

CONTRIBUTORS TO THIS VOLUME

J. H. Dunlop

R. D. Gillard

R. Juza

M. F. Lappert

R. V. Parish

D. F. Peppard

H. Pyszora

A. A. Woolf

Advances in
INORGANIC CHEMISTRY
AND
RADIOCHEMISTRY

EDITORS

H. J. EMELÉUS

A. G. SHARPE

*University Chemical Laboratory
Cambridge, England*

VOLUME 9

1966

ACADEMIC PRESS



New York and London

COPYRIGHT © 1966, BY ACADEMIC PRESS INC.

ALL RIGHTS RESERVED.

NO PART OF THIS BOOK MAY BE REPRODUCED IN ANY FORM,
BY PHOTOSTAT, MICROFILM, OR ANY OTHER MEANS, WITHOUT
WRITTEN PERMISSION FROM THE PUBLISHERS.

ACADEMIC PRESS INC.

111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by

ACADEMIC PRESS INC. (LONDON) LTD.

Berkeley Square House, London W.1

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 59-7692

PRINTED IN THE UNITED STATES OF AMERICA

LIST OF CONTRIBUTORS

Numbers in parentheses indicate the pages on which the authors' contributions begin.

- J. H. DUNLOP (185), *Department of Chemistry, The University, Sheffield, England*
- R. D. GILLARD (185), *Department of Chemistry, The University, Sheffield, England*
- R. JUZA (81), *Institut für anorganische Chemie der Universität Kiel, Kiel, Germany*
- M. F. LAPPERT (133), *The Chemical Laboratory, University of Sussex, Brighton, England*
- R. V. PARISH (315), *Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester, England*
- D. F. PEPPARD (1), *Chemistry Division, Argonne National Laboratory, Argonne, Illinois*
- H. PYSZORA (133), *The Distillers Company, Epsom, England*
- A. A. WOOLF (217), *Department of Chemistry, Bristol College of Science and Technology, Bristol, England*

LIQUID-LIQUID EXTRACTION OF METAL IONS

D. F. Peppard

Chemistry Division, Argonne National Laboratory, Argonne, Ill.

I. Introduction	1
II. Single-Stage Extraction	4
A. Principles	4
B. Mathematical Treatment	5
III. Multiple Extraction and Multiple Scrubbing	7
A. Principles	7
B. "Push-Through" Method of Operation	8
C. "Countercurrent Extraction" Method of Operation	15
D. Comparison of "Push-Through" and "Countercurrent Extraction" Methods of Operation	23
IV. Systems Involving Neutral Phosphorus-Based Extractants	25
A. Mononuclear Extractants	25
B. Dinuclear Extractants	32
V. Systems Involving Acidic Phosphorus-Based Extractants	34
A. Mononuclear Extractants	34
B. Dinuclear Extractants	47
VI. Systems Involving Sulfonic Acids, $(\text{G})\text{SO}_2(\text{OH})$, as Extractants	48
VII. Systems Involving Amines and Amine Oxides as Extractants	49
A. General	49
B. Amines and Amine Oxides	50
VIII. Miscellaneous Systems	56
A. Organic Extractant (in Diluent) vs. Fused Salt	56
B. Partition Chromatography	57
IX. Synergism and Antisynergism	64
X. Investigation of Complexes	68
XI. Concluding Comments	71
References	72

I. Introduction

"A good technique is worth a thousand theories" is a debatable statement, certain to provoke a lively and acrimonious discussion at any gathering of scientists. Without attempting to resolve the argument, let it be said that development of a new and powerful technique has often opened to exploration an area of research previously inaccessible, and has frequently made it possible to prove or disprove a theory otherwise unamenable to testing.

Considering only a few of the winners of the Nobel Prize in Chemistry, it seems safe to say that, despite their many accomplishments in basic science, these men will be remembered by chemists at large because of the far-reaching consequences of techniques associated with their discoveries: V. Grignard and P. Sabatier (use of organometallic compounds in organic syntheses), H. C. Urey (separation of isotopes), W. F. Libby (dating of samples of geological importance by carbon-14 analysis), A. J. P. Martin and R. L. M. Synge (development of partition chromatography), and E. M. McMillan and G. T. Seaborg (development of procedures for production, separation, and characterization of man-made elements).

Correspondingly, in the field of liquid-liquid extraction, H. Peligot will be remembered for his observation (in 1842) that uranyl nitrate may be extracted into diethyl ether, J. W. Rothe for his study (reported in 1892) of the extraction of ferric ion from concentrated hydrochloric acid into diethyl ether, and L. C. Craig for his development of equipment for "countercurrent distribution," an operational technique of immediate value in biological and medical research and of long-term influence upon diverse chemical separations investigations.

The rapidly expanding field of liquid-liquid extraction of metal ions is now so extensive that a review of other than book length must be severely limited. On the assumption that the most valuable result of a survey may be the stimulation of further research in the field, the present treatment is largely restricted to recently reported systems not reviewed in the dual context of basic chemistry and separations application.

For analysis and discussion of the chemical and structural problems involved, up to date and thorough reviews are those by Morrison and Freiser (187), "Solvent extraction," 1959; Diamond and Tuck (59), "Extraction of inorganic compounds into organic solvents," 1960; Fomin (88), "Chemistry of extraction processes," 1962; Marcus (170), "Solvent extraction of inorganic species," 1963; and Katzin (141), "Solvent extraction of inorganic species," 1965.

The chemical systems, the methods of operation, and the pertinent mathematics are considered in the reviews by Martin and Holt (174), "Liquid-liquid extraction in inorganic chemistry," 1959; Irving and Williams (127), "Liquid-liquid extraction," 1961; and von Metzsch (286), "Solvent extraction," 1961.

The yearly journal reviews, "Extraction" in *Analytical Chemistry* and "Liquid extraction" in *Industrial and Engineering Chemistry*, are helpful complements to these fuller treatments.

"Old and new processes of multiplicative distribution (liquid-liquid extraction)," 1964, is an analysis of various ways in which multiplication of a separation effect in liquid-liquid extraction may be achieved, presented by Fischer *et al.* (85).

"Purification by solvent extraction" by Fletcher (87), 1957, treats of large-scale potentialities. Analytical applications are described by Morrison and Freiser in *Solvent Extraction in Analytical Chemistry* (186), 1957, and in "Extraction" (188), 1964, and preceding reviews of the series, and by Belcher *et al.* (19) in the chapter "Solvent extraction" in *New Methods of Analytical Chemistry*, 1964.

Freiser (92) has surveyed "Solvent extraction in radiochemical separations," and Dyrssen (72) has reviewed "The use of solvent extraction techniques in the study of chemical equilibria."

In "Automatic countercurrent distribution equipment," Craig *et al.* (51) describe in detail the design and function of the equilibration cell which made possible automation of countercurrent distribution, and Verzele and Alderweireldt (283) report a modification which permits both phases to flow through the train of contactors.

The extraction of mineral acids and of water, by organic phases consisting of neutral phosphorus-based extractants in an organic diluent, has been reviewed by Diamond (59) and Marcus (170).

In "The partition law in solvent extraction," 1963, McKay and Miles (162) compare the ratio of the independently measured activities of a solute in two immiscible liquid phases with measured partition data for the solute in the system employing these two liquid phases mutually in contact. This appears to be the first test of the thermodynamic partition law.

Complete and rigorous mathematical treatment of liquid-liquid extraction is given by Alders (3), Craig (50), and Treybal (275).

In addition to emphasizing chemical systems which seem of prime interest, or potential prime interest, in the field of metals separations, the present review stresses the importance of a familiarity with the various ways in which a single-stage separation effect may be multiplied.

An imposing collection of basic data concerning the extraction of metals has been gathered by liquid-liquid extraction investigators. However, with the exception of very large-scale metallurgical separations and of certain separations involved in processing in atomic energy installations, the field of applications has been left to practitioners of reversed-phase partition chromatography.

The latter statement is made not in anger but in sorrow, for in many instances a straightforward application of the "push-through" or the "countercurrent extraction" method of operation is the most efficient solution to a given separations problem. Unfamiliarity with the mechanical manipulations and the mathematical treatment appears to be the basic cause of the lack of such applications.

It is hoped that presentation of these methods of multiplication of a single-stage separation effect may lead to expanded use of liquid-liquid extraction in radiochemistry, in analytical chemistry, and in any investiga-

tion in which the degree of separation of one metal from another is a determining factor in deciding the fate of the study.

Meanwhile, reversed-phase partition chromatographers are to be commended for having established so many valuable metal separations schemes on the basis of liquid-liquid extraction data.

II. Single-Stage Extraction

A. PRINCIPLES

In its essentials, liquid-liquid extraction is an operation in which a dissolved substance expresses its preference between two liquids simultaneously present and available to the substance. This preference is determined by chemical and physical principles which are inviolable but in most instances are identified in a qualitative fashion only.

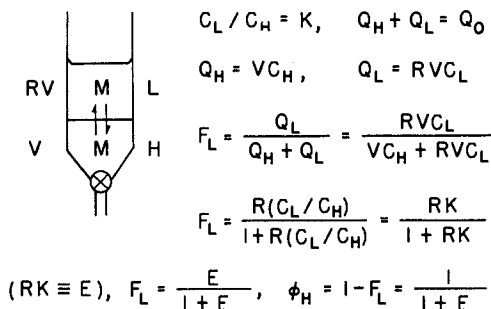
Consequently the behavior of a given solute in a given extraction system cannot be predicted in any but the roughest manner. However, this behavior, once determined, can be relied upon in any future experiment.

Two liquids which, following thorough mutual physical mixing, separate into two liquid phases upon becoming quiescent together constitute a *liquid-liquid extraction system*. If a solute, M, soluble in each of these liquids separately, is introduced into this system, it will (at equilibrium) *distribute* itself between the *two liquid phases* in a precise and reproducible manner. This *distribution* (or *partition*) is described mathematically by the *distribution ratio* (or *partition ratio*), for which a wide variety of symbols and defining expressions have been used.

Assume that the separatory funnel of Fig. 1 contains two liquids (L for *lighter* and H for *heavier*) which, in a settling period following thorough intermixing, will separate into two layers. A solute, M, is allowed to dissolve in this mixture and distribute between the two liquid phases during a mixing period sufficiently long to assure *empirical equilibrium distribution* (i.e., a distribution indistinguishable from the true *thermodynamic distribution* by the available methods of *measurement*).

Following a settling period to permit phase disengagement, each of the phases is analyzed for M content. Assume that a series of similar experiments, in which each variable except the quantity of M added is kept constant, has been performed, and that the quantity of M added was varied over a wide range. If the *two solutions* behave *ideally*, the ratio of the concentration of M in the light phase to that in the heavy phase will have the same value for each of the experiments, that is, $C_L/C_H = K$. (This constancy of C_L/C_H is frequently approximated very closely in practice if the solute has the same state of aggregation in the two liquid phases, and if the concentration of solute is sufficiently below the "saturated" concen-

tration in each phase. For example, tracer-level radioactive lanthanides(III) exhibit a constant C_L/C_H over a wide range of concentration in many systems, that is, over a range in which the highest concentration in a given phase may be 10,000 times as great as the lowest, although both are in the "tracer-level" range.)



$$C_L / C_H = K, \quad Q_H + Q_L = Q_0$$

$$Q_H = VC_H, \quad Q_L = RVC_L$$

$$F_L = \frac{Q_L}{Q_H + Q_L} = \frac{RVC_L}{VC_H + RVC_L}$$

$$F_L = \frac{R(C_L / C_H)}{1 + R(C_L / C_H)} = \frac{RK}{1 + RK}$$

$$(RK \equiv E), \quad F_L = \frac{E}{1 + E}, \quad \phi_H = 1 - F_L = \frac{1}{1 + E}$$

FIG. 1. Single-stage extraction of metal M in the system: light phase (L) and heavy phase (H) of respective volumes RV and V .

B. MATHEMATICAL TREATMENT

From consideration of material balance it follows that the quantity of M in the L phase plus the quantity of M in the H phase must equal the total quantity (Q_0) of M added, that is:

$$Q_L + Q_H = Q_0 \quad (1)$$

The volumes of the H and L phases (Fig. 1) are, respectively, V and RV . Therefore, recalling that "concentration" is "quantity per unit volume," in any arbitrary units:

$$Q_H = VC_H, \quad Q_L = RVC_L \quad (2)$$

The fraction of the total quantity of M in the separatory funnel found in the light phase (F_L) is thus:

$$F_L = Q_L / Q_0 = Q_L / (Q_L + Q_H) = RVC_L / (RVC_L + VC_H) \quad (3)$$

For the case in which the distribution ratio is a constant:

$$K = C_L / C_H \quad (4)$$

Therefore, following division of both numerator and denominator of Eq. (3) by (VC_H) and substitution of K for C_L / C_H , the fraction of the quantity of M in the L phase is expressed as

$$F_L = RK / (RK + 1) = E / (E + 1) \quad (5)$$

where the *effective distribution ratio*, E , is defined by the expression:

$$E = RK \quad (6)$$

Similarly, since the sum of the two fractions must equal unity, the fraction of the total quantity of M in the H phase (Φ_H) is expressed as:

$$\Phi_H = 1 - F_L = 1/(RK + 1) = 1/(E + 1) \quad (7)$$

Evidently if $E = 1$, $F_L = \Phi_H = 0.5$. If E is greater than unity, F_L exceeds 0.5 (M preferentially in L phase) and, if less, Φ_H exceeds 0.5 (M preferentially in H phase). These interrelationships illustrate the importance of considering E (i.e., RK), not K , in the devising of a separations scheme for solutes M and N, having respective distribution ratios K_M and K_N , $K_M > K_N$.

The technological contributions of liquid-liquid extraction techniques have involved the separation of one or more solutes from a mixture. In essence, all such separations are equivalent to the mutual separation of solutes M and N. This mutual separation is dependent upon operating the extraction system under conditions such that the RK product, E , for M is greater than unity and that for N is less than unity. It is evident that if E for solute M is *far greater* than unity and that for N is *far less* than unity, then M will appear almost exclusively in the L phase and N almost exclusively in the H phase. That is, M and N will be separated from each other quite efficiently.

Expressed in another way, the greater the ratio of their E values, the more readily may M and N be mutually separated—*provided that the two E values are suitably related to unity*. For example, if the two E values are 10,000 and 100, respectively, the N in the H phase will be purified reasonably well with respect to contamination by M (the ratio of M to N having been reduced by a factor of nearly 100), but will be obtained in only approximately 1% yield. The purification of M, with respect to N, in the L phase will be negligible.

For fixed values of E , it may be shown that maximum mutual separation of M and N is obtained when the E values are mutually reciprocal (33):

$$E_M E_N = 1, \text{ that is, } E_M = 1/E_N \quad (8)$$

By reference to the definition of E , Eq. (6), it is seen that the ratio of the E values is identical with the ratio of the corresponding K values. Therefore the ratio of K values of the solutes, M and N, may be considered a measure of their mutual separability. This ratio, frequently called the *separation factor*, is symbolized as β and is defined by:

$$\beta = K_M/K_N \quad (9)$$

Assuming the solutes M and N have respective K values of 100 and 0.01 ($\beta = 10,000$) and equal volumes of L and H phases are employed

($R = 1$), substitution in Eq. (5) indicates that 99.01% of the total M and only 0.9901% of the total N will be found in the L phase. Therefore the M-product has been obtained in 99.0% yield and has been *decontaminated* with respect to N by a factor of 100. (Similarly, N will be found in 99.0% yield, *decontaminated* with respect to M by a factor of 100, in the H phase.)

The *decontamination factor* is a numerical measure of the efficiency with which a *product* has been *cleaned up* with respect to an *undesirable impurity*. Assuming M the product and N the impurity, the decontamination factor (DF) is defined as the ratio of the quantity (Q_N/Q_M) in the starting material (feed) to the quantity (Q_N/Q_M) in the M-product. (The ratio of the quantity (Q_M/Q_N) in the M-product to the quantity (Q_M/Q_N) in the feed, sometimes called the *clean-up factor*, is an equivalent definition.)

By reference to Eq. (3), it is clear that:

$$DF = (F_M/F_N), \quad \text{for M-product in L phase} \quad (10)$$

Similarly, if N is the product and M the contaminant:

$$DF = (\Phi_N/\Phi_M), \quad \text{for N-product in H phase} \quad (11)$$

III. Multiple Extraction and Multiple Scrubbing

A. PRINCIPLES

Suppose that, in the system described, a DF of 100 is not sufficiently large or that a yield of 99% of product is not acceptable. What can be done?

By reference to Fig. 1 and Eq. (5) it will be seen that by draining the H phase, replacing it with a fresh *barren* (containing no M or N) H phase of the same volume, and agitating the phases, the M and N in the L phase (*extract*) will redistribute between the L phase and the fresh H phase (*scrub*), producing an L phase (*scrubbed extract*) containing 98.0% of the original M and only 0.0098% of the original N.

That is, the DF for M with respect to N is 10,000 after a *single extraction* followed by a *single scrub* as opposed to only 100 after a *single extraction without scrub*. (Contacting an *extract phase* with *barren opposing phase* is called *scrubbing*. In general the extract phase is primarily organic in nature and the barren opposing phase, the scrub, primarily aqueous; but this is purely a matter of definition.)

The penalty paid for increasing the DF from 100 to 10,000 by use of a single scrub was a loss in yield, the yield falling from 99.0% to 98.0%. A second scrub would result in a 97.0% yield of M-product with a DF with respect to N of 1,000,000. It is evident that *multiple scrubbing* is an effective technique for increasing the DF.

Considering the arbitrary nature of the definition of K and DF , that is, considering the L phase the extractant and M the product rather than the H phase the extractant and N the product, it is apparent from the symmetry relationships in Eqs. (5) and (7) that what *multiple scrubbing* does for DF , *multiple extraction* will do for yield, considering M as product. (Equivalent reasoning applies to N as product in the H phase.)

The answer to the demand for both increased yield and a larger DF (assuming that β cannot be increased) is the use of both *multiple extraction* and *multiple scrubbing*.

B. "PUSH-THROUGH" METHOD OF OPERATION

1. General

One method of operation incorporating both multiple extraction and multiple scrubbing is illustrated in Fig. 2. Because of the confusion of terms

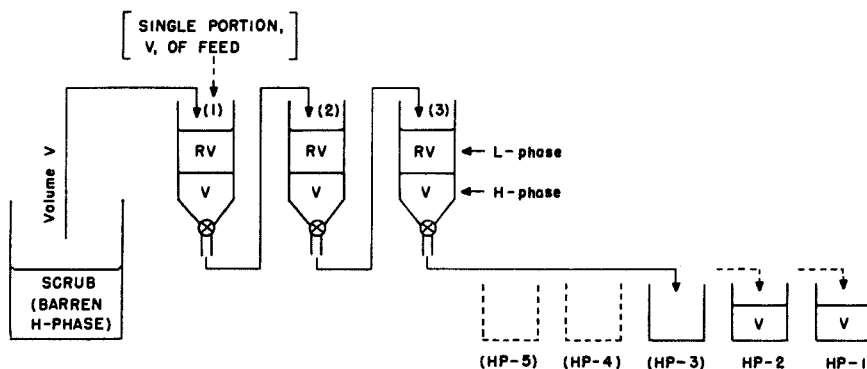


FIG. 2. Multiple extraction and multiple scrubbing: "push-through."

associated with it in the literature, this will be identified as the *push-through* technique in reference to the fact that a single portion of feed is *pushed* through the system by a series of scrubs. It constitutes a special case of "countercurrent distribution," which has been treated exhaustively, both experimentally and mathematically, by Craig (50). Its consideration here is justified on the basis of the relative simplicity of its mathematical treatment and its ready applicability to research-scale separation of radioactive nuclides.

In Fig. 2, the three separatory funnels are numbered consecutively to the right, and the "flow" of H phase is to the right, the L phase being stationary with respect to the overall assembly.

Consider each funnel to initially contain a volume RV of barren L phase. A volume V of Feed (H phase) is introduced into Funnel 1. Follow-

ing a mixing and settling cycle, the H phase is drained from Funnel 1 to Funnel 2 and a volume V of Scrub (barren H phase) is added to Funnel 1. Following a mixing and settling cycle for each of the two Funnels, the H phase of Funnel 2 is drained to Funnel 3 and that from Funnel 1 then drained to Funnel 2, following which a volume V of Scrub is added to Funnel 1. This sequence of mixing, allowing to settle, transferring N phase to the right (necessarily progressing from right to left with the transfers unless holding containers are used so that draining is not directly to a funnel), and adding a portion of Scrub is continued until the desired number of Scrubs have been employed. Note that when the depleted Feed is in Funnel 3 and ready to be drained as the first product phase, HP-1, the first Scrub is in Funnel 2 and the second Scrub in Funnel 1.

2. Operation and Mathematical Treatment

By a generalization of this treatment it may be shown that, after the passage of n portions of H phase through an assembly of c funnels, i.e., n H-products numbered consecutively from HP-1 to HP- a and c L-products numbered consecutively (to correspond to Funnel numbers) from LP-1 to LP- c , the fraction of solute M added to this assembly in the single portion of Feed to be found in a given product is expressed as

$$\Phi_{\text{HP}-n} = B_{(c,n)} E^{n-1} / (E + 1)^{c+n-1} \quad (12)$$

for the n th H-product (c contactor), and as

$$F_{\text{LP}-n} = B_{(q,a)} E^a / (E + 1)^{q+a-1} \quad (13)$$

for the q th L-product (a portions of H phase passed through the q th contactor). The multiplier, $B_{(q,n)}$, in the above equation is expressed as:

$$B_{(q,n)} = (q + n - 2)! / [(q - 1)!(n - 1)!] \quad (14)$$

Considering an assembly of these contactors ($c = 3$) (see Fig. 2), after a total of five H phases have traversed the assembly ($a = 5$) the funnels from left to right will contain LP-1, LP-2, and LP-3, and five products, HP-1 to HP-5, will have been withdrawn. The fraction of total M introduced into the system reporting to each of these eight products is shown in Table I.

Substitution of specific numerical values for E in the F and Φ expressions of Table I generates the F and Φ values of Table II.

For $E = 1$: The Φ value, proceeding from HP-1 to HP-5, is seen to increase to a maximum at HP-2 and HP-3, the total fraction of M reporting to the composite H-product being 0.774. The F values, proceeding from LP-1 to LP-3, increase throughout.

TABLE I

FRACTION OF TOTAL M INTRODUCED INTO THE SYSTEM REPORTING TO EACH
OF THE 8 PRODUCTS RESULTING FROM TRANSFERS OF 5 PORTIONS ($\alpha = 5$)
OF H PHASE THROUGH 3 STATIONARY PORTIONS ($c = 3$) OF L PHASE:
GENERAL CASE

L Phase		H Phase	
Product	F	Product	Φ
LP-1	$E^5/(E+1)^5$	HP-1	$1/(E+1)^3$
LP-2	$5E^5/(E+1)^6$	HP-2	$3E/(E+1)^4$
LP-3	$15E^5/(E+1)^7$	HP-3	$6E^2/(E+1)^5$
		HP-4	$10E^3/(E+1)^6$
		HP-5	$15E^4/(E+1)^7$

TABLE II

FRACTION OF TOTAL M INTRODUCED INTO THE SYSTEM REPORTING TO EACH
OF THE 8 PRODUCTS RESULTING FROM TRANSFER OF 5 PORTIONS ($\alpha = 5$)
OF H PHASE THROUGH 3 STATIONARY PORTIONS ($c = 3$) OF L PHASE:
SPECIFIC VALUES OF E

Product	F (or Φ)			
	$E = 1$	$E = 2$	$E = 9$	$E = 0.1$
LP-1	0.0313	0.132	0.590	6.2×10^{-6}
LP-2	0.0781	0.219	0.295	2.8×10^{-5}
LP-3	0.117	0.219	0.089	7.7×10^{-5}
	0.226	0.570	0.974	0.000111
HP-1	0.125	0.0370	0.00100	0.751
HP-2	0.188	0.0740	0.00270	0.205
HP-3	0.188	0.0988	0.00486	0.0373
HP-4	0.156	0.110	0.00729	0.00564
HP-5	0.117	0.110	0.00984	0.000770
	0.774	0.430	0.026	1.000

For $E = 2$: The Φ value increases to 0.110 at both HP-4 and HP-5, the total fraction of M reporting to the composite H-product being 0.430. The F values behave similarly.

For $E = 9$: The Φ values increase throughout, the total fraction of M in the composite H-product being only 0.026. The LP-1 product contains better than half of the M content of the system.

For $E = 0.1$: The HP-1 product contains 75% of the total M of the system. The composite L-product contains approximately 0.011% of the total M.

3. Applications

A linear plot of the Φ data of Table II for a given E vs. the number of the H-product bears a formal resemblance to an ion-exchange elution curve. Similarly, a linear plot of the F data for a given E vs. the number of the L-product is formally analogous to a plot of equi-spaced sections of an ion-exchange column, sectioned after development.

From Table II it is evident that, if the Feed contained two substances, M and N, with respective E values of 9 and 0.1, the LP-1 contains 59.0% of the added M, decontaminated with respect to N by a factor of 9.5×10^4 . (The DF is less in LP-2 and still less in LP-3.) The composite L-product contains 97.4% of the M with a DF of 8.8×10^3 . Similarly, the HP-1 contains 75.1% of the N decontaminated with respect to M by a factor of 751.

Sometimes the analogy of gradient elution may be used in the push-through technique. Suppose, under three sets of conditions differing only in the composition of the H phase employed, the E values for substances A, B, C are (1) $E_A < 1$, $E_B \gg 1$, $E_C \gg 1$; (2) $E_B < 1$, $E_C \gg 1$; (3) $E_C < 1$. Then, by using the proper number of portions of H phase corresponding to conditions (1), (2), and (3) in succession, A, B, and C will be removed, successively, from the assembly of funnels.

Such a "gradient" separation of Th(IV), Pa(V), and U(VI), i.e., UO_2^{++} , is shown in Fig. 3. (The data used in deriving the procedure are presented in Table III.)

In this separation, the method of operation presented in Fig. 2 was employed. Each of three funnels contained 25 ml tributyl phosphate, $(n\text{-C}_4\text{H}_9\text{O})_3\text{PO}$ (TBP), and the feed and all scrubs were used in 25-ml portions. The feed and the immediately following three scrubs were 5.0 M

TABLE III
EXTRACTION OF Th(IV), Pa(V), AND U(VI) INTO UNDILUTED TBP, $(n\text{-C}_4\text{H}_9\text{O})_3\text{PO}$,
FROM EQUILIBRATED AQUEOUS PHASES OF VARIOUS COMPOSITION^a

Equilibrated aqueous phase	K		
	Th(IV)	Pa(V)	U(VI)
5.0 M HCl	0.006	41	50
5.0 M HCl + 0.5 M HF	—	0.13	39
4.0 M HCl	—	3.7	25
4.0 M HCl + 1.0 M HF	—	—	10.4
0.5 M HCl	—	—	0.040
0.5 M HCl + 1.0 M HF	—	—	0.0076

^a See reference (207).

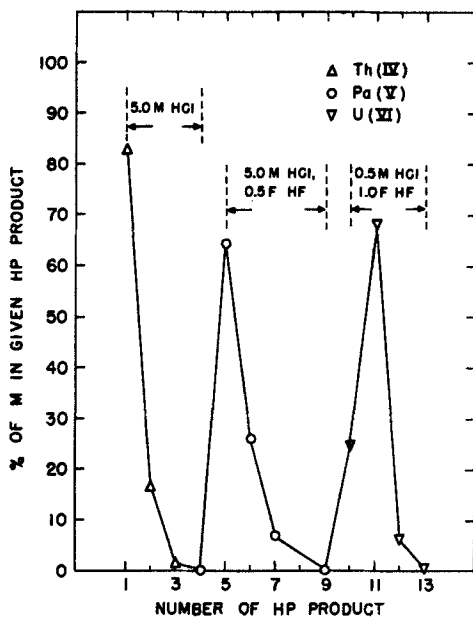


FIG. 3. "Gradient" separation of Th(IV), Pa(V), and U(VI): "push-through" (three contactors, 25 ml TBP in each, 25-ml portions of aqueous phase) (207).

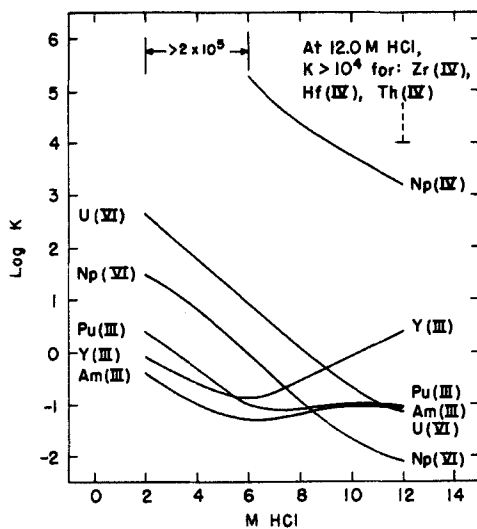


FIG. 4. Variation of $\log K$ with concentration of HCl for selected M(III), M(IV), M(VI) in the system: 0.48 F H_2MEHP (in toluene) vs. HCl (218). F = No. formula weights solute/liter solution.

in HCl, the next five scrubs were 5.0 *M* in HCl and 0.5 *M* in HF, and the final four scrubs were 0.5 *M* in HCl and 1.0 *M* in HF. For each of the nuclides, better than 60% yield is found in a single-product phase.

In general, separations involving metals in mutually different valence states are readily accomplished, Fig. 4 illustrating this fact for a system involving mono-2-ethyl hexyl phosphoric acid, $(C_2H_5 \cdot C_6H_{12}O)PO(OH)_2$ (H_2MEHP), as the extractant (218). (All lanthanides(III) lie within or close to the general region bracketed by Am(III) and Y(III); U(IV) and Pu(IV) are comparable to Th(IV) in behavior, exact data throughout the range of HCl concentration being difficult to obtain because of the problems of valence control, U(VI) and Pu(III) constituting the respective interferences.)

It is evident that neptunium, as Np(IV), is readily separable from U(VI) and from actinides(III), lanthanides(III), and Y(III) under properly chosen conditions. However, experimentally the decontamination factor (DF) of the Np product phase with respect to uranium contamination frequently levels off, with continued scrubbing with 12 *M* HCl, at approximately 500. That is, further scrubbing with 12 *M* HCl fails to remove an appreciable portion of the uranium remaining in the product. This effect has been shown to be due to the presence of U(IV), the "oxidized uranium" in 12 *M* HCl having been demonstrated, by extraction experiments, to contain 0.3–2% U(IV) after an aging period of several hours.

Following a bromate "oxidation" scrub, a further DF of approximately 500 may be obtained. Consequently, through suitable insertion of bromate oxidation scrubs in the scrub sequence, a DF with respect to uranium of any desired value may be reached. (It may be noted that if a loss in neptunium yield of 1–2% may be tolerated, only a single contactor (funnel) is required. In practice, it may be desirable to transfer the organic phase to a fresh contactor after approximately half of the scrubs have been employed, because of the tendency of trace contaminants to adhere to the walls.)

The "leveling off" of the DF of the neptunium product with respect to uranium contamination, frequently at approximately 500, due to the presence of U(IV), forcefully illustrates the importance of valence control in systems involving elements of variable valence. For example, it is extremely difficult to maintain the Pu(IV) to Pu(III) ratio in 1–6 *M* HCl below a value of 10^{-3} . Consequently, although the data of Fig. 4 indicate the ready separability of U(VI) and Pu(III) at 6 *M* HCl, a high DF of uranium product with respect to plutonium contaminant requires the presence of a reductant in the 6 *M* HCl scrubs, this reductant serving to reduce Pu(IV) in the extract to Pu(III) as Pu(III) is removed by scrubbing.

It is evident from Fig. 4 that Np(VI) is readily separable from Th(IV). Since Th exists in such systems only as Th(IV), no difficulty in purification of Np is to be expected. However, the yield of Np is dependent upon the maintenance of the hexavalent state.

Gindler *et al.* (93) used this H_2MEHP (in toluene) vs. HCl system in the purification of daughter ^{229}Th from parent ^{233}U and from other fissionable material in the determination of the thermal neutron fission cross-section of ^{229}Th .

A comparison of the extraction behavior of a given element in different states of oxidation is instructive. From a comparison of β values (ratio of the two K values) for a given element in two states of oxidation, as calculated from the data of Table IV, it is tempting to generalize that K values may be ordered:

$$M(IV) > M(III) \sim M(VI) > M(II)$$

However, it must be noted that even the Eu and Bk data are not strictly comparable, since the chemical systems employed are not the same. (The former data were obtained in a HCl system so that Eu(II) could be maintained, and the latter in a HNO_3 system so that Bk(IV) could be stabilized.) Further, in certain systems involving neutral extractants, such as the tributyl phosphate, $(n-C_4H_9O)_3PO$ (TBP), vs. HNO_3 system and the diethyl ether vs. NH_4NO_3 system, the K for U(VI) exceeds that for U(IV).

Although a sweeping generalization may not be made, the fact that the β for Eu(III) with respect to Eu(II), for Bk(IV) with respect to Bk(III),

TABLE IV
COMPARISON OF K VALUES FOR M IN TWO DIFFERENT VALENCE STATES
UNDER SELECTED OPERATING CONDITIONS^a

M	K			
	M(II)	M(III)	M(IV)	M(VI)
Eu ^b	3.0×10^{-3}	2.2×10^3	—	—
Bk ^c	—	2.3×10^{-3}	1.9×10^3	—
Np ^d	—	—	1.7×10^3	1.2×10^{-2}
U ^d	—	—	$>7 \times 10^3$	6.3×10^{-2}

^a Acidic phosphorus-based extractants in carrier diluents vs. an aqueous mineral acid phase.

^b 0.40 F $HEH(\phi P)$, i.e. $(C_2H_5-C_6H_{12}O)(C_6H_5)PO(OH)$, 2-ethyl hexyl hydrogen phenyl phosphonate, in toluene vs. 0.05 M HCl (201).

^c 0.15 F $HDEHP$, i.e. $(C_2H_5-C_6H_{12}O)_2PO(OH)$, di-2-ethyl hexyl phosphoric acid, in n -heptane vs. 10 M HNO_3 (219).

^d 0.48 F H_2MEHP , i.e. $(C_2H_5-C_6H_{12}O)PO(OH)_2$, mono-2-ethyl hexyl phosphoric acid, in toluene vs. 12 M HCl (218).

and for Np(IV) with respect to Np(VI) approximates 10^5 in the systems represented in Table IV suggests that the mutual separation of two elements present in different valence states should be readily accomplished. The fact that M(IV) and M(III) respond differently to varying operating conditions (see Fig. 3) may be employed in effecting their mutual separation.

C. "COUNTERCURRENT EXTRACTION" METHOD OF OPERATION

1. General

Separations based upon β values of 10^5 (assuming the E values bear the proper relationship to unity) are readily accomplished. Those based upon β values approximating 100 may be achieved by use of multiple extraction and multiple scrubbing by the push-through technique, utilizing only a small number of contactors and relatively few scrubs; those based upon a β value of approximately 10 are in the "challenging" area.

However, a separation based upon a β value in the range 2-5 requires a method of operation not yet discussed. Such a method of operation is required for the efficient mutual separation of adjacent lanthanides(III). In the lanthanide (rare earth) series, the 15 members, differing successively by one in atomic number, are chemically similar and exist preferentially as lanthanide(III) ions. Cerium(IV) and europium(II) are sufficiently stable for study, but the usual state for each of these elements is the trivalent one.

The data of curve A of Fig. 5 pertain to one of the more promising systems with respect to the mutual separation of lanthanides(III) (209). The average β for one member with respect to the adjacent member one unit lower in atomic number, Z , is 2.8. (Noting that β , β^2 , β^3 , β^4 , and β^5 are, respectively, 2.8, 7.8, 22, 61, and 172, it is evident that even the push-through technique will suffice to mutually separate lanthanides(III) which differ by four or more units in atomic number.)

The push-through method of operation may be applied to a number of solutes so as to produce a number of product phases in which the various solutes tend to concentrate discretely. (Compare the peaks of an ion-exchange elution plot.) However, the purity of a given product is not high, unless the β for the solute with respect to immediately preceding and following solutes is greatly different from unity.

In order to achieve greater discrimination (more thorough mutual separation with respect to a given pair of solutes) the advantage of multiple "product" phases must be sacrificed. In the method of operation about to be described, here referred to as *countercurrent extraction*, at *steady state* operation of the system, two product phases, L and H, each of constant composition with respect to time, are obtained.

The *cut*, among a number of solutes, may be made at any predetermined point, but the isolation of a single solute (other than one of the two terminal ones in the sequence of ascending extractability under a given set of conditions) requires *two passes* through the system. In one of these passes, this solute reports to the L phase, all solutes less extractable reporting to the H phase. In the other pass, it reports, singly, to the H phase, all solutes more extractable reporting to the L phase.

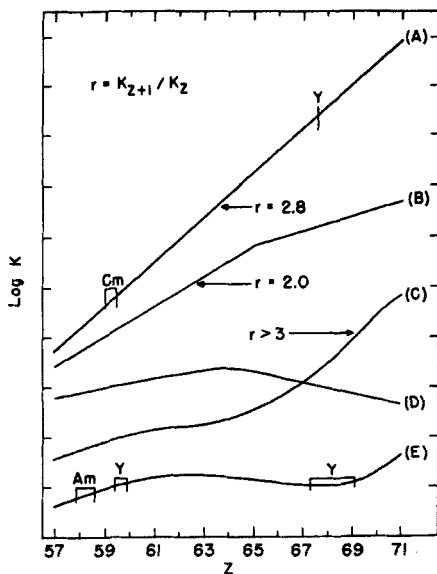


FIG. 5. Variation of $\log K$ with Z for lanthanides(III) in selected systems (smoothed curves; $\log K$ values at Z axis, respectively for curves A-E, are -7 , -4 , -2 , -5 , and 1). (A) $1.0 F$ HEH[Φ P] (in toluene) vs. $2.0 M$ HCl (209); (B) undiluted TBP vs. $15.6 M$ HNO_3 (113); (C) $0.0375 F$ HDHoEP (in benzene) vs. $0.25 M$ $HClO_4$ (208); (D) $0.71 F$ TBP (in CCl_4) vs. $1.96 M$ HNO_3 (199); and (E) $0.10 F$ H_2MEHP (in toluene) vs. $0.25 M$ HCl (177). F = No. formula wts. solute/liter solution.

(The terms "reports" and "singly" are used relatively, it being understood that each product phase contains some of each of the solutes present in the original feed, since no liquid-liquid extraction separation is "absolute.")

2. Operation and Mathematical Treatment

Countercurrent extraction is illustrated for a five-contactor system in Fig. 6. In a method of operation used in the author's laboratory the funnels are clamped in fixed equi-spaced position, mixing of the phases being accomplished by glass "pump-mix" stirrers driven by motors mounted

above the funnels. The seven beakers, numbered 0-6, are placed in shallow cups attached to a board which moves easily (on glides or rollers) in a left-right line, its movement being limited by stops at the left and right, so that positions corresponding to (A) and (B) of Fig. 6 may be obtained rapidly and precisely. The position corresponding to (C) may be stabilized by use of a pin inserted to prevent movement of the board.

In the general case, any number of funnels may be employed, and the Feed may be introduced into any one. However, in the interest of mathematical simplicity, an *odd* number of funnels with Feed entry at the *central position* has been chosen for the illustration of the principle of countercurrent extraction.

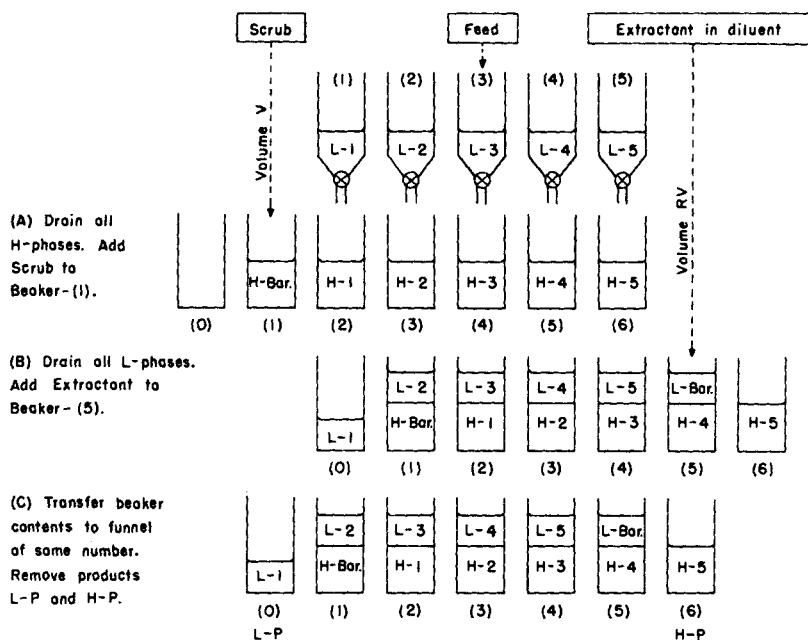


FIG. 6. Multiple extraction and multiple scrubbing: "countercurrent extraction."

Assume that at the start of the operation each of the funnels of Fig. 6 contains a volume RV of Extractant phase (L phase) and a volume V of barren Scrub phase (H phase). A portion of Feed (a volume *temporarily* considered to be negligible by comparison with V and RV) is introduced into Funnel 3. (Note that the Feed may be introduced as a solution in L or in H. In theory, a solid Feed may be introduced, but this is in general undesirable due to difficulties in assuring complete dissolution.)

Following equilibration of phases in Funnel 3, the H phase is drained to Beaker 4 (Subcycle A). The L phase is then drained to Beaker 2 (Sub-

cycle B). (The heavy and light phases of the other funnels have meanwhile been transferred correspondingly, but at this point contain no solutes. Also, a portion, V , of Scrub (barren H phase) has been added to Beaker 1; and a portion, RV , of Extractant (barren L phase) has been added to Beaker 5.)

When the beakers are moved into Position C, Beaker 0 contains a volume RV of L phase, Beaker 6 contains a volume V of H phase, and each of the intervening beakers contains a volume RV of L phase and a volume V of H phase. The content of each beaker is then transferred to the funnel with the corresponding number.

As the result of the manipulations involved in Subcycles A, B, and C, each portion of L phase has moved one position to the left and each portion of H phase one position to the right. Note that Funnel 2 and Funnel 4, but no other funnels, now contain solutes from the Feed. A fresh portion of Feed is introduced into Funnel 3 and the entire cycle performed repetitively.

Just before addition of the third portion of Feed, solutes from *Feed portion-1* will be in *Funnels 1, 3, 5* and solutes from *Feed portion-2* will be in *Funnels 2, 4*. From consideration of Fig. 6, it is evident that all Feed portions of *odd number* will mutually interact as will all Feed portions of *even number* in an identical fashion. But odd and even *cannot* mutually interact. Therefore, if individual products, represented by Beaker 0 and Beaker 6, are kept separate as steady state operation is approached, it will be found that each odd-numbered product has an even-numbered counterpart of identical composition.

(Mathematically, the system is represented by a *double-diamond*, as opposed to a *single-diamond*. This point is stressed since, if it is mistakenly analyzed as a single diamond, it will be concluded that a given approximation to steady state operation has been reached with p through-puts (i.e., product phases produced) whereas $2p$ will be required.)

Considering a solute, M , for which RK , i.e. E , is equal to unity, it is evident that after the first transfer of Feed portion-1, the M of Feed portion-1 will be equally distributed between Funnel 2 and Funnel 4. Following the next transfer, it will be distributed in Funnels 1, 3, 5 in the ratio 1:2:1. Therefore, since M distributes equally between opposing phases, 12.5% will appear in the first L-product and 12.5% in the first H-product.

Meanwhile, 50% of the M content of Feed portion-1 has been joined by 100% of the M of Feed portion-3 in Funnel 3. Continuation of this reasoning leads to the conclusion that the M content of each funnel builds up to a limiting value which may be expressed in terms of the quantity Q present in a single portion of Feed. These limiting values are: Q for Funnel 1 and Funnel 5, $2Q$ for Funnel 2 and Funnel 4, and $3Q$ for Funnel 3.

When these limiting values have been reached, the system is operating at steady state *with respect to M which has an E of 1*.

The approach to steady state operation of a given system is a function of *E*. Therefore the system may be at "steady state" with respect to one solute present but not with respect to another. It has been shown that the number of through-puts required to approach steady state operation to a given approximation in such a system increases as *E* approaches unity, from either side (221). Therefore the behavior of the solute with *E* closest to unity may be used to establish the reliability of "steady state" data.

By definition, at steady state the quantity of solute M leaving the system in an L-product plus that in an H-product, must equal the quantity of M, Q_0 , in a single portion of Feed, that is:

$$Q_{L-P} + Q_{H-P} = Q_0 \quad (15)$$

Defining "fractional yields" as before:

$$F_L = Q_{L-P}/Q_0, \quad \Phi_H = Q_{H-P}/Q_0 \quad (16)$$

In an extension of the mathematical analysis of liquid-liquid extraction by Hunter and Nash (118, 119), Bush and Densen (33), Golumbic (96), Compere and Ryland (46), Auer and Gardner (9), Scheibel (240-242), and Peppard and Peppard (221), it has been shown by Peppard *et al.* (216) that for the general case of:

q contactors

Feed entry at n th contactor

Scrub entry at 1st contactor

Extractant entry at q th contactor

$RK = U$, in contactors 1, \dots , $(n-1)$

$RK = P$, in contactor n

$RK = E$, in contactors $(n+1)$, \dots , q

$$F_L = PU^{n-1} \sum_0^{q-n} E^i / \left[\sum_0^{n-1} U^i + PU^{n-1} \sum_0^{q-n} E^i \right] \quad (17)$$

$$\Phi_H = \sum_0^{n-1} U^i / \left[\sum_0^{n-1} U^i + PU^{n-1} \sum_0^{q-n} E^i \right] \quad (18)$$

Assuming that all solutes are present in tracer-level concentration and that opposing L and H phases are mutually pre-equilibrated except with respect to the solutes to be studied, no volume changes will occur throughout the system. Therefore, since the Feed must be introduced in a

finite volume, P may be made equal to U or to E , dependent upon the Feed being L phase or H phase, respectively.

If the volume of Feed is a sufficiently small fraction of V and of RV and if K is truly constant, then, approximately,

$$U = P = E$$

and Eqs. (17) and (18) approach:

$$F_L = E^n \sum_0^{q-n} E^i / \left[\sum_0^{n-1} E^i + E^n \sum_0^{q-n} E^i \right] \quad (19)$$

$$\Phi_H = \sum_0^{n-1} E^i / \left[\sum_0^{n-1} E^i + E^n \sum_0^{q-n} E^i \right] \quad (20)$$

Specifically, for a system with an odd number of contactors (stages) with Feed entry at the center contactor, i.e., $q = 2n - 1$, these equations reduce to the readily manipulated forms:

$$F_L = E^n / (1 + E^n) \quad (21)$$

$$\Phi_H = 1 / (1 + E^n) \quad (22)$$

For the system presented in Fig. 6, therefore, in which the Feed entry is at number 3 contactor of an assembly of five contactors:

$$F_L = E^3 / (1 + E^3) \quad (23)$$

$$\Phi_H = 1 / (1 + E^3) \quad (24)$$

The mutual separability of two solutes, M and N, $K_M > K_N$, is illustrated in Table V for β values of 2, 4, and 8. Feed entry is at the center stage, $E_M = 1/E_N$, and Eqs. (21) and (22) are applicable. Note that, as the result of this symmetrical method of operation, the "product N" in the H phase is of the same relative yield and purity as the "product M" in the L phase.

With a β value of 2, each solute is obtained in 66.7% yield with a DF of 2.0 with respect to the other solute in a 3-stage system. A 27-stage system is required to produce a 99.2% yield of product with a DF of 127.

With a β value of 8, products in 99.8% yield with DF values of 512 are obtained in an 11-stage system; in a 27-stage system, products in greater than 99.99% yield with DF values of 2.1×10^6 are obtained.

3. Applications

Specific applications of countercurrent extraction to the mutual separation of lanthanides(III) may be envisioned by reference to Table V and Fig. 5. In Fig. 5, the variation of $\log K$ with atomic number for lantha-

TABLE V
THEORETICAL MUTUAL SEPARABILITY OF SOLUTES M AND N,
WITH VARIOUS β VALUES, AS EXPRESSED BY F_L AND Φ_H ^a

$2n - 1$		M		N	
β	(q)	F_L	Φ_H	F_L	Φ_H
2	3	0.6667	0.3333	0.3333	0.6667
	7	0.8000	0.2000	0.2000	0.8000
	11	0.8889	0.1111	0.1111	0.8889
	15	0.9412	0.05882	0.05882	0.9412
	19	0.9697	0.03030	0.03030	0.9697
	23	0.9846	0.01538	0.01538	0.9846
	27	0.9922	7.752×10^{-3}	7.752×10^{-3}	0.9922
4	3	0.8000	0.2000	0.2000	0.8000
	7	0.9412	0.05882	0.05882	0.9412
	11	0.9846	0.01538	0.01538	0.9846
	15	0.9961	3.891×10^{-3}	3.891×10^{-3}	0.9961
	19	0.9990	9.756×10^{-4}	9.756×10^{-4}	0.9990
	23	0.9998	2.440×10^{-4}	2.440×10^{-4}	0.9998
	27	>0.9999	6.103×10^{-5}	6.103×10^{-5}	>0.9999
8	3	0.8889	0.1111	0.1111	0.8889
	7	0.9846	0.01538	0.01538	0.9846
	11	0.9980	1.949×10^{-3}	1.949×10^{-3}	0.9980
	15	0.9998	2.440×10^{-4}	2.440×10^{-4}	0.9998
	19	>0.9999	3.052×10^{-5}	3.052×10^{-5}	>0.9999
	23	>0.9999	3.815×10^{-6}	3.815×10^{-6}	>0.9999
	27	>0.9999	4.768×10^{-7}	4.768×10^{-7}	>0.9999

^a Feed entry at n th stage of $(2n - 1)$ stages, $U = P = E$, $E_M = 1/E_N$. $F_L = E^n / (1 + E^n)$, $\Phi_H = 1 / (1 + E^n)$.

nides(III) is shown for selected systems exhibiting widely differing separations possibilities.

Curve (B) is essentially two straight lines joining at approximately $Z = 64$ (gadolinium) (113). The steep left-hand portion represents a value of r (i.e., β for adjacent members) of approximately 2.0. Therefore, in this region, a pair of elements differing by one, two, and three in atomic numbers will have β values approximating 2, 4, and 8, i.e. β^1 , β^2 , β^3 , which are the values treated in Table V.

Curve (D) represents the same basic chemical system as Curve (B), with different values of the operating variables (199). The plot is approximately symmetrical about $Z = 64$. Therefore, for each element on the left leg of the curve, there is a matching element of essentially the same K value on the right leg. Obviously the separations applications of such a system are limited.

Mathematically, curve (C) (208) resembles the curve which would result by turning curve (B) through 180° about an axis passing through the ends. That is, the right leg now offers separations possibilities, whereas the left is unpromising.

Curve (E) exhibits a maximum followed by a minimum (177). The total range of K values is approximately 8. (In a system recently reported (176) in which the curve is similar, the total range of K values is less than 4.)

Curve (A) represents a nearly constant r value for adjacent members of 2.8 throughout the lanthanide series (209). The total range of K values is 1×10^6 .

A second system, with a straight-line plot and indicating an r of 2.5, has been reported (217).

A third promising system, with a "straight line of best fit plot" indicating an r for adjacent members of 2.7 and having a total K range of 1×10^6 , is reported to exhibit an odd-even effect (213). Selected specific respective β values are: Tm(69)/Er(68), 1.5; Er(68)/Ho(67), 6.7; Tm(69)/Ho(67), 10. The 1.5 is discouragingly small, the 6.7 is far better than any previous r , and 10 is the largest r^2 value reported.

Although it is evident that adjacent members of the lanthanide series, in the trivalent state, may be separated mutually by liquid-liquid extraction, it is also evident that the amount of manipulation required in using manually operated equipment is prohibitive. Fortunately, the "continuous flow" analog of the "intermittent flow" system pictured in Fig. 6 has been automated.

One device utilizing continuous flow is the vertical column in which the barren H phase is introduced at the top and flows downward, the barren L phase is introduced at the bottom and flows upward, and the Feed is introduced at an intermediate point. The designs of such columns differ widely, including packed, rotating, and oscillating types (273, 274, 277), but the function is always the same: to allow H and L phases to intimately mix, disengage, and flow countercurrently, each infinitesimal portion of each phase then to repeat the cycle. The two products issue from the ends of the column.

Another device, of wide popularity, is the mixer-settler (273, 274, 276), which in essence is an alternating assembly of pairs of mixing and settling chambers. The arrangement is such that the physical mixture of phases from the mixing chamber of stage X flows into a settling chamber from which the discrete L and H phases then flow, respectively, into the mixing chambers of stages $(X - 1)$ and $(X + 1)$. The net result is that the L and H phases flow countercurrently and continuously. The barren L and H phases are introduced at the terminal stages, from which the two products also issue; the Feed is introduced at an intermediate stage.

D. COMPARISON OF "PUSH-THROUGH" AND "COUNTERCURRENT EXTRACTION" METHODS OF OPERATION

A comparison of "push-through" and "countercurrent extraction" techniques, with respect to areas in which one is manifestly superior to the other, is instructive.

The former has become widely accepted by analytical chemists and nuclear chemists because of its easy implementation, if a chemical system exhibiting a sufficiently large β is available. Even though a quantitative yield of the desired product may not be attainable in a system with only a few contactors, frequently the yield may be determined accurately and be sufficiently reproducible to permit use of a trustworthy correction or normalization factor. Consequently, accurate analysis is possible. Such an extraction-separation may be made solely for the purpose of eliminating interfering elements, or for effecting a concentration of the component to be determined, or for both purposes.

Sometimes a high DF with respect to one or more contaminants is the only requirement, yield being of no concern. For example, suppose an inexpensive, readily available radionuclide, A, is contaminated with radionuclide B which has a K one ninth that of A. If the E values are set at 3 and $1/3$, a single extraction, followed by 11 scrubs, will produce A in 3.2% yield with a DF of 5×10^5 with respect to B. If two contactors (i.e., two portions of L phase) and a total of 12 portions of H phase are employed, A will be obtained in 12.8% yield with a DF of 2×10^6 . Such a separations approach is of obvious application in obtaining a sample of radionuclide for disintegration scheme studies and half-life determination and in securing a "pure" sample for radiotracing experiments.

If the β value is sufficiently large and if the E values are properly related to unity, both high yield and large DF may be obtained with a single contactor and multiple scrubbing, as illustrated by the purification of Np based upon the data of Fig. 4.

If the β value is in the neighborhood of 3 or less, countercurrent extraction is the more feasible of the two techniques. This is especially true if the mutual separation of M and N is required, or if only M of a mixture of M, N, O, P . . . is a desired product. In general, it is the preferred "production," as contrasted with "research," method of operation.

Consider an example from actinide technology. The mutual separation of americium (Am, $Z = 95$) and curium (Cm, $Z = 96$) is a challenging problem whose solution is of great importance. A variety of uses for Cm, produced by neutron bombardment of Am, have been proposed. These include power supplies for satellites and other devices requiring a self-contained, dependable, long-lived, rugged, and light-weight energy source.

Further bombardment of Cm by neutrons and by other fundamental particles to produce radionuclides for basic studies is of importance also (244).

In many instances the utilization of Cm requires a preceding Cm-Am separation. Sometimes a high DF is required, but a low yield may be tolerated. In other cases a high yield is of prime importance, but a moderate DF value will suffice. In still other cases both high yield and a large DF are considered fundamental to the success of the proposed utilization.

Although few data for both Am and Cm in liquid-liquid extraction systems have been reported, it appears that the β value is in general less than 2, Cm extracting the better in most systems (120). If a β value of 2 may be realized in a system with acceptable physical operating characteristics, then mutual Cm-Am separation by countercurrent extraction, employing automatic equipment such as a mixer-settler, is attainable, as may be seen by reference to Table V.

Although there appears little hope of stabilizing Cm at any oxidation state other than the trivalent in a system employing an aqueous phase (267), the existence of Am as Am(VI) in aqueous solution has been well established (8, 289). Consequently an attractive possibility in effecting the Cm-Am separation is a system separating Am(VI) from Cm(III) (267). From the data of Table IV and the pertinent discussion of the effect of oxidation state upon K , it may be predicted that a liquid-liquid extraction system may be devised in which the β for Am(VI) with respect to Am(III), and therefore for Am(VI) with respect to Cm(III), should be in the range 10^2 – 10^3 or perhaps even higher.

Such predictions have not been realized effectually, because of the difficulty encountered in maintaining Am as Am(VI) in the extraction system. In the author's laboratory, it has been found difficult to maintain ^{241}Am as Am(VI) in an aqueous phase if the Am concentration is appreciably below 0.1 mg per ml. This difficulty becomes more pronounced as the Am concentration becomes lower. Consequently, in a system in which Am(VI) extracts far better than does Cm(III), the Am(VI) extract may be scrubbed to remove contaminant Cm(III), thereby producing a "pure" Am product. However, multiple extraction to remove contaminant Am(VI) from Cm(III) fails, because of the instability of Am(VI) at low concentration. Therefore a pure Cm product cannot be obtained.

Therefore, although Cm-Am separation based upon different states of oxidation of the two elements appears promising, successful application awaits development of a system in which Am(VI) is stable at low concentration.

Meanwhile, mutual separation of Cm and Am in a system showing a β value of 2 is feasible, using countercurrent extraction. With a β of 4 (see Table V) the difficulty of the problem is decreased dramatically.

It is suggested that β values of 4 or greater might be realized if the dual effects of differential extractability and of differential aqueous phase complexing of the "bare" M(III) ions can be made mutually reinforcing. Other possibilities are systems in which one of these elements extracts as a "mixed complex" and the other does not, possibly as $\text{MX}(\text{extnt.})_2$ and $\text{M}(\text{extnt.})_3$, where X is Cl^- , ClO_4^- , NO_3^- , etc., or in which the extractant dependencies for the two elements differ, the extracted entities perhaps being $\text{M}(\text{extnt.})_3$ and $\text{H}[\text{M}(\text{extnt.})_4]$. These approaches are presently under investigation at the author's laboratory.

IV. Systems Involving Neutral Phosphorus-Based Extractants

A. MONONUCLEAR EXTRACTANTS

Extraction with neutral extractants, presumably embodying the equivalent of ion pair association plus true metal-extractant coordination, has been treated in detail by Diamond and Tuck (59). To the historically important and still valuable ethers, ketones, alcohols, and carboxylic esters has been added a wide range of neutral phosphorus-based extractants. These are listed in general form in Table VI, along with other phosphorus compounds, some of which have also been reported as extractants, which are included for structural comparisons.

The vertical columns, identified as A, B, and C, of Table VI, classify the phosphorus-based compounds as neutral, monoacidic, and diacidic by

TABLE VI
GENERAL CLASSIFICATION^a OF MONONUCLEAR PHOSPHORUS-BASED "EXTRACTANTS,"
PROVED AND POTENTIAL

Bonding class	Neutral A	Monoacidic B	Diacidic C
1	$(\text{GO})_3\text{P}$	$[(\text{GO})_2\text{P}(\text{OH})]^b$	$[(\text{GO})\text{P}(\text{OH})_2]^b$
2	$(\text{GO})_3\text{PO}$	$(\text{GO})_2\text{PO}(\text{OH})$	$(\text{GO})\text{PO}(\text{OH})_2$
3	$(\text{GO})_2(\text{G})\text{PO}$	$(\text{GO})(\text{G})\text{PO}(\text{OH})$	$(\text{G})\text{PO}(\text{OH})_2$
4	$(\text{GO})(\text{G})_2\text{PO}$	$(\text{G})_2\text{PO}(\text{OH})$	—
5	$(\text{G})_3\text{PO}$	—	—
6	$(\text{GO})_2(\text{H})\text{PO}$	$(\text{GO})(\text{H})\text{PO}(\text{OH})$	—
7	$(\text{GO})(\text{G})(\text{H})\text{PO}$	$(\text{G})(\text{H})\text{PO}(\text{OH})$	—
8	$(\text{G})_2\text{HPO}$	—	—
9	$(\text{GO})(\text{H})_2\text{PO}$	—	—
10	$(\text{G})(\text{H})_2\text{PO}$	—	—

^a G is a generalized organic group containing a C atom attached directly to P or to an oxygen atom which is attached to P. For simplicity, G, G', and G'' have been represented as G, it being understood, for example, that $(\text{GO})(\text{G})\text{PO}(\text{OH})$ may be $(\text{GO})(\text{G}')\text{PO}(\text{OH})$, and $(\text{GO})(\text{G})_2\text{PO}$ may be $(\text{GO})(\text{G}')(\text{G}'')\text{PO}$, etc.

^b Brackets indicate nonexistence of this structure, Class 1B and Class 1C being found, respectively, as Class 6A and Class 6B.

reference to the formula. The horizontal groupings, identified by the numerals 1, 2, . . . 10, are based upon types of bond involved. (Class 1 includes "tricoordinate" phosphorus and all others "tetracoordinate" phosphorus, assuming the simple monomeric formula.)

For example, Class 1 and Class 2 involve no C-P or H-P bonds; Class 3, one C-P bond; Class 4, two C-P bonds; Class 7, one C-P bond and one H-P bond; Class 9, two H-P bonds; etc. In general, the nomenclature which will be used in referring to these compounds is that used in *Chemical Abstracts*.

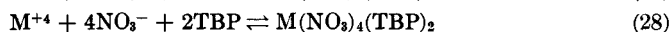
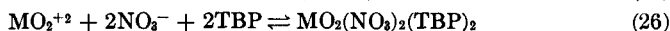
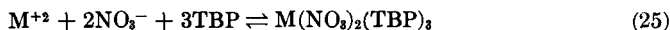
The most widely studied of these neutral phosphorus-based extractants is tributyl phosphate, i.e., tri-*n*-butyl phosphate, $(n\text{-C}_4\text{H}_9\text{O})_3\text{PO}$, an example of Class 2A of Table VI. Accepted usage has established TBP as the symbolic representation of this compound.

It is generally assumed to function as an extractant through metal coordination involving the unique oxygen (32), thereby occupying one coordination position on the metal (111). For example, Healy and McKay (111) consider Am(III) to be hexacoordinate in the extracted species, $\text{Am}(\text{NO}_3)_3(\text{TBP})_3$.

In some studies and applications, undiluted TBP has been employed. However, the extractant phase is more generally a solution of TBP in a carrier diluent such as an aliphatic or aromatic hydrocarbon or carbon tetrachloride (the term carrier diluent is used, rather than inert diluent, since the *K* for a given element under otherwise identical sets of conditions may vary widely as the diluent is changed) (4, 270).

The first recorded instance of the application of TBP as an extractant for metal ions was the extraction of Ce(IV) from an aqueous nitrate phase into undiluted TBP, reported by Warf (290).

Typical extraction stoichiometries from an aqueous nitrate phase might be represented as



the charged species being considered to be in the aqueous phase and the uncharged in the organic phase, respectively assumed to be H and L phases. (Whether the organic is L or H phase is dependent upon the diluent employed and the nature of the aqueous phase, i.e., salt content, etc. Usually the TBP extractant phase is the L phase.)

Extracted metallic species shown to conform to these stoichiometries are (Eq. 25) Co(II) (110); (Eq. 26) U(VI), Np(VI), and Pu(VI) (111); (Eq. 27) Am(III) and Y(III) (111), Pu(III) (22), and lanthanides(III) in

general (113, 239); and (Eq. 28) Th(IV), Np(IV), and Pu(IV) (2), Zr(IV) (1).

Consider the extraction represented by Eq. (26). If MO_2^{+2} is the only M(VI) species present in the aqueous phase and $\text{MO}_2(\text{NO}_3)_2(\text{TBP})_2$ the only M(VI) species present in the organic phase, then

$$K = [\text{MO}_2(\text{NO}_3)_2(\text{TBP})_2]_{\text{O}} / [\text{MO}_2^{+2}]_{\text{A}} \quad (29)$$

Hence, from mass law consideration,

$$K = k[\text{NO}_3^-]_{\text{A}}^2[\text{TBP}]_{\text{O}}^2 \quad (30)$$

The assumption that $K \propto [\text{TBP}]^q$ was utilized in deriving all of the quoted stoichiometries. However, whether the K is proportional to $[\text{NO}_3^-]^p$ is dependent upon whether appreciable complexing of the metal by nitrate occurs in the aqueous phase.

The complexing of UO_2^{+2} by nitrate at unit ionic strength is small (55), and therefore Eq. (30) holds very well for both the NO_3^- and TBP for U(VI) (212). On the other hand, complexing of Th(IV) by nitrate in the aqueous phase may not be ignored (56, 90, 91, 304). Therefore, the K for Th is expressed as

$$K = [\text{Th}(\text{NO}_3)_4(\text{TBP})_2] / \{[\text{Th}^{+4}] + [\text{Th}(\text{NO}_3)^{+3}] + \dots\} \quad (31)$$

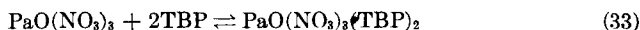
from which it follows that

$$K = k\{1 + k_1[\text{NO}_3^-] + \dots\}^{-1}[\text{NO}_3^-]^4[\text{TBP}]^2 \quad (32)$$

where k_1 is the stability constant for $\text{Th}(\text{NO}_3)^{+3}$, etc. Fomin and Maiorova (90, 91) have used a TBP vs. aqueous nitrate extraction system in determining the stability constants of the various nitrate complexes of Th.

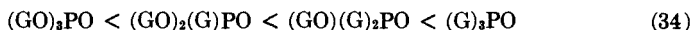
In addition to M(II,III,IV,VI), M(V) as exemplified by Pa(V) is of both practical and theoretical importance in TBP vs. HNO_3 extraction systems (106). Hardy *et al.* (106) reported the K for Pa(V) into a solution of TBP in odorless kerosene from aqueous HNO_3 solutions to be second-power dependent upon the concentration of TBP. They suggest the possibility that a series of nitrate complexes, ranging from $\text{Pa}(\text{OH})_2(\text{NO}_3)^{+2}$ to $\text{Pa}(\text{OH})_2(\text{NO}_3)_4^{-1}$, in rapid equilibrium with one another, are present in the aqueous phase and that $\text{Pa}(\text{OH})_2(\text{NO}_3)_3$ is extracted by TBP. (For purposes of this discussion, the equivalence of $\text{Pa}(\text{OH})_2^{+3}$ and PaO^{+3} is assumed.)

Accordingly, in terms of concentration of nitrate ion and of TBP, the equation for the extraction of Pa(V) is of the form of Eq. (32). However, it is perhaps more instructive to represent the extraction, as postulated by Hardy *et al.* (106), as:



An extensive investigation of 100% TBP (i.e., without diluent) as an extractant for metals from solutions of HNO_3 and $\text{Ca}(\text{NO}_3)_2$ was reported by Bernström and Rydberg (21). The cations studied were those of $\text{Ca}(\text{II})$, $\text{Sr}(\text{II})$, $\text{La}(\text{III})$, $\text{Zr}(\text{IV})$, $\text{Th}(\text{IV})$, $\text{Pu}(\text{IV})$, $\text{Nb}(\text{V})$, $\text{U}(\text{VI})$, and $\text{Pu}(\text{VI})$. The extraction curves were “. . . discussed with respect to the different complexes formed and to the possibility of using the investigated systems for separating plutonium and uranium from the fission products.”

Extractants of Class 5A have been shown to function much as those of Class 2A, except that for identical G groups the phosphine oxides (Class 5A) are better extractants than the phosphates (Class 2A). Assuming the extracting ability of the molecule to be determined by the ability of the oxygen atom of the $\text{P} \rightarrow \text{O}$ to accept hydrogen bonds, i.e., by the basicity of this oxygen, the K , for a given metallic cation in an otherwise fixed system of extractant (in carrier diluent) vs. an aqueous nitrate phase, should increase with successive removal of O atoms, in the sequence:



This was first shown to be true for the extraction of $\text{U}(\text{VI})$ and $\text{Pu}(\text{IV})$ by Burger (32), who correlated the K values with phosphoryl-bond stretching frequencies.

As TBP is the most widely studied phosphate, TOPO, tri-*n*-octyl phosphine oxide, $(n\text{-C}_8\text{H}_{17})_3\text{PO}$, is the most frequently reported phosphine oxide in metals extraction studies. In general, Eqs. (26–28) are applicable. For example, in a TOPO vs. aqueous nitrate system, Ishimori *et al.* (134) found the K values for $\text{Am}(\text{III})$ and $\text{Eu}(\text{III})$ to be essentially third-power extractant dependent; Martin *et al.* (173) reported the K values for $\text{Pu}(\text{IV})$ and $\text{Pu}(\text{VI})$ as second-power extractant dependent. Similarly, Saisho (235) reported second-power extractant dependencies for $\text{Zr}(\text{IV})$ and $\text{Hf}(\text{IV})$. However, Zingaro and White (305) found a third-power TOPO dependency for $\text{Th}(\text{IV})$, to be compared with the second-power TBP dependency.

The higher K for a given metallic cation in an otherwise identical system shown by phosphine oxides (Class 5A) as compared with phosphates (Class 2A) is paralleled by a higher K for HNO_3 (292). Consequently, in the interpretation of extractant and nitrate dependency data, corrections for tie-up of extractant by HNO_3 are even more important than in TBP vs. aqueous nitrate systems.

A study of tri-*n*-butyl phosphine oxide, $(n\text{-C}_4\text{H}_9)_3\text{PO}$ (TBPO), in carbon tetrachloride as extractant for $\text{Pu}(\text{III})$ and $\text{Pu}(\text{IV})$ from HNO_3 has been reported by Umezawa (278).

The monograph by White and Ross (292) reviews a large portion of the TOPO literature preceding 1961. From this review it is evident that TOPO vs. aqueous mineral acid systems offers great promise in separations of

interest to the nuclear chemist. However, it must be emphasized that, for many separations applications, ridding the TOPO of acidic impurities is imperative. In the author's laboratory, a sample of TOPO obtained from a commercial source showed zero titer in a titration with standard NaOH. However, a portion of this was treated by a procedure designed to remove acidic impurities, possibly di-*n*-octyl phosphinic acid (see Class 4B of Table VI). Under otherwise identical conditions, ^{230}Th was extracted from an aqueous nitrate solution by the purified sample with a K of 0.2 and by the "as received" sample with a K of 7×10^2 .

Dialkyl alkyl phosphonates (Class 3A) have been studied as extractants, from aqueous mineral acids, of U(VI) (212, 250, 264), Mo(VI) (194), Th(IV) (166, 250), and Zr(IV) and Hf(IV) (299).

Burger (32) reported the extraction of Pu(IV) and Pu(VI) from an aqueous nitrate phase by butyl dibutyl phosphinate and by ethyl dihexyl phosphinate, examples of Class 4A. However, studies of members of this class are sparse, probably because the compounds have not been readily available.

How widely applicable the proposed generalization of Eq. (34) will prove, when tested for a variety of metallic cations for a large range of electronegativities for G, for both minimal and maximal steric effects in G, and for systems employing various diluents, should prove of great interest. Compounds of Classes 2A, 3A, and 5A are commercially available. Certain Class 4B compounds are commercially available and may be esterified by the carbodiimide technique (149-151) to form the corresponding Class 4A compound. Consequently the initial phases of such a study should not prove difficult.

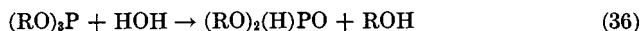
Of the remaining neutral, or A, compounds of Table VI, only those of Class 1A have been reported as extractants, to the author's knowledge. Handley and Dean (104) studied the extraction of Cu(I) halides from an aqueous halide phase into a solution of triphenyl phosphite, $(\text{C}_6\text{H}_5\text{O})_3\text{P}$, in carbon tetrachloride. From their saturation data, indicating a 1:1 ratio of extractant to Cu in the extracted entity, and from data on extraction of bromide-82 with the Cu(I), it may be concluded that the extraction stoichiometry is:



Presumably the bonding is through the electron pair on the P, but this has not been demonstrated.

It should be pointed out that such a study is possible because of the stability of triphenyl phosphite in an aqueous mineral acid system. Presumably stability is to be expected of other aromatic phosphites also. However, the investigation cannot be extended to include alkyl phosphites,

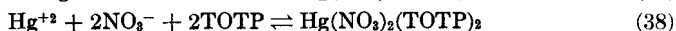
because they react in contact with aqueous mineral acid (7), to form members of Class 6A:



The $(\text{RO})_2(\text{H})\text{PO}$ may very well be a valuable extractant in its own right, but it is important that its properties not be mistaken for those of $(\text{RO})_3\text{P}$. Postulation of the product as $(\text{RO})_2\text{P}(\text{OH})$ has been shown to be in error (6, 53). The structure is discussed at length by Doak and Freedman (60).

Although the utility of $(\text{GO})_3\text{P}$ in liquid-liquid extraction is limited by the instability of so many members, the corresponding compounds without C-O-P bonds, i.e. $(\text{G})_3\text{P}$, $(\text{G})_2(\text{H})\text{P}$, and $(\text{G})(\text{H})_2\text{P}$, may be widely applicable. Although these compounds have been studied as addends in coordination chemistry, they have not been exploited as extractants. If triphenyl phosphite, $(\text{C}_6\text{H}_5\text{O})_3\text{P}$, functions as an extractant because of the pair of electrons on the P, then presumably triphenyl phosphine, $(\text{C}_6\text{H}_5)_3\text{P}$, should be the better of the two extractants. (Triphenyl phosphine oxide, $(\text{C}_6\text{H}_5)_3\text{PO}$, is a far better extractant than is triphenyl phosphate, $(\text{C}_6\text{H}_5\text{O})_3\text{PO}$.)

Monothio compounds, in which S replaces the unique O of the Class A compounds of Table VI, should offer an entirely different range of separations possibilities, since the electron-donating tendency of S in the $\text{P} \rightarrow \text{S}$ group is very small compared with that of the O in the $\text{P} \rightarrow \text{O}$ group. Handley and Dean (103) have reported the extraction of Ag(I) and Hg(II) by triisooctyl thiophosphate, $(\text{C}_8\text{H}_{17}\text{O})_3\text{PS}$ (TOTP), from aqueous HNO_3 . From the observed extractant dependencies, they postulate:



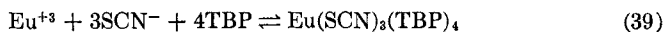
(These stoichiometries are not intended to imply first- and second-power nitrate dependencies of the respective distribution ratios, since nitrate dependencies at constant ionic strength were not reported.) The system was found to be highly selective for Ag(I) and Hg(II) from the 35 elements listed, including Ca(II), Zn(II), La(III), Th(IV), Zr(IV), Nb(V), and Mo(VI).

Although a large proportion of the "neutral phosphorus extractant" systems reported employ an aqueous nitrate phase, aqueous chloride, perchlorate, and thiocyanate phases have also been shown to be effective. Kertes and Halpern (148) showed TBP to extract U(VI) from an aqueous chloride solution as $\text{UO}_2\text{Cl}_2(\text{TBP})_2$. Peppard *et al.* demonstrated the mutual separation of Sc(III), Th(IV), and Zr(IV) (216) and of Th(IV), Pa(V), and U(VI) (207) in a TBP vs. HCl system. Reznik *et al.* (231) employed TBP vs. aqueous HNO_3 , HCl, and mixed HNO_3 -HCl phases in a study of Zr(IV)

extraction. They reported $\text{Zr}(\text{NO}_3)_4(\text{TBP})_2$ and $\text{ZrCl}_4(\text{TBP})_2$ and "mixed nitrate-chloride complexes" corresponding to $\text{Zr}(\text{NO}_3)_3\text{Cl}(\text{TBP})_2$ and $\text{Zr}(\text{NO}_3)_2\text{Cl}_2(\text{TBP})_2$ as the respective extracted species. Ishimori and Sammour (135) studied the countercurrent separation of fission products in the TBP vs. HCl system; Majumdar and De (164) report $\text{FeCl}_3(\text{TBP})_3$ and $\text{H}[\text{FeCl}_4(\text{TBP})_2]$ as extractable species from 2 *M* and 6 *M* HCl, respectively. Ishimori *et al.* (139) made "a radiochemical survey on the extraction behavior of almost sixty chemical elements" in the 1% TBPO, tributyl phosphine oxide, $(n\text{-C}_4\text{H}_9)_3\text{PO}$, in toluene vs. HCl system.

Distribution ratios for Ce(III), La(III), Y(III), Zr(IV), and Th(IV) from perchloric acid solution into TBP were reported by Siekierski (254). Hesford and McKay (114) postulated $\text{UO}_2(\text{ClO}_4)_2(\text{TBP})_2$ as an extracted entity in a TBP vs. aqueous perchlorate system but point out that other solvates may also form. Naito and Suzuki (192) report $\text{UO}_2(\text{ClO}_4)_2(\text{TBP})_4$.

Yoshida (301) studied the extraction of lanthanides(III) into a kerosene solution of TBP from an aqueous thiocyanate phase. He pictured the extraction of Eu(III) as:



His plot of $\log K$ vs. Z for the lanthanide(III) series, excepting Pm(III), has a saw-tooth appearance, suggestive of an odd-even effect, especially in the $Z = 62\text{--}69$ region.

The first odd-even effect in the extraction of lanthanides(III) to be noted was reported by Hesford *et al.* (113) for the TBP vs. dilute HNO_3 system. In reference to their observation of "an alternation in extractability between elements of odd and even atomic number" they state, "Our impression is . . . that a single smooth curve can always be drawn through the points for the odd- Z elements, but that there is often a discontinuity at gadolinium among the results for the even- Z elements."

Structural effects have been reported by Siddall in "The effects of altering alkyl substituents in trialkyl phosphates on the extraction of actinides" (251), and by Nomura and Hara in "The effect of organic substituents and structure of organophosphorus compounds on their extraction abilities for uranium" (197). Examples of specific metals separations applications of TBP systems are "Separating hafnium from zirconium, solvent extraction with tributyl phosphate" (49); "Separation of monazite rare earths by solvent extraction" (25); "Recovery of neptunium-237 from process residues by solvent extraction" (86); and "Separation of trans-curium elements from large quantities of curium, by liquid-liquid extraction" (129).

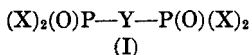
Ishimori and Sammour (136) report the separation of ^{233}U and ^{233}Pa from irradiated thorium in the tributyl phosphine oxide (TBPO) vs. HCl

system by a "discontinuous countercurrent extraction technique"; Siddall (252) devotes a chapter to "Solvent extraction processes based on tri-*n*-butyl phosphate."

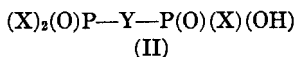
B. DINUCLEAR EXTRACTANTS

If neutral mononuclear phosphorus-based extractants function as coordinating ligands through the unique O, i.e. the O of $P \rightarrow O$, then presumably a dinuclear compound with the $P \rightarrow O$ groupings suitably joined to permit chelation through the two O atoms to the metal atom to be extracted should be an even more effective extractant.

Saisho (234) studied the extraction of Zr(IV), Y(III), and lanthanides(III) as nitrates by tetra-*n*-butyl ethylene diphosphonate (TBEDP), which is a representative of



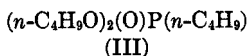
where Y is $-\text{CH}_2\text{CH}_2-$, and X is $n\text{-C}_4\text{H}_9\text{O}-$. Since the "TBEDP . . . was used without further purification," i.e., as received from a commercial supplier, it must be considered suspect with respect to acidic impurities. Such an acidic impurity, perhaps



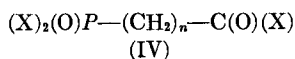
i.e., tri-*n*-butyl hydrogen ethylene diphosphonate, would, if present even in the parts per thousand range, probably be the dominant extractant for tracer-level radionuclides in the low acid range. In addition, it would probably impose an inverse hydrogen ion dependency.

Consequently, whether the high *K* values for lanthanides(III) in the acidity region of approximately 0.1–0.5 *M* HNO_3 are due to the main extractant or to acidic impurity or impurities is open to serious question, as pointed out by Siddall (253).

Siddall (253), working with the same extractant without diluent, found the *K* for Ce(III) to rise steadily from 0.4 *M* HNO_3 to 4 *M* HNO_3 , whereas Saisho reported the *K* to decrease in this range in the 0.2 *M* extractant (kerosene) vs. HNO_3 system. In a study of the effect of the length of Y, Siddall (253) used four compounds in which X was $n\text{-C}_4\text{H}_9\text{O}-$ and Y was $-\text{CH}_2-$, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$, and $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$. As extractants for Ce(III) from aqueous HNO_3 , the last two diphosphonates were only slightly superior to dibutyl butyl phosphonate, which may be written as



to emphasize the resemblance to the diphosphonate structure. At 5 *M* HNO₃, in the ethylene diphosphonate and the methylene diphosphonate systems, the *K* for Ce(III) was, respectively, 20 and 200 times that in the dibutyl butyl phosphonate system. Presumably a stable six-membered ring is formed by chelation of the methylene diphosphonate with a central M atom, resulting in a relatively high *K* value. However, as the ring size increases to 7, 8, and 9 members, the effectiveness of a diphosphonate approaches that of a phosphonate. In the same study, the effectiveness of a combined phosphoryl and carbonyl extractant was demonstrated for Ce(III), the compounds being

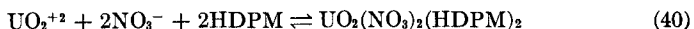


where *n* was 0 or 1, and X was *n*-C₄H₉O

The major objection to a diphosphonate as an extractant in basic studies is that contamination by an acidic impurity, which may well be the dominant extractant for a tracer-level metal, is difficult to avoid. (An extractant which is of acceptable purity at the beginning of a determination of *K* may undergo sufficient hydrolysis during equilibration with the aqueous mineral acid phase to form an acidic extractant which then controls the extraction.)

Consequently the diphosphine oxides, structurally equivalent to the diphosphonate except that X is attached to P by a C-P bond, should be more trustworthy in studies involving tracer-level metals. These compounds have been investigated as extractants by Mrochek *et al.* (190), who refer to them as *gem*-bis(disubstituted phosphinyl)alkanes. Specifically, bis(di-*n*-hexyl phosphinyl)methane, [(C₆H₁₃)₂P(O)]₂CH₂ (symbolized as HDPM), in 1,2-dichlorobenzene diluent was studied as an extractant for U(VI) from the four aqueous mineral acids HCl, HClO₄, H₂SO₄, and HNO₃. Throughout the region 1–9 *M* HClO₄, the *K* into 0.05 *M* extractant is greater than 4,000. Correspondingly, the *K* into 0.05 *M* TOPO, (*n*-C₈H₁₇)₃PO, decreases from 7 to 0.6. However, in the HNO₃ system, TOPO is somewhat the more effective of the two as an extractant for U(VI) throughout the 1–7 *M* acid region.

In the presence of excess extractant, the extraction of U(VI) from HNO₃ is described by:



Since UO₂⁺² has been shown to extract in the TBP vs. HNO₃ system with a second-power dependence upon TBP concentration, it might have been expected that Eq. (40) would involve only one HDPM. Mrochek *et al.* (190) report a monosolvate, but conclude that a disolvate is formed in the presence of excess extractant.

V. Systems Involving Acidic Phosphorus-Based Extractants

A. MONONUCLEAR EXTRACTANTS

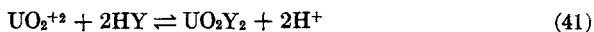
1. General

Acidic phosphorus-based extractants, as extractants for metallic cations, were discovered by accident. In at least two instances the discovery resulted from observation of interferences in TBP vs. mineral acid extraction systems.

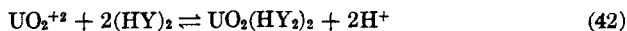
For example, in early experiments with tracer-level Th(IV) in the undiluted TBP vs. HCl system in the author's laboratory, the dependence of K upon concentration of HCl was studied, using eight approximately equi-spaced concentrations varying from 1.0 M to 12 M . In each experiment, the α -active ^{230}Th was initially in the aqueous phase. The K values increased from $\sim 4 \times 10^{-4}$ at 1.0 M HCl to ~ 20 at 12 M HCl. All of the separated organic extracts in the $K > 0.1$ range were set aside for determination of K values by the reverse or scrubbing technique the following day. Each of these extracts, approximately 18 hours old, was then contacted with the pertinent barren scrub (aqueous HCl of the same concentration as initially used). The resultant K values were all greater than 500. These "anomalous" reverse K values were shown to be due to hydrolysis products of TBP.

Concurrently, in U. S. Atomic Energy-sponsored investigations, certain interferences in the TBP vs. HNO_3 metals separation process were shown to be due to hydrolysis products of TBP.

Stewart and Hicks (269) first reported, in a U.S.A.E.C. classified document issued in 1950 and declassified in 1957, the extraction of U(VI) by dibutyl ether solutions of dibutyl phosphoric acid, $(n\text{-C}_4\text{H}_9\text{O})_2\text{PO}(\text{OH})$ (HDBP), and of monobutyl phosphoric acid, $(n\text{-C}_4\text{H}_9\text{O})\text{PO}(\text{OH})_2$ (H_2MBP), from an aqueous mineral acid phase. From their extractant dependency and hydrogen ion dependency data and the fact that K did not vary as the nitrate concentration varied from zero to 0.5 M , in a 0.5 M constant ionic strength nitrate plus perchlorate medium, they concluded that the extraction with HDBP could be represented as



where HY represents HDBP, and the charged species are in the aqueous phase and the uncharged species in the organic phase. Assuming HDBP to be dimeric in dibutyl ether, Eq. (41) should be rewritten as:



(Although no state of aggregation study has been reported for dibutyl

ether as a diluent, it seems probable, on the basis of diisopropyl ether data (77), that HDBP is dimeric in this diluent.)

The method of mutually separating mono- and diacidic esters of phosphoric acid reported by Stewart and Hicks (269) and Stewart and Crandall (268), based upon distribution between two mutually immiscible liquid phases such as dibutyl ether and diethylene glycol, has proved invaluable in obtaining extractants of the required purity.

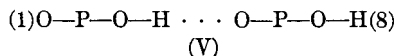
Scadden and Ballou (238) reported the use of a dibutyl ether solution of mixed mono- and dibutyl phosphoric acids in the isolation of zirconium and niobium from other fission products, and in the separation of the "yttrium group" lanthanides from the "lanthanum group" lanthanides.

Dyrssen *et al.* (68, 74, 77) have shown HDBP to be dimeric in *n*-hexane, carbon tetrachloride, chloroform, isopropyl ether, methyl isobutyl ketone, and TBP, and to be essentially monomeric in methyl isobutyl carbinol. Peppard *et al.* (200) have shown di-2-ethyl hexyl phosphoric acid, $(2\text{-C}_2\text{H}_5\cdot\text{C}_6\text{H}_{12}\text{O})_2\text{PO}(\text{OH})$ (HDEHP), to be dimeric and mono-2-ethyl hexyl phosphoric acid, $(2\text{-C}_2\text{H}_5\cdot\text{C}_6\text{H}_{12}\text{O})\text{PO}(\text{OH})_2$ (H_2MEHP), to be polymeric in dry benzene. They further reported both HDEHP and H_2MEHP to be monomeric in methyl alcohol and dimeric in acetone, and H_2MEHP to be hexameric in benzene (82). Baes (11) reported HDEHP as primarily dimeric (partially trimeric) in *n*-octane.

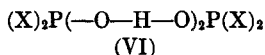
Peppard *et al.* (82) found several members of Class 3B, $(\text{GO})(\text{G})\text{PO}(\text{OH})$, to be dimeric in benzene. Kosolapoff and Powell (155) reported $(\text{G})_2\text{PO}(\text{OH})$, representative of Class 4B, to be dimeric in naphthalene; they also reported $(\text{G})(\text{H})\text{PO}(\text{OH})$, Class 7B, to be trimers and $(\text{G})\text{PO}(\text{OH})_2$, Class 3C, to be polymers approximating hexamers in naphthalene.

Generalizing from the examples of Table VI and the reported states of aggregation, letting X represent G or GO, the compounds $(\text{X})_2\text{PO}(\text{OH})$ tend to approximate dimers in all diluents except alcohols, in which they are monomers; the compounds $(\text{X})\text{PO}(\text{OH})_2$ tend to approximate (or exceed) hexamers in hydrocarbons, etc., dimers in ketones, and monomers in alcohols. It must be realized that these generalizations are based upon a very modest collection of data.

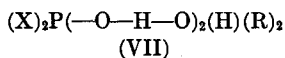
The dimers of $(\text{X})_2\text{PO}(\text{OH})$ are considered to be based upon the $\text{PO}(\text{OH})$ function, by analogy with the dimers of carboxylic acids based upon the $\text{CO}(\text{OH})$ function. The bonding is pictured as



with the O(1) joined in similar fashion to the H(8) to form an eight-membered ring which may be shown, without distinction as to the origin of the H atoms, for the molecule as:



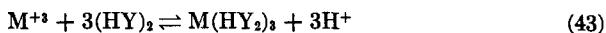
Perhaps the monomer, in alcohol, should be postulated similarly as



assuming the formula $X_2PO(OH) \cdot 2ROH$.

2. Monoacidic Extractants, $(X)_2PO(OH)$

The studies of HDBP by Stewart and Hicks (269) and Scadden and Ballou (238) were followed by an investigation of di-2-ethyl hexyl phosphoric acid, $(2-C_2H_5 \cdot C_6H_{12}O)_2PO(OH)$ (HDEHP), as an extractant for lanthanides(III) by Peppard *et al.* (217). The $\log K$ vs. Z curve in the 0.75 F HDEHP (toluene) vs. 0.5 M HCl system was represented as a straight line of slope 0.40, i.e., average separation factor for adjacent members of 2.5 (cf. Fig. 3). Their representation of the extraction is in error, since they were unaware of the dimeric nature of HDEHP. In a later paper (206) they represent the extraction as



analogous to Eq. (42).

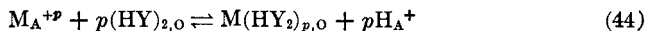
In both Eq. (42) and Eq. (43) and in others to be discussed, HY_2^- is to be considered equivalent to $Y^- \cdot HY$, so that $M(HY_2)_3$, $M(Y)(HY_2)_2(HY)$, $MY_2(HY_2)(HY)_2$, and $MY_3(HY)_3$ are alternate representations of the extracted species. The choice of HY_2^- in the formula as written is based upon the supposition, not in any way proved, that mono-ionized dimers are present in the extracted entity.

In a similar study of HDBP in dibutyl ether, Duyckaerts *et al.* (63) reported the separation factor for adjacent rare earths to be 2.6 in the "heavy" region and 1.95 in the "light." The plots are presented in a later paper (62). They found the extraction to be represented by Eq. (43) (63). The same extraction stoichiometry for Eu(III) in HDBP (diluent) vs. HNO_3 was found by Dyrssen and Liem (78) for n -hexane, carbon tetrachloride, chloroform, and diisopropyl ether as diluent. In methyl isobutyl carbinol, in which the HDBP is primarily monomeric, they postulated two extracted entities, MY_3 and $MY_3(HY)_3$, the latter being an alternative representation of $M(HY_2)_3$, and suggested that the former is dominant at low concentrations of extractant. Dyrssen (67) also showed the extraction of Y(III) from HNO_3 into a chloroform solution of HDBP to follow Eq. (43).

From the reports of Dyrssen and Krasovec (75) on HDBP vs. aqueous perchlorate, Baes *et al.* (13) on HDEHP vs. aqueous perchlorate, Sato

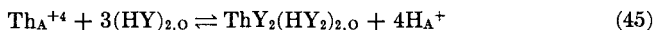
(236) on HDEHP vs. aqueous sulfate, and Peppard *et al.* (212) on HDEHP vs. aqueous perchlorate, nitrate, and chloride, the extraction of U(VI) in systems employing a nonmonomerizing diluent may be represented by Eq. (42).

Consideration of Eqs. (42–43) suggests the generalized expression



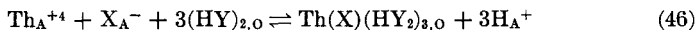
for the extraction of a cation with charge $+p$, the subscripts A and O referring, respectively, to the equilibrated aqueous and organic phases, and HY, in this instance, representing a Class 2B compound of Table VI, i.e., $(GO)_2PO(OH)$.

However, the K for the extraction of Th(IV) into a toluene solution of di[*p*-(1,1,3,3-tetramethyl butyl)phenyl] phosphoric acid (*p*-C₈H₁₇·C₆H₄O)₂-PO(OH) (HDO ϕ P), from aqueous perchlorate, chloride, and nitrate phases is third-power extractant dependent, not fourth-power. The expected inverse fourth-power hydrogen ion dependency is observed (214). The extraction is thus represented as



without intent to imply a proved structure of the extracted entity, which may be $ThY_4(HY)_2$, etc.

In an otherwise similar system in which HDEHP is the extractant, the extraction of Th(IV) from aqueous perchlorate and chloride phases of low acidity is represented by Eq. (45), but the extraction from an aqueous nitrate phase involves a "mixed complex" (214),



where $X^- = NO_3^-$.

At 0.1 M H^+ the K for Th(IV) from 1.0 M (HX + NaX) into a toluene solution of HDEHP of fixed concentration is in the approximate ratio 0.3:1:50 for $X = Cl^-$, ClO_4^- , NO_3^- , respectively. (The corresponding ratios in the HDO ϕ P system are approximately 0.3:1:0.2.)

Presumably in the HDEHP (toluene) vs. aqueous nitrate system the extraction stoichiometries represented by Eq. (45) and Eq. (46) are both involved, but the latter is dominant throughout the range of hydrogen ion concentrations investigated. The data for the chloride and perchlorate systems in the high concentration of hydrogen ion region are consistent with the postulation of both $ThY_2(HY_2)_2$ and $Th(X)(HY_2)_3$, the dominant extraction being expressed by Eq. (45) in the low acidity region and by Eq. (46) in the high (214).

Dyrssen and Liem (79) in analogous studies with HDBP report the Th(IV) mixed perchlorate complex and mixed nitrate complex to extract essentially identically.

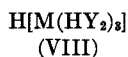
Dreze and Duyckaerts (61) report $\text{Th}(\text{NO}_3)_2(\text{HY}_2)_2$, where HY is di-*n*-butyl phosphoric acid (HDBP), as the extracted species in a benzene solution of HDBP.

In contrast to the K for Th(IV) which has an extractant dependency smaller than the charge on the cation, the K for Ca(II), Sr(II), and Ba(II) has an extractant dependency greater than the charge on the cation. In the HDEHP (xylene) vs. aqueous chloride system, the extraction of Ca(II) may be represented (215) as



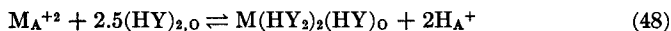
recalling that the extracted entity might be written alternatively as $\text{M}(\text{Y})(\text{HY}_2)(\text{HY})_3$, etc.

Considering the coordination number of Ca(II) to be 6, the extracted entity might be postulated as $\text{M}(\text{HY}_2)_2(\text{HY})_2$ containing two mono-ionized dimers, each occupying two coordination positions, and two un-ionized monomers, each occupying one, by analogy with the Sr(II) compound, $\text{Sr}(\text{oxine})_2(\text{H oxine})_2$, reported by Dyrssen (65). One difficulty presented by this postulation is that presumably there would be a "free" OH group, i.e., not hydrogen-bonded, on each of these un-ionized monomers. Considering the strong tendency toward hydrogen bond formation by $(\text{X})_2\text{PO}(\text{OH})$ (83), free OH groups seem unlikely. Perhaps one OH is hydrogen-bonded to the other, as in ROH dimers and trimers. If so, the structure would be formally similar to

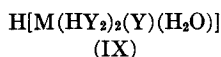


in which the "unique" H is coordinated to a specific O which then has a coordination number of 3.

This postulation must be modified in order to explain the 2.5-power extractant dependency of the K for Ca(II) and for Sr(II) in the HDOΦP (xylene) vs. aqueous chloride system (215):



One possibility is that the $\text{M}(\text{HY}_2)_2(\text{HY})$ contains 1 mole of H_2O , the formulation then being equivalent to

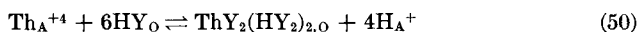


by analogy with compound VIII, it being understood again that the "unique" H is coordinated to one of the O atoms. In this system, the K for Ba(II) is 3.0-power extractant dependent (215).

In the same system, Eu(II) is extracted with a third-power extractant dependency, the extraction being represented by Eq. (47) (201). The ex-

traction of Eu(III) is also third-power extractant dependent, being represented by Eq. (43) (206).

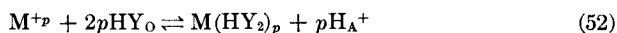
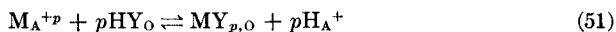
Mason *et al.* (176) studied the extraction of M^{+2} , M^{+3} , and Th^{+4} in the HDEHP (*n*-decyl alcohol) vs. aqueous chloride system. Since this extractant in alcohol solution is primarily monomeric, extractant dependencies less than the charge on the cation should be impossible unless the extracted species contains chloride. The extractant dependency of the K for Th(IV) was analyzed as a composite of fourth-power and sixth-power, the extraction being represented as:



Note that the extractant dependency in Eq. (50) is not twice that of Eq. (49) but twice that found in a "dimer mechanism" extraction, Eq. (45).

Similarly UO_2^{+2} was shown to extract with second-power and fourth-power extractant dependencies and lanthanides(III), Y(III), Sc(III), and Am(III) with third-power and sixth-power extractant dependencies. Both UO_2^{+2} and Ca^{+2} are extracted with second-power and fourth-power extractant dependencies in the HDO ϕ P (*n*-decyl alcohol) vs. aqueous chloride system (176).

Consequently the "monomeric" extraction of U(VI), Ca(II), lanthanides(III), Y(III), Sc(III), and Am(III) may be represented as:



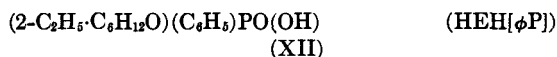
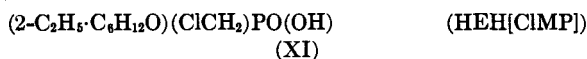
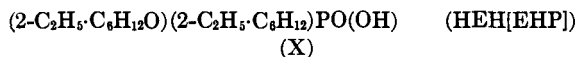
It is apparent that the extraction represented by Eq. (52) becomes more important, relative to that represented by Eq. (51), as the concentration of extractant is increased.

If the plot of observed K values, as a $\log K$ vs. $\log F$ of extractant plot, is analyzed into two straight-line plots corresponding to the extraction represented by Eqs. (51–52), the two straight lines intersect. The point of intersection, in terms of $\log F$ of extractant, varies with variation in M (III). In the lanthanide(III) series, this point of intersection shifts toward lower concentration of extractant with increasing Z .

As a consequence of this difference in operational extractant dependency of the K values for two lanthanides(III), the β for the pair of elements is a function of the concentration of extractant. For example, in the HDEHP (*n*-decyl alcohol) vs. 0.025 M HCl system, the β for Tm(III) with respect to Eu(III) is approximately 2 at 0.06 F HDEHP and approximately 100 at 0.6 F HDEHP. Exploitation of such differences in extractant dependencies for two elements in their mutual separation seems promising.

In both the HDO ϕ P and HDEHP systems, i.e., extractant (in *n*-decyl alcohol) vs. 0.025 *M* HCl, the plot of log *K* vs. *Z* for lanthanides(III) is best represented as separate odd-*Z* and even-*Z* curves.

Class 3B extractants (Table VI), (GO)(G)PO(OH), have not been investigated extensively, but reported studies indicate stoichiometries similar to those found in (GO)₂PO(OH) systems. For example (209), the extraction of Pm(III), Cm(III), and Cf(III) is represented by Eq. (43) in the HG[GP] (toluene) vs. aqueous chloride system, where HG[GP] is 2-ethyl hexyl hydrogen 2-ethyl hexyl phosphonate (HEH[EHP], X), 2-ethyl hexyl hydrogen chloromethyl phosphonate (HEH[CIMP], XI), or 2-ethyl hexyl hydrogen phenyl phosphonate (HEH[ϕ P], XII):

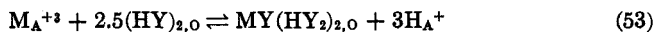


The HEH[ϕ P] (toluene) vs. 1.0 *M* (NaCl + HCl) system has been demonstrated to differentiate in favor of Cf with respect to Cm by a factor of approximately 105 (209, 210). This β value of 105 may be compared with that of 47 reported for the HDEHP (toluene) vs. 0.25 *M* HCl system (205).

In the 1.0 *F* HEH[ϕ P] (toluene) vs. 2.0 *M* HCl system (Fig. 5), the β for a given lanthanide(III) with respect to the adjacent member of lower *Z* is approximately 2.8 (209). With respect to β values throughout the lanthanide series, this is the most promising liquid-liquid extraction separations system yet reported.

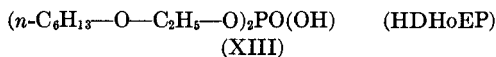
In Th(IV) experiments with HEH[EHP] (X), extraction of mixed complexes appears to be favored more than in HDEHP systems, the separate extracted species containing one nitrate group, two nitrate groups, one chloride group, and one perchlorate group being reported (220).

Like those of Class 3B, extractants of Class 4B, (G)₂PO(OH) (Table VI), have not been investigated in depth. In a study of di-*n*-octyl phosphinic acid, (*n*-C₈H₁₇)₂PO(OH) (H[DOP]), in benzene solution, the extractant dependency of *K* from an aqueous acidic chloride medium was found to be 2.0-power for U(VI) but 2.5-power, rather than the expected 3.0-power, for Ce(III), Eu(III), Tm(III), Yb(III), Y(III), Am(III), and Cm(III) (213). The extraction of U(VI) was found to follow Eq. (42), but that of the M(III) examples was represented as:



For comparison, it may be noted that the extraction of Eu(III) and Am(III) in the bis(hexoxy-ethyl) phosphoric acid (HDHoEP, XIII) in

benzene vs. aqueous perchlorate or chloride system (208) is also expressed by Eq. (53). Both H[DOP] (213) and HDHoEP (208) have been proved dimeric in dry benzene.



Blake *et al.* (24) showed the extraction of U(VI) from aqueous sulfate solution into a carbon tetrachloride solution of extractant to be better by a factor approximating 2 for (G)₂PO(OH) as compared with (GO)₂PO(OH), where G is *n*-C₈H₁₇ or 2-C₂H₅·C₆H₁₂.

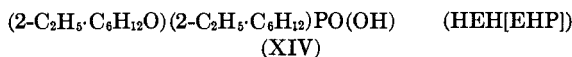
Baes (10) has surveyed "The extraction of metallic species by dialkyl phosphoric acids," treating the effects of varying the diluent, varying the G in (GO)₂PO(OH), adding synergists, and varying the ion size and ion charge of the cation to be extracted. Among more restricted reviews pertinent to this discussion are "Some mechanisms of extraction of M(II), (III), (IV), (VI) metals by acidic organophosphorus compounds" (202), "Structural aspects of organophosphorus extractants and their metallic complexes as deduced from spectral and molecular weight studies" (83), and "Types of acidic organophosphorus extractants and their applications to transuranic separations" (178).

"Mutual separation of yttrium-91 and promethium-147 by counter-current solvent extraction in pulse column" by use of the HDEHP (toluene) vs. aqueous HNO₃ system has been reported by Mandil *et al.* (165).

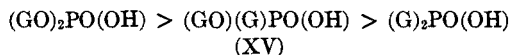
The HDOϕP (toluene) vs. 1.0 *M* (HX + HClO₄) system, where X⁻ is Cl⁻ or NO₃⁻, has been used in determining the stability constant of MX⁺² in the aqueous phase for La, Ce, Pr, Eu, Tm, Yb, Lu, and Am (211).

Blake *et al.* (24) reported "relative acidity" data, defined as apparent pH at half-neutralization in 70% ethanol, for a variety of (X)₂PO(OH), where X is G or GO. The respective values reported for (*n*-C₈H₁₇O)₂PO(OH) and (*n*-C₈H₁₇)₂PO(OH) are 2.9 and 5.2, and those for (2-C₂H₅·C₆H₁₂O)₂PO(OH) and (2-C₂H₅·C₆H₁₂)₂PO(OH) are 3.2 and 5.6. In a system employing carbon tetrachloride as diluent and an aqueous sulfate solution as opposing phase, the phosphinic acid, (G)₂PO(OH), extracted U(VI) with a *K* approximately twice that found for the dialkyl phosphate, (GO)₂PO(OH).

This small difference in *K* for U(VI) associated with an apparent acidity difference of approximately 2.3 p*K* units is surprising. In support of this finding, 2-ethyl hexyl hydrogen 2-ethyl hexyl phosphonate (HEH[EHP], XIV), which would be expected to have a p*K* between that of the corresponding phosphate and phosphinic acid, has been shown to extract U(VI) with a *K* approximately twice that shown by HDEHP for aqueous perchlorate, nitrate, or chloride solutions (212).



In contrast to U(VI), the M(III) elements reported by Peppard *et al.* (213) show a marked decrease in K as C-P bonds replace C-O-P, the order being:



Perhaps a detailed study of K for a variety of elements under a standard set of conditions as a function of the "acidity" of the extractant may furnish a clue concerning the bonding present in the extracted species. Consider the equation

$$K_{\text{obs}} = K_S F_{\text{ex}}^b / [\text{H}^+]_A^p \quad (54)$$

as relating the observed K , K_{obs} , of M^{+p} as a function of the concentration of extractant, F_{ex} , in the organic phase, expressed in formality units, and the concentration of hydrogen ion in the aqueous phase, $[\text{H}^+]_A$. It is evident that if the diluent, ionic strength of the aqueous phase, and the temperature are fixed, then K_S values for a given cation in systems involving different extractants may be compared if both p and b have the same values in each of the systems considered. (Note that p and b may be but are not necessarily equal to each other.)

Such a compilation of K_S values for a number of cations could then be considered as a function of the "acidity" of the extractant in the hope of finding useful correlations. A study of the "Variation of the $\text{p}K_A$ of $(\text{X})(\text{Y})\text{PO}(\text{OH})$ with X and Y in 75 and 95% ethanol" recently reported (204) may prove useful here. The average effect of interposing an oxygen atom between G and P to transform a G-P structure to a G-O-P structure was found to be -1.10 $\text{p}K$ units where G is cyclo-hexyl. Therefore the difference to be expected for two such interpositions is -2.20 $\text{p}K$ units. Specifically, for $(\text{cyclo-C}_6\text{H}_{11}\text{-O})_2\text{PO}(\text{OH})$ and $(\text{cyclo-C}_6\text{H}_{11})_2\text{PO}(\text{OH})$ the $\text{p}K$ values as measured are 3.81 and 5.92 (in 75% ethanol) and 4.43 and 6.64 (in 90% ethanol), the respective $\text{p}K$ differences corresponding to interposition of two oxygen atoms being -2.12 and -2.21 . These differences may be compared with the value of -2.3 observed by Blake for the *n*-octyl compounds (24).

In this $\text{p}K_A$ study, Peppard *et al.* (204) assigned a values to the groups phenoxy (ϕO), hydrogen (H), cyclo-hexoxy (CHO), phenyl (ϕ), and cyclo-hexyl (CH) to be used in the $\text{p}K_A$ expressions for $(\text{X})(\text{Y})\text{PO}(\text{OH})$:

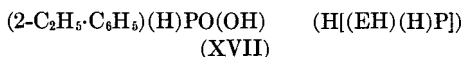
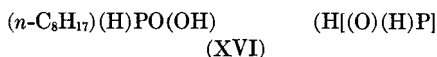
$$\text{p}K_A = 2.00 - \sum a, \text{ in } 75\% \text{ C}_2\text{H}_5\text{OH} \quad (55)$$

$$\text{p}K_A = 2.60 - \sum a, \text{ in } 95\% \text{ C}_2\text{H}_5\text{OH} \quad (56)$$

The values are: ϕO (0.30), H (0.00), CHO (-0.85), ϕ (-1.05), and CH (-1.95).

The difference in measured pK_A values for $(\text{cyclo-C}_6\text{H}_{11})_2\text{PO}(\text{OH})$ and $(\text{cyclo-C}_6\text{H}_{11})(\text{H})\text{PO}(\text{OH})$ is 2.01 in 75% ethanol and 2.11 in 95% ethanol. Consequently it would be expected that in general an alkyl hydrogen phosphinic acid (Class 7B of Table VI) would be considerably more acidic, perhaps by approximately two pK units, than the corresponding dialkyl phosphinic acid, Class 4B. (Analogously, an aryl hydrogen phosphinic acid might be predicted to be more acidic than the corresponding diaryl phosphinic acid by perhaps one pK unit.)

If it is assumed that increasing acidity, as measured by decreasing pK_A values, is accompanied by increasing K_S values, as defined by Eq. (54), for M(III) cations, then *n*-octyl hydrogen phosphinic acid, $\text{H}[(\text{O})(\text{H})\text{P}]$, and 2-ethyl hexyl hydrogen phosphinic acid, $\text{H}[(\text{EH})(\text{H})\text{P}]$, should be far better extractants than the corresponding dialkyl phosphinic acids.



Unpublished investigations in the author's laboratory show that in systems involving $\text{H}[(\text{O})(\text{H})\text{P}]$, XVI, in benzene vs. aqueous chloride phase, Am(III), Cm(III), and Pm(III) are extracted according to Eq. (43), assuming the extractant to be dimeric. However, the extractant dependency for lanthanides(III) decreases with increasing Z , being 3.0 for Pm, 2.7 for Eu, 2.3 for Tm, and 2.3 for Lu. The hydrogen ion dependencies are all inverse third-power. The variation of extractant dependency with Z is even more noticeable in the system utilizing $\text{H}[(\text{EH})(\text{H})\text{P}]$, XVII. Here, the power of the extractant dependency is: Ce (2.9), Pm (2.7), Eu (2.6), Tm (2.2), and Lu (2.2). The corresponding actinide values are: Am (2.7) and Cm (2.7).

As a result of the variation of extractant dependence with Z , the dependence being smaller at higher Z , the $\log K$ vs. Z curve for lanthanides(III) is "steeper" in the 0.0187 F extractant vs. 0.100 M HCl system than in the 0.300 F extractant vs. 0.25 M HCl system.

In a 0.10 F extractant (benzene) vs. 0.25 M HCl system, the K for Y(III) in the $\text{H}[(\text{O})(\text{H})\text{P}]$ system is at least 500 times as great as that in the $\text{H}[\text{DOP}]$ system. It is therefore imperative that the $\text{H}[\text{DOP}]$ used in studying tracer-level M(III) elements be scrupulously freed from $\text{H}[(\text{O})(\text{H})\text{P}]$.

Handley and Dean (105) report *O,O'*-dialkyl phosphorodithioc acids, $(\text{RO})_2\text{PS}(\text{SH})$, as extractants (in carbon tetrachloride) for metal ions from HCl and H_2SO_4 . In this "... preliminary survey of the distribution of elements as dialkyl phosphorodithioates into CCl_4 from HCl and H_2SO_4

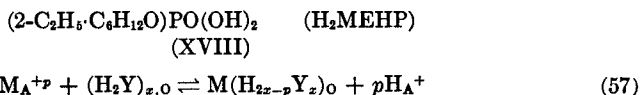
media . . . ,” 42 elements were studied. Stoichiometric parameters were not reported in detail except for Zn(II), for which the K was found to vary directly as the square of the concentration of extractant and inversely as the square of the hydrogen ion concentration.

3. Diacidic Extractants, $(X)PO(OH)_2$

Reported studies of $(X)PO(OH)_2$ compounds, either $(GO)PO(OH)_2$, Class 1C of Table VI, or $(G)PO(OH)_2$, Class 2C, as extractants for metallic cations are few.

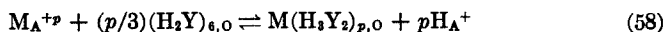
Blake *et al.* (24) presented extraction data for U(VI) from an aqueous sulfate phase into carbon tetrachloride or kerosene solutions of seven $(GO)PO(OH)_2$ samples. They point out, “In extractions by monoalkyl phosphoric and phosphonic acids, the U(VI) extraction coefficient varies as the first to second power of the extractant concentration. This indicates that the U(VI) extraction complexes contain at least as many organophosphorus groups as the aggregates of the unreacted organophosphoric acid. Since these monoalkyl acids (H_2X) are considerably more associated than the dialkyl acids, this means that the extraction complex cannot be the simple salt UO_2X or $UO_2(HX)_2$, but must contain additional molecules of the extractant.”

Peppard *et al.* (206) have postulated an “infinite polymer” mode of extraction of lanthanides(III), actinides(III), scandium(III), and yttrium(III) from aqueous mineral acid phases into a toluene solution of mono-2-ethyl hexyl phosphoric acid (H_2MEHP , XVIII). The extraction was expressed as



assuming that x is a large number, i.e., that H_2MEHP is a very large polymer in “wet” toluene, since it was shown that contacting a toluene solution of H_2MEHP with pure water results in the formation of a gel-like solid.

Alternatively, if it is assumed that $x = 6$ in the equilibrated organic phase, i.e., wet toluene, as it is in dry benzene (82) and that the extractant is attached to M as mono-ionized dimers, $H_3Y_2^-$, then the extraction may be represented as:



In Eq. (57) the indicated extractant dependency is first-power for all values of p , whereas in Eq. (58) it is first-power for M^{+3} but 4/3-power for M^{+4} , such as Th(IV), and 2/3-power for M^{+2} , such as UO_2^{+2} and Ca^{+2} .

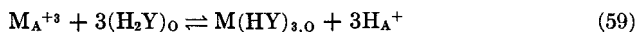
Both Eq. (57) and Eq. (58) are consistent with the observed first-power extractant dependencies in the extraction of M(III) cations. However, Eq. (57) is favored, since a highly polymeric form of H₂MEHP in the equilibrated organic phase seems likely.

Although in their report of the extraction of M(III) cations by H₂MEHP in toluene, Peppard *et al.* (206) present their hydrogen ion dependency data as pertaining to constant ionic strength in the aqueous phase, this presentation is almost certainly in error.

In an extension of the H₂MEHP work, accompanying an H₂[EHP] study, the *K* values for these M(III) cations were found to have an inverse hydrogen ion dependency slightly in excess of third-power for nonconstant ionic strength conditions, i.e., the aqueous phase containing only HX, the log *K* vs. log [H⁺] plot being closely approximated by a straight line. However, in the corresponding 1.0 *M* (HX + NaX) system, the inverse hydrogen ion dependency is much less than third-power. Although these data were obtained with a sample of H₂MEHP different from that used in the reported study, and the reported data may therefore be in error due to the action of unidentified impurities, it seems more likely that nonconstant ionic strength data were mistakenly identified as constant ionic strength data in the preparation of the manuscript.

Equations (57) and (58) should therefore be considered as pertaining to nonconstant ionic strength aqueous phases containing only HX.

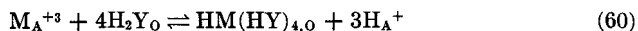
In later work with H₂MEHP (XVIII) (in *n*-decyl alcohol) vs. 0.05 *M* HCl, the extraction of Am(III) and Eu(III) by a monomer mechanism was demonstrated (177), the extraction being presented as



with the extractant dependency exceeding third-power in the region beyond 0.3 *F* H₂MEHP.

The variation of *K* value with diluent in this instance is dramatically large, the *K* value for Eu(III) for a 0.1 *F* H₂MEHP (in diluent) vs. 0.05 *M* HCl system being at least 10⁵ times greater with toluene as diluent than with *n*-decyl alcohol as diluent.

Warren and Suttle (291), working with (GO)PO(OH)₂ where G is *n*-C₃H₇, *n*-C₄H₉, *n*-C₆H₁₁, *n*-C₈H₁₃, and *n*-C₈H₁₇, in *n*-amyl alcohol as diluent, reported the extraction of Y(III) and La(III) from aqueous HNO₃ as



and that of Sc(III) as in Eq. (59).

Their conclusions and those of Mason *et al.* (177), although in apparent conflict, are seen to be compatible when it is noted that their Sc data were

obtained in the extractant concentration range lower than that employed by Mason *et al.* (177), and therefore Eq. (59) is obeyed, but their Y and La data were obtained in the extractant concentration range in which Mason *et al.* (177) noted an increasing extractant dependency.

The large diluent effect found in replacing a hydrocarbon by an alcohol has been utilized in returning a cation of otherwise awkwardly high K from a solution of H_2MEHP in hydrocarbon diluent to an aqueous phase, the extract being diluted with 2-ethyl hexanol-1 which serves as an antisynnergist or negative synergist (203). For example, a solution of H_2MEHP in a diluent such as carbon tetrachloride, chlorobenzene, toluene, or *n*-heptane is contacted with a sample of acidified human urine in analysis for certain M(III), M(IV), and M(VI) radioactive metals. The antisynnergistic effect of 2-ethyl hexanol-1 may then be used in effecting the removal to the aqueous phase of M(III), followed by M(VI), followed by M(IV), as the concentration of antisynnergist is increased (203).

Some of the metals separations possibilities inherent in the H_2MEHP (toluene) vs. aqueous HCl system are shown in Fig. 4. In this system, the K for Np(IV) is approximately first-power dependent upon the concentration of extractant. Therefore dilution of the extract with toluene is without effect in aiding the return of Np to an aqueous phase, since the RK product remains essentially constant. Oxidation to Np(VI) and re-extraction of the element in this state of oxidation are a feasible solution to the problem. A more direct solution, however, is addition of the antisynnergist. For example, in the 0.24 F H_2MEHP (toluene) vs. 1.0 M H_2SO_4 system, the K for Np(IV) is 2×10^4 . In an otherwise similar system in which the extractant is 0.24 F H_2MEHP + 1.8 F TBP, the K is ~ 0.15 . As an antisynnergist the TBP depresses the K for Np(IV) in this system by a factor exceeding 10^6 (218).

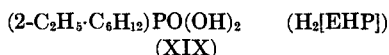
In the 0.48 F H_2MEHP (toluene) vs. HCl system, the K for Pm(III) is larger than that for Am(III) throughout the range of HCl concentration greater than 2.0 M . In the plot of $\log K$ vs. M HCl, the curves for both M(III) elements display a flat minimum in the 5–7 M HCl region. However, to the right of this region the curves diverge. Consequently, although the β for Pm with respect to Am is less than 2 at 2.0 M HCl (218), it is approximately 6 at 12.0 M HCl (178). At 13.5 M HCl, the β in the same system at 2°C is 20 (205).

Baybarz and Leuze (17) replaced the aqueous HCl phase by an aqueous 10 M LiCl solution containing HCl and used xylene as the diluent. They reported, "Rare earth elements are extracted from 10 M LiCl solutions (with HCl ranging from 0.5 to 1.0 M) into 0.5 M mono-2-ethyl hexyl orthophosphoric acid in xylene carrier. The americium and curium remain in the lithium chloride solution. Americium is separated from all rare earths, and curium from all rare earths except lanthanum by countercurrent extraction." (Note that their expression 0.5 M H_2MEHP means 0.5 F H_2MEHP .)

Mason and Peppard (178) report that in the 0.5 *F* H₂MEHP (toluene) vs. 10.3 *M* NH₄CNS system, the respective *K* values for Pm and Am(III) are 8.3 and 0.163, the β value being 51.

In regard to extraction of metallic cations by solutions of phosphonic acids, Class 2C of Table VI, Peppard and Mason (202) state, "A study now in progress in the authors' laboratory of H₂[EHP], (EH)PO(OH)₂, shows many similarities but some striking differences with respect to the H₂MEHP studies. For example, hydrogen ion dependencies in the chloride and perchlorate systems (nonconstant ionic strength, utilizing only HX) are parallel, being slightly greater than third-power for lanthanides(III) and actinides(III). However, the extractant dependency for lanthanides(III) and actinides(III) in the H₂[EHP] system employing toluene as carrier diluent is approximately second-power, not first-power, as with H₂MEHP. The log *K* vs. *Z* curve appears similarly unpromising for H₂[EHP], from a separations viewpoint." The detailed study upon which these comments were based has not yet been published.

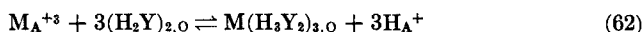
Rao *et al.* (230) have studied the extraction of Am(III), Eu(III), Tm(III), Ca(II), and U(VI) by 2-ethyl hexyl phosphonic acid, H₂[EHP] (XIX), and by H₂MEHP in a dimerizing diluent from aqueous HCl. The diluent was methyl isobutyl ketone.



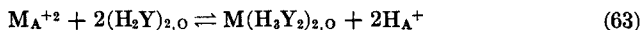
The extraction of M(III) by H₂MEHP was presented as



and by H₂[EHP] as



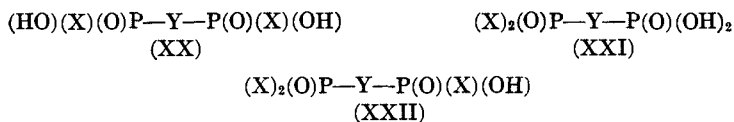
and that of Ca(II) and U(VI) by both H₂MEHP and H₂[EHP] as:



Both systems show some promise for application to mutual separations of lanthanides(III) in the Ho-Lu region.

B. DINUCLEAR EXTRACTANTS

The acidic dinuclear compounds,



where Y is an alkyl chain or an oxygen atom, are considered together. It may be noted that the dinuclear compounds, XX and XXI, are mutually

isomeric. Of these, only XX has been reported as an extractant, and no extractions by the monoacidic compound XXII have been noted.

Grdenic and Korpar (100) reported the extraction of U(IV) into a ligroin solution of symmetrical di-*n*-octyl pyrophosphoric acid, a specific example of XX with $Y = O$ and $X = n-C_8H_{17}O$, from aqueous sulfuric acid solution. They concluded that the extractable species is a complex compound defined by the formula $U(Oct_2HP_2O_7)_4$, or, if XX is symbolized by H_2Z , as $U(HZ)_4$.

Gorican and Grdenic (98) then studied symmetrical di-*n*-octyl methylene diphosphonate, an example of XX, with $Y = CH_2$ and $X = n-C_8H_{17}O$, stating, "Although dioctyl dihydrogen pyrophosphate can be used as a complex-forming agent in liquid-liquid extraction of uranium, it has the serious inconvenience of being easily hydrolyzed by the acid aqueous phase." For $M(IV) = U, Th, Zr, \text{ or } Ce$ in the quadrivalent state, they reported the extractable species as $H_4[MZ_4]$, which may be considered equivalent to $M[HZ]_4$, where H_2Z represents un-ionized XX. They also isolated Na_4ThZ_4 , where the X in XX was C_2H_5O .

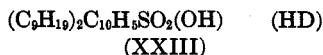
Grdenic and Jagodic (99) in a study of "Separation of germanium from arsenic by solvent extraction with dioctyl methylene bisphosphonic acid" suggest the formulation of the extracted germanium species as $H_2[GeZ_3]$ and that of a mixed sodium-germanium compound as $Na_2[GeZ_3]$, where H_2Z represents XX. With excess $GeCl_4$ a gelatinous precipitate, "probably a polymer" (99), with a composition corresponding to GeZ_2 was formed.

In the absence of data concerning the state of aggregation of H_2Z and of extractant dependency data, expressions for the extractions discussed cannot be written.

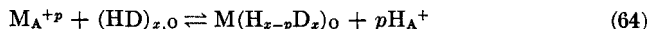
VI. Systems Involving Sulfonic Acids, $(G)SO_2(OH)$, as Extractants

Reported studies of $(G)SO_2(OH)$ compounds, where G is a generalized organic group attached directly to the sulfur atom, as extractants for metallic cations are few.

Boyd and Lindenbaum (28), in discussing liquid-liquid extraction systems from the ion-exchange viewpoint, considered solutions of di-2-ethyl hexyl phosphoric acid (HDEHP) and of dinonyl naphthalene sulfonic acid, later symbolized by White *et al.* (294) as HD (XXIII), as respective analogs of weak-acid and strong-acid resinous cation exchangers.

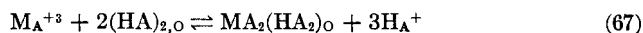
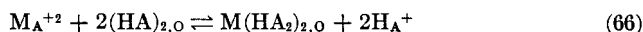
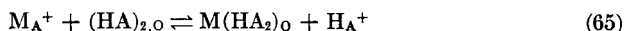
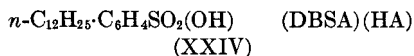


White *et al.* (294), employing a *n*-heptane solution of HD vs. aqueous perchloric acid system, found the extraction of Co(II), Zn(II), Mn(II), Fe(III), and In(III) to be represented as:



Note the similarity of Eq. (64) to Eq. (57), which is one representation of the extraction of M^{+p} by H_2MEHP . Both H_2MEHP and HD are assumed to be highly polymeric in these interpretations. Note also that Eq. (64) pertains to aqueous $HClO_4$, not to $(HClO_4 + NaClO_4)$ of constant ionic strength.

Ishimori *et al.* (132), using dodecyl benzene sulfonic acid (DBSA) as the extractant in a diluent composed of diethyl ether and ethyl acetate (1:1), reported the extraction of M^+ , M^{+2} , and M^{+3} from mineral acids to be represented as



assuming the extractant to be dimeric in the organic phase.

The assumptions of polymers in *n*-heptane by White *et al.* (294), and of dimers in a diethyl ether-ethyl acetate diluent by Ishimori *et al.* (132), correspond roughly to the previously discussed assumptions that H_2MEHP is highly polymeric in wet toluene but dimeric in methyl isobutyl ketone.

The dodecyl benzene sulfonic acid (DBSA) study was extended by Ishimori *et al.* (133) to include approximately 60 elements, the extraction system being a 3% DBSA solution in a 1:1 diethyl ether-ethyl acetate mixture vs. aqueous HCl .

Using DBSA in (1:1) diethyl ether-ethyl acetate vs. aqueous HCl , HNO_3 , and $HClO_4$, Nakamura (193) studied the extraction of $Np(IV)$, (V) , and (VI) and compared the results with those for $Th(IV)$, $Pa(V)$, and $U(VI)$. He concluded, "To sum up, the ionic charges of $Np(IV)$, (V) , and (VI) were shown to be +4, +1, and +2, and the chemical species in dilute acid solutions are supposed to be Np^{+4} , NpO_2^+ , and NpO_2^{+2} . A dissimilarity was recognized between $Np(V)$ and $Pa(V)$."

VII. Systems Involving Amines and Amine Oxides as Extractants

A. GENERAL

In 1948 Smith and Page (260) reported their study of "The acid-binding properties of long-chain aliphatic amines." They considered the system of amine in hydrocarbon diluent vs. an immiscible aqueous phase as analogous to a resinous anion exchanger vs. an aqueous phase, and demonstrated the mutual separation of hydrohalic acid and glutamic acid, the former reporting to the amine phase.

In his investigation "Long-chain amines, versatile acid extractants," Moore (179) suggests, "The acid-binding properties of these bases depend on the fact that their salts with acids are almost insoluble in water, but readily soluble in organic solvents such as chloroform. In its simplest form the reaction is thought to be as follows:



where R = a long chain aliphatic or aromatic group, and A = the anion of either a simple acid or a complex metal acid, such as $FeCl_4^-$."

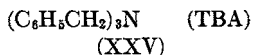
In 1952 Leddicotte and Moore (158) reported "A new solvent extraction method for the separation of niobium and tantalum," stating, "We wish to make a preliminary report of the separation of niobium and tantalum by a new solvent extraction technique. It has been found that niobium may be extracted essentially quantitatively from strong hydrochloric acid with a solution of methyldioctylamine in xylene. Under these conditions the extraction of tantalum appears to be negligible. The niobium may then be 'stripped' from the organic phase with nitric acid, sulfuric acid or dilute hydrochloric acid."

With this report, the currently rapidly expanding field of extraction of metals into an amine solution from an aqueous solution of a mineral acid and/or its salt, or of a carboxylic acid and/or its salt, was opened.

The stoichiometry of extraction by amine oxides is considered to resemble that of extraction by amines very closely.

B. AMINES AND AMINE OXIDES

In an extension of the Leddicotte and Moore (158) work, Ellenburg *et al.* (80) in 1954 demonstrated a β for Nb(V) with respect to Ta(V) of 3.4×10^4 for the system 8% tribenzylamine (XXV) in methylene chloride



vs. 11 M HCl, the respective K values being 80.50 and 2.3×10^{-3} . In a system involving the same organic phase but 4.5 M H_2SO_4 , the β was 1.9×10^2 , the respective K values being 0.58 and 3×10^{-3} .

Moore (180) followed in 1958 with the paper, "Liquid-liquid extraction of uranium and plutonium from hydrochloric acid solution with triisooctylamine." He pointed out, "Inasmuch as thorium does not form anionic complexes with the chloride ion, it was reasoned that the extraction of anionic uranyl complexes from hydrochloric acid solutions would result in a clean separation of these two elements."

He reported that the K values for Th(IV) and U(VI) in the 5% triisooctylamine in xylene vs. 6 M HCl system were respectively 1×10^2 and

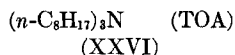
$\sim 1 \times 10^{-2}$, adding that Sr(II), lanthanides(III), Am(III), and Cm(III) did not extract appreciably, whereas "Those elements which form anionic complexes at the particular hydrochloric acid concentration used for the extraction of uranium would, of course, extract also."

His observation that triisooctylamine-xylene solution, previously saturated with hydrochloric acid, extracted U(VI) at least as efficiently as did the untreated amine was of far-reaching consequence, since it led to the investigation of solutions of amine hydrochloride vs. aqueous LiCl. These latter systems show great promise in actinide-lanthanide separations.

The paper "Solvent extraction with alkyl amines" by Coleman *et al.* (45) treats the "control of extraction by amine structure," one example being "Whereas rare earth sulfates are extracted only by primary amines . . . , the nitrates are extracted only by tertiary amines."

The extraction isotherms for U(VI) in the amine (in aromatic diluent) vs. an aqueous sulfate phase indicated a limiting association of each uranium atom with 4-6 formula weights of amine. But the K of U(VI) was approximately first-power. Coleman *et al.* (45) suggested, "The obvious hypothesis to account for this is that the amine salts associate into aggregates, which remain in stable colloidal dispersion but in effect constitute a separate phase of nearly constant composition. However, direct evaluation of the average molecular weights . . . shows that not all of the amine salts concerned are aggregated, and hence the explanation cannot be quite so simple."

Keder (142) considers the hydrochloride of tri-*n*-octylamine (XXVI)



as monomeric in wet xylene when he represents the extraction of M^{+p} in the tri-*n*-octylamine in xylene vs. aqueous HCl system as:

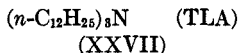


From a study of K vs. vol% TOA in xylene, he concludes that $n = 2$ for U, Np, and Pu in both the tetravalent and hexavalent states, the complex anions in the extracted species presumably being MCl_6^{-2} and $MO_2Cl_4^{-2}$, respectively.

Similarly, Wilson and Keder (297) conclude that U(IV), which is extracted from 4 *M* HNO₃ by TOA in xylene with a second-power extractant dependency, is extracted as $U(NO_3)_6^{-2}$.

The question of the state of aggregation of the amine salt in the organic phase is an important one currently under investigation in a number of laboratories. Keder and Wilson (144), quoting the work of Högfeldt *et al.* (115) on polymers of the type $(TLA \cdot HNO_3)_i$ found in solutions of trilauryl-

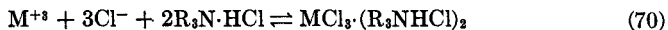
amine (XXVII), state, "In *m*-xylene the degree of aggregation found is small, but in *n*-octane solutions the aggregates are perhaps a factor of ten higher."



If the state of aggregation of the amine salt is strongly dependent upon the nature of the diluent, then an extraction stoichiometry, as deduced from extraction dependency data, for a given metal in an otherwise fixed system may be expected to vary with the diluent employed. This important point must be kept in mind when considering reported stoichiometries which appear to be in mutual conflict. An example is noted by Keder *et al.* (143), who state, ". . . the amine dependence of extraction of U(VI) from 4 *M* HNO₃ by TOA-nitrobenzene solutions is greatly different from that by TOA-xylene solutions."

Duyckaerts *et al.* (64), studying TLA·HCl, the hydrochloride of XXVII, in benzene and toluene, concluded, "The amine salt exists partially in an associated form." However, the assumption of monomeric TLA·HCl does not lead to appreciable error, the authors concluding from their study of actinides(III), "The extraction coefficients of actinides increase with the second power of amine salt concentration in the organic phase which means that the complex contains two molecules of amine per metal atom."

The extraction of lanthanides(III) and actinides(III), in a toluene solution of the hydrochloride of TLA (XXVII) vs. an aqueous chloride solution, has been interpreted by Müller *et al.* (191) as equivalent to



where the charged species are considered to be in the aqueous phase and the uncharged in the organic.

Without attempting to distinguish between $\text{MCl}_3\cdot(\text{R}_3\text{NHCl})_2$, $(\text{R}_3\text{NH})\cdot(\text{MCl}_4)\cdot(\text{R}_3\text{NHCl})$, and $(\text{R}_3\text{NH})_2\text{MCl}_5$ as the proper representation of the extracted species in Eq. (70), it may be noted that Eq. (70) is Eq. (69) with $p = 3$ and $n = 2$. It is concluded that, if the tertiary amine is monomeric, the extraction of actinides in the tertiary amine hydrochloride (in diluent) vs. aqueous chloride solution system is second-power dependent upon the concentration of amine salt in the organic phase for M(III), M(IV), and M(VI).

Moore (183) first reported the application of amine extractants to the separation of actinides(III) from lanthanides(III), the system being triisooctylamine in xylene vs. a concentrated LiCl plus dilute HCl aqueous solution. In an extension of the study Baybarz *et al.* (18), using the hydrochloride of Alamine 336 (a commercial tertiary amine with three straight-chain alkyls, principally C₈H₁₇ and C₁₀H₂₁, obtained from General

Mills, Inc., Kankakee, Ill.) in diethyl benzene vs. aqueous 10 *F* LiCl solution, showed the group β for actinides(III) with respect to lanthanides(III) to be at least 100. See the (B) curves of Fig. 7.

The comparison of this "anionic" system with a "cationic" system employing a monoacidic phosphorus-based extractant (209), the (A) curves presented in Fig. 7, accents the following points:

(1) The lanthanide(III) curves differ greatly in the two systems, the one system showing great promise, the other no promise, for mutual separation of lanthanides.

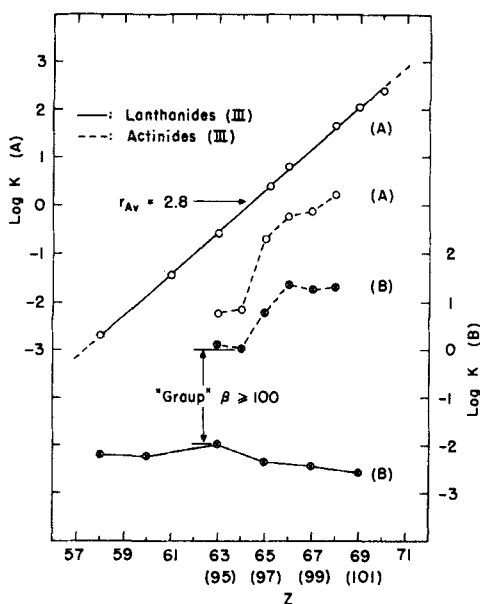


FIG. 7. Variation of $\log K$ with Z for lanthanides(III) and actinides(III) in the systems: (A) 1.0 *F* HEH[Φ P] (in toluene) vs. 2.0 *M* HCl, (B) 0.6 *F* "Alamine 336" hydrochloride (in diethyl benzene) vs. 10.0 *F* LiCl [(A), lanthanides, Peppard *et al.* (209); (A), actinides, Baybarz (16), "normalized" to benzene diluent; (B), both curves, Baybarz *et al.* (18).]

(2) The actinide(III) curves resemble each other somewhat, both showing promise for mutual actinide(III) separations in the $Z = 96-98$ region.

(3) The relative order of extraction of Am and Cm, and of 98 and 99, differs in the two systems.

(4) As plotted, the relative positions of actinide and lanthanide curves differ in the two systems.

(5) The concept of group β is meaningless in considering the (A) curves, since for each actinide there is one or more lanthanides with a nearly identical K , whereas the group β for the (B) curves is at least 100.

Baybarz *et al.* (18) reported the K values for M(III) to be directly proportional to the square of the amine hydrochloride concentration in the organic phase and to the 17th power of the LiCl concentration in the aqueous phase and inversely proportional to the 1.3–2.0 power of the acid concentration in the aqueous phase.

In studying the effect of diluent in the 0.5 F triisooctylamine hydrochloride (diluent) vs. 8 N LiCl + 2 N AlCl₃ system, they found the respective K values for Am(III) to be 0.27, 0.45, 0.65, 1.35, and 1.80 for benzene, toluene, xylene, diethyl benzene, and diisopropyl benzene. With carbon tetrachloride as diluent the K was less than 0.001.

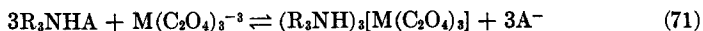
A far-ranging study of the diluent effect in such systems has been reported by Smulek and Siekierski (261) in their paper, "The influence of diluent on the extraction of iron(III) from hydrochloric acid solutions by tertiary amines."

Baybarz *et al.* (18) describe a process, based upon the tertiary amine hydrochloride (diluent) vs. LiCl system, for recovery of transplutonium elements, summarizing, "The flowsheet has been tested in batch counter-current extraction and in mini mixer-settlers with tracer-level runs. With 6 extraction and 6 scrub stages an americium recovery of 99.99% with a rare earth decontamination factor of $>10^4$ was consistently achieved."

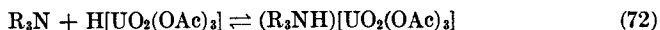
In a paper titled "Application of amine and phosphonate extractants to transplutonium element production," Leuze *et al.* (160) discuss a production-scale separations scheme in which the two systems presented in Fig. 7 are integrated into a composite process.

Extraction by a tertiary amine (in diluent) from an aqueous nitrate solution has been reported by Sato (237), Lloyd and Mason (161), Baroncelli *et al.* (14), Verstegen (282), and Vdovenko *et al.* (280) for U(VI); by Wilson (296) for Pu(IV); and by Verstegen (282) for Cu(II), Cd(II), Fe(III), and Th(IV).

The extraction of oxalato complexes of Ni(II), Co(II), Co(III), and Fe(III) by long-chain alkyl amines has been investigated by Bryan and Good (31). The extraction of Co(III) and of Fe(III) was represented as:



Moore (181) considered the extraction of U(VI) from an aqueous acetate solution into a xylene solution of triisooctylamine to be equivalent to:



The extraction of Pu(IV) from an aqueous H_2SO_4 solution by TOA (XXVI) in carbon tetrachloride was represented by Shevchenko and Zhdanov (249) as:



Vdovenko *et al.* (281) in a similar study employing a primary amine (a mixture of C_7 to C_9 aliphatic amines) considered the extraction of Pu(IV) as equivalent to:



Wilson *et al.* (295) in their paper, "Solvent extraction with quaternary ammonium halides," liken the extraction from concentrated hydrochloric acid to anion exchange, on a resinous exchanger, in the same aqueous medium. They summarize, "A comparison of the characteristic curves of all the metals studied in this paper . . . with those studied by Kraus *et al.* suggests that the mechanism of distribution by solvent extraction with quaternary ammonium halides is similar to the mechanism of distribution by elution chromatography with anion exchange resins. These quaternary ammonium halides can be called 'liquid anion exchangers.' Also, qualitative predictions about separations in one system should apply to the other system." (The Kraus (156) study referred to is the paper "Anion exchange studies of the fission products.") Good *et al.* (97) also consider such extractions as occurring through "liquid anion exchange."

Maack *et al.* (163) made a survey study of the extraction of 57 metallic ions by three quaternary amines, tetrapropyl, tetrabutyl, and tetrahexyl, in methyl isobutyl ketone diluent from five aqueous media, HNO_3 , H_2SO_4 , HF , HCl , and NaOH . The data should prove useful in the derivation of analytical separations schemes.

Similar survey studies have been made by Ishimori *et al.* for tertiary amines (in xylene) vs. HCl systems (137), and for tertiary amine (in xylene) vs. H_2SO_4 systems (130).

Kennedy and Perkins (147) found a tertiary amine oxide, Alamine 336 oxide, to differ only marginally from the corresponding tertiary amine, Alamine 336, in extraction behavior with respect to U(VI). The system was extractant in dibutyl carbitol (DBC) vs. HNO_3 .

Outstanding general reviews in the field are "High molecular weight amines, versatile modern extractants" by Moore (184), "Amine extraction in reprocessing" by Coleman (43), and "Recent uses of liquid ion exchangers in inorganic analysis" by Green (101).

The needs of the nuclear chemist with vexing separations problems are more specifically met by "Liquid-liquid extraction with high-molecular-weight amines" by Moore (182).

VIII. Miscellaneous Systems

A. ORGANIC EXTRACTANT (IN DILUENT) VS. FUSED SALT

The observation by Gruen *et al.* (102), that certain transition metal ions including Co(II), Fe(III), Nd(III), and U(VI) may be extracted nearly quantitatively from fused $\text{LiNO}_3\text{-KNO}_3$ eutectic at 150°C into undiluted tri-*n*-butyl phosphate (TBP), appears to be the first literature reference to a system composed of organic extractant vs. fused salt. In an extension of this study, Isaac *et al.* (128) used a mixture of polyphenyls as carrier diluent for the TBP extractant.

Isaac *et al.* (128) report the dependence of K upon the concentration of TBP in the organic phase to be second-power for Li(I), Co(II), and U(VI) and third-power for Nd(III), Eu(III), Am(III), and Cm(III). It was found difficult to operate the system with an acceptable material balance with respect to the tracer metal ion under investigation, the authors stating, ". . . all the distribution coefficients listed . . . were determined using concentrations of metal ions in the range $10^{-3} M$ or with tracer concentrations supported by a suitable carrier. Carriers were found to be necessary to maintain tracer quantities of any of the elements investigated in the molten salt solutions. A reaction between the molten $\text{LiNO}_3\text{-KNO}_3$ phase and the Pyrex container was postulated to account for the lack of material balances when tracer quantities of metal ions were used without carrier. Different container materials such as quartz, Teflon, and stainless steel were tried, without significantly changing the results obtained with Pyrex. . . . The best results were obtained when a Pyrex tube, which had been contacted two or three times with the molten salt phase, was employed with radioactive tracer."

They report a separation factor, β , of 3.2 for Cm(III) with respect to Am(III), pointing out that it "is the best ever found in liquid-liquid extractions." It will be recalled (from Section III,D) that the β for this pair is usually less than 2. A value of 3.2 therefore seems excitingly large.

However, it should be noted that their data in a system involving 1.4% by weight of NH_4NO_3 in the eutectic are inconsistent with this value, the β apparently being less than unity. (If the K for Cm in their Table IV is "normalized" to 0.084 M free TBP, on the assumption of a third-power TBP dependence, so that it may be compared with that for Am, the respective Cm and Am values are 9.3 and 10.3, corresponding to a β value of 0.90.) The data of their Table VI are also inconsistent with a Cm(III)/

Am(III) β value of 3.2, but this is presumably due to errors in the table, specifically in the Eu(III)/Am(III) β values.

Considering the acknowledged material balance difficulties encountered in the study, a β value based upon Cm and Am K values determined in separate experiments, not involving a normalizing element, must be considered suspect.

If Eu(III) had been present in both the Cm(III) and Am(III) experiments, then if the two K values for Eu were nearly identical the ratio of the normalized Cm and Am K values should be reasonably accurate. Note that Cm and Am are α -active and Eu β -active, so that the radiometric assays are readily made.

Another approach is the determination of K values, through α pulse analysis, of Cm and Am simultaneously present. A β value thus determined in a single experiment is directly applicable to separations calculations.

B. PARTITION CHROMATOGRAPHY

1. *Neutral Phosphorus-Based Stationary Phase*

Application of partition chromatography to the mutual separation of metals appears to date from the publication in 1959 of a paper by Siekierski and Kotlinska (256), titled "Separation of mixtures of zirconium and niobium by reversed-phase partition chromatography." The authors present the rationale, "An extraction technique which allows for separating substances having similar chemical properties is often used for separating mixtures of inorganic cations. But in the case where the distribution constants differ only slightly, however, the extraction process must be repeated through quite a few runs on the countercurrent principle using a series of separatory funnels, for example, or an extraction tower. These methods are not very convenient, so that the ion-exchange technique is most often resorted to under laboratory conditions. The merits of extraction and of the chromatographic technique are combined in partition chromatography, particularly in reversed-phase partition chromatography, where the organic solvent phase is the stationary phase."

Using tributyl phosphate (TBP) adsorbed on "siliconated silica gel" as the stationary phase and aqueous nitric acid as eluting agent, they demonstrated the mutual separation of Nb and Zr, Nb appearing first. Although the Nb fraction was purified acceptably well, the tailing of Nb resulted in a Zr product of poor grade. This difficulty was eliminated through use of a nitric acid eluting agent containing H_2O_2 , the Nb tailing being eliminated.

The authors conclude, "Separation of a mixture of cations having similar chemical properties by means of partition chromatography using

TBP as the stationary phase is thus entirely within the realm of possibility. Since many cations in the form of different salts (nitrates, chlorides, bromides) are extracted with the aid of TBP, it may be anticipated that the technique described above will prove to be of more extended value. At the present time, studies are in progress in our laboratory on the application of this technique to the separation of rare earths."

Siekierski and Fidelis (255) followed in 1960 with the paper "Separation of some rare earths by reversed-phase partition chromatography," describing the use of TBP as the stationary phase and aqueous HNO_3 as the mobile phase. They state, "... reversed-phase partition chromatography in the system TBP- HNO_3 may be successfully applied to the separation of small quantities of some rare earths. It is possible to separate the neighboring rare earths from Pm to Tb, and with a change of acid concentration from Ce to Tb, excluding Pr. It should be emphasized that the effluent from the column in this method does not contain any salts but only HNO_3 which is readily removed by evaporation and that the procedure is not time-consuming and may be carried out at room temperature." They emphasize the very low value of the separation factor for the Eu-Gd pair.

Martynenko *et al.* (175) in 1959 reported "Chromatographic separation of rare earth elements by means of tributyl phosphate," differing from the preceding techniques in that a TBP solution of rare earth nitrates was fed to a column of particulate silica gel and followed by TBP as eluting agent.

Fidelis and Siekierski (84) in 1961 showed the applicability of the TBP (stationary phase) vs. HNO_3 (mobile phase) system to the separation of heavy rare earths, demonstrating the mutual separation of all of the members Gd-Lu by elution with 11.5 *M* HNO_3 . (The position of Y was between Er and Tm.) They calculate separation factors of pairs of neighboring members with 12.3 *M* HNO_3 as eluting agent to be: Tb-Dy (1.5), Dy-Ho (1.33), Ho-Er (1.4), Er-Tm (1.53), Tm-Yb (1.4), and Yb-Lu (1.23). They point out that the factor 1.23 for Yb-Lu is exceptionally small, and that the Yb-Lu pair "... plays the same role among the heavy rare earths as the Eu-Gd pair does among the light rare earths."

They also studied the TBP (stationary phase) vs. aqueous HCl (mobile phase) system for the heavy rare earths, reporting separation factors (a) with 11.8 *M* HCl Er-Tm (1.6), Tm-Yb (1.94), and Yb-Lu (1.48), and (b) with 12.3 *M* HCl Er-Tm (1.86) and Tm-Yb (2.52). Again the Yb-Lu pair has a smaller separation factor than does the Tm-Yb pair. Note that the value 2.52 for Tm-Yb in the 12.3 *M* HCl elution is unusually large.

Reasoning "... from the fact that scandium is well extracted into TBP from HCl solutions (216) and extraction of calcium should be much worse, since there is generally a significant difference in extractability

between di- and trivalent cations," Siekierski and Sochacka (257) successfully applied the TBP (stationary phase) vs. HCl (mobile phase) to the separation of carrier-free Ca(II) from macro amounts of Sc(III).

Beranová and Novák (20), employing a sorbent "formed by swelling the styrene divinyl benzene copolymer in tributyl phosphate solution" and aqueous HNO_3 as eluting agent, studied uranium and the fission products ^{116}Ru , $^{95}\text{Zr-Nb}$, $^{90}\text{Sr-Y}$, ^{144}Ce , and ^{137}Cs and concluded that the technique ". . . appears suitable for the decontamination of uranium from the fission products in 5 *M* nitric acid medium."

Cerrai and Testa (39) used tri-*n*-octyl phosphine oxide (TOPO) on Whatman No. 1, type CRL/1, chromatographic paper as support and three different mineral acids as eluents. They made a systematic study and reported, "Curves of the R_F values as functions of the acidity of the eluent are given for about fifty metal ions. The acids used were HCl, HNO_3 and H_2SO_4 Generally, the higher the extraction coefficient E_a° of TOPO for a given element at the selected acidity, the lower the R_F value."

Kennedy (145) used the solid polymer of triallyl phosphate, $(\text{CH}_2=\text{CH}-\text{CH}_2\text{O})_3\text{PO}$, symbolizing it as $\overline{\text{TAP}}$, as adsorbent for uranyl nitrate, cobaltous nitrate, lithium chloride, and ferric chloride from solutions of the salts in acetone, acetone-ether, and alcohol. He points out that the distribution coefficients for these salts between $\overline{\text{TAP}}$ and acetone are high, 10–1,000 in favor of the polymer.

2. Acidic Phosphorus-Based Stationary Phase

Pierce and Peck (225) observed, "Investigations into the use of alkyl phosphoric acids as metal extractants have shown that there are relatively large differences between the stabilities of the complexes of individual rare earths with di(2-ethylhexyl) orthophosphoric acid (HDEHP), the separation factor for any adjacent pair being about 2.5 (217). This figure suggests that it should be feasible to devise a comparatively simple scheme for rare earth separations based on a multi-stage extraction procedure utilizing HDEHP as extractant."

They immobilized the HDEHP on a poly(vinyl chloride/vinyl acetate) copolymer as column packing and used aqueous perchloric acid as eluting agent. At 60°C a mixture of all of the irradiated lanthanides(III) from La to Gd (with the exception of Pm) was separated by gradient elution, the concentration of HClO_4 ranging from 0.320 to 0.810 *M*. (The first element to appear in the effluent is La.) The authors conclude, ". . . gradient elution greatly reduced overlap of the elements in the effluent, and permitted a separation to be achieved, even for the europium-gadolinium pair. . . ."

The same authors (226) followed with a paper describing the separation of all 15 lanthanides(III) in a similar system employing gradient elution by HClO_4 ranging in concentration from 0.195 to 6.87 M . They comment, "It can be seen that the elements terbium to lutetium, like the light rare earths, are eluted in the order of increasing atomic number, which is also the order of increasing distribution ratio for the lanthanides, when partitioning between aqueous hydrochloric acid and a solution of HDEHP in toluene, at constant acidity and HDEHP concentration" (217).

In two succeeding papers, Pierce and Hobbs (223) and Pierce *et al.* (227) explore the HDEHP (stationary phase) vs. aqueous HClO_4 (mobile phase) in detail.

The reaction between metal ion and column material is considered to be



where the subscripts A and O refer to aqueous and solid phases and HL represents HDEHP in this instance.

In terms of the zone migration parameter, R_M , Pierce and Hobbs (223) express the reaction as equivalent to

$$R_M = K_c + p \log [\text{HL}]_{\text{O}} - n \log [\text{H}^{+}]_{\text{A}} \quad (77)$$

where K_c is a constant characteristic of the specific column employed, and R_M is defined (15) as

$$R_M = \log (1/R_F - 1) \quad (78)$$

R_F being the experimentally determined ratio of the rate of movement of the fronts of solute and eluting agent (40, 159, 224). Note that if the solute front moves as rapidly as the eluting agent front, $R_F = 1$. [In the Pierce and Hobbs paper (223, p. 78), the definition of R_M is a misprint, the term "log" having been omitted.]

If the concentration of hydrogen ion is varied but all other conditions remain fixed, a plot of R_M vs. $\log [\text{H}^{+}]$ should have a slope of -3 for M^{+3} , according to Eq. (77). This hydrogen ion dependence was demonstrated for Eu^{+3} at six different loadings of HDEHP ranging over a factor of 6. With respect to the dependence of R_M upon concentration of HDEHP the authors state, "No attempt was made to relate R_M to $[\text{HL}]_{\text{O}}$ since the nature of the non-aqueous phase is not yet known, but . . . an increase in column loading is accompanied by an increase in R_M ."

Pierce *et al.* (227) studied the variation of R_M with $\log [\text{H}^{+}]$ for all 15 lanthanides(III), in both HClO_4 and HCl systems, and found the slope of R_M vs. $\log [\text{H}^{+}]$ to have an average value of -3.13 ± 0.29 for the HClO_4 system and -2.73 ± 0.37 for the HCl system. (Note that these experiments included only HX , not $\text{HX} + \text{NaX}$ at constant ionic strength.)

Their plot of $3 \log[H^+]$, at $R_M = 1$, vs. Z for the 15 lanthanides(III) is represented reasonably well by a straight line corresponding to an average separation factor for adjacent members of 2.44 and 2.11 in $HClO_4$ and HCl systems, respectively.

They summarize a comprehensive comparison of liquid-liquid extraction data and reversed-phase chromatographic data, ". . . it can be seen that the relative positions of the points derived from solvent extraction results correspond well with those taken from elution measurements. . . . Thus, generally, similar separation factors are obtained in the two systems, which is of interest, since liquid-liquid measurements are derived from equilibrium determinations with the HDEHP dissolved in toluene, whereas for elutions, the aqueous phase flowed past the reagent which was immobilized on a solid. Further, the results suggest that it should be possible to predict the behavior of elements on these columns from liquid-liquid results, if the position of the elution maximum for one element is known at a given acidity, together with the liquid extraction data for this and the other elements to be eluted."

In evaluating their reversed-phase system with respect to conventional ion exchangers they point out, "A disadvantage of the reversed phase system described in this paper compared with conventional ion-exchangers for the separation of macro quantities of rare earths is . . . the relatively low capacity of HDEHP-Corvic columns for the extraction of metals Nevertheless, the reliability of the system, the order of elution of the elements, the simplicity of the eluting phase and the generally higher separation factors for adjacent elements have resulted in the reversed phase partition technique providing a more satisfactory means for the routine separation of rare earths, prior to analytical determination, in several cases."

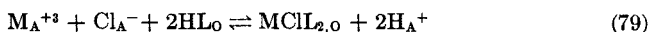
Cerrai *et al.* (41) report a similar study involving HDEHP immobilized on cellulose powder as the stationary phase and aqueous HCl as eluent. Winchester (298), using aqueous HCl or HNO_3 as eluent vs. HDEHP (which he symbolized as DEP), "held on dichlorodimethylsilane-treated diatomaceous silica columns," reports, "Separation factors observed are similar to those in solvent extraction using DEP, and the kinetics of the elution are rapid. Columns are easily prepared and are stable and long-lived." He concludes, "Application of the DEP rare earth chromatographic procedure to neutron activation analysis in geochemistry is now in progress."

Sochacka and Siekierski (262) studied the factors affecting plate height in the HDEHP (on kieselguhr) vs. aqueous HCl or HNO_3 system. They found that with up to 10% of HDEHP (with respect to the mass of kieselguhr) the height of the plate is about 0.33 mm, making it possible to obtain

very efficient separation of adjacent rare earths at room temperature. However, the width of the elution peak of a heavy rare earth is much greater with HCl than with HNO₃ as eluting agent, especially at room temperature.

Siekierski and Sochacka (258), in a detailed lanthanide(III) study of the factors affecting the height of the plate in HDEHP (on kieselguhr) vs. aqueous HNO₃, HClO₄, HCl, and H₂SO₄, showed that the plate height is essentially independent of *Z* in HNO₃ and HClO₄ systems, being in the 0.3–0.5 mm range. The plate height in the HCl system is 0.3–0.4 mm for the members La–Gd, but the succeeding values are (in mm): Tb (0.78), Dy (1.4), Ho (1.7), Er (4.0), Tm (3.6), Yb (6.0), Lu (4.4), and Y (6.0). Comparable results are presented for the H₂SO₄ system. The authors explain the larger plate height associated with the heavy rare earths as being due to kinetic effects, suggesting that Cl[−] and SO₄[−] anions are held in the inner coordination shell of the cation in the aqueous phase and must be displaced before the cation becomes fixed in the HDEHP phase. The NO₃[−] and ClO₄[−] anions are assumed to be in the outer coordination sphere and therefore more readily dislodged.

However, it should be noted that Pierce *et al.* (227) found the average of the slopes of R_M vs. $\log[H^+]$ to be -2.73 ± 0.37 in the HCl system, but those of the heavier rare earths were flatter than those of the lighter. (In liquid-liquid extraction studies of HDEHP, he found the average slope of $\log K$ vs. $\log[H^+]$ to be -3.57 ± 0.25 . Since the study involved only HCl, not a constant ionic strength medium, a slope more steep than -3.0 is to be expected.) Consequently, an alternative explanation of the higher plate heights for the heavy rare earths may be based upon the assumption that MCl^{+2} rather than, or in addition to, M^{+3} is fixed in the HDEHP phase. The reaction might be represented as:



The relative importance of Eq. (79) is assumed to be a function of *Z*. A similar explanation of the H₂SO₄ data might be offered. (Compare Eqs. (80) and (81) in a later discussion.)

Moskvin (189) used a Jones reductor in conjunction with the HDEHP (fixed on Teflon) vs. aqueous HCl + NH₄Cl system, demonstrating the separation of europium, as Eu(II), from lanthanides(III), the Eu(II) being in the early fractions. The author points out, "In those cases when europium is present in trace amounts it cannot be separated. This is evidently explained by the presence in the solutions of elementary oxygen, which oxidizes the europium after it has passed through the reducer."

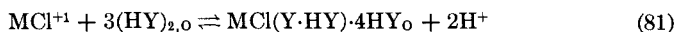
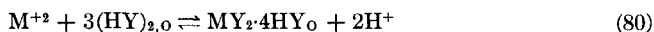
This technique may be compared with the corresponding liquid-liquid extraction technique reported by Peppard *et al.* (201), in which Eu(II)

reports preferentially to the aqueous phase and lanthanides(III) to the HDEHP (in toluene) phase. In this latter system, the separation of Eu(II) in the 10^{-10} *M* range was demonstrated, Cr(II) being employed as a holding reductant. Perhaps the Moskvin (189) separation might be extended into the tracer range by use of a holding reductant.

Hulet (117) demonstrated the mutual separation of Am and Cm, as Am(VI) and Cm(III), by use of the HDEHP (immobilized on a diatomaceous silica product) vs. aqueous HNO₃ system, using (NH₄)₂S₂O₈ as holding oxidant. Similarly, Bk was isolated as Bk(IV) from "all transuranic elements and fission products except cerium."

Kooi and Boden (154) used a similar system in the mutual separation of Bk(III) and Ce(III).

In their study of alkaline earths in the system HDEHP (immobilized on paper) vs. HCl, Cerrai and Ghersini (35) noted that the plot of $\log(1/R_F - 1)$ vs. $\log[H^+]$ had in general a slope less steep than -2 . In explanation, they postulated the extraction as a composite of:



Cerrai and Ghersini (36) later demonstrated the applicability of the same system to the separation of the M(III) elements Al, Ga, In, and Tl.

Separation of lanthanides(III) by the HDEHP (immobilized) vs. HCl system was adapted to thin-layer chromatography (TLC) by Pierce and Flint (222). The results may be compared with those of Daneels *et al.* (54), who used silica gel impregnated with buffers or acids as the stationary phase and a solution of HDEHP in carbon tetrachloride as the eluent in a TLC separation of lanthanides(III).

3. Amine Stationary Phase

Testa (272) first reported the separation of metallic cations by use of the amine (immobilized on paper) vs. aqueous HCl system. He correlated his R_F values with distribution ratios reported for the same elements in anion resin vs. aqueous HCl systems (156) and summarized, "Chromatographic paper treated with a liquid anion exchange (tri-*n*-octylamine) behaves like an anionic resin film; consequently many separations of cations that form anionic complexes can also be carried out by means of this new chromatographic procedure. Many examples are reported, among which the separation of the very similar elements zirconium and hafnium is of great significance. It is anticipated that it will be possible to isolate traces of complexed metals from large quantities of non-complexed elements."

Cerrai and Testa (37) followed with a report of the chromatographic separation of U(VI), Th(IV), and lanthanides(III) using the tri-*n*-octylamine (TOA, XXVI) impregnated paper vs. aqueous HNO₃ system. They suggest the possibility of using columns filled with cellulose powder treated with TOA as anionic resin columns.

In a closely following paper they (38) report the use of tri-*n*-octylamine cellulose (TOAC) in metals separations using HCl and HNO₃ as eluents. They describe the preparation of TOAC and the procedure used for determining exchange capacity. This exchange capacity was found to be 3–4 times lower than that of the common anionic resins. They point to its stability in 8–10 *M* HCl and 5–7 *M* HNO₃ as an advantage of TOAC.

Brinkman and de Vries (29) applied the thin-layer technique using amine-impregnated silica gel on glass microscope slides, the eluent being aqueous HCl.

4. General Treatment of the Technique

For historical background and a rigorous introduction, the papers by Martin and Synge (171) and Martin (172) are highly recommended. In addition to papers quoted in preceding sections, those by Vink (284, 285) on the theory of partition chromatography and on numerical calculations will be found valuable.

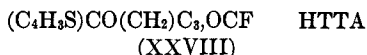
Familiarity with thin-layer chromatography (TLC) may be gained from the papers by Bolliger and Bolliger (27), Peifer (198), and Russel (233).

Cerrai (34), in a paper "Liquid ion exchangers: separation on inert supports impregnated with liquid ion exchangers," reviews the work on TOPO, HDEHP, and TOA as stationary phases. In his conclusions he states, "The results presented in this review show . . . what can be accomplished in the field of chemical separation by reversed-phase partition chromatography The principal merits of such processes are their simplicity and versatility The development of these techniques has allowed not only the separation of many similar elements from one another, but also the separation of ions of the same element, present in two different states of valency. Further development may also be concerned with processes involving electron exchange chromatography."

IX. Synergism and Antisynergism

In 1954 Cuninghame *et al.* (52) in a study of the extraction of Nd(III) and Pr(III) by the β -diketone, thenoyltrifluoroacetone (HTTA, XXVIII), noted a greatly enhanced extraction in a system containing a small concentration of tri-*n*-butyl phosphate (TBP) in the organic phase. For exam-

ple, in the 0.2 *F* HTTA (in kerosene) vs. an aqueous $\text{HNO}_3 + 1\text{ }M\text{ } \text{NH}_4\text{NO}_3$ phase of pH 3.55 system in which the organic phase contained TBP in

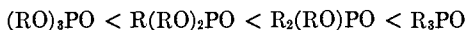


various concentrations (expressed in formality units), the *K* for Nd(III) increased with the formality, *F*, of TBP: 0.30 (no TBP), 0.87 (0.005 *F*), 2.6 (0.01 *F*), 9.4 (0.02 *F*), and 110 (0.04 *F*). Note that at the highest TBP concentration the ratio of TBP to HTTA, in formality units, is only 0.20. The *K* for Nd(III) into 0.04 *F* TBP (in the absence of HTTA) from the same aqueous phase is not reported, but from the reported data for 100% TBP it might be expected to be less than 0.01.

This enhancement of the *K* by a factor of approximately 350 appears to be the first recorded instance of a very large synergistic effect in the liquid-liquid extraction of metals.

In 1958 Blake *et al.* (24) reported the enhanced extraction of U(VI) in the presence of neutral organophosphorus reagents, in dialkyl phosphoric acid (in hydrocarbon diluent) vs. aqueous mineral acid systems. Specifically, neutral phosphates, phosphonates, phosphinates, and phosphine oxides, respectively members of Classes 2A, 3A, 4A, and 5A of Table VI, were shown to increase the *K* for U(VI) in the system 0.1 *F* HDEHP (in kerosene) vs. 0.5 *F* aqueous sulfate at pH 1.0. For example, in the presence of 0.05 *F* tri-*n*-butyl phosphine oxide (TBPO) the *K* for U(VI) is 7.0×10^3 , and in the absence of synergist is 1.35×10^2 . The synergistic enhancement factor is approximately 50.

The authors state, "An important property of the dialkylphosphoric acids is that in combination with neutral organophosphorus reagents a strong (synergistic) enhancement of U(VI) extraction can be obtained, the extraction power of the mixture being greater than the sum of the extraction powers of the separate reagents. . . . The order of synergistic enhancement is seen to be



which is also the order of increasing base strength of the phosphoryl oxygen. . . . The property of synergistic enhancement of extraction coefficient seems limited to dialkylphosphoric acid-neutral reagent combinations. The phosphinic acids tested show no synergistic enhancement. . . ."

They suggest that the effect is due to addition of the neutral reagent (synergist) to the uranyl-dialkyl phosphate complex through hydrogen bonding, and that hydrogen bonding between the synergist and the extractant accounts for the antisnergistic effect noted in systems containing a high concentration of the neutral reagent.

In this paper and in another by Blake *et al.* (23), it is reported that with monoalkyl phosphoric acids, Class 2C of Table VI, an immediate antagonistic decrease in K , that is, an antisynergistic effect, is found upon addition of a neutral reagent.

This enhancement effect, variously called the "synergic" and "synergistic" effect, has been studied for U(VI) in systems employing a monoacidic extractant of Class 2B of Table VI as extractant and a neutral compound of Class 2A or Class 5A of Table VI as synergist by Dyrssen and Kuca (76), Deane *et al.* (58), Kennedy and Deane (146), Siekierski and Taube (259), Baes (12), and Zangen (302). Siekierski and Taube (259) and Taube (271) extended the study to Pu(IV) and Pu(VI); Zangen (303) studied Ca(II) and Ba(II), selected lanthanides(III) and actinides(III), and Th(IV). Zangen concludes, ". . . only lanthanides with $Z > 64$ and Ba failed to show any synergistic phenomena. In general, the synergism was much less pronounced than in the case of U(VI)."

Each of these studies in general reports a region of positive effect followed by one of negative effect, that is, synergistic and antisynergistic regions.

The antisynergistic effect of TBP upon the extraction of Np(IV) by mono-2-ethyl hexyl phosphoric acid (H_2MEHP , XVIII) (in toluene) from an aqueous HCl solution was reported by Peppard *et al.* (218). The study of H_2MEHP as extractant was extended by Mason *et al.* (177), who employed *n*-decanol, TBP, and TOPO as synergistic agents in the extraction of selected lanthanides(III), Y(III), Am(III), Cm(III), Th(IV), and U(VI). In no instance was a large positive effect noted, but the negative effects were quite large.

In 1959 Irving and Edgington (121) reported a preliminary survey of the extraction of U(VI) into 0.02 F HTTA (in cyclohexane) from 0.01 M HNO_3 as affected by the presence of TBP or TBPO in the organic phase. They noted that 0.003 F TBP enhanced the K for U(VI) 5000-fold and that TBPO is even more effective. The extracted species were shown to be $UO_2(TTA)_2(TBP)$ and $UO_2(TTA)_2(TBPO)_3$.

They (122) reported an extension of this work in 1960 and included a penetrating analysis of various proposed explanations of "synergism" in liquid-liquid extraction, concluding, "Synergic effects are well known in many biochemical systems where the association of two drugs, two insecticides, two germicides or a toxic and a non-toxic component exert effects which would not have been predicted from the behavior of the substances considered severally. No general explanation of such complex phenomena has been given and indeed no such universal explanation is to be expected, for to take a special case, particular physiological symptoms may be produced by several different stimuli. For similar reasons we would not suppose that all cases of synergic enhancement of solvent extraction will be ex-

plicable in the same terms, even using the rather general model we have proposed. . . ."

In 1961 the same authors (123) report the synergistic enhancement by TBP, in the HTTA (in cyclohexane) vs. aqueous HNO_3 system, of the extraction of Pu(VI), Np(IV), Th(IV), Am(III), Pm(III), and Eu(III). When TBP was replaced by TBPO, the extracted species were $\text{M}(\text{TTA})_3(\text{TBPO})$ and $\text{M}(\text{TTA})_2(\text{NO}_3)(\text{TBPO})_3$ where $\text{M} = \text{Eu}^{+3}$, Am^{+3} . Similarly, in explaining the extraction of Np(IV) and Pu(IV) the extracted species were considered to be $\text{M}(\text{TTA})_4$, $\text{M}(\text{TTA})_3(\text{NO}_3)(\text{TBP})$, and $\text{M}(\text{TTA})_2(\text{NO}_3)_2(\text{TBPO})_2$. They conclude in part, "That the basic reasons for the enhancement in solvent extraction will not always be due simply to a replacement of coordinated water by a less hydrophilic group, or to a simple increase in coordination number due to the attachment of a neutral hydrophobic ligand will be obvious from the variety of behaviour indicated above. Clearly the interplay of these factors with steric and stability considerations must now be regarded as the basis of any comprehensive theoretical treatment of the phenomena which have yet to be fully exploited in analytical chemistry."

Perhaps the final dozen words of the preceding statement will prove most prophetic. Almost certainly, synergism in liquid-liquid extraction, in both its positive and negative aspects, will prove important in the field of separations chemistry of vital interest to the analytical chemist.

Irving and Edgington, in three other papers dealing with synergic effects in HTTA extraction, report upon trivalent plutonium, americium, and europium (126), upon tetravalent actinides (124), and upon plutonium(VI) and neptunium(V) (125).

Also in 1961 Healy (107) reported "Synergism in the solvent extraction of di-, tri-, and tetra-valent metal ions—I. Synergic effects of different phosphate esters," in which the HTTA (in benzene) vs. aqueous HCl system was used. His results and conclusions were very similar to those of Irving and Edgington. He accompanied this study with ". . . II. Synergic effects in so-called inert diluents" (108) and concluded, "The extracted species $\text{M}(\text{TTA})_n\text{S}_x$ is the same, whatever 'inert' diluent is used, but the partition coefficients of the metal ion vary over several powers of ten, sometimes by a factor much greater than that obtained by the synergic effect itself. The effect, on the extraction, of so-called 'inert' diluent such as cyclohexane, hexane, carbon tetrachloride, benzene and chloroform has been studied under various conditions. In all cases, the distribution ratio decreases as the diluent is changed from cyclohexane in the above sequence, chloroform giving the lowest partition coefficient."

An extensive study of antisnergism in HTTA systems was reported by Healy *et al.* (112), and Healy and Ferraro (109) reported ultraviolet and visible absorption spectrophotometric measurements of dilute solutions

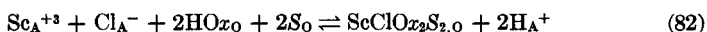
of the uranyl, thorium, and neodymium complexes. Ferraro and Healy (81) followed with a study of the infrared spectra.

Manning (167), in a study of the HTTA (in kerosene) vs. HNO_3 system, found steric effects (as exhibited by the synergists) to be important, concluding, "Both steric and synergic effects operate in the extraction of the lanthanides, yttrium and scandium by mixtures of HTTA and coordinating organophosphorus reagents. The former effects lead to poor separation factors, and synergic systems generally would seem to possess little practical application to the improved separation of the metals. An exception might be in cases where the lower lanthanide chelates form disolvates and the higher, monosolvates."

Similar systems, in which tri-*n*-octylamine (TOA) serves as the synergist, have been reported by Newman and Klotz (195, 196); Walker and Li (288) have reported the preparation of $\text{Zn}(\text{TTA})_2(\text{TOPO})$ and $\text{Cu}(\text{TTA})_2(\text{TOPO})$.

Dyrssen (73) utilized the antisnergistic effect of an alcohol, methyl isobutyl carbinol, to return Y(III) from the HDBP (in chloroform) extract to an aqueous phase.

In a study of the extraction of Sc(III) by mixtures of oxine (8-quinolinol) and neutral organophosphorus reagents in hexone (methyl isobutyl ketone) from dilute HCl, Manning and Pranowo (169) represent the extraction as



where *S* is the synergist. The extraction of the "mixed complex" containing chloride from aqueous $1.24 \times 10^{-3} M$ HCl indicates the need for caution in interpreting synergism data, and for precise determinations of hydrogen ion dependency data.

The synergistic behavior of protactinium in mixed solvents has been reported by Goble and Maddock (94). This study was concerned with extraction from aqueous HCl by a variety of two component mixtures of neutral solvents.

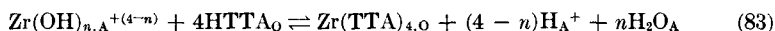
X. Investigation of Complexes

In 1949 Connick and McVey (47), working with Zr(IV), inaugurated the HTTA extraction method of determining complexity constants. In their rationale they explain, "From a search of the literature we have been forced to the conclusion that the formula of not a single aqueous zirconium(IV) species has been unambiguously identified up to the present time The purpose of the present research was to determine the formulas of the zirconium species existing in acidic aqueous solutions and to study the complexing of zirconium(IV) by a number of the more common anions The usual procedures for the determination of the

formulas of species in solution . . . are not readily applicable in the case of zirconium because of the great tendency for hydrolysis to take place except in quite acidic solutions."

They outline the procedure, "The experimental method involves the measurement of an equilibrium in which zirconium(IV) is distributed between the aqueous phase being investigated and an organic phase containing a chelating agent. The zirconium is inappreciably complexed by the chelating agent when in the aqueous phase, yet forms a chelate which is soluble in the organic phase and which is in equilibrium with whatever species exist in the aqueous phase. Any complexing of species in the aqueous phase is quantitatively reflected in a decrease of the extraction of the zirconium in the organic phase."

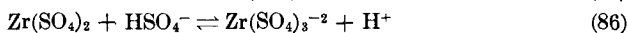
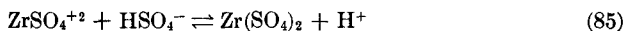
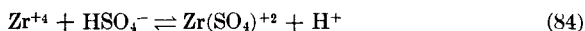
In essence the extraction into HTTA (in benzene) from perchloric acid was represented as:



They concluded that at low zirconium concentrations the average zirconium species lies between Zr^{+4} and Zr(OH)^{+3} .

(Connick and Reas (48) extended the method to the study of the hydrolysis and polymerization of zirconium in perchloric acid solution.)

By studying the effect of incremental replacement of HClO_4 by H_2SO_4 , keeping the ionic strength essentially constant, Connick and McVey (47) evaluated the respective equilibrium constants for



as 4.6×10^{-2} , 53, and 1.

Similarly, through use of HF in place of H_2SO_4 , the complexes ZrF^{+3} , ZrF_2^{+2} , and ZrF_3^+ were shown to be unusually stable. The ZrCl^{+3} and $\text{Zr(NO}_3\text{)}^{+3}$ complexes were shown to have small stability constants, perhaps 2.0.

Prophetically, the authors suggest, "The method used in the present study is clearly a powerful one and it should find applications in the study of many similar systems."

In 1950 Day and Stoughton (56) reported stability constants for Th(IV) complexes, with chloride, fluoride, nitrate, chlorate, bromate, iodate, acetate, chloroacetate, dichloroacetate, and trichloroacetate ions, using the HTTA (in benzene) vs. ($\text{HClO}_4 + \text{HX}$) system. They cited evidence for the existence of $\text{Th(NO}_3\text{)F}^{+2}$ and $\text{Th(NO}_3\text{)F}_2^+$.

In their study of acetate complexing they found, ". . . the presence of acetic acid in the aqueous phase increases the extractability of the chelated

product formed between thorium and TTA." For example, under otherwise identical conditions the K from a 0.5 M acetic + 0.5 M HClO_4 phase is 1.4 times that from 0.5 M HClO_4 . This effect has been reported in detail by Goldstein *et al.* (95).

Similar HTTA studies of complexing of metals by a variety of common anions have been reported for Th(IV) by Zebroski *et al.* (304) and Waggener and Stoughton (287), for Hf(IV) by Varga and Hume (279), for U(IV) by Day *et al.* (57), for U(VI) by Day and Powers (55), and for Eu(III) by Manning and Monk (168).

Analogously, Bogucki *et al.* (26) used the HTTA (in cyclohexane) vs. a buffered aqueous phase containing 1,2-pyrocatechol-3,5-disulfonic acid ("Tiron") to determine the molecular complexity in the aqueous phase of the 1:1.5 Th(IV)-Tiron chelate. Their results show it to be binuclear at pH 4.3.

In an approach somewhat less direct than that used in HTTA systems, extraction by TBP has been used by Solovkin (263) in the determination of hydrolysis constants of Zr(IV) and of stability constants of Zr(IV) complexes with nitrate and chloride ions. Similarly, Prokhorova and Brezhneva (229) determined the stability constants of the nitrate complexes of Hf(IV).

Extraction by TBP was used in the study of the nitrate complexes of Th(IV) by Fomin and Maiorova (90, 91), of Ce(III) by Fomin *et al.* (89), and of Pu(III) by Shevchenko *et al.* (248) and Laxminarayanan *et al.* (157).

Peppard *et al.* (211) determined the stability constants of MX^{+2} for La, Ce, Pr, Eu, Tm, Yb, Lu, and Am, where $\text{X} = \text{Cl}^-$, NO_3^- , using the di[*p*-(1,1,3,3-tetramethyl butyl)phenyl] phosphoric acid ($\text{HDO}\Phi\text{P}$) (in toluene) vs. ($\text{HClO}_4 + \text{HX}$) system. In essence the theory is that utilized in the HTTA system.

White *et al.* (293) studied the chloride and nitrate complexes of Fe(III) and In(III) by use of the dinonyl naphthalene sulfonic acid (HD, XXIII) (in benzene) vs. ($\text{HClO}_4 + \text{HX}$) system. Choppin and Unrein (42) determined similarly the stability constants of CeCl^{+2} , CeBr^{+2} , EuCl^{+2} , EuBr^{+2} , EuI^{+2} , YCl^{+2} , and YBr^{+2} .

Extraction by a mixture of secondary amines (in toluene) from an aqueous ($\text{NaNO}_3 + \text{NaClO}_4 + 0.2 M \text{HNO}_3$) phase, $\mu = 6.7$, was used by Brothers *et al.* (30) in their investigation of the complexing of Pu(IV) by nitrate ion.

Sekine (245) has demonstrated the use of a "synergistic" system, employing HTTA and TBP, in the study of trivalent La, Eu, Lu, and Am complexes with oxalate, sulfate, chloride, and thiocyanate ions.

Antikainen and Dyrssen (5) studied the hydrolysis of Ag^+ by varying the concentration of OH^- in the extraction system quinoline (in benzene) vs. 3 M ($\text{NaClO}_4 + \text{NaOH}$).

The extent of hydration of salts, as measured by liquid-liquid extraction techniques, has been reported by Rozen *et al.* (232) and Yates *et al.* (300).

Further examples of liquid-liquid extraction as a tool in the study of metal complexes may be found in the review "Investigation of complex formation in solution by the distribution method" by Zozulya and Peshkova (306).

XI. Concluding Comments

Because of space limitations this review has not included extraction of water and of mineral acids by neutral phosphorus-based extractants. For an excellent survey of this important field, the chapter by Diamond and Tuck (59) is recommended.

Important recent comprehensive papers, concerning extractants other than phosphorus-based compounds and amines, are "Systematic study of the solvent extraction of metal β -diketonates," by Starý and Hladký (266); "Systematic study of the solvent extraction of metal oxinates," by Starý (265); "A theoretical approach to the solvent extraction of metal chelates," by Schweitzer (243); "A summary of TTA extraction coefficients," by Poskanzer and Foreman (228); and a series of papers on the use of tropolone and β -isopropyl tropolone as extractants for metal ions by Dyrssen *et al.* (66, 69-71, 246, 247).

Moore, who made the pioneering applications of amine vs. chloride systems to the separation of actinides(III) as a group from lanthanides(III) as a group (Section VII,B), has recently described a "New approach to separation of trivalent actinide elements from lanthanide elements, selective liquid-liquid extraction with tricaprylmethylammonium thiocyanate" (185).

Baybarz and Leuze (17) have reported "Separation of transplutonium and rare earth elements by liquid-liquid extraction," and Horner *et al.* (116) have described "Fission product recovery from waste solutions by solvent extraction."

A "periodic table" type of survey has been made by Kimura (152, 153) for the HDEHP (in toluene) vs. HCl system, by Ishimori and Watanabe (138) for the 100% TBP vs. HNO₃ system, by Ishimori *et al.* (140) for the 100% TBP vs. HCl system, by Ishimori *et al.* (131) for various systems employing neutral phosphates and phosphine oxides and amines as extractants, and by Ishimori *et al.* (130) for various amine vs. H₂SO₄ systems.

In recent reviews Coleman *et al.* (44) and Green (101) have assessed the use of liquid ion exchangers in inorganic analysis. These papers are especially recommended because of the breadth of treatment which makes them of immediate value to the working analyst.

And finally, to deliver the coup de grace to the term "inert diluent," the diluent effect has been elucidated by Taube (270) in "The influence of

diluent polarity on the extraction of neptunium and uranium compounds to organic media," by Alimarin and Zolotov (4) in "The influence of the nature of the organic solvent on the extraction of chelate compounds," and by Smulek and Siekierski (261) in "The influence of diluent on the extraction of iron(III) from hydrochloric acid solutions by tertiary amines."

REFERENCES

1. Alcock, K., Bedford, F. C., Hardwick, W. H., and McKay, H. A. C., *J. Inorg. Nucl. Chem.* **4**, 100 (1957).
2. Alcock, K., Best, G. F., Hesford, E., and McKay, H. A. C., *J. Inorg. Nucl. Chem.* **6**, 328 (1958).
3. Alders, L., "Liquid-Liquid Extraction, Theory and Laboratory Practice," 2nd rev. ed. Elsevier, Amsterdam, 1959.
4. Alimarin, I. P., and Zolotov, Y. A., *Talanta* **9**, 891 (1962).
5. Antikainen, P. J., and Dyrssen, D., *Acta Chem. Scand.* **14**, 86 (1960).
6. Arbuzov, A. E., Dissertation, Kazan, 1905.
7. Arbuzov, A. E., *J. Russ. Chem. Soc.* **46**, 291. *Chem. Abstr.* **8**, 10 (1914).
8. Asprey, L. B., Stephanou, S. E., and Penneman, R. A., *J. Am. Chem. Soc.* **73**, 5715 (1951).
9. Auer, P. L., and Gardner, C. S., *Ind. Eng. Chem.* **46**, 39 (1954).
10. Baes, C. F., Jr., *J. Inorg. Nucl. Chem.* **24**, 707 (1962).
11. Baes, C. F., Jr., *J. Phys. Chem.* **66**, 1629 (1962).
12. Baes, C. F., Jr., *Nucl. Sci. Eng.* **16**, 405 (1963).
13. Baes, C. F., Jr., Zingaro, R. A., and Coleman, C. F., *J. Phys. Chem.* **62**, 129 (1958).
14. Baroncelli, F., Scibona, G., and Zifferero, M., *J. Inorg. Nucl. Chem.* **24**, 547 (1962).
15. Bate-Smith, E. C., and Westall, R. G., *Biochim. Biophys. Acta* **4**, 427 (1950).
16. Baybarz, R. D., *Nucl. Sci. Eng.* **17**, 463 (1963).
17. Baybarz, R. D., and Leuze, R. E., *Nucl. Sci. Eng.* **11**, 90 (1961).
18. Baybarz, R. D., Weaver, B. S., and Kinser, H. B., *Nucl. Sci. Eng.* **17**, 457 (1963).
19. Belcher, R., Wilson, C. L., and West, T. S., "New Methods of Analytical Chemistry," 2nd ed., Chapt. VIII. Chapman & Hall, London, 1964.
20. Beranová, H., and Novák, M., *Collection Czech. Chem. Commun.* **30**, 1073 (1965).
21. Bernström, B., and Rydberg, J., *Acta Chem. Scand.* **11**, 1173 (1957).
22. Best, G. F., McKay, H. A. C., and Woodgate, P. R., *J. Inorg. Nucl. Chem.* **4**, 315 (1957).
23. Blake, C. A., Jr., Baes, C. F., Jr., and Brown, K. B., *Ind. Eng. Chem.* **50**, 1763 (1958).
24. Blake, C. A., Jr., Baes, C. F., Jr., Brown, K. B., Coleman, C. F., and White, J. C., *Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva, 1958* Vol. 28, p. 289. I.D.S., Columbia Univ. Press, New York, 1959.
25. Bochinski, J., Smutz, M., and Spedding, F. H., *Ind. Eng. Chem.* **50**, 157 (1958).
26. Bogucki, R. F., Murakami, Y., and Martell, A. E., *J. Am. Chem. Soc.* **82**, 5608 (1960).
27. Bolliger, A., and Bolliger, J. E., *Proc. Roy. Australian Chem. Inst.* **29**, 78 (1962).
28. Boyd, G. E., and Lindenbaum, S., *Abstr. 134th Meeting, Am. Chem. Soc., Chicago, Illinois, 1958* No. 42, p. 17-I (1958).
29. Brinkman, U. A. T., and de Vries, G., *J. Chromatog.* **18**, 142 (1965).
30. Brothers, J. A., Hart, R. G., and Mathers, W. G., *J. Inorg. Nucl. Chem.* **7**, 85 (1958).

31. Bryan, S. E., and Good, M. L., *J. Inorg. Nucl. Chem.* **21**, 339 (1961).
32. Burger, L. L., *J. Phys. Chem.* **62**, 590 (1958).
33. Bush, M. T., and Densen, P. M., *Anal. Chem.* **20**, 121 (1948).
34. Cerrai, E., *Chromatog. Rev.* **6**, 129 (1964).
35. Cerrai, E., and Ghersini, G., *J. Chromatog.* **15**, 236 (1964).
36. Cerrai, E., and Ghersini, G., *J. Chromatog.* **18**, 124 (1965).
37. Cerrai, E., and Testa, C., *J. Chromatog.* **5**, 442 (1961).
38. Cerrai, E., and Testa, C., *J. Chromatog.* **6**, 443 (1961).
39. Cerrai, E., and Testa, C., *J. Chromatog.* **7**, 112 (1962).
40. Cerrai, E., and Testa, C., *J. Chromatog.* **8**, 232 (1962).
41. Cerrai, E., Testa, C., and Triulzi, C., *Energia Nucl.* **9**, 193 (1962).
42. Choppin, G. R., and Unrein, P. J., *J. Inorg. Nucl. Chem.* **25**, 387 (1963).
43. Coleman, C. F., *At. Energy Rev.* **2**, No. 2, 3 (1964).
44. Coleman, C. F., Blake, C. A., Jr., and Brown, K. B., *Talanta* **9**, 297 (1962).
45. Coleman, C. F., Brown, K. B., Moore, J. G., and Crouse, D. J., *Ind. Eng. Chem.* **50**, 1756 (1958).
46. Compere, E. L., and Ryland, A. L., *Ind. Eng. Chem.* **46**, 24 (1954).
47. Connick, R. E., and McVey, W. H., *J. Am. Chem. Soc.* **71**, 3182 (1949).
48. Connick, R. E., and Reas, W. H., *J. Am. Chem. Soc.* **73**, 1171 (1951).
49. Cox, R. P., Peterson, H. C., and Beyer, G. H., *Ind. Eng. Chem.* **50**, 141 (1958).
50. Craig, L. C., in "Technique of Organic Chemistry" (A. Weissberger, ed.), Vol. 3, Chapt. 4. Wiley (Interscience), New York, 1950.
51. Craig, L. C., Hausmann, W., Ahrens, E. H., Jr., and Harfenist, E. J., *Anal. Chem.* **23**, 1236 (1951).
52. Cuninghame, J. G., Scargill, P., and Willis, H. H., Harwell (England) Unclassified Rept. AERE C/M 215 (1954).
53. Daasch, L. W., *J. Am. Chem. Soc.* **80**, 5301 (1958).
54. Daneels, A., Massart, D. L., and Hoste, J., *J. Chromatog.* **18**, 144 (1965).
55. Day, R. A., Jr., and Powers, R. M., *J. Am. Chem. Soc.* **76**, 3895 (1954).
56. Day, R. A., Jr., and Stoughton, R. W., *J. Am. Chem. Soc.* **72**, 5662 (1950).
57. Day, R. A., Jr., Wilhite, R. N., and Hamilton, F. D., *J. Am. Chem. Soc.* **77**, 3180 (1955).
58. Deane, A. M., Kennedy, J., and Sammes, P. G., *Chem. Ind.* **79**, 443 (1960).
59. Diamond, R. M., and Tuck, D. G., *Prog. Inorg. Chem.* **2**, 109-192 (1960).
60. Doak, G. O., and Freedman, L. D., *Chem. Rev.* **61**, 31 (1961).
61. Dreze, P., and Duyckaerts, G., "Euratom" Report EUR 436.f, 1963.
62. Duyckaerts, G., and Dreze, P., *Bull. Soc. Chim. Belges* **71**, 306 (1962).
63. Duyckaerts, G., Dreze, P., and Simon, A., *J. Inorg. Nucl. Chem.* **13**, 332 (1960).
64. Duyckaerts, G., Fuger, J., and Müller, W., "Euratom" Report EUR 426.f, 1963.
65. Dyrssen, D., *Svensk Kem. Tidskr.* **67**, 311 (1955).
66. Dyrssen, D., *Acta Chem. Scand.* **9**, 1567 (1955).
67. Dyrssen, D., *Acta Chem. Scand.* **11**, 1277 (1957).
68. Dyrssen, D., *Acta Chem. Scand.* **11**, 1771 (1957).
69. Dyrssen, D., *Proc. Intern. Symp. Chem. Co-ord. Compounds, Rome, 1957*, p. 291, IUPAC.
70. Dyrssen, D., *Acta Chem. Scand.* **15**, 1614 (1961).
71. Dyrssen, D., *Trans. Roy. Inst. Technol., Stockholm*, **188** (1962).
72. Dyrssen, D., *Nucl. Sci. Eng.* **16**, 448 (1963).
73. Dyrssen, D., and Ekberg, S., *Acta Chem. Scand.* **13**, 1909 (1959).
74. Dyrssen, D., Ekberg, S., and Liem, D. H., *Acta Chem. Scand.* **18**, 135 (1964).

75. Dyrssen, D., and Krasovec, F., *Acta Chem. Scand.* **13**, 561 (1959).
76. Dyrssen, D., and Kuca, L., *Acta Chem. Scand.* **14**, 1945 (1960).
77. Dyrssen, D., and Liem, D. H., *Acta Chem. Scand.* **14**, 1091 (1960).
78. Dyrssen, D., and Liem, D. H., *Acta Chem. Scand.* **14**, 1100 (1960).
79. Dyrssen, D., and Liem, D. H., *Acta Chem. Scand.* **18**, 224 (1964).
80. Ellenburg, J. Y., Leddicotte, G. W., and Moore, F. L., *Anal. Chem.* **26**, 1045 (1954).
81. Ferraro, J. R., and Healy, T. V., *J. Inorg. Nucl. Chem.* **24**, 1463 (1962).
82. Ferraro, J. R., Mason, G. W., and Peppard, D. F., *J. Inorg. Nucl. Chem.* **22**, 285 (1961).
83. Ferraro, J. R., and Peppard, D. F., *Nucl. Sci. Eng.* **16**, 389 (1963).
84. Fidelis, I., and Siekierski, S., *J. Chromatog.* **5**, 161 (1961).
85. Fischer, W., Biesenberger, K., Heppner, J., and Neitzel, U., *Angew. Chem. Intern. Ed. English* **3**, 791 (1964).
86. Flanary, J. R., and Goode, J. H., *Ind. Eng. Chem.* **51**, 55 (1959).
87. Fletcher, J. M., *Symp. Extraction Met. Some Less Common Metals, 1956 Paper No. 2*, Inst. of Mining and Metallurgy, London, 1957.
88. Fomin V. V., "Chemistry of Extraction Processes." Translated and published for the National Science Foundation, Washington, D. C., and the Department of Commerce by the Israel Program for Scientific Translations, 1962. PST Cat. No. 802.
89. Fomin, V. V., Kartushova, R. E., and Rudenko, T. I., *Zh. Neorgan. Khim.* **3**, 2117 (1958).
90. Fomin, V. V., and Maiorova, E. P., *Russ. J. Inorg. Chem. (English Transl.)* **1**, No. 8, 1703 (1956).
91. Fomin, V. V., and Maiorova, E. P., *Russ. J. Inorg. Chem. (English Transl.)* **1**, No. 12, 2749 (1956).
92. Freiser, H., and Morrison, G. H., *Ann. Rev. Nucl. Sci.* **9**, 221 (1959).
93. Gindler, J. E., Flynn, K. F., and Gray, J., Jr., *J. Inorg. Nucl. Chem.* **15**, 1 (1960).
94. Goble, A. G., and Maddock, A. G., *Trans. Faraday Soc.* **55**, 591 (1959).
95. Goldstein, G., Menis, O., and Manning, D. L., *Anal. Chem.* **32**, 400 (1960).
96. Golumbic, C., *Anal. Chem.* **23**, 1210 (1951).
97. Good, M. L., Srivastava, S. C., and Holland, F. F., Jr., *Anal. Chim. Acta* **31**, 534 (1964).
98. Gorican, H., and Grdenic, D., *Proc. Chem. Soc.* p. 288 (1960).
99. Grdenic, D., and Jagodic, V., *J. Inorg. Nucl. Chem.* **23**, 167 (1964).
100. Grdenic, D., and Korpar, B., *J. Inorg. Nucl. Chem.* **12**, 149 (1959).
101. Green, H., *Talanta* **11**, 1561 (1964).
102. Gruen, D. M., Fried, S., Graf, P., and McBeth, R. L., *Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva, 1958* Vol. 28, p. 112. I. D. S., Columbia Univ. Press, New York, 1959.
103. Handley, T. H., and Dean, J. A., *Anal. Chem.* **32**, 1878 (1960).
104. Handley, T. H., and Dean, J. A., *Anal. Chem.* **33**, 1087 (1961).
105. Handley, T. H., and Dean, J. A., *Anal. Chem.* **34**, 1312 (1962).
106. Hardy, C. J., Scargill, D., and Fletcher, J. M., *J. Inorg. Nucl. Chem.* **7**, 257 (1958).
107. Healy, T. V., *J. Inorg. Nucl. Chem.* **19**, 314 (1961).
108. Healy, T. V., *J. Inorg. Nucl. Chem.* **19**, 328 (1961).
109. Healy, T. V., and Ferraro, J. R., *J. Inorg. Nucl. Chem.* **24**, 1449 (1962).
110. Healy, T. V., Kennedy, J., and Waind, G. M., *J. Inorg. Nucl. Chem.* **10**, 137 (1959).
111. Healy, T. V., and McKay, H. A. C., *Rec. Trav. Chim.* **75**, 730 (1956).

112. Healy, T. V., Peppard, D. F., and Mason, G. W., *J. Inorg. Nucl. Chem.* **24**, 1429 (1962).
113. Hesford, E., Jackson, E. E., and McKay, H. A. C., *J. Inorg. Nucl. Chem.* **9**, 279 (1959).
114. Hesford, E., and McKay, H. A. C., *J. Inorg. Nucl. Chem.* **13**, 165 (1960).
115. Högföldt, E., Bolander, B., and Fredlund, F., *Proc. 7th Intern. Conf. Coord. Chem., Stockholm, 1962* Paper 7M4. Butterworths, London (1963).
116. Horner, D. E., Crouse, D. J., Brown, K. B., and Weaver, B., *Nucl. Sci. Eng.* **17**, 234 (1963).
117. Hulet, E. K., *J. Inorg. Nucl. Chem.* **26**, 1721 (1964).
118. Hunter, T. G., and Nash, A. W., *J. Soc. Chem. Ind. (London)* **51**, 285T (1932).
119. Hunter, T. G., and Nash, A. W., *J. Soc. Chem. Ind. (London)* **53**, 95T (1934).
120. Hyde, E. K., *Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva, 1955* Vol. 7, p. 281. I. D. S., Columbia Univ. Press, New York, 1956.
121. Irving, H., and Edgington, D. N., *Proc. Chem. Soc.* p. 360 (1959).
122. Irving, H., and Edgington, D. N., *J. Inorg. Nucl. Chem.* **15**, 158 (1960).
123. Irving, H., and Edgington, D. N., *Chem. Ind. (London)* p. 77 (1961).
124. Irving, H., and Edgington, D. N., *J. Inorg. Nucl. Chem.* **20**, 321 (1961).
125. Irving, H., and Edgington, D. N., *J. Inorg. Nucl. Chem.* **20**, 314 (1961).
126. Irving, H., and Edgington, D. N., *J. Inorg. Nucl. Chem.* **21**, 169 (1961).
127. Irving, H., and Williams, R. J. P., in "Treatise on Analytical Chemistry" (I. M. Kolthoff and P. J. Elving, eds.), Vol. III, Sect. C, Chapt. 31. Wiley (Interscience), New York, 1961.
128. Isaac, N. M., Fields, P. R., and Gruen, D. M., *J. Inorg. Nucl. Chem.* **21**, 152 (1961).
129. Isaac, N. M., Wilkins, J. W., and Fields, P. R., *J. Inorg. Nucl. Chem.* **15**, 151 (1960).
130. Ishimori, T., Akatsu, E., Cheng, W., Tsukuechi, K., and Osakabe, T., *Japan At. Energy Res. Inst. Res. Rept.* **1062** (1964).
131. Ishimori, T., Kimura, K., Nakamura, E., Watanabe, K., Fujino, T., Akatsu, J., Ono, R., Murakami, H., Izumi, T., Tsukuechi, K., Kobune, T., Osakabe, T., Ueno, K., Chang, C., Cheng, W., Chen, Y., and Sammour, H. M., *Japan At. Energy Res. Inst. Res. Rept.* **1047**, (1963).
132. Ishimori, T., Nakamura, E., and Murakami, H., *J. At. Energy Soc. Japan* **3**, 193 (1961).
133. Ishimori, T., Nakamura, E., and Murakami, H., *J. At. Energy Soc. Japan* **3**, 590 (1961).
134. Ishimori, T., Rhee, C. T., and Fujino, T., *J. At. Energy Soc. Japan* **4**, 837 (1962).
135. Ishimori, T., and Sammour, H. M., *J. At. Energy Soc. Japan* **3**, 344 (1961).
136. Ishimori, T., and Sammour, H. M., *J. At. Energy Soc. Japan* **3**, 410 (1961).
137. Ishimori, T., Sammour, H. M., Kimura, K., Murakami, H., and Izumi, T., *J. At. Energy Soc. Japan* **3**, 698 (1961).
138. Ishimori, T., and Watanabe, K., *Bull. Chem. Soc. Japan* **33**, 1443 (1960).
139. Ishimori, T., Watanabe, K., and Fujino, T., *J. At. Energy Soc. Japan* **3**, 19 (1961).
140. Ishimori, T., Watanabe, K., and Nakamura, E., *Bull. Chem. Soc. Japan* **33**, 636 (1960).
141. Katzin, L. I., in "The Chemistry of Non-Aqueous Solvents" (J. J. Lagowski, ed.), p. 173. Academic Press, New York.
142. Keder, W. E., *J. Inorg. Nucl. Chem.* **24**, 561 (1962).

143. Keder, W. E., Ryan, J. L., and Wilson, A. S., *J. Inorg. Nucl. Chem.* **20**, 131 (1961).
144. Keder, W. E., and Wilson, A. S., *Nucl. Sci. Eng.* **17**, 287 (1963).
145. Kennedy, J., *J. Appl. Chem.* **9**, 26 (1959).
146. Kennedy, J., and Deane, A. M., *J. Inorg. Nucl. Chem.* **19**, 142 (1961).
147. Kennedy, J., and Perkins, R., *J. Inorg. Nucl. Chem.* **26**, 1601 (1964).
148. Kertes, A. S., and Halpern, M., *J. Inorg. Nucl. Chem.* **16**, 308 (1961).
149. Khorana, H. G., *Chem. Rev.* **53**, 145 (1953).
150. Khorana, H. G., *J. Am. Chem. Soc.* **76**, 3517 (1954).
151. Khorana, H. G., and Todd, A. R., *J. Chem. Soc.* p. 2257 (1953).
152. Kimura, K., *Bull. Chem. Soc. Japan* **33**, 1038 (1960).
153. Kimura, K., *Bull. Chem. Soc. Japan* **34**, 63 (1961).
154. Kooi, J., and Boden, R., *Radiochim. Acta* **3**, 226 (1964).
155. Kosolapoff, G. M., and Powell, J. S., *J. Chem. Soc.* p. 3535 (1950).
156. Kraus, K. A., and Nelson, F., *Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva, 1955* Vol. 7, p. 113. I. D. S., Columbia Univ. Press, New York, 1956.
157. Laxminarayanan, T. S., Patil, S. K., and Sharma, H. D., *J. Inorg. Nucl. Chem.* **26**, 1001 (1964).
158. Leddicotte, G. W., and Moore, F. L., *J. Am. Chem. Soc.* **74**, 1618 (1952).
159. Lederer, M., and Kertes, S., *Anal. Chim. Acta* **15**, 226 (1956).
160. Leuze, R. E., Baybarz, R. D., and Weaver, B., *Nucl. Sci. Eng.* **17**, 252 (1963).
161. Lloyd, P. J., and Mason, E. A., *J. Phys. Chem.* **68**, 3120 (1964).
162. McKay, H. A. C., and Miles, J. H., *Nature* **199**, 65 (1963).
163. Maeck, W. J., Booman, G. L., Kussy, M. E., and Rein, J. E., *Anal. Chem.* **33**, 1775 (1961).
164. Majumdar, S. K., and De, A. K., *Talanta* **7**, 1 (1960).
165. Mandil, M. A., Mason, G. W., and Peppard, D. F., *Ind. Eng. Chem., Process Design Develop.* **2**, 106 (1963).
166. Manning, P. G., *Can. J. Chem.* **40**, 1684 (1962).
167. Manning, P. G., *Can. J. Chem.* **41**, 658 (1963).
168. Manning, P. G., and Monk, C. B., *Trans. Faraday Soc.* **58**, 938 (1962).
169. Manning, P. G., and Pranowo, *Can. J. Chem.* **42**, 708 (1964).
170. Marcus, Y., *Chem. Rev.* **63**, 139 (1963).
171. Martin, A. J. P., and Synge, R. L. M., *Biochem. J.* **35**, 1358 (1941).
172. Martin, A. J. P., *Ann. Rev. Biochem.* **19**, 517 (1950).
173. Martin, B., Ockenden, D. W., and Foreman, J. K., *J. Inorg. Nucl. Chem.* **21**, 96 (1961).
174. Martin, F. S., and Holt, R. J. W., *Quart. Rev. (London)* **13**, 327 (1959).
175. Martynenko, L. I., Eremin, G. K., and Kamenev, A. I., *Russ. J. Inorg. Chem. (English Transl.)* **4**, 2639 (1959).
176. Mason, G. W., Lewey, S., and Peppard, D. F., *J. Inorg. Nucl. Chem.* **26**, 2271 (1964).
177. Mason, G. W., McCarty, S., and Peppard, D. F., *J. Inorg. Nucl. Chem.* **24**, 967 (1962).
178. Mason, G. W., and Peppard, D. F., *Nucl. Sci. Eng.* **17**, 247 (1963).
179. Moore, F. L., *Anal. Chem.* **29**, 1660 (1957).
180. Moore, F. L., *Anal. Chem.* **30**, 908 (1958).
181. Moore, F. L., *Anal. Chem.* **32**, 1075 (1960).
182. Moore, F. L., Liquid-liquid extraction with high-molecular-weight amines. *U.S. At. Energy Comm. NAS-NS 3101* (1960).

183. Moore, F. L., *Anal. Chem.* **33**, 748 (1961).
184. Moore, F. L., "Analytical Chemistry 1962" (P. W. West, A. M. G. MacDonald, and T. S. West, eds.), pp. 345-355. Elsevier, Amsterdam, 1963.
185. Moore, F. L., *Anal. Chem.* **36**, 2158 (1964).
186. Morrison, G. H., and Freiser, H., "Solvent Extraction in Analytical Chemistry." Wiley, New York, 1957.
187. Morrison, G. H., and Freiser, H., in "Comprehensive Analytical Chemistry" (C. L. Wilson and D. W. Wilson, eds.), Vol. 1A, Chapt. 7. Elsevier, New York, 1959.
188. Morrison, G. H., and Freiser, H., *Anal. Chem. Ann. Rev.* **36**, 93R (1964).
189. Moskvina, L. N., *Radiochemistry (USSR) (English Transl.)* **5**, 708 (1963).
190. Mroczek, J. E., O'Laughlin, J. W., Sakurai, H., and Banks, C. V., *J. Inorg. Nucl. Chem.* **25**, 955 (1963).
191. Müller, W., Fuger, J., and Duyckaerts, G., *Proc. 8th Intern. Conf. Coord. Chem., Vienna, 1964* L. Vanmelle S.A. Ghent, Brussels (1964) EURATOM 2169. e.
192. Naito, K., and Suzuki, T., *J. Phys. Chem.* **66**, 989 (1962).
193. Nakamura, E., *J. At. Energy Soc. Japan* **3**, 684 (1961).
194. Nenarokomov, E. A., and Slepchenko, I. G., *Russ. J. Inorg. Chem. (English Transl.)* **8**, No. 12, 1459 (1963). (Russ. p. 2785.)
195. Newman, L., and Klotz, P., *J. Phys. Chem.* **65**, 796 (1961).
196. Newman, L., and Klotz, P., *J. Phys. Chem.* **67**, 205 (1963).
197. Nomura, S., and Hara, R., *Anal. Chim. Acta* **25**, 212 (1961).
198. Peifer, J. J., *Mikrochim. Acta* p. 529 (1962).
199. Peppard, D. F., Driscoll, W. J., Sironen, R. J., and McCarty, S., *J. Inorg. Nucl. Chem.* **4**, 326 (1957).
200. Peppard, D. F., Ferraro, J. R., and Mason, G. W., *J. Inorg. Nucl. Chem.* **4**, 371 (1957).
201. Peppard, D. F., Horwitz, E. P., and Mason, G. W., *J. Inorg. Nucl. Chem.* **24**, 429 (1962).
202. Peppard, D. F., and Mason, G. W., *Nucl. Sci. Eng.* **16**, 382 (1963).
203. Peppard, D. F., Mason, G. W., and Andrejasich, C. M., *J. Inorg. Nucl. Chem.* **25**, 1175 (1963).
204. Peppard, D. F., Mason, G. W., and Andrejasich, C. M., *J. Inorg. Nucl. Chem.* **27**, 697 (1965).
205. Peppard, D. F., Mason, G. W., Driscoll, W. J., and McCarty, S., *J. Inorg. Nucl. Chem.* **12**, 141 (1959).
206. Peppard, D. F., Mason, G. W., Driscoll, W. J., and Sironen, R. J., *J. Inorg. Nucl. Chem.* **7**, 276 (1958).
207. Peppard, D. F., Mason, G. W., and Gergel, M. V., *J. Inorg. Nucl. Chem.* **3**, 370 (1957).
208. Peppard, D. F., Mason, G. W., and Giffin, G., *J. Inorg. Nucl. Chem.* **27**, 1683 (1965).
209. Peppard, D. F., Mason, G. W., and Hucher, I., *J. Inorg. Nucl. Chem.* **18**, 245 (1961).
210. Peppard, D. F., Mason, G. W., and Hucher, I., "Radioisotopes in the Physical Sciences and Industry," pp. 541-554. Intern. At. Energy Agency, Vienna, 1962.
211. Peppard, D. F., Mason, G. W., and Hucher, I., *J. Inorg. Nucl. Chem.* **24**, 881 (1962).
212. Peppard, D. F., Mason, G. W., Hucher, I., and Brandao, F. A. J. A., *J. Inorg. Nucl. Chem.* **24**, 1387 (1962).
213. Peppard, D. F., Mason, G. W., and Lewey, S., *J. Inorg. Nucl. Chem.* **27**, 2065 (1965).

214. Peppard, D. F., Mason, G. W., and McCarty, S., *J. Inorg. Nucl. Chem.* **13**, 138 (1960).
215. Peppard, D. F., Mason, G. W., McCarty, S., and Johnson, F. D., *J. Inorg. Nucl. Chem.* **24**, 321 (1962).
216. Peppard, D. F., Mason, G. W., and Maier, J. L., *J. Inorg. Nucl. Chem.* **3**, 215 (1956).
217. Peppard, D. F., Mason, G. W., Maier, J. L., and Driscoll, W. J., *J. Inorg. Nucl. Chem.* **4**, 334 (1957).
218. Peppard, D. F., Mason, G. W., and Sironen, R. J., *J. Inorg. Nucl. Chem.* **10**, 117 (1959).
219. Peppard, D. F., Moline, S. W., and Mason, G. W., *J. Inorg. Nucl. Chem.* **4**, 344 (1957).
220. Peppard, D. F., Namboodiri, M. N., and Mason, G. W., *J. Inorg. Nucl. Chem.* **24**, 979 (1962).
221. Peppard, D. F., and Peppard, M. A., *Ind. Eng. Chem.* **46**, 34 (1954).
222. Pierce, T. B., and Flint, R. F., *Anal. Chim. Acta* **31**, 595 (1964).
223. Pierce, T. B., and Hobbs, R. S., *J. Chromatog.* **12**, 74 (1963).
224. Pierce, T. B., and Peck, P. F., *J. Chromatog.* **6**, 248 (1961).
225. Pierce, T. B., and Peck, P. F., *Nature* **194**, 84 (1962).
226. Pierce, T. B., and Peck, P. F., *Nature* **195**, 597 (1962).
227. Pierce, T. B., Peck, P. F., and Hobbs, R. S., *J. Chromatog.* **12**, 81 (1963).
228. Poskanzer, A. M., and Foreman, B. M., Jr., *J. Inorg. Nucl. Chem.* **16**, 323 (1961).
229. Prokhorova, N. P., and Brezhneva, N. E., *Russ. J. Inorg. Chem. (English Transl.)* **7**, No. 8, 953 (1962). (Russ. p. 1846.)
230. Rao, G. S., Mason, G. W., and Peppard, D. F., *J. Inorg. Nucl. Chem.* **28**, 887 (1966).
231. Reznik, A. M., Rozen, A. M., Korovin, S. S., and Apraksin, I. A., *Radiochemistry (USSR) (English Transl.)* **5**, No. 1, 40 (1963). (Russ. p. 49.)
232. Rozen, A. M., Sabaev, I. Y., and Shokin, I. N., *Russ. J. Inorg. Chem. (English Transl.)* **9**, No. 6, 788 (1964). (Russ. p. 1455.)
233. Russel, J. H., *Rev. Pure Appl. Chem.* **13**, 15 (1963).
234. Saisho, H., *Bull. Chem. Soc. Japan* **34**, 859 (1961).
235. Saisho, H., *Bull. Chem. Soc. Japan* **35**, 514 (1962).
236. Sato, T., *J. Inorg. Nucl. Chem.* **24**, 699 (1962).
237. Sato, T., *J. Inorg. Nucl. Chem.* **26**, 1295 (1964).
238. Scadden, E. M., and Ballou, N. E., *Anal. Chem.* **25**, 1602 (1953).
239. Scargill, D., Alcock, K., Fletcher, J. M., Hesford, E., and McKay, H. A. C., *J. Inorg. Nucl. Chem.* **4**, 304 (1957).
240. Scheibel, E. G., *Ind. Eng. Chem.* **44**, 2942 (1952).
241. Scheibel, E. G., *Ind. Eng. Chem.* **46**, 16 (1954).
242. Scheibel, E. G., *Ind. Eng. Chem.* **46**, 43 (1954).
243. Schweitzer, G. K., *Anal. Chim. Acta* **30**, 68 (1964).
244. Seaborg, G. T., *Phys. Today* **15**, 19 (1962).
245. Sekine, T., *J. Inorg. Nucl. Chem.* **26**, 1463 (1964).
246. Sekine, T., and Dyrssen, D., *J. Inorg. Nucl. Chem.* **26**, 2013 (1964).
247. Sekine, T., and Dyrssen, D., *J. Inorg. Nucl. Chem.* **26**, 1727 (1964).
248. Shevchenko, V. B., Timoshev, V. G., and Volkova, A. A., *J. Nucl. Energy: Pt. B* **1**, 211 (1960).
249. Shevchenko, V. B., and Zhdanov, Y. F., *Radiochemistry (USSR) (English Transl.)* **3**, Nos. 3 and 4, 231 (1962).
250. Siddall, T. H., III, *Ind. Eng. Chem.* **51**, 41 (1959).

251. Siddall, T. H., III, *J. Inorg. Nucl. Chem.* **13**, 151 (1960).
252. Siddall, T. H., III, in "Chemical Processing of Reactor Fuels" (J. H. Flagg, ed.), Chapt. 5. Academic Press, New York, 1961.
253. Siddall, T. H., III, *J. Inorg. Nucl. Chem.* **25**, 883 (1963).
254. Siekierski, S., *J. Inorg. Nucl. Chem.* **12**, 129 (1959).
255. Siekierski, S., and Fidelis, I., *J. Chromatog.* **4**, 60 (1960).
256. Siekierski, S., and Kotlinska, B., *Atomnaya Energ.* **7**, 160 (1959).
257. Siekierski, S., and Sochacka, R. J., *Polish Acad. Sci. Inst. Nucl. Res. Rept.* **262/V** (1961).
258. Siekierski, S., and Sochacka, R. J., *J. Chromatog.* **16**, 385 (1964).
259. Siekierski, S., and Taube, M., *Nucleonika* **6**, 489 (1961).
260. Smith, E. L., and Page, J. E., *J. Soc. Chem. Ind. (London)* **67**, 48 (1948).
261. Smulek, W., and Siekierski, S., *Polish Acad. Sci. Inst. Nucl. Res. Rept.* **303/V** (1962).
262. Sochacka, R. J., and Siekierski, S., *J. Chromatog.* **16**, 376 (1964).
263. Solovkin, A. S., *Russ. J. Inorg. Chem. (English Transl.)* **2**, No. 3, 611 (1957).
264. Solovkin, A. S., Konarev, M. I., and Adaev, D. P., *Russ. J. Inorg. Chem. (English Transl.)* **5**, 903 (1959). (Russ. p. 1861.)
265. Starý, J., *Anal. Chim. Acta* **28**, 132 (1963).
266. Starý, J., and Hladký, E., *Anal. Chim. Acta* **28**, 227 (1963).
267. Stephanou, S. E., and Penneman, R. A., *J. Am. Chem. Soc.* **74**, 3701 (1952).
268. Stewart, D. C., and Crandall, H. W., *J. Am. Chem. Soc.* **73**, 1377 (1951).
269. Stewart, D. C., and Hicks, T. E., Univ. Calif. Radiation Lab. Rept. UCRL 861 (1950).
270. Taube, M., *J. Inorg. Nucl. Chem.* **15**, 171 (1960).
271. Taube, M., *Radiochemistry (USSR) (English Transl.)* **4**, No. 3, 237 (1962). (Russ. p. 260.)
272. Testa, C., *J. Chromatog.* **5**, 236 (1961).
273. Treybal, R. E., *Ind. Eng. Chem.* **53**, 161 (1961).
274. Treybal, R. E., *Ind. Eng. Chem.* **54**, 55 (1962).
275. Treybal, R. E., "Liquid Extraction," 2nd ed. McGraw-Hill, New York, 1963.
276. Treybal, R. E., "Liquid Extraction," 2nd ed. Chapt. 10. McGraw-Hill, New York, 1963.
277. Treybal, R. E., "Liquid Extraction," 2nd ed. Chapt. 11. McGraw-Hill, New York, 1963.
278. Umezawa, H., *J. At. Energy Soc. Japan* **2**, 478 (1960).
279. Varga, L. P., and Hume, D. N., *Inorg. Chem.* **2**, 201 (1963).
280. Vdovenko, V. M., Kovaleva, T. V., and Ryazanov, I. A., *Radiochemistry (USSR) (English Transl.)* **5**, No. 5, 573 (1963). (Russ. p. 619.)
281. Vdovenko, V. M., Lipovskii, A. A., and Nikitina, S. A., *Radiochemistry (USSR) (English Transl.)* **3**, Nos. 3 and 4, 143 (1962).
282. Versteegen, J. M. P. J., *J. Inorg. Nucl. Chem.* **26**, 1589 (1964).
283. Verzele, M., and Alderweireldt, F., *Nature* **174**, 702 (1954).
284. Vink, H., *J. Chromatog.* **15**, 448 (1964).
285. Vink, H., *J. Chromatog.* **18**, 25 (1965).
286. von Metzsch, F. A., in "Physical Methods in Chemical Analysis" (W. G. Berl, ed.), Vol. IV. Academic Press, New York, 1961.
287. Waggener, W. C., and Stoughton, R. W., *J. Phys. Chem.* **56**, 1 (1952).
288. Walker, W. R., and Li, N. C., *J. Inorg. Nucl. Chem.* **27**, 411 (1965).
289. Ward, M., and Welch, G. A., *J. Chem. Soc.* p. 4038 (1954).

290. Warf, J. C., *J. Am. Chem. Soc.* **71**, 3257 (1959).
291. Warren, C. G., and Suttle, J. F., *J. Inorg. Nucl. Chem.* **12**, 336 (1960).
292. White, J. C., and Ross, W. J., Separations by solvent extraction with tri-n-octylphosphine oxide. *U.S. At. Energy Comm. NAS-NS 3102* (1961).
293. White, J. M., Kelly, P., and Li, N. C., *J. Inorg. Nucl. Chem.* **16**, 337 (1961).
294. White, J. M., Tang, P., and Li, N. C., *J. Inorg. Nucl. Chem.* **14**, 255 (1960).
295. Wilson, A. M., Churchill, L., Kiluk, K., and Hovsepien, P., *Anal. Chem.* **34**, 203 (1962).
296. Wilson, A. S., *Prog. Nucl. Energy Ser. III* **3**, 211 (1961).
297. Wilson, A. S., and Keder, W. E., *J. Inorg. Nucl. Chem.* **18**, 259 (1961).
298. Winchester, J. W., *J. Chromatog.* **10**, 502 (1963).
299. Yagodin, G. A., and Mostovaya, O. A., *J. Appl. Chem. USSR (English Transl.)* **33**, No. 11, 2426 (1960). (Russ. p. 2459.)
300. Yates, P. C., Laran, R., Williams, R. E., and Moore, T. E., *J. Am. Chem. Soc.* **75**, 2212 (1953).
301. Yoshida, H., *J. Inorg. Nucl. Chem.* **24**, 1257 (1962).
302. Zangen, M., *J. Inorg. Nucl. Chem.* **25**, 581 (1963).
303. Zangen, M., *J. Inorg. Nucl. Chem.* **25**, 1051 (1963).
304. Zebroski, E. L., Alter, H. W., and Heumann, F. K., *J. Am. Chem. Soc.* **73**, 5646 (1951).
305. Zingaro, R. A., and White, J. C., *J. Inorg. Nucl. Chem.* **12**, 315 (1960).
306. Zozulya, A. P., and Peshkova, V. M., *Russ. Chem. Rev. (English Transl.)* **2**, 101 (1960). (Russ. p. 234.)

NITRIDES OF METALS OF THE FIRST TRANSITION SERIES

R. Juza

Institut für anorganische Chemie der Universität Kiel, Kiel, Germany

I. Introduction	81
II. Binary Compounds	82
A. Phases	82
B. Preparative Methods	94
C. Properties	98
D. Bonding in Transition Metal Nitrides	108
III. Ternary Compounds	116
A. Ternary Metallic Phases	116
B. Polar Ternary Compounds	125
References	127

I. Introduction

Transition metal nitrides have been widely studied recently. From the original and somewhat generalized concept of metallic intercalation compounds, several different types have now emerged, which often have quite different characteristics. Titanium nitride, for example, is a substance with the electrical conductivity of a good metallic conductor and the hardness of diamond. Regular and at the same time big changes in the properties of nitrides occur with increasing atomic number in the transition metal series, and there are also marked crystallographic regularities. The nitrides of chromium, manganese, and iron are also of theoretical interest because of the incidence of ferromagnetism, antiferromagnetism, and ferrimagnetism.

Quite a new concept of the bonding in these substances has also emerged as a result of improvements in older techniques, such as X-ray crystallography and magnetic measurements, and the introduction of new methods, such as neutron diffraction, for the elucidation of magnetic structures. Interpretation of the results of these studies has been greatly helped by further developments in theories of the chemical bond, particularly the Valence Bond and Molecular Orbital theories, and also by applications of the theory of metallic bonding. The study of nitrides has also been greatly stimulated by technical developments. Applications will not in general be discussed in this article, although those which have stimulated scientific research will be referred to briefly.

Nitrides of metals of the fourth and fifth groups have long been of importance in high-melting cermets, as have some of the carbides. In

combination with a metal such as cobalt they have found widespread use as hard-cast alloys. Fashioning is done by the methods of powder metallurgy, involving sintering and hot-pressing at high temperatures. Their notably high melting points and relatively good nonscaling properties have made these materials of interest in connection with problems of jet propulsion and rocket technology. In addition to the preparation of sintered products, the production of thin coatings on metallic or ceramic base materials is also important. The high melting points, coupled with the possibility of fashioning by the methods of powder metallurgy, have also resulted in the manufacture of refractory vessels for metallurgical work which can be used in melting alloys of the b-group metals. In this connection the use of ternary compounds which contain metal from the b-groups as well as a transition metal may be noted. The chemical resistance and high electrical conductivity lead to applications as electrode materials in fused salt electrolysis. The compounds are also interesting as superconductors because of their relatively high transition temperatures.

Study of the nitrides of metals in Groups 6–8, especially double nitrides and carbidenitrides of these metals, has been stimulated by *inter alia* the steel industry. Such phases play a key role in nitrided steels, although they occur independently of the process of hardening by nitriding.

II. Binary Compounds

A. PHASES

Before discussing the chemical and physical properties of these compounds their constitutions will be dealt with. If they were ionic the formulas would be a sufficient indication. It is also necessary in this case to specify, where possible, stability ranges and, as far as is known, the dependence of these on temperature. The crystal structure is also required as a means of characterizing a particular compound.

1. Survey of Interstitial Structures

G. Hägg recognized that there is a common structural principle for the metallic nitrides (51). The structure is determined by the metal atoms, which are substantially bigger than the nitrogen atom. In the vast majority of compounds the metal atoms are arranged in either cubic or hexagonal close packing. Nitrogen atoms are intercalated in the octahedral holes in the metal structure and this is the origin of the terms "intercalation compound" and "intercalation phase" introduced by Hägg.

In the close-packed cubic unit cell (Fig. 1) there are four octahedral holes situated in the center of the cell and in the middle of the edges. The octahedron of metal atoms associated with the nitrogen in the $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ position

is illustrated. A simple geometrical relationship shows that the nitrogen atoms just fit into these holes when the radii of nitrogen and metal are in the ratio $r_N:r_{Me} = 0.41$. If the nonmetal does not fill the holes, which is so in the case of metallic hydrides, it goes into the smaller tetrahedral holes. If the nonmetal is somewhat too large the metal atom lattice is expanded and metal-metal contact is lost. Expansion of the metal lattice is observed up

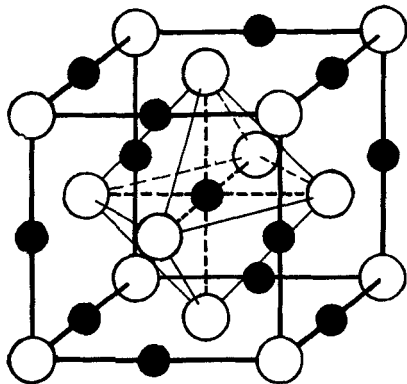


FIG. 1. Lattice of nitrides of the type MeN (NaCl type): \circ Me; \bullet N.

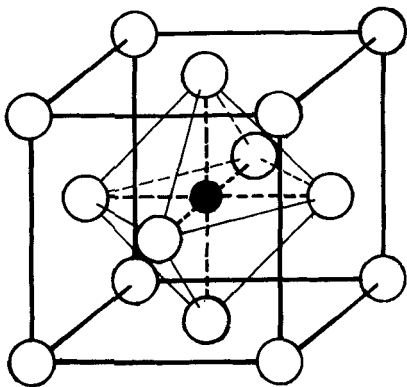


FIG. 2. Lattice of nitrides of the type Me_4N (perovskite type): \circ Me; \bullet N.

to the value $r_N:r_{Me} = 0.59$. If this value is exceeded, as for example in Fe_3C , more complex structures result.

Two types of compound may be derived from the cubic close-packed arrangement. If all octahedral holes in the cubic face-centered metal atom lattice are occupied, the composition is MeN (type B1, *sodium chloride lattice*). A substantial percentage of the positions in the nitrogen sublattice may remain unoccupied when, as is generally the case, the metal lattice is fully populated. The vacancies are then distributed statistically and one

again speaks of a "NaCl lattice," although the composition may deviate very appreciably from MeN .

If only the $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ position in the face-centered cubic unit cell is occupied by nitrogen (Fig. 2), the composition becomes Me_4N . Only one quarter of the available octahedral holes are then occupied. This occurs in such a way that only one of two neighboring octahedral holes contains nitrogen. The four metal atoms are no longer equivalent with respect to nitrogen, the atom in the 000 position being more distant. This is reflected in the properties of the nitrides: they are now called "*perovskite-type nitrides*." Their analogy to perovskite is expressed by the formula $\text{Me}_c\text{N}(\text{Me}_f)_3$ (type L'10), where Me_c is the atom at the corner of the cube and Me_f represents the three in the middle of the faces.

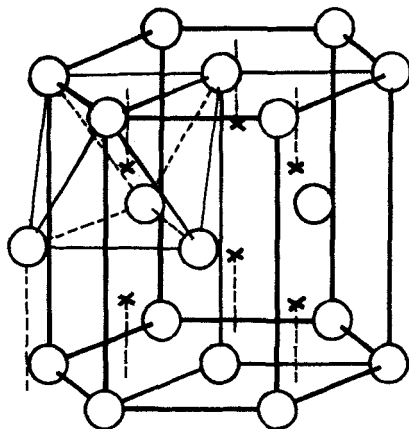


FIG. 3. Hexagonal close packing of metal atoms in the nitrides Me_3N to $\sim\text{Me}_2\text{N}$: \circ Me; \times octahedral holes.

The framework for nitrides which crystallize in the hexagonal system is provided by metal atoms with a *hexagonal close-packed* arrangement, compositions varying in the first transition series between Me_3N and Me_2N . The triple hexagonal close-packed unit cell shown in Fig. 3 contains six octahedral holes for six metal atoms: these are indicated in the figure by crosses. One octahedron formed by the six neighboring metal atoms is shown. It includes one metal atom from the neighboring cell. Octahedral holes are, however, filled by nitrogen to the extent of only 33–50%, corresponding with the formulas Me_3N and Me_2N . When nitrogen is distributed statistically the unit cell of the nitride is the same as that for the hexagonal close-packed metal lattice. With ordered arrangements of nitrogen, superstructures occur, which will be discussed for the hexagonal iron nitrides (cf. Section II, A, 2f).

2. Nitrides of the Metals

Table I summarizes the phases, their compositions, and structural data. Where the phase limits are known they are given with their lattice constants, measured at room temperature and shown by a cross. It is difficult to avoid a certain measure of inconsistency in writing the formulas.

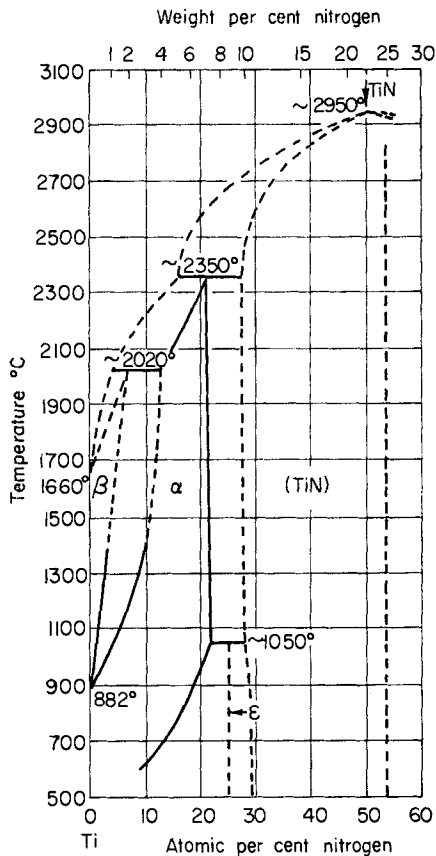


FIG. 4. The titanium/nitrogen system (55).

a. Scandium. The only compound of *scandium* to exist is ScN , which crystallizes with an NaCl lattice and is thus in line with the MeN phases of subsequent elements. Unlike them, however, scandium nitride has a stoichiometric composition (8) or a very narrow stability range (147).

b. Titanium. The system *titanium/nitrogen* (cf. Fig. 4) (55) is typical of intercalated structures in the sense of Hägg's formulation (50, 51). Hexagonal close-packed α -titanium takes up nitrogen in solid solution

TABLE I
STRUCTURAL DATA

Phase	Structural type and space group	Composition ^a	Lattice constants (Å)			Reference	Additional readings
			<i>a</i>	<i>b</i>	<i>c</i>		
ScN	B1, O_h^5	ScN	4.45	—	—	(8)	—
		ScN _{0.970}	4.499	—	—	(147)	—
δ-TiN	B1, O_h^5	Ti _{0.875} N	4.21	—	—	(14)	(14, 60, 117, 131)
		x TiN _{1.00}	4.234	—	—	(28)	—
		x TiN _{0.42}	4.215	—	—	(28)	—
ε-Ti ₂ N	Tetragonal, D_{4h}^{14}	TiN _{0.50}	4.945	—	3.034	(60)	(127)
γ-VN	B1, O_h^5	VN _{1.00}	4.126	—	—	(53)	(15, 33)
		VN _{0.71}	4.064	—	—	(53)	—
β-V ₃ N	L'3, D_{6h}^4	x VN _{0.43}	2.835	—	4.541	(53)	—
		x VN _{0.37}	2.831	—	4.533	(53)	—
γ-CrN	B1, O_h^5	CrN _{1.0}	4.140	—	—	(11)	(34, 135)
CrN antif.	Orthorhombic, D_{2h}^{16}	CrN _{1.0}	5.757	2.964	4.134	(26)	—
β-Cr ₂ N	L'3, D_{6h}^4	x Cr ₂ N _{1.0}	2.768	—	4.469	(34)	(137)
		x Cr ₂ N _{0.75}	2.742	—	4.429	(34)	—
MnN ?	Cubic ?	MnN _{1.04}	4.435	—	—	(126)	—
θ-Mn ₆ N ₅	Tetragonal	x Mn ₆ N _{5.25}	4.2218	—	4.1136	(107)	—
	face-centered	x Mn ₆ N ₅	4.2145	—	4.1486	(107)	—
η-Mn ₃ N ₂	L'6, D_{4h}^{17}	x Mn ₃ N _{2.08}	4.2074	—	4.0410	(107)	(49, 126)
		x Mn ₃ N _{1.85}	4.2044	—	4.0464	(107)	—

ζ -Mn ₂ N	L'3, D_{6h}^4	x Mn ₂ N _{1.06}	2.8179	—	4.5346	(107)	(19, 49, 50)
		x Mn ₂ N _{0.79}	2.7757	—	4.5284	(107)	—
ϵ -Mn ₄ N	L'1, O_h^5	x Mn ₄ N	3.863	—	—	(87)	(18, 49)
		x Mn ₄ N _{0.435}	3.763	—	—	(87)	—
δ -Mn ₂ N	Tetragonal	Mn _{9.2} N	3.764	—	3.729	(87)	—
	face-centered	Mn _{26.3} N	3.765	—	3.610	(87)	—
ζ -Fe ₂ N	Orthorhombic	Fe ₂ N _{1.0}	5.512	4.820	4.416	(72)	(17, 20, 21)
ϵ -Fe ₂ N	L'3, D_{6h}^4	x Fe ₂ N _{1.0}	2.77	—	4.42	(48)	—
ϵ -Fe ₃ N	L'3, D_{6h}^4	x Fe ₃ N _{1.0}	2.695	—	4.362	(48)	—
	L'3, D_3^1	Fe ₂ N	$2.765 \times \sqrt{3}$	—	4.41	(136)	(20, 21)
	D_3^1	Fe ₂₄ N ₁₀	$2.764 \times 2\sqrt{3}$	—	4.420	(67)	—
γ' -Fe ₄ N	O_h^5	x Fe ₃ N _{1.1}	3.793	—	—	(132)	(48, 67, 136, 176)
		x Fe ₄ N _{0.89}	3.783	—	—	(132)	—
α'' -Fe ₃ N	L'6, D_{4h}^{17}	Fe ₈ N _{1.0}	5.72	—	6.29	(71)	(52, 69)
CoN	Cubic (blende)	CoN	4.28	—	—	(78)	—
	Cubic (NaCl type)	—	4.27	—	—	(154)	—
Co ₂ N	Orthorhombic, D_{2h}^{12}	Co ₂ N _{1.0}	2.848	4.636	4.339	(89)	(25)
Co ₃ N	L'3, hexagonal	Co ₃ N _{1.06}	$2.663 \times \sqrt{3}$	—	4.360	(89)	(170)
Co ₄ N	L'1, O_h^5	Co ₄ N _{1.0}	3.738	—	—	(170)	—
Ni ₃ N	L'3, hexagonal	Ni ₃ N _{1.0}	$2.670 \times \sqrt{3}$	—	4.307	(90)	(69)
Ni ₄ N	L'1, O_h^5	Ni ₄ N _{1.0}	3.72	—	—	(169)	(9)
Cu ₃ N	D _{0h} , O_h^1	Cu ₃ N _{1.0}	3.807	—	—	(82)	—

^a Symbol x indicates lattice constants of the specimen at the phase boundaries.

and thus forms an "intercalated mixed crystal." Because of this intercalation, the hexagonal close-packed arrangement of the metal, which is transformed into a cubic body-centered arrangement at 882°C for the pure metal, is stabilized at higher temperatures, probably to about 2350°C. Nitrogen is situated in the octahedral holes of the hexagonal close-packed titanium lattice (cf. Fig. 3).

The solubility of nitrogen in body-centered cubic β -titanium, which is stable above 882°C, is substantially lower. Only highly distorted "octahedral holes" are available in this type of structure, and the relatively complicated process of intercalation of a nonmetal in such holes has been studied only for the system iron-nitrogen (Section II,A,2).

Apart from these two solid solutions, the diagram is dominated by the δ -phase, TiN, which extends from $\text{TiN}_{0.42}$ to $\text{TiN}_{1.00}$ (28). Comparison of the pyknometric density with that derived by X-ray methods leads to the conclusion that the cubic face-centered titanium lattice in $\text{TiN}_{0.42}$ is fully populated, but that the nitrogen lattice corresponding with this composition contains vacancies. For the stoichiometric composition both lattices have 4% of vacancies (28). In preparations with a nitrogen content up to $\text{TiN}_{1.16}$, the excess of nitrogen is readily lost by thermal dissociation and up to 20% of the titanium lattice sites are unoccupied (Section II,B,2) (14).

In addition to the above, an ϵ -phase exists, which has been little studied. The composition has been given as Ti_3N (131) or Ti_2N (60), and it is known to crystallize in an anti-rutile lattice (60), in which nitrogen is again surrounded by deformed octahedra of titanium atoms.

c. *Vanadium*. The solubility of nitrogen in cubic body-centered crystalline vanadium is very small at low temperatures. The γ -phase, VN, which again crystallizes in the NaCl lattice, has a narrower phase range than TiN (15, 32, 33, 53). It also differs from TiN in having no appreciable concentration of lattice vacancies: pyknometric densities for the γ -phase agree very well with values deduced from X-ray measurements (53). The hexagonal intercalated phase is represented in this case by an intermediate β -phase, V_3N (53), whereas in the system titanium/nitrogen the same structure occurs as intercalated mixed crystals of α -Ti.

d. *Chromium*. The same intermediate phases occur in the system chromium/nitrogen. These are the cubic γ -phase, CrN, the stability range of which is unknown, and the hexagonal close-packed β -phase, Cr_2N (11, 34, 135). Cubic CrN is orthorhombically deformed below 0°C (26). This change is associated with the incidence of antiferromagnetism (cf. Section II,C,4,b). A hexagonal phase CrN has also been described, but cannot be considered as fully established (137).

e. *Manganese*. Phase studies in the system manganese/nitrogen (Fig. 5) are more extensive, although again not conclusive. The tetragonal face-

centered δ -phase, Mn_6N_5 , is the richest in nitrogen. With increasing nitrogen content the ratio c/a approaches unity and extrapolation to MnN gives $c/a = 1$ (107). A cubic face-centered phase MnN has also been reported (126), although a lattice constant is given which it is impossible to reconcile with the extrapolation mentioned above.

As the nitrogen content is decreased, the η -phase, Mn_3N_2 , appears. Its range of existence has been established, at least at low temperatures, and it is again *tetragonal face-centered*. Between it and the nitrogen-richer δ -phase there is a two-phase region in which the axial ratio c/a in the η -

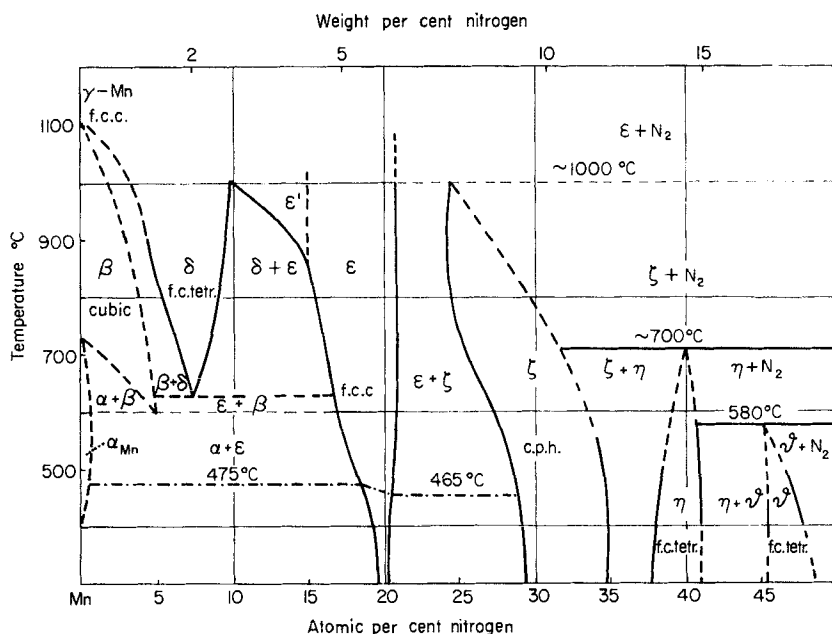


FIG. 5. The manganese/nitrogen system (55, 87, 107).

and the δ -phase alters with decreasing nitrogen content in the opposite sense (49, 107).

While the two tetragonal phases mentioned are structurally like the cubic MeN phases of Groups 3-6, it is found that, with lower nitrogen contents, a *hexagonal* ξ -phase with the composition Mn_2N occurs (19, 49, 107). The ranges of existence of the phases referred to above become narrower in all three cases as the temperature is increased.

An ϵ -phase follows which, at lower temperatures, has the composition Mn_4N and a small stability range (49, 87). Here a structure of the *perovskite* type (cf. Section A,II,1) occurs for the first time. At higher temperatures

the ϵ -phase region extends in the direction of lower nitrogen contents. An ϵ' -phase follows, which differs from the ferrimagnetic ϵ -phase in being paramagnetic (87). Extrapolation of the lattice constants of the ϵ - and ϵ' -phases gives the lattice constants of the cubic face-centered high-temperature γ -Mn phase (1095°–1134°C) (87). In the literature the Mn_4N phase is frequently described as having a smaller range and decomposing peritectically with rising temperature at 700°C (55). This would correspond with the behavior of Fe_4N , which will be discussed later, but the statement is very probably incorrect.

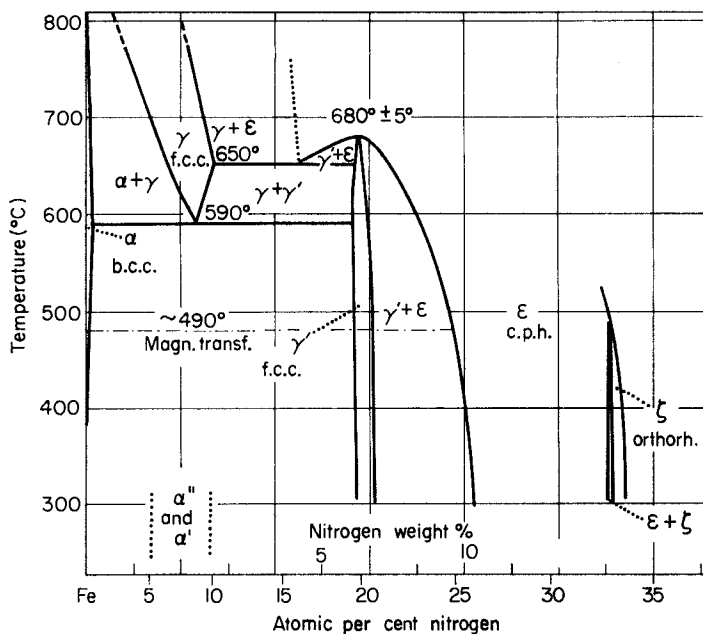


FIG. 6. The iron/nitrogen system (55, 70).

With 4–10 atom% of N in a specimen that has been annealed at 1000° or 800° and very rapidly quenched, a *tetragonal face-centered* δ -phase is found (49, 87). Its lattice constants would, with increasing nitrogen contents, approximate to those of the cubic ϵ -phase and, with decreasing nitrogen content—by extrapolation, to those of the tetragonal face-centered low temperature γ -Mn phase. There are thus close relationships between the γ -Mn high-temperature phase and the ϵ - and ϵ' -phases, and also between the γ -Mn low-temperature phase and the δ -phase.

There is also the possibility that a unique phase extends at high temperatures from high-temperature γ -Mn to Mn_4N ; that is, γ -Mn is progres-

sively stabilized with increase in its nitrogen content, and exists as Mn_4N even down to room temperatures (180). On this basis Mn_4N is not an intermediate phase but a high-temperature γ -Mn mixed crystal. Occurrence of the δ -phase could then be attributed to incomplete stabilization at low nitrogen contents and to transition, notwithstanding very rapid quenching, to the tetragonal low-temperature γ -Mn phase.

f. Iron. The fact that the iron/nitrogen system is relatively well known is due particularly to the investigation of Lehrer (106), Eisenhut and Kaupp (29), and Jack (67, 70, 71, 72). For low concentrations of nonmetal there is an extensive analogy with the iron/carbon system.

Nitrogen has a low solubility in cubic body-centered α -iron. This reaches a maximum of 0.4 atom% N at 590°C. On the other hand, solubility in cubic face-centered γ -iron, which exists above 910°C, is high, and this phase is stabilized to lower temperatures by intercalation of nitrogen. The maximum nitrogen content is 10.3 atom% at 650°C and there is a eutectoid at 590°C, 8.75% N (106). Since the γ -phase corresponds with austenite in the Fe/C system it is called "*nitrogen austenite*." With about 1 atom of nitrogen to 10 atoms of iron, about 10% of the octahedral holes of the cubic face-centered iron lattice are statistically occupied by nitrogen.

Further nitriding at higher temperatures, e.g., 700°C, leads at about 18 atom% N to the one-phase region of the ϵ -phase. This has a hexagonal close-packed arrangement of iron atoms with nitrogen distributed statistically in the octahedral holes. When a specimen of the hexagonal phase with 20 atom% N is cooled below 680°C a cubic γ' -phase Fe_4N results, while at somewhat lower nitrogen contents the ϵ -phase decomposes in a eutectoid reaction to the γ - and γ' -phases.

If nitrogen austenite (γ -phase) is cooled slowly it goes over eutectically to a mixture of the γ' -phase with α -iron. With quick cooling "*nitrogen martensite*" (α' -phase) is formed. In this, as in martensite, the iron atoms have a tetragonal body-centered arrangement. The nitrogen atoms are distributed statistically in the $\frac{1}{2}\frac{1}{2}0$ and $00\frac{1}{2}$ positions with a maximum of 9.4 N to 100 Fe (70).

When nitrogen martensite is annealed at somewhat over 200°C it is converted to $\text{Fe}_4\text{N} + \alpha\text{-Fe}$, just as martensite goes to $\text{Fe}_3\text{C} + \alpha\text{-Fe}$. When the annealing is done at a lower temperature (120°C), however, an intermediate α'' -phase is formed which may be considered as an *ordered nitrogen martensite*. Its decomposition results only on prolonged annealing (71). The phase changes are represented in Fig. 7.

Figure 8 shows the structure corresponding to the ideal composition of ordered nitrogen martensite (α'' -phase, Fe_{16}N_2). It is possible, however, for up to 50% of the nitrogen sites in the lattice to be unoccupied without change in the dimensions of the elementary cell. When iron atoms are

displaced in the direction of the c -axis, deformed octahedral holes (71) are formed from the holes of the original cubic body-centered or tetragonal body-centered elementary cell.

The structure of the α'' -phase, Fe_{16}N_2 , may also be derived from Fe_4N : each second Fe_4N -cell contains one nitrogen atom; tetragonal deformation of the elementary cell of Fe_4N is compensated by displacement of iron atoms in the direction of the c -axis, so that a true coordination number of 6 results (71).

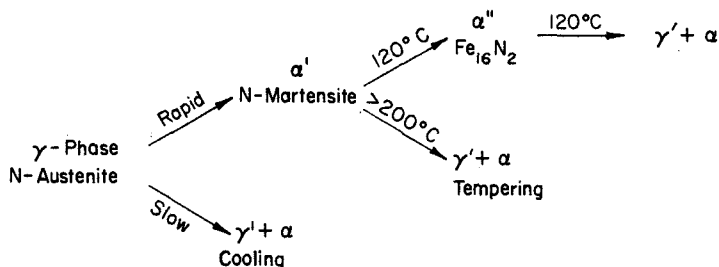


FIG. 7. Transitions of the γ -phase in the iron/nitrogen system at lower temperatures.

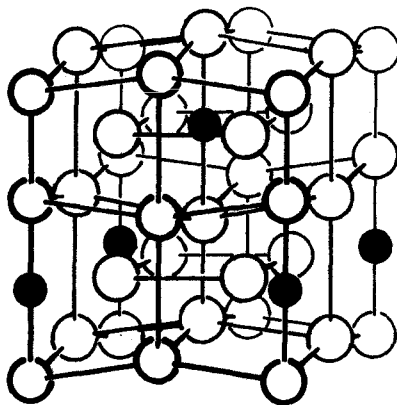


FIG. 8. Lattice of Fe_{16}N_2 (α'' -phase of ordered nitrogen martensite): \circ Fe; \bullet N.

The *hexagonal* ϵ -phase contains $\text{Fe}_2\text{N}_{0.66}$ in the unit cell when the composition is Fe_3N ; this is valid for a statistical distribution of nitrogen atoms over the two available octahedral holes of the cell. In actual fact a superstructure (Fe_6N_2) of 3 times the volume with $a' = a\sqrt{3}$ is found. Figure 9(A) shows the positions of nitrogen atoms, according to Hendricks and Kostling (57), in the triple elementary cell with a lattice constant of $a\sqrt{3}$. Positions of the nitrogen atoms are shown. Iron atoms are shown only for the environment of one N atom with $z = 0$. They have $z = \frac{1}{4}$ or $z = -\frac{1}{4}$.

Nitrogen atoms are arranged so that neighboring octahedral holes are unoccupied in the direction of the c -axis and at right angles to it.

The hexagonal phase reaches almost the composition Fe_2N . In it there is the same superstructure cell; half of the octahedral holes corresponding to a composition that is somewhat poorer in nitrogen than Fe_3N_4 are occupied in such a way that there is a lattice vacancy above and below each nitrogen atom [cf. Fig. 9(B)]. In addition, there is one N atom in the "nitrogen layer" with $z = \frac{1}{2}$ and two in the other (with $z = 0$).

There is also an *orthorhombic* ξ -phase, Fe_2N , separated from this hexagonal phase by a very narrow two-phase region and with almost the

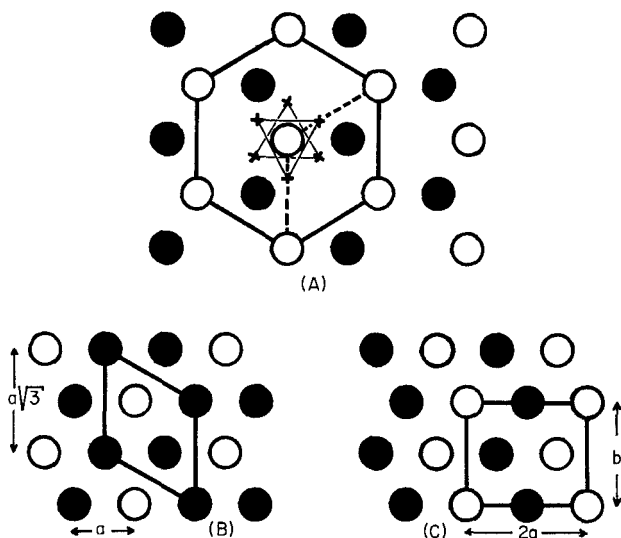


FIG. 9. Projections of the nitrogen sites on the x, y planes of iron nitride Fe_3N – Fe_2N . (A): $\epsilon\text{-Fe}_3\text{N}$; (B) $\epsilon\text{-Fe}_2\text{N}$; (C) $\xi\text{-Fe}_2\text{N}$; \circ N in $z = 0$; \bullet N in $z = \frac{1}{2}$; \times Fe in $z = \pm\frac{1}{4}$.

same composition. The iron atoms in it have basically the same arrangement as in the hexagonal phase, but the orthohexagonal cell is somewhat deformed in the sense of becoming orthorhombic. Nitrogen atoms, however, are arranged differently. The two nitrogen layers referred to previously now each contain the same number of atoms. Figure 9(C) shows the structure of the orthorhombic elementary cell (Fe_3N_4). Neighboring octahedral holes are now filled by nitrogen in *one* direction, leading to an expansion in this direction compared with the original hexagonal form (67, 72).

With intermediate nitrogen contents in the hexagonal phase, a superstructure with an even larger elementary cell makes its appearance as a result of ordered nitrogen layers. For the composition $\text{Fe}_{24}\text{N}_{10}$ the unit cell has $a'' = a \cdot 2\sqrt{3}$ for the same value of c .

g. Cobalt. In the system *cobalt/nitrogen* there is a similar situation: Co_3N is found as a hexagonal intercalated structure with a superstructure cell that has 3 times the volume (25, 89). With higher nitrogen contents this is succeeded by a broad two-phase region, followed by the stoichiometric phase Co_2N , having an orthorhombic deformed hexagonal close-packed arrangement like the ξ -phase of iron (89). Electron diffraction also reveals on cobalt surfaces a cubic phase, to which the composition Co_4N has been assigned, with a structure analogous to that of Fe_4N (170). A poorly crystallized CoN has also been described to which a NaCl structure (154) or, in more recent work, a zinc blende structure (78) has been attributed.

h. Nickel. In the system *nickel/nitrogen* there is a hexagonal Ni_3N phase of small breadth which, because of the ordered nitrogen layers, again requires a 3-fold increase in the unit cell size (69, 90). Electron diffraction has detected the Ni_4N phase (169), which is analogous to the case of cobalt. The nitride Ni_3N_2 , formed by thermal decomposition of the amide, is amorphous (173).

i. Copper. It might be expected that this series would also include a corresponding nitride of *copper*. The compound Cu_3N has indeed been prepared, but has nothing in common with the nitrides of iron, cobalt, and nickel of the same composition. The compound shows no metallic conduction and crystallizes with the ReO_3 lattice. It must be considered as a compound of Cu(I) which is partly polar in character (82). It will not be further considered.

B. PREPARATIVE METHODS

The most diverse methods are available for preparing metallic nitrides. This is due primarily to great differences in thermal stability and, associated with this, in enthalpies of formation. Thermal properties are described (Section II,C,1). It may be noted, however, that TiN , for example, has an enthalpy of formation of -79.7 kcal (59) and can be heated in nitrogen at 1 atm up to 2900°C . Both enthalpy of formation and thermal stability decrease with increase in the atomic number of the metal; Ni_3N has an enthalpy of formation of -0.2 kcal (54) and decomposes rapidly at 400°C . Indeed, this decomposition would occur at lower temperatures if it were not kinetically hindered.

In the following pages relevant preparative methods will be discussed with examples [cf. (93)], without, however, attempting a complete coverage of the literature.

1. Nitriding of Metals

This method is of the greatest importance today because metals of high purity are available.

(a) In nitriding with *nitrogen* it follows that only that phase will be obtained that is in equilibrium at the given temperature with the pressure of nitrogen used. The nitrides TiN (1, 28), VN (53), and CrN (11) may be prepared with nitrogen at 1 atm. For complete nitriding it is necessary to employ temperatures between 1100° and 1600°C, depending on the fineness of division of the metal and the duration of the treatment. In the system manganese/nitrogen a nitrogen pressure of 1 atm at 750°C gives a product with about 22 atom% N (153) whereas, at 200 atm and 740°C, 32 atom% N is reached (47). In the case of elements of the eighth group, nitriding with nitrogen at pressures which can be attained without special facilities is no longer possible.

(b) A substantially higher degree of nitriding is attained by use of *streaming ammonia*. If ammonia at, say, 500°C is passed at a sufficiently high streaming rate over iron, it is found that the degree of dissociation in the gas phase is far short of the equilibrium value. Calculations from the equilibrium constant would indicate very high equilibrium pressures of nitrogen. In fact, the dissociation equilibrium in the gas phase is established slowly, whereas equilibrium between ammonia and metal, leading to the formation of nitride and hydrogen, is established rapidly. In this way it is possible from the metal and streaming ammonia to prepare nitrides of iron (105), cobalt (89), or nickel (90), all of which have a very low enthalpy of formation and also a very high equilibrium pressure of nitrogen at the temperature of their preparation.

A further preparative route is the use of a mixture of *ammonia* and *hydrogen*. With ammonia at 1 atm and for a given flow rate and temperature only a fixed nitrogen content can be attained. Variation in the volume ratio $\text{NH}_3:\text{H}_2$ in the gas taken enables lower nitrogen pressures to be set up, and this makes possible the preparation of less highly nitrified material. For example, a mixture of 98% NH_3 and 2% H_2 , at 500°C and 1 atm, corresponds with a nitrogen pressure of about 8×10^9 atm, and a mixture of 70% NH_3 and 30% H_2 with a nitrogen pressure of about 1.2×10^6 atm (36). The formation of Fe_4N may be mentioned as an example. This requires an NH_3/H_2 mixture at 500°C with 20 vol% NH_3 , corresponding with a dissociation pressure of about 5.2×10^3 atm N_2 . This method of working has been important in establishing the Fe-N phase diagram (105, 132).

2. Nitriding of Metallic Compounds

(a) The classical method for preparing metallic nitrides is the reaction of *metallic oxides*, e.g., TiO_2 , with *nitrogen* in presence of *carbon*. This process was used in the fundamental researches of Friederich and Sittig (40), although it is applicable only to nitrides of high thermal stability and does not lead to pure products. With titanium, for example, reaction

above 1600°C with 1 atm N_2 leads to titanium carbide and, below this temperature, to titanium nitride. The ability of TiN to form mixed crystals with TiC and TiO also makes the thermodynamic treatment of the reaction very difficult (117). VN and CrN may also be made by this process, although contamination with carbide occurs even more readily.

(b) In many cases it has proved advantageous to nitride *amalgams, hydrides, oxides, and halides* with ammonia. The principle is well illustrated by the nitriding of manganese amalgam. As the temperature is increased the amalgam decomposes and the resulting very finely divided metal reacts with ammonia that is passing over it. This method may be operated at relatively low temperatures and yields products which are highly nitrated (107). Reaction with titanium hydride or vanadium hydride occurs similarly. They react with nitrogen or, better, with ammonia at 1000°C (37).

Ammonia has an additional role as a reducing agent in the conversion of oxides and halides. From NH_4VO_3 it is possible to make VN by reaction with ammonia at 900°–1000°C (21). Fe_3O_4 also reacts with ammonia at 430°C to form Fe_2N (58). Fluorides of cobalt and nickel, which have the advantage that they do not form amines, are likewise reacted with ammonia (89, 90). Other halides may be transformed after intermediate formation of an ammine or following ammonolysis. Thus $TiCl_4$, for example, yields TiN of stoichiometric composition if the reaction temperature is increased to 1400°–1600°C (14). At lower temperatures material is produced with up to 20% of vacancies in the titanium sublattice, i.e., with an excess of nitrogen (14).

(c) Mention may also be made of experiments to prepare nitrides in the *plasma beam*. In a plasma burner fed with a mixture of 36 vol% N_2 and 64 vol% Ar, $TiCl_4$ is introduced with the nitrogen stream. Small crystallites of TiN separate in the cooled anode cavity. Since the elements are ionized in the beam the use of hydrogen may be dispensed with, although it is necessary in the growth process discussed below (130, 165).

3. Growth Processes

(a) The van Arkel process for the thermal decomposition of transition metal halides on a tungsten wire heated to a high temperature has also been used for making metallic nitrides. In preparing titanium nitride, $TiCl_4$ in an atmosphere of nitrogen and hydrogen is decomposed on a very thin tungsten wire heated electrically to 1000°–1400°C. Knowledge of the equilibrium underlying the reaction, which depends little on the temperature, allows the reaction temperature to be lowered still further. It is possible in this way to obtain 1–2-mm thick wires of TiN (115, 117, 118, 171a).

(b) Basically the same process is used to coat carrier materials such as steel or corundum with a thin surface layer of TiN (24). The temperature

may be lowered to about 1000°C and well adhering layers with thicknesses of 6μ , for example, may be obtained on sheet steel (117).

Using the same method, VN may be prepared from VCl_4 , nitrogen, and hydrogen at 1400°–1600°C on tungsten wires (115), and VN layers may be put onto carriers at 1100°–1600°C (24).

4. Thermal Decomposition

(a) Thermal decomposition of metallic *nitrides* (also discussed in Section II,C,1) offers the possibility of preparing nitrides of lower nitrogen content by thermal decomposition of a highly nitrated product. Thus it is possible to submit Co_2N , which is the most highly nitrated compound, to careful degradation and so obtain Co_3N (89). Since, however, thermal decomposition is not generally done under equilibrium conditions, there is the danger of forming nonhomogeneous products.

(b) Nitrogen-rich nitrides may be prepared by thermal decomposition of *amides* obtained by precipitation from liquid ammonia. For example, CoN may be made from $\text{Co}(\text{NH}_2)_3$ (154) or Ni_3N_2 from $\text{Ni}(\text{NH}_2)_2$ (173). Equilibrium reactions are not involved and the products are not crystalline.

5. Reactions in the Solid State

(a) When stability relationships permit, preparations of medium nitrogen content may be obtained quite simply by heating the metal with a nitrogen-rich nitride. Reaction is favored by the use of fine grain sizes and pressing the mixed reactants. If sufficient attention is paid to homogenizing the material, this approach may be used in studying the systems titanium-, vanadium-, chromium-, and manganese-nitrogen.

(b) In this connection mention may be made of sintering and hot-pressing, a prerequisite of which is the production of material of small particle size by special processes. Temperatures of 1300°–1600°C and pressures of 70–150 kg/mm² are used. The process, which has long been of importance in laboratory and technical practice, is dealt with fully by Kieffer and Schwarzkopf (94). Contributions to the theory of sintering have also been made by Hüttig (64). The thermodynamics of the sintering process in the presence of carbon has been treated for TiN (12).

6. Melting

The preparation of nitrides in melts is not in general possible because the compounds either undergo thermal dissociation too readily or have very high melting points. The system titanium/nitrogen has been investigated with the aid of arc melting for products of low nitrogen content (131).

C. PROPERTIES

1. Chemical and Thermal Properties

Scandium nitride represents a bridge between polar calcium nitride and TiN, a typical transition metal nitride with metallic character. Saltlike nitrides are hydrolyzed by water with formation of ammonia, and this is true to a small extent of ScN. It is a strongly exothermic compound, although the only value for the enthalpy of formation, -67.5 kcal/mole (125), is an estimate based on interpolation. Collected values of enthalpies of formation and free enthalpies of formation are given in Table II. As for many transition metal nitrides, the melting point of ScN, 2627°C (40), is substantially higher than that of the metal (1400°C).

TABLE II
THERMODYNAMIC DATA

Phase	ΔH_{298} (kcal/1N)	ΔG_{298} (kcal/1N)	Reference	Additional readings
ScN	-67.5	—	(152)	—
TiN	-79.67	—	(104)	(59, 63, 125)
	—	-72.52	(104)	(159)
VN	-51.88	-45.7	(112)	—
γ -CrN	-29.01	—	(104)	(124, 151)
Cr ₂ N	-30.8	-24.2	(111)	—
ζ -Mn _{2,5} N	-24.1	—	(110)	(160)
ϵ -Mn ₄ N	-30.3	—	(110)	—
ζ -Fe ₂ N	-3.0	—	(23)	(1, 70, 92, 120)
γ' -Fe ₃ N	-4.5	—	(23)	(22, 92)
Ni ₃ N	-0.2	—	(54)	—
Cu ₃ N	+17.84	—	(83)	—

In *titanium nitride* the chemical properties of the transition metal nitrides as high melting cermets are well developed. Indeed, it has the greatest chemical and thermal resistance of any of the compounds in the series under consideration. In the cold it is attacked only by aqua regia but, on warming, slow attack occurs with acids or alkalies to yield ammonium salts or ammonia. TiN is resistant to chloride melts and metallic melts of iron, aluminum, or copper, but will not withstand oxide slags.

The scaling resistance in air is not very good. Systematic studies have shown that TiN in air undergoes a weight increase due to oxidation of 1 mg/cm^2 in 6 hours at 800°C . From kinetic studies it shows that two processes are operating at about the same rate: on scaling, rutile is being formed at the TiN/TiO₂ interface with an activation energy of 24.5 kcal/

mole, while oxygen and nitrogen diffuse through the rutile layer with an activation energy of 46.4 kcal/mole (119).

The enthalpy of formation of TiN determined by the Knudsen effusion method is $\Delta H_{298} = -79.7$ kcal/mole (104) and is the highest in the series of compounds under consideration. The same is true of the free enthalpy of formation ($\Delta G_{298} = -72.5$ kcal/mole) (104). In the effusion method, solid TiN vaporizes as titanium and nitrogen. With this method a nitrogen partial pressure of 32.2×10^{-6} atm is measured at 1968°C (59). Mass spectrographic studies also show that TiN is thermally dissociated at about 1800°C and does not evaporate as molecules (2, 3). The melting point, 2947°C (1), is particularly high. The sample must, of course, be melted in a nitrogen atmosphere as TiN dissociates in vacuum at high temperatures.

With increasing atomic number the chemical and thermal resistance of the nitrides decreases fairly steadily. *Vanadium nitride*, VN, is insoluble in nonoxidizing acids, but dissolves in either nitric or concentrated sulfuric acid. Part of the nitrogen appears as an ammonium salt and the remainder as elementary nitrogen. This behavior is also observed with the other nitrides. They are decomposed by strong alkalis with evolution of ammonia. V_3N is less resistant chemically than is VN (53). A value of 2050°C has been given for the melting point of VN, although it also undergoes decomposition (40). The enthalpy of formation of VN, determined by combustion calorimetry, is -51.88 kcal/mole (112), which is appreciably less than that of the preceding nitrides. The same is true of the free enthalpy of formation (-45.7 kcal/mole) (112).

The *chromium nitrides* CrN and Cr_2N dissolve in concentrated hydrochloric acid, part of the nitrogen being liberated as such. The enthalpies of formation of CrN and Cr_2N , determined by direct nitriding under pressure or by combustion calorimetry, are almost the same [CrN, -29.0 kcal/mole (104); Cr_2N , -30.8 kcal/mole (111)]. The free enthalpy of formation of Cr_2N is -24.2 kcal/mole (111). It is possible to prepare CrN with nitrogen at 1 atm, but melting points cannot be determined since CrN and Cr_2N decompose at about 1500°C without melting.

The *manganese nitrides* dissolve in dilute nonoxidizing acids with formation of ammonium salts and are also decomposed slowly by water. Enthalpies of formation are only a little lower than for the chromium compounds (ζ - $Mn_{2.5}N$, -24.1 ; ϵ - Mn_4N , -30.3 kcal/mole) (110). Equilibrium pressures are, however, substantially higher; the phase Mn_4N at 540°C has a nitrogen pressure of about 3 torr (153).

The *iron nitrides* are only slightly exothermic. Enthalpies of formation have been determined by solution calorimetry (ζ - Fe_2N , -3.0 ; γ' - Fe_4N , -4.5 kcal/mole) (23). The equilibrium between ammonia and iron leading to formation of the various iron nitrides and hydrogen has been studied

repeatedly (31, 132). Equilibrium nitrogen pressures may be calculated from these experiments. It is found, for example, that Fe_4N at 525°C has a nitrogen fugacity of 5600 atm (31), a value which, compared with equilibrium pressure of Mn_4N already cited, illustrates the low stability of the iron nitrides. Nitrogen dissociation pressures have also been measured directly in high-pressure apparatus. The phases $\alpha\text{-Fe}$ and Fe_4N exist in equilibrium with one another at the following pressures: 300°C , 2100 atm; 400°C , 2300 atm; 500°C , 2700 atm. This is in approximate agreement with the results of phase analysis by the X-ray and magnetic methods and with the equilibrium measurements already referred to (100). At room temperature the iron nitrides are metastable; the rate of decomposition becomes measurable only at higher temperatures, which depend on particle size and nitrogen content.

A minimum in chemical and thermal stability is reached in the *nitrides of cobalt and nickel*. Ni_3N has an enthalpy of formation of -0.2 kcal/mole (54) and Cu_3N is actually endothermic with a value of 17.8 kcal/mole (83).

2. Mechanical Properties

The mechanical properties of nitrides are at least as important for their technical applications as chemical and thermal stability. It is not surprising therefore that this aspect of the subject has been studied intensively, particularly in the cases of TiN used as a metallic cermet and of the nitrides which are encountered in steel.

Scandium nitride, with a hardness of 7–8 on Moh's scale (40), is already decidedly hard. With *titanium nitride* a hardness almost equal to that of diamond is reached. The results of measurements are not, however, always concordant, and depend on the conditions of preparation and the purity of the specimens. With fused TiN , values of 9–10 (37) and 8–9 (14) have been recorded. Determinations of the microhardness of TiN layers evaporated onto steel gave Vickers hardness values of 1700–1900 kg/mm² (117). Titanium nitride is, however, extraordinarily brittle and as a result finds no uses as a cermet in its pure form. It may be sintered with a metal such as cobalt to give a satisfactory product or may be used as a surface coating. Compact TiN and evaporated layers of TiN on molded bodies may be polished with corundum powder (117).

Vanadium nitride, VN , is about as hard as TiN : values of 9–10 on Moh's scale have been found for specimens that have been melted (7, 40). Comparative measurements of the microhardness on specimens subjected to varying degrees of nitriding and subsequently sintered have shown a relationship between the hardness and changes in bonding with progres-

sive nitriding ($\text{VN}_{0.338}$, 1900; $\text{VN}_{0.74}$, 1520; $\text{CrN}_{0.47}$, 1571; $\text{CrN}_{0.99}$ 1093 kg/mm^2) (149).

Reference may also be made to nitrided *chromium* surfaces, which are very hard and possess high thermal stability and corrosion resistance, as well as a high resistance to abrasion. They are characterized by micro-brittleness, which hinders cold welding and seizing (109, 175). These films find applications because of their corrosion resistance. Quite apart from nitride formation, incorporation of nitrogen in metallic chromium increases brittleness because of local distortions in the metal lattice. The cold brittleness boundary is also lowered as a result of local distortions in the chromium lattice (96, 174). The influence of nitrogen is very much greater than that of oxygen (172).

The hardness of the *manganese nitrides* varies greatly. The ϵ -phase, Mn_4N , has a microhardness of 850–950 kg/mm^2 at room temperature (6). Above 700°C it becomes ductile and the ductility increases progressively as the nitrogen content of the ϵ -phase is decreased. The nitrogen-poor δ -phase obtained by quenching is also ductile, as is the low-temperature modification of γ -manganese itself (87, 180). Manganese nitrides are also used as nitrogen-containing intermediate alloys in steel making.

There are no exact hardness measurements for the *iron nitrides* because sintered specimens cannot be prepared from them. Determinations of the microhardness of nitride deposits on iron gave the following values: nitrogen-containing α -Fe, 160; $\epsilon + \gamma$ -phase, 280; nitrogen-martensite, 580; γ -phase 260 kg/mm^2 (98). A 0.5-mm thick nitride layer containing the α -, ϵ -, and γ -phases had a Vickers hardness of 927 kg/mm^2 (138).

These results show that the hardness of the iron nitrides is much below that of the nitrides so far discussed. In spite of this they are of considerable technical significance. This does not, however, depend directly on the properties of the iron nitrides. The hardness and other mechanical properties of nitrogen-containing iron obtained by surface nitriding are associated with iron lattice defects arising from nitride deposits; blocking of the glide planes results (41). Electron microscope studies also show that the hardness is due to deformation of the iron lattice resulting from nitride separation (65).

A further substantial increase in hardness is obtained by nitride formation in nitrated alloy steels. These contain particularly chromium, titanium, or vanadium, binary or ternary nitrides of which are produced in the process of surface nitriding. These phases, in conjunction with the effects associated with iron itself, produce the great hardness.

There is no information on the nitrides of *cobalt* and *nickel*, which cannot be obtained in the sintered form. It will be seen, however, that a

decrease in hardness is to be expected by analogy with the decrease in chemical and thermal stability in the nitrides from titanium to nickel.

3. *Electrical and Optical Properties*

All binary nitrides have a high *electrical conductivity*. This is often of the same order of magnitude as the conductivity of the pure metal and the temperature coefficient is always negative.

Scandium nitride, ScN, which may be considered as having a polar structure, has a small specific resistance ($300 \times 10^{-6} \Omega \text{ cm}$). This value was obtained with a sintered specimen containing 4.5% Sc_2O_3 (40). TiN has the lowest specific resistance, with a value of $17.3 \times 10^{-6} \Omega \text{ cm}$, measured on rods of high purity made by the van Arkel growth process. The temperature coefficient of resistance is positive from 20° to 800°C (117). As the atomic number of the metal increases so does the specific resistance of the nitrides. For VN it is 200×10^{-6} (40), for $\text{VN}_{0.93}$ 85×10^{-6} (149), and for $\text{VN}_{0.338}$ $123 \times 10^{-6} \Omega \text{ cm}$ (149). The specific resistances of $\text{CrN}_{0.926}$ (640×10^{-6}) and $\text{CrN}_{0.497}$ ($79 \times 10^{-6} \Omega \text{ cm}$) differ sharply (149). Among the nitrides of the later elements in the series, only Ni_3N ($2800 \times 10^{-6} \Omega \text{ cm}$) has been studied (88). Exact values cannot be obtained for nitrides of the eighth group as only powders are available for the measurements.

Cu_3N is a semiconductor; its electrical behavior shows that it does not belong to the transition metal nitrides (88). Measurements have also been made of the resistance of thin nitride films made by evaporation in the glow discharge in nitrogen, to which the formulas Fe_3N_2 and Ni_3N_2 have been assigned (77).

Superconductivity has been found in TiN below 4.2°K (117) or 5.6°K (56) and in VN below 8.2°K (56). The transition temperature in the case of TiN falls with increase in the oxygen content as a result of the incorporation of oxygen in the nitrogen sublattice. TiO itself is not a superconductor. A dependence on the oxygen content of the specimen is also observed in the case of VN if VN-VO mixed crystals are present (56). CrN does not show superconductivity down to 1.2°K (56).

The differential *thermoelectric coefficients* for the following nitrides have been measured: $\text{TiN}_{0.98} - 10.8$; $\text{VN}_{0.34} - 5.3$; $\text{VN}_{0.93} - 4.6$; $\text{CrN}_{0.50} - 2.3$; $\text{CrN}_{0.926} - 92 \mu\text{V/degree}$. All were examined in the sintered form (149).

Hall coefficients for the same five compounds were -0.67 , -0.9 , -0.45 , -0.72 , $-264 \text{ cm}^3/\text{coul}$. (149). Trends in the values for the Hall coefficient, electrical conductivity, and thermoelectric coefficient of the nitrides have been correlated with the progressive filling of the 3d shell of the metal atom (149) (cf. Section II,D,2).

The *color* of nitrides varies greatly with the particle size. Powdered finely crystalline preparations are light brown (TiN), dark brown (VN), or

dark gray to black (nitrides from chromium to nickel). Well-crystallized specimens, made by the growth process (TiN, VN) or by sintering (TiN, VN, CrN), are golden yellow or bronze in color. They exhibit a metallic luster, which is enhanced by polishing. Recrystallized ScN, which is known only with a Sc_2O_3 content of 4.5%, is dark blue in color (40). Specimens of TiN containing oxide are likewise blue to blue-black (40). Materials prepared at relatively low temperatures from titanium tetrachloride and ammonia, which have a nitrogen content in excess of that corresponding to TiN and in which titanium is therefore present in part in an oxidation state of +4, are dark blue (14). In very thin transparent TiN films deposited on so-called "sapphire windows" consisting of ground Al_2O_3 plates, absorption has been measured in the range 200–1000 $\text{m}\mu$. The absorption minimum is at 400 $\text{m}\mu$. Contrary to what is observed visually, no difference is found between pure metallic TiN and semiconducting TiN containing oxygen (cf. Section III,A,3). The reflecting power in the infrared appears to be somewhat different for the two nitrides (117).

The *X-ray emission spectra* of some nitrides (TiN, VN, CrN, and Cr_2N) have been measured and compared with those of a large number of related compounds. The spectrum of TiN, for example, shows, in addition to the $\text{K}\beta_5$ line, a satellite at longer wavelengths which does not occur in the spectrum of titanium metal. The spectra of TiN, VN, CrN, and Cr_2N are explained by the splitting of the $3d$ level into t_{2g} and e_g levels by the crystal field in the octahedral environment (123).

The question of the charge on the nitrogen atom in intercalation compounds is difficult to answer. X-ray determination of the atomic scattering factor for nitrogen in Mn_4N shows that nitrogen is not an electron donor: results are consistent with N^0 or N^{1-} , but not with N^{3+} . The absence of low-angle reflections, from which the distinction between the different oxidation states is normally made, makes it impossible to differentiate between N^0 and N^{1-} (103). These results obtained by Kuriyama (103) do not agree with Elliott's determinations of the atomic scattering factor in Fe_4N (30), which show N^{3-} to be the probable species. They are, however, consistent with the general concept of a covalent metal-nitrogen bond (cf. Section II,D).

4. Magnetic Properties

In the transition metal nitrides one finds not only paramagnetism (e.g., in TiN) but also antiferromagnetism (CrN), ferromagnetism (Fe_4N , $\epsilon\text{-Fe}_2\text{N}$), and ferrimagnetism (Mn_4N). Some of the compounds with the last three properties have been studied in very great detail as they are very important for theories of magnetism and the chemical bond (they are further discussed in Section II,D,2).

a. Paramagnetism. For nitrides of the type MeN, susceptibility values are known only in the case of TiN and CrN. Molecular susceptibilities, χ_{Mol} in cgs units, are

$$\begin{aligned}\text{TiN (20°C)} & 89 \times 10^{-6} \text{ (97, 117)} \\ \text{CrN (24°C)} & 763 \times 10^{-6} \text{ (26)}\end{aligned}$$

The paramagnetic susceptibility of TiN decreases somewhat with increasing temperature (117). CrN becomes antiferromagnetic below 0°C (cf. subsection b). Further susceptibility measurements on CrN and Cr₂N are difficult to correlate with those quoted (122).

The hexagonal ζ -phase in the system manganese/nitrogen (composition MnN_{0.41}) obeys the Curie-Weiss law of the form

$$\chi_{\text{Mol}} = \frac{0.0316}{T + 1070}$$

between -180° and 530°C, leading to a value of χ_{Mol} for MnN_{0.41} at 20° of 1405×10^{-6} (179). This gives a magnetic moment of 3.94 μ_B , which is only a little greater than that corresponding with the spin moment of three unpaired electrons. For preparations of the ζ -phase richer in nitrogen (MnN_{0.48}) and for the tetragonal η -phase (MnN_{0.66}), measured values are 949×10^{-6} and 784×10^{-6} , respectively (18).

The orthorhombic ζ -phase Fe₂N is also paramagnetic (17). The magnetic moment is 0.19 μ_B per Fe atom (178). The hexagonal ϵ -phase is normally ferromagnetic (cf. Section II,C,4,c), but nitrogen-rich specimens (Fe_{2+x}N, where $0 < x \leq 1$) have a low Curie point so that they are paramagnetic at room temperature (17).

A thermomagnetic study of the paramagnetic phase Ni₃N has yielded information on its decomposition temperature. It has also been found that nickel formed in the decomposition has a Curie point that is lowered by about 18° because of intercalated nitrogen (9).

b. Antiferromagnetism. The only antiferromagnetic nitride identified so far is CrN below 273°K, which has been fully studied. Following the increase of susceptibility with decreasing temperature, there is a sharp drop in susceptibility at the Néel point of about 273°K. The structure of antiferromagnetic CrN is derived from that of the paramagnetic high-temperature modification (NaCl type) by orthorhombic deformation of the original cubic elementary cell. The orthorhombic *a*- and *b*-axes result from the face diagonals of the rock salt lattice, while the orthorhombic *c*-axis corresponds with the cubic axis. Figure 10 shows the structure. Only the Cr positions are shown, with $z = 0$ as points and $z = \frac{1}{2}$ as circles. The crystallographic orthorhombic elementary cell is shown by dotted lines, and the relationship to the original cubic elementary cell is also

indicated. One of the diagonals of the cubic face (a_{1h}) is shortened by about 1% and the other ($2b_{rh}$) is lengthened by the same amount. Alternating two (h00) planes are moved somewhat nearer together, as indicated by brackets in the diagram.

Neutron diffraction photographs at 77°K show a magnetic superstructure with 4 times the volume of the crystallographic cell; the a - and b -axes have to be doubled. Figure 10 also indicates the arrangement of spins. All spins lie parallel to the rhombic b -axis. In CrN we have one of the two possible "antiferromagnetic structures of the fourth order" (26). The spin moments of the atoms of *one* rhombic (h00) plane are all parallel. The

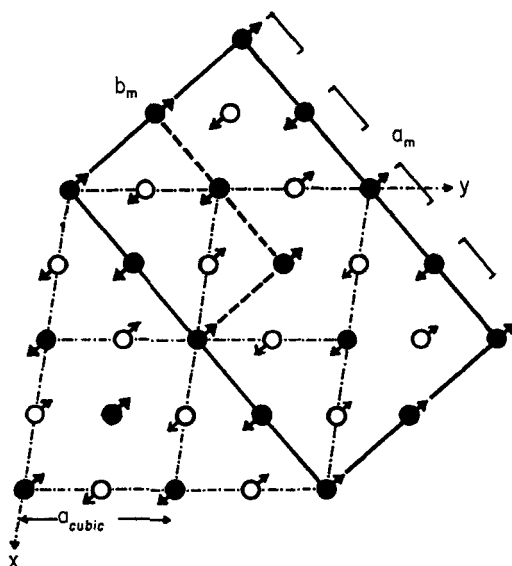


FIG. 10. Projection of chromium sites of antiferromagnetic CrN on the x, y planes: ○ Cr in $z = \frac{1}{2}$; ● Cr in $z = 0$.

resulting moments of these planes are, as one progresses in the [100] direction, arranged in the sequence $++--++--$. The interaction of the planes is thus alternately ferromagnetic and antiferromagnetic in type.

c. Ferromagnetism. Binary ferromagnetic transition metal nitrides are so far known only in the system iron/nitrogen. Ternary ferromagnetic nitrides may also be derived from them (cf. Section III,A,1).

Hexagonal ϵ -iron nitride at low temperatures is ferromagnetic over the whole phase range, but at room temperature only specimens with a low nitrogen content exhibit this property. The Curie point rises from -200°C for $\text{Fe}_{2.05}\text{N}$ to $+270^\circ\text{C}$ for $\text{Fe}_{2.8}\text{N}$ (106). The magnetic moment per iron

atom, obtained from saturation measurements, rises in the same sense. Following the paramagnetic rhombic ζ -Fe₂N phase, the moment at first rises sharply, then more slowly, until in the region from Fe_{2.1}N to Fe_{2.5}N the rise is linear from 1.1 μ_B to 1.9 μ_B . It remains constant from Fe_{2.5}N to Fe₃N (178). Since the nitrogen content is related to the lattice dimensions, both the Curie point and the magnetic moment may also be represented as a function of the lattice dimensions (17).

The magnetic structure of a specimen of the ϵ -phase with the composition Fe₃N_{1.17} (Fe₂₄N_{9.36}) has been studied in detail by Robbins and White (139). The hexagonal unit cell determined by X-rays contains in the ideal case 24 Fe atoms and 10 N atoms (cf. Section II,A,2,f). Since the distribution of N atoms in the octahedral holes has no bearing on the magnetic structure, the description of the arrangement of spin vectors for the metal atoms requires only a unit cell containing two Fe atoms. The following expressions describe the relationships between the axes of the two unit cells: $2a_{\text{magn}}\sqrt{3} = a_{\text{cryst}}$; $c_{\text{magn}} = c_{\text{cryst}}$. From neutron diffraction observations, the spin moments of the Fe atoms all have the same orientation and are parallel to the c -axis: this means that the compound is ferromagnetic. Neutron diffraction gives a moment of 1.5 μ_B per iron atom and extrapolation of the magnetization curve to 0°K gives 1.33 μ_B (139). This low value has been taken as proof that nitrogen is acting as an electron donor. The same conclusion is reached from structural data, for, taking the radius of the iron atom as 1.26 Å, that of nitrogen is found to be 0.66 Å. This is considerably smaller than the radius of N^{±0}, which the authors take as 0.77 Å (139).

The cubic γ' -phase, Fe₄N, has also been fully studied. The Curie point for the stoichiometric composition Fe₄N is at 488°C (46). Between Fe₄N_{0.97} and Fe₄N_{1.04}, which is the region of the γ' -phase, the Curie point varies from 481° to 508°C (17). Fe₄N has a magnetic moment of 8.86 μ_B per unit formula at 0°K (46). The mean value per atom of Fe agrees with that for α -Fe (2.22 μ_B) (161). On the basis of saturation measurements, Wiener and Berger have given an interpretation of the magnetic structure of Fe₄N which is also supported by measurements on the ternary compounds Fe₃NiN and Fe₃PtN (cf. Section III,A,1) (176). Frazer (39) has verified the structure proposed by neutron diffraction: iron atoms in the corners of the cube (cf. Fig. 11) have spin moments that are parallel to one another; the moment per Fe_c is 3 μ_B . A second magnetic sublattice is formed by the three face-centered iron atoms; the moment per Fe_f is 2 μ_B . The interaction between these two sublattices is also ferromagnetic. This model has also been verified by NMR studies with ⁵⁷Fe₄N (4). The relationship of the magnetic moments could also be established by interpreting the Mössbauer effect for Fe₄N (158).

d. Ferrimagnetism. The Curie point for the stoichiometric composition Mn_4N is at 483°C , and over the range $\text{Mn}_4\text{N}_{1.04}$ to $\text{Mn}_4\text{N}_{0.77}$ varies from 473° to 513°C (86). Measurements of saturation magnetization with Mn_4N gave a magnetic moment of $1.14 \mu_B$ per unit formula at 0°K , corresponding to a mean moment of $0.3 \mu_B$ per Mn atom (47, 86). Guillaud and Wyart recognized that the low moment of manganese was due to a partial paral-

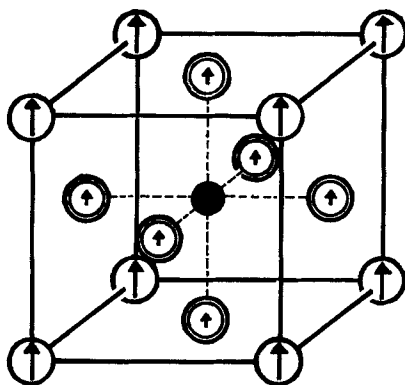


FIG. 11. Magnetic structure of Fe_4N : \circ Fe_c ; \odot Fe_f ; \bullet N.

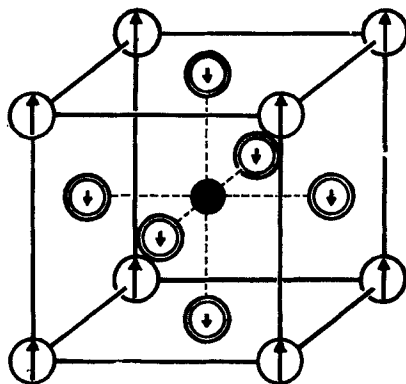


FIG. 12. Magnetic structure of Mn_4N : \circ Mn_c ; \odot Mn_f ; \bullet N.

lel—or antiparallel—arrangement of the spin moments, that is, to an uncompensated antiferromagnetism (47), which Néel (121) has termed ferrimagnetism. More certain indications of the magnitude and direction of the moments at the Mn positions were obtained in studies with polarized neutrons at 77°K (167, 168). Manganese atoms at the corners (Mn_c) and those at the centers of faces (Mn_f) both form a magnetic sublattice (cf. Fig. 12). Within the sublattice there is a ferromagnetic coupling of the

spin moments, and the moments between the two sublattices are coupled antiferromagnetically. For Mn_6 and Mn_7 the moments are $+3.84 \mu_B$ and $-0.90 \mu_B$, respectively. The residual moment of $+1.14 \mu_B$ per Mn_4N gives rise to ferrimagnetism (cf. Section II,D,2).

D. BONDING IN TRANSMISSION METAL NITRIDES

There is as yet no complete theory of bonding in transition metal nitrides. Concepts developed up to the present are based essentially on intercalation compounds of the types MeN , with the NaCl structure, and Me_4N , with the perovskite structure. Two approaches are apparent, one based mainly on the theory of the covalent bond and the other on the band theory of bonding in metals. The latter has been extended by inclusion of elements of the covalent bond model.

1. Covalent Model

Pauling (133, 134) explains bonding in the above two groups of nitrides in terms of his theory of the metallic bond, which he considers to be closely related to the covalent bond. Each atom of a metal forms covalent bonds with the neighboring atoms. Since the number of these is greater than the number of electron pairs available for covalent bonds, resonance occurs between the possible canonical forms. The electrical conductivity of metallic substances is based on this resonance.

Pauling's system of metallic valency and metallic single-bond radii $R(1)$, together with the bond number n (the quotient of the number of electron pairs available for bonds and the number of possible canonical forms), makes it possible by using the relationship

$$R(1) - R(n) = 0.300 \log n$$

either to calculate the *lattice dimensions* $R(n)$ from tabulated single-bond radii, assuming reasonable bond numbers, or, using X-ray determinations of the lattice dimensions, to calculate and interpret the bond order.

Applying these concepts to nitrides, it is assumed that nitrogen has the $2s$ orbital and three $2p$ orbitals available for bonding. Bonding in the NMe_6 octahedra is brought about by the five valency electrons of nitrogen and $6/2$ electrons of the neighboring metal. This gives a bond order $n = 4/6$, i.e., four bonds distribute themselves by resonance over six canonical forms. As an example, in vanadium nitride each vanadium atom has, after forming bonds to nitrogen, two further electrons that are available for the vanadium-vanadium bond. The bond order in the cubic face-centered vanadium sublattice is accordingly $n = 2/12$, when electrons of the neighboring atoms are taken into account.

Calculation of interatomic distances by the use of Pauling's single-bond radius of 0.70 Å for the nitrogen and the bond order referred to above leads, in the case of vanadium nitride, to good agreement with the values found by X-ray analysis. This method of calculation fails, however, when applied to ScN, TiN, and γ -CrN. Systematic deviations occur, depending on the atomic number of the metal. Thus in ScN and TiN the calculated Me-Me distances are too large and in CrN they are too small. Calculation of the bond order from distances based on X-ray analysis likewise yields results which are only qualitatively useful. In the case of Me_4N results are equally inexact. In spite of these large deviations, later authors have continued to use the basic concept of resonance in the covalent bond between nitrogen and the transition metal and of the multiple canonical forms in resonance for the covalent bonds between metal atoms.

Rundle's model (142) is a development of that proposed by Pauling. He limited his treatment to intercalation compounds of the type MeN and MeC with a rock salt structure formed by transition metals of Groups 3-5. However, he introduced additional postulates about the hybridization on both the nonmetal and the metal. It was concluded, on the basis of the increased Me-Me distance in the cermets compared with that in the pure metals, that electrons were withdrawn from the Me-Me bonds and used in Me-N bonds. High melting points were explained by Rundle in terms of strong Me-N bonds, and both hardness and brittleness were associated with the presence of directed covalent bonds.

The preferential occurrence of the NaCl structure with its octahedral coordination is due to use of the three nitrogen p orbitals which are at right angles to one another. The two electrons in the nitrogen s orbitals do not in most cases participate in bonding, so that six *half-bonds* are formed from the metal to nitrogen and the bond order $n = \frac{1}{2}$. The metal atom has hybridized d^2sp^3 orbitals available for bonding to nitrogen. If the nonmetal is less strongly electronegative with respect to the metal, sp hybridization occurs on the nonmetal so that two two-electron bonds and four half-bonds can be formed by using both the remaining $2p$ orbitals. The bond order n is then equal to $\frac{2}{3}$. Whether $n = \frac{1}{2}$ or $\frac{2}{3}$ can be estimated from the Me-N distances. For $n = \frac{1}{2}$ the Pauling single-bond radii will be exceeded by ~ 0.18 Å and for $n = \frac{2}{3}$ by ~ 0.10 Å. This distinction is, however, somewhat too rigid. Electrical conductivity is attributed to bond resonance as in the Pauling model.

Hume-Rothery (61), in contrast to Rundle, considers the arrangement of metal atoms as the factor determining the occurrence of an NaCl structure for nitrides of the type MeN . Nitrogen enters preferentially the octahedral holes in the cubic close-packed metal atom lattice, but not those in the hexagonal close-packed lattice. According to Hume-Rothery, the

environment of the metal atom is a determinative factor as well as the electron-deficient bonds based on the three $2p$ orbitals of nitrogen. In the NaCl type, d^2sp^3 hybridization allows octahedral coordination of nitrogen around the metal atom, whereas in the hexagonal close-packed metal lattice the metal atoms would be surrounded by nitrogen atoms in a trigonal prismatic arrangement. This arrangement is not observed for the nitrides in Groups 3-5.

The drop in melting point in going from TiN to VN is believed to be due to weakening of the bonding with increase in the electron concentration, as was also suggested by Rundle.

Samsonov has made a detailed study of the effect of electron concentration on bonding in cermetes (145, 146). He considers the nitrides as intercalation compounds with metallic character, in which isolated atoms of nonmetal are intercalated in the metal lattice. For one and the same nonmetal, bonding is then determined by the extent to which the incompletely filled d shell of the transition metal atom is occupied and by its position in the Periodic Table. The possibility of electron transfer from the nonmetal to the vacant orbitals of the metal atom is then expressed in terms of the "acceptor ability," $1/N_d n_d$, where N_d is the principal quantum number of the partly filled d shell, and n_d the number of electrons in this shell. It will be seen that the acceptor ability decreases with increasing atomic number. Various properties of the material vary systematically with the magnitude of this quantity. For example, with decreasing acceptor ability, for a certain number of intercalation compounds of Groups 4-6 there is a decrease in electrical conductivity (148), heat of formation, lattice energy (123), and hardness (123).

The treatments of Pauling, Rundle, and Hume-Rothery involve only σ -bonds between the metal and nitrogen in which the two e_g orbitals of the metal participate. Krebs (99) has suggested a resonance system of π -bonds between the three p orbitals of nitrogen and the t_{2g} orbitals of the metal, and this also should provide an explanation of the occurrence of the NaCl structure and of electrical conductivity.

A more precise application of the concept of the covalent bond to intercalation compounds of the type MeN and MeC is due to Bilz (10), who treated isolated XMe_6 coordination polyhedra within the lattice as " XMe_6 molecules" and provided a molecular orbital scheme of their bonding. Only σ -bonds were discussed. In each Me only that of the six d^2sp^3 hybrid orbitals is considered which is oriented toward the central nonmetal atom and is almost completely localized in this direction. Molecular orbitals involving the s orbital of the nonmetal and the corresponding metal orbitals gave little localized $\frac{1}{6}$ -bonds, whereas molecular orbitals from p orbitals of

the nonmetal and the corresponding metal orbitals are localized half-bonds. This provided a more precise picture of Rundle's $\frac{2}{3}$ -bonds.

Metal-metal bonds were not taken into account in the molecular model. Bilz therefore tried to broaden the concept of the pure molecular model by introducing the separate "XMe₆ molecules" into the lattice so that the orbitals overlapped. In the authors' view, the covalent model expanded in this way by introducing elements of the band model is still unsatisfactory.

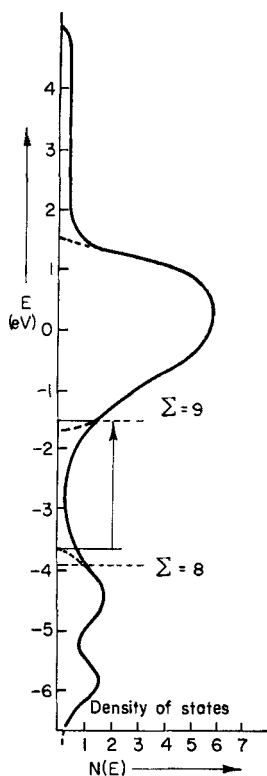


FIG. 13. Band scheme of TiN and TiC (10).

2. Band Model

Bilz (10) appended to his discussion of the covalent model a calculation of the electronic states for cermet MeX, based on the band theory of metals. The calculation was made for the [100], [111], and [110] directions in the K-space. From this the pattern of density of states was derived (cf. Fig. 13).

The low-lying *p*-band with strongly oriented *eigen* functions below the Fermi limit for $\Sigma(\text{valency electrons}) = 8$ (TiC or ScN) corresponds with the valency bond in the covalent model. The metallic bond corresponds to the very broad *s*-band with a low density of states which overlaps both the narrow *p*-bands, with a higher density of states, and the *d*-band, the functions of which are less dependent on direction. It is therefore to be expected that the metallic character will increase with increased electron occupation of the *d*-band in the series ScN, TiN, VN. This is supported by Kume and Yamagishi's nuclear magnetic resonance measurements on ScN and VN (102), which reveal more metallic character for VN and show ScN to resemble a half-metal. Presumably this may be correlated with the more polar character of ScN. The increase in metallic character required by Bilz's treatment is not, however, shown in the trend of electrical conductivities.

Between the *p*- and *d*-bands there is a marked minimum in the density of states at the Fermi boundary of $\Sigma(\text{valency electrons}) \simeq 8.5$. According to Bilz, this minimum is essential for comparing the band model with the observed properties of the materials: directed bonding of the *p*-band determines hardness and band overlapping the electrical conductivity. The latter becomes higher the higher the Fermi boundary lies. It is possible in this way to explain why the specific conductivity of TiN is greater than that of TiC. In the system TiC/TiN a minimum in conductivity in passing through the Fermi boundary would be expected as a result of a minimum density of states at about the composition $\text{TiC}_{0.5}\text{N}_{0.5}$. Experimentally, a conductivity minimum is found for the composition $\text{TiC}_{0.25}\text{N}_{0.75}$ (108). On the same basis a mixed phase $\text{TiC}_{0.5}\text{N}_{0.5}$ should show a melting point maximum with respect to its components TiN and TiC (1).

Incomplete occupation of the lattice of a cermet, which is often observed, especially among nitrides, is explicable in terms of a tendency to lower the Fermi boundary as far as possible below $\Sigma(\text{valency electrons}) = 8.5$. This allows extensive occupation of only the *p*-states. The light absorption of TiN and the color change of TiN/TiC mixed crystals with increase in the TiC content have also been correlated with the special Fermi boundary of $\Sigma(\text{valency electrons}) = 8.5$ (10).*

In describing bonding in nitrides with the rock salt or perovskite structure, Goodenough (44) starts from the metallic bond in transition metals. According to Mott (116), the distribution of electrons between the localized and the more delocalized bonding states is determined by a critical distance R_c : when the distance of the transition metal atoms in the lattice exceeds this value, the electrons are localized. When R_c is not exceeded "collective" electrons are present. Goodenough (43) gives a value of $R_c \lesssim 2.9 \pm 0.1 \text{ \AA}$. In the face-centered cubic metals Ni and Co, for example, the distance to

* New discussion of band structure of TiC, TiN, and TiO (34a).

the twelve nearest neighbors, $R_{nn} \sim 2.5 \text{ \AA}$, which is $< R_c$. That to the six next-nearest neighbors $R_{nnn} \sim 3.5 \text{ \AA}$, i.e., $> R_c$. Bonding to the next-nearest neighbors occurs through e_g orbitals ($d_{x^2-y^2}$, d_{z^2}), i.e., through extensively localized electrons which are in directed bonds involving narrow bands with a high density of states. Bonding to nearest neighbors is through t_{2g} orbitals (d_{xy} , d_{xz} , d_{yz}), which give a broad t_{2g} -band. There is also a very broad band with a low density of states which is formed by s and p orbitals. It is in these two bands that the collective electrons are found. A band scheme has been proposed for the cubic face-centered metals, Mn, Fe, Co, and Ni (43).

Nitrides with a *rock salt* structure were described by Goodenough as "ionic compounds with metallic conductivity" and in particular related to the oxides (44). In these compounds the band is partly ionic in character, because of the electronegativity difference between metal and nitrogen, and also partly covalent. Electrical conductivity is associated with partial filling of the t_{2g} -bands by collective electrons and is limited to compounds in which the metal-metal distances are less than R_c (as is the case for nitrides).

Nitrides crystallizing in the sodium chloride lattice are then formed only if three or less d electrons are available in the formally trivalent cation, so that the e_g orbitals are empty and the t_{2g} orbitals are either half or less than half filled. With large differences in electronegativity there is a large forbidden zone and the bonding electrons belong largely to the nitrogen sublattice; the bonding s and p - e_g electrons are predominantly on the nitrogen (ScN). With decreasing electronegativity difference the bonding electrons take on a stronger e_g character. The increasing covalent character of the bond may lead to cation-anion-cation exchange interaction (e.g., CrN).

Special bonding relationships intermediate between the two extremes described above exist in γ -chromium nitride, CrN. This modification, which crystallizes in the NaCl lattice and is stable at room temperature, has a magnetic moment corresponding essentially with the spin-only value for the Cr^{3+} ion. The covalent part in the bonding is not localized. Below 0°C CrN is antiferromagnetic with the magnetic structure given (Section II,C,4,b) (cf. Fig. 10). Transition from cubic to orthorhombic symmetry is associated with localization of the covalent bond. Cations in the (h00) planes (orthorhombic indication) have spin moments that are parallel to one another. In the [100] direction the spin arrangement for the (h00) planes alternates (cf. Fig. 10).

The covalent part of the Cr—N bond is now localized in the direction of the z -axis. Formation of a Cr—Cr bonding band occurs through d_{zz} and d_{yz} orbitals, which are inclined at 45° to the c -axis and are directed toward the neighboring Cr atoms (x and y being the axes of the original cubic lat-

tice). The magnetic arrangement is as follows: cation-anion-cation interactions along the z -axis are ferromagnetic, but are antiferromagnetic within a (001) plane. Cation-cation interaction between cations that are close together and bonded by d_{yz} and d_{zx} orbitals is antiferromagnetic, while for those which are more separated it is ferromagnetic. The d_{xy} orbital is not involved in bonding (42).

Nitrides of the *perovskite* type Me_4N are classified by Goodenough as interstitial alloys (44). The $\text{Me}-\text{N}$ bond in these substances is predominantly covalent in character, i.e., nitrogen is probably present in the lattice as a neutral atom. The concept of a covalent metal-nitrogen bond accords with Kuriyama's determination of the atomic scattering factor of nitrogen in Mn_4N (103) (cf. Section II,C,3), which shows nitrogen to be present as either N^0 or N^{1-} . Nitrogen has the $2s$ orbital and three $2p$ orbitals available for bonding, as in nitrides of the type MeN , and the metal has the e_g and t_{2g} orbitals. Me_c-Me_f , the distance between metal atom nearest neighbors (M_c is the metal atom at the corner of the cube and M_f that in the center of a face), is far below the critical distance. These bands therefore involve a broad t_{2g} -band containing collective electrons. As a result, good electrical conductivity is observed. In considering bonding to the next-nearest neighbor metal atoms two cases arise: bonding of the type Me_c-Me_c occurs through localized electrons in the e_g -band, and that of the type $\text{Me}_f-\text{N}-\text{Me}_f$, involving metal atoms in the centers of cubic faces, occurs via nitrogen atoms.

In the bonding Fe_f-N band of ferromagnetic γ' -iron nitride, Fe_4N (cf. Section II,C,4,c and Fig. 11) there are spin-paired states involving a p electron of nitrogen, so that only one e_g electron per Fe_f can contribute to the atomic moment. A further contribution comes from an unpaired t_{2g} electron, so that Fe_f has a moment of $2 \mu_B$; 0.95 electron is given up to the $4s$ -band. $\text{Fe}_f-\text{N}-\text{Fe}_f$ interactions are all ferromagnetic and, in this way, a magnetic Fe_f sublattice comes into being. A second sublattice involving Fe_c also has spins which are parallel. The atomic moment of Fe_c is $3 \mu_B$, i.e., $1 \mu_B$ more than that of Fe_f , because the absence of spin pairing with a p electron of nitrogen produces an increase in moment. Interactions between the two sublattices Fe_f and Fe_c are also ferromagnetic in character. The ferromagnetic interaction of the two sublattices is explained by Goodenough's rule (43, 44). This states that ferromagnetic coupling between the sublattices of a cubic face-centered arrangement of metal atoms will occur if n , the number of t_{2g} electrons, is greater than 5 but equal to or less than 6. This is true here as the $4s$ -band of iron has 0.95 electron per iron atom and there are two electrons in the e_g -band.

Following the neutron diffraction study of ϵ -manganese nitride, Mn_4N , by Takei *et al.* (cf. Section II,C,4,a) (167, 168), Mekata (114) has given a

qualitative band scheme for this substance. It is a modification of Goodenough's scheme for cubic face-centered manganese, but differs in the energetic arrangement of the e_g - and t_{2g} -bands relative to one another.

This scheme, shown in Fig. 14, relates to manganese (Mn_c) at the corner of the unit cell (Fig. 14a) and at the center of faces (Mn_f) (Fig. 14b) Mn_c forms one of the magnetic sublattices and the three Mn_f atoms the other. Spin moments of the two sublattices are antiparallel to one another. This is in agreement with Goodenough's rule, according to which anti-ferromagnetic coupling of the sublattices occurs if the number, n , of t_{2g} electrons is greater than 3 but not more than 5 (44). The diagram takes

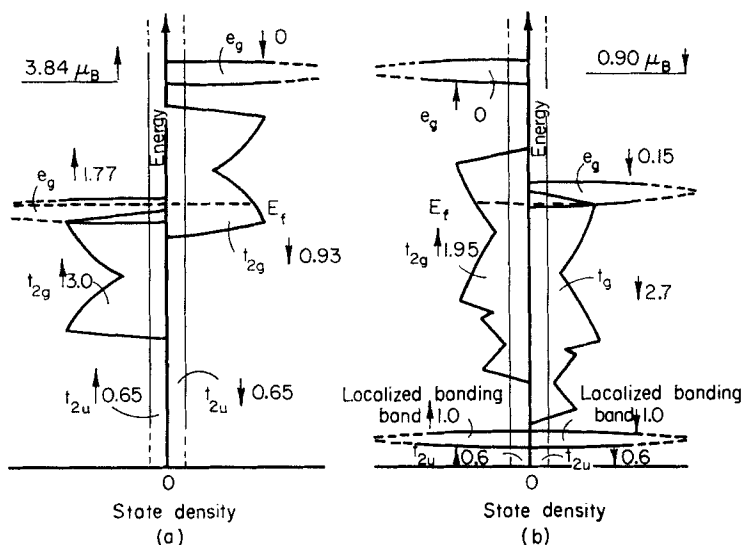


FIG. 14. The schematic state density curves of the energy bands in Mn_4N : (a) corner site Mn, and (b) face-centered Mn (114).

into account experimentally determined values of $3.84 \mu_B$ for Mn_c and $0.90 \mu_B$ for Mn_f .

The degree of occupation of the sub-bands is usually different for the two directions of spin (drawn in each figure to left and right) since these are displaced energetically relative to one another. Intraatomic exchange increases with localization of the electrons. Consequently the displacement is greater for the e_g sub-band than for the t_{2g} sub-band.

The scheme shows that from Mn_c there is a broad t_{2g} -band with a low density of states to the next manganese neighbor (Mn_f), this band being occupied by "collective electrons." The number of electrons in the t_{2g} -band is shown in the figure, account being taken of the spin orientation. A narrow

e_g -band with a high density of states is also present. This is directed toward the next-nearest neighbor manganese, i.e., from Mn_c to Mn_c . A very broad t_{2g} -band, made up from $4s$ and $4p$ orbitals and occupied by electrons with oppositely directed spins, overlaps the other bands. The density of states in this band is very small and it is shown on a much larger scale.

The band scheme for Mn_I is shown on the right. The low-lying narrow e_g -band with a high density of states brings about bonding between Mn_I and nitrogen. One of the two electrons is supplied by nitrogen. There are three electron pairs available per nitrogen atom and these have to participate in six bands. They correspond with the half-bonds postulated by Rundle (142) (cf. Section II,D,1). The t_{2g} -band is broader than for Mn_c because the site symmetry of Mn_I is tetragonal with each Mn_I enclosed by two N atoms. Mn_c and Mn_I are also not equivalent, so that the crystal field acting on Mn_I has tetragonal symmetry. The t_{2g} -band again serves to bond the manganese atom to the nearest neighbor at the corner of the cube, i.e., Mn_I to Mn_c .

III. Ternary Compounds

The binary compounds that have been discussed are all members of a single group. More recently many investigations have been made in which the influence of a third element, either metallic or nonmetallic, in combination with binary nitrides has been examined. Ternary compounds are obtained which belong to very different classes of substance.

If a transition metal is partly exchanged for a neighboring transition metal, the properties of the ternary compound differ little from those of the binary nitride. Introduction of one of the b-group metals has a significantly greater effect.

Partial substitution of nitrogen by carbon or oxygen may change the properties of the starting material to a greater extent than substitution of the metal by a neighboring transition metal. This is related to the strong influence of the nonmetal on the nature of the bonding in the interstitial alloy.

Quite different products, which are polar in character, are formed if the third component is a very base metal or a strongly electronegative nonmetal. The classification adopted in the following pages is based on these general considerations.

A. TERNARY METALLIC PHASES

1. Double Nitrides

a. *Mixed Crystals of the NaCl Type.* The close relationship between binary nitrides that crystallize in the sodium chloride lattice leads to the

expectation that a range of mixed crystals will be formed. They may in fact be prepared from mixtures of the nitrides by hot-pressing in a nitrogen atmosphere at 2000°–2400°C (27, 128). Alternatively, alloys may be nitrided with ammonia at 650°–950°C (157). In binary combinations of TiN, VN, ZrN, and NbN complete miscibility is always observed, except in the system VN/ZrN where the lattice constants of the binary components differ markedly. Lattice constants in the mixed crystal ranges show only a small positive deviation from Vegard's rule. TaN, which is irregular in that it crystallizes in the hexagonal system, does not display unlimited solubility in the above nitrides. Metals of the first transition series may be replaced by tantalum only up to the limits $\text{Ti}_{0.9}\text{Ta}_{0.1}\text{N}$, $\text{V}_{0.75}\text{Ta}_{0.25}\text{N}$, and $\text{Cr}_{0.75}\text{Ta}_{0.25}\text{N}$ (157).

Study of these mixed crystals shows that their properties are by no means always additive. In the comparable system TiC/VC a study of the Hall effect has revealed that the density of charge carriers does not increase linearly with the vanadium content, but passes through a well-defined maximum. The number of conduction electrons increases from about 0.2 for TiC, through a maximum of about 1.8 to 1.2 for VC. This observation may be explained in terms of a disturbance of the lattice periodicity of the titanium-vanadium alloys. The strict band model is no longer adequate to explain the effect. There is no such disturbance of lattice periodicity when carbon is replaced by nitrogen (cf. Section III,A,2) in the system TiC/TiN, in which the number of conduction electrons increases only a little from TiC to $\text{TiC}_{0.5}\text{N}_{0.5}$ and then rises more rapidly and linearly with the nitrogen content (66).

b. Hexagonal Phases. The metals Mn, Fe, Co, and Ni are able to replace tantalum partially in the hexagonal lattice of ϵ -tantalum nitride, TaN. The compounds Ta_3MnN_4 , $\sim\text{Ta}_2\text{FeN}_{2.5}$, $\sim\text{Ta}_2\text{CoN}_{2.5}$, $\sim\text{Ta}_2\text{NiN}_{2.5}$ have small ranges. Their crystal structures are derived from that of TaN. Metal atoms are arranged hexagonally with the layer sequence ABACABAC. The ordered distribution of metal atoms explains the occurrence of superstructures. Whereas the elementary cell of Ta_3MnN_4 contains four metal atoms, the arrangement in the $\text{Ta}_2\text{MeN}_{2.5}$ compounds is such that there are 12 metal atoms in the elementary cell. δ -Tantalum nitride, $\text{TaN}_{0.8-0.9}$, also forms with manganese a further hexagonal ternary phase. Nitrogen is octahedrally coordinated in all these double nitrides. They are prepared when a metal alloy of the corresponding composition is melted at 1500°C in a high-frequency induction furnace and then nitrided in a stream of ammonia at 650°–950°C (157).

Quite irregular structures occur for $\text{Ti}_{0.7}\text{Co}_{0.3}\text{N}$, $\text{Ti}_{0.7}\text{Ni}_{0.3}\text{N}$, $\text{Mo}_{0.8}\text{Co}_{0.8}\text{N}_{0.9}$, and $\text{Mo}_{0.8}\text{Ni}_{0.8}\text{N}_{0.9}$. These nitrides, which crystallize in the hexagonal system, have the tungsten carbide lattice. The metal atoms are

in a simple hexagonal arrangement and the structure has been related to that of nickel arsenide (156).

It will be impossible here to deal with the numerous ternary nitrides that have been isolated from special steels, although some carbidenitrides which occur in steels will be discussed (Section III,A,2). The effect of nitrogen on steel has been the subject of much research in, for example, the cases of chromium-, chromium/nickel-, and chromium/manganese-steels, and steels both with and without a substantial carbon content have been considered (113).

c. Mixed Crystals of the Perovskite Type. Mixed crystals of the composition $\text{Mn}_{4-x}\text{Me}_x\text{N}_{1-x/4}\square_{x/4}$ (where Me = Cr, Mn, Ni, Cu, or Zn, and \square denotes holes in the nitrogen sublattice), derived from Mn_4N , the ϵ -phase in the system Mn/N, have been investigated. Incorporation of Me depends on the stability of the binary nitrides of the competing metals. Chromium substitutes manganese in the middle of the face of the unit cell to form a nitrogen-chromium bond. The incorporation of manganese is reflected in the breadth of the Mn_4N phase (cf. Section II,A,2,e). Nickel, copper, and zinc are incorporated in the 000 sites, which does not allow nitrogen-metal bonds to be formed. In addition, nitrogen is substituted by carbon. Lattice constants decrease with incorporation of Cr and Mn (cf. Fig. 15) and rise with that of Ni, Cu, and Zn. Like Mn_4N , the mixed crystals are ferromagnetic. Curie points rise somewhat as the Mn, Cr, and C content is increased and fall as a result of the incorporation of Cu, Zn, and Ni. Magnetic moments per unit cell depend systematically on the foreign metal content, as may be seen from Fig. 15 (80, 86).

Detailed conclusions about spin distribution among separate atom sites cannot be drawn on the basis of saturation measurements. But the systematic changes in saturation magnetism may be explained as follows: the moment of Mn_4N may, on the basis of neutron diffraction studies, be formulated as the difference of two sublattices (167):

$$1.14\mu_B = \frac{(3.84}{\text{Mn}_c} - 3 \times \frac{0.90}{\text{Mn}_f})\mu_B$$

Substitution of nitrogen by carbon involves the withdrawal of one electron per atom of nonmetal (13, 168). A hole at a nitrogen site leads to a loss of three electrons, and replacement of Mn_f by Cr results in a further loss of one electron, in addition to the effect associated with the nitrogen hole. Reduction in the electron concentration in the Mn_f lattice leads to increase of the Mn_f moment with spin decoupling and a lowering of the resulting total moment of the unit cell.

Nickel, copper, and zinc may be substituted for Mn_c . These metals give an increase in the electron concentration in the Mn_c lattice with spin

pairing and also produce a decrease in the total moment by creating nitrogen vacancies. The overall result is a lowering of both the Mn_c moment and the total moment of the unit cell (86).

Neutron diffraction studies of two specimens with vacancies in the nitrogen sublattice are in agreement with this concept as far as the total moment is concerned, but they cast doubt on the interpretation suggested (168). Results with the mixed crystals $Mn_{4-x}In_xN$ and $Mn_{4-x}Sn_xN$ (114) are not in good agreement with those above. There are, however, special considerations which explain the discrepancy: these mixed crystals have no vacancies in the nitrogen sublattice, the substituting atoms are very much

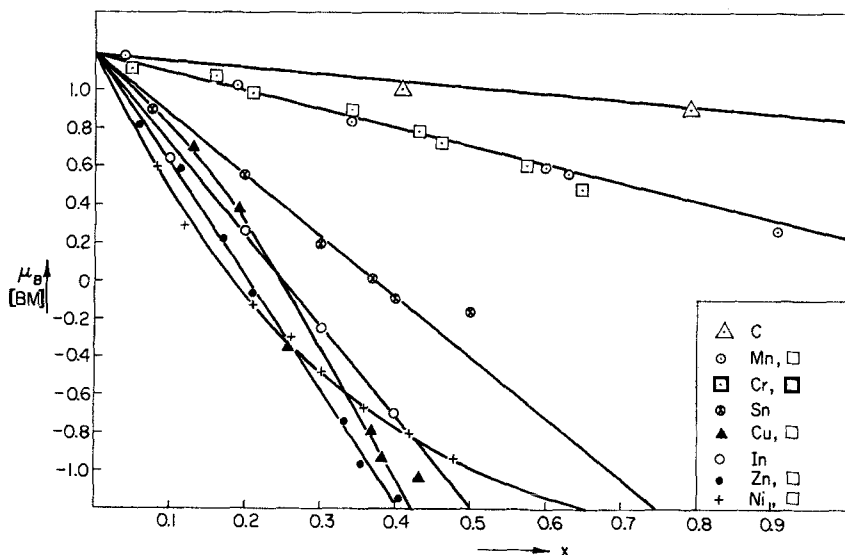


Fig. 15. Magnetic moments of the mixed crystals $Mn_{4-x}Me_xN_{1-x/4}\square_{x/4}$ and $Mn_{4-x}N_{1-x/4}C_{x/4}$ (80, 86), $Mn_{4-x}In_xN$ and $Mn_{4-x}Sn_xN$ (114).

larger, and the number of electrons transferred to a band for Group 3b and 4b elements is certainly not proportional to the group number.

Ternary ferromagnetic compounds may be derived from Fe_4N in which iron in the 000 position is replaced by nickel or platinum. These were prepared by Wiener and Berger with the object of elucidating the magnetic structure of Fe_4N (176). Mixed crystals of the type $Fe_{4-x}Ni_xN$ with $0 \leq x \leq 3$ were subject to detailed magnetic investigation over the whole composition range (45). The Curie point of $NiFe_3N$ is at $487^\circ C$ and that of Fe_3PtN at $369^\circ C$ (176). From the saturation magnetization the magnetic moment per unit formula was found to be $7.2 \mu_B$ for Fe_3NiN and $7.76 \mu_B$ for Fe_3PtN . The three iron atoms at the face centers retain their magnetic

moments of $2 \mu_B$ per Fe and, for nickel and platinum in 000, $1 \mu_B$ is to be expected, leading to a total of $7 \mu_B$ per unit formula for both compounds. The differences of $+0.2 \mu_B$ and $0.76 \mu_B$ between the measured magnetic moments and those to be expected from the model are to be associated with the contributions from the *s*-bands of the crystals (44).

Further nickel may be substituted for iron in the face centers (5); these nickel atoms have a moment of $0 \mu_B$ because the metal-nitrogen bond is covalent (44). When yet more nitrogen is incorporated, the tetragonal compound FeNiN is formed. This no longer has the perovskite structure, although structurally it is directly related to $\text{Fe}_{4-x}\text{Ni}_x\text{N}$ (5, 171). This additional nitrogen increases the concentration of electrons so much that ferromagnetic coupling disappears and FeNiN is paramagnetic (45).

d. T/M Phases. A group of double nitrides has been discovered recently whose structures are determined by the coexistence of a transition metal (T) and a b-group element (M). The symbols T and M will be used in this section in place of Me. The phases may be derived from those of binary transition metal nitrides that have been discussed so far as follows: nitrogen in the T/M phases is again surrounded by six transition metal atoms in what is essentially an octahedral arrangement, and the b-group atom is not bonded to nitrogen (64).

"Perovskite phases," T_2MN : The perovskite phases T_2MN and mixed crystals of the perovskite type (discussed in Section III,A,1,c) have much in common. Indeed, from the point of view of crystallography the two sections belong together, but are discussed here from the point of view of chemistry. Table III sets out the T_2MN phases prepared by Stadelmaier which are of interest here (162-164). The b-group metal belongs to Groups 1-4. The phases appear to occur preferentially for the elements from manganese to nickel. Compounds with the same structure, however, have been prepared with transition elements of lower atomic number. Thus reaction

TABLE III
T/M PHASES OF THE PEROVSKITE TYPE^a

Ib	Mn_2CuN^b Mn_2AgN^b			
IIb	Mn_2ZnN	Fe_2MgN Fe_2ZnN	Co_2ZnN	Ni_2ZnN
IIIb	Cr_2GaN^b Mn_2GaN^b Mn_2InN	Fe_2AlN Fe_2GaN Fe_2InN	Co_2GaN Co_2InN	Ni_2AlN
IVb		Fe_2GeN Fe_2SnN	Co_2GeN Co_2SnN	

^a From Stadelmaier (162, 163); ^b Samson *et al.* (144).

of GaN with chromium gives Cr_3GaN (144), and Ti_3InN and Ti_3TlN have been prepared from titanium (76).

Most of the investigations leave open the question of the extent to which the nitrogen sublattice is occupied (144, 163). In the extreme case, when there is no nitrogen in the compound, the perovskite phase goes over to the ordered Cu_3Au phase, in which Au occupies the corners of the cubes. One can, in fact, speak of the perovskite phase as a Cu_3Au phase that is stabilized by nitrogen.

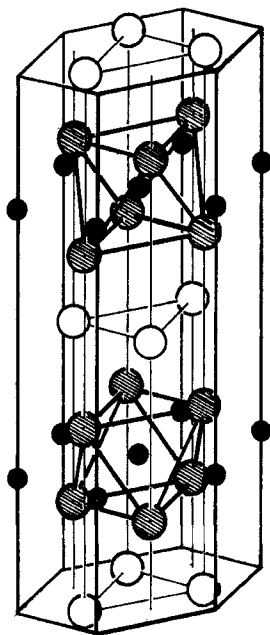
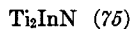


FIG. 16. Lattice of "H phases," T_2MN : \circ M; \bullet T; \bullet N.

"H phases," T_2MN : A further group of ternary phases found by Nowotny has the composition T_2MN . These are designated as "H phases" because they are hexagonal. Compounds of this sort in the first transition series are



These are isotypic with Cr_2AlC and Ti_2SC (101). Their structures (cf. Fig. 16) are reminiscent of hexagonal close-packed crystalline intercalated structures, such as Fe_3N , from which they may be derived. Nitrogen atoms are present in the octahedral holes between two transition metal layers that

are perpendicular to the c -axis of the hexagonal elementary cell. Above and below these TNT layers there is a layer of atoms of the b-group metal M. The metal atoms are approximately in a hexagonal close-packed arrangement (with the layers A and B) so that in the direction of the c -axis there is the sequence $M_A T_B N T_A M_B T_A N T_B M_A$. Incidence of H phases is restricted to transition metals of Groups 4 and 5, but the nature of the b-group element may vary greatly. If it belongs to 2b or 3b, the structure has a high c/a ratio and is near to hexagonal close packing. The compound is also predominantly metallic in character. When the b-group element belongs to Group 4 (germanium) or even Group 6 (sulfur, although this is found only in carbides) the axial ratio is smaller and metallic character is less pronounced (129).

" *β -Manganese phases*," T_3M_2X : β -Manganese crystallizes in the cubic system with eightfold and twelvefold position. Double nitrides are derived from this elementary cell. $Mo_{18}Fe_7N_4$, which approximates to $Mo_{12}Fe_8N_4$ or Mo_3Fe_2N , was found (35). It has recently been discovered that corresponding compounds may be prepared (V_3Zn_2N and V_3Ga_2N) (73) which contain a b-group metal instead of a transition metal at the eightfold position. The number of compounds of this type so far prepared is not large.

" *η_2 -Carbide phases*," T_4M_2N : Ternary nitrides may also be derived from the $E9_8$ type of structure (W_3Fe_3C) or, more precisely, from the " η_2 -carbide type" (Mo_4Fe_2C) (95). The compound Ti_4Zn_2N may be cited (73). In this, transition metal atoms are partly replaced by a b-group atom (Zn). Corresponding oxygen compounds have, for example, the composition Ti_4Cu_2O . In the η_2 -carbide phases the nonmetal is in the center of a deformed octahedron.

In all T/M phases formed from a transition metal and a b-group metal that have been described above, it is clear that the metal atom lattice has been stabilized by partially filling the octahedral holes formed by the transition metal atoms.

2. Carbidenitrides

Wöhler (177) described a golden yellow lustrous material that he called *Hochofenwürfel*, containing 0.2 of C and 0.8 of N to 1 of Ti. This has since been repeatedly studied, and was shown by X-ray methods to consist of mixed crystals. A continuous series of mixed crystals $Ti(N,C)$ is indeed formed by heating together TiN and TiC to $2400^\circ C$. Isotypic nitrides and carbides form such continuous series in many combinations, one proviso being that the radii of the metal atoms shall differ by less than 15%. The same is often true when the metal and nonmetal are varied simultaneously, as in the following combinations: TiN with HfC , VC , NbC ; VN with TiC , NbC . Lattice constants of the mixed crystals follow Vegard's rule with

minor deviations (27). The carbidenitride systems of Group 4 and 5 transition metals are also interesting technically because, in part accidentally, materials prepared for cermets often contain carbon and nitrogen together.

A detailed phase study of the ternary system in the metal-rich range has been made for *titanium* (166). Systematic investigations of electrical properties in TiN/TiC alloys show conductivity to depend mainly on the 4s electrons of titanium and to some extent on holes of the 3d band. Defect conductivity becomes more pronounced in going from TiN to TiC (108). There is a marked minimum in the conductivity for the composition $\text{TiN}_{0.75}\text{C}_{0.25}$, as is required by the Bilz band scheme in connection with the low density of states at the Fermi boundary of about 8.5 electrons (cf. Section II,D,2). The charge carrier concentration in TiC/TiN mixed crystals, determined by the Hall effect (referred to in Section III,A,1,a), may be interpreted in the same way (66).

Systematic study of the *vanadium* carbide nitride system VN/VC/V shows a broad one-phase region for V(N,C), which crystallizes with the NaCl lattice and extends to about $\text{V(N,C)}_{0.72}$. In addition, a broad area corresponding to hexagonal close-packed $\text{V}_2(\text{N,C})$ joins the two binary phases V_2N and V_2C without gaps (16). Specimens were obtained from vanadium powder and carbon by repeated grinding, followed by pressing, heating to 1400°–2000°C, and finally nitriding with nitrogen at 1250°C.

Carbidenitrides of chromium with the NaCl lattice may be obtained from nitrided steels. They are usually isolated by an electrolytic method in which the alloy containing nitride is made the anode (62). Since an isotypic chromium carbide does not exist, only part of the nitrogen can be replaced by carbon.

Replacement of nitrogen by carbon in *ε-manganese* nitride, Mn_4N , may be effected up to the composition $\text{Mn}_4\text{N}_{0.2}\text{C}_{0.8}$ by solid-state reaction of the mixture of binary compounds. Saturation magnetization of the mixed crystals, which, like Mn_4N , are ferrimagnetic, falls linearly in accordance with the assumed spin distribution and the decrease in number of valency electrons when nitrogen is replaced by carbon. This decrease leads to an increase in the magnetic moment of the negatively charged sublattice of manganese atoms at face centers, and thus to a lowering of the resultant moment (13, 86) (cf. Fig. 12).

Carbidenitrides of *iron* have been very fully studied and have an important bearing on the properties of special steels. Because of their low thermal stability they cannot be prepared by starting from the two binary compounds. Either the corresponding nitride, made by nitriding with ammonia, is carbided with carbon monoxide, or an iron carbide is nitrided by heating in ammonia (68).

As may be seen from the studies of Jack, the results of which are represented in Fig. 17, the composition and structure of carbidenitrides are

directly related to what has been said about the binary nitrides of iron. Orthorhombic nonmetal-rich ζ -carbidenitride extends from Fe_2N to $\text{Fe}_2\text{C}_{0.75}\text{N}_{0.25}$ (68). Unlike $\zeta\text{-Fe}_2\text{N}$, this iron carbidenitride is ferromagnetic. Its Curie point increases with the carbon content and lies between 288° and 350°C (17).

The hexagonal carbidenitride, which corresponds to the ϵ -phase in the iron/nitrogen system, has a phase range from $\text{Fe}_3(\text{C,N})$ to $\text{Fe}_2(\text{C,N})$ and contains a maximum of 16 atom% of C (68). It is also ferromagnetic with Curie points in the range -90° to 388°C , depending on the composition (17).

In the γ' -phase, Fe_4N , very little nitrogen can be replaced by carbon (17, 68). The carbon-containing Fe_4N phase is also ferromagnetic with a

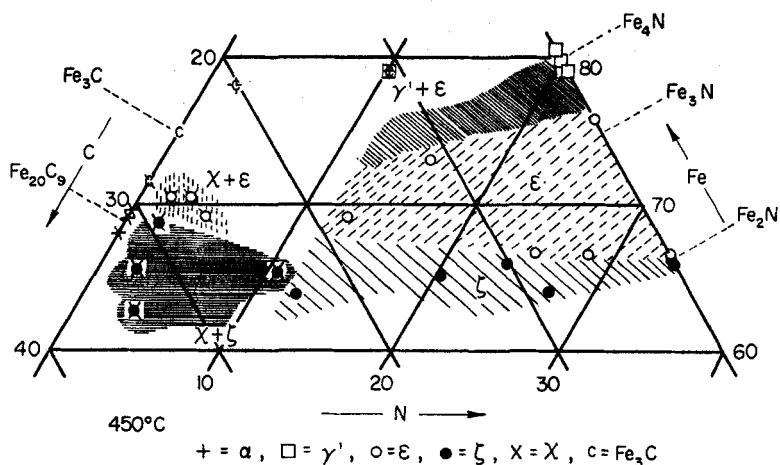


FIG. 17. The iron/carbon/nitrogen system (68).

Curie point between 471° and 490°C , depending on the N/C ratio (17). It is found by thermomagnetic methods that the γ' type of carbidenitride loses carbon on heating to form hexagonal $\text{Fe}_3(\text{C,N})$, which has a high carbon content. There also appears $\alpha\text{-Fe}$ containing a little N and C.

Knowledge of iron carbidenitrides is of interest *inter alia* because they enter into the carbonitriding of steels. These processes use baths containing fused alkali cyanides or, in the case of gas cementation, mixtures of nitriding and carbiding gases. In carbonitriding it is thought that the quick-acting nitrogen accelerates subsequent carbiding. This is important because every effort is made to carry through the process at as low a temperature as possible and to do the subsequent hardening operation by relatively mild quenching, e.g., in air or a stream of gas.

Carbidenitrides of *cobalt* are closely comparable with those of iron. The phase richest in nitrogen in the system Co/N is Co_2N , which, like Co_2C , crystallizes in the orthorhombic system. The lattice constants of the two compounds differ little. As a result it is possible when carbiding Co_2N with CO at 340°C gradually to replace all of the nitrogen by carbon. Lattice constants for mixed crystals of $\text{Co}_2(\text{N},\text{C})$ change uniformly with the N/C ratio. There is no isotypic carbide Co_3C corresponding to hexagonal Co_3N . As a result, only partial replacement of N by C in Co_3N can be achieved (25).

Nickel nitride, Ni_3N , may also be carbided (69): both Ni_3N and Ni_3C crystallize in the hexagonal system and their lattice dimensions are almost the same.

3. Nitride Oxides

Little is known about nitrides of the first transition series containing oxygen as a second nonmetal. TiN and TiO differ in lattice constants by only about 2% and would therefore be expected to form series of mixed crystals. X-ray studies show, however, that $\text{Ti}(\text{N},\text{O})$ specimens, prepared from the binary compounds by sintering at 1700°C , exhibit the unchanged lattice constant of TiN from TiN to $\text{TiN}_{0.5}\text{O}_{0.4}$. A decrease in the lattice constant to that of TiO follows, indicating a limited solubility of TiN in TiO , but not of TiO in TiN . Pyknometric density determinations, which can give information on the number of vacancies in the cation lattice, provide no further clarification (155).

The influence of oxygen on the electrical properties of TiN has been investigated up to about $\text{TiN}_{0.5}\text{O}_{0.5}$. The specific resistance passes through a minimum at about 40 mole % TiO , while the differential thermoelectric power and Hall coefficient have a minimum at about 20%. The temperature dependence of the specific resistance was also examined: it is first strongly positive and from above about 1200°C strongly negative (150). These resistance measurements are not, however, reconcilable with experiments on thin TiN films with a small oxygen content, which were found to be semiconducting (117). Further results on nitride oxides are available for vanadium (140), chromium (141), and cobalt (89). Compounds of the metals in question were first nitrized and then oxidized, or vice versa. The products were believed to contain nitride oxides in addition to oxides and nitrides. These nitride oxides could not, however, be made in an equilibrium reaction.

B. POLAR TERNARY COMPOUNDS

Brief reference may be made to ternary compounds containing, in addition to a transition metal and nitrogen, another base metal (lithium) or a very electronegative nonmetal (a halogen). The nature of such ternary

compounds is determined largely by the tendency of these elements to go over to the ionic state.

1. Polar Double Nitrides

When lithium nitride is heated in a nitrogen atmosphere with finely divided cobalt, nickel, or copper, the metal enters the Li_3N lattice and is simultaneously nitrified to an oxidation state of $+1$. While Co_3N , Ni_3N , and Cu_3N cannot be obtained from the metal and nitrogen (Section II,C,1), nitrogen uptake occurs during the process of incorporation in lithium nitride. The heavy metal atom is taken up on $00\frac{1}{2}$ sites in hexagonal Li_3N up to a composition of about $\text{Li}_{2.5}\text{Me}_{0.5}\text{N}$. The mixed crystals retain the predominantly saltlike character of Li_3N (143).

Corresponding reactions of Li_3N with titanium, vanadium, chromium, manganese, and iron, or reaction with the binary nitrides of these metals, lead in a nitrogen atmosphere to compounds in which one finds oxidation states of the metal with respect to nitrogen which do not occur in the binary nitrides: e.g., Li_5TiN_3 (91), Li_7VN_4 (81), Li_9CrN_5 (84), Li_7MnN_4 (79), Li_3FeN_2 (38). Whereas the limiting composition in the binary nitrides of titanium, vanadium, and chromium is MeN , these three metals here occur in their highest oxidation states. This is, however, not so for manganese and iron, although oxidation states of five or three with respect to nitrogen are stabilized. The electrovalent composition, high melting points, and ready hydrolysis of the compounds indicate that they have predominantly polar structures.

In these ternary nitrides no complex ions occur in spite of the high charge on the transition metal. This is because of the high charge on the N^{3-} ion. The compounds from titanium to manganese crystallize with a superstructure of the antifluorite lattice. The equivalent lattice positions are known for Li_5TiN_3 , Li_7VN_4 , and Li_7MnN_4 . In all cases nitrogen ions are cubically close packed; metal ions are in the tetrahedral holes and, unlike nitrogen atoms in intercalation compounds, the nitrogen ions are surrounded by eight cations. There are always two cations per anion. The "AB₂ character" of the compounds is emphasized by the fact that mixed crystals are formed with Li_2O , which also crystallizes with an antifluorite lattice (91).

2. Nitride Halides

The nitride halides TiNCl , TiNBr , and TiNI may be obtained by ammonolysis of the halides at elevated temperatures. These titanium compounds decompose at high temperatures and hydrolyze very readily. The corresponding compounds of the heavier metals zirconium and especially thorium are much more stable thermally and chemically.

The titanium compounds mentioned crystallize isotypically with FeOCl and thus have a pronounced layer lattice. In the rhombic elementary cell the sequence HalTiNNTiHal occurs in the direction of the c -axis. Lattice dimensions within the layers are determined by the two close-packed layers of large halogen ions. Thus it happens that both close-packed nitrogen layers are pushed together into a doubly occupied corrugated layer. It may be assumed that the halogens are present as ions. Within the cationic layer $(\text{TiNNTi})_n^{2n+}$ the polar component of the bond should, however, be small (85).

ACKNOWLEDGMENT

I thank Dr. H. Seidel and Dipl.-Chem. H. Jacobs for their enthusiastic help in preparing this article.

REFERENCES

1. Agte, C., and Moers, K., *Z. Anorg. Allgem. Chem.* **198**, 233 (1931).
2. Akishin, P. A., and Klodeev, Y. S., *Zh. Neorgan. Khim.* **7**, 941 (1962).
3. Akishin, P. A., and Klodeev, Y. S., *Russ. J. Inorg. Chem. (English Transl.)* **7**, 486 (1962).
4. Amaya, K., Ajiro, Y., Yasuoka, H., Abe, H., Matsuura, M., and Hirai, A., *J. Phys. Soc. Japan* **19**, 413 (1964).
5. Arnott, R. J., and Wold, A., *Phys. Chem. Solids* **15**, 152 (1960).
6. Baratashvili, J. B., Fedotov, V. P., Samarin, A. M., and Berethiani, J. B., *Fiz. Khim. Osnovy Proizv. Stali, Akad. Nauk SSSR, Inst. Met. Tr. 6-oi Eshestoi J. Konf., Moscow* p. 294 (1961).
7. Becker, K., *Z. Physik* **34**, 185 (1933).
8. Becker, K., and Ebert, F., *Z. Physik* **31**, 268 (1925).
9. Bernier, R., *Ann. Chim. (Paris)* [12] **6**, 104 (1951).
10. Bilz, H., *Z. Physik* **153**, 338 (1958).
11. Blix, R., *Z. Physik. Chem.* **B3**, 229 (1929).
12. Blum, A., *Planseeber. Pulvermet.* **10**, 72 (1962).
13. Bouchaud, J. P., and Fruchart, R., *Bull. Soc. Chim. France* No. 2, 1579 (1964).
14. Brager, A., *Acta Physicochim. URSS* **11**, 617 (1939).
15. Brauer, G., and Schnell, W. D., *J. Less-Common Metals* **6**, 326 (1964).
16. Brauer, G., and Schnell, W. D., *J. Less-Common Metals* **7**, 23 (1964).
17. Bridelle, R., *Ann. Chim. (Paris)* [12] **10**, 824 (1955).
18. Brisi, C., *Met. Ital.* **47**, 405 (1955).
19. Brisi, C., and Abbattista, F., *Ric. Sci.* **29**, 1402 (1959).
20. Burdese, A., *Met. Ital.* **47**, 357 (1955).
21. Burdese, A., *Met. Ital.* **49**, 195 (1957).
22. Burdese, A., *Met. Ital.* **50**, 529 (1958).
23. Burdese, A., and Abbattista, F., *Atti Accad. Sci. Torino, Classe Sci. Fis. Mat. Nat.* **93**, 340 (1958-1959).
24. Campbell, I. E., Powell, C. F., Nowicki, D. H., and Gonser, B. W., *J. Electrochem. Soc.* **96**, 318 (1949).
25. Clarke, J., and Jack, K. H., *Chem. Ind. (London)* p. 1004 (1951).
26. Corliss, L. M., Elliott, N., and Hastings, J. M., *Phys. Rev.* **117**, 929 (1960).
27. Duwez, P., and Odell, F., *J. Electrochem. Soc.* **97**, 299 (1950).

28. Ehrlich, P., *Z. Anorg. Chem.* **259**, 1 (1949).
29. Eisenhut, O., and Kaupp, E., *Z. Elektrochem.* **36**, 392 (1930).
30. Elliott, N., *Phys. Rev.* **129**, 1120 (1963).
31. Emmett, P. H., Hendricks, S. B., and Brunauer, S., *J. Am. Chem. Soc.* **52**, 1456 (1930).
32. Epelbaum, V., and Brager, A., *Acta Physicochim. URSS* **13**, 595 (1940).
33. Epelbaum, V., and Ormont, B., *Acta Physicochim. URSS* **22**, 319 (1947).
34. Eriksson, S., *Jernkontorets Ann.* **118**, 530 (1934).
- 34a. Ern, V., and Switendick, A. C., *Phys. Rev.* **137**, A1927 (1965).
35. Evans, D. A., and Jack, K. H., *Acta Cryst.* **10**, 769 (1957).
36. Fast, J. D., *Philips Tech. Rev.* **10**, 27 (1948).
37. Foster, L. S., AECD 2942 (1945).
38. Frankenburger, W., Andrussov, L., and Dürr, F., *Z. Elektrochem.* **34**, 632 (1928).
39. Frazer, B. C., *Phys. Rev.* **112**, 751 (1958).
40. Friederich, E., and Sittig, L., *Z. Anorg. Allgem. Chem.* **143**, 293 (1925).
41. Fry, A., *J. Iron Steel Inst. (London)* **125**, 191 (1932).
42. Goodenough, J. B., *Phys. Rev.* **117**, 1442 (1960).
43. Goodenough, J. B., *Phys. Rev.* **120**, 67 (1960).
44. Goodenough, J. B., "Magnetism and the Chemical Bond." Wiley (Interscience), New York, 1963.
45. Goodenough, J. B., Wold, A., and Arnott, R. J., *J. Appl. Phys.* **31**, Suppl., 342 (1960).
46. Guillaud, C., and Creveaux, H., *Compt. Rend.* **222**, 1170 (1946).
47. Guillaud, C., and Wyart, J., *J. Rech. Centre Natl. Rech. Sci. Lab. Bellevue (Paris)* **3**, 123 (1947).
48. Hägg, G., *Nova Acta Regiae Soc. Sci. Upsaliensis* [4] **7**, No. 1, 95 (1929).
49. Hägg, G., *Z. Physik. Chem.* **B4**, 346 (1929).
50. Hägg, G., *Z. Physik. Chem.* **B6**, 229 (1929).
51. Hägg, G., *Z. Physik. Chem.* **B12**, 33 (1931).
52. Hägg, G., *IVA* **24**, 345 (1953).
53. Hahn, H., *Z. Anorg. Chem.* **258**, 58 (1949).
54. Hahn, H., and Konrad, A., *Z. Anorg. Allgem. Chem.* **264**, 181 (1951).
55. Hansen, M., "Constitution of Binary Alloys," 2nd ed. McGraw-Hill, New York, 1958.
56. Hardy, G. F., and Hulm, D. K., *Phys. Rev.* **93**, 1004 (1954).
57. Hendricks, S. B., and Kosting, P. K., *Z. Krist., Abt. A Z. Krist. Mineral. Petrog.* **74**, 511 (1930).
58. Hilpert, R. S., Hoffmann, A., and Huch, F. H., *Ber. Deut. Chem. Ges.* **72B**, 848 (1939).
59. Hoch, M., Dingley, D. P., and Johnston, L., *J. Am. Chem. Soc.* **77**, 304 (1955).
60. Holmberg, B., *Acta Chem. Scand.* **16**, 1255 (1962).
61. Hume-Rothery, W., *Phil. Mag.* [7] **44**, 1154 (1953).
62. Hume-Rothery, W., Raynor, G. V., and Little, A. T., *J. Iron Steel Inst. (London)* **145**, 129 (1942).
63. Humphrey, G. L., *J. Am. Chem. Soc.* **73**, 2261 (1951).
64. Hüttig, G. F., *Kolloid-Z.* **97**, 281 (1941).
65. Imai, Y., and Ishizaki, T., *Sci. Rept. Res. Inst. Tohoku Univ. Ser. A* **14**, 203 (1962).
66. Ito, F., Tsuchida, T., and Takaki, H., *J. Phys. Soc. Japan* **19**, No. 1, 136 (1964).
67. Jack, K. H., *Proc. Roy. Soc.* **A195**, 34 (1948).
68. Jack, K. H., *Proc. Roy. Soc.* **A195**, 41 (1948).
69. Jack, K. H., *Acta Cryst.* **3**, 392 (1950).
70. Jack, K. H., *Proc. Roy. Soc.* **A208**, 200 (1951).

71. Jack, K. H., *Proc. Roy. Soc.* **A208**, 216 (1951).
72. Jack, K. H., *Acta Cryst.* **5**, 404 (1952).
73. Jeitschko, W., Nowotny, H., and Benesovsky, F., *Monatsh. Chem.* **95**, 156 (1964).
74. Jeitschko, W., Nowotny, H., and Benesovsky, F., *Monatsh. Chem.* **94**, 1198 (1963).
75. Jeitschko, W., Nowotny, H., and Benesovsky, F., *Monatsh. Chem.* **95**, 178 (1964).
76. Jeitschko, W., Nowotny, H., and Benesovsky, F., *Monatsh. Chem.* **95**, 436 (1964).
77. Janeff, W., *Z. Physik* **142**, 619 (1955).
78. Joyner, T. B., and Verhoek, F. H., *J. Am. Chem. Soc.* **83**, 1070 (1961).
79. Juza, R., Anschütz, E., and Puff, H., *Angew. Chem.* **71**, 161 (1959).
80. Juza, R., Deneke, K., and Puff, H., *Z. Elektrochem.* **63**, 551 (1959).
81. Juza, R., Gieren, W., and Haug, J., *Z. Anorg. Allgem. Chem.* **300**, 61 (1959).
82. Juza, R., and Hahn, H., *Z. Anorg. Allgem. Chem.* **239**, 282 (1938).
83. Juza, R., and Hahn, H., *Z. Anorg. Allgem. Chem.* **241**, 172 (1939).
84. Juza, R., and Haug, J., *Z. Anorg. Allgem. Chem.* **309**, 276 (1961).
85. Juza, R., and Heners, J., *Z. Anorg. Allgem. Chem.* **332**, 159 (1964).
86. Juza, R., and Puff, H., *Z. Elektrochem.* **61**, 810 (1957).
87. Juza, R., Puff, H., and Wagenknecht, F., *Z. Elektrochem.* **61**, 804 (1957).
88. Juza, R., and Rabenau, A., *Z. Anorg. Allgem. Chem.* **285**, 212 (1956).
89. Juza, R., and Sachsze, W., *Z. Anorg. Chem.* **253**, 95 (1947).
90. Juza, R., and Sachsze, W., *Z. Anorg. Allgem. Chem.* **251**, 201 (1943).
91. Juza, R., Weber, H. H., and Meyer-Simon, E., *Z. Anorg. Allgem. Chem.* **273**, 48 (1953).
92. Kelley, K. K., *U.S. Bur. Mines, Bull.* No. 407, 66 (1937).
93. Kieffer, R., and Benesovsky, F., "Hartstoffe." Springer, Wien, 1963.
94. Kieffer, R., and Schwarzkopf, P., "Hartstoffe und Hartmetalle." Springer, Wien, 1953.
95. Kiessling, R., 1952, *Proc. Intern. Symp. Reactivity Solids, Gothenburg, 1952* p. 1065. Elanders Boktryckeri Actiebolag, Gothenburg, Sweden (1954).
96. Kischkin, S. T., and Panassjuk, J. O., *Dokl. Akad. Nauk SSSR* **113**, 1263 (1957).
97. Klemm, W., and Schüth, W., *Z. Anorg. Allgem. Chem.* **201**, 24 (1931).
98. Kontorowitsch, J. E., and Ssowalow, G. A., *Izv. Akad. Nauk SSSR, Otd. Tekhn. Nauk* p. 1675 (1949).
99. Krebs, H., *Acta Cryst.* **9**, 95 (1956).
100. Krichevskii, I. R., and Khazanova, N. E., *Zh. Fiz. Khim.* **21**, 719 (1947).
101. Kudielka, H., and Rohde, H., *Z. Krist.* **114**, 447 (1960).
102. Kume, K., and Yamagishi, H., *J. Phys. Soc. Japan* **19**, 414 (1964).
103. Kuriyama, M., Hosoya, S., and Suzuki, T., *Phys. Rev.* **130**, 898 (1963).
104. Landolt, H., and Börnstein, R., "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik," 6th ed., Vol. 2, Pt. 4. Springer, Berlin, 1961.
105. Lehrer, E., *Z. Elektrochem.* **36**, 383 (1930).
106. Lehrer, E., *Z. Elektrochem.* **36**, 460 (1930).
107. Lihl, F., Ettmayer, P., and Kutzelnigg, A., *Z. Metallk.* **53**, 715 (1962).
108. L'vov, S. M., Nemchenko, V. F., and Samsonov, G. V., *Ukr. Fiz. Zh.* **7**, 331 (1962).
109. McGee, S. W., and Sump, C. H., *ASTM Bull.* **217**, 58 (1956).
110. Mah, A. D., *J. Am. Chem. Soc.* **80**, 2954 (1958).
111. Mah, A. D., *U.S. Bur. Mines, Rept. Invest.* **5529**, (1960).
112. Mah, A. D., *U.S. Bur. Mines, Rept. Invest.* **6177**, 1-8 (1963).
113. Maratray, F., *Publ. Inst. Rech. Siderurgie (Saint-Germain-en-Laye) Ser. B.* No. 75, 47 (1954).
114. Mekata, M., *J. Phys. Soc. Japan* **17**, 796 (1962).

115. Moers, K., *Z. Anorg. Allgem. Chem.* **198**, 243 (1931).
116. Mott, N. F., *Nuovo Cimento* [10] **7**, Suppl., 312 (1958).
117. Münster, A., *Angew. Chem.* **69**, 281 (1957).
118. Münster, A., and Ruppert, W., *Z. Elektrochem.* **57**, 564 (1953).
119. Münster, A., and Schlamp, C., *Z. Physik. Chem. (Frankfurt)* [N.F.], **13-15**, 59 and 176 (1957-1958).
120. National Bureau of Standards, Washington 1947-1959, Selected values of chemical thermodynamic properties. *Natl. Bur. Std. (U.S.) Circ.* 500, reprint 1961.
121. Néel, L., *Ann. Phys. (Paris)* [12] **3**, 137 (1948).
122. Nemnonow, S. A., and Menschikow, A. Z., *Izv. Akad. Nauk SSSR, Ser. Fiz.* **23**, 578 (1959).
123. Neshpor, V. S., in "Refractory Transition Metal Compounds; High Temperature Cermets" (G. V. Samsonov, ed.), pp. 62-106. Academic Press, New York, 1964 (translated from Russian).
124. Neumann, B., Kröger, C., and Haebler, H., *Z. Anorg. Allgem. Chem.* **196**, 65 (1931).
125. Neumann, B., Kröger, C., and Kunz, H., *Z. Anorg. Allgem. Chem.* **218**, 379 (1934).
126. Nishiyama, Z., and Iwanaga, R., *Mem. Inst. Sci. Ind. Res., Osaka Univ.* **9**, 74 (1952).
127. Nowotny, H., Benesovsky, F., Brukl, C., and Schob, O., *Monatsh. Chem.* **92**, 403 (1961).
128. Nowotny, H., Benesovsky, F., and Rudy, E., *Monatsh. Chem.* **91**, 348 (1960).
129. Nowotny, H., Jeitschko, W., and Benesovsky, F., *Planseeber. Pulvermet.* **12**, 31 (1964).
130. Opfermann, W., *Monatsber. Deut. Akad. Wiss. (Berlin)* **6**, 92 (1964).
131. Palty, A. E., Margolin, H., and Nielsen, J. P., *Trans. Am. Soc. Metals* **46**, 312 (1954).
132. Paranjpe, V. G., Cohen, M., Bever, M. B., and Floe, C. F., *Trans. J. Metals* **188**, 261 (1950).
133. Pauling, L., *J. Am. Chem. Soc.* **69**, 542 (1947).
134. Pauling, L., "The Nature of the Chemical Bond." Cornell Univ. Press, Ithaca, New York, 1960.
135. Pinsker, Z. G., and Abrosimowa, L. N., *Kristallografiya* **3**, 28 (1958).
136. Pinsker, Z. G., and Kaverin, S. V., *Dokl. Akad. Nauk SSSR* **95**, 519 (1954).
137. Pinsker, Z. G., and Kaverin, S. V., *Kristallografiya* **2**, 386 (1957).
138. Ratner, A. W., and Leonowa, L. G., *Teploenergetika* **7**, No. 1, 59 (1960).
139. Robbins, M., and White, J. G., *Phys. Chem. Solids* **25**, 717 (1964).
140. Roubin, M. P., and Pâris, J. M., *Compt. Rend.* **260**, 3088 (1965).
141. Roubin, M. P., and Pâris, J. M., *Compt. Rend.* **260**, 3981 (1965).
142. Rundle, R. E., *Acta Cryst.* **1**, 180 (1948).
143. Sachsze, W., and Juza, R., *Z. Anorg. Chem.* **259**, 278 (1949).
144. Samson, C., Bouchaud, J. P., and Fruchart, R., *Compt. Rend.* **259**, 392 (1964).
145. Samsonov, G. V., *Dokl. Akad. Nauk SSSR* **83**, 689 (1953).
146. Samsonov, G. V. (ed.), in "Refractory Transition Metal Compounds; High Temperature Cermets," pp. 1-12. Academic Press, New York, 1964 (translated from Russian).
147. Samsonov, G. V., Kosolapova, T. Y., Lyutana, M. D., and Marenko, G. N., *Redkozem. Elementy, Akad. Nauk SSSR, Inst. Geokhim. i. Analit. Khim.* p. 8 (1963).
148. Samsonov, G. V., and Neshpor, V. S., *Vopr. Poroshkovoi Met i. Prochnosti Materialov, Akad. Nauk Ukr. SSR* No. 7, 99 (1959).

149. Samsonov, G. V., and Verkhoglyadova, T. S., *Dokl. Akad. Nauk SSSR* **142**, 608 (1962).
150. Samsonov, G. V., Verkhoglyadova, T. S., L'vov, S. M., and Nemschenko, V. F., *Dokl. Akad. Nauk SSSR*, **142**, 862 (1962).
151. Sano, K., *J. Chem. Soc. Japan* **58**, 981 (1937).
152. Satô, S., *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)* **34**, 1356 (1938).
153. Schenk, R., and Kortengraber, A., *Z. Anorg. Allgem. Chem.* **210**, 273 (1933).
154. Schmitz-Dumont, O., *Z. Elektrochem.* **60**, 866 (1956).
155. Schmitz-Dumont, O., and Steinberg, K., *Naturwissenschaften* **41**, 117 (1954).
156. Schönberg, N., *Acta Met.* **2**, 427 (1954).
157. Schönberg, N., *Acta Chem. Scand.* **8**, 213 (1954).
158. Shirane, G., Takei, W. J., and Ruby, S. L., *Phys. Rev.* **126**, 49 (1962).
159. Shomate, C. H., *J. Am. Chem. Soc.* **68**, 310 (1946).
160. Shomate, C. H., and Young, F. E., *J. Am. Chem. Soc.* **66**, 771 (1944).
161. Shull, C. G., Wollan, E. O., and Koehler, W. C., *Phys. Rev.* **84**, 912 (1951).
162. Stadelmaier, H. H., and Fraker, A. C., *Z. Metallk.* **53**, 48 (1962).
163. Stadelmaier, H. H., *Z. Metallk.* **52**, 758 (1961).
164. Stadelmaier, H. H., and Tong, S. Y., *Z. Metallk.* **52**, 477 (1961).
165. Stokes, C. S., and Knipe, W. W., *Ind. Eng. Chem.* **52**, 287 (1960).
166. Stone, L., and Margolin, M., *J. Metals* **5**, 1498 (1953).
167. Takei, W. J., Shirane, G., and Frazer, B. C., *Phys. Rev.* **119**, 122 (1960).
168. Takei, W. J., Heikes, R. R., and Shirane, G., *Phys. Rev.* **125**, 1893 (1962).
169. Terao, N., *Naturwissenschaften* **45**, 620 (1958).
170. Terao, N., *Mem. Sci. Rev. Met.* **57**, 96 (1960).
171. Terao, N., *J. Phys. Soc. Japan* **17**, Suppl. BII, 242 (1962).
- 171a. van Arkel, A. E., and de Boer, J. H., *Z. Anorg. Allgem. Chem.* **148**, 345 (1925).
172. Wain, H. L., Henderson, F., Johnstone, S. T. M., and Louat, N., *J. Inst. Metals* **86**, Pt. 6, 281 (1958).
173. Watt, G. W., and Davies, D. D., *J. Am. Chem. Soc.* **70**, 3753 (1948).
174. Weaver, C. W., *Nature* **180**, 806 (1957).
175. Westphal, R. C., and Glatter, J., *Mater. Methods* **40**, 100 (1954).
176. Wiener, G. W., and Berger, J. A., *J. Metals* **7**, *AIME Trans.* **203**, 360 (1955).
177. Wöhler, F., *Ann. Chem.* **73**, 34 (1850).
178. Wold, A., Arnott, R. J., and Menyuk, N., *J. Phys. Chem.* **65**, 1068 (1961).
179. Yousef, Y. L., Girgis, R. K., and Mikhail, H., *J. Chem. Phys.* **23**, 959 (1955).
180. Zwicker, U., *Z. Metallk.* **42**, 274 (1951).

PSEUDOHALIDES OF GROUP IIIB AND IVB ELEMENTS

M. F. Lappert and H. Pyszora

The Chemical Laboratory, University of Sussex, Brighton, England
and The Distillers Company, Epsom, England

I. Introduction	133
II. Azides	133
A. Introduction	134
B. Preparation	136
C. Properties	139
III. Cyanides and Isocyanides	142
A. Preparation	142
B. Structures	149
C. Properties	150
IV. Isocyanates	152
A. Preparation	152
B. Structures	159
C. Properties	160
V. Isothiocyanates	165
A. Preparation	165
B. Structures	170
C. Properties	172
References	178

I. Introduction

This review deals with the azides, cyanides, isocyanates, and isothiocyanates of the nontransition elements of Groups III and IV, and their isomers (e.g., MNC as well as MCN) when these exist. The literature is covered to the beginning of 1966 (see also *183a*).

The aim has been to provide a substantially complete account of published work, including a general description of the chemistry for each class of pseudohalide (Sections II–V). Individual compounds, with numerical data and references, are listed in Tables I–IV.

The term "pseudohalide" was originally (*31a*, *40a*) coined collectively to describe groups such as cyanide, thiocyanate, azidothiocarbonate, selenocyanate, tellurocyanate, cyanate, azide, and their structural isomers, in order to emphasize the physical and chemical resemblances between them and the halides. It is perhaps useful to consider the structural and electronic features which they have in common. These are that they are polyatomic, linear, electronegative (i.e., will exert a $-I$ effect when covalently bound to

a Group IIIB or IVB element), and capable of participating in intramolecular π -bonding with a neighboring electrophilic center. This $+M$ effect is made possible by virtue of their unsaturation and/or the possession of formally nonbonding electrons on the atom which provides the donor site. With groups other than azide, the donor site may in principle be one of two (e.g., N or O in $M-N=C=O$ and $M-O-C\equiv N$), and this presents us with the possibility of structural isomerism. A geometric consequence of strong π -interaction between the element M and the pseudohalide is linearity at the donor site; for example, in $H_3SiN=C=S$ the $SiNC$ angle is 180° , indicating substantial Si—N multiple-bond character (see Section V). There seems to have been only a single study relating to the comparative electronic effects of halide and pseudohalide (so far only $-NCO$ and $-NCS$) groups when attached to Group IIIB and IVB elements, and this is for boron compounds (114, 150). Acceptor strengths, with respect to both pyridine (calorimetric data) and ethyl acetate (infrared spectroscopic data), decreased in the series $\text{>B-Br} > \text{>B-Cl} > \text{>B-NCS} > \text{>B-NCO} > \text{>B-F}$, and this probably reflects the inverse ability of these halides and pseudohalides to π -bond with boron. The same order was found also for (a) the electronegativity (from 1H n.m.r.) of nitrogen in $(XBNC_2H_5)_3$ (e.g., 3.1 for $X = F$ and 3.56 for $X = Br$), and (b) the intensity of the NH infrared stretching mode in $(XBNH)_3$. No results are yet available to throw light on relative electronegativities of the groups X. In the boron series, ^{11}B nuclear magnetic resonance measurements on both >B-X and >BX may prove informative.

A further consequence of unsaturation in the pseudohalide group X is the possibility of addition reactions. In this way, X may behave as a functional group rather than a halide. This problem is analyzed (Section III,C).

II. Azides

A. INTRODUCTION

Hydrazoic acid was discovered in 1890 (50). Many inorganic and organic derivatives have been prepared. Reviews (29, 39, 180b) relating to these compounds have been published, but only recently was attention turned to the preparation of organometallic azides. Some of these have proved remarkably stable to thermal decomposition. (See Table I.)

TABLE I
DATA ON AZIDES*

Compound	M.P. (°C)	B.P. (°C)/mm	Reference	Other properties ^a
B(N ₃) ₃	—	—	(199)	—
LiB(N ₃) ₄	—	—	(200)	—
(Me ₂ N) ₂ BN ₃	—	38–42/2	(128, 138a, 141)	B (128, 141)
(Et ₂ N) ₂ BN ₃	—	90–93/12	(128, 141)	B (141)
Me ₂ NB(N ₃) ₂	—	53–55/12	(128, 141)	B (141)
Et ₂ NB(N ₃) ₂	—	75–77/12	(128, 141)	B (141)
Ph ₂ BN ₃	—	—	(140, 140a)	—
Ph ₂ BN ₃ ·C ₆ H ₅ N	—	89–92/HV	(139, 140)	—
PhB(N ₃) ₂ ·C ₆ H ₅ N	—	140/HV	(140)	—
B(N ₃) ₃ ·C ₆ H ₅ N	—	130/HV	(140)	—
(Cl ₂ BN ₃) ₃	67	—	(140a, 140b)	B, H (140b)
(Br ₂ BN ₃) ₃	94.5	—	(140b)	B, H (140b)
[HNB(N ₃)] ₃	—	—	(138)	—
[Bu ⁺ NB(N ₃)] ₄	275–7	—	(185, 185a)	—
[Am ⁺ NB(N ₃)] ₄	261–3	—	(185, 185a)	—
H ₃ N ₂ B ₃ (N ₃)Cl ₂	70–73	—	(128)	—
Me ₂ N ₂ B ₃ (N ₃)Cl ₂	—	—	(128)	—
Et ₂ AlN ₃	—	—	(143a)	—
Al(N ₃) ₃	—	—	(100, 197)	—
MeAl(N ₃) ₂	—	—	(199)	—
MeOAl(N ₃) ₂	—	—	(199)	—
Ga(N ₃) ₃	—	—	(202)	—
Me ₂ TlN ₃	—	—	(109b)	—
TlN ₃	c. 334	—	(213)	—
PhTl(N ₃) ₂	d. 200	—	(44)	—
Ph ₂ TlN ₃	d. 321	—	(30a)	—
H ₃ SiN ₃	–81.8	–28/760	(61)	—
D ₃ SiN ₃	—	—	(61)	—
Me ₂ SiN ₃	–95	92–93/760	(32, 33, 35, 36, 47, 151, 155a, 178, 179a, 180c, 182, 196, 205)	A, B, (47, 180c), D (47), E
Me ₂ SiClN ₃	—	—	(179a, 180)	—
MeSiCl ₂ N ₃	—	100.5/760	(179a, 180)	—
Ph ₃ SiN ₃	79–80	—	(36, 151, 179a, 181, 196, 203–207)	B (207)
Ph ₂ MeSiN ₃	—	196–198/47	(155a)	—
PhMe ₂ SiN ₃	—	70/15	(196)	—
2-PhC ₆ H ₄ SiMe ₂ N ₃ ^b	—	152/65	(80a)	—
Me ₂ Si(N ₃) ₂	—	144.3/760	(151, 178, 179a)	B (178)
MeSiCl(N ₃) ₂	—	47/20	(179a, 180)	—
Ph ₂ Si(N ₃) ₂ ^c	—	85–90/0.01	(151, 179a, 203, 206)	C (206)
MeSi(N ₃) ₃	—	70–73/30	(151, 179a)	—
PhSi(N ₃) ₃	—	63/0.01	(151, 179a, 182)	—

TABLE I (Continued)

Compound	M.P. (°C)	B.P. (°C)/mm	Reference	Other properties ^a
Si(N ₃) ₄	—	—	(201)	—
Me ₃ GeN ₃	-65	138/760	(155, 157, 180c, 182)	A (182), B (180c, 182)
Ph ₃ GeN ₃	102-103	—	(151, 157a, 181)	—
Me ₂ Ge(N ₃) ₂	-14	43.5/2	(155, 157)	—
Me ₃ SnN ₃	119.5-121.5	—	(96, 96a, 123, 180c, 182)	A (182), B (180c, 182), J (96a)
Bu ⁿ ₃ SnN ₃ ^d	—	118-120/0.18	(123)	B
(PhCM ₂ CH ₂) ₃ SnN ₃	96-96.5	—	(96, 151a)	J
Ph ₃ SnN ₃	115-116	—	(96, 96a, 123, 151, 181)	B (123), J (96a)
Cl ₃ SnN ₃	—	—	(53)	B
Me ₂ Sn(N ₃) ₂	—	—	(154)	—
Ph ₃ PbN ₃	186-187	—	(118, 119a, 151, 181)	A (119a, 181), B (118, 181)
Pb ₂ Pb(N ₃) ₂	—	—	(119a)	A
Pb(N ₃) ₂	—	—	(51)	—
Me ₃ PbN ₃	—	—	(180c, 182)	A, B

^a For all tables: A = ultraviolet; B = infrared; C = nuclear magnetic resonance; D = vapor pressure; E = heat of vaporization; F = Trouton constant; G = microwave spectrum; H = Raman spectrum; I = electron diffraction; J = Mössbauer spectrum. K = X-ray diffraction.

^b $n_D = 1.5887$, 20°C.

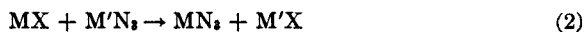
^c $n_D = 1.5097$, 25°C.

^d $n_D = 1.5745$, 25°C.

* See data added in proof, p. 184.

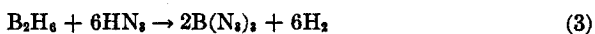
B. PREPARATION

Two methods have been used for the preparation of the majority of organometallic azides, and these are summarized in Eqs. (1) and (2):



where M = B, Al, Ga, or Si; M' = Li, Na, or K; and X = F or Cl.

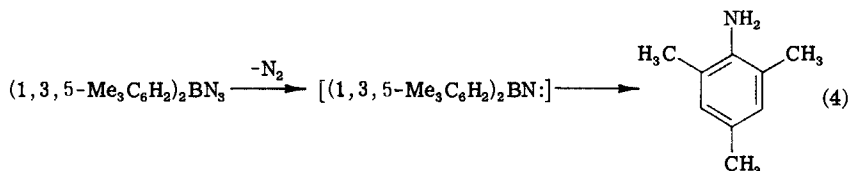
Triazidoborane was synthesized by passing diborane into a cooled ether solution containing excess hydrazoic acid and allowing the mixture to attain room temperature (199). Rapid evolution of hydrogen began at 20° and the reaction afforded high yields of triazidoborane:



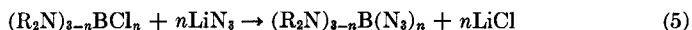
Addition of trimethylamine to the ether solution gave HB(N₃)₂ and H₂BN₃, isolated as stable addition compounds with the amine. It has also been claimed that the acid HB(N₃)₄ is formed during the preparation of triazidoborane, but this was supposed stable only at low temperature.

Hydrazoic acid readily reacted with lithium borohydride yielding (90%) lithium tetraazidoborate, $\text{LiB}(\text{N}_3)_4$. The triazidoborane and lithium azide were assumed to be intermediates in the formation of this compound (200).

Using Eq. (2), other boron azides were prepared. The reaction of sodium azide and aluminum chloride with dimesitylfluoroborane in tetrahydrofuran yielded dimesitylazidoborane. This, however, was not isolated, but was hydrolyzed to give mesidine, thus indicating that a Curtius rearrangement had taken place (117):



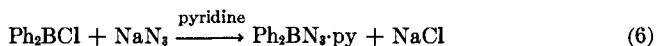
From dialkylaminochloroboranes and lithium azide, in refluxing benzene or toluene, moderate yields of the azidoboranes were obtained (128, 141); similarly prepared were Ph_2BN_3 (140) and Cl_2BN_3 (140a, 140b), from Ph_2BCl and BCl_3 , respectively:



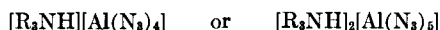
where $\text{R} = \text{Me}$ or Et , and $n = 1$ or 2 .

Likewise, using *B*-trichloroborazine and *B*-trichloro-*N*-trimethylborazine with one equivalent of lithium azide gave the *B*-azido-*B'*,*B''*-dichloroborazines (128). $[(\text{N}_3)\text{BNH}]_3$ (138) and two azidoborazocines (185, 185a) [derivatives of $(\text{HBNH})_4$] have been reported, the latter prepared using NaN_3 in a polar solvent.

The interaction of chlorodiphenylborane and sodium azide, using pyridine as a solvent, resulted in a 90% yield of pyridine-azidodiphenylborane, after the mixture had been stirred for several days at room temperature (139):



Various aluminum azides were synthesized by using Eqs. (1) and (2). An almost quantitative yield of aluminum azide was obtained from the interaction of aluminum hydride and hydrazoic acid at -116° , using ether as a solvent. Addition compounds, such as $\text{AlH}_3\cdot\text{NMe}_3$ and $\text{AlH}_3\cdot 2\text{NMe}_3$, under similar conditions, yielded insoluble (THF) products, and these were assumed (197) to be complex azides:



Sodium azide and aluminum chloride reacted readily at 20° in tetrahydrofuran (THF) yielding (89%) aluminum triazide (100).

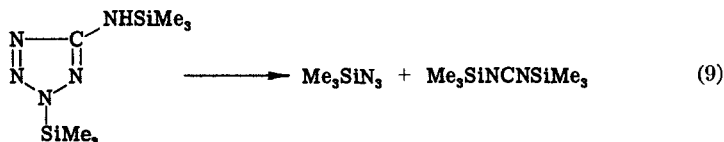
Alkyl and alkoxy aluminum azides were obtained by reactions according to Eqs. (7) and (8), respectively (199):



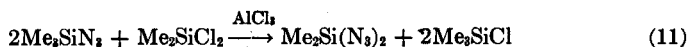
A procedure identical with that used in the synthesis of aluminum triazide yielded gallium triazide from GaH_3/HN_3 (202); gallium hydride is stable only in complexed form.

Equation (2) has been used for all the azidosilanes prepared to date. From various silyl chlorides and sodium or lithium azide, tetraazidosilane (201), trimethyl- (32, 47, 178, 196) and triphenyl- (196, 203, 204) azidosilanes, dimethyl- (178) and diphenyl- (204) diazidosilanes, and phenyl-triazidosilane (203) were obtained. Various other derivatives of silicon (179a, 180, 205, 206), germanium (155, 157), tin (181, 182), and lead (151, 181, 182) have been prepared similarly. Among the less common solvents were pyridine (206) and tetrahydrofuran (205), while from chlorosilanes and NaN_3 , using molten salts as solvents, $\text{MeCl}_2\text{SiN}_3$, $\text{MeClSi}(\text{N}_3)_2$, and $\text{Me}_2\text{ClSiN}_3$ were obtained (179a, 180).

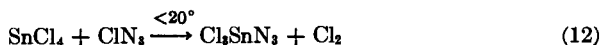
Trimethylazidosilane was also prepared by thermolysis of 1-(*N*-trimethylsilylamino)-3-trimethylsilyltetrazole [likewise, the 1,2-isomer gave $\text{Me}_3\text{SiN}_3 + \text{Me}_3\text{SiNHCN}$ (61)], and by interaction of hydrazoic acid and hexamethyldisilazane (32). Silylamine and hydrazoic acid gave H_3SiN_3 (61).



Interaction of trimethylazidosilane and dimethyldichlorosilane, in the presence of aluminum chloride, gave dimethyldiazidosilane in almost quantitative yield (178):



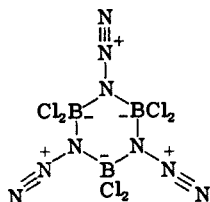
Trimethyl-, tri-*n*-butyl-, and triphenyl-tin azides were obtained from the corresponding chlorides and sodium azide (123). Attempts to prepare the tetraazide by the interaction of tin(IV) chloride with sodium azide resulted in the formation of $\text{Na}_2\text{Sn}(\text{N}_3)_6$ (201). An azidochlorostannane was made using Eq. (12) (53):



Triphenyllead(IV) azide was obtained when an ethanolic suspension of the hydroxide was treated with a chloroform solution of hydrazoic acid (118, 119a); $\text{Ph}_2\text{Pb}(\text{N}_3)_2$ was prepared similarly from $(\text{Ph}_2\text{PbO})_n$.

C. PROPERTIES

The triazides of boron, aluminum, and gallium, and tetraazidosilane are all solids, soluble in some polar organic solvents (e.g., tetrahydrofuran). They are very reactive, hydrolyze rapidly, and are extremely sensitive to percussion. The only compounds reported as oligomeric or polymeric are some tin azides and $(\text{Cl}_2\text{BN}_3)_3$ and $(\text{Br}_2\text{BN}_3)_3$ (140a, 140b), for which a cyclic structure was proposed:

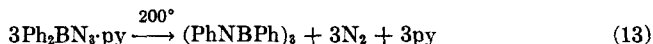


Some tin azides R_3SnN_3 have been regarded as polymeric in the solid state with tin in a bipyramidal five-coordinate environment and azide bridging groups, on the basis of infrared (123) and Mössbauer (96a) spectral data; the hindered $(\text{PhCMe}_2\text{CH}_2)_3\text{SnN}_3$, however, is monomeric (151a).

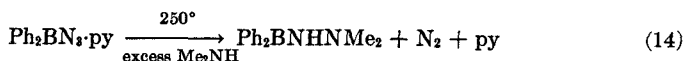
The alkyl and aryl azido compounds of silicon, tin, and lead, bisdimethylaminoazidoborane, and the azidoborazines, on the other hand, have high thermal stability. Evolution of nitrogen was slow even at elevated temperatures; thus, triphenylazidosilane was recovered quantitatively after heating at 400° in the presence of copper powder (203), and the azidoborazines lost nitrogen very slowly when heated at 200° (128).

The stability of the phenylazidosilanes was attributed to $p\pi-d\pi$ NSi bonding, which may also be responsible for the expected linearity of the $\equiv\text{SiN}_3$ skeleton. The proton magnetic resonance spectrum of triphenylazidosilane was said to indicate a marked degree of overlap of the d orbitals of the silicon atom with the π -system of the benzene ring. That this is not the sole factor contributing to the stability of the azide is clear from the high stability of the alkyl derivatives. The infrared spectra of the series Me_3MN_3 ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{and Pb}$) have been examined (180c).

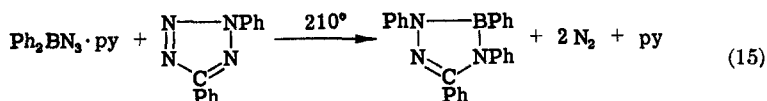
Pyridine-azidodiphenylborane underwent a number of reactions at 200° – 250° in sealed tubes (139, 140). A nearly quantitative yield of hexaphenylborazine was obtained from simple pyrolysis of the azide (139). Clearly, this involves migration of a phenyl anion from boron to nitrogen:



Heating the azide with excess dimethylamine gave a low yield of 1-phenyl-2,2-dimethylhydrazine, indicating that Ph_2BN (analogous to a carbene) may have been an intermediate in the decomposition:



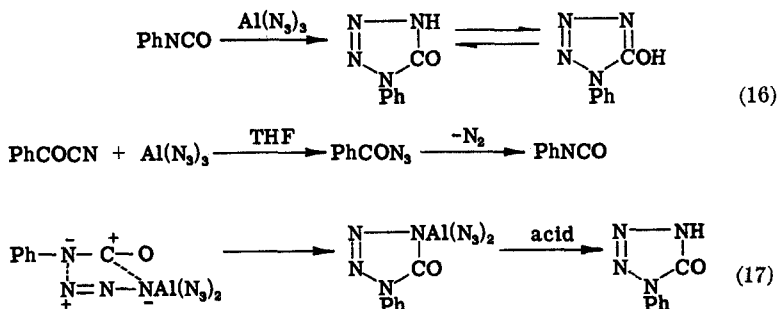
The presence of another intermediate, $\text{PhB}=\text{NPh}$, was postulated (139) to account for the formation in low yield of 1,2,3,5-tetraphenyl-1,3,4-triaza-2-borole, when the pyrolysis was carried out in the presence of 2,5-diphenyltetrazole, which is known to be a source of the 1,3-dipole $\text{PhC}=\text{N}^+-\text{N}^--\text{Ph}$:



Pyrolysis of Ph_2BN_3 in the absence of pyridine gave $(\text{PhBNPh})_2$ and nitrogen (140); $(\text{Me}_2\text{N})_2\text{BN}_3$ after 17 hours at 220° gave N_2 , Me_2NH , and a resin (141); $(\text{Et}_2\text{N})_2\text{BN}_3$ after 18 hours at 280° afforded N_2 , $\text{B}(\text{NEt}_2)_3$, and a resin; $\text{R}_2\text{NB}(\text{N}_3)_2$ ($\text{R} = \text{Me}$ or Et) at 210° gave N_2 corresponding to one azide group; and Cl_2BN_3 at 200° yielded N_2 , BCl_3 , and $(\text{ClBNCl})_3$ (140a).

Aluminum triazide reacted with benzonitrile to give 5-phenyltetrazole in high yield (198).

1-Phenyl-5(4H)-tetrazolinone was obtained from the interaction of benzoyl cyanide (Eq. 16), or phenyl isocyanate (Eq. 17), and aluminum triazide (99), and also from the isomerization of phenylcarbamyl azide, when aluminum azide was the catalyst (119).

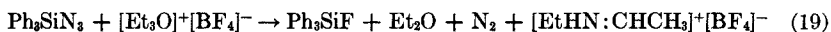


The azidosilanes are hydrolyzed more slowly than the corresponding chlorides, and the hydrolysis is catalyzed by both acids and bases.

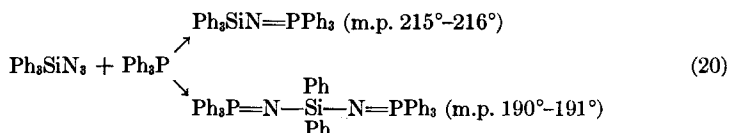
Triphenylazidosilane was completely decomposed by ultraviolet irradiation at 30° . Both photolysis and thermal degradation were believed to occur

by the same mechanism as for organic azides, namely, through the formation of azene intermediates (167, 168). Some doubt, however, was expressed (47) as to the validity of this interpretation when, from the pyrolysis of trimethylazidosilane, a complex mixture was isolated (including methane, ethane, acetylene, ethylene, hydrogen cyanide, hydrazoic acid, ammonium azide, hydrogen, and nitrogen). Azido-2-biphenyldimethylsilane, RMe_2SiN_3 , upon photolysis gave nitrogen and 9,10-azasiladihydrophenanthrene (80a).

Azide-halogen exchange has been demonstrated for the following examples:



The phenylazidosilanes formed 1:1 complexes with triphenylphosphine (196). Triphenylazidosilane decomposed (203, 204) slowly in benzene (50°) or ether (100°) in the presence of triphenylphosphine, to give *N*-silyl-phosphinimines:



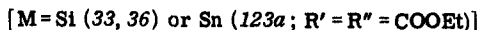
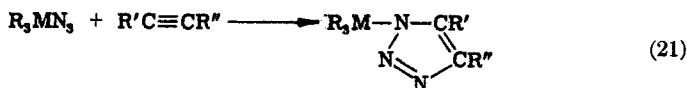
The loss of nitrogen did not follow first order kinetics, and only a maximum of 50% nitrogen was evolved. Side reactions resulting in the formation of $(\text{Ph}_3\text{P}=\text{NH}_2)^+\text{N}_3^-$ were postulated.

Other silicon (35, 181, 194, 206) as well as germanium (181, 194) and tin (194) azides also reacted with phosphines, either to form 1:1 adducts (181) or stable phosphinimines (181, 194). However, silyl azide and halo-phosphines reacted by azide-halogen exchange, and the unstable azido-phosphines readily lost nitrogen to afford cyclophosphazenes (109, 109a).

Whereas Ph_3SiN_3 afforded $(\text{Ph}_2\text{SiNPh})_2$ on pyrolysis, Ph_3SnN_3 and Ph_3PbN_3 gave Ph_4Sn or Ph_4Pb , respectively (151). It has been suggested that thermal decomposition of metallic monoazidochlorides may be utilized for preparing corresponding nitrides (53).

Group IV azides react with acetylenes to form triazoles; however, $\text{Bu}^n\text{SnN}_3/\text{HOCC}\equiv\text{CCOOH}$ gave $\text{Bu}^n\text{SnOCOC}\equiv\text{CCOOSnBu}^n$ and hydrazine (123).

A number of 1:1 Lewis Acid adducts of Group IVB azides, such as $\text{Ph}_3\text{MN}_3\cdot\text{BBr}_3$ and $\text{Ph}_3\text{MN}_3\cdot\text{SnCl}_4$ ($\text{M} = \text{Si, Ge, or Sn}$) have been prepared (183). The complexes $\text{R}_3\text{SiN}_3\cdot\text{SbCl}_5$ ($\text{R} = \text{CH}_3$ or C_6H_5) (183) are highly unstable (see Eq. 18) (208), while H_3SiN_3 and BF_3 afford SiH_4 and SiH_3F (61).

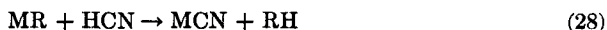
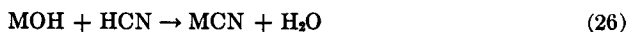
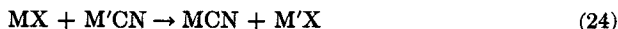
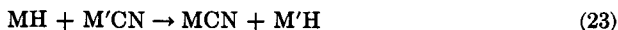


III. Cyanides and Isocyanides

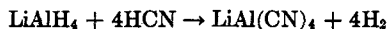
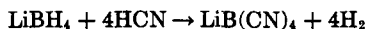
A. PREPARATION

There is some doubt as to whether the covalent organometallic cyanides of Group IIIB and IVB elements have the normal cyanide ($M-C\equiv N$) or the isocyanide ($M-N\equiv C$) structure. In this section (A) the formulas and names will be written as they appear in the original publications and no structural implications are intended. (See Table II.)

Eight general types of reaction (Eqs. 22-28a) are available for the preparation of organometallic cyanides:



Interaction of lithium boro- (211) or aluminum (210) hydrides and hydrogen cyanide at low temperature afforded the tetracyanides of boron and aluminum:

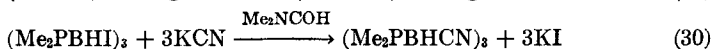


Treatment of lithium borohydride with a dioxane solution of hydrogen cyanide at 100° afforded lithium monocyanoborohydride, crystallizing with 2 moles of dioxane and, unlike $LiAl(CN)_4$, stable in aqueous solution (210).

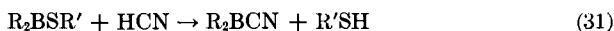
Attempts (30a, 43) have been made to repeat the synthesis of tri-cyanoborane, first reported in 1931 (142). The reaction of trihaloboranes (Cl or Br), either with hydrogen cyanide or with silver cyanide, yields highly unstable products which cannot be characterized.

Tricyanoborazine (40, 52) and *P*-hexamethyl-*B*-tricyanoborophane (191) have been synthesized from the corresponding chloride (Eq. 29) and

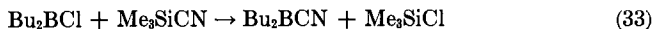
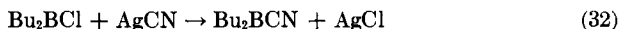
iodide (Eq. 30), using a polar solvent; other cyanoborazines have been obtained similarly (94):



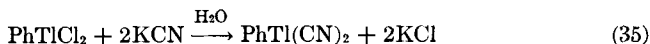
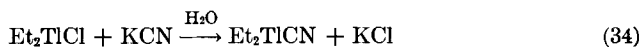
Di-*n*-butyl-, di-*i*-butyl-, and di-*i*-amyl-cyanoboranes were obtained according to Eq. (31) (135):



Di-*n*-butylcyanoborane has been prepared from the chloride by the metathetical reactions (32) and (33) (65a):



Interaction of potassium cyanide and diethylthallium chloride or phenylthallium dichloride in water afforded (Eqs. 34, 35) the corresponding cyano derivatives (31, 44); Me_2TlF and KCN behaved similarly (45):



Phenylthallium dichloride reacted with 4 moles of potassium cyanide to give $\text{K}[\text{PhTl(CN)}_3]$, which on boiling in water gave hydrocyanic acid and a precipitate of diphenylthallium cyanide (44).

Dimethylmetal cyanides of Al, Ga, In, and Tl were obtained by route (28) (45).

Many organocyanosilanes are known and have usually been obtained by use of reaction routes (23) and (24).

By passing the vapor of halosilanes over silver cyanide at room temperature, or by the interaction of silver or mercury(II) cyanides and halosilanes in solution, a number of cyanosilanes have been prepared. Thus, H_3SiCN (129), H_2SiMeCN (64), HSiMe_2CN (111), $\text{H}_3\text{SiSiH}_2\text{CN}$ (48), and $\text{Me}_3\text{SiSiMe}_2\text{CN}$ were synthesized using the vapor phase reaction; and Me_3SiCN (37, 48, 56), Cl_3SiCN (105), Et_3SiCN (37, 56), $\text{Et}_2\text{Si(NC)}_2$ (176), and $\text{Me}_2\text{Si(CN)}_2$ (126, 127) were obtained by the solution technique.

It is often advantageous not to use a solvent, from the standpoints of reaction times and yields (57).

In the synthesis of trichlorocyanosilane from hexachlorodisilane and mercuric cyanide, pentachlorocyanodisilane was postulated as an intermediate (105). Cleavage of the Si—Si bond gave a polymeric chloride and

TABLE II
DATA ON CYANIDES AND ISOCYANIDES

Compound	M.P. (°C)	B.P. (°C)/mm	n_D	°C	d_4	°C	Reference	Other properties ^a
LiB(CN) ₄	—	—	—	—	—	—	(211)	—
LiBH ₃ CN	—	—	—	—	—	—	(211)	—
NaPh ₃ BCN	—	—	—	—	—	—	(212)	—
(H ₂ BCN) _n	—	—	—	—	—	—	(65)	—
B(CN) ₃	—	—	—	—	—	—	(43, 142)	—
Bu ⁿ ₂ BCN	57–58	—	—	—	—	—	(65a, 135)	B (65a, 135)
Bu ⁱ ₂ BCN	145	—	—	—	—	—	(135)	—
Am ⁱ ₂ BCN	—	—	—	—	—	—	(135)	—
(HNBCN) ₃	—	—	—	—	—	—	(40, 52)	—
(MeNBCN) ₃	150	—	—	—	—	—	(94)	—
(PhNBCN) ₃	220	—	—	—	—	—	(94)	—
Me ₃ N ₂ B ₃ (CN) ₂ Bu ⁿ	40	—	—	—	—	—	(94)	—
Me ₃ N ₂ B ₃ (CN)Bu ⁿ ₂	—	130/0.001	—	—	—	—	(94)	—
(Me ₂ PBHCN) ₃	—	—	—	—	—	—	(191)	—
LiAl(CN) ₄	—	—	—	—	—	—	(210)	—
Al(CN) ₃	—	—	—	—	—	—	(210)	—
Me ₂ AlCN	89	—	—	—	—	—	(45)	B
Me ₂ GaCN	79	—	—	—	—	—	(45)	B
In(CN) ₃	—	—	—	—	—	—	(98a)	—
Me ₂ InCN	147	—	—	—	—	—	(45)	B
Me ₂ TiCN	275 decomp.	—	—	—	—	—	(45, 94b)	B (45), C (94b)
Et ₂ TiCN	—	—	—	—	—	—	(31)	—
Ph ₂ TiCN	318 decomp.	—	—	—	—	—	(44)	—
PhTi(CN) ₂	228	—	—	—	—	—	(44)	—

H ₃ SiCN	32.4	49.6/760	—	—	—	—	(58, 70, 129, 137, 177)	B (70), C (58), G (137)
D ₃ SiCN	—	—	—	—	—	—	(120)	—
MeSiH ₂ CN	23.1	—	—	—	—	—	(64)	—
Me ₂ SiHCN	-60.9	—	—	—	—	—	(111)	—
Me ₂ PhSiCN	—	230-232/760	1.49983 ^b	—	0.95733 ^b	—	(125)	—
Me ₃ SiCN	11.5	117.8/760	1.3883	26	0.7834	20	(37, 56, 57, 65, 70, 100a, 126, 127, 162, 179, 189)	B (5, 70, 162)
Et ₃ SiCN	5.5	182/760	1.4270	26	—	—	(37, 56, 70, 100a)	B (70)
Pr ⁿ ₃ SiCN	-8	229/760	—	—	—	—	(56, 70)	B (70)
<i>n</i> -HeptylSiH ₂ CN	—	204/760	1.4349	20	0.830	20	(26)	—
Ph ₃ SiCN	135-137	210/5	—	—	—	—	(37, 70, 125)	B (70)
Cl ₃ SiCN	-46.2	73.2/760 (extr.)	—	—	—	—	(105)	—
Me ₂ Si(NMe ₂)CN	—	—	—	—	—	—	(100a)	—
MeSi(NMe ₂) ₂ CN	—	—	—	—	—	—	(100a)	—
MeSi(NEt ₂) ₂ CN	—	—	—	—	—	—	(100a)	—
Me ₂ Si(NEt ₂)CN	—	—	—	—	—	—	(100a)	—
H ₃ SiSiH ₂ CN	—	—	—	—	—	—	(48)	—
Me ₃ SiSiMe ₂ CN	—	176.4/760 (extr.)	1.4374	30	0.8136	30	(48)	B, D, E, F
Me ₃ Si(SiMe ₂) ₃ CN	—	—	—	—	—	—	(187)	—
Me ₃ Si(SiMe ₂) ₄ CN	—	—	—	—	—	—	(187)	—
Me ₂ Si(CN) ₂	84-85	168-169/760	—	—	—	—	(126, 127)	—
Et ₂ Si(CN) ₂	33	214/760	—	—	—	—	(56)	—
Ph ₂ Si(CN) ₂	46-48	142/2	1.5599 ^b	—	1.0904 ^b	—	(103, 125)	—
H ₃ GeCN	45-46.8	—	—	—	—	—	(85, 110, 171, 172, 175, 176)	B (85, 172, 175)
D ₃ GeCN	—	—	—	—	—	—	(85, 110, 175)	B (85, 175)
Me ₃ GeCN	38-38.5	—	—	—	—	—	(162, 172)	B (162, 172)

TABLE II (Continued)

Compound	M.P. (°C)	B.P. (°C)/mm	n_D	°C	D_4	°C	Reference	Other properties ^a
Et ₃ GeCN	18	213/760	1.4509	20	1.111	20	(16, 25)	—
Pr ⁿ ₃ GeCN	-13	253/760	1.4544	20	1.041	20	(16, 22)	—
Pr ⁱ ₃ GeCN	—	—	—	—	—	—	(22)	—
Bu ⁿ ₃ GeHCN	—	108-110/8	1.4527	20	1.050	20	(24)	—
Pr ⁱ ₂ Ge(CN) ₂	—	—	—	—	—	—	(22)	—
Ge(CN) ₄	—	—	—	—	—	—	(37, 132)	—
Me ₃ SnCN	184.5-186	—	—	—	—	—	(157a, 162)	B (162), K (157a)
Et ₃ SnCN	163.5-165	249/760	—	—	—	—	(28, 41, 122a, 124, 162, 188)	B
Et ₂ Sn(CN)I	—	—	—	—	—	—	(41)	—
Pr ⁿ ₃ SnCN	—	—	—	—	—	—	(42)	—
Bu ⁿ ₃ SnCN	90-93	—	—	—	—	—	(49, 122a, 124)	—
Ph ₃ SnCN	260	—	—	—	—	—	(122a, 215)	—
Me ₂ Sn(CN) ₂	>400	—	—	—	—	—	(122a)	B
Et ₂ Sn(CN) ₂	—	—	—	—	—	—	(122a, 215)	—
Pr ⁿ ₂ Sn(CN) ₂	—	—	—	—	—	—	(55)	—
Bu ⁿ ₂ Sn(CN) ₂	220	—	—	—	—	—	(122a)	B
Ph ₂ Sn(CN) ₂	265	—	—	—	—	—	(122a)	B
Et ₂ PbCN	189 decomp.	—	—	—	—	—	(95, 116a)	—
Pr ⁿ ₂ PbCN	135	—	—	—	—	—	(156)	—
Ph ₂ PbCN	—	—	—	—	—	—	(63, 116a)	B
Ph ₂ Pb(CN) ₂	245-255 decomp.	—	—	—	—	—	(116a, 195)	—
Ph ₂ Pb(OH)CN	—	—	—	—	—	—	(116a)	—

^a See Table I for symbols used.^b Density and refractive index measured on supercooled liquid.

trichlorocyanosilane. The hypothesis is supported by the observation that pentamethylcyanodisilane gave a high yield of trimethylcyanosilane by thermal decomposition (Eq. 36) at 115°–130° (48):



n-Heptylcyanosilane was obtained by reaction (37) (26):



Trimethylcyanosilane was formed (Eq. 38) when trimethylchloromethylsilane was treated with silver cyanide (144), and when sodium and acetonitrile were reacted (Eq. 39) with trimethylchlorosilane in ether (145):



Dichlorosilanes and silver cyanide behave differently. Refluxing Ph_2SiCl_2 and AgCN in benzene, or in the absence of solvent, was said to provide no reaction, whereas under the same conditions, with LiCN , $\text{Ph}_2\text{Si}(\text{CN})_2$ was obtained in 68% yield (103). However, R_2SiCl_2 ($\text{R}_2 = \text{Me}, \text{Ph}$, or $\text{Me}, \text{CH}_2=\text{CH}$) and AgCN in benzene or ether gave a polymeric carbodiimide, $(\text{R}_2\text{SiNCN})_n$ ($n = 6.7\text{--}8.4$) (147).

Triethyl- and triphenyl-cyanosilanes have been prepared according to Eq. (40) (37). Methyl trimethylacetate was continuously removed by distillation:



When hexamethyldisilazane was treated with an ethereal solution of hydrogen cyanide, trimethylcyanosilane was obtained (Eq. 41) (37):



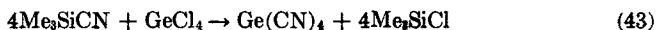
From organogermanium halides and silver or mercury(II) cyanides, with or without solvent, the following cyanogermanes were obtained: $\text{EtGe}(\text{CN})_3$ (12), Et_3GeCN (16), Pr_3GeCN (16, 22), Pr_3GeCN (22), Me_3GeCN (161, 162), H_3GeCN (171, 176), D_3GeCN (175), and $\text{Ge}(\text{CN})_4$ (37, 132).

The addition of mercury(II) cyanide to $\text{Bu}^n_2\text{GeH}_2$ (1:2) gave di-*n*-butylcyanogermane in 74% yield (132).

High yields of cyanogermanes were also reported from the interaction (Eq. 42) of bis(trialkylgermanium) oxides and hydrogen cyanide (144):



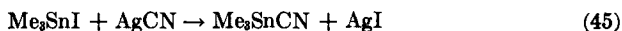
Tetracyanogermane was obtained from trimethylcyanosilane and germanium tetrachloride (Eq. 43), by heating in xylene and removing the chlorosilane as it was formed (37):



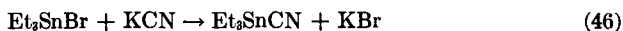
Triethylgermanium sulfonate provided a source (Eq. 44) for the cyanide (25):



Silver cyanide was the reagent used in the synthesis (Eq. 45) of trimethyltin cyanide from trimethyltin iodide in benzene (161, 162):

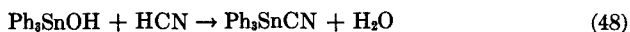


In another synthesis (Eqs. 46, 47), aqueous potassium cyanide and ethereal solutions of organotin halides were employed (124, 188):



Absolute ethanol has also been used as a solvent (55).

Attempts to prepare triphenyltin cyanide from the hydroxide and aqueous hydrogen cyanide (route 26), or from triphenyltin chloride and potassium cyanide (route 24), failed. However, by passing anhydrous hydrogen cyanide into triphenyltin hydroxide and washing the product with anhydrous hydrogen cyanide, triphenyltin cyanide was obtained (Eq. 48) in 95% yield (215):



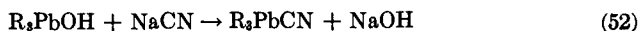
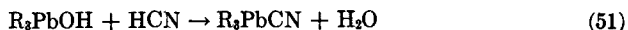
Likewise, bis(triethyltin) oxide and anhydrous liquid hydrogen cyanide gave (Eq. 49) triethyltin cyanide (28):



Interaction of anhydrous hydrogen cyanide and either R_3SnNEt_2 or $\text{R}_2\text{Sn}(\text{NEt}_2)_2$ ($\text{R} = \text{Me}, \text{Et}, \text{Bu}^n$, or Ph) gave diethylammonium cyanide and R_3SnCN or $\text{R}_2\text{Sn}(\text{CN})_2$, respectively (122a).

Organic derivatives of silicon, germanium, and tin have been shown to interchange cyanide groups (28, 57, 171).

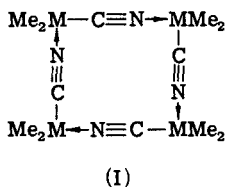
For the preparation of organolead cyanides, reactions (50–52) have been used (3, 63, 95, 156):



B. STRUCTURES

We have here essentially three problems. These are (i) covalent versus ionic character [in the event, only the thallium derivatives are ionic; Me_2TlCN is soluble in water and its electrical conductance indicates it to be a strong 1:1 electrolyte, $\text{Me}_2\text{Tl}^+\text{CN}^-$ (45)]; (ii) degree of association (oligomeric and polymeric species are found only with B, Al, Ga, and In derivatives); and (iii), in covalent monomeric species, cyanide ($\text{M}-\text{C}\equiv\text{N}$) versus isocyanide ($\text{M}-\text{N}=\text{C}$) structures.

Tricyanoborane appears to be an unstable, polymeric solid which curiously showed no absorption band in the $2000\text{--}2300\text{ cm}^{-1}$ range (43, 94a), while $(\text{Bu}^n_2\text{BCN})_{20}$ is a low molecular weight polymer, as indicated by cryoscopy in benzene (65a). Compounds $(\text{Ar}_2\text{BCN})_n$ are likewise polymeric (114a). The cyanodimethylmetallanes of Al, Ga, and In, on similar evidence, are tetrameric in benzene solution, and structure I has been proposed (45). Infrared spectra show CN stretching vibrations at 2213 cm^{-1} (Al), 2202 cm^{-1} (Ga), and 2101 cm^{-1} (Tl).



The proton nuclear magnetic resonance spectra of H_3SiCN and Me_3SiCN are consistent with a normal $\text{M}-\text{CN}$ structure, on the basis of comparative chemical shifts (within 0.02 p.p.m.), in $\text{H}_3\text{SiC}\equiv\text{N}$ and $\text{H}_3\text{SiC}\equiv\text{CH}$ (58). Bonding through nitrogen would probably require larger downfield shifts; thus the values in H_3SiNCO , H_3SiNCS , and $\text{Me}_3\text{SiNCNSiMe}_3$ are $\sim 0.7\text{ p.p.m.}$ lower than in $\text{H}_3\text{SiC}\equiv\text{CH}$.

Spectroscopic evidence for H_3SiCN and D_3SiCN strongly suggested the normal structure (120), and this was further supported by the examination of the microwave spectrum of H_3SiCN (137, 165). Similarly, infrared spectral data favored the normal structure for a number of R_3SiCN ($\text{R} = \text{H, Me, Et, } n\text{-Pr, Ph}$) derivatives (70). The structures of trimethylcyano-silane (37, 57, 91, 121, 126, 127), trimethyl(iso)cyanogermane (162), and trimethyltin cyanide (162) have been the subject of much discussion in recent years, and it is now assumed on the basis of infrared spectra (37, 162) and chemical studies (162) that these trimethyl derivatives may consist of equilibrium mixtures of the iso ($\text{M}-\text{NC}$) and normal ($\text{M}-\text{CN}$) structures. Comparison of the infrared spectra of Me_3SiCN and Me_3GeCN revealed

two significant absorption bands in each case, at 2108 and 2198 cm^{-1} for the silicon compound, and at 2100 and 2197 cm^{-1} for the germanium compound, the first band being attributed to isocyanide, the second to the normal cyanide. The optical density of the $\text{—C}\equiv\text{N}$ band in trimethylcyanosilane and trimethylcyanogermane was about 4.5 times as great as that of the $\text{—N}=\text{C}$ band. Similar observations have been made on pentamethylcyanodisilane, where two maxima at 2183 and 2101 cm^{-1} , with the relative intensity ratio of $\sim 3.2:1$, have been noted, the former absorption band being due to the normal and the latter to the iso isomer. Triethyltin cyanide showed only one absorption band in the $\text{—C}\equiv\text{N}$ region at 2175 cm^{-1} . The absence of a second band does not exclude the possibility of the isocyanide isomer being present in very low concentration. The chemical and physical properties of trimethyltin cyanide are, however, more in line with those of a highly polar compound $\text{Me}_3\text{Sn}-\overset{\delta+}{\text{C}}\overset{\delta-}{\text{N}}$ rather than those of a mixture of covalent isomers, as in the case of the analogous silicon and germanium compounds, although chemical support for the iso structure in Bu_3SnNC has been forthcoming (49).

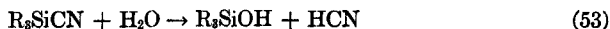
Evidence for the normal structure in germyl cyanide has been provided by vibrational studies on H_3GeCN and D_3GeCN , using also ^{13}C and ^{15}N enrichment (85); a simple linear $\text{M}-\text{C}\equiv\text{N}$ or $\text{M}-\text{N}=\text{C}$ model was taken, using a valence force field with no interaction constants. Potential energy and rotation-distortion constants and thermodynamic properties for these two molecules were calculated (110).

C. PROPERTIES

Aluminum tricyanide is stable for a short period when exposed to the atmosphere, but is hydrolyzed readily in water (210).

Dimethylaluminum, gallium, and indium cyanides, $(\text{Me}_2\text{MCN})_4$, are all sensitive to moisture (45), while Me_2TiCN behaves as a salt in aqueous solution. $(\text{Me}_2\text{GaCN})_4$, upon exposure to air, slowly liquefied, depositing crystals of $(\text{Me}_2\text{GaOH})_4$; $(\text{Me}_2\text{InCN})_4$ behaved similarly (45).

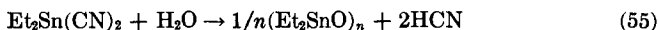
Trimethyl- and triethyl-cyanosilanes (133) and cyanogermane and its deuterio analog (175, 176) reacted rapidly with water, according to Eqs. (53) and (54):



Study of the second reaction has been extended to hydrolysis in D_2O . Spectroscopic evidence excludes the possibility of H_3GeOD formation, as no $\text{D}-\text{O}$ absorption was observed in the 2500 cm^{-1} region. Formation of digermyl ethers was suggested (175).

Attempts to exploit triethyltin cyanide as a source of triethyltin

carboxylic acid failed (124). Diethyltin dicyanide and triphenyltin cyanide decomposed (Eq. 55) readily in water (215). On the other hand, hydrolysis of dipropyltin dicyanide has been claimed to yield ammonia, and Eq. (56) was proposed (55):



Di-*n*-butylcyanoborane afforded $\text{Bu}^n_2\text{BNH}_2$ with ammonia (65a), while amines (PhNH_2 , *n*- BuNH_2 , or $\text{C}_6\text{H}_5\text{N}$) and $(\text{R}_2\text{BCN})_n$ gave monomeric 1:1 adducts (114a, 135). Similar complexes were obtained from $(\text{Me}_2\text{AlCN})_4$ or $(\text{Me}_2\text{GaCN})_4$ and Me_3N (45).

Trimethyl- and triphenyl-cyanosilanes (133), dimethylphenylcyanosilane (125), and trimethylcyanogermane (162) readily added sulfur (Eq. 57):



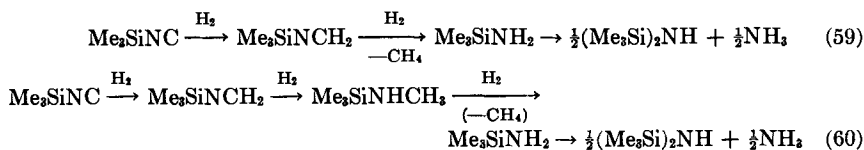
This was taken as evidence for the presence of the iso isomers in these compounds. In contrast, cyanosilane (H_3SiCN) did not add sulfur at room temperature, but complex formation occurred upon heating (120). Trimethyltin cyanide was also converted to the isothiocyanate by treatment for 1 hour at 150° – 160° . However, this should not be taken as support for the presence of the iso structure, since it is known that ionic cyanides react readily with sulfur at high temperatures to form thiocyanates (166), and tin cyanides would be expected to be highly polar [$\text{Sn}(\delta+) - \text{CN}(\delta-)$]. This is supported by data on the crystal structure of Me_3SnCN ; much ionic character was indicated for $\text{Sn} \cdots \text{CN}$ bond (157a). The structure is polymeric, with infinite chains: $\cdots \text{CN} \cdots \text{Me}_3\text{Sn} \cdots \text{CN} \cdots$.

Trimethylcyanosilane and trimethyltin cyanide displaced carbon monoxide from $\text{Fe}(\text{CO})_5$ (161), to give (Eq. 58) crystalline tetracarbonyl derivatives (161):

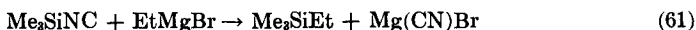


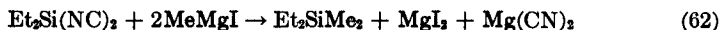
and thus resemble isonitriles (98).

Under high pressure and at elevated temperature using Raney nickel, reduction of trimethylcyanosilane occurred. The reaction sequence postulated (126, 127) was Eq. (59) or (60):

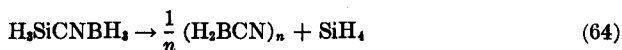
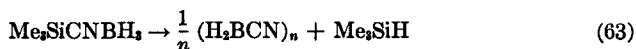


Organocyanosilanes reacted with Grignard reagents in a manner (Eqs. 61, 62) analogous to that of the halides (126, 127):

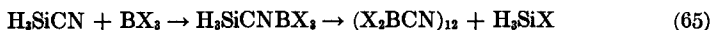




Diborane formed addition compounds with cyanosilane (65), cyano-germane (176), and trimethylcyanosilane (65). The addition compounds $\text{Me}_3\text{SiCNBH}_3$ and $\text{H}_3\text{SiCNBH}_3$ decomposed (Eqs. 63, 64) at 100° , giving polymeric materials, $(\text{H}_2\text{BCN})_n$, remarkably stable to water, oxygen, and heat (65):



Similarly (Eqs. 65, 66), haloboranes (F, Cl, and Br) reacted at low temperature with cyanosilanes (H_3SiCN and Me_3SiCN) (65b) and cyano-germanes [H_3GeCN (176) and Me_3GeCN (162)] (with BF_3 only), to give addition products which decomposed slowly at or below room temperature. The infrared spectra of $\text{H}_3\text{SiCN} \cdot \text{BF}_3$ and $\text{H}_3\text{GeCN} \cdot \text{BF}_3$ have been examined (177).



The effect of heating pentamethylcyanodisilane for 7 hours at 175° has been studied (Eq. 67; $n = 3, 4$, and 7) (187):

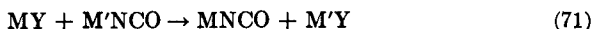
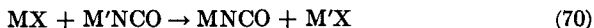
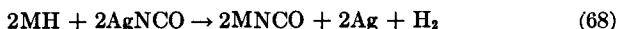


IV. Isocyanates

A. PREPARATION

The MNCO derivatives of the Group IIIB and IVB elements discussed in this section will be referred to as isocyanates, although in the original publications the normal structure may sometimes have been inferred from either their physical properties or chemical behavior. Most substances earlier described as cyanates have proved on re-examination to be the isomeric iso compounds. (See Table III.)

Four general methods (Eqs. 68-71) are available for the synthesis of organometallic isocyanates:

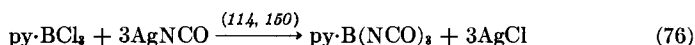
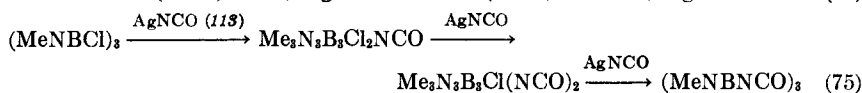
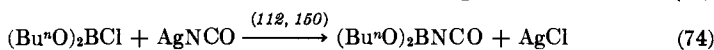
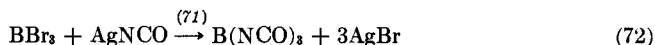


Reaction (70) refers to the transformation of a Group IIIB or IVB halide into the corresponding isocyanate, using the silver, mercury(II), lead(II), sodium, or potassium salt of cyanic acid. Reaction (71) refers to a

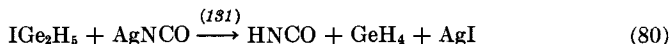
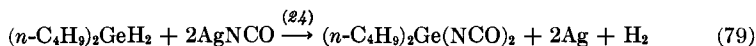
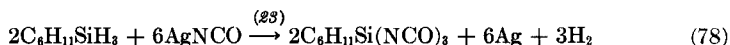
"conversion" or "volatility" series, established for boron (115), silicon (57), germanium (13, 171), and tin (28), whereby interchange of NCO, NCS, X, and other groups may be effected, usually by careful removal by fractionation of the most volatile component of an equilibrium mixture.

Examples of the use of reaction (70) in boron chemistry are shown in Eqs. (72-76).

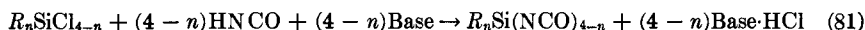
In general, only with silver salts was benzene an effective solvent; sodium or lead salts reacted slowly, if at all, in nonpolar media or in the absence of a solvent such as acetonitrile or acetone (112-115). $\text{Me}_3\text{N}\cdot\text{BCl}_3$ reacted neither with silver cyanate in benzene nor with sodium cyanate in acetone, and this is probably due to the exceptionally strong $\text{N} \rightarrow \text{B}$ linkage (150).



Reaction (68) has been demonstrated for the cases shown in Eqs. (77-79). However, an anomalous system was reaction (80).



Reaction (69) has so far been demonstrated only for a series of chlorosilanes, and the bases used were tertiary amines or amides (Eq. 81) (186, 194a):



Treatment of organosilicon or germanium halides (Br or Cl) with a variety of salts of cyanic acid in solvents such as benzene, hexane, acetonitrile, and nitromethane has provided a route to isocyanates, according to Eq. (70) (8-11, 14, 26, 57, 60, 71, 72, 77, 78, 81, 116, 136, 171, 173, 186, 192). Molten alkali halides have also been used as reaction media (179). No reaction took place between trimethylchlorosilane and potassium cyanate

TABLE III
 DATA ON ISOCYANATES

Compound	M.P. (°C)	B.P. (°C)/mm	n_D	°C	d_4	°C	Reference	Other properties ^a
B(NCO) ₃	—	—	—	—	—	—	(71)	—
Me ₂ BNCO	-118, -119	41.3/760 (extr.)	—	—	1.146	-78	(87)	B (87)
(MeO) ₂ BNCO	—	48/88	1.3856	20	—	—	(115)	—
(Bu ⁿ O) ₂ BNCO	—	65-66/2.5	1.4155	20	0.9613	20	(112, 115, 150)	B (150)
(Bu ⁿ O)(Pr ⁱ N)BNCO	—	64/0.1	1.4265	20	—	—	(115, 150)	B (150)
(Bu ⁿ O)(Pr ⁱ N)BNCO	—	32/0.05	1.4213	20	—	—	(115, 150)	B (150)
(C ₆ H ₁₁ O)(Pr ⁱ N)BNCO	—	90/0.25	1.4529	20	—	—	(115, 150)	B (150)
(Me ₂ N) ₂ BNCO	—	30/0.3	1.4499	20	—	—	(112, 115, 150)	B (150)
(Et ₂ N) ₂ BNCO	—	61/0.1	1.4475	20	0.8678	20	(115, 150)	B (150)
(Pr ⁱ N) ₂ BNCO	—	73-75/0.005	1.4502	20	0.8933	20	(115, 150)	B (150)
(Pr ⁱ N)Bu ^t NHBNCO	—	41-43/0.01	1.4453	20	—	—	(115, 150)	B (150)
(Bu ^t NH) ₂ BNCO	—	72/0.1	1.4376	20	—	—	(115, 150)	B (150)
(CH ₂ NPr ⁿ) ₂ BNCO	—	61/0.9	1.4575	20	—	—	(115)	—
(PhMeN)(Pr ⁱ N)BNCO	—	80/0.1	1.5051	20	—	—	(115)	—
<i>o</i> -C ₆ H ₄ O ₂ BNCO	—	54/0.2	1.5277	20	—	—	(47a, 112, 115, 150)	A (150), B (150)
Ph ₂ BNCO	—	89/0.01	1.6092	20	1.105	20	(112, 115, 150)	B (150)
Pr ⁱ NB(NCO) ₂	—	74/2	1.4529	20	—	—	(115, 150)	B (150)
PhB(NCO) ₂	—	60/0.2	1.5527	20	1.187	20	(112, 115, 150)	B (150)
PhB(NR ₂)NCO	—	—	—	—	—	—	(97)	—
PhB(NMe ₂)NCO	—	—	—	—	—	—	(114)	B, C
(HNBNCO) ₂	166	—	—	—	—	—	(112, 113, 150)	B (150)
(MeNBNCO) ₂	85-86	112/0.03	—	—	—	—	(113, 150)	B (150)
(EtNBNCO) ₂	36	102/0.01	—	—	—	—	(113, 114, 150)	B (150), C (114)
(Pr ⁿ NBNCO) ₂	—	118/0.003	1.4499	20	1.094	20	(113, 150)	A (150), B (150)
(Bu ⁿ NBNCO) ₂	30	140/0.02	—	—	—	—	(113, 150)	B (150)

(Bu ⁺ NBNCO) ₃	—	134/0.01	1.4901	20	1.060	20	(113, 150)	B (150)
(PhNBNCO) ₃	151–152	—	—	—	—	—	(113, 150)	A (150), B (150)
Me ₂ N ₃ B ₃ Cl ₂ (NCO)	56–57	—	—	—	—	—	(113, 150)	B (150)
Me ₂ N ₃ B ₃ Cl(NCO) ₂	95	—	—	—	—	—	(113, 150)	B (150)
Et ₂ N ₃ B ₃ Cl(NCO) ₂	—	98/0.025	—	—	—	—	(113, 150)	B (150)
[Me ₂ PBH(NCO)] ₃	71–72	—	—	—	—	—	(191)	B
(Bu ⁺ NBNCO) ₄	237–238	—	—	—	—	—	(185, 185a)	B (185a)
(Am ⁺ NBNCO) ₄	240.5/245.5	—	—	—	—	—	(185, 185a)	B (185a)
B(NCO) ₄ ·C ₅ H ₅ N	34	154/0.02	—	—	—	—	(150)	B
<i>o</i> -C ₆ H ₄ O ₂ BNCO·C ₅ H ₅ N	—	97/0.03	—	—	—	—	(150)	B
Ph ₂ BNCO·C ₅ H ₅ N	172–175	—	—	—	—	—	(150)	B
PhB(NCO) ₂ ·C ₅ H ₅ N	143–145	—	—	—	—	—	(150)	A, B
PhB(NCO) ₂ ·EtOAc	—	(dissociates at 20/15)	—	—	—	—	(150)	B
H ₃ SiNCO	—	—	—	—	—	—	(58, 60)	A, B, C (58), D, E, F
Me ₃ SiNCO	–49	91/760	1.3960	20	0.867	20	(34, 78, 79, 89, 90, 106b, 146, 148, 174, 176, 179, 180c, 214)	B (89, 180c), I (106b)
Et ₃ SiNCO	—	165.1/760	1.4295	20	0.889	20	(9–11)	—
Ph ₃ SiNCO	95	372/760	—	—	—	—	(78, 79, 81)	—
F ₃ SiNCO	—	–6/760	—	—	—	—	(75)	—
Cl ₃ SiNCO	–69	86.8/760	1.4262	25	1.445	25	(3)	—
(MeO) ₃ SiNCO	—	137.6/760	1.3839	20	1.123	20	(72, 73)	—
(EtO) ₃ SiNCO	—	172.9/760	1.3922	20	1.015	20	(78, 79)	—
MeCOOCH ₂ SiMe ₂ NCO	—	51/12	1.4272	20	—	—	(34)	—
Me ₃ SiSiMe ₂ NCO	—	159.4–160/760	1.4337	30	0.8537	30	(186)	B, D, E, F
(OCNCH ₂ CH ₂ O) ₂ SiNCO	—	—	—	—	—	—	(66)	—
CyclohexylSiH ₂ NCO	—	163.7/760	1.4668	20	0.990	20	(23)	—
Me ₂ Si(NCO) ₂	–31.2	139.2/760	1.4221	20	1.076	20	(78, 79, 89, 174, 209)	B (89)
Et ₂ Si(NCO) ₂	—	176.7/760	1.4348	20	1.022	20	(9–11)	—
Bu ⁺ ₃ Si(NCO) ₂	—	96/3	1.4428	25	—	—	(194a)	—

TABLE III (Continued)

Compound	M.P. (°C)	B.P. (°C)/mm	n_D	°C	d_4	°C	Reference	Other properties ^a
Ph ₂ Si(NCO) ₂	22.9	319.6/760	1.5675	20	1.188	20	(78, 79, 194a)	—
F ₂ Si(NCO) ₂	-75	68.6/760	1.3536	20	1.437	20	(75)	—
Cl ₂ Si(NCO) ₂	-80	117.8/760	1.4380	25	1.437	25	(3)	—
(MeO) ₂ Si(NCO) ₂	—	152.1/760	1.4028	20	1.208	20	(72, 73)	—
(EtO) ₂ Si(NCO) ₂	—	175.4/760	1.4046	20	1.108	20	(78, 79, 194a)	—
MeSi(NCO) ₃	2.7	170.8/760	1.4430	20	1.267	20	(78, 79, 89)	B (89)
EtSi(NCO) ₃	—	183.5/760	1.4468	20	1.219	20	(9-11)	—
Pr ⁿ Si(NCO) ₃	—	192.2/760	1.4462	20	1.173	20	(11)	—
Pr ⁱ Si(NCO) ₃	—	192/760	1.4444	20	1.163	20	(11)	—
Bu ⁿ Si(NCO) ₃	—	215.5/760	1.4479	20	1.141	20	(78, 79)	—
FSi(NCO) ₃	-29.2	134.3/760	1.4161	20	1.456	20	(75)	—
ClSi(NCO) ₃	-35	152/760	1.4507	—	1.437	25	(3)	—
MeOSi(NCO) ₃	—	168.4/760	1.4287	20	1.313	20	(72, 73)	—
EtOSi(NCO) ₃	—	179.6/760	1.4251	20	1.236	20	(78, 79)	—
PhOSi(NCO) ₃	—	251.9/760	1.5210	20	1.273	20	(78, 79, 194a)	—
<i>n</i> -HeptylSi(NCO) ₃	—	258/760	1.4516	20	1.077	20	(26)	—
CyclohexylSi(NCO) ₃	—	253/760	1.4787	25	1.208	—	(23)	—
[(OCN) ₂ Si] ₂ O	—	—	—	—	—	—	(76, 89, 149)	B (89)
(Me ₂ Si) ₂ NSi(NCO) ₃	-2	81/1	1.4647	20	1.088	20	(192)	B
Si(NCO) ₄	26	185.6/760	1.4610	25	1.434	25	(71, 89, 136, 174, 194a, 179)	A (136), B (89, 136), H (89, 136)
H ₂ GeNCO	-44 ± 0.5	71.5/760 (extr.)	—	—	—	—	(171, 172)	B (172), E (171), F (171)
Me ₃ GeNCO	—	122/760	—	—	—	—	(180c)	B
Et ₃ GeNCO	—	200/760	1.454	20	—	—	(8, 15, 25)	—
Pr ⁿ ₃ GeNCO	-19	247/760	1.4574	20	1.055	20	(15)	—
Pr ⁱ ₃ GeNCO	—	—	—	—	—	—	(21)	—
Bu ⁿ ₃ GeNCO	—	283/760	1.4595	20	1.044	20	(17)	—

Cl_2GeNCO	—	112/760	—	—	—	—	(74)	—
$\text{Et}_2\text{Ge}(\text{NCO})_2$	—	226/760	1.4619	20	1.330	20	(8)	—
$\text{Pr}^i_4\text{Ge}(\text{NCO})_2$	—	239/760	1.464	20	1.225	20	(104)	—
$\text{Bu}^n_2\text{Ge}(\text{NCO})_2$	—	273/760	1.4634	20	1.179	20	(24)	—
$\text{EtGe}(\text{NCO})_3$	-31	225 4/760	1.4739	20	1.534	20	(8)	—
$[(\text{OCN})_2\text{Ge}]_2\text{O}$	—	—	—	—	—	—	(104)	—
$\text{Ge}(\text{NCO})_4$	-8	195-199/760	1.4793	25	1.7694	24	(8, 72, 116, 136)	A (136), B (136) D (72, 116), E (116), H (136)
Me_3SnNCO	105-107	—	—	—	—	—	(180c)	B
Et_3SnNCO	48	120-121/11	—	—	—	—	(28, 173a)	B (173a)
Et_3SnOCN	214	—	—	—	—	—	(20, 41, 146)	—
$\text{Bu}^n_3\text{SnNCO}$	—	144-7/13	1.490	20	—	—	(136a, 173a)	B (173a)
$\text{Bu}^i_3\text{SnNCO}$	—	103/0.3	1.489	21	—	—	(173a)	—
$\text{Me}_2\text{Sn}(\text{NCO})_2$	—	—	—	—	—	—	(82, 154)	—
$\text{Bu}^n_2\text{Sn}(\text{NCO})_2$	48-51	—	—	—	—	—	(136a)	—
Ph_3SnNCO	98-99	—	—	—	—	—	(136a, 173)	—
Me_3PbNCO	220 decomp.	—	—	—	—	—	(180c)	B
Et_3PbNCO	—	—	—	—	—	—	(95)	—

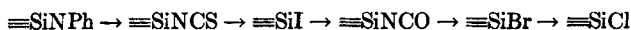
* See Table III for symbols used.

in a nonpolar solvent, but in the absence of solvent a good yield of isocyanatosilane resulted (38).

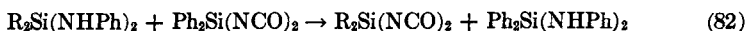
Triethyllead isocyanate has been prepared by refluxing triethyllead chloride and potassium cyanate in alcohol (95).

For boron compounds, the following "conversion" (Eq. 71) series has been proposed (115): $\text{>BBr} \rightarrow \text{>BS} \rightarrow \text{>BCN} \rightarrow \text{>BCl} \rightarrow \text{>BNCS} \rightarrow \text{>BNCO} \rightarrow \text{>BO—}$. Thus, in general, it was possible to convert a compound on the left to one further on the right by the use of either a silver or a mercury(II) salt. It should be noted, however, that the system 2>BNCS/HgO provided an anhydride, $\text{>B—O—B</>/Hg(NCS)}_2$, and not the isocyanate.

For triethylsilyl compounds, conversion (71) may be effected (14, 17, 27) in the following directions:

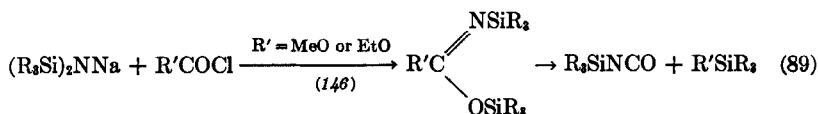


Examples of other such reactions are shown in Eqs. (82) (19), (83) (20), and (84) (25):



These reactions are not of especial value for the preparation of isocyanates, because the starting materials are usually synthesized from the halides, and these can be converted directly to the isocyanates by means of Eq. (70).

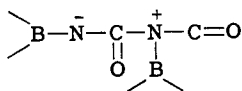
In addition to the general methods (Eqs. 68–71), isocyanatosilanes have been obtained by other routes, as illustrated in Eqs. (85–90). The urea procedure (analogous to Eq. 85) was unsuccessful in the boron field (115). For reaction (85), in the case of $\text{R}=\text{Me}$, $[\text{Me}_3\text{SiNHCONH}_3^+]\text{Cl}^-$



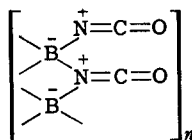
was proposed as an intermediate, while for reaction (90) the molecular rearrangement was believed to proceed by the intermediate $\text{MeCOOSiMe}_2\text{CH}_2^+\text{NCO}^-$. When the reagents of Eq. (88) were mixed in 1:1 stoichiometry, the product was the substituted urea. The reaction of urea with R_3SnOH or $(\text{R}_3\text{Sn})_2\text{O}$ in a molten state ($130\text{--}140^\circ\text{C}$) furnished R_3SnNCO ($\text{R} = \text{Et}$ or Bu^t) in high yields (173a). With R_3SnCl , the results were poorer and $(\text{Bu}^t_2\text{SnO})_n$ afforded $[\text{Bu}^t_2\text{SnOSn}(\text{NCO})_2]_n$. The distannoxanes and isocyanic acid at $70\text{--}80^\circ\text{C}$ gave R_3SnNCO ($\text{R} = \text{Et}$ or Bu^t and water which was removed and an azeotrope with benzene, cyanuric acid gave the complexes $(\text{R}_3\text{SnNCO})_3$. The urea reaction does not proceed through buret because adequate rate of reaction required more heating ($160\text{--}170^\circ\text{C}$).

B. STRUCTURES

The compounds prepared to date are clearly covalent. The problem of molecular association has been seriously encountered only with derivatives of 3-coordinate boron. Propensity for polymerization among these compounds appears to decrease as follows: (i) $\text{R}_2\text{BNCO} > \text{Ar}_2\text{BNCO} > (\text{R}_2\text{N})_2\text{BNCO} > (\text{RO})_2\text{BNCO}$, (ii) $\text{>BNCO} > \text{>BNCS}$, (iii) $\text{B}(\text{NCO})_3$ (only known as a polymer) $> \text{XB}(\text{NCO})_2 > \text{X}_2\text{BNCO}$, and (iv) acyclic $>$ cyclic (borazine) (113–115). These are largely qualitative observations, depending on the appearance after comparable times of solid precipitates from freshly prepared monomeric species. The relative tendencies toward polymerization (i–iv) would indicate that the greater the electron density at boron the greater is the stability of the monomer. Detailed information on the structures of the polymers is not available, except for infrared spectral data (87, 115). These show the presence of both —NCO and C=O functions. Cyclic and linear structures are possible (115), but only the latter are indicated in structures II and III. Evidence in favor of polymers



(II)



(III)

not directly involving boron (except in the side chains), as in structure II, is that (a) isocyanates of carbon, silicon, and phosphorus polymerize also (although less readily), (b) each of (i)–(iv) is explained, and (c) the spectral characteristics are appropriate. On the other hand, a point of contrast between boron and many other isocyanates is that the isocyanatoboranes do not depolymerize on heating. Infrared spectral data on Me_3SnNCO suggest a polymeric structure for the solid, since γ_{as} shifts to highest frequency in solution (180c).

The infrared spectra of Me_2BNCO (87), $(\text{MeO})_2\text{BNCO}$ (112, 114, 150), $(\text{HNBNC})_3$, $(\text{MeNBNC})_3$, $\text{Si}(\text{NCO})_4$ (136), $\text{Me}_{4-n}\text{Si}(\text{NCO})_n$ (89), $(\text{Me}_3\text{Si})_2\text{NSi}(\text{NCO})_3$ (192), $\text{Me}_3\text{SiSiMe}_2\text{NCO}$ (186), $\text{Ge}(\text{NCO})_4$ (136), and Me_3MNCO ($\text{M} = \text{Si, Ge, Sn, or Pb}$) (180c) have been recorded with full assignments of vibrational modes.

In isocyanatoboranes $\nu_{as}(\text{NCO})$ was found at $2273 \pm 30 \text{ cm}^{-1}$ and $\nu_{sym}(\text{NCO})$ at $1526 \pm 20 \text{ cm}^{-1}$ for a wide range of compounds (87, 112, 114, 150). The relatively high value for the latter mode, and calculations of force constants (86), have been taken as evidence for substantial BN π -bonding in $\text{B}-\text{NCO}$, while the intensities and band widths at half-height showed close correspondence with those found in organic isocyanates rather than cyanates (87, 112, 114, 150). The number of observed fundamental frequencies in Me_2BNCO agreed with that for a molecule having C_{2v} symmetry (87).

The infrared and Raman spectra of $\text{Si}(\text{NCO})_4$ and $\text{Ge}(\text{NCO})_4$ in the range $4000\text{--}80 \text{ cm}^{-1}$ are very simple, indicating that these molecules are highly symmetrical (89, 136). For the former, results are consistent with a tetrahedral model, while the spectrum of $\text{Ge}(\text{NCO})_4$ deviates slightly from that expected for a molecule belonging to the point group T_d .

The proton nuclear magnetic resonance spectrum of H_3SiNCO showed a line at lower field ($\sim 0.7 \text{ p.p.m.}$) than found in $\text{H}_3\text{SiC}\equiv\text{CH}$ and H_3SiCN , but similar to H_3SiNCS and $\text{H}_3\text{SiNCNSiH}_3$; this was taken as evidence

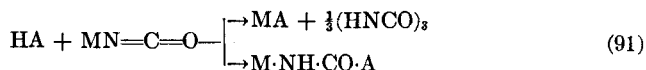
for the $\begin{array}{c} \diagup \\ \text{—Si—N=C=O} \\ \diagdown \end{array}$ rather than the cyanato structure (58).

The molecular structure of Me_3SiNCO in the gaseous state has been determined by electron diffraction (106b): $r_g(\text{C—H}) = 1.10 \pm 0.02$, $r_g(\text{C=O}) = 1.18 \pm 0.01$, $r_g(\text{N=C}) = 1.20 \pm 0.01$, $r_g(\text{Si—N}) = 1.76 \pm 0.02$, $r_g(\text{C—Si}) = 1.89 \pm 0.01\text{\AA}$, and $\angle(\text{Si—N—C}) = 150 \pm 3^\circ$. It is interesting to note the substantial deviations from linearity.

C. PROPERTIES

The isocyanates of Groups IIIB and IVB vary in stability from the unstable dimethylisocyanatoborane, which polymerizes rapidly at 20° , through isocyanatogermane, stable at room temperature but decomposing at $50^\circ\text{--}200^\circ$ into polymeric hydrides and hydroacids [${}_n\text{H}_3\text{GeNCO} \rightarrow (\text{GeH}_2)_n + {}_n\text{HNCO}$], to triphenylisocyanatosilane which can be distilled at 372° without decomposition.

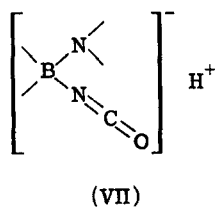
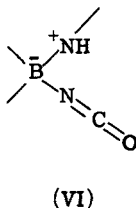
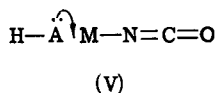
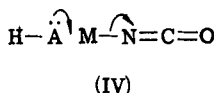
Reactions of isocyanates with protic reagents HA have been discussed (113). These are of interest primarily to determine whether there is a prevalence of substitution (pseudohalide behavior) or addition (functional group behavior) for a given class of compounds. This may be illustrated by Eq. (91):



Under $\text{S}_{\text{N}}1$ conditions, when $\text{M}-\text{N}$ heterolysis is rate-determining, substitution will of necessity prevail; but under bimolecular conditions, product control is determined by competition between the two electrophilic sites, the central carbon atom (see Eq. 92) and M :

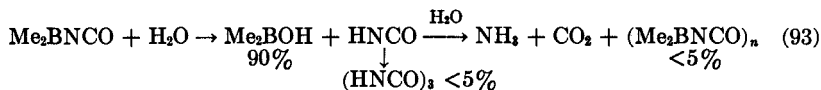


The nature of the transition state in the latter case depends on M , but it may in general require initial formation of a complex (as in structure V), or it may involve synchronous bond-making and bond-breaking (as in structure IV). The former is the relevant mechanism in the case of a trigonal



boron pseudohalide, and the complex with a primary or secondary amine as the reagent may be pictured as in structure VI or VII. The competition between the boron atom and the carbon atom for the attacking nucleophile is affected also by the nature of the attacking reagent. This is so, because substitution at trigonal boron depends on both basicity and steric factors, whereas attack at digonal carbon is likely to be controlled largely by a combination of basicity and polarizability of the nucleophile [a simple illustration is the relative reactivity, generally $\text{H}_2\text{O} > \text{NH}_3 > \text{R}\cdot\text{NH}_2 > \text{R}_2\text{NH}$ for trigonal boron compounds, but $\text{NH}_3 > \text{H}_2\text{O}$ for carbonyl carbon (in *p*-nitrophenyl acetate)].

In order to have effective competition for the substitution, steric hindrance both in the substrate and in the reagent is helpful. From the electronic aspect, either M should not have available vacant low-energy orbitals, or the reorganization energy for change in hybridization should be high. This analysis appears to explain satisfactorily the results not only for the boron pseudohalides, but also for derivatives of other elements (as summarized in the tabulation, together with data on related isothio-



BEHAVIOR OF SOME COMMON ISOCYANATES AND ISOTHIOCYANATES WITH ALCOHOLS
AND AMINES:

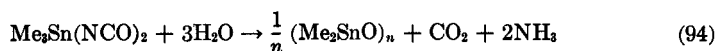
Class	With ROH	With R·NH ₂	Reference
>B·NCO	>B·OR	>B·NHR	(87, 115)
—			
>B·NCO	>B·OR	>B·NH·CO·NHR	(114, 150)
(R'·N·B·NCO) ₃	>B·OR	(R'·N·B·NH·CO·NHR) ₃	(113)
(R'·N·B·NCS) ₃	>B·OR	(R'·N·B·NHR) ₃	(113)
>C·NCO	>C·NH·CO ₂ R	>C·NH·CO·NHR	(28a)
>C·NCS	>C·NH·CS·OR	>C·NH·CS·NHR	(106a)
>Si·NCO	>Si·OR	>Si·NH·CO·NHR	(88, 90)
>Ge·NCO	>Ge·OR	—	(8)
>PO·NCO	>PO·NH·CO ₂ R	>PO·NH·CO·NHR	(106c, 165a)
>PO·NCS	>PO·NH·CS·OR	>PO·NH·CS·NHR	(62a)
[PN(NCS) ₂] _{3,4}	(addition)	(addition)	(180a)
SVI·NCO	SVI·NH·CO ₂ R	SVI·NH·CO·NHR	(28b)

cyanates). The lower additive reactivity of isothiocyanates than of isocyanates is attributed to the low polarity of the thiocarbonyl compared with the carbonyl bond (113).

Dimethylisocyanatoborane reacted readily (Eq. 93) with water, affording dimethylhydroxyborane, ammonia, carbon dioxide, cyanuric acid, and a polymeric boron compound (87). Likewise, hydrolysis of triisocyanatoborane gave boric acid, ammonium sulfate, and carbon dioxide whence the normal cyanate structure was inferred (71); this is clearly inappropriate, as the isocyanate would give the same products.

Silicon isocyanates are readily hydrolyzed to silanols. Some, such as triphenyl- or triethyl-isocyanatosilane, are relatively stable to water, but this stability is associated with their insolubility; thus hydrolysis is rapid when carried out in the presence of acetone or alcohol (57, 77, 81). Tendency for hydrolysis decreased in the series $\text{MeSi}(\text{NCO})_3 > \text{Me}_2\text{Si}(\text{NCO})_2 > \text{Me}_3\text{SiNCO}$, and this effect is also probably associated with a progressive decrease in the solubility of these isocyanates in water (79). For germanium compounds, a similar effect was observed $[\text{Ge}(\text{NCO})_4 > \text{EtGe}(\text{NCO})_3 > \text{Et}_2\text{Ge}(\text{NCO})_2 > \text{Et}_3\text{GeNCO}]$ (8).

Dimethyltin diisocyanate was hydrolyzed according to Eq. (94). The diisocyanates of tin appear to be particularly sensitive to moisture, and hydrolysis products of types $\text{Bu}^n_3\text{Sn}_4(\text{NCO})_4\text{O}_2$, $\text{Bu}^n_3\text{Sn}_4(\text{NCO})_2(\text{OH})_2\text{O}_2$, and $\text{Ph}_4\text{Sn}_2(\text{NCO})_2(\text{OH})_2$ have been isolated (136a).



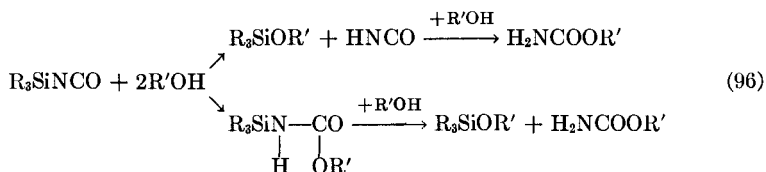
Alcoholysis of the isocyanates of boron (87), silicon (34, 90), and germanium (8) proceeds readily, to afford corresponding alkoxy derivatives and substituted carbamates.

This was demonstrated for Me_2BNCO (a small yield of $(\text{Me}_2\text{BNCO})_n$ was also obtained) (87), as well as for numerous other 3-coordinate mono- (115) and poly- (borazine derivatives) (113) nuclear boranes, and also for 4-coordinate species, such as $\text{py} \cdot \text{B}(\text{NCO})_3$ (114, 150).

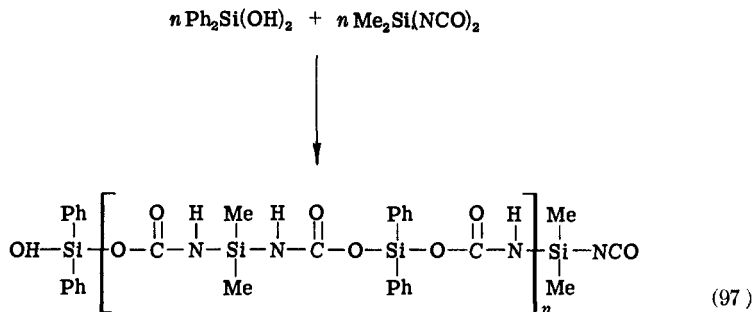
The ethylisocyanatogermanes reacted quantitatively with ethanol and butanol according to Eq. (95):



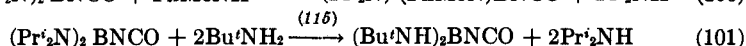
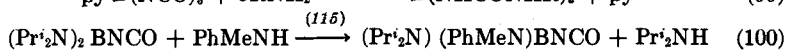
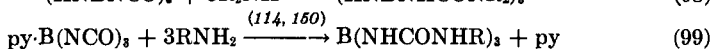
The silicon isocyanates needed more forcing conditions. Thus, unreacted trimethylisocyanatosilane ($\sim 20\%$) was recovered from the reaction with excess ethanol after 3 hours at room temperature, although quantitative yields of both trimethylmethoxysilane and methyl carbamate were obtained when the reaction was carried out at a higher temperature (90). Change of alcohol, solvent, temperature, concentration, and molar ratios produced qualitatively the same results, i.e., no silicon urethanes were obtained. Reaction sequence (96) was postulated (90). With higher or more highly branched alcohols (*n*-amyl, *i*-propyl, and *t*-butyl) or phenol, reaction rates decreased. For example, after 2 hours at 70° significant proportions of starting materials may be recovered. Likewise, structural changes in the silicon substrates have similar implications; e.g., triphenylisocyanatosilane was unaffected by ethanol in boiling benzene (81).



A contrasting report is provided by a patent, in which the formation of poly(silicourethanes) is claimed, prepared according to Eq. (97) (209):



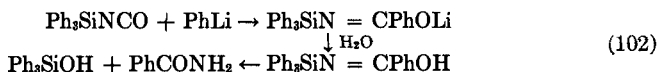
The reactions of isocyanatoboranes and amines have been investigated in some detail (87, 112-115, 150). In general, addition or substitution behavior may be found depending on variations in electronic and steric factors, in accordance with the general principles outlined above for MNCO/HA systems. Representative examples are shown in Eqs. (98-101). 4-Coordinate species did not invariably yield ureidoboranes. Thus, the pyridine complexes of $\text{PhB}(\text{NCO})_2$ or Ph_2BNCO both gave the substitution products, $\text{PhB}(\text{NHR})_2$ and Ph_2BNHR .



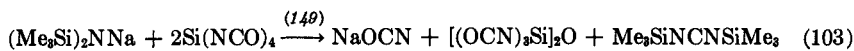
Silicon isocyanates appear invariably to give silicoureas (88).

The order of reactivity for various amines and isocyanato-borazines (113) or -silanes (88) was similar to that observed for organic isocyanates, i.e., $\text{RNH}_2 > \text{R}_2\text{NH} > \text{ArNH}_2 \gg \text{ArNHR}$.

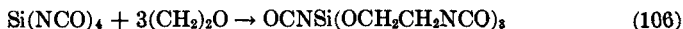
Phenyllithium or phenylmagnesium bromide and triphenylisocyanatosilane gave, after hydrolysis, triphenylhydroxysilane and benzamide, according to Eq. (102) (81); the silicon derivative thus behaved in an analogous fashion to phenyl isocyanate. Attempts to make methylisocyanatosilanes from tetraisocyanatosilane and Grignard reagents failed (79), and likewise there was no reaction between triethylisocyanatosilane and methylmagnesium iodide (57).



Isocyanatosilanes have provided routes to silylcarbodiimides, as shown in Eqs. (103-105):

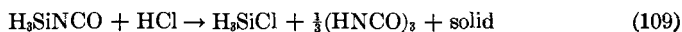
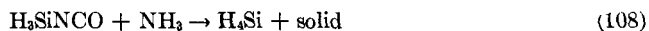
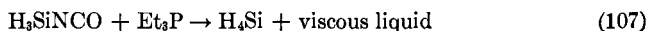


Ethylene oxide was cleaved by reaction with $\text{Si}(\text{NCO})_4$, as shown in Eq. (106) (66):

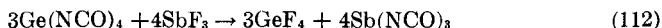


The behavior of H_3SiNCO with various acids and bases, under mild conditions, has been examined, as summarized in Eqs. (107-111) (60).

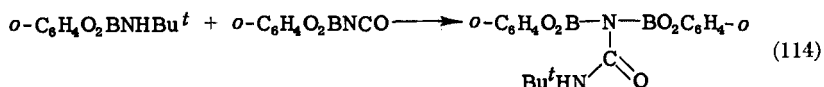
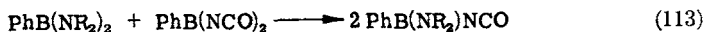
There was no reaction with diborane or phosphine; sodium hydroxide afforded various decomposition products, and with sulfuric acid carbon dioxide was evolved.



Tetraisocyanatogermane reacted with antimony(III) fluoride according to Eq. (112), but the GeF_4 was isolated as a constant boiling mixture with Ge(NCO)_4 (10, 76):



A further reaction in which the isocyanate group behaves as a pseudohalide is exemplified by Eq. (113) (97, 114); on the other hand, an addition reaction has been observed in a related system (Eq. 114) (47a):



Pyrolysis of $o\text{-C}_6\text{H}_4\text{O}_2\text{BNCO}$ (114) or Ph_2BNCO (98b) did not lead to elimination of carbon dioxide and carbodiimide formation, even in the presence of 3-methyl-1-phenylphospholene (98b), and this is a further point of contrast with organic isocyanates. Ethanethiol did not react with isocyanatoboranes (113).

The acceptor properties of 3-coordinate isocyanatoboranes toward ligands such as ethyl acetate or pyridine, relative to related compounds, are $\text{>BBr} > \text{>BCl} > \text{>BNCS} > \text{>BNCO} > \text{>BF}$, as determined by thermochemical (heats of complex formation) and infrared spectral measurements (114, 150).

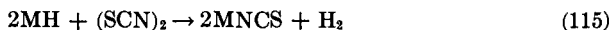
V. Isothiocyanates

A. PREPARATION

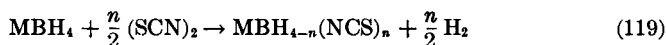
Physical properties such as molecular refractions, boiling points, and infrared, Raman, and microwave spectra indicate that the organometallic thiocyanates of Group IIIB and IVB elements have the iso ($\text{M}-\text{N}=\text{C}=\text{S}$) structure. These compounds are therefore named isothiocyanates, even

when reference is made to publications in which the normal ($M-S-C\equiv N$) structure was originally postulated. (See Table IV.)

Four general types of reaction (Eqs. 115–118) are available for the preparation of isothiocyanates of Groups IIIB and IVB:



Scheme (115) is illustrated by Eq. (119) ($M=Li$ or Na), using tetrahydrofuran or ether at somewhat below room temperature (107, 108):



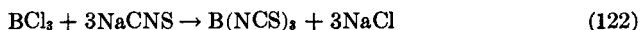
With sodium borohydride the number of hydrogens displaced by $-NCS$ groups never exceeds three. Lithium tetraisothiocyanatoborate was not isolated, owing to its instability, but from the ether solution an insoluble complex, $[LiB(NCS)_4 \cdot 2C_4H_8O_2]$, could be precipitated. Lithium aluminum hydride and thiocyanogen in ether behaved similarly, to afford a solvated complex of $LiAl(NCS)_4$, which decomposed at $\sim 50^\circ$ (108).

Modifications of scheme (115) are shown in Eqs. (120) and (121) (1):

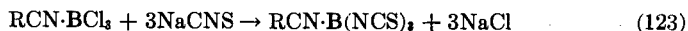


Apart from $B(NCS)_3$, the first isothiocyanatoboranes to be prepared were obtained by route (116), from halo- (Cl, Br) boranes and Ag, Na, or Pb salts of thiocyanic acid (112–115, 150). With the silver salts high yields were realized by using nonpolar solvents such as benzene, but with sodium or lead thiocyanates it was necessary to use a polar medium.

The preparation of triisothiocyanatoborane, originally reported (46) in 1906, was carried out according to route (116), from tribromoborane and silver thiocyanate in benzene solution. The product was described as an unstable crystalline solid. However, more recently triisothiocyanatoborane was obtained as a distillable liquid (38%, according to Eq. 122), from trichloroborane and potassium or sodium thiocyanate, in sulfur dioxide at -30° (170):

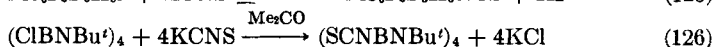
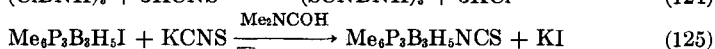


Using similar reaction conditions, a number of 4-coordinate isothiocyanatoboranes have been synthesized, as shown in Eq. (123) ($R = CH_3$, C_6H_5 , or $C_6H_5CH_2$) (170):

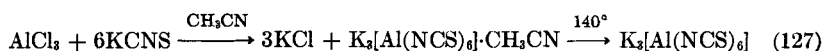


These isothiocyanatoboranes were also obtained by the addition of the nitriles to triisothiocyanatoborane, and analogous procedures afforded pyridine- and triethylamine-triisothiocyanatoboranes. The latter compounds could not be prepared from the appropriate BCl_3 complexes, as these failed to react with sodium thiocyanate, using sulfur dioxide as solvent at -30° . On the other hand, $\text{py} \cdot \text{BCl}_3$ (unlike $\text{Me}_3\text{N} \cdot \text{BCl}_3$) and AgNCS in benzene gave the $\text{Base} \cdot \text{B}(\text{NCS})_3$ product (114, 150).

B-Triisothiocyanatoborazine (40, 93), *P*-hexamethyl-*B*-isothiocyanatoborophane (191), and tetra-*B*-isothiocyanatotetra-*N*-*t*-butylborazocine $(\text{Bu}^t\text{NBNCs})_4$ (184, 185a) have been synthesized [see Eqs. (124–126)]:



2-Isothiocyanato-1,3,2-dioxaborinane $[(\text{CH}_2)_3\text{O}_2\text{BNCS}]$ (68), 2-isothiocyanato-1,3,2-dioxaborolane $[(\text{CH}_2)_2\text{O}_2\text{BNCS}]$ (69), and butoxyisothiocyanatophenylborane $[\text{PhB}(\text{OBu}^n)\text{NCS}]$ (122) were obtained from the interaction of silver thiocyanate and the corresponding chlorides. A hexaiso-thiocyanatoaluminate has been made by the procedure of Eq. (127) (158):

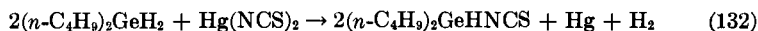
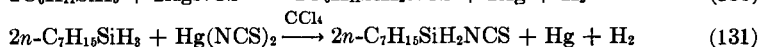


The only other isothiocyanates of Group IIIB elements at present known are diethylisothiocyanatothallium (Eq. 128) (84), diisothiocyanatophenylthallium (Eq. 129) (44), and indium(III) isothiocyanate (obtained from $\text{Ba}(\text{CNS})_2/\text{In}_2(\text{SO}_4)_3$ in aqueous solution and removal of the insoluble BaSO_4) (141a).

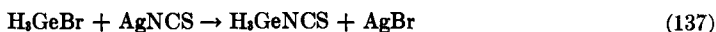
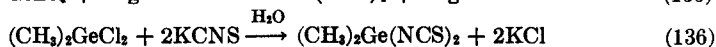
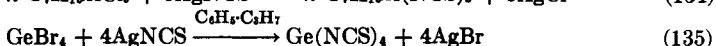
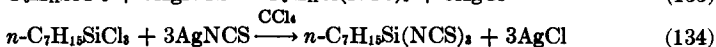


For the preparation of silicon and germanium isothiocyanates, all four general methods have been used extensively.

Interaction of cyclohexyl- (23) or *n*-heptyl- (26) silane, or di-*n*-butylgermane (24) and silver or mercury thiocyanate, in the presence of solvent, gave the corresponding isothiocyanates, as shown in Eqs. (130–132); from the second and third reactions, isothiocyanic acid, a mixture of organo-silanes and germanes, and some starting materials were also isolated:



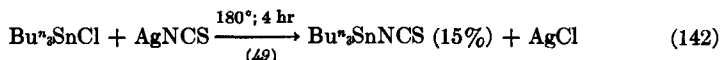
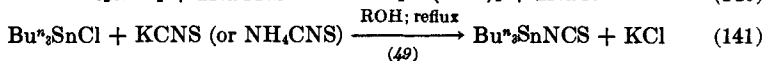
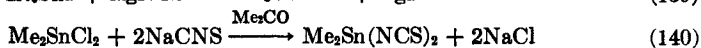
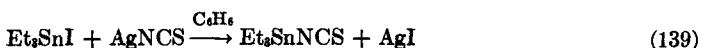
Treatment of organogermanium or organosilicon halides (Cl, Br, or I), with a variety of salts of thiocyanic acid in the vapor phase, or in solvents such as benzene, carbon tetrachloride, hexane, acetonitrile, nitromethane, or water, resulted in high yields of germanium or silicon isothiocyanates (15, 23, 26, 134, 152, 153, 171). Examples are shown in Eqs. (133–137):



A vapor phase reaction, passing silyl iodide over silver thiocyanate, has been used for the preparation of silyl isothiocyanate (130). Fused alkali metal salts have been employed as reaction media, as shown in Eq. (138) (179):

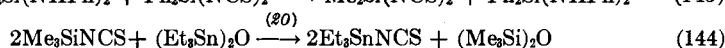


The interaction of organotin halides and metal thiocyanates has provided routes to tin derivatives, under the conditions of Eqs. (139–142). Triphenyllead isothiocyanate has similarly been obtained from $\text{Ph}_3\text{PbI}/\text{AgNCS}$ (173) or $\text{Ph}_3\text{PbCl}/\text{KCNS}/\text{EtOH}$ (63), and triethyllead isothiocyanate from $\text{Et}_3\text{PbCl}/\text{KCNS}/\text{EtOH}$ (95).



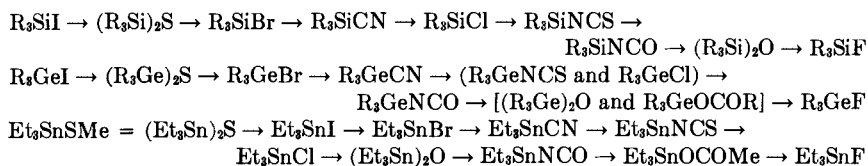
For the preparation according to Eq. (140), liquid sulfur dioxide or acetonitrile has been suggested as a more suitable solvent, as they are less reactive than acetone toward the chlorides used as starting materials (93). These media dissolve appreciable amounts of ammonium and potassium thiocyanates, while the chlorides are only sparingly soluble.

Organic derivatives of silicon, germanium, and tin often interchange isothiocyanate, isocyanate, halogen, and other groups at the boiling point of the mixture, when the most volatile component can be distilled out as it forms. For the triethylsilyl compounds, conversion may be affected in the following direction (14, 17, 27) (for example, as shown in Eqs. 143, 144), $\equiv\text{SiNHPh} \rightarrow \equiv\text{SiNCS} \rightarrow \equiv\text{SiI} \rightarrow \equiv\text{SiNCO} \rightarrow \equiv\text{SiBr} \rightarrow \equiv\text{SiCl}$.

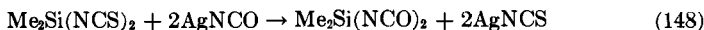
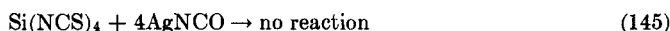


However, these reactions are not of great value for the synthesis of isothiocyanates, since the starting materials are usually prepared from the halides, and these may be converted directly to the isothiocyanates by use of metal salts.

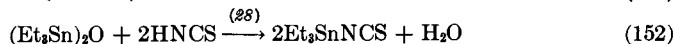
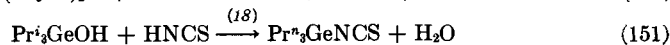
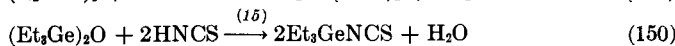
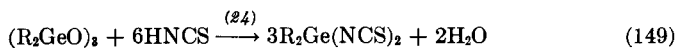
"Conversion series" for boron (115), silicon (25, 57), germanium (15, 25, 171), and tin (28) have been proposed. Using dry silver salts, with or without an inert solvent such as benzene, carbon tetrachloride, or toluene, any compound on the left may be converted to one on the right within a series. For silicon, germanium, and tin these "conversion series" are (for boron, see Section IV):



Anomalies have been noted, and sometimes are ascribed to steric factors (10). Examples are shown in Eqs. (145–148):



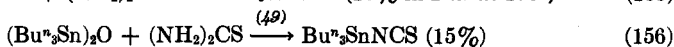
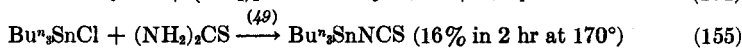
Thiocyanic acid has been shown to react readily with organometallic oxides or hydroxides, to give isothiocyanates in high yields. Examples are shown in Eqs. (149–152):



Trimethyl- and triphenyl-cyanosilanes (133), dimethylphenylcyano-silane (125), trimethylcyano-germane and -stannane (162), and tri-*n*-butylcyanostannane (49) added sulfur readily, to afford the corresponding isothiocyanates, as shown in Eq. (153) (see also Section III):



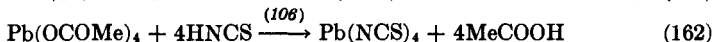
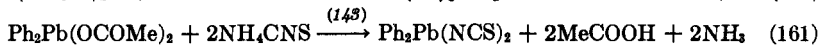
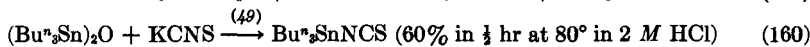
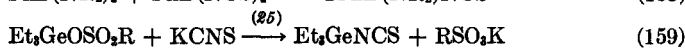
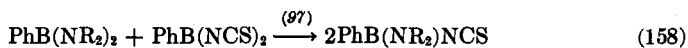
Thiourea has proved a possible starting material for isothiocyanates, as shown in Eqs. (154–156):



Silyl isothiocyanate was obtained from the interaction of disilylcyanamide and silver thiocyanate, as shown in Eq. (157) (59):



Miscellaneous methods for preparing isothiocyanates are illustrated in Eqs. (158–162). There was no reaction between isocyanatoboranes with either mercury(II) or phosphorus(V) sulfide (115):



B. STRUCTURES

Isothiocyanatoboranes are monomeric in benzene solutions and, unlike corresponding >BNCO derivatives (see Section IV), show little tendency for polymerization (112–115, 150). On the other hand, the difference in boiling point between the isothiocyanatoboranes and corresponding chloroboranes ($\sim 100^\circ$ at 760 mm, per group) is far greater than between the isothiocyanates and chlorides of silicon or phosphorus ($\sim 65^\circ$ at 760 mm per group) (115). This must be due to enhanced molecular association for the boron compounds, probably due to increased polarization of the —N=C=S group, as a result of conjugation with boron.

The molar refractivities of isothiocyanatoboranes, obtained from refractive indices and liquid densities, agree well with values calculated on a >B—N=C=S model, but not with $\text{>B—S—C}\equiv\text{N}$ (115). A detailed comparison of the electronic (NCS chromophore) and infrared spectra of isothiocyanatoboranes with those of organic thiocyanates and isothiocyanates points also to the >B—N=C=S structure (112, 114, 150). The preference for the former may be related to B—N π -bonding (114, 150).

The infrared spectra of many isothiocyanato-boranes (69, 93, 107, 112, 114, 150, 170), -silanes (40b, 62, 92, 93, 169), -germanes (172), and -stannanes (93) have been recorded, and full assignments for some compounds proposed [e.g., the series Me_3MNCS ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{or Pb}$) (180c)].

All the spectra showed strong absorption in the regions 2080–1940 cm^{-1} and 1070–920 cm^{-1} , and these bands are associated with the asymmetrical and symmetrical stretching vibration of the $-\text{N}=\text{C}=\text{S}$ group. In

>BNCS derivatives these fall within the narrower ranges of 2089 ± 31 and 995 ± 30 cm^{-1} (112, 114, 150). Vibrational spectra for $\text{Si}(\text{NCS})_4$ indicate T_d symmetry with linearity of the $\text{Si}-\text{N}=\text{C}=\text{S}$ chain (40b).

Linearity of the $\text{>Si}-\text{N}=\text{C}=\text{S}$ chain was established in isothiocyanatosilane, from microwave (101, 102) and infrared (62) spectra. From the microwave spectrum, C_{3v} symmetry of the molecule was deduced and the following structural parameters were determined:

$$\begin{aligned}\text{Si}-\text{N} &= 1.714 \pm 0.010 \text{ \AA} \\ \text{N}-\text{C} &= 1.211 \pm 0.010 \text{ \AA} \\ \text{Si}-\text{H} &= 1.489 \pm 0.010 \text{ \AA} \\ \text{H}-\text{Si}-\text{H} &= 111^\circ 22' \pm 10' \\ \text{C}-\text{S} &= 1.560 \text{ \AA (assumed)}\end{aligned}$$

On the other hand, an electron-diffraction study of Me_3SiNCS shows a substantial deviation from linearity (106b); the molecular parameters are: $r_g(\text{C}-\text{H}) = 1.09 \pm 0.02$, $r_g(\text{C}-\text{S}) = 1.56 \pm 0.01$, $r_g(\text{N}-\text{C}) = 1.18 \pm 0.01$, $r_g(\text{Si}-\text{N}) = 1.78 \pm 0.02$, $r_g(\text{C}-\text{Si}) = 1.87 \pm 0.01 \text{ \AA}$, and $\angle(\text{Si}-\text{N}-\text{C}) = 154 \pm 2^\circ$.

The linearity of the $\equiv\text{SiNCS}$ skeleton in H_3SiNCS may be a consequence of $p_\pi-d_\pi$ bonding. Consequently, a short $\text{Si}-\text{N}$ bond distance is to be expected, and the value of 1.714 \AA is significantly lower than the calculated value of 1.87 \AA obtained by adding Pauling single-bond radii. The $\text{N}-\text{C}$ bond distance of 1.211 \AA is very similar to that found in HNCS (54) and CH_3NCS (30).

The C_{3v} symmetry of silyl isothiocyanate has been confirmed by a study of infrared and Raman spectra of this compound and its deuterated analog (62). Similar spectroscopic work on derivatives of silicon (58, 70) and tin (49) likewise points to the iso structure. The proton resonance in H_3SiNCS was very close to that for H_3SiNCO and $\text{H}_3\text{SiNCNSiH}_3$, but about 0.7 p.p.m. to lower field from the H_3Si resonance found in H_3SiCN and $\text{H}_3\text{SiC}\equiv\text{CH}$. This offers independent support for $\text{Si}-\text{N}$ bonding (58).

Further evidence for the iso structure ($\text{M}-\text{N}=\text{C}=\text{S}$) in the isothiocyanatosilanes is obtained from molecular refractions and boiling points (7, 9, 76).

C. PROPERTIES

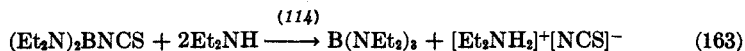
The isothiocyanates of Groups IIIB and IVB vary in stability from the unstable (at 0°) isothiocyanatomethylsilane (MeH_2SiNCS) (111), through isothiocyanatogermane, stable at room temperature but decomposing completely when heated for 20 hours at 50° into germanes and thiocyanic acid [$n\text{H}_2\text{GeNCS} \rightarrow (\text{GeH}_2)_n + n\text{HNCS}$] (171), to methyltriisothiocyanatosilane, which can be distilled at 267° with no decomposition (190). The presence of M—H bonds in either silicon or germanium isothiocyanates reduces the stability of these compounds. Tri-*n*-butylisothiocyanatostannane withstood prolonged heating *in vacuo* at 180° (49). Tetraisothiocyanatolead readily disproportionates to produce thiocyanogen and lead(II) isothiocyanate (106).

From reaction of boron isothiocyanate and aniline a solid, containing no boron, was isolated (46), which on treatment with boiling water was converted to phenylthiocarbamide. It was therefore concluded that the original compound had the thiocyanate structure. However, the evidence is ambiguous, as $\text{B}(\text{NCS})_3$ would also be expected to yield $\text{B}(\text{NHPh})_3$.

Triisothiocyanatoborane and nitriles or tertiary amines formed 1:1 complexes at low temperature (170). The acceptor properties ($\text{BBr} > \text{BCl} > \text{BNCS} > \text{BNCO} > \text{BF}_3$) of related boranes toward EtOAc and $\text{C}_5\text{H}_5\text{N}$ have been examined (114, 150). Pyridine, quinoline, and isoquinoline formed 2:1 complexes with $\text{Si}(\text{NCS})_4$ (159, 160); from conductivity and infrared spectral data these were formulated as $[\text{Si}(\text{NCS})_2(\text{Base})_2](\text{SCN})_2$. $\text{Bu}_3\text{Sn}(\text{NCS})_2$ formed a 1:1 complex with 2,2'-dipyridyl (2), and similar complexes of the methyl, ethyl, and *n*-propyl homologs have been prepared (190a). The anions $[\text{MeSn}(\text{NCS})_5]^{2-}$, $[\text{Me}_2\text{Sn}(\text{NCS})_4]^{2-}$, and $[\text{Me}_3\text{Sn}(\text{NCS})_3]^-$ are known (41a).

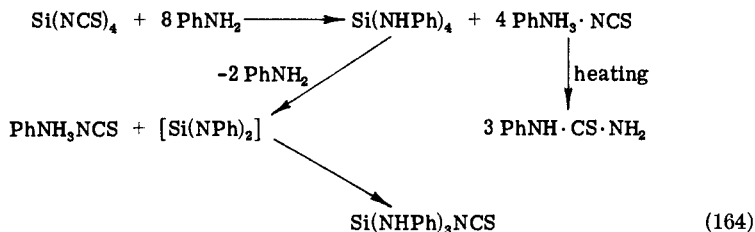
Silicon isothiocyanates are readily hydrolyzed to silanols, and the case of hydrolysis is dependent upon the nature of other substituents and the number of isothiocyanate groups directly attached to silicon (57, 133).

The reactions of isothiocyanatoboranes with alcohols or amines invariably lead to substitution products (see also Section IV) (e.g., Eq. 163) (113–115, 150):

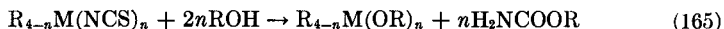


Tetraisothiocyanatosilane and aniline, when kept for 10 days at room temperature, gave tetraanilinosilane and anilinium thiocyanate, which on heating gave *N*-phenylthiourea. The anilinosilane lost two molecules of

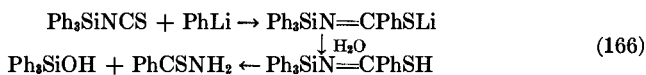
aniline, to give a diimide, which added one molecule of aniline thiocyanate (152). These reactions are illustrated in scheme (164).



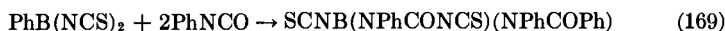
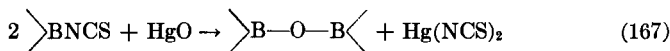
Isothiocyanatosilanes and isothiocyanatogermanes reacted with alcohols according to Eq. (165) (9, 133):



Phenyllithium with triphenylisothiocyanatosilane gave, after hydrolysis, triphenylsilanol and thiobenzamide; tetraphenylsilane was also isolated (81). The reaction sequence (166) was proposed:



Isothiocyanatoboranes reacted with mercury(II) oxide according to Eq. (167) (114, 150), and with organic isocyanates to give addition products (Eqs. 168–170) (100b). In the addition reactions they resemble chloroboranes (111a), and it is interesting that $\text{Ph} > \text{NCS}$ is migratory aptitude.



Diisothiocyanatophenylthallium, when refluxed in water, gave isothiocyanatobenzene, and, with potassium iodide, iodobenzene (44).

Various other reactions of isothiocyanates of silicon are illustrated in Eqs. (171–175):

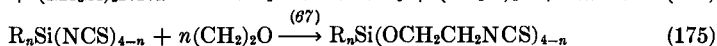
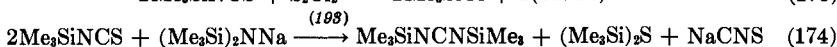
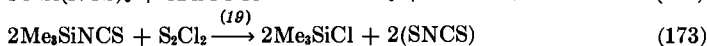
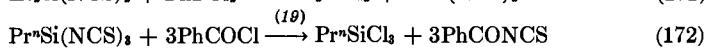
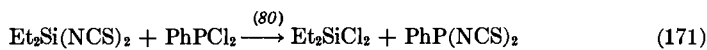


TABLE IV
 DATA ON ISOTHIOCYANATES*

Compound	M.P. (°C)	B.P. (°C)/mm	n_D	°C	d_4	°C	Reference	Other properties ^a
B(NCS) ₃	—	92/0.1	—	—	—	—	(46, 170)	B (170)
(CH ₂) ₂ O ₂ BNCS	—	—	—	—	—	—	(69)	B
(CH ₂) ₂ O ₂ BNCS	—	58–60/0.01	—	—	—	—	(68, 69)	B (69)
PhB(OBu ^o)NCS	—	94–100/0.6	—	—	—	—	(122)	B
PhB(NMe ₂)NCS	—	—	—	—	—	—	(114)	B, C
PhB(NR ₂)NCS	—	—	—	—	—	—	(97)	—
(Bu ^o O) ₂ BNCS	—	64.5–65/0.25	1.4449	20	0.9488	20	(112, 115, 150)	A (112), B (150)
(Me ₂ N) ₂ BNCS	—	50/0.4	1.5231	20	0.9941	20	(112, 115, 150)	B (150)
(Et ₂ N) ₂ BNCS	—	65/0.1	1.5032	20	0.943	20	(115, 150)	B (150)
<i>o</i> -C ₆ H ₄ O ₂ BNCS	—	84/0.7	1.6048	20	1.2814	20	(112, 115, 150)	A (112), B (150)
Ph ₂ BNCS	—	114–116/0.02	1.6714	20	1.119	20	(115, 150)	B (150)
(HNBNCs) ₃	154	—	—	—	—	—	(40, 93, 112, 113, 150)	A (112), B (93, 150)
(MeNBNCs) ₃	202–204	—	—	—	—	—	(113, 150)	A (150), B (150)
(EtNBNCs) ₃	87–88	130/0.01	—	—	—	—	(113, 150)	A (150), B (150)
(Pr ⁿ NBNCs) ₃	121	—	—	—	—	—	(113, 150)	B (150)
(Bu ⁿ NBNCs) ₃	54	—	—	—	—	—	(113, 150)	B (150)
(PhNBNCs) ₃	212–214	—	—	—	—	—	(113, 150)	B (150)
(Bu ⁿ NBNCs) ₄	291–295 (decomp.)	—	—	—	—	—	(184, 185, 185a)	B (184, 185a)
Me ₃ P ₂ B ₃ H ₃ (NCS) ₃	63–64	—	—	—	—	—	(191)	B
B(NCS) ₃ ·C ₃ H ₅ N	118–120	—	—	—	—	—	(170)	B
B(NCS) ₃ ·Et ₃ N	102–104	—	—	—	—	—	(170)	B
B(NCS) ₃ ·CH ₃ CN	137 (decomp.)	—	—	—	—	—	(170)	B
B(NCS) ₃ ·PhCN	105 (decomp.)	—	—	—	—	—	(170)	B
B(NCS) ₃ ·PhCH ₂ CN	95–96 (decomp.)	—	—	—	—	—	(170)	B
PhB(NCS) ₂ ·C ₃ H ₅ N	153–155	—	—	—	—	—	(150)	B

PhB(NCS) ₂ ·EtOAc	46-48	—	—	—	—	—	(150)	B
BrB(NCS) ₂	—	80/0.15	—	—	1.3721	20	(112, 115, 150)	B (150)
Br ₂ BNCS	—	40/5	—	—	—	—	(100a)	B
NaBH(NCS) ₃	—	—	—	—	—	—	(107, 108)	B (107, 108)
K ₃ [Al(SCN) ₆]	—	—	—	—	—	—	(158)	—
In(NCS) ₃	—	—	—	—	—	—	(141a)	—
Me ₂ TlNCS	—	—	—	—	—	—	(94b)	C
Et ₂ TlNCS	—	—	—	—	—	—	(84, 94b)	C (94b)
PhTl(NCS) ₂	—	—	—	—	—	—	(44)	—
H ₃ SiNCS	-51.8	84/760	—	—	—	—	(58, 59, 62, 70, 101, 102, 126)	B (62, 70), C (58), G (102), H (62)
D ₃ SiNCS	—	—	—	—	—	—	(62)	B, H
MeSiH ₂ NCS	—	—	—	—	—	—	(111)	—
Me ₃ SiNCS	-32.8	143.1/760	1.4820	20	0.931	20	(51, 70, 76, 89, 92, 93, 106b, 169, 179, 180c, 190)	B (70, 89, 93, 169, 180c), I (106b)
Et ₃ SiNCS	—	210.5/760	1.4944	20	0.934	20	(9, 70, 190)	B (70)
Pr ⁿ ₃ SiNCS	—	—	—	—	—	—	(70)	B
PhMe ₂ SiNCS	—	252-254/760	1.5556	30	1.0384	30	(128)	—
<i>n</i> -HeptylSiH ₂ NCS	—	235/760 (decomp.); 75-77/1	1.4939	20	0.921	20	(26)	—
CyclohexylSiH ₂ NCS	—	231/760; 91-91.8/1	1.5336	20	1.018	20	(23)	—
Ph ₃ SiNCS	76 ± 1	396/760	—	—	—	—	(7, 70, 81)	B (70)
Me ₃ SiHNCS	—	—	—	—	—	—	(102)	—
Cl ₃ SiNCS	-75	129.5/760	1.5091	20	1.461	24	(4, 92)	—
(MeO) ₃ SiNCS	—	170.5/760	1.4426	20	1.134	20	(5)	—
(EtO) ₃ SiNCS	—	205.8/760	1.4431	20	1.036	20	(10)	—

TABLE IV (Continued)

Compound	M.P. (°C)	B.P. (°C)/mm	n_D	°C	d_4	°C	Reference	Other properties ^a
Me ₂ Si(NCS) ₂	18	217.3/760; 55/0.08	1.5677	20	1.142	20	(10, 57, 76, 92, 93, 169, 179, 190)	B (93, 169)
Et ₂ Si(NCS) ₂	—	245.5/760	1.5540	20	1.089	20	(9, 190)	—
Ph ₂ Si(NCS) ₂	46	376/760	—	—	—	—	(7)	—
MeSi(NCS) ₃	72	267.5/760	—	—	1.304	—	(57, 76, 93, 169, 179, 190)	B (169)
EtSi(NCS) ₃	—	276/760	1.6195	20	1.264	20	(9)	—
Pr ⁿ Si(NCS) ₃	—	289.5/760	1.6014	20	1.2248	20	(11, 19)	—
Bu ⁿ Si(NCS) ₃	-0.5	300.6/760	1.5928	20	1.189	20	(10)	—
<i>n</i> -HeptylSi(NCS) ₃	—	347/760; 174/1	1.5739	20	1.129	20	(26)	—
CyclohexylSi(NCS) ₃	—	348/760; 172-173/1	1.6179	20	1.231	20	(23)	—
PhSi(NCS) ₃	52	339.6/760	—	—	—	—	(7, 190)	—
PhCH ₂ Si(NCS) ₃	36	348.9/760	—	—	1.28	20	(10, 190)	—
CH ₂ =CH—CH ₂ Si(NCS) ₃	—	126-128/2.5	1.6140	26	—	—	(83)	B
CH ₂ =CH—Si(NCS) ₃	—	134-138/3	1.6350	26	—	—	(83)	B
<i>p</i> -MeC ₆ H ₄ Si(NCS) ₃	—	182-185/3.5	1.6490	26	—	—	(83)	B
[(SCN) ₃ Si] ₂ O	120-121	—	—	—	—	—	(76)	—
Si(NCS) ₄	146	313/760	—	—	1.41	20	(6, 40b, 92, 93, 134, 152, 169, 179, 190)	A (40b), B (40b, 93, 169)
Si(NCS) ₄ ·2C ₆ H ₅ N	—	—	—	—	—	—	(159, 160)	B (159, 160)
Si(NCS) ₄ ·2 quinoline	—	—	—	—	—	—	(159, 160)	B (159, 160)
Si(NCS) ₄ ·2 isoquinoline	—	—	—	—	—	—	(159, 160)	B (159, 160)
H ₂ GeNCS	18.6 ± 0.3	150/760 (extr.)	—	—	—	—	(171)	D, F
Me ₃ GeNCS	—	—	—	—	—	—	(162, 172, 180c)	B (172, 180c)
Et ₃ GeNCS	-46	252/760; 113-114/8	1.517	20	1.184	20	(15, 25)	—

$\text{Pr}^{\text{III}}_3\text{GeNCS}$	—56	287/760; 143–144/9	1.5063	20	1.105	20	(15)	—
$\text{Pr}^{\text{III}}_3\text{GeNCS}$	18	277/760	1.512	20	1.112	20	(18, 25)	—
$\text{Bu}^{\text{III}}_3\text{GeNCS}$	—	319/760; 135–136/2	1.5039	20	1.071	20	(15)	—
$\text{Bu}^{\text{II}}_2\text{GeHNCS}$	—	96–98/1	1.5097	20	1.123	20	(24)	—
$\text{Me}_2\text{Ge}(\text{NCS})_2$	45.5–47	266–268/760	—	—	—	—	(153)	—
$\text{Et}_2\text{Ge}(\text{NCS})_2$	16	298/760; 113–116/1	—	—	1.356	20	(15)	—
$\text{Pr}^{\text{IV}}_2\text{Ge}(\text{NCS})_2$	—	296/760; 105–107/1	1.558	20	1.234	20	(25)	—
$\text{Bu}^{\text{II}}_2\text{Ge}(\text{NCS})_2$	—	337/760; 140–141/1	1.5501	20	1.210	20	(24)	—
$\text{EtGe}(\text{NCS})_3$	—	—	—	—	—	—	(12)	—
$\text{Ge}(\text{NCS})_4$	—	—	—	—	—	—	(15, 93)	B (93)
Me_3SnNCS	108.5	—	—	—	—	—	(162, 180c)	B —
Et_3SnNCS	33	130/1	1.5825	20	—	—	(20, 28, 41)	—
$\text{Bu}^{\text{III}}_3\text{SnNCS}$	—	160–162/0.8	1.543	20	1.2350	20	(49)	B —
Ph_3SnNCS	172–173	—	—	—	—	—	(173)	—
$\text{Me}_2\text{Sn}(\text{NCS})_2$	198.6–199.4	—	—	—	—	—	(163)	—
$\text{Et}_2\text{Sn}(\text{NCS})_2$	—	—	—	—	—	—	(41)	—
$\text{Bu}^{\text{II}}_2\text{Sn}(\text{NCS})_2$	144–145	—	—	—	—	—	(93, 163, 190a)	B (93)
$(\text{CH}_2=\text{CH})_2\text{Sn}(\text{NCS})_2$	163.5–165	—	—	—	—	—	(164)	—
$\text{Sn}(\text{NCS})_4$	—	—	—	—	—	—	(93)	B (93)
$\text{Bu}^{\text{II}}_3\text{Sn}(\text{NCS})_2 \cdot 2,2'$ - bipyridine	152.5/153	—	—	—	—	—	(2)	—
Me_3PbNCS	145 decomp.	—	—	—	—	—	(180c)	B —
Et_3PbNCS	35	—	—	—	—	—	(95, 116a)	—
Ph_3PbNCS	—	—	—	—	—	—	(63, 173)	B (63)
$\text{Ph}_2\text{Pb}(\text{NCS})_2$	—	—	—	—	—	—	(116a, 143)	—

* See Table I for symbols used.

* See data added in proof, p. 184.

REFERENCES

1. Aftandilian, V. D., Miller, H. C., and Muetterties, E. L., *J. Am. Chem. Soc.* **83**, 2471 (1961).
2. Alleston, D. L., and Davies, A. G., *J. Chem. Soc.* p. 2050 (1962).
3. Anderson, H. H., *J. Am. Chem. Soc.* **66**, 934 (1944).
4. Anderson, H. H., *J. Am. Chem. Soc.* **67**, 223 (1945).
5. Anderson, H. H., *J. Am. Chem. Soc.* **67**, 2176 (1945).
6. Anderson, H. H., *J. Am. Chem. Soc.* **69**, 3049 (1947).
7. Anderson, H. H., *J. Am. Chem. Soc.* **70**, 1220 (1948).
8. Anderson, H. H., *J. Am. Chem. Soc.* **71**, 1799 (1949).
9. Anderson, H. H., *J. Am. Chem. Soc.* **71**, 1801 (1949).
10. Anderson, H. H., *J. Am. Chem. Soc.* **72**, 193 (1950).
11. Anderson, H. H., *J. Am. Chem. Soc.* **72**, 196 (1950).
12. Anderson, H. H., *J. Am. Chem. Soc.* **72**, 2089 (1950).
13. Anderson, H. H., *J. Am. Chem. Soc.* **72**, 2761 (1950).
14. Anderson, H. H., *J. Am. Chem. Soc.* **73**, 2351 (1951).
15. Anderson, H. H., *J. Am. Chem. Soc.* **73**, 5439 (1951).
16. Anderson, H. H., *J. Am. Chem. Soc.* **73**, 5440 (1951).
17. Anderson, H. H., *J. Am. Chem. Soc.* **73**, 5800 (1951).
18. Anderson, H. H., *J. Am. Chem. Soc.* **75**, 814 (1953).
19. Anderson, H. H., *J. Am. Chem. Soc.* **75**, 1576 (1953).
20. Anderson, H. H., *J. Org. Chem.* **19**, 1766 (1954).
21. Anderson, H. H., *J. Org. Chem.* **20**, 536 (1955).
22. Anderson, H. H., *J. Am. Chem. Soc.* **78**, 1692 (1956).
23. Anderson, H. H., *J. Am. Chem. Soc.* **81**, 4785 (1959).
24. Anderson, H. H., *J. Am. Chem. Soc.* **83**, 547 (1961).
25. Anderson, H. H., *Inorg. Chem.* **3**, 910 (1964).
26. Anderson, H. H., and Hendifar, A., *J. Org. Chem.* **26**, 3033 (1961).
27. Anderson, H. H., Seaton, D. L., and Rudnicki, R. P. T., *J. Am. Chem. Soc.* **73**, 2144 (1951).
28. Anderson, H. H., and Vasta, J. A., *J. Org. Chem.* **19**, 1300 (1954).
- 28a. Arnold, R. G., Nelson, J. A., and Verbane, J. J., *Chem. Rev.* **57**, 47 (1957).
- 28b. Appel, R., and Gerber, H., *Chem. Ber.* **91**, 1200 (1958).
29. Audrieth, L. F., *Chem. Rev.* **15**, 169 (1934).
30. Beard, C. I., and Dailey, B. P., *J. Am. Chem. Soc.* **71**, 929 (1949).
- 30a. Beck, W., Schuierer, E., and Feldl, K., *Angew. Chem.* **78**, 267 (1966).
- 30b. Bertsch, C. R., and Miller, H. C., ASTIA Rept. 227931.
31. Birch, S. F., *J. Chem. Soc.* p. 1132 (1934).
- 31a. Birkenbach, L., and Kellermann, K., *Ber. Deut. Chem. Ges.* **58**, 786, 2377 (1925).
32. Birkofer, L., Ritter, A., and Richter, P., *Angew. Chem.* **74**, 293 (1962).
33. Birkofer, L., Ritter, A., and Richter, P., *Chem. Ber.* **96**, 2750 (1963).
34. Birkofer, L., Ritter, A., and Schramm, J., *Chem. Ber.* **95**, 426 (1962).
35. Birkofer, L., and Kim, S. M., *Chem. Ber.* **97**, 2100 (1964).
36. Birkofer, L., Ritter, A., and Uhlenbrauck, H., *Chem. Ber.* **96**, 3280 (1963).
37. Bither, T. A., Knoth, W. N., Lindsey, R. V., and Sharkley, W. H., *J. Am. Chem. Soc.* **80**, 4151 (1958).
38. Bluestein, B. A., U. S. Patent 2,559,340 (1951).
39. Boyer, J. H., and Canter, F. C., *Chem. Rev.* **51**, 1 (1954).
40. Brennan, G. L., Dahl, G. H., and Schaeffer, R., *J. Am. Chem. Soc.* **82**, 6248 (1960).
- 40a. Browne, A. W., Hoel, A. B., Smith, G. B. L., and Swezey, F. H., *J. Am. Chem. Soc.* **45**, 2541 (1923).

- 40b. Carlson, G. L., *Spectrochim. Acta* **18**, 1529 (1962).
41. Cahours, A., *Ann. Chem.* **122**, 48 (1862).
41a. Cassol, A., Portanova, R., and Barbien, R., *J. Inorg. Nucl. Chem.* **27**, 2275 (1965).
42. Cahours, A., *Compt. Rend.* **76**, 133 (1873).
43. Chaigneau, M., *Compt. Rend.* **239**, 1220 (1954).
44. Challenger, F., and Richards, O. V., *J. Chem. Soc.* p. 405 (1934).
45. Coates, G. E., and Mukherjee, R. N., *J. Chem. Soc.* p. 229 (1963).
46. Cocksedge, H. E., *J. Chem. Soc.* **93**, 2177 (1908).
47. Connolly, J. W., and Urry, G., *Inorg. Chem.* **1**, 718 (1962).
47a. Cragg, R. H., Lappert, M. F., and Tilley, B. P., *J. Chem. Soc.* p. 2108 (1964).
48. Craig, A. D., Urenovitch, J. V., and MacDiarmid, A. G., *J. Chem. Soc.* p. 548 (1962).
49. Cummins, R. A., and Dunn, D., *Australian J. Chem.* **17**, 411 (1964).
50. Curtius, T., *Chem. Ber.* **23**, 3023 (1890).
51. Curtius, T., *Chem. Ber.* **24**, 3341 (1891).
52. Dahl, G. H., *Dissertation Abstr.* **21**, 1751 (1961).
53. Dehnicke, K., *Angew. Chem. Intern. Ed. English* **3**, 142 (1964).
54. Dousmanis, G. C., Sanders, T. M., Townes, C. H., and Zeiger, H. J., *J. Chem. Phys.* **21**, 1416 (1953).
55. Druce, J. G. F., *Rec. Trav. Chim.* **44**, 340 (1925).
56. Eaborn, C., *J. Chem. Soc.* p. 2755 (1949).
57. Eaborn, C., *J. Chem. Soc.* p. 3077 (1950).
58. Ebsworth, E. A. V., and Frankiss, S. G., *J. Chem. Soc.* p. 661 (1963).
59. Ebsworth, E. A. V., and Mays, M. J., *J. Chem. Soc.* p. 4879 (1961).
60. Ebsworth, E. A. V., and Mays, M. J., *J. Chem. Soc.* p. 4844 (1962).
61. Ebsworth, E. A. V., and Mays, M. J., *J. Chem. Soc.* p. 3450 (1964).
62. Ebsworth, E. A. V., Mould, R., Taylor, R., Wilkinson, G. R., and Woodward, L. A., *Trans. Faraday Soc.* **58**, 1069 (1962).
62a. Elmore, D. T., and Ogle, J. R., *J. Chem. Soc.* p. 2286 (1959).
63. Emel us, H. J., and Evans, P. R., *J. Chem. Soc.* p. 510 (1964).
64. Emel us, H. J., Onyszchuk, M., and Kuchen, W., *Z. Anorg. Allgem. Chem.* **283**, 74 (1956).
65. Evers, E. C., Freitag, W. O., Keith, J. N., Kriner, W. A., MacDiarmid, A. G., and Sujishi, S., *J. Am. Chem. Soc.* **81**, 4493 (1959).
65a. Evers, E. C., Freitag, W. O., Kriner, W. A., and MacDiarmid, A. G., *J. Am. Chem. Soc.* **81**, 5106 (1959).
65b. Evers, E. C., Freitag, W. O., Kriner, W. A., MacDiarmid, A. G., and Sujishi, S., *J. Inorg. Nucl. Chem.* **13**, 239 (1960).
66. Fielding, H. C., and Pollock, J. M., British Patent 923,581 (1963).
67. Fielding, H. C., and Pollock, J. M., British Patent 923,582 (1963).
68. Finch, A., Gardner, P. J., Lockhart, J. C., and Pearn, E. J., *J. Chem. Soc.* p. 1428 (1962).
69. Finch, A., Hendra, P. J., and Pearn, E. J., *Spectrochim. Acta* **18**, 51 (1962).
70. Foerster, W., and Kriegsmann, H., *Z. Anorg. Allgem. Chem.* **327**, 309 (1964).
71. Forbes, G. S., and Anderson, H. H., *J. Am. Chem. Soc.* **62**, 761 (1940).
72. Forbes, G. S., and Anderson, H. H., *J. Am. Chem. Soc.* **65**, 2271 (1943).
73. Forbes, G. S., and Anderson, H. H., *J. Am. Chem. Soc.* **66**, 1703 (1944).
74. Forbes, G. S., and Anderson, H. H., *J. Am. Chem. Soc.* **67**, 1911 (1945).
75. Forbes, G. S., and Anderson, H. H., *J. Am. Chem. Soc.* **69**, 1241 (1947).
76. Forbes, G. S., and Anderson, H. H., *J. Am. Chem. Soc.* **69**, 3048 (1947).
77. Forbes, G. S., and Anderson, H. H., *J. Am. Chem. Soc.* **69**, 3049 (1947).

78. Forbes, G. S., and Anderson, H. H., *J. Am. Chem. Soc.* **70**, 1043 (1948).
79. Forbes, G. S., and Anderson, H. H., *J. Am. Chem. Soc.* **70**, 1222 (1948).
80. Franks, A. W., *Chem. Rev.* **61**, 389 (1961).
- 80a. Gaidis, J. M., and West, R., *J. Am. Chem. Soc.*, **86**, 5699 (1964).
81. Gilman, H., Hofferth, B., and Melvin, H. W., *J. Am. Chem. Soc.* **72**, 3045 (1950).
82. Gingold, K., Rochow, E. G., Seyferth, D., Smith, A. C., and West, R., *J. Am. Chem. Soc.* **74**, 6306 (1952).
83. Glowacki, G. R., and Post, H. W., *J. Org. Chem.* **27**, 634 (1962).
84. Goddard, A. E., *J. Chem. Soc.* **119**, 672 (1921).
85. Goldfarb, T. D., and Zafonte, B. P., *J. Chem. Phys.* **41**, 3653 (1964).
86. Goubeau, J., *Angew. Chem.* **73**, 305 (1961).
87. Goubeau, J., and Gräbner, H., *Chem. Ber.* **93**, 1379 (1960).
88. Goubeau, J., and Heubach, E., *Chem. Ber.* **93**, 1117 (1960).
89. Goubeau, J., Heubach, E., Paulin, D., and Widmaier, I., *Z. Anorg. Allgem. Chem.* **300**, 194 (1959).
90. Goubeau, J., and Paulin, D., *Chem. Ber.* **93**, 1111 (1960).
91. Goubeau, J., and Reyhling, J., *Z. Anorg. Allgem. Chem.* **294**, 92 (1958).
92. Goubeau, J., and Reyhling, J., *Z. Anorg. Allgem. Chem.* **294**, 96 (1958).
93. Green, B. S., Sowerby, D. B., and Wihksne, K. Y., *Chem. Ind. (London)* p. 1306 (1960).
94. Gutmann, V., Meller, A., and Schaschel, E., *Monatsh. Chem.* **95**, 1188 (1964).
- 94a. Guy, R., and Chaigneau, M., *Bull. Soc. Chim. France* p. 257 (1956).
- 94b. Haffon, J. V., *J. Chem. Phys.* **40**, 933 (1964).
95. Heap, R., and Saunders, B. C., *J. Chem. Soc.* p. 2983 (1949).
96. Herber, R. H., *Chem. Eng. News* **44** (28), 66 (1964).
- 96a. Herber, R. H., Stöckler, H., and Reichle, W. T., *J. Chem. Phys.* **42**, 2447 (1965).
97. Heying, T. L., and Smith, H. D., *U.S. Govt. Res. Rept.* **38**, 12 (1963).
98. Hieber, W., and Pigenot, D., *Chem. Ber.* **89**, 193 (1956).
- 98a. Hodgman, C. D., and West, R. C., "Handbook of Chemistry and Physics." The Chemical Rubber Publishing Co., Cleveland 43rd ed. 1961.
- 98b. Horder, J. R., and Lappert, M. F., Unpublished work, 1965.
99. Horowitz, J. P., Fisher, B. E., and Tomaszewski, A. J., *Abstr. Papers 134th Meeting Am. Chem. Soc., Chicago, 1958*, p. 19 P (1958).
100. Huisgen, R., and Ugi, I., *Chem. Ber.* **90**, 2914 (1957).
- 100a. Hundek, J., *Angew. Chem. Intern. Ed. Engl.* **4**, 977 (1965).
- 100b. Jefferson, R., and Lappert, M. F., Unpublished work, 1965.
101. Jenkins, D. R., Kewley, R., and Sudgen, T. M., *Proc. Chem. Soc.* p. 220 (1960).
102. Jenkins, D. R., Kewley, R., and Sudgen, T. M., *Trans. Faraday Soc.* **58**, 1284 (1962).
103. Johns, I. B., and Di Pietro, H. R., *J. Org. Chem.* **29**, 1970 (1964).
104. Johnson, O. H., *Chem. Rev.* **48**, 259 (1951).
105. Kaczmarczyk, A., and Urry, G., *J. Am. Chem. Soc.* **81**, 4112 (1959).
106. Kaufmann, H. P., and Kögler, F., *Ber. Deut. Chem. Ges.* **59**, 178 (1926).
- 106a. Kharasch, N., "Organic Sulfur Compounds," Vol. I, p. 326. Macmillan (Pergamon), New York, 1961.
- 106b. Kimura, K., Katada, K., and Bauer, S. H., *J. Am. Chem. Soc.* **88**, 416 (1966).
- 106c. Kirsanov, A. V., and Marenets, M. S., *Zh. Obshch. Khim.* **29**, 2256 (1959).
107. Klanberg, F., *Proc. Chem. Soc.* p. 203 (1961).
108. Klanberg, F., *Z. Anorg. Allgem. Chem.* **316**, 197 (1962).
109. Kratzer, R. H., and Paciorek, K. L., *Abstr. Papers 148th Meeting Am. Chem. Soc. Chicago, 1964* p. 390 (1964).
- 109a. Kratzer, R. H., and Paciorek, K. L., *Inorg. Chem.* **4**, 1767 (1965).

- 109b. Krause, E., and Von Grosse, A., "Die Chemie der Organometallischen Verbindungen," p. 240, Borntraeger, Berlin, 1933.
110. Krishna Pillai, M. G., and Perumal, A., *Bull. Soc. Chim. Belges* **73**, 29 (1964).
111. Kuchen, W., *Z. Anorg. Allgem. Chem.* **288**, 101 (1956).
- 111a. Lappert, M. F., and Prokai, B., *J. Chem. Soc.* p. 4223 (1963).
112. Lappert, M. F., and Pyszora, H., *Proc. Chem. Soc.* p. 350 (1960).
113. Lappert, M. F., and Pyszora, H., *J. Chem. Soc.* p. 1744 (1963).
114. Lappert, M. F., and Pyszora, H., Unpublished work, 1963.
- 114a. Lappert, M. F., Prokai, B., and Pyszora, H., Unpublished work, 1963.
115. Lappert, M. F., Pyszora, H., and Rieber, M., *J. Chem. Soc.* p. 4256 (1965).
116. Laubengayer, A. W., and Reggel, L., *J. Am. Chem. Soc.* **65**, 1783 (1943).
- 116a. Leeper, R. W., Summers, L., and Gilman, H., *Chem. Rev.* **54**, 101 (1954).
117. Leffler, J. E., and Todd, L. J., *Chem. Ind. (London)* p. 512 (1961).
118. Lieber, E., and Keane, F. M., *Chem. Ind. (London)* p. 747 (1961).
119. Lieber, E., and Nambury, C. N. V., *Chem. Ind. (London)* p. 883 (1959).
- 119a. Lieber, E., Rao, C. N. R., and Keane, F. M., *J. Inorg. Nucl. Chem.* **25**, 631 (1963).
120. Linton, H. R., and Nixon, E. R., *Spectrochim. Acta* **10**, 299 (1958).
121. Linton, H. R., and Nixon, E. R., *J. Chem. Phys.* **28**, 990 (1958).
122. Lockhart, J. C., *J. Chem. Soc.* p. 1197 (1962).
- 122a. Lorberth, J., *Chem. Ber.* **98**, 1201 (1965).
123. Luijten, J. G. A., Janssen, M. J., and van der Kerk, G. J. N., *Rec. Trav. Chim.* **81**, 202 (1962).
- 123a. Luitjen, J. G. A., and van der Kerk, G. J. N., *Rec. Trav. Chim.* **83**, 295 (1964).
124. Luijten, J. G. A., and van der Kerk, G. J. N., "A Survey and the Chemistry and Application of Organotin Compounds." Tin Res. Inst., Greenford, England 1955.
125. McBride, J. J., *J. Org. Chem.* **24**, 2029 (1959).
126. McBride, J. J., and Beachell, H. C., *J. Org. Chem.* **28**, 991 (1958).
127. McBride, J. J., and Beachell, H. C., *J. Am. Chem. Soc.* **74**, 5247 (1952).
128. McCloskey, A. L., "Research on Inorganic Polymer Systems." WADC Technical Report U.S. Borax Res. Corp., 1960.
129. Mackay, K. M., and Roebuck, P. J., *J. Chem. Soc.* p. 1195 (1964).
130. MacDiarmid, A. G., *J. Inorg. Nucl. Chem.* **2**, 88 (1956).
131. MacDiarmid, A. G., and Maddock, A. G., *J. Inorg. Nucl. Chem.* **1**, 411 (1955).
132. Menzer, W., *Angew. Chem.* **70**, 656 (1958).
133. Michalowski, Z., *Wiadomosci Chem.* **13**, 543 (1959).
134. Miguel, M., *Ann. Chim. Phys.* **5**, 343 (1877).
135. Mikhailov, B. M., and Bubnov, Y. N., *Dokl. Akad. Nauk SSSR* **127**, 571 (1959).
136. Miller, F. A., and Carlson, G. L., *Spectrochim. Acta* **17**, 977 (1961).
- 136a. Mufti, A. S., and Poller, R. C., *J. Chem. Soc.* p. 5055 (1965).
137. Muller, N., and Bracken, N. C., *J. Chem. Phys.* **32**, 1577 (1960).
138. Muszkat, K. A., Hill, L., and Kirson, B., *Israel J. Chem.* **1**, 27 (1963).
- 138a. Newsom, H. C., U.S. Patent 3,161,659 (1964).
139. Paetzold, P. I., *Angew. Chem.* **74**, 506 (1962).
140. Paetzold, P. I., *Z. Anorg. Allgem. Chem.* **326**, 53 and 58 (1963).
- 140a. Paetzold, P. I., *Z. Anorg. Allgem. Chem.* **326**, 47 (1963).
- 140b. Paetzold, P. I., Gayoso, M., and Dehnicke, K., *Chem. Ber.* **98**, 1173 (1965).
141. Paetzold, P. I., and Maier, G., *Angew. Chem. Intern. Ed. English* **3**, 315 (1964).
- 141a. Patel, S. J., and Tuck, D. G., Personal communication, 1965.
142. Pohland, E., *Z. Anorg. Allgem. Chem.* **201**, 282 (1931).
143. Polis, A., *Ber. Deut. Chem. Ges.* **20**, 333 (1887).
- 143a. Prince, M. I., and Weiss, K., *J. Organomet. Chem.* **5**, 584 (1966).
144. Prober, M., *J. Am. Chem. Soc.* **77**, 3224 (1955).
145. Prober, M., *J. Am. Chem. Soc.* **78**, 2274 (1956).

146. Pump, J., and Rochow, E. G., *Chem. Ber.* **97**, 627 (1964).
147. Pump, J., and Rochow, E. G., *Z. Anorg. Allgem. Chem.* **330**, 101 (1964).
148. Pump, J., and Wannagat, U., *Ann. Chem.* **652**, 21 (1962).
149. Pump, J., and Wannagat, U., *Angew. Chem.* **74**, 117 (1962).
150. Pyszora, H., Ph. D. Thesis, Manchester University, 1963.
151. Reichle, W. T., *Inorg. Chem.* **3**, 402 (1964).
151a. Reichle, W. T., *Inorg. Chem.* **5**, 87 (1966).
152. Reynold, J. E., *J. Chem. Soc.* **89**, 397 (1906).
153. Rochow, E. G., and Allred, A. L., *J. Am. Chem. Soc.* **77**, 4489 (1955).
154. Rochow, E. G., Seyferth, D., and Smith, A. C., *J. Am. Chem. Soc.* **75**, 3099 (1953).
154a. Ruhlmann, K., Reiche, A., and Becker, M., *Chem. Ber.* **98**, 1814 (1965).
155. Ruidisch, I., and Schmidt, M., *J. Organomet. Chem.* **1**, 493 (1964).
155a. Ruhlmann, K., Reiche, A., and Becker, M., *Chem. Ber.* 1814 (1965).
156. Saunders, B. C., and Stacey, G. J., *J. Chem. Soc.* p. 919 (1949).
157. Scherer, O. J., and Schmidt, M., *J. Organomet. Chem.* **1**, 490 (1964).
157a. Schlemper, E. O., and Britton, D., *Inorg. Chem.* **5**, 507 (1966).
158. Schmitz-Dumont, O., and Ross, B., *Angew. Chem. Intern. Ed. English* **3**, 586 (1964).
159. Schnell, E., and Wersin, G., *Monatsh. Chem.* **92**, 647 (1961).
160. Schnell, E., and Wersin, G., *Monatsh. Chem.* **93**, 65 (1962).
161. Seyferth, D., and Kahlen, N., *J. Am. Chem. Soc.* **82**, 1080 (1960).
162. Seyferth, D., and Kahlen, N., *J. Org. Chem.* **25**, 809 (1960).
163. Seyferth, D., and Rochow, E. G., *J. Am. Chem. Soc.* **77**, 1302 (1955).
164. Seyferth, D., and Stone, F. G. A., *J. Am. Chem. Soc.* **79**, 515 (1957).
165. Sheridan, J., and Turner, A. C., *Proc. Chem. Soc.* p. 21 (1960).
165a. Shevchenko, V. I., Shtepanek, A. S., and Kirsanov, A. V., *Zh. Obshch. Khim.* **31**, 3062 (1961).
166. Sidgwick, N. V., "The Chemical Elements and their Compounds," p. 675. Oxford Univ. Press, London and New York, 1950.
167. Smolinsky, G., *J. Am. Chem. Soc.* **82**, 4717 (1960); **83**, 2489 (1961).
168. Smolinsky, G., *J. Org. Chem.* **26**, 4108 (1961).
169. Sowerby, D. B., *J. Inorg. Nucl. Chem.* **22**, 205 (1961).
170. Sowerby, D. B., *J. Am. Chem. Soc.* **84**, 1831 (1962).
171. Srivastava, T. N., Griffiths, J. E., and Onyszchuk, M., *Can. J. Chem.* **40**, 739 (1962).
172. Srivastava, T. N., Griffiths, J. E., and Onyszchuk, M., *Spectrochim. Acta* **18**, 142 (1962).
173. Srivastava, T. N., and Tandon, S. K., *Indian J. Appl. Chem.* **25**, 171 (1963).
173a. Stamm, W., *J. Org. Chem.* **30**, 693 (1965).
174. Steyermark, P. R., *J. Org. Chem.* **28**, 586 (1963).
175. Sujishi, S., and Goldfarb, T. D., *Abstr. Papers 140th Meeting Am. Chem. Soc., Chicago, 1961* p. 35 N (1961).
176. Sujishi, S., and Keith, J. N., *Abstr. Papers 134th Meeting Am. Chem. Soc., Chicago, 1958* p. 44 N (1958).
177. Sujishi, S., Raider, S., and Goldfarb, T. D., *Abstr. Papers 148th Meeting Am. Chem. Soc., Chicago, 1964* p. 40 O (1964).
178. Sundermeyer, W., *Angew. Chem. Intern. Ed. English* **1**, 552 (1962).
179. Sundermeyer, W., *Z. Anorg. Allgem. Chem.* **313**, 290 (1962).
179a. Sundermeyer, W., *Chem. Ber.* **96**, 1293 (1963).
180. Sundermeyer, W., *Angew. Chem.* **75**, 684 (1963).

- 180a. Tesi, G., Oho, R. J. A., Sherif, F. G., and Audrieth, L. F., *J. Am. Chem. Soc.* **80**, 5894 (1958).
- 180b. Thayer, J. S., *Organomet. Chem. Rev.* **1**, 157 (1966).
- 180c. Thayer, J. S., and Strommer, D. P., *J. Organomet. Chem.* **5**, 383 (1966).
181. Thayer, J. S., and West, R., *Inorg. Chem.* **3**, 406 (1964).
182. Thayer, J. S., and West, R., *Inorg. Chem.* **3**, 889 (1964).
183. Thayer, J. S., and West, R., *Inorg. Chem.* **4**, 114 (1965).
- 183a. Thayer, J. S., and West, R., *Adv. Organomet. Chem.* **5**, in press.
184. Turner, H. S., and Warne, R. J., *Proc. Chem. Soc.* p. 69 (1962).
185. Turner, H. S., and Warne, R. J., British Patent 946,989 (1964).
- 185a. Turner, H. S., and Warne, R. J., *J. Chem. Soc.* p. 6421 (1965).
186. Urenovitch, J. V., and MacDiarmid, A. G., *J. Chem. Soc.* p. 1091 (1963).
187. Urenovitch, J. V., and MacDiarmid, A. G., *J. Am. Chem. Soc.* **85**, 3372 (1963).
188. van der Kerk, G. J. M., and Luijten, J. G. A., *J. Appl. Chem. (London)* **6**, 49 (1956).
189. van der Kerk, G. J. M., Luijten, J. G. A., and Janssen, M. J., *Chimia (Aarau)* **16**, 10 (1962).
190. Voronkov, M. G., and Dolgov, B. N., *Zh. Obshch. Khim.* **24**, 1082 (1954).
- 190a. Wada, M., Nishimo, M., and Okawara, R., *J. Organomet. Chem.* **3**, 70 (1965).
- 190b. Wada, M., Kawakami, K., and Okawara, R., *J. Organomet. Chem.* **4**, 159 (1965).
191. Wagner, R. I., Research on Inorganic Polymers. WADC Technical Report 61-05 (1961).
192. Wannagat, U., Behmel, K., and Bürger, H., *Chem. Ber.* **97**, 2029 (1964).
193. Wannagat, U., Pump, J., and Bürger, H., *Monatsh. Chem.* **94**, 1013 (1963).
194. Washburn, R. M., and Baldwin, R. A., U. S. Patent 3,112,331 (1963).
- 194a. Weisse, G. K., and Thomas, R. M., U. S. Patent 3,093,451 (1963).
195. Werner, A., and Pfeiffer, P., *Z. Anorg. Chem.* **17**, 82 (1898).
196. West, R., and Thayer, J. S., *J. Am. Chem. Soc.* **84**, 1763 (1962).
197. Wiberg, E., and Michaud, H., *Z. Naturforsch.* **9b**, 495 (1954).
198. Wiberg, E., and Michaud, H., *Z. Naturforsch.* **9b**, 496 (1954).
199. Wiberg, E., and Michaud, H., *Z. Naturforsch.* **9b**, 497 (1954).
200. Wiberg, E., and Michaud, H., *Z. Naturforsch.* **9b**, 499 (1954).
201. Wiberg, E., and Michaud, H., *Z. Naturforsch.* **9b**, 500 (1954).
202. Wiberg, E., and Michaud, H., *Z. Naturforsch.* **9b**, 502 (1954).
- 202a. Wiberg, N., and Neruda, B., *Chem. Ber.* **99**, 740 (1966).
203. Wiberg, N., and Raschig, F., *Angew. Chem. Intern. Ed. English* **1**, 335 (1962).
204. Wiberg, N., Raschig, F., and Sustmann, R., *Angew. Chem. Intern. Ed. English* **1**, 551 (1962).
205. Wiberg, N., Raschig, F., and Sustmann, R., *Angew. Chem.* **74**, 388 (1962).
206. Wiberg, N., Raschig, F., and Sustmann, R., *Angew. Chem.* **74**, 716 (1962).
207. Wiberg, N., and Schmid, K. H., *Angew. Chem. Intern. Ed. English* **3**, 444 (1964).
208. Wiberg, N., and Schmid, K. H., *Angew. Chem. Intern. Ed. English* **3**, 444 (1964).
209. Wilson, J. C., Nadler, M. A., Katz, I., and Walti, A., U. S. Pat. 2,932,586 (1960).
210. Wittig, G., and Bille, H., *Z. Naturforsch.* **6b**, 226 (1951).
211. Wittig, G., and Raff, P., *Z. Naturforsch.* **6b**, 225 (1951).
212. Wittig, G., and Raff, P., *Ann. Chem.* **573**, 195 (1951).
213. Yoffe, A. D., *Proc. Roy. Soc.* **A208**, 188 (1951).
214. Zhinkin, D. Y., Morgunova, M. M., Popov, K. K., and Andrianov, K. A., *Dokl. Akad. Nauk. SSSR* **158**, 641 (1964).
215. Zimmer, H., and Lübke, K., *Chem. Ber.* **85**, 1119 (1952).

Data Added in Proof

TABLE I (Continued)
DATA ON AZIDES

Compound	M.P. (°C)	B.P. (°C)/mm	Reference	Other properties
Si(N ₃) ₄	—	—	(201)	—
Et ₃ SiN ₃ ^a	—	104/95	(202a)	B
Bu ⁿ ₃ SiN ₃ ^b	—	88/0.01	(202a)	B
(Me ₂ N) ₃ SiN ₃ ^c	—	76/11	(202a)	B
(MeO) ₃ SiN ₃ ^d	—	18/4	(202a)	B
F ₃ SiN ₃	—	—	(202a)	B
(1,3,5-Me ₃ C ₆ H ₂) ₂ SiMeN ₃	65–68	—	(202a)	B
(1,3,5-Me ₃ C ₆ H ₂) ₂ Si(NPPPh ₃)N ₃	189	—	(202a)	B
(1,3,5-Me ₃ C ₆ H ₂ Si(N ₃) ₂	87.5	—	(202a)	B
Me ₂ Ge(N ₃) ₂	–14	43.5/2	(155, 157)	—

^a *n*_D = 1.4424, 20°C. ^b *n*_D = 1.4522, 22°C. ^c *n*_D = 1.4494, 20°C. ^d *n*_D = 1.3969, 26°C.TABLE IV (Continued)
DATA ON ISOTHIOCYANATES

Compound	M.P. (°C)	Reference
Bu ⁿ ₂ Sn(NCS) ₂ ·2,2'-bipyridine	152.5/153	(2)
Pr ⁿ ₂ Sn(NCS) ₂	135–136	(190a)
Et ₂ Sn[OSn(OH)Et ₂]NCS	170–176 decomp.	(190a)
(Et ₂ SnNCS) ₂ O	178–179	(190a)
Me ₂ Sn(OC ₂ H ₅ N)NCS	123–124	(190a)
Pr ⁿ ₂ Sn(OC ₂ H ₅ N)NCS	144	(190b)
Et ₂ PnNCS	35	(95, 116a)
Ph ₃ PbNCS	—	(63, 173a), B (63)
Ph ₂ Pb(NCS) ₂	—	(116a, 143)

STERESELECTIVITY IN COORDINATION COMPOUNDS

J. H. Dunlop and R. D. Gillard

Department of Chemistry, The University, Sheffield, England

I. Introduction	185
A. Nomenclature	186
B. Stereoselectivity	187
II. Complexes of Diamines	188
A. Historical	188
B. Conformational Theory	189
C. Recent Work	192
III. Complexes of Amino Acids	204
A. Introduction	204
B. One Amino Acid	206
C. Two Amino Acids	207
D. Three Amino Acids	209
IV. Other Ligands	211
V. Conclusion	212
References	213

I. Introduction

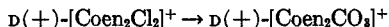
Biological aspects of inorganic chemistry are becoming increasingly important. Many of the most striking effects observed require an understanding of the subtle details of some inorganic stereochemistry not previously reviewed. Further, in classical coordination chemistry, it has become increasingly clear that a good deal of valuable information is to be obtained from the interplay of optical configuration and spectroscopy. For example, it is possible to characterize spectroscopic levels from measurements of circular dichroism if the absolute optical configuration of the compound is known.

The time is therefore ripe for an exposition of the ways in which stereospecific effects arise from the interaction in transition metal complexes of several sources of asymmetry.

The behavior of molecular diastereoisomers has been known as stereospecificity or stereoselectivity in organic chemistry for some years, and this is the sense in which we use the term stereoselectivity. Unfortunately, in coordination chemistry as in organic chemistry, the term has also been applied to other types of behavior, such as retention of geometrical configuration, e.g.,



and retention of optical configuration, e.g.,



We use the term "stereoselectivity" to refer only to the behavior of molecular diastereoisomers, i.e., asymmetric metal complexes containing further centers of asymmetry. This definition covers the transition state of many reactions of optically active complexes with optically active ligands, such as the reaction of $(+)[Coen_2CO_3]^+$ with $(+)$ tartaric acid; such reactions have usually been called stereospecific in the past.

There is a rapidly growing tendency among organic chemists for reactions of the type formerly called stereospecific to be called stereoselective ("stereospecific" being reserved for reactions which are 100% stereoselective). Although this usage does not represent a fixed state of affairs (today's stereospecific reaction may be tomorrow's 99% stereoselective reaction, as experimental methods improve), we have revised the common inorganic usage whereby stereospecificity refers to one molecular diastereoisomer having different properties from another, and call such effects stereoselective, in accordance with modern organic practice.

A. NOMENCLATURE

Although no description of basic principles of optical activity is given in this review, a few points of nomenclature are necessary. First, the absolute optical configuration of complexes: it is now known by the Bijvoet method (11) of anomalous diffraction of X-rays that the Fischer convention for D-glyceraldehyde corresponds to reality. It has further been shown (78) in a similar way that the enantiomer of the trisethylenediaminecobalt(III) cation, which is dextrorotatory at the sodium D line ($[\alpha]_D = +90^\circ$), has the absolute configuration shown in Fig. 1a. This configuration may be called D (43), Λ (82), or $S(C_3)R(C_2)$ (19, 21). Second, a positive Cotton effect for an isolated electronic transition is shown in Fig. 1b. Curves are given for both the more commonly measured optical rotatory dispersion, and the rather more informative circular dichroism. Both phenomena, the inverse rotatory dispersion curve and the circular dichroism band, are included under the name Cotton effect. The intimate connection between configuration and Cotton effect will be clear from Fig. 1.

In naming complexes, we adopt the following rules:

(a) Any sign of rotation given, whether for complex or for ligand, refers to sodium yellow light (589 m μ) unless otherwise specified, e.g., $(+)[Coen_2(NCS)(H_2O)]^{2+}$, $(+)_{5461}[Coen_2(NCS)Cl]^+$, $(+)[Coen_2(+tartrate)]^{2+}$.

(b) Absolute configurations for complex or ligand are given where known in an accepted nomenclature, e.g., $D(+)-[Co(+pn)_3]^{3+}$, $(+)[Co(L(+)-alaninate)_3]$.

(c) Abbreviations for ligands are as in a recent book (58), except as follows: diamines are abbreviated as in (37), EDTA denotes the ethylenediaminetetraacetate ion, PDTA the propylenediaminetetraacetate ion, CHXTA the *trans*-1,2-cyclohexanediaminetetraacetate ion, Ala the alaninate anion, and hmc the hydroxymethylenecamphorate anion.

B. STERESELECTIVITY

Optical enantiomers react at exactly equal rates with symmetric reagents to form exactly similar products, distinguishable only by some measurement with an asymmetric technique. Rephrasing this statement, symmetrical properties of enantiomers are exactly equal. Thus, the electronic and infrared spectra of the enantiomers of tartaric acid or of trisethylenediaminecobalt(III) chloride are superposable.

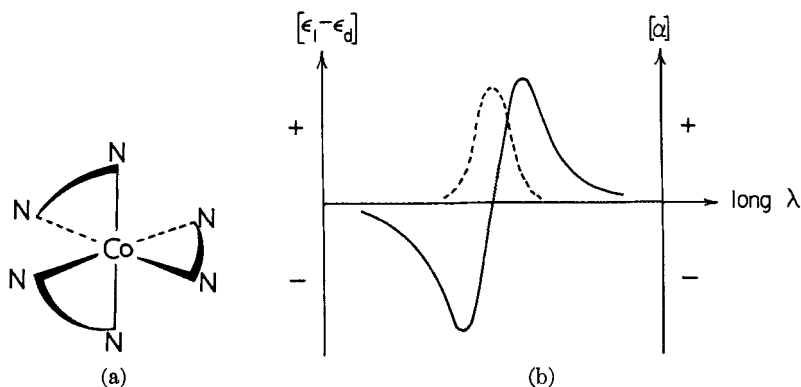
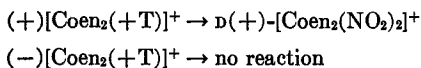


FIG. 1(a) The D configuration, as in $(+)[\text{Coen}_3]^{3+}$. This has left-handed helicity about the C_2 axis, right-handed about any C_2 axis, i.e., $D \equiv S(C_2)R(C_2)$. (b) A positive Cotton effect: — optical rotatory dispersion; - - - - circular dichroism ($\epsilon_1 - \epsilon_d$).

Molecules with more than one (say n) element of asymmetry may obviously form enantiomers, where all n elements of asymmetry differ in optical configuration from one enantiomer to the other. However, such molecules may also form diastereoisomers, in which at least one and at most $(n - 1)$ elements of asymmetry have the same optical configurations. Examples of such diastereoisomers are common in coordination chemistry; an illustrative series is $D\text{-}[\text{Co}(-\text{pn})_3]^{3+}$, $D\text{-}[\text{Co}(-\text{pn})_2(+\text{pn})]^{3+}$, $D\text{-}[\text{Co}(-\text{pn})(+\text{pn})_2]^{3+}$, and $D\text{-}[\text{Co}(+\text{pn})_3]^{3+}$. These are diastereoisomers; their respective enantiomers are, of course, $L\text{-}[\text{Co}(+\text{pn})_3]^{3+}$, $L\text{-}[\text{Co}(+\text{pn})_2(-\text{pn})]^{3+}$, $L\text{-}[\text{Co}(+\text{pn})(-\text{pn})_2]^{3+}$, and $L\text{-}[\text{Co}(-\text{pn})_3]^{3+}$. In the case of diastereoisomers, there is no reason to suppose that symmetrical properties will be similar. This is, of course, the basis of the well-known method of resolution by means of forming diastereoisomeric salts, in which a racemic

cation, $\pm C$, is caused to form a salt with an asymmetric anion, say $(+)A$. The possible salts $(+)C(+)A$ and $(-)C(+)A$ are diastereoisomers, and not enantiomers (the enantiomer of $(+)C(+)A$ is $(-)C(-)A$, and there is no $(-)A$ in the system). The properties of the diastereoisomers will differ in many respects. Because there will be differences in interaction between cation and anion in the solid state, lattice energies and hence solubilities will differ. Crystallization of the mixture of $(+)C(+)A$ and $(-)C(+)A$ will therefore lead to the less soluble diastereoisomer crystallizing first.

In cases where the separate elements of asymmetry are contained within the same molecule or ion, the diastereoisomers may show surprising differences in properties. For example, the mixture obtained (57) from the reaction of $(+)$ tartaric acid with DL-carbonatobisethylenediaminecobalt(III) cation contains both possible diastereoisomers. These react at strikingly different rates with nitrite ion, to such effect that the nitrite-containing product is optically pure:

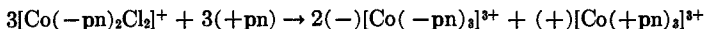


The remainder of this review is concerned with individual types of system in which stereoselective differences have been observed between diastereoisomeric molecules. No attempt has been made to include all the work which has appeared, although relevant literature has been searched to May 1965. The aim has been to set out the areas of agreement, and to point out the paucity of data in places where information would be of the utmost value. In particular, the lack of quantitative data is emphasized.

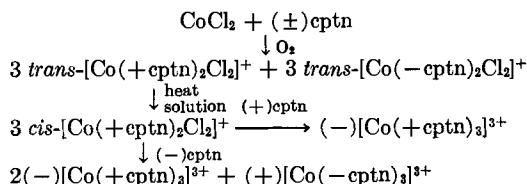
II. Complexes of Diamines

A. HISTORICAL

It has been recognized for many years that, in the complexes of transition metals with optically active diamines, there are marked stereoselective effects. The earliest demonstrations of this matter rested on the isolation from reaction mixtures of less diastereoisomers than the predicted number. Indeed, it was for many years thought that, in tris complexes of optically active diamines, this stereospecificity was complete, and that, using a diamine such as $(+)$ propylenediamine, only one complex cation, say $(+)[M(+pn)_3]^{3+}$, was formed. For example, the following reaction was discovered (94) very early, and confirmed (8) more recently.



Similarly, Smirnoff (92) was able to isolate only two series of salts from the oxidation of cobalt(II) chloride in the presence of racemic propylenediamine. These contained $(-)[\text{Co}(-\text{pn})_3]^{3+}$ and $(+)[\text{Co}(+\text{pn})_3]^{3+}$. It was clear that one of the possible diastereoisomers, said by Jaeger (53) to be the most symmetrical, is the most stable, although whether this stability was kinetic or thermodynamic was not known. Similar work has been performed on complexes of other diamines. Jaeger and Blumendal found (56) that, using racemic *trans*-cyclopentanediamine, the reactions observed were:



Similar results were found for the complexes of rhodium(III), and later the work was extended (55) to complexes of *trans*-1,2-cyclohexanediamine, which gave rise to exactly similar stereospecific formation of favored isomers.

Although all this early work relied on isolation of complexes, and more recent work, discussed in subsequent sections, shows that the stereoselective effects are not nearly so absolute as was earlier thought, there is a great deal of evidence that one diastereoisomer, usually the most symmetrical, is a good deal more stable than the others. This has been explained (15) as a thermodynamic effect in terms of conformational analysis, although it appears likely that many of the stereoselective effects observed in complexes of ligands other than diamines may have a kinetic origin.

B. CONFORMATIONAL THEORY

1. Conformation of a Five-Membered Chelate Ring

As pointed out by earlier workers (38), chelation of a 1,2-diamine results in a nonplanar structure. In their remarkable paper (15) on the conformational analysis of chelate rings, Corey and Bailar calculated the preferred conformation of a chelate ring formed by ethylenediamine, using the best values for bond lengths available. The resulting carbon-carbon backbone is very similar to the side of a cyclohexane ring. There is now a great deal of evidence (38) that chelate rings formed by 1,2-diamines have, to a very good approximation, just this preferred conformation. For example, in the crystal structures of $\text{D}(+)\text{-2}[\text{Coen}_3]\text{Cl}_3 \cdot \text{NaCl} \cdot 6\text{H}_2\text{O}$ (78), $\text{D}(+)\text{-}[\text{Coen}_3]\text{Br}_3 \cdot \text{H}_2\text{O}$ (77), $\text{L}(-)\text{-}[\text{Co}(-\text{pn})_3]\text{Br}_3$ (86), and *trans*-

$[\text{Co}(-\text{pn})_2\text{Cl}_2](\text{H}_6\text{O}_2)\text{Cl}_2$ (52) the chelate rings are always *gauche*, and the detailed stereochemistry is, within a small amount, that calculated by conformational analysis.

2. Interaction of Three Chelate Rings

It was early realized (85) that a 1,2-disubstituted ethane in the *gauche* form is, in principle, a resolvable compound, since it has no center, plane, or alternating axis of symmetry. Although the only attempt (91) to resolve a monoethylenediamine compound— $[\text{Coen}(\text{NH}_3)_4]^{3+}$ —failed, this can be attributed to rapid inversion of the chelate ring. It is clear from Fig. 2 that a chelated diamine molecule is asymmetric. The forms shown, which might be called *d* and *l*, or (+) and (−), were in fact called (15) *k* and *k'* by Corey and Bailar, the *k* form being part of a right-handed helix, and the *k'* form part of a left-handed helix. One might expect these right-handed helices to pack better around a left-handed helix than around a right-

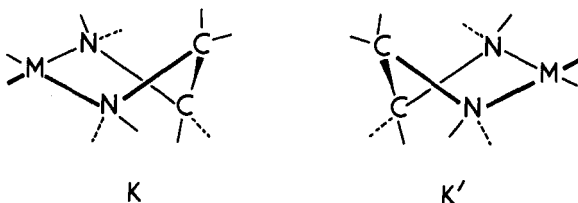


FIG. 2. Mirror image conformations of a diamine chelate ring.

handed one. Corey and Bailar were able to show (15) that three *k*-form diamine ligands would exhibit less H—H repulsion when packed into a complex of *D* configuration, which of course has a left-handed principal threefold axis, $S(C_3)$, than when packed around a right-handed helix as in the *L* complexes. The result of packing three *k*-form diamine ligands is shown in Fig. 3; this complex was named “*lel*” because its threefold axis is parallel with the C—C bonds in the ligands. The diastereoisomeric complex, with *k'*-form ligands, was called “*ob*,” because the threefold axis was obverse to the C—C bond direction (see Fig. 3).

This prediction (15) of a stable form with three *k*-form ligands in a complex of *D* configuration is valid for ethylenediamine itself; the energy difference calculated between the *D*(*kkk*) (*lel*) form and the *D*(*k'k'k'*) (*ob*) form was ca. 1.8 kcal/mole. This difference represents the stabilization of *D*(*kkk*)- $[\text{Coen}_3]^{3+}$ relative to its diastereoisomer *D*(*k'k'k'*)- $[\text{Coen}_3]^{3+}$, or of *L*(*k'k'k'*)- $[\text{Coen}_3]^{3+}$ relative to *L*(*kkk*)- $[\text{Coen}_3]^{3+}$. It is certainly true that in all the crystal structures so far reported* of trisdiamine metal complexes,

* These are $2[\text{Coen}_3]\text{Cl}_3 \cdot \text{NaCl} \cdot 6\text{H}_2\text{O}$ (78), $[\text{Coen}_3]\text{Br}_3 \cdot \text{H}_2\text{O}$ (77), $L(-)-[\text{Co}(-\text{pn})_3]\text{Br}_3$ (86), and $[\text{Ni en}_3](\text{NO}_3)_2$ (93).

there has been a genuine threefold axis of rotation through the metal atom, in keeping with the conformational prediction that all three chelate rings will be equivalent.

In complexes of optically active diamines, the *k* and *k'* forms of ethylenediamine now correspond to the (+) and (−) enantiomers of the diamine. The absolute configurations of (+)- and (−)-propylenediamine are shown in Fig. 4. Now, in addition to the hydrogen repulsions of the N-H groups in nonbonded *cis* positions, there is the additional factor, stabilizing the

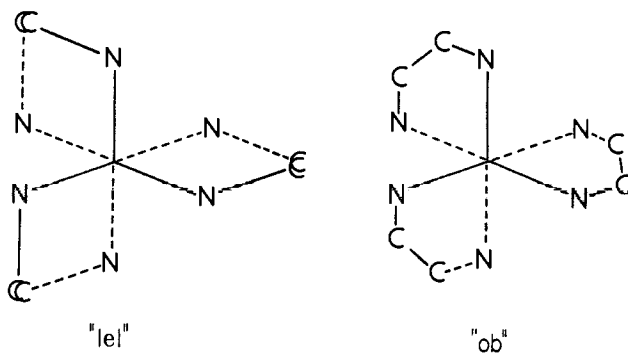


FIG. 3. The "ob" and "lel" isomers.

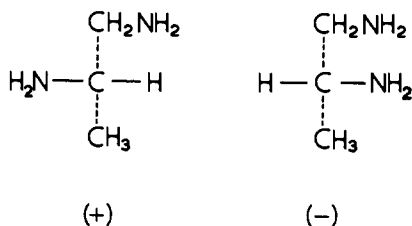
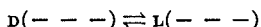


FIG. 4. The absolute configurations of (+)- and (−)-propylenediamine.

k form for (+)pn or the *k'* form for (−)pn, that the methyl group will be much more stable as an equatorial substituent. Here is the explanation of the observed stereospecificity in complexes of optically active diamines—it is only in the $\text{D}-[\text{M}(+\text{pn})_3]^{n+}$ complex diastereoisomer that the methyl groups can be equatorial. Similar arguments may be used for other optically active diamines, and those, say (+)AA, with the optical configuration related to that of (+)pn will give as the most stable diastereoisomer $\text{D}-[\text{M}(+\text{AA})_3]^{n+}$. This offers a method of deducing optical configurations of ligands or metal complexes, and examples of such deductions are discussed later.

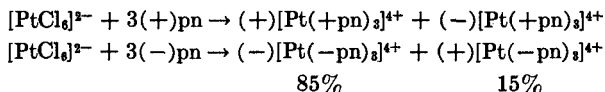
C. RECENT WORK

Since the appearance of the conformational theory outlined above, a good deal of careful work has been performed by Dwyer and his students on stereoselectivity in trisdiamine systems. They found (25) more isomers than had previous workers. Trispropylenediaminecobalt(III) cation was obtained (25) as a mixture of the $L(---)$, $D(---)$, $D(+++)$, and $L(+++)$ forms. Using a charcoal catalyst to establish equilibrium rapidly, the reaction,



was shown to have an equilibrium constant, $K = 5.75$. The free energy is thus -1.02 ± 0.05 kcal/mole, which is the order of magnitude expected for conversion from the *kkk* form to a less conformationally stable form.

An early explanation for the nonisolation of the less stable diastereoisomers in systems involving cobalt(III) was that disproportionation occurred. On the ground that such an explanation would not be reasonable for the inert complexes of rhodium(III), where stereoselective effects also occur, Dwyer argued (25) that the difficulties in cobalt(III) systems could arise from intermediates of coordination number higher than 6, and the presence of labilizing cobalt(II) compounds. Such complications are less likely to arise in complexes of platinum, and some quantitative work (23) on the diastereoisomeric trispropylenediamine complexes of platinum(IV) has been done:



The pairs of diastereoisomeric cations formed in each reaction were separated by means of the fractional crystallization of their oxalates, which are sparingly soluble in water. The relative amounts of stable and unstable diastereoisomers show that the energy difference between them is about that predicted for a conformational $kkk \rightarrow k'k'k'$ change.

Dwyer also made a careful study of the mixed products obtained from reactions of propylenediamine and ethylenediamine with cobalt(III). The results (28) are collected in Table I. It is clear that the results may readily be rationalized on the basis that $D(kkk)$ isomers are more stable than $D(k'k'k')$.

The complexes of cobalt(III) with resolved *trans*-1,2-cyclopentanediamine have very recently been re-examined (81), and several corrections were made to the early work. However, although the ion previously formulated as trisdiaminecobalt(III) was in fact shown to contain a poly-

nuclear species, the stereoselectivity of the formation of the complex was confirmed.

1. Applications

Configurations: From the conformational theory of stereospecificity, it is clear that a given hand of an optically active 1,2-diamine gives a most stable diastereoisomeric tris complex with any metal which has the same optical configuration. This was first demonstrated experimentally by Jaeger, who showed (54) that the stable diastereoisomers $[M(-\text{chxn})_3]^{3+}$, where $M = \text{Co}$, Rh , and Cr , had related optical configurations, since they formed mixed crystals of the same space group as their optically active parents, rather than partial racemates. He also showed that the dissym-

TABLE I
COMPOSITION OF "MIXED" TRISDIAMINE SPECIES^a

Product	Products (%)			
	From [Coen ₂ Cl ₂]Cl	From [Coen ₂ (NO ₂) ₂]Cl	Direct synthesis	
			(-)pn/en = 1:2	(-)pn/en = 2:1
(-)[Coen ₂ (-pn)] ³⁺	27	28	27	15
(-)[Coen(-pn) ₂] ³⁺	10	17	18	37
(-)[Co(-pn) ₃] ³⁺	13	4	6	30
(+)[Coen ₂ (-pn)] ³⁺	17.5	15.5	13	7
(+)[Coen(-pn) ₂] ³⁺	1	3.5	3	5
(+)[Co(-pn) ₃] ³⁺	1	1	1	2

^a From reference (22).

metries of spots were similar on a Laue picture taken with X-radiation directed from 000 $\bar{1}$ to 0001 for the three isomorphous nitrates.

Several applications are possible of this stereospecific induction of configuration by optically active diamines. Knowing the absolute configuration of the diamine, it is obviously possible to predict which diastereoisomer of the trisdiamine complex will be the more stable. A prerequisite is the knowledge of the configurations of 1,2-diamines. These may be related by comparing the Cotton effects of their metal complexes, such as the blue (or yellow) Lifschitz salts, $[\text{Ni}(\text{diamine})_2]\text{X}_2$, X being an anion. A self-consistent correlation on these lines has been obtained (37) for all the diamines which have been used in stereospecific studies. Those having the optical configuration related to that of (+)propylenediamine (itself related to L(+)alanine) are (37) (+)pn, (+)bn, (+)cptn, (+)chxn, (+)phenen, and (-)stien. The more stable diastereoisomer of complexes containing three of any of these diamines will have the D configuration.

A good deal of use has been made of this principle. The general method has been to decide which diastereoisomer is the more stable, e.g., $\text{D}(+)\text{[Co}(+)\text{pn}]_3^{3+}$. The nature of the Cotton effects of this diastereoisomer is then determined, and compared with those of resolved complexes of inactive diamines, such as $(+)\text{[Coen}_3]^{3+}$. Since the spectroscopic levels in the ligand field region are extremely similar for such closely related compounds, a direct comparison of optical configuration is possible. For example (21, 43), the more stable diastereoisomer, $\text{D}(+)\text{[Co}(+)\text{pn}]_3^{3+}$, has Cotton effects exactly similar to those of $(+)\text{[Coen}_3]^{3+}$, which is known to have the D configuration by Bijvoet analysis. The optical configuration of the more stable diastereoisomer has recently been confirmed directly by a full Bijvoet method analysis (86) of the stable diastereoisomer $(-)\text{[Co}(-\text{pn})_3]^{3+}$, which was found to have the L configuration. In another example (21), the more stable diastereoisomer of $\text{Rh}(-\text{pn})_3^{3+}$, which must

TABLE II
CONFIGURATIONS OF TRISDIAMINE COMPLEXES

Cation	D configuration ^a	Circular dichroism		$(+)\text{T}^b$	A.R. ^c
		$m\mu$	$\epsilon_1 - \epsilon_d$		
$[\text{Coen}_3]^{3+}$	(+)	493	+1.9	(+)	(+)
$[\text{Rhen}_3]^{3+}$	(-)	310	+1.4	(-)	(-)
$[\text{Iren}_3]^{3+}$	(-)	315	+0.4	—	—
$[\text{Cren}_3]^{3+}$	(+)	460	+1.7	—	—

^a From stereoselectivity (21).

^b Relative configurations from less soluble diastereoisomers.

^c Relative configurations from the method of active racemates (16a).

have the L configuration, shows a circular dichroism spectrum very similar to that of the cation $(+)\text{[Rhen}_3]^{3+}$, which therefore also has the L configuration. Work of this kind has been performed for complexes of cobalt(III) (21, 43), chromium(III) (19), rhodium(III) (43), and platinum(IV) (20) and the results are summarized in Table II. Results obtained by such classical methods (16a) as partial racemate formation are confirmed by this stereospecific method.

2. Spectroscopy

A brief summary of the spectroscopy of dihedral complexes is necessary. For d^6 spin-paired complexes, such as those of cobalt(III), with pure octahedral symmetry, O_h , the ground state is ${}^1A_{1g}$, $(e_g)^6$, from which triply degenerate spin-allowed transitions may occur within the $d-d$ manifold to

${}^1T_{1g}$ (Band I) at lower energy, and ${}^1T_{2g}$ (Band II) at higher energy, the excited states arising from $(e_g)^5(t_{2g})^1$. Band I is magnetic-dipole-allowed, and therefore gives rise to a much larger rotational strength than Band II, which is magnetic-dipole-forbidden. In a trischelate complex, the highest element of symmetry is the threefold axis; complexes of ligands such as 1,2-diamines also have three twofold axes, so that such complex ions as $[\text{Coen}_3]^{3+}$ belong to the point group D_3 . This is equivalent to the statement that there is a trigonal distortion about the cobalt atom. The threefold degeneracy of the excited states is lifted, and both Bands I and II become split into an A and an E state. Under Band I for such complexes, two transitions therefore occur, each giving rise to a Cotton effect (${}^1A_1 \rightarrow {}^1E_a + {}^1A_2$). It may be predicted that these will be of opposite signs. For $\text{D}(+)\text{-}[\text{Coen}_3]^{3+}$ it has been shown (9) that the E_a transition has a positive rotational strength. This leads to the rule that if the E_a transition gives a positive Cotton effect, the complex has the D configuration. Conversely, absolute configurations may be used to deduce spectroscopic information, since, if the complex has the D configuration, then the positive Cotton effect under Band I arises from ${}^1A_1 \rightarrow {}^1E_a$. This offers a method of assessing small spectroscopic splittings, and it has been shown (19) in this way that the splittings of Band I in trisdiamine complexes of cobalt(III), rhodium(III), and chromium(III) are all in the same sense, the $A \rightarrow E$ component falling at lower energy than the $A \rightarrow A$ component.

A number of studies have appeared on the spectroscopic splittings in trisdiamine complexes; it has been suggested (97) that the two components observed under Band I are not in fact due to ${}^1A_1 \rightarrow {}^1A_2$ and ${}^1A_1 \rightarrow {}^1E_a$ of a trigonal complex, but to the "lel" and "ob" conformations of the complex. However, the more stable diastereoisomer $\text{D}(+)\text{-}[\text{Co}(+\text{pn})_3]^{3+}$, which exists purely in the "lel" conformation by virtue of the equatorial requirement of the methyl groups, shows (21) two bands, in the same way as $(+)\text{[Coen}_3]^{3+}$. A similar pair of Cotton effects of opposed signs is observed for the stable diastereoisomers of $[\text{Rh}(-\text{pn})_3]^{3+}$ (21) and of $[\text{Co}(-\text{chxn})_3]^{3+}$ (83). It has recently been suggested (67) that the sign of the Cotton effect which arises from the charge transfer absorption at ca. 220 $\text{m}\mu$ is related to the k or k' configuration of the ligand.

Configurational relationships based on the effect of forming ion pairs with polarizable anions are in agreement with the earlier work using stereospecificity. In particular, the similar behavior with phosphate ions of $\text{D}(+)\text{-}[\text{Coen}_3]^{3+}$ and $\text{D}(+)\text{-}[\text{Co}(+\text{pn})_3]^{3+}$ may be attributed (71) to the possibility of stabilizing the "lel" conformation in both by hydrogen bonding. $\text{L}(-)\text{-}[\text{Co}(+\text{pn})_3]^{3+}$, the less stable diastereoisomer, behaves in a totally different manner.

3. Two Asymmetric Diamines

When two asymmetric ligand molecules combine with a metal salt to produce a *cis* complex with an asymmetric metal atom, then the six possible optical isomers that can be produced, arranged in pairs of enantiomers, are:

$D(++)$ and $L(--)$

$D(+-)$ and $L(+-)$

$D(--)$ and $L(++)$

If only one enantiomer of the ligand has been used in the reaction, say the $(-)$ form, then the possible products are limited to the $D(--)$ and the $L(--)$ isomers, which are not enantiomers but diastereoisomers. The diastereoisomers should be separable by fractional crystallization or by chromatographic techniques. If the metal complex which results from the combination of the racemic ligand with the metal is planar or tetragonal, e.g., $[Pt(diamine)_2]Cl_2$ or *trans*- $[Co(diamine)_2Cl_2]Cl$, then the possible products are $(++)$, $(--)$, and $(+-)$. The first two isomers are enantiomeric and have no center of symmetry. The $(+-)$ isomer has a center of symmetry and should therefore be physically different from the pair of enantiomers. However, it has been pointed out (95) that this difference in symmetry, and hence in "allowedness" of the electronic transitions, will be too small to be observed experimentally, and a similar observation is that the electronic spectra of solutions of racemic copper(II) alaninate and of optically active copper(II) alaninate are identical (39), despite an earlier report (17) of differences.

4. Evidence for Stereoselectivity

Tetragonal complexes: There is a good deal of evidence that the equatorial preference of substituents on 1,2-diamine chelate rings gives rise to considerable effects on stabilities. For example, complexes of *meso*- and *dl*-1,2-diamines, such as stilbenediamine, differ in thermodynamic stability (38) because the *meso* complexes have at least one substituent which is axial on the *gauche* chelate ring. A similar explanation applies to the greater preparative stability (31) of copper complexes of the 1,2-amino-alcohol, ψ -ephedrine, than for ephedrine itself. Unfortunately, there is no thermodynamic information whatsoever on the relative stabilities of such complexes as *trans*- $[M(+AA)_2]^{n+}$ and *trans*- $[M(+AA)(-AA)]^{n+}$. The theory (15) of Corey and Bailar predicts that the complexes containing two molecules of diamine of the same hand (*kk*) will be more stable than the mixed *meso* complex containing one ligand of each optical hand (*kk'*). There are some early preparative studies which suggest that this is true.

Jaeger and Blumendal (56) found no mixed isomers in the reaction products of cobalt(II) chloride and *trans*-1,2-cyclopentanediamine. Optically inactive *trans*-dichloro-1,2-cyclopentanediaminecobalt(III) chloride was prepared (1) by mixing equimolar amounts of *trans*-[Co(-cptn)₂Cl₂]Cl and *trans*-[Co(+cptn)₂Cl₂]Cl, and (2) from the racemic base.

The compounds produced by the two methods were identical in physical properties. In the first reaction there was no reason to expect that equilibration had occurred. Therefore they concluded that no mixed isomers had been formed. However, it appears (81) that the *trans*-1,2-cyclopentanediamine used by Jaeger was impure. When the pure diamine was used (81), several of Jaeger's reactions could not be repeated.

Corey and Bailar showed (15) that in planar and tetragonal complexes only the hydrogen-hydrogen interactions of the neighboring amine groups were significantly different between the *kk* and the *kk'* forms, i.e., between the optically active and the *meso* forms. Calculations showed that the *kk* form was more stable than the *kk'* form by about 1 kcal/mole. Therefore the *kk* form will predominate at equilibrium by a factor of about 5. The early failure to find the mixed isomer, which must form only a small percentage of the total reaction product, may be because the complete reaction product was not examined. It has been suggested (79) that Hurlimann's work (48) on the *cis*-dinitrobispropylenediaminecobalt(III) ion actually referred to the *trans* isomer. However, he found no mixed isomers, whatever the complex he studied.

Cis-bisdiamine complexes: It is clear from the treatment of conformations by Corey and Bailar (15) that the hydrogen-hydrogen repulsions and the equatorial preference of substituents in the chelate rings, which dictate the details of stereochemistry in the trisdiamine complexes, will also be present in *cis*-bisdiamine complexes, although the effect is expected to be smaller in the bis complexes. There is a good deal of evidence that this is so, and that there is a more stable diastereoisomer of the pair $D-[M(+AA)_2XY]^{n+}$ and $L-[M(+AA)_2XY]^{n+}$. Mere occurrence of a Cotton effect for the *d-d* transitions of the equilibrium mixture does not prove this, since there is no reason why the rotatory powers of the two diastereoisomers should be equal. Even a 1:1 mixture will therefore give a net Cotton effect. The preferred method of procedure is to isolate both diastereoisomers pure, as salts of inactive anions, and to use their rotatory properties to analyze the equilibrium mixture (which may be the original synthetic product or, more commonly, the product of equilibrating either diastereoisomer.)

Unfortunately a good deal of the early work is severely qualitative in nature. For example, when a solution of *trans*-dichlorobis(+)cyclopentanediaminecobalt(III) chloride was heated, the product is (-)*cis*-dichlorobis(+)cyclopentanediaminecobalt(III) chloride. This reacted (56) with a

further mole of (+)base to give the favored tris(+)base complex. However, this does not prove that the *cis*-bis complex contained an excess of one diastereoisomer.

Hurlimann (48) could isolate only two isomers from a compound which he regarded as a *cis*-dinitrobispropylenediaminecobalt(III) salt. These isomers were designated D(--) and L(++). However, optical rotatory dispersion (79) showed that his compound was largely the *trans* isomer. Similarly, Jaeger and Blumendal (56) could not find mixed isomers in *cis*-dichlorobispropylenediaminecobalt(III) chloride, or in *cis*-dichlorobis-cyclopentanediaminecobalt(III) chloride.

Since the work (15) of Corey and Bailer on the conformation of chelate rings, greater care has been taken in the examination of products of reactions of metal ions with asymmetrical ligands. It was suggested (15) that, in many such reactions, especially those where there were labile intermediates, thermodynamic equilibria would be found, so that "mixed isomers," which had previously been overlooked, should be detectable by careful examination of the products.

Dwyer and Sargeson (30) reacted (-)propylenediamine with tetrachloroethylenediamineplatinum(IV) in dimethylformamide. In this solvent the product is precipitated as soon as it is formed. The product will therefore be kinetically controlled. As the complexes of platinum(II) are not labile, platinum(II) impurities would not produce the thermodynamically controlled product. The product was resolved, and it was shown (30) that the ratio of the (+) and (-) forms of ethylenediaminebis(-)propylenediamineplatinum(IV) chloride was 55:45 in favor of the (+) form. Dwyer *et al.* (28) prepared bis(-)propylenediamine-ethylenediaminecobalt(III) chloride in the presence of charcoal, and separated the products by paper chromatography. They found that the ratio of the D(--) to the L(--) isomer was 13.4:86.6. From the equilibrium constant, the free energy difference between the isomers was 1.2 kcal/mole, the value expected from the conformational theory. As the reaction started from a cobalt(II) salt in the presence of activated charcoal, the ratio of the products was not determined kinetically, but by the relative thermodynamic stabilities of the products.

The oxalatobis(-)propylenediaminecobalt(III) ion was prepared and separated into its diastereoisomers by the same workers (27). The equilibrium constant $K = D(--) / L(--)$ was calculated from the rotation of the mixture. This showed (27) that there was $42 \pm 2\%$ of the L(--) form at equilibrium; the difference in free energy between the diastereoisomers is 200 cal/mole. The ratio of the amounts of the diastereoisomers obtained from the equilibrium studies was the ratio obtained from the recovery of the reaction products. The reaction product was therefore at thermodynamic equilibrium.

A preparation which is absolutely stereospecific has been reported by Dwyer and McDermott (26). The reaction of cobalt(II) chloride, (–)propylenediamine, and carbon dioxide in the presence of lithium carbonate gave optically pure L-carbonatobis(–)propylenediaminecobalt(III) chloride on crystallization from aqueous acetone. The lower solubility of the L diastereoisomer and the equilibrium, which must exist between the D and the L diastereoisomers, are the cause of the absolute stereospecificity in this preparation. This “second order asymmetric synthesis” shows how dangerous it is to argue from the isolated solid products back to the nature of the equilibria in solution. Martinette and Bailar (70) had previously attempted to separate the diastereoisomers by fractional crystallization. This was only partially successful, but they did show that the impure diastereoisomers differed markedly in optical rotatory dispersion, although their electronic absorption spectra and conductivities were the same.

5. Applications to Absolute Configuration

Iwasaki and Saito have determined (52) the absolute configuration of *trans*-dichlorobis(–)propylenediaminecobalt(III) chloride by the Bijvoet method. The (–)propylenediamine chelate rings were found to be in the *kk* conformation, as predicted (15) by Corey and Bailar. However, work by Saito and his co-workers shows that in *trans*-dichlorobisethylenediaminecobalt(III) chloride (76) and in *trans*-dichlorobis(+–)propylenediaminecobalt(III) chloride (52a) the chelate rings are in the *kk'* conformation. Results on solids are not a completely reliable guide to the nature of solutions. The equilibrium studies of other types of system in solution by Dwyer and his co-workers agree well with the predictions of Corey and Bailar.

The conformational theory can therefore be used (43) to assign the absolute configuration of bisdiamine complexes in the same way as it has been used for the trisdiamine complexes.

If the conditions of a reaction are such that a thermodynamic equilibrium is achieved, then conformational analysis will show which isomer is the more stable and will thus predict the predominant isomer in the reaction product. Table III shows the ratio of the diastereoisomers calculated from the free energy values.

In trisdiamine complexes and in bisdiamine complexes, the more stable isomer predominates by a considerable margin. However, in complexes with only one diamine this predominance is reduced because the physical difference between the diastereoisomers is much less. There is therefore a greater degree of uncertainty. There have been no assignments of the absolute configuration of complexes with only one asymmetric diamine ligand. Indeed, in contrast to the increasing use of stereoselectivity in

TABLE III
FREE ENERGY DIFFERENCES AND RATIOS OF DIASTEREISOMERS

ΔG (cal/mole)	%D(+++)	%L(+++)	$K = D(+++)/L(+++)$
1800	95.2	4.8	18.94
1200	88	12	7.33
600	73	27	2.70

complexes with three asymmetric diamine ligands, there has been only one report (43) on the use of stereoselectivity to assign the absolute configuration of complexes of bisdiamines. The argument is essentially similar to that for the trisdiamine complexes; the stable diastereoisomer $(-)[Co(-pn)_2CO_3]^+$, from the conformational theory, has the L configuration. This diastereoisomeric cation has a rotatory dispersion curve essentially enantiomorphous with that of resolved $(+)$ carbonatobis-ethylenediaminecobalt(III) cation, which may therefore be assigned (43) the D configuration.

Qualitative work on $[Co(AA)_2X_2]^{n+}$ complexes by Mathieu (73) showed that the more stable diastereoisomers of nine complexes of the type $(+)[Co(+pn)_2(NO_2)_2]^+$ had positive rotatory dispersion curves. Since these complexes have the D configuration induced by the equatorial requirement of the methyl groups, their Cotton effects serve as a reference for determining the absolute configurations of the analogous complexes of ethylenediamine, which are (43) $D(+)-[Coen_2(NO_2)_2]^+$ and $D(+)-[Coen_2(H_2O)_2]^{3+}$. These last complexes have since been related chemically, together with all the intermediate complexes (34).

6. Reactions

Bailar and McReynolds prepared (7) *cis*-dichlorobis $(-)$ propylenediaminecobalt(III) chloride and the corresponding carbonato complex. The two diastereoisomers of the carbonato complex were not of equal stability. The conversion between these diastereoisomers has been extensively studied, with various experimental conditions (69, 70).

Several workers (8, 56) have tried to prepare mixed trisdiamine complexes by the reaction of the bis active diamine complex with either the racemic diamine, or the other enantiomer of the base. They failed to isolate any mixed isomers. This failure is explained by later work which showed (33) that trisdiaminecobalt(III) complexes would be racemized in basic solutions. Therefore any excess of the diamine will cause the mixed isomers that might have been formed initially to rearrange into the equilibrium mixture which is the result of the conformational interactions of the puck-

ered diamine rings. The mixed isomers form a very small percentage of this mixture and considerable experimental dexterity is required to isolate and identify them.

Active carbonato complexes have been used (44) for the partial resolution of several organic acids. Carbonatobis(−)propylenediaminecobalt(III) chloride reacts at a different rate with the (+) form of the organic acid than with the (−) form. Excess of the racemic acid was used and the unreacted acid was found to be partially resolved. The amount of resolution, which in the most successful experiment was only 30%, should be considerably increased if optically pure $L\text{-[Co(−pn)}_2\text{CO}_3]\text{Cl}$ were used. A similar reaction between racemic alanine and *trans*-dichlorobis(−)propylenediaminecobalt(III) chloride was unsuccessful. There was no preferential coordination of one enantiomer of the alanine in the metal complex formed. Tartratobisdiaminecobalt(III) complexes also show a difference in the stability and reactivity between the diastereoisomers. This difference has been used (45, 57) to obtain partial resolutions of racemic tartaric acid and racemic propylenediamine.

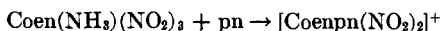
During some interesting work (75) on the asymmetric synthesis of threonine, glycinatobis(−)propylenediaminecobalt(III) iodide (probably a mixture of diastereoisomers) was caused to react with acetaldehyde at controlled pH at room temperature. A very small amount of threonine was obtained with an asymmetric yield of 8%. When (−)glycinatobisethylenediaminecobalt(III) iodide was used, the asymmetric yield dropped to 1%. (−)Threonine was formed in preference to the (+) enantiomer. Reactions of this Knoevenagel type, between acetaldehyde and a methylene group in an amino acid chelate ring, also occur readily (40) in complexes of cobalt(III) with peptides.

Only one reaction of a trisdiamine complex has been reported (8). (+)Trisethylenediaminechromium(III) bromide, or tris(−)propylenediaminechromium(III) chloride, was allowed to react with an excess of racemic phenylalanine for several hours. A polynuclear complex of phenylalanine with chromium(III) was obtained, and the unreacted phenylalanine showed no optical activity.

7. One Asymmetric Ligand

The predominance of one optical isomer in the equilibrium mixture of the products of a reaction which could produce several diastereoisomers is less marked when there is only one asymmetric ligand per metal atom than when there are two or more asymmetric ligands. Werner (96) claimed to have isolated the eight possible isomers of the *cis*-dinitroethylenediaminepropylenediaminecobalt(III) cation. Bailar confirmed this work, but found that there was no stereoselectivity. However, Sargeson (87) has cast some

doubt on the chemical isomerism of all the products of the reaction used to form this complex, which is allegedly:



The "isomers," separated by chromatography, do not all have optical rotatory dispersion spectra similar to those of $[\text{Co}(\text{AA})_2(\text{NO}_2)_2](\text{NO}_2)$, where AA = en or pn.

It has also been pointed out (38, 37) that the compound (+)bisethylenediamine-1,2-cyclopentanediaminecobalt(III) chloride, which Jaeger (56) claimed to have made, is likely to be a mixture of (+)trisethylenediaminecobalt(III) chloride and (+)tris-1,2-cyclopentanediaminecobalt(III) chloride, because the reaction of *cis*-dichlorobisethylenediaminecobalt(III) chloride with (+)propylenediamine gives (37) a product whose stoichiometry is $[\text{Coen}_2\text{pn}]\text{Cl}_3\text{H}_2\text{O}$ and which remains unchanged after several recrystallizations. This "isomer" is a solid solution of $\text{D-}[\text{Coen}_3]\text{Cl}_3\text{H}_2\text{O}$ and $\text{D-}[\text{Copen}_3]\text{Cl}_3\text{H}_2\text{O}$. The components cannot be separated by crystallization of the product of this reaction in methanol. However, 1% of the product was made up of cobalt(II) compounds. The presence of cobalt in this kinetically labile state may explain the failure of the attempts to isolate the mixed isomers. Dwyer *et al.* (28) reacted cobalt(II) chloride, (–)propylenediamine, ethylenediamine, and hydrochloric acid at 25° in the presence of charcoal while air was bubbled through the mixture. The composition of the products depended on the ratio of ethylenediamine to propylenediamine in the reaction mixture. The ratio of the products was that given by a statistical treatment assuming that the two bases are equivalent. The products of the reaction were separated by chromatography and then resolved. In the equilibrium mixture, the ratio of the (+) to the (–) diastereoisomer of bisethylenediamine(–)propylenediaminecobalt(III) chloride was 1 to 2.1. The free energy difference between the isomers is 450 cal/mole. From the conformational theory, one might expect about 600 cal/mole.

The only other case where one diastereoisomer has been shown to predominate at equilibrium was reported (27) by the same authors. They found stereoselectivity in the formation of potassium bisoxalato(–)propylenediaminecobaltate(III) from cobalt(II) acetate. The diastereoisomers were separated and separately equilibrated with activated charcoal. At equilibrium there was 38 ± 2% of the (–)[(–)] diastereoisomer. This was also the percentage found in the initial reaction product. The free energy difference between the (–)[(–)] and the (+)[(–)] diastereoisomers was 270 cal/mole.

In mixed diamine complexes of platinum(IV) in dimethylformamide solution, where the ratio of the products is determined by the kinetics of the

reaction, the two diastereoisomers of the bisethylenediamine(−)propylenediamineplatinum(IV) chloride were formed (30) in equal amounts. Bailer and his co-workers (14) prepared and resolved *cis*-dinitroethylenediamine-(+)2,3-butanediaminecobalt(III) chloride as the bromocamphorsulfonate; the rates of racemization of the two diastereoisomers were different.

The experimental work on the diamine complexes of metals, discussed here, suggests that the initial products of a reaction involving asymmetric molecules are determined kinetically. The ratio of these products will be given by the statistical chance of their formation, and they will be found in this ratio if they are immediately isolated, or if there is no means by which the thermodynamically unstable isomers may rearrange to the more stable isomers. The work of Dwyer and his associates has shown that the mixed isomers in the case of cobalt(III) are kinetically stable and will not rearrange to the thermodynamically favored ratio of isomers unless they are treated with activated charcoal, which will racemize (18, 88) trisdiamine complexes of cobalt. The mechanism involved is probably reduction to labile cobalt(II) complexes, which will rearrange. Reoxidation will reform cobalt(III) complexes but with a different ratio of isomers. Popplewell has observed (84) that the rate of exchange of C¹⁴-ethylenediamine with coordinated ethylenediamine in the [Coen₃]³⁺ ion on charcoal is slower than the rate of racemization of (+)[Coen₃]³⁺ under the same conditions. The racemization must therefore proceed, at least in part, by an intramolecular process. In basic solution, trisethylenediaminecobalt(III) ions are in equilibrium (33) with *cis*- and *trans*-bisethylenediaminecobalt(III) ions. (+)[Coen₃]³⁺ will therefore be racemized in such solutions. The use of excess diamine in the preparation of diamine complexes of cobalt(III) will ensure that the products will be isolated in the thermodynamically favored ratios. Further, the presence (29) of cobalt(II) compounds in a reaction mixture apparently involving only cobalt(III) compounds is evidence of equilibration via a redox mechanism.

8. 1,2-Diaminetetraacetic Acids as Ligands

One of the very few cases where absolute stereospecificity has been observed is in complexes of substituted ethylenediaminetetraacetate ions. Two of these have been studied to date, those derived from propylenediamine (PDTA) and from *trans*-cyclohexanediamine (CHXTA). The stability constants (51) of (−)- and of (±)PDTA with such metals as magnesium and calcium are equal. When (+)PDTA forms a complex with a metal, for the methyl substituent on the *N,N'*-chelate ring to be equatorial, only one diastereoisomer is possible. It is found (12) that (−)₅₄₆₁[Co(+PDTA)][−] forms with complete stereospecificity; there is no evidence whatsoever for the other diastereoisomer (where the methyl

group would be axial). A similar situation occurs (24) in the complexes of CHXTA. The absolute configuration of (+)PDTA is known from its relationship with (+)pn, and so the absolute configuration of the $(-)\text{}_{5461}[\text{Co}(+\text{PDTA})]^-$ may be deduced (35) as that in Fig. 5. By comparison of the observed circular dichroism curves, as in Table IV, the absolute configuration of $(-)\text{}_{5461}[\text{Co}(\text{EDTA})]^-$ is shown (35) to be that derived from Fig. 5, by replacing the methyl group with a hydrogen atom. Similar deductions have been made (36) for the absolute configurations of rhodium(III) complexes of EDTA, using the stereospecifically formed $[\text{Rh}(+\text{PDTA})(\text{H}_2\text{O})]$ as a reference point. It was also possible to show in this way that the analogous energy levels in the analogous complexes of chromium(III) and cobalt(III) did not occur in the same order (36).

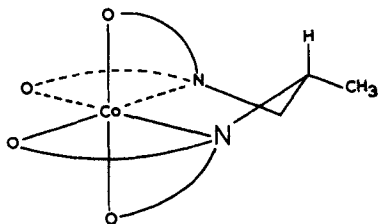
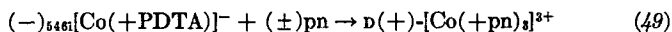
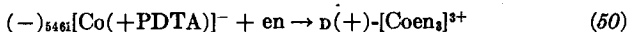


FIG. 5. The absolute configuration of $(-)\text{}_{5461}[\text{Co}(+\text{PDTA})]^-$.

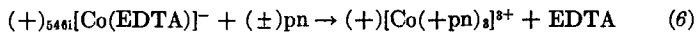
Two stereoselective reactions of $[\text{Co}(+\text{PDTA})]^-$ were discovered by Irving and Gillard; these were



and



Some analogous reactions of the analogous complex of EDTA are also known:



Mechanistic studies (12) of reactions of this type have not so far led to full steric details of transition states, but the results so far available are encouraging.

III. Complexes of Amino Acids

A. INTRODUCTION

The ring formed by an α -amino acid chelated to a transition metal is more nearly planar than that formed by a 1,2-diamine. Any stereo-

TABLE IV
CIRCULAR DICHROISMS OF DIAMINOTETRACARBOXYLATOCOBALTATES(III)^a

Compound	Band I				Band II			
	ν_{\max}	Sign	ν_{\max}	Sign	ν_{\max}	Sign	ν_{\max}	Sign
(-) _{546.1} [Co(EDTA)] ⁻	17,010	+ve	19,420	-ve	23,801	+ve	27,470	+ve
(-) _{546.1} [Co(+PDTA)] ⁻	17,040	+ve	19,420	-ve	23,870	+ve	27,550	+ve

^a From reference (35).

selectivity that occurred in complex compounds with α -amino acid ligands might be expected to be smaller than that in complexes of diamines. The easy separation of three of the four possible geometrical-optical isomers of tris- α -L-alaninatocobalt(III) by Lifschitz was considered to be the result either of a smaller free energy difference between the diastereoisomers than in trisdiamine complexes, or of a greater difference in solubility of the diastereoisomers. Others have suggested (2) that the high stability of the α -amino acid chelate ring will prevent the rearrangement of the isomers once formed. This argument is reasonable for the complexes of cobalt(III) but will not hold for the much more labile complexes of α -amino acids with nickel(II) and copper(II). It is with these labile complexes that the quantitative work has been done (10, 39, 46, 47, 68).

It is impossible to study equilibria in the trisamino-acidate complexes of cobalt(III) and rhodium(III) for several reasons (20). The principal hindrance is the extreme insolubility of one of the isomers in the alanine cobalt system, which prevents (20) the attainment of true equilibrium between the isomers. The very great solubility (20) of the trisaspartate and the trisglutamate complexes has so far prevented the complete separation of the isomers. The stability of the α -amino acid chelate rings is the other obstacle to equilibration studies. The optical rotation is unaffected by dissolution of the complexes in 50% sulfuric acid. The optical activity of Co(L-alaninate)_3 is also unaffected (20) by boiling with a trace of cobalt(II) chloride or by warming with activated charcoal at 80°. If the α -isomers, that is, the (1,2,6)-isomers, are boiled with activated charcoal they are quantitatively converted (20) to the very insoluble $\beta(+)$ -isomer. Therefore no equilibrium can be detected between the α - and β -isomers.

Certain tartrate complexes have been discussed in this section because the conformations of complexes of α -hydroxy acids bear some resemblance to those of α -amino acids.

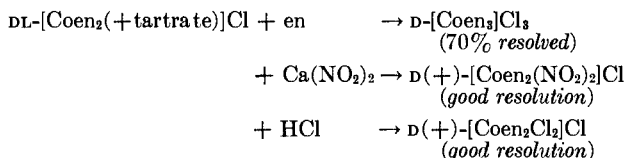
B. ONE AMINO ACID

When only one amino acid is present in a complex, little stereoselectivity is expected. For example, Lifschitz (64) made compounds of the type $[\text{Coen}_2(\alpha\text{-amino-acidate})]\text{Cl}_2$, with glycine, D-alanine, and L-leucine. They were "resolved"* with (+)bromocamphorsulfonic acid and with (+)tartaric acid. Lifschitz showed that no dissymmetric synthesis had occurred, i.e., that the amounts of D and L $[\text{Coen}_2(\text{L-amino-acidate})]^{2+}$ were equal within experimental error. Similar results were obtained by Mathieu (72). The circular dichroisms of these complexes have recently been reported

* This is not in fact a resolution, but a fractional crystallization; the resolving agent is *not* essential in separating the diastereoisomers, whose salts with inactive anions often have different solubilities.

(13) over an extended range. The optical rotatory dispersion of "racemic" (synthetic) $[\text{Coen}_2(\text{L-ala})]\text{I}_2$ changes (20) when fractional crystallization is carried out in aqueous ethanol, one diastereoisomer being less soluble than the other. This illustrates one of the difficulties of studies of stereoselectivity—the product from the reaction mixture, after recrystallization, is not representative of the reaction mixture.

A compound (57) which should be very similar to the monoamino acid complex is $[\text{Coen}_2(+)\text{tartrate}]\text{Cl}$. The two diastereoisomers were not completely separated but it was shown that the partially separated compounds had different reactivities, solubilities, and stabilities. For example, the difference in reactivity of the diastereoisomers was used (57) to give partially resolved complexes:



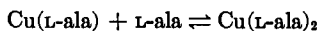
The high stereoselectivity of these reactions arose because only one of the diastereoisomers underwent reaction at room temperature. The more stable diastereoisomer, $\text{L}(+)$, was more abundant and therefore more stable than the $\text{D}(+)$ isomer. This means that there were stereoselective influences in the preparation of the complex, which is not unexpected from a polydentate ligand such as the tartrate anion. The asymmetric reactions (75) of $[\text{Co}(-)\text{pn}_2\text{glycinate}]\text{I}_2$ and $(-)[\text{Coen}_2\text{glycinate}]\text{I}_2$ have been discussed (Section II). The salt, $\text{D}(+)\text{[Coen}_2(\text{L-glutamate})]\text{ClO}_4$, is formed stereoselectively from $\text{DL-}[\text{Coen}_2\text{CO}_3]\text{ClO}_4$ and L-glutamic acid (20).

C. TWO AMINO ACIDS

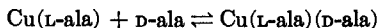
There has been a good deal of quantitative work on bis- α -amino acid metal chelates. The compounds, $\text{Cu}(\alpha\text{-amino acid})_2$, are easily prepared. They are planar and could exist as either *cis* or *trans* geometrical isomers. All the structural evidence* shows that the complexes of asymmetric amino acids have the *trans* configuration. The planar $\text{M}(\text{dl-amino-acidate})_2$ will be centrosymmetric and should therefore differ from the $\text{M}(\text{d-amino-acidate})_2$ which is not centrosymmetric. Dijkgraaf (17) claimed to have observed this difference manifested as a difference in the oscillator strength in the electronic absorption band at 620 $\text{m}\mu$. In fact, this difference is spurious, and arises because the molecular formulas of the two diastereo-

* Although a recent X-ray analysis (32) of $\text{Cu}(\text{glycinate})_2$ shows it to be a *cis* complex, and two crystalline forms of $\text{Cu}(\text{L-alaninate})_2$ and of its enantiomer have been obtained (42).

isomers are different (39). On mixing equimolar solutions of the two enantiomers, Cu(D-alanine)_2 and Cu(L-alanine)_2 , the electronic spectrum does not change. It has also been shown (39) that the stability constants, K_2 , for the equilibria



and



are equal. Bennett had previously shown (10) that the optically pure diastereoisomers were favored in an apparently similar system. He obtained the formation constants for the mixed and the optically pure diastereoisomers of copper(II) with asparagine by potentiometric titration. The values he obtained were:

$$\text{Nonmixed complex (dd or ll)} \quad K_2 = 2.82 \times 10^6$$

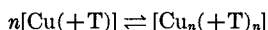
$$\text{Mixed complex (dl)} \quad K_2 = 7 \times 10^6$$

Using the contact shifts of protons in the ligands, all the isomers in certain equilibrium mixtures have been detected. By studying the systems over a temperature range, thermodynamic constants for all the species present could be obtained. This technique, of course, depends on the complex being paramagnetic and is therefore not applicable to cobalt(III) complexes. McDonald and Philips (68) studied the proton contact shifts of the cobalt(II) bishistidine complex in deuterium oxide. They found that the DD and the LL complexes had identical contact shifts. If the optically pure complexes are mixed, then new peaks appear which have larger contact shifts. Equilibrium studies showed that in this system the mixed complex is the more stable, since it is in greater concentration at equilibrium than the DD or the LL isomers. The difference (68) in free energies for the 2:1 octahedral histidine cobalt(II) complexes is 0.7 kcal/mole. Holm and his co-workers (47) studied the bis(5-methyl-*N*-sec-butylsalicylaldehyde)-nickel(II) complex. For this complex containing a Schiff base the proton contact shifts for the (+ +) and (− −) isomers were again the same, but when the optically pure complexes were mixed a new set of peaks appeared at once. These were identified as being due to the (+ −) complex. The spectrum was measured from -40° to 100° , giving thermodynamic constants for the equilibrium, planar \rightleftharpoons tetrahedral, as shown in Table V.

The bis-L-aspartic acid complex of cobalt(III) has been used to obtain partly resolved alanine from the racemic amino acid (89). Sodium bis-L-aspartatocobaltate(III) was mixed with an excess of DL-alanine at pH 9.5–10 at 20° – 40° . Activated charcoal was added to the reaction mixture. The excess alanine was removed from the precipitated tris-L- α -alaninato-cobalt(III). The alanine was 13% resolved, the D enantiomer having been

preferentially coordinated. If cellulose powder was also added to the reaction mixture, then the resolution was increased to 30%.

There is obviously a contradiction between the results (39) in the copper α -alanine system, where the stabilities of the mixed isomer and the optically active isomer are equal, and the asparagine (10) or histidine (68) system. A possible clue to the reason for this arises from the study of stereoselective effects in the copper(II) tartrate system. It was noticed by Cotton (16) that alkaline solutions of copper(II) mono(+)tartrate and copper(II) mono(\pm)tartrate were of differing blue colors. It has recently been shown (20) that this is due to polymerization, the equilibrium constant for



differing from that for

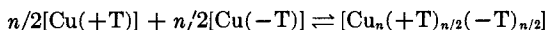


TABLE V
THERMODYNAMIC DATA^a FOR A SCHIFF BASE COMPLEX

	Complex	
	(++) or (--)	(+-)
ΔH	1,240 cal/mole	1,590 cal/mole
ΔS	1.58 e.u.	2.41 e.u.
ΔG	709 cal/mole	789 cal/mole

^a From reference (47).

Similar stereoselective effects are found (20) for vanadyl tartrate species; the common assumption that asymmetric syntheses occur in the formation of such complexes as tris(+)tartratochromium(III) is probably warranted. The stereoselective effects described above for complexes of the tridentate ligands histidine and asparagine may also possibly arise from the presence of polymeric complexes.

D. THREE AMINO ACIDS

Three molecules of bidentate α -amino acid may be coordinated to a transition metal atom in two ways to give an octahedral complex. These two geometrical isomers designated α and β (see Fig. 6) could in principle give a maximum of eight optical isomers for each geometrical isomer. However, if an optically active amino acid is used the number of isomers is limited to four, α -D(LLL), α -L(LL), β -D(LLL), and β -L(LL). Lifschitz (62) claimed to have isolated the two α -isomers and one β -isomer of tris-L- α -alaninatocobalt(III). The single β -isomer was so insoluble that he could not tell whether it was a mixture of diastereoisomers or an optically pure

compound. He also reported (63) the rotatory dispersion spectra of all four isomers of the tris-L-glutamato-cobaltate(III) anion. The salts of these are, unfortunately, very soluble, and the compounds have not so far been obtained in crystalline form. However, Lifschitz found (63) that by varying the preparative method he obtained either the two D isomers (α and β) or the two L isomers. Presumably, then, the nature of the product is kinetically determined (although there is doubt (20) about the optical purity of Lifschitz' isomers, this suggestion about kinetic control is not affected). In the same way, the ratio of the amounts of α -isomers to β -isomers in the tris-L-alaninato-cobalt(III) system depends (60, 74) on the preparative method.

No crystalline derivatives of the tris-L-aspartato-cobaltate(III) were isolated (66), and isomerism was not discussed fully. Ley found (59) that in the tris-N-methylalanine cobalt(III) system, solubility difficulties hindered the work on isomerism.

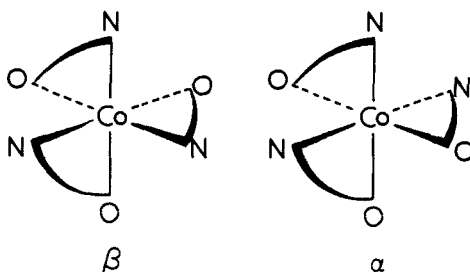


FIG. 6. The geometrical isomers of $\text{Co}(\text{amino-acidate})_3$.

The difference in free energy between the two diastereoisomers of one geometrical isomer will depend only on the interactions between the substituents on the α -carbon atom in the amino acid, because of the planarity of the carboxylate part of the chelate ring. This interaction will be greater in the optically pure (1,2,3)-isomers than in the optically pure (1,2,6)-isomers, because in the former all three substituent groups are pointing in the same direction along the threefold rotation axis (C_3 axis), while in the (1,2,6)-isomer one substituent points away from the other two and steric interference will be reduced. The steric interaction will depend on the size of the substituent on the α -carbon atom. In alanine complexes this substituent is a methyl group, in aspartic acid complexes it is a $-\text{CH}_2-\text{CO}_2\text{H}$ group, and in glutamic acid complexes it is a $-\text{CH}_2-\text{CH}_2-\text{CO}_2\text{H}$ group.

The stereoselectivity of a reaction depends on the size of the free energy difference between the diastereoisomers, which the reaction produces. If the stereoselectivity arises from the interaction of substituents on the α -carbon atom of the ligand, then it will be least in the $\alpha\text{-Co}(\text{L-alaninate})_3$

complex and greatest on the β -[Co(L-glutamate)₃]³⁻ ion of the complexes so far studied. We have shown that there is little stereoselectivity in the first complex. Lifschitz claimed (63) that there is considerable stereoselectivity in the glutamic acid complexes, but that the predominating isomer depends on the method of preparation. This is rather surprising. In our work on the Co(L-alaninate)₃ complexes we obtained (20) the optical rotatory dispersion curves of all four isomers (+) α , (-) α , (+) β , and (-) β . These isomers were optically pure. The optical rotatory dispersion of the (+) α -isomer was approximately the mirror image of that of the (-) α -isomer. The same was true of the β -isomers. The optical rotatory dispersion curves reported (66) for the (+) α and the (-) α complexes with the L-aspartic acid were also enantiomorphous. However, the optical rotatory dispersion curves, which Lifschitz reported (63) for the L isomers of the [Co(L-glutamate)₃]³⁻ complexes, appear to be very similar to the curves for the D isomers. From a comparison of the optical rotatory curves (63), which Lifschitz obtained for the glutamate complexes, with the curves obtained (20) for the Co(L-alaninate)₃ complexes, it appears that [Co(L-glutamate)₃]³⁻ isomers with the D configuration were the principal products obtained by Lifschitz in his study of this system. Stereoselectivity is therefore considerable in the glutamate complexes. A study is currently being made (42) on the corresponding complexes with valine and leucine, which also have large substituents on the α -carbon atom in the chelate ring, to see if this trend is continued.

IV. Other Ligands

Very little work has been done on stereospecific effects in complexes of ligands other than diamines or amino acids. The possible effects in complexes of such ligands as amino-alcohols or diols have been overlooked. However, some data are available (20, 65) on complexes of (+)hydroxymethylenecamphor, which acts as a β -diketone. It is certainly true that an apparently stereospecific reaction occurs with cobalt(III). The circular dichroism of a typical product shows (71a) 710 m μ , $\epsilon_l - \epsilon_d = -0.50$; 603 m μ , $\epsilon_l - \epsilon_d = +6.20$. From the relative sizes of these Cotton effects and those in fully resolved cobalt(III) complexes, it seems likely that a stereospecific synthesis has taken place, and that the product is not the 1:1 mixture of the diastereoisomers D-Co(+hmc)₃ and L-Co(+hmc)₃ that would arise in the absence of stereospecific interactions, but one or the other of them almost pure. From chromatographic work (20) it is clear that one diastereoisomer is present as ca. 95% of the mixture, so that the formation of tris(+)-hydroxymethylenecamphorato-cobalt(III) occurs with very marked stereoselectivity. This is extremely interesting, in view of the fact that the chelate rings in these β -diketonato complexes are virtually

planar, and interactions of the type discussed by Corey and Bailer (15) for puckered rings are not present. In the case of the trishydroxymethylenecamphor complexes (20) of cobalt(III) and rhodium(III), it appears that one diastereoisomer is a good deal more stable than the other. In the case (65) of $\text{Cr}(+\text{hmc})_3$, both diastereoisomers are formed, with the (+) isomer in large excess. These may be separated, but, on allowing a methanol solution of either pure diastereoisomer to stand for a day, the equilibrium mixture is again obtained.

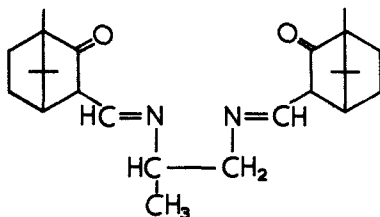


FIG. 7. Bishydroxymethylenecamphorpropylenediimine.

When hydroxymethylenecamphor condenses with propylenediamine to form the Schiff base, shown in Fig. 7, there are several diastereoisomers possible (42a, 80); calling the ligand HPH, those of interest are (+)H(+)P(+)H, (+)H(+)P(-)H, and (+)H(-)P(-)H. The complexes of these three individual tetradentate ligands are of different colors. This may be explained by differing steric requirements of the different ligands.

The only other optically active ligand which has been used at all extensively is (+)tartaric acid. For example, it is often said that when an aqueous solution of a chromium(III) salt reacts with three equivalents of (+)tartaric acid, a stereospecific synthesis occurs. It may well be true that a stereoselective process occurs, in view of the rather large Cotton effects observed for the reaction product, but it is not necessarily true. Tartrate systems are difficult to elucidate because of the presence of polynuclear complexes. This dominates (1) the tartratocopper(II) and tartratovanadyl systems, and renders dubious the stability constants measured in such systems. It is significant that solutions of the so-called "chromitartrate" ion do not obey the Beer-Lambert law, and show a strong absorption at ca. 350 m μ , suggesting the intervention of polynuclear species.

V. Conclusion

A great deal of new experimental work is required in this fascinating field. A large number of stereoselective effects is already known, but the number of these which have been explained is small. The detailed results on

amino acid and peptide complexes of cobalt(III) are only beginning to appear, and studies of metals other than cobalt are generally conspicuous by their absence. A most interesting observation (61) is that the stabilities of the complexes of cobalt(II) with L-alanyl-D-alanine differ from those with L-alanyl-L-alanine. The remarkable biochemical stereospecific effects observed include the differential action of enantiomers of complexes with living systems, and the foundations for further work on such effects are only partially laid. It has recently been shown (41) that in the nonheme iron protein isolated from clostridia and other bacteria, ferredoxin, chemical reduction by sodium dithionite in the presence of α,α' -bipyridyl gives optically inactive tris- α,α' -bipyridyliron(II) salts whereas, when the protein is treated with 8 M urea in the presence of bipyridyl, $(-)[\text{Fe}(\text{bipy})_3]^{2+}$ is formed stereospecifically.

It is said (90) that when such racemic substrates as catechin or 3,4-dihydroxyphenylalanine are allowed to react with oxygen in the presence of optically active cobalt(III) complexes, such as the $(-)$ bromoaminebis-ethylenediaminecobalt(III) cation, one hand of the substrate is oxidized very much faster than the other. The similarity of the stereoselective effects in these comparatively simple systems to those observed in enzymatic processes suggests that the behavior of optically active diastereoisomeric complexes may provide convenient models for much more complex biological systems.

REFERENCES

1. Atherton, N. M., Dunlop, J. H., and Gillard, R. D., unpublished work, 1965.
2. Bailar, J. C., *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)* **10**, 21 (1949).
3. Bailar, J. C., and Auten, R. W., *J. Am. Chem. Soc.* **56**, 774 (1934).
4. Bailar, J. C., Jonassen, H. B., and Gott, A. D., *J. Am. Chem. Soc.* **74**, 3131 (1952).
5. Bailar, J. C., Jonelis, F. G., and Huffman, E. H., *J. Am. Chem. Soc.* **58**, 2224 (1936).
6. Bailar, J. C., Kirschner, S., and Wei, Y. K., *J. Am. Chem. Soc.* **79**, 5877 (1957).
7. Bailar, J. C., and McReynolds, J. P., *J. Am. Chem. Soc.* **61**, 3199 (1939).
8. Bailar, J. C., Stieglmann, C. A., Balthis, J. H., and Huffman, E. H., *J. Am. Chem. Soc.* **61**, 2402 (1939).
9. Ballard, R. E., McCaffery, A. J., and Mason, S. F., *Proc. Chem. Soc.* p. 331 (1962).
10. Bennett, W. E., *J. Am. Chem. Soc.* **81**, 246 (1959).
11. Bijvoet, J. M., Peerdeman, A. F., and van Bommel, A. J., *Nature* **168**, 271 (1951).
12. Busch, D. H., Cooke, D. W., Swaminathan, K., and Yong Ae Im., in "Advances in the Chemistry of the Coordination Compounds" (S. Kirschner, ed.), p. 139. Macmillan, New York, 1959.
13. Chong Tan Liu and Douglas, B. E., *Inorg. Chem.* **3**, 1356 (1964).
14. Cooley, W. E., Chiu Fan Liu, and Bailar, J. C., *J. Am. Chem. Soc.* **81**, 4189 (1959).
15. Corey, E. J., and Bailar, J. C., *J. Am. Chem. Soc.* **81**, 2620 (1959).
16. Cotton, A., *Trans. Faraday Soc.* **26**, 377 (1930).
- 16a. Delepine, M., and Charonnat, R., *Bull. Soc. franc. minéral* **53**, 73 (1930).
17. Dijkgraaf, C., *Spectrochim. Acta* **20**, 1227 (1964).
18. Douglas, B. E., *J. Am. Chem. Soc.* **76**, 1020 (1954).

19. Dunlop, J. H., and Gillard, R. D., *J. Inorg. Nucl. Chem.* **27**, 361 (1965).
20. Dunlop, J. H., and Gillard, R. D., unpublished work, 1965.
21. Dunlop, J. H., Gillard, R. D., and Wilkinson, G., *J. Chem. Soc.* p. 3160 (1964).
22. Dwyer, F. P., in "Advances in the Chemistry of the Coordination Compounds" (S. Kirschner, ed.), p. 17. Macmillan, New York, 1961).
23. Dwyer, F. P., and Garvan, F. L., *J. Am. Chem. Soc.* **81**, 1043 (1959).
24. Dwyer, F. P., and Garvan, F. L., *J. Am. Chem. Soc.* **83**, 2610 (1961).
25. Dwyer, F. P., Garvan, F. L., and Shulman, A., *J. Am. Chem. Soc.* **81**, 290 (1959).
- 25a. Dwyer, F. P., Gyarfas, E. C., and Mellor, D. P., *J. Phys. Chem.* **59**, 296 (1955).
26. Dwyer, F. P., and McDermott, T. E., *Inorg. Chem.* **3**, 871 (1963).
27. Dwyer, F. P., McDermott, T. E., and Sargeson, A. M., *J. Am. Chem. Soc.* **85**, 661 (1963).
28. Dwyer, F. P., McDermott, T. E., and Sargeson, A. M., *J. Am. Chem. Soc.* **85**, 2913 (1963).
29. Dwyer, F. P., and Sargeson, A. M., *J. Am. Chem. Soc.* **81**, 5269 (1959).
30. Dwyer, F. P., and Sargeson, A. M., *J. Am. Chem. Soc.* **81**, 5272 (1959).
31. Foldi, Z., Foldi, T., and Foldi, A., *Acta Chim. Acad. Sci. Hung.* **16**, 185 (1958).
32. Freeman, H. C., Snow, M. C., Nitta, I., and Tomita, K., *Acta Cryst.* **21**, 1463 (1964).
33. Friend, J. A., and Nunn, E. K., *J. Chem. Soc.* p. 1567 (1958).
34. Garbett, K., and Gillard, R. D., *J. Chem. Soc.*, p. 6084 (1965).
35. Gillard, R. D., *Nature* **198**, 580 (1963).
36. Gillard, R. D., *Spectrochim. Acta* **20**, 1431 (1964).
37. Gillard, R. D., *Tetrahedron* **21**, 503 (1965).
38. Gillard, R. D., and Irving, H. M., *Chem. Rev.* **65**, 603 (1965).
39. Gillard, R. D., Irving, H. M., Parkins, R. M., Payne, N. C., and Pettit, L. D., *Chem. Commun.* **1**, 81 (1965).
40. Gillard, R. D., and McKenzie, E. D., unpublished work, 1964.
41. Gillard, R. D., McKenzie, E. D., Mason, R., Mayhew, S. J., Peel, J. L., and Stangroom, J., *Nature* **208**, 769 (1965).
42. Gillard, R. D., and Payne, N. C., unpublished work, 1965.
- 42a. Gillard, R. D., and Ugo, R., unpublished work, 1965.
43. Gillard, R. D., and Wilkinson, G., *J. Chem. Soc.* p. 1368 (1964).
44. Gott, A. D., and Bailar, J. C., *J. Am. Chem. Soc.* **74**, 4820 (1952).
45. Hamilton, N. H., Thesis, Illinois, 1947.
46. Holm, R. H., Dudek, G. D., and Chakravorty, A., *J. Am. Chem. Soc.* **85**, 821 (1963).
47. Holm, R. H., Dudek, G. D., and Chakravorty, A., *J. Am. Chem. Soc.* **86**, 379 (1964).
48. Hurlimann, H., Thesis, Zurich, 1918.
49. Irving, H. M., and Gillard, R. D., *J. Chem. Soc.* p. 5266 (1960).
50. Irving, H. M., and Gillard, R. D., *J. Chem. Soc.* p. 2249 (1961).
51. Irving, H. M., and Gillard, R. D., unpublished work, 1960.
52. Iwasaki, H., and Saito, Y., *Bull. Chem. Soc. Japan* **35**, 1131 (1962).
- 52a. Iwasaki, H., and Saito, Y., in "Advances in the Chemistry of the Coordination Compounds" (S. Kirchner, ed.), p. 543. Macmillan, New York, 1959.
53. Jaeger, F. M., "Optical Activity and High Temperature Measurements." McGraw-Hill, New York, 1930.
54. Jaeger, F. M., *Bull. Soc. Chim. France* **4**, 1201 (1937).
55. Jaeger, F. M., and Bijkerk, I., *Proc. Koninkl. Akad. Wetenschap. Amsterdam* **40**, 116 (1937).
56. Jaeger, F. M., and Blumendal, H. B., *Z. Anorg. Allgem. Chem.* **175**, 161 (1928).
57. Jonassen, H. B., Bailar, J. C., and Huffman, E. H., *J. Am. Chem. Soc.* **70**, 756 (1948).

58. Lewis, J., and Wilkins, R. G., "Modern Coordination Chemistry," Wiley (Interscience), New York, 1960.
59. Ley, H., and Temme, T., *Ber. Deut. Chem. Ges.* **59**, 2712 (1926).
60. Ley, H., and Winkler, H., *Ber. Deut. Chem. Ges.* **42**, 3894 (1909).
61. Li, N. C., Miller, G. W., Solony, N., and Gillis, B. T., *J. Am. Chem. Soc.* **82**, 3737 (1960).
62. Lifschitz, I., *Z. Physik. Chem.* **114**, 485 (1925); *Proc. Koninkl. Akad. Wetenschap. Amsterdam* **27**, 721 (1924).
63. Lifschitz, I., *Proc. Koninkl. Akad. Wetenschap. Amsterdam* **39**, 1192 (1936).
64. Lifschitz, I., *Rec. Trav. Chim.* **58**, 785 (1939).
65. Lifschitz, I., *Rec. Trav. Chim.* **69**, 1495 (1950).
66. Lifschitz, I., and Froentjes, W., *Rec. Trav. Chim.* **60**, 225 (1941).
67. McCaffery, A. J., Mason, S. F., and Norman, B. J., *Chem. Commun.* **1**, 49 (1965).
68. McDonald, C. C., and Phillips, W. D., *J. Am. Chem. Soc.* **85**, 3736 (1963).
69. Martinette, M., private communication to J. C. Bailar, quoted in ref. 2.
70. Martinette, M., and Bailar, J. C., *J. Am. Chem. Soc.* **74**, 1054 (1952).
71. Mason, S. F., and Norman, B. J., *Proc. Chem. Soc.* p. 339 (1964).
- 71a. Mason, S. F., *Quart. Rev. (London)* **17**, 20 (1963).
72. Mathieu, J. P., *Bull. Soc. Chim. France* [5] **6**, 873 (1939).
73. Mathieu, J. P., *Ann. Phys. (Paris)* [11] **19**, 335 (1944).
74. Mori, M., Shibata, M., Kyuno, E., and Kanaga, M., *Bull. Chim. Soc. Japan* **34**, 1837 (1961).
75. Murakami, M., and Takahashi, K., *Bull. Chem. Soc. Japan* **32**, 308 (1959).
76. Nakahara, A., Saito, Y., and Kuroya, H., *Bull. Chem. Soc. Japan* **25**, 331 (1952).
77. Nakatsu, K., *Bull. Chem. Soc. Japan* **35**, 832 (1962).
78. Nakatsu, K., Shiro, M., Saito, Y., and Kuroya, H., *Bull. Chem. Soc. Japan* **30**, 158 (1957); *Acta Cryst.* **8**, 729 (1955).
79. O'Brien, T. D., McReynolds, J. P., and Bailar, J. C., *J. Am. Chem. Soc.* **70**, 749 (1949).
80. Pfeiffer, P., Christeleit, W., Hesse, T., Pfitzner, H., and Thielert, H., *J. Prakt. Chem.* **150**, 261 (1938).
81. Philips, J. F., and Royer, D. J., *Inorg. Chem.* **4**, 616 (1965).
82. Piper, T. S., *J. Am. Chem. Soc.* **83**, 3908 (1961).
83. Piper, T. S., and Karipides, A. G., *J. Am. Chem. Soc.* **86**, 5039 (1964).
84. Popplewell, D. S., Thesis, Sheffield, 1956.
85. Quagliano, J. V., and Mizushima, S-I., *J. Am. Chem. Soc.* **75**, 6084 (1953).
86. Saito, Y., Iwasaki, H., and Ota, H., *Bull. Chem. Soc. Japan* **36**, 1543 (1963).
87. Sargeson, A. M., in "Chelating Agents and Metal Chelates" (F. P. Dwyer and D. P. Mellor, eds.), p. 183. Academic Press, New York, 1964.
88. Sen, D. C., and Fernellius, W. C., *J. Inorg. Nucl. Chem.* **10**, 269 (1959).
89. Shibata, M., Fujita, Y., Naito, M., and Hori, K., *Bull. Chem. Soc. Japan* **36**, 485 (1963).
90. Shibata, Y., *Bull. Chem. Soc. Japan* **2**, 273 (1934) and references therein.
91. Shimura, Y., *Bull. Chem. Soc. Japan* **31**, 311 (1958).
92. Smirnov, A. P., *Helv. Chim. Acta* **3**, 177 (1920).
93. Swink, L. N., and Atoji, M., *Acta Cryst.* **13**, 639 (1960).
94. Tchugaev, L., and Sokolov, W., *Ber. Deut. Chem. Ges.* **42**, 55 (1909).
95. Wentworth, R. A. D., and Piper, T. S., *Inorg. Chem.* **4**, 202 (1965).
96. Werner, A., *Helv. Chim. Acta* **1**, 5 (1918).
97. Woldbye, F., *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)* **24**, 197 (1963).

HETEROCATIONS

A. A. Woolf

Department of Chemistry, Bristol College of Science and Technology, Bristol, England

I. Introduction	217
A. Definition of Ions	218
B. Recognition of Ions	219
C. Generation of Cations	224
D. Classification of Heterocations	230
II. Cations of Nontransition Elements	233
A. Group III	233
B. Group IV	237
C. Group V	243
D. Group VI	262
E. Group VII	267
III. The Proton in Heterocations	279
A. Aqueous Solutions	279
B. Solutions in Sulfuric Acid	282
C. Solutions in Anhydrous Hydrogen Fluoride	283
D. Solutions in Liquid Hydrogen Chloride	286
E. Solutions in Fluorosulfuric Acid	287
IV. Cations with Metal-Carbon and Metal-Metal Bonding	287
V. Ions in the Gas Phase	292
VI. Heterocations in Aqueous Solution	298
A. Ion Pairing	298
B. Hydrolytic Equilibria	300
C. Structures in Solution	303
VII. Concluding Remarks	305
References	306

I. Introduction

A large part of inorganic chemistry is essentially the chemistry of ions. It follows that any review article about ions of a reasonable length cannot treat every aspect of the topic in depth. In this article some of the heterocations containing two or more different elements, and which have been studied since 1950, are considered. Only the main lines of progress, biased to some extent by the author's particular interests, can be delineated. Solvated cations are dealt with under a number of headings, the main emphasis being directed away from the solvation of simple metal cations toward those solvated cations in which the element is stabilized in an otherwise inaccessible state. While the derivation of cation structures by

direct physical methods is accentuated, their deduction from chemical reactivity, although never unequivocal, is also described. Attention is drawn to the effect of the physical method on the event being measured.

A. DEFINITION OF IONS

Every chemist "knows" what is meant by an ion but a comprehensive definition is impossible without discursive qualifications. It is inevitably linked to theoretical concepts and often to the mode of generation of the ion. Thus, in the gas phase, one can define an ion almost mechanistically as a molecule, radical, or atom from which one or more electrons have been completely separated. In practice, the ion must survive for a long enough period to be detected, which in a mass spectrometer is normally of the order of microseconds or orders of magnitude larger than vibration times of the hetero species. An even lower temporal restriction on the definition of an ion is encountered in solution when rapid exchange of charge is occurring. For example, in water the charge on the positive ion species is fluctuating rapidly and any particular hydronium cation can be regarded as having a lifetime of 10^{-12} second (87). If there is a reasonable concentration of these cations, as in a solution of a strong acid, the short life does not prohibit recognition of the species, whereas if such a short-lived entity is a reaction intermediate with a low stationary concentration, then indirect methods may be required to identify the species.

A spatial restriction on the definition is just as difficult to impose because in certain structures there is no apparent limitation to the size of the cation. In titanyl sulfate, for example, discrete sulfate ions link together infinite chains of oxygen and titanium atoms (199). At the other extreme, difficulties arise in defining cations when they are approached by anions. At some stage the composite begins to differ in physical and chemical behavior from the separate ions. There may not be a point of inflection in the observable properties, and consequently a somewhat arbitrary limit, albeit guided by theory, is set for the definition of such a complex ion. In condensed phases, even more difficult problems of definition arise when there is an incomplete separation of charge. Ideally the electron distribution should be accurately determined by experiment or, alternatively, a model of the structure calculated on wave mechanical principles using appropriate experimental parameters, so that charge distribution is measured quantitatively and the definition of an ion suitably modified. Neither approach is feasible at present. The structure of the compound ISbCl_8 as determined by X-ray analysis is a simple example. It consists of octahedral (SbCl_6) groups and angular (ICl_2) units. The former are distorted with a pair of Sb-Cl distances longer than the rest. The chlorine atoms on these bonds are weakly linked to the iodine atoms, and complete a distorted square of

chlorine atoms around each iodine. In this arrangement the structure lies between $\text{ICl}_2^+\text{SbCl}_6^-$ and $\text{ICl}_4^-\text{SbCl}_4^+$ (322).

B. RECOGNITION OF IONS

The main experimental methods applied to the detection of ions are discussed briefly in order to appreciate the particular aspect of ionicity being examined and, as important, any influence exerted by the method on the measurement.

1. *Ion Transport*

The most obvious property of an ion is the possession of unbalanced charge, which when placed in unidirectional magnetic or electric fields will undergo transport in a direction governed by the sign of charge. Thus in a time-of-flight mass spectrometer the cations move linearly in an electric field, the kinetic energy of the ion being balanced by the field energy, or in a more conventional mass spectrometer on a circular arc in a magnetic field. In both instances the cations of constant mass-to-charge ratio are collected in time or spatial sequence (205). Provided the instrument resolution is high enough, the mass of the cation and its identity are readily established, often aided by the presence of satellite peaks due to the less abundant isotopes. For many inorganic applications a low-resolution instrument suffices (56). Spurious background from extraneous material can usually be discounted by observing the effects of shielding the ion source, varying the pressure in the system, and altering the conditions of ion generation. However, only matter in the gas state can be examined; although solids and liquids can be vaporized and ionized in suitable sources, the observed ionic distribution will not correspond to that in the solid or liquid state even when the same ions are formed. The method does not provide quantitative information on the distribution of cations in liquids or solids, because of the processes required to separate ions. Nevertheless the simple ions present in liquids or solids can in general be detected qualitatively in mass spectrometers.

In liquids the presence of ions is recognized by electrical conductivity measurements, although a clear distinction is not always possible on these grounds alone. Under normal conditions even hydrocarbons are imperfect insulators, because of the natural ionizing background (195). Many ionizing solvents, such as dinitrogen tetroxide, also have very low conductivities of the same order. The full recognition of ionization in these pure liquids relies on their ability to interact with solutes to form acid or base analogs within certain limits of strength. Ionization in solids can be recognized by their dissolution and dissociation in these ionizing solvents and by the magnitude of the conductivity produced. However, the energies involved

in dissolution or solvation may be enough to provoke ionization in a solid or liquid which was un-ionized, or only partly ionic, in the crystal state. Ionization in solution or melt is not an unfailing criterion of ionization in the solid.

Conversely, the melt from an ionic solid is not always conducting. Certainly with many heterocations it is unsafe to extrapolate ionicity from one state of matter to another. The nature of the electrical conductivity has also to be considered because modes of charge transport other than by ions are possible. The temperature variation of conductivity provides this information. Ionic conductivity in the liquid state usually possesses a positive and linear temperature coefficient. The conductivity decreases sharply and discontinuously at the melting point. Electronic conduction varies exponentially with temperature without a sharp discontinuity on change of state. Ionic composition and charge have often been deduced from electrolytic transport measurements, but these results can be fully interpreted only if a complete mass balance and knowledge of the ionic equilibria are available. The meaning of transport in molten salts is less clear-cut, because there is no solvent to act as a frame of reference.

A direct influence of the method of measurement on the measurement itself has been pointed out by Wyatt (339) with respect to highly conducting liquids, such as sulfuric acid. Application of the field required to measure conductivity causes dissociation in the field direction. This effect is a result of the reduced energy difference between neutral molecules and complex of solvated ion pairs in the field direction. It has been calculated that about one third of the observed conductance in sulfuric acid is due to this asymmetrical dissociation.

Electrical conductance is in general the most widely accepted property for the recognition of ionization and, provided precautions are taken in measurement and interpretation, is a reliable indicator.

2. Interaction with Radiation

In another group of methods for identifying ions, the possession of charge is not recognized as such, but rather the geometrical groupings around a central element. The most generally applicable method is X-ray diffraction by solids. The electron distribution in the solid by cooperative scattering produces well-defined maxima, modified somewhat by physical and chemical imperfections, from the amplitude and direction of which the periodicity of the structure is deduced. The results of such analysis are presented in the form of projections contoured at equal electron intervals on particular planes through the structure. In these projections the heterocation is usually recognized as a finite group of simple shape separated from similar groups by distances greater than the distances within the group.

However, it is not possible to sum the electron density completely enough to assess the charge in a group, mainly because the observed intensities and the atomic structure factors cannot be extrapolated to zero angle of incidence (35). In the structure of solid phosphorus pentachloride (Fig. 1) distinct tetrahedral and octahedral groups of chlorine atoms around phosphorus can be seen, but recourse to our knowledge of electron configuration of atoms and theory of bonding is needed to show that the octahedral grouping cannot be a positive entity. (Auxiliary experiments, in which

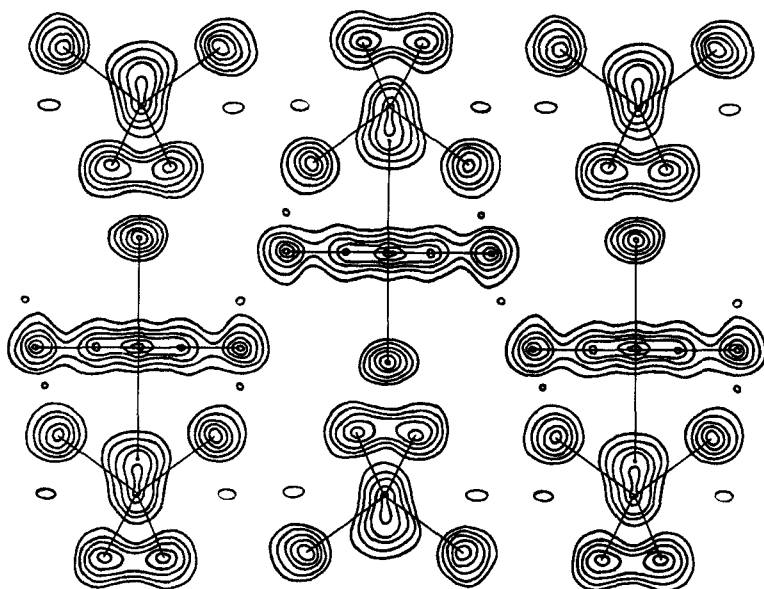


FIG. 1. Fourier synthesis on (100). Tetrahedral PCl_4 and octahedral PCl_6 groups shown by ruled lines.

the direction of electrical transport in a solvent is determined, are a useful confirmation of the polarity, but as mentioned previously due regard must be given to the power of the solvent in inducing polarity or changing the direction of polarity in borderline systems.)

X-ray diffraction has also been used to examine ions in solution. Again there is coherent scattering in preferred directions, the difference from a solid being the deduction of average distributions only, in the form of radial distribution curves because of the constant movement of atoms in the liquid. If the areas under the peaks of such curves can be resolved, it is possible to calculate the coordination around a particular atom and from a postulated structure to calculate the expected radial distribution (42). The location of hydrogen atoms is usually assumed in the X-ray diffraction

technique. The most refined measurements can reveal small inflections, or peaks, in the electron-density maps corresponding to the hydrogen positions.

Electron and neutron diffraction methods provide a surer location of hydrogen atoms and for simple geometrical arrangements the best method utilizes proton magnetic resonance (p.m.r.) (253). The last technique has been described in detail in an earlier volume (220). Briefly, by applying an oscillatory magnetic field at right angles to a permanent field in which nuclei with nonintegral spins are oriented, it is possible to induce nuclear transitions with resonant absorption of energy. The position of the transition is influenced by the surroundings of the particular nucleus, because the nucleus sees, as it were, a magnetic field which differs from the externally applied field. Electron motions near the nuclei screen the latter and produce characteristic chemical shifts. In addition, the presence of neighboring nuclei may modify the field at the central nucleus and produce characteristic fine structure in the absorption of energy. The geometrical arrangement of hetero-ions in solution is deduced by interpreting these spectra. In the solid state the interactions of like and unlike nuclei cause energy absorption over a broader field. The general shape of the absorption curve can be calculated for different geometrical arrangements, and an exact fit obtained by appropriate choice of interatomic distances. Since these factors are not completely independent, it is usual to assume an exact shape for the ion and then calculate precise interatomic distances. The dimensions of the H_3O^+ , PH_4^+ , and N_2H_5^+ ions have been found in this manner (248, 254).

The interpretation of infrared spectra, and the complementary Raman spectra, is the most generally applicable method for determining the configuration of ionic compounds, and as such has been fully described in numerous texts (e.g., 224). Again, the methods do not reveal ions, insofar as the electron distribution is not measured directly. However, similarity in distribution is readily shown by similarity in force constants and geometry in isoelectronic series, such as the tetrahedral species PH_4^+ , CH_4 , BH_4^- , or in isoelectronic pairs, such as PFCl_3^+ , SiFCl_3 ; CH_3CO^+ , CH_3CN ; NO_2^+ , CO_2 . For simple ions the shapes can be deduced quite rigorously from group theory and normal coordinate analysis, but in many instances only a partial interpretation of spectra is possible. This may arise because a species is reactive and the spectra are poor and incomplete, or theoretically because of its complexity. This partial assignment has often led to the same spectra being interpreted in different ways, by making analogies with what are regarded as corresponding compounds (112, 241). From the point of view of identifying ionic structures, much needless controversy has arisen when a structure is incompletely ionized and an equilibrium exists between ionic and molecular forms. The nondetection of ionization by examination of infrared spectra, even when clearly indicated by conductivity measure-

ments, is expected when the ionization is small. The extent of ionization when large, however, can be measured quantitatively by infrared or Raman spectroscopy (70).

3. Colligative Behavior

Ionization, besides leading to an increase in charge or a change in shape which can be detected by one of the methods described, increases the number of particles in a system and thus affects colligative properties. The depression of freezing point of dilute solutions is one of the most accurately measurable of such properties and for an ideal solution is proportional to the mole fraction of solute. Ionization is inferred by an increased depression over that calculated. In the most extensive study in recent years by this technique, the solvent employed was sulfuric acid (119). This has a considerable self-ionization, as well as internal dehydration and subsequent ionization, so not surprisingly the interpretation of ionization in this solvent has been a disputed subject. Originally the deviations from ideality were collected in a single van't Hoff factor, or ratio of the observed depression to that of an equimolecular solution of the ideal nonelectrolyte, which was identified with the number of kinetically separated particles. The factor is actually a combination of this and the interparticulate forces. Gillespie introduced another factor to represent the number of particles, quite separately from these deviations from ideality (116). The solvent ionization was repressed in earlier work, but later the ionization was allowed for by means of equilibrium constants obtained from conductivity measurements. When a solute is largely dissociated, the small value of interionic forces in this medium of high dielectric constant is neglected, and the Gillespie factor is sufficiently close to integral values to formulate stoichiometric equations with the equilibrium almost entirely on the ionic side. Certain compounds, which are nonelectrolytes according to spectrophotometric evidence, have been found to give greater depressions than expected for nonelectrolytes in sulfuric acid. This effect has been described as a salt effect since small amounts of electrolytes were also present. Other equilibrium methods, employed to investigate the successive formation of complex cations in solution, are considered later (Section VI).

4. Kinetic Behavior

Kinetic measurements rank equal in importance with equilibrium methods for identifying actual or potential ionic species in reactions, often without the need to isolate them. This holds particularly for electrophilic entities in organic substitution reactions. Thus the following kinetic results are sufficient to identify the nitronium ion as a nitrating entity: the increase in order of reaction in organic solvents to unity with increasing reactivity

of aromatic substances, the acceleration of rate by sulfuric acid and retardation by nitrate ions, and the increasing rate of nitration by specific medium effects which favor ionization (155). Closely related are some of the reactive entities in Friedel-Crafts types of reaction, such as acylations, for which most evidence suggests an acylium cation as intermediate. Some workers prefer to regard the carbonium ion as a limiting state which is not achieved before attack on the substrate commences, but nevertheless it has proved possible to isolate some of these limiting states in the form of ionic salts (230).

The kinetics of metal dissolution have also been used in a semiquantitative fashion to detect the generation of cations in a variety of solvents. The increased rate of metal solution in liquid ammonia by addition of ammonium chloride, of uranium in bromine trifluoride by addition of antimony pentafluoride, or of the same metal in nitrogen tetroxide by addition of amines, is associated with increasing "acidity" of these solvents by generation of cations.

Exchange kinetics of certain nuclei within an entity, or between entities, can be followed by observations of nuclear magnetic resonance (n.m.r.) spectra. The fine structure of a multiplet will often be resolvable only at low temperatures, because the rate of exchange at higher temperatures is sufficient to coalesce the separate peaks. Thus the F^{19} n.m.r. spectrum of sulfur tetrafluoride at -98° consists of a pair of triplets resulting from the interaction of pairs of nonequivalent fluorine atoms. As the temperature increases the spectrum is reduced to a doublet and finally a broad single peak (219). In this instance a clear decision between an intermolecular exchange via an ionization, or by association, was not possible, although the ready ionization of sulfur or selenium tetrachloride would be compatible with the former.

Kinetic methods can be applied in a negative way to disprove the existence of ions and with less certainty in the reverse way. Thus if isotopic tracers are incorporated into a solute, then a slow rate or absence of exchange with a solvent implies the absence of ionic intermediaries in the equilibria between solute and solvent. A rapid exchange allows the presence of ions, especially when supported by rate laws appropriate to a feasible exchange mechanism (312). The possibility of exchange by nonionic mechanisms, especially in heterogeneous systems, can never be neglected.

C. GENERATION OF CATIONS

1. *Ions in the Gas Phase*

The generation of cations necessarily produces species of opposite charge, which in the solid or liquid associate in stable arrays held by

coulombic forces. In the gas phase this stabilization is very limited, and it is usual to make cations by direct ejection and rapid withdrawal of electrons. The free cations are reactive entities and their reactions with molecules can be studied most conveniently by mass spectrometry, although in normal low-pressure operation such reactions are avoided. Appreciable amounts of cations are formed at high temperatures in flames or plasmas or more conveniently at ordinary temperatures in low-pressure discharges. These sources can be sampled by suitable probes and the cations examined inside the mass spectrometer. For example, the ions formed from a glow discharge in water vapor have been measured at various points in the discharge. A series of ions $\text{H}(\text{H}_2\text{O})_n^+$ ($n = 1-6$) were observed, with the H_3O_4^+ ion as a particularly stable species (170). Ion production in mass spectrometers is mainly for the purpose of identifying their precursors; stability is not particularly important, provided the ions last long enough to record their presence. The stability, and thermodynamic quantities associated with the ion, can be studied *in situ* as they are produced.

Chemical synthesis has recently been attempted with ion beams of reactive cations directed immediately after generation onto a target (305). Nitrogen dioxide at 10^{-3} to 10^{-4} torr was ionized by electron impact in a magnetron ion source. The kinetic energy and the ionizing potential of the nitronium ions were controllable. It was possible to generate milliamperage ion currents of 99% nitronium ion content with which to nitrate benzene in good yield. Although the quantities involved were only of the order of microliters, it marks a significant development in controlled ion synthesis. Other types of plasma device such as constricted arcs, high-frequency induced plasmas, and electrically assisted flames generally operate at too high a temperature to generate heterocations directly; larger ions can form only in cooler regions.

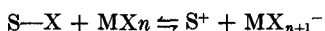
2. Ions in Solution

In the liquid state, the principal method of generating ions is by means of ionizing solvents which can directly heterolyze part of the dissolved molecule, or transfer ions from the solvent itself to generate heterocations and the associated complex anions. (The solution or melting of an ionic compound is not regarded as generation of ions in this sense because of preformation elsewhere.) The driving force is obviously the enhanced stability of a regular arrangement of oppositely charged ions aided by the relative ease of charge separation in media of high dielectric constant. The inevitable presence of large dipoles in such solvents limits their applicability because the solvent molecule tends to participate in the ion which is generated. The participation may be limited, as in solvation which helps to spread the ionic charge, or more complete in solvolysis when the ion is

replaced by a solvent species. The solvating propensity can be unequal for similar ions of opposite charge if one end of the solvent dipole is sterically hindered, as for example with dimethyl sulfoxide which tends to solvate cations preferentially (235). The heterocation can also be sterically hindered with respect to solvent participation, as in the phenyl-substituted ions $(C_6H_5)_3C^+$, $(C_6H_5)_3As^+$, etc. There are enough solvents available to strike a reasonable compromise between solvation and solvolysis and indeed for some ions the choice is very wide. The nitronium ion has been prepared in solvents as diverse as HNO_3 , H_2SO_4 , CH_3NO_2 , CH_3COOH , SO_2 , $NOCl$, HF , and BrF_3 .

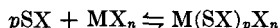
Heterocations containing halogen or oxygen atoms can usually be generated from the corresponding halide or oxyhalide by abstraction of a halide ion. The abstracting entity may be the solvent or a similar molecule, such as a Lewis acid (an electron pair acceptor), which can form a stable anion. Only wide generalizations concerning the extent of ionization and the nature of the Lewis acid are possible. It is greatest for fluorides, least for iodides; Lewis acids which can be converted to four- and six-coordinated anions are favored compared with odd coordinations. Apart from this, each ionization has to be considered individually and there is no unique order of ionizing ability for Lewis acids. (A closely related problem is that of arranging Lewis acids in order of activity for Friedel-Crafts reactions.)

In solvents of lower dielectric constant the nature of the ions generated is not always easy to assess since the processes of solvation, ionization, and dissociation are intimately linked. One approach is to consider that all ionizing solvents are parent acid-base systems analogous to water or liquid ammonia, and to regard ionization in these solvents as hydrogen ion, halide ion, or oxide ion transfers. Species which become cationic are defined as acids in the particular system. Lewis acids are fitted into this scheme as ansolvo acids which generate the system acid indirectly by combining with the solvent anion and shifting the solvent equilibrium to compensate for this, i.e.,

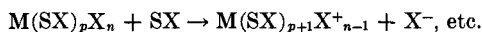


Solvation is not specifically introduced, except when it is obviously incorrect to omit the solvent molecule, as for example the solvation of a proton in acidic solvents. In organic chemistry much more attention has had to be paid to the effect of solvation because of the smaller tendency to ionization in organic systems, and recently Drago and his co-workers have re-emphasized the importance of solvation in inorganic systems. They have proposed a coordination model which focuses attention on the solvating ability of the solvent (79). Groenveld proposed much the same ideas more qualitatively (131, 133). There is in effect competition between the solvat-

ing ability of a solvent and its donor or acceptor strength. When a Lewis acid is dissolved in a solvent the primary step, according to Drago, is the formation of a solvate,

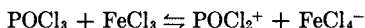


formulated with solvent around the less electronegative atom. The next stage is a stepwise displacement of the more negative group X, as an anion, by more solvent molecules:

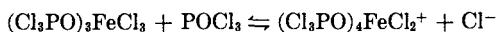
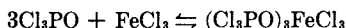


The extent of displacement depends on the overall energetics of the system. Although this can be subdivided into simple steps, not all the energy terms can be found experimentally so that only trends can be predicted.

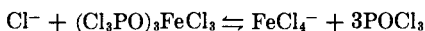
Consider the two approaches when applied to the ionization of ferric chloride in phosphorus oxychloride. On the solvent system concept, the ferric chloride becomes anionic and acts as an acid by increasing the cation content of the solvent:



On the coordination model, assuming octahedral coordination of iron, the following stages are postulated:

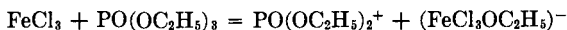


Similarly, for $(Cl_3PO)_3FeCl_2^+$ and $(Cl_3PO)_6Fe^{3+}$ cations



The theories predict different cations; in particular, on the solvent system theory all the ionized iron is expected to be anionic, whereas on the coordination theory part is cationic.

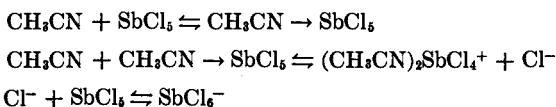
If the solvent phosphorus oxychloride is replaced by triethylphosphate, a solvent with approximately the same dielectric constant and solvating ability, the ionization of ferric chloride to the tetrachloroferrate anion still occurs, although it is no longer possible to express the ionization as a chloride ion transfer from the solvent. An equilibrium of the type



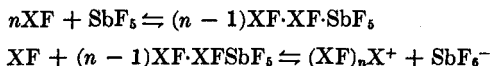
would be required. However, according to the coordination theory, substituting an ethoxy group for chlorine in the above equations leads to essentially similar products and there is no difficulty in understanding the formation of the $FeCl_4^-$ anion. In fact solvents for ferric chloride can be arranged in order of donating and solvating ability, and related to the ionization induced in ferric chloride. At one extreme, weakly donating and

solvating solvents produce mainly $\text{FeCl}_2(\text{solvent})_4^+$ and FeCl_4^- ; at the other extreme, for strongly donating and solvating solvents, only chloride ion and the solvated ferric ion are formed. There are many other examples in which solvation is essential to stabilize cations and in this respect the above theory is satisfactory.

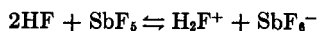
The generation of a tetrachlorostibonium ion by dissolving antimony pentachloride in methyl cyanide can also be formulated according to the coordination theory (24, 181):



However, with antimony pentahalides in halide-containing solvents, the antimony is found in the anion only. Thus a solution of antimony pentafluoride in anhydrous hydrogen fluoride behaves similarly to a solution of an alkali hexafluoroantimonate. Similarly, the antimony is anionic in fluoro-sulfuric acid and in halogen fluorides. The coordination theory has then to be formulated as

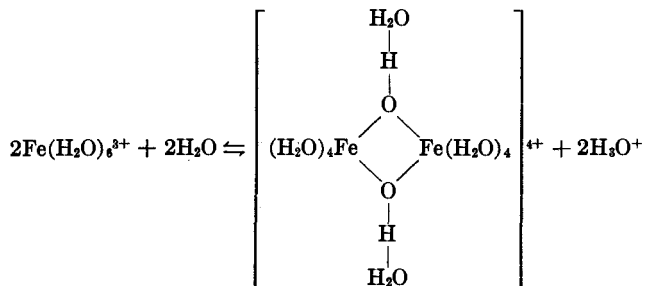


where XF is HF, BrF_3 , IF_5 , AsF_3 , which, except for the intermediate adduct, is no different in essence from the solvent system formulation. This would be given more simply, as for example in hydrogen fluoride, by



and this is to be preferred since there are strong objections against formulating an un-ionized intermediate, which is anything other than a short-lived transition state in these highly polar media.

The solvation of cations when an ionic solid is dissolved in a solvent will not be considered, but the further reactions with solvents which solvolyze these ions will be described later. Ferric ions in water, for example, are hydrolyzed to a binuclear cation (212):

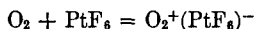


The formation of complex cations, when part of the primary solvation shell is replaced by simple anions, is similar to the above, and is studied by analogous methods. Generally a series of substituted ions coexist and it is impossible to isolate a simple species. The methods of investigation provide no information on the extent of solvent participation. Thus in the hydrolyzed ion above, the octahedral water coordination is assumed to persist from the simple solvated cation.

3. Ions in the Solid Phase

Solid ionic compounds can be generated without solvent participation by merely bringing together volatile nonionic halides and oxyhalides. Admittedly liquids such as halogenated hydrocarbons are sometimes used, but these are inert heat-transfer and collecting media which facilitate the removal of reaction heat and enable solids to be collected conveniently. Thus gaseous sulfur tetrafluoride reacts with boron trifluoride or arsenic pentafluoride to form solid trifluorosulfonium salts (286). If one of the halides or oxyhalides is reactive it can act as a halogenating agent and generate a second halide *in situ* to combine with an excess of the first component. Nitrosyl chloride behaves in this way with metals, forming the metal chlorides which then combine with excess nitrosyl chloride to produce nitrosonium salts (237). Similar reactions occur with nitril fluoride and metals (11). However, heterogeneous reactions involving solids are less efficient than solution reactions because of limited diffusion rates in solids. Higher temperatures are generally needed and heat transfer is more difficult to control. Alternative solution reactions are therefore preferable, provided solvent participation in the product can be overcome.

The majority of reactions leading to ionic solids involve ion transfers or pairwise electron transfers. It is also possible to form ionic solids by simple electron transfer or mutual oxidation-reduction. A good example is Bartlett and Lohmann's preparation of the oxygenyl ion by electron transfer between oxygen and platinum hexafluoride (20):



Other free radicals, such as NF_2^* , NO_2^* , SO_3F^* , ClO_2^* , can also interact between themselves and with halides although not necessarily to produce ionic compounds (200, 279). Nitronium perchlorate was prepared from nitrogen dioxide, chlorine dioxide, and ozone, presumably by a radical reaction (124). Reactions with metals must involve electron transfer in the initial stages, the transferred electron usually being carried off as a volatile species. Thus nitric oxide is liberated in the formation of a nitrosonium complex nitrate from nitrogen tetroxide and zinc or copper, and the fluorination of dinitrogen tetroxide and gold in bromine trifluoride to nitronium

tetrafluoroaurate liberates bromine. In the first example the dinitrogen tetroxide is cleaved unsymmetrically to form the heterocation. Other examples of unsymmetrical molecular cleavage are known; in particular the boron hydrides, such as diborane, can be ionized as $\text{BH}_2^+\text{BH}_4^-$ when the cation is stabilized by solvation.

D. CLASSIFICATION OF HETEROCATIONS

A short survey of the heterocations is now given to show their interrelation, before describing some in more detail. A purely geometrical classification is less informative than one based on the Periodic Table and a formal method of generating ions. The small stable cations are concentrated in earlier periods and toward the center of the periodic classification. There is a tendency for polymeric cations in later periods and for ion pairs with elements of metallic character. In the earlier groups the heterocations also tend to form ion pairs and simple solvated cations. In Fig. 2 these tendencies are represented diagrammatically.

Group \ Period	1	2	3	4	5	6	7
2							
3							
4							
5							
6							
7							

FIG. 2. Cations in relation to the Periodic Table.

The heterocation contains a core element and in order to attain a positive charge the surrounding elements or groups must be of greater electronegativity even if not potentially anionic. Consequently the halogens and oxygen are the main negative functions. This immediately precludes binary oxycations in Group 2; they need to be at least binuclear with respect to the core element. The other main negative species is hydrogen or an analogous group, such as the phenyl group.

Generation of cations can be started formally from carbon tetrachloride. Withdrawal of the chloride ion would leave the trichlorocarbonium cation. In practice this tendency is small in solution, because the inductive effect of three halogens on the heterolysis of the remaining bond will leave the

species with a negative charge. Thus the trifluoromethyl group tends to act as a negative substituent or pseudofluoride in many compounds. In the gas phase, however, the generation of CF_3^+ by a homolytic route is feasible and this ion is identified mass spectrometrically as a common product from the breakdown of fluorocarbons. More stable carbonium ions result when alkyl or aryl groups replace halogens. The triphenylcarbonium (trityl) ion is stabilized in numerous salts, but even here the ease of formation of free triphenylmethyl radicals shows how finely balanced are the factors leading to the carbonium ion.

The hydrogen or halogen can also be replaced by oxygen. There is evidence for the formylium cation in some reactions; other acylium or arylium cations are well authenticated. There is no convincing evidence for COCl^+ or CO^{++} , although postulated for reactions in solution. These formal relationships are summarized in Fig. 3.

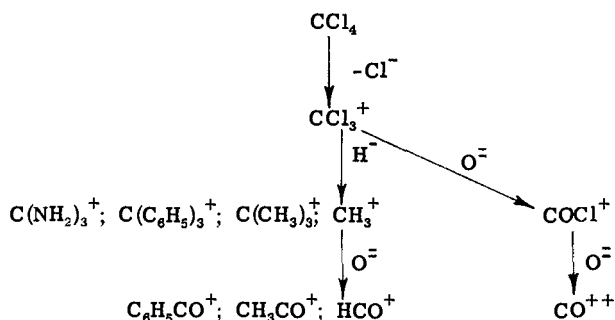


FIG. 3. Formal generation of ions from CCl_4 .

The nonclassical carbonium ions, of importance as intermediates in organic chemistry, are not discussed.

Silicon is unable to form this array of small hetero-ions, and the tendency with oxygen is toward polymeric structures as in various forms of silica or in silicones. Simple ions, SiO^+ , Si_2O_2^+ , are encountered only in the gas phase. In the subgroup polymerized oxycations are the rule; the halocations are generally monomeric (e.g., ZrF_2^{2+} , ZrF_3^+ , ZrCl_3^+).

In Group 3, boron can form simple heterocations containing hydrogen or halogen, provided the tetrahedral boron coordination is achieved with extra solvent molecules [e.g., $\text{BH}_2(\text{solvent})^+$, $\text{B}(\text{C}_6\text{H}_5)_2(\text{solvent})^+$, $\text{BCl}_2(\text{solvent})^+$]. With oxygen the tendency to three-coordination predominates and results in polymer formation. Boron oxyhalides are cyclic trimers, not salts containing BO^+ cations. With aluminum there is a greater tendency to polymeric cations, especially with oxygen, but thallium again forms dihalo and dialkyl cations.

On the other side of carbon there is a profusion of heterocations in

Group 5, which can be related to phosphorus pentachloride $\text{PCl}_4^+\text{PCl}_6^-$ by substituting elements or groups of elements for chlorine in the PCl_4^+ cation. This is shown in Fig. 4. Many other more complex phosphonium salts are known.

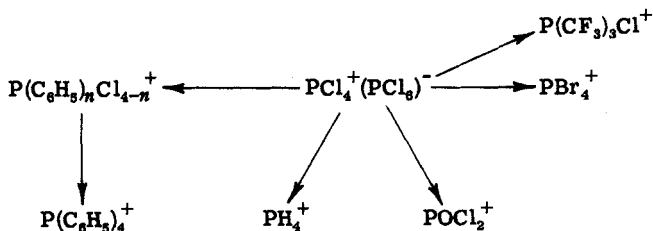


FIG. 4. Formal generation of ions from PCl_5 .

The nitrogen heterocations are less extensive in substituents if not in number of salts isolated (e.g., NH_4^+ , NO^+ , NO_2^+ , NF_2^+ , N_2F^+). Monomeric tetrahalo cations exist with As, Sb, V, Nb, Ta, as well as polyhalo cations, such as $\text{Nb}_6\text{Cl}_{12}^{2+}$, in later periods of the group. This polymeric tendency is also shown in oxygen derivatives.

In the next group, while there is only contentious evidence for sulfur and selenium oxycations, there is no doubt concerning the halo derivatives which include SeCl_3^+ , TeCl_3^+ , SeF_3^+ , SCl_3^+ , SCl^+ , S(alkyl)_3^+ . The transition elements in this group again follow the trend from the previous group in forming polynuclear oxyions and some polyhalo cations (e.g., $\text{Mo}_6\text{Cl}_6^{4+}$).

Group 7 heterocations consist mainly of the interhalogen cations and those derived from oxyfluorides (e.g., ClF_2^+ , BrF_2^+ , ICl_2^+ , $\text{I}^+(\text{solvent})$, IF_4^+ , ClO_2^+ , IO_2^+). Fluorine is too electronegative to be the core element and no fluoronium salts have yet been prepared.

The hydrogen content of heterocations so far mentioned has been electronegative. The positive side of its behavior is even more important, not in the form of the bare proton but associated with water and other protonic solvents or aromatic molecules, as $\text{H(H}_2\text{O)}_n^+$, H(HX)_n^+ , and H(ArH)^+ ions. The extensive work on this aspect of heterocations merits separate discussion (p. 279).

The principal developments in cation chemistry in the period under consideration can be summarized:

(1) Identification of cations in the gas phase relying mainly on measurement of their mass-to-charge ratio and appearance potential. Little direct information on structure can be obtained for inorganic species.

(2) Production of cations in nonaqueous systems and their isolation as salts. The mechanism of cation production in these systems is the subject of controversy concerning the role of solvation.

(3) Recognition and quantitative measurement of polynuclear complex cations in aqueous solution. The full composition of these species is unknown; they appear as a result of fitting experimental curves with a minimum number of species of different stabilities. More direct experimental methods have provided confirmation for some of these species and shown the reality of the concepts involved.

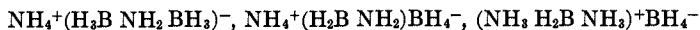
These developments are not fundamentally different in kind, in that most of the methods and theoretical background already existed. However, the correlation of structural units in the different states of matter can be regarded as novel. Thus large cation units which exist in the solid have now been recognized in the liquid and gaseous states. Presumably the same forces maintain structural integrity.

II. Cations of Nontransition Elements

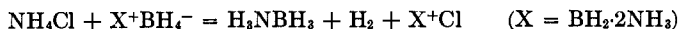
A. GROUP III

1. Boron Cations

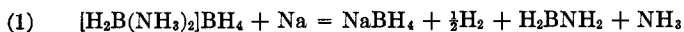
The known cations are solvated dihydro or dihalo boronium ions with tetrahedral coordination. Of particular interest are the ions derived from boron hydrides which contain hydroboro anions as well as cations. Parry and his co-workers made a thorough re-examination of the diammoniate of diborane which is admittedly saltlike, but which can be formulated in more than one way by movement of single hydrogen:



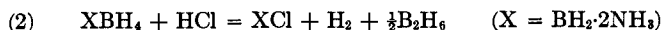
The second formula was originally adopted because ammonium borohydride is unstable; the separation of the ions was supposed to stabilize them. It was shown to be a borohydride, and not an ammonium salt, by its reaction with a slurry of solid ammonium chloride in ether. Hydrogen was evolved, a chloride, later identified as $\text{BH}_2(\text{NH}_3)_2^+\text{Cl}^-$, was isolated, and also a borine amine of only half the molecular weight of the original $\text{B}_2\text{H}_6\cdot 2\text{NH}_3$. The reaction can be regarded as a double decomposition reaction (280),



followed by breakdown of the unstable $\text{NH}_4^+\text{BH}_4^-$. Other reactions which confirmed the borohydride formulation were



a cation displacement carried out at -78° in liquid ammonia, and the anion displacement,



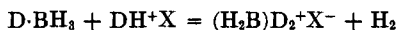
Further evidence came from tracer experiments with deuterated compounds which showed that in the sodium reduction (1) the B-H bonds in BH_4^- remained intact whereas the N-H was broken. The presence of the borohydride ion was also established by Raman spectroscopy on a solution of $\text{B}_2\text{H}_6\cdot 2\text{NH}_3$ in liquid ammonia at low temperatures.

The diammoniate of tetraborane, made by adding ammonia to a cold ethereal solution of excess tetraborane, was shown to be $\text{H}_2\text{B}(\text{NH}_3)_2^+\text{B}_3\text{H}_8^-$ by analogous methods. Thus in reaction (1) the salt NaB_3H_8 was isolated in 60-70% yield, and from reaction (2) the same XCl salt as from the diammoniate of diborane could be recovered. The B_3H_7 fragment was isolated as the etherate $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{B}_3\text{H}_7$ (171).

The crystal structure of the salt $\text{BH}_2(\text{NH}_3)_2\text{Cl}$ consists of puckered layers of chloride ions interleaved with the cations. Although the hydrogen atoms were not located the B-H distances, equal within experimental error and inclined at 106° , were consistent with a tetrahedral cation. The ammonia groups were surrounded by a distorted square of chlorine atoms with N-Cl distances from 3.39 to 3.45 Å, similar to those in ammonium chloride (226). A series of salts with the ammonia in the $\text{BH}_2(\text{NH}_3)_2^+$ cation replaced by amines has been prepared.

Unsymmetrical cleavage of diborane can also be brought about by reaction with dimethyl sulfoxide in the diluent methylene chloride at -78° . The structure of the product was shown to be $\text{BH}_2[\text{OS}(\text{CH}_3)_2]_2^+\text{BH}_4^-$ by BH_2^+ peaks in the Raman spectrum and the quintet due to BH_4^- in the B^{11} n.m.r. spectrum. The compound, however, is not stable above -33° (201). A systematic synthesis of a whole range of stable borane cations has now been achieved. Their stability is highlighted by one of the general synthetic methods carried out at temperatures up to 180° . The solvates include tertiary amines, phosphines, arsines, dialkylsulfides, as well as bidendate ligands. The salt anions include halide, polyhalide, fluorophosphate, chloroaurate, and dodecaborane anion $\text{B}_{12}\text{H}_{12}^-$. Three synthetic methods were used (215):

- (1) Base boranes + onium salt of large anions at 100° - 180° :



If the onium salt was unstable the equivalent $\text{D} + \text{HX}$ mixture was substituted.

- (2) Displacement of the solvate or base in the cation by a stronger base. This could occur simultaneously in the previous method. The displacement series found was diamines > amines > phosphines > arsines > sulfides.

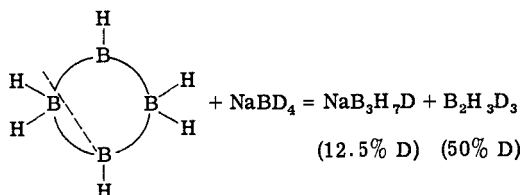
- (3) Base borane and diborane.

The cations were thoroughly characterized by the infrared spectra, by the B^{11} n.m.r. spectra, which consisted of 1:2:1 triplets expected from

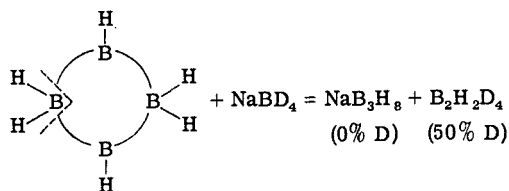
equivalent B-H bands in BH_2 , and by the retention of the base in the cation on ion exchange. Substitution reactions in the cation enable the hydrogen to be replaced. Thus SF_6Cl , NCl_3 , and aqua regia all monochlorinate, ICl dichlorinates, F_2 with nitrogen difluorinates, and F_2 with the chloride ion can chlorofluorinate. It is even possible to "fluorosulfate" with peroxydifluorosulfate $\text{S}_2\text{O}_6\text{F}_2$. The series of solvated cations of BH_2^+ , BHCl^+ , BCl_2^+ , BClF^+ , BF_2^+ , and $\text{B}(\text{SO}_3\text{F})_2^+$ is now available.

The mechanism of formation of these ions from boranes has been studied and indicates that the initial cleavage of the borane is symmetrical (236). Thus tetraborane and sodium tetradeuteroborate in ethylene glycol-dimethyl ether exchange deuterium in the amounts required by the first and not the second equation:

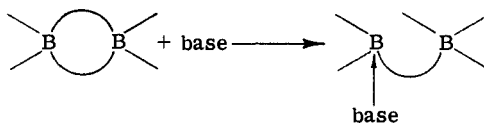
Symmetrical cleavage



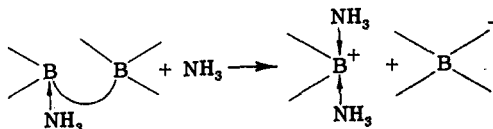
Unsymmetrical cleavage



The reaction of diborane with a base is therefore formulated as a symmetrical bridge opening followed by nucleophilic attack by a second molecule of base:



The nature of the nucleophile, and of the base already attached, decides whether the product is symmetrical or not. For ammonia the slow second step is:

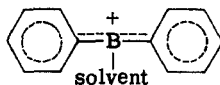
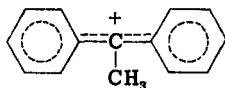


An n.m.r. examination of tetraborane in tetrahydrofuran, on the other hand, suggests an initial nonsymmetrical cleavage. At -68° the B^{11} resonances of tetraborane are observed. They disappear at -50° and at -20° are replaced by a clearly resolved septuplet with the chemical shift and coupling constants of the B_3H_8^- ion (269).

Lipscomb has discussed the possible borane ions from a topological viewpoint and indicated the possibility of purely ionic hydrides, which has now been realized. The $\text{B}_6\text{H}_{11}^+$ ion has been predicted as one of the triad analogous to the aromatic sequence (198). The cations B_3H_6^+ and $\text{B}_4\text{H}_{10}^{2+}$ were also predicted.

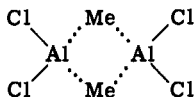
 B_4H_7^-  B_5H_9  $\text{B}_6\text{H}_{11}^+$

The cations described previously and the chelated cations of boron, with for example acetylacetone, are tetrahedral. Davidson and French (74) made a planar cation by dissolving diphenylboron chloride in methyl ethyl ketone and adding aluminum chloride. The production of ions was indicated by a 1000-fold increase in conductivity, equivalent to about 1% ionization. The ultraviolet absorption spectrum had a maximum very close to that of diphenylmethyl bromide in the presence of aluminum chloride. The correspondence of the isoelectronic π systems was taken as evidence for a planar boronium ion.

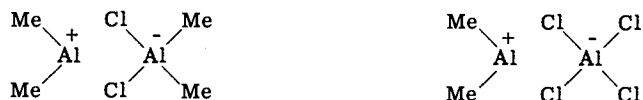


2. Other Cations in the Subgroup

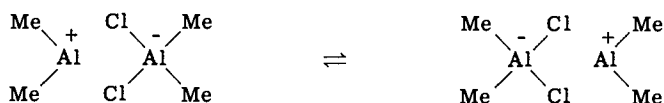
There is some evidence of cations produced by unsymmetrical cleavage of dimeric halides, or substituted halides, with other elements in the subgroup. The dimethyl- and tetramethylaluminum chlorides have been formulated with methyl bridged structures:



Glick and Zwickel maintain that the Raman spectra are consistent with ionic structures (122):

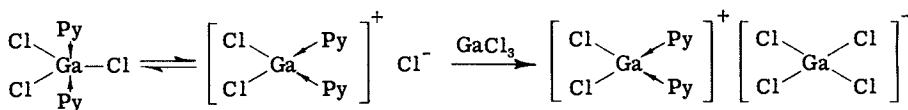


Although the methyl groups are not equivalent in the former ionic structure, they are not distinguished in p.m.r. spectra, presumably because of halogen exchange.

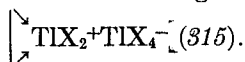


In order to obtain C_{2v} symmetry with bridging methyl groups in the tetramethyl compound the *cis* structure is required. The correct symmetry follows more naturally from the ionic formulation. The dipole moment of 1.9 D is also inconsistent with methyl bridging. This is an interesting illustration of an ion of limited life detected by Raman spectroscopy in the form of an ion pair, but not by n.m.r. because of the time scale of chlorine exchange. The dissolution of aluminum chloride in donor molecules can also induce unsymmetrical ionization. The ion pair $(\text{AlCl}_2 \cdot n\text{CH}_3\text{CN})^+ \cdot \text{AlCl}_4^-$ seems more likely than the ionization $(\text{Al}_2\text{Cl}_5 \cdot n\text{CH}_3\text{CN})^+ \cdot \text{AlCl}_4^-$ originally proposed (276).

The pyridine adducts of gallium trihalides ionize to a small extent when molten. The amount of ionization with $\text{GaCl}_3 \cdot 2\text{C}_5\text{H}_5\text{N}$ has been estimated at about 7%. The 1:1 adduct is the more stable and ionization of an initial trigonal bipyramidal adduct has been suggested (130).



Bidentate ligands on thallic halides can induce similar ionization

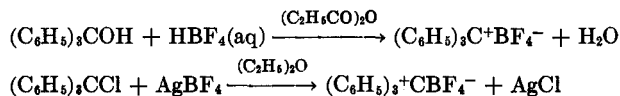


B. GROUP IV

An extensive account of recent progress in the field of carbonium ions has appeared (76), and only a few topics of more general interest are covered here.

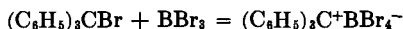
1. *Trityl and Related Cations*

Salts of the triphenylmethyl (trityl) and substituted cations are well established. They can be easily prepared by neutralization of the carbinol, or by removal of a chloride ion from trityl chloride by means of a silver salt (73). Thus for the tetrafluoroborate:



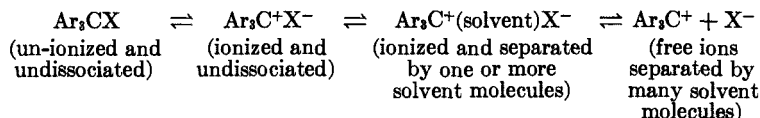
The salts of the complex fluoro anions PF_6^- , SbF_6^- , NbF_6^- , and SO_3F^- are particularly stable in the solid state. Delocalization and stabilization of charge in the trityl ion would be optimized if the ion were symmetrical and planar, but the *ortho*-hydrogen atoms on adjacent rings prevent this. A compromise propeller-like structure, with the rings tilted in sequence at 30° to each other, is indicated by both infrared and n.m.r. spectra (33). A full interpretation of the former spectra has not been carried out, but qualitatively the main features are accounted for on D_3 rather than D_{3h} symmetry. The absence of covalent bonding between cation and the anions is shown by the characteristic anion absorption bands as in alkali salts. Any distortion of these highly symmetrical ions would lead to splitting of the peaks (297).

Less stable tetrahalogenoborates have been prepared by mixing the trityl halide with the boron trihalide in nonionizing solvents, such as methylene chloride or cyclohexane. Thus



This salt is able to extract a hydride ion from cycloheptatriene to form the tropenium salt $\text{C}_7\text{H}_7^+\text{BBr}_4^-$ (138, 139).

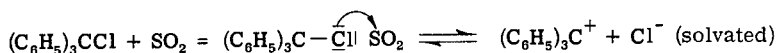
There has been a continuous interest in the ionization of triaryl methyl compounds in solvents. In particular, the distinction between ionization and dissociation, and their variation with substituents in the aromatic portion, or of the group X, has been argued:



The method of measurement employed determines which of these stages is detected. Thus conductometry detects the discrete ions in the last stage, and possibly the solvent-separated ions when the ion pairing is weak, whereas spectrophotometry, on a triaryl carbonium absorption peak, is less dependent on the cation-anion separation and both ion pair and free ion are measured.

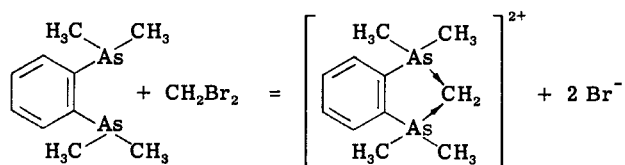
Fairbrother and Wright measured the extent of ionization spectrophotometrically when dilute solutions of arsenic tribromide in various solvents were added to trityl bromide solutions (95). The equilibrium constants for ion pair formation varied from about 0.1 to 10 as the solvent was changed from benzene to ethyl bromide. The equilibrium constants, for the stage ion pairs to separated ions, were of the order 10^{-7} to 10^{-4} in these solvents. Even in dilute solutions very few ions were free (e.g., a 0.005 *M* solution in benzene had 0.09% of free ions). With mercuric chloride in benzene there was no evidence for free ions but only for ion pairs. In nitromethane considerable ion pair formation and some dissociation have been claimed (22), but this has been disputed by Pocker (243), who detected an interaction with the solvent to form hydrogen chloride which contributed to the conductivity and color of solutions. He believes that trityl chloride is ionized in this solvent.

The displacement of chloride in trityl chloride solutions in benzene has been interpreted solely in terms of ion pair formation without dissociation (154), but generally the solvent takes a more intimate role in the ionization of trityl compounds, apart from providing a polar medium. This can be appreciated by comparing the minute dissociation of trityl chloride in nitrobenzene (dielectric constant 24.5) with its extensive ionization and dissociation in liquid sulfur dioxide or hydrogen chloride (dielectric constants 15.3 and 9.3, respectively). In the latter solvent, specific interaction by hydrogen bonding to the $(\text{Cl}-\text{H}-\text{Cl})^-$ anion is likely; in the former, while direct formation of the SO_2Cl^- anion is improbable, the existence of a charge transfer complex between the chloride ion and sulfur dioxide is shown by intensification of the electronic spectrum of the latter (196, 197), i.e.,

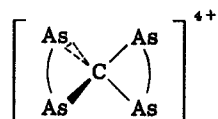


This interaction would considerably reduce the energy required for ionization.

Ionic salts of the methyl cation are not known in the solid state, but it has proved possible to make simple carbonium derivatives chelated with diarsines:

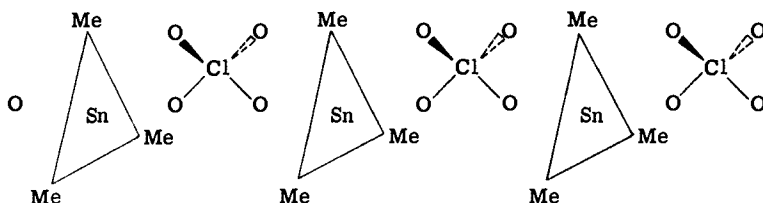


Similarly from carbon tetraiodide the chelated ion results.



Conductivity measurements confirm the cation charges (64). There is evidence mainly from n.m.r. spectra for secondary and tertiary alkyl cations produced from the corresponding fluoroalkanes dissolved in antimony pentafluoride (231). The planar $\text{C}(\text{NH}_2)_3^+$ cation has been confirmed by X-ray analysis (142).

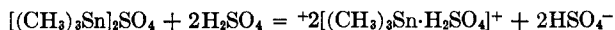
There are no corresponding stable series of triaryl cations of other Group IVb elements. Thus triphenylsilyl chloride does not ionize in nitrobenzene even in the presence of strong Lewis acids (316). Conflicting reasons have been advanced to explain this (23). (In Group IVa, delocalization of charge from metal ion to ring systems can form stable cations; these metal-carbon bonded configurations are discussed later.) The full ionicity of many trimethyltin compounds has also been disputed. These volatile solids were formulated as salts $(\text{CH}_3)_3\text{Sn}^+\text{X}^-$ where $\text{X}^- = \text{halide}, \text{NO}_3^-, \text{CH}_3\text{COO}^-, \text{ClO}_4^-, \text{BF}_4^-, \text{AsF}_6^-, \text{or } \text{PF}_6^-$. However, the perchlorate consists of planar trimethyltin groups bridged by bidendate perchlorate groups to form chains (57).



The symmetry of the perchlorate group, according to the infrared spectrum, is lowered from the T_d symmetry of the perchlorate ion to C_{2v} . A similar behavior was observed with anhydrous copper perchlorate (144). The nitrate contains a unidendate nitrate group, as distinct from the bidendate nitrate group encountered in basic beryllium nitrate, and the tin is tetrahedrally coordinated. The Raman spectra of other halides show halogen bridging between tin groups (186). This partial covalent bonding is removed on solvation. Thus the diammoniate of trimethyltin nitrate contains the free nitrate ion and is $(\text{CH}_3)_3\text{Sn}(\text{NH}_3)_2^+\text{NO}_3^-$. Tetramethylstannane dissolves in concentrated sulfuric acid with evolution of methane and ionization of the residue to a solvated trimethyltin cation:



Trimethyltin sulfate in sulfuric acid produces four particles according to cryoscopic measurements, two of which are shown to be bisulfate ions by conductivity measurements (119):



2. Acylium and Arylium Cations

The main interest in these ions has been in conjunction with their role as reaction intermediates, particularly in the Friedel-Crafts reaction for which Fairbrother's classic experiment on radioactive chlorine exchange during the acetylation of benzene provided *prima facie* evidence of acylium ions (94). Although stable salts of these ions have been isolated, a detailed examination of the infrared spectra reveals additional lines which indicate some interaction between cation and anion. Susz and co-workers examined the spectrum of acylium fluoroborate, a compound first isolated by Seel from the component fluorides in liquid sulfur dioxide (314). The lines of the fluoroborate anion appeared at frequencies close to those of potassium fluoroborate after precautions were taken to avoid formation of the anion by possible attack on the cell windows by fluoroboric acid. This acid could arise from traces of moisture and partial dissociation of the salt. A strong absorption at 2299 cm^{-1} was ascribed to the cation $\text{CH}_3\text{C}\equiv\text{O}^+$. The carbonyl frequencies in acetyl fluoride appeared at 1851 and 1879 cm^{-1} . The assignment was supported by analogy with the bands in $\text{NO}^+\text{AlCl}_4^-$ and NOCl , which occur at 2236 and 1800 cm^{-1} , respectively (108). However, a further absorption occurred at 1619 cm^{-1} and this was interpreted as a contribution from a carbonyl stretching frequency perturbed by an electron drift from oxygen to boron. Similar shifts in carbonyl frequencies occurred when ketones were complexed with Lewis acids (50). The lowering of frequencies with various Lewis acids is given in Table I; the uncomplexed ketone frequencies are in parentheses.

TABLE I
LOWERING OF C=O FREQUENCIES BY LEWIS ACIDS

Lewis acid	$\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$ (1657)	$\text{C}_6\text{H}_5\text{COCH}_3$ (1675)	CH_3COCH_3 (1710)
HgCl_2	—	18	—
ZnCl_2	—	47	—
BF_3	112	107	70
TiCl_4	144	118	—
SnCl_4	—	—	75
AlCl_3	122	120	—
FeCl_3	145	130	—
AlBr_3	142	130	85

Thus the main spectral evidence for the acetylium cation rests on the assignment of the 2300 cm^{-1} band, which appears when acetyl halides are mixed with Lewis acids, and similarly a band at 2200 cm^{-1} for arylum ions. However, Cook points out that with some complexes both of these bands are obtained. In $\text{CH}_3\text{COCl}\cdot\text{AlCl}_3$ or $\text{CH}_3\text{COCl}\cdot\text{GaCl}_3$, for example, there is a strong band at 2300 cm^{-1} and a weak one at 2199 cm^{-1} , as well as a 1616 cm^{-1} band associated with oxygen donation to the halides. He presents evidence for equating the lower frequency with the stretching frequency of CH_3CO^+ , and the higher frequency with the carbonyl stretch in a complex $[\text{CH}_3\text{CO} \cdots \text{GaCl}_3]^+\text{Cl}^-$ (67).

Among the arguments advanced are:

(1) The avoidance of postulating different coordinations, i.e., from oxygen or halogen to the Lewis acid, when the organic chloride is changed and the Lewis acid remains constant in a series, or vice versa. Complex formation always occurs with oxygen on this view.

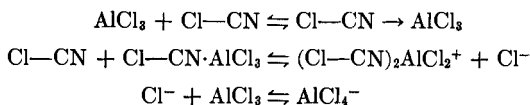
(2) The mechanism of acetylation requires a more sterically hindered entity than the small CH_3CO^+ cation.

(3) The production of aluminum at both electrodes on the electrolysis of aluminum halides in acyl halide solution.

Much further evidence is needed before the structure of these acylium salts can be satisfactorily resolved. In particular, a study of metal-halogen frequencies should indicate the validity of ionic-coordinated species suggested by Cook, or even further ionization of the Lewis acid in line with Drago's coordination theory (e.g., $[\text{CH}_3\text{COGaCl}_2]^+\text{Cl}^-$). Certainly X-ray structural data are required. The coexistence of more than one species is of course possible, e.g., an equilibrium between ionic species and donor-acceptor complexes.

The evidence for the cations COCl^+ and CN^+ relies on the ionizations induced by Lewis acid chlorides in the corresponding chlorides COCl_2 and CNCl . Solvates of aluminum chloride can be isolated from solutions in both halides (111). The analogies between cyanogen and nitrosyl halides have been discussed (333). Thus both chlorides form 1:1 compounds with AuCl_3 , BCl_3 , AlCl_3 , SbCl_5 , and FeCl_3 , and 1:2 compounds with TiCl_4 . It is therefore tempting to formulate the cyanogen chloride compounds as salts of the cyanogen cation. A comparison of the energetics of salt formation between the cyanogen and nitrosyl positive ions shows that the former is far less favorable, mainly because of the higher ionization potential to produce the cyanogen cation, and the greater dissociation energy of CN-Cl to produce the cyanogen radical. This rules out the cyanogen cation in solid compounds.

The high conductivities of Lewis acid chlorides in solution and transport of aluminum or iron to the anode on electrolysis could be explained by ionization of the solvates without involving a solvent ionization, i.e.,



and similarly for ferric chloride solutions. However, a partial polarization of the cyanogen-halogen bond, which is greater than in the formation of solvates, may be involved in Friedel-Crafts substitutions with cyanogen chloride and bromide. The solvates $\text{CNCl} \cdot \text{AlCl}_3$ and $\text{CNBr} \cdot \text{AlBr}_3$ produce cyanobenzene with benzene, and the yield increases in a more polar medium such as nitromethane (333).

C. GROUP V

The nitronium and nitrosonium cations are probably the most intensively studied of all heterocations apart from protonated species. A wide range of other hetero-ions belonging to this group has also been studied but in much less detail.

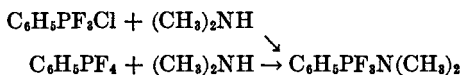
1. Halogenated Phosphonium Cations

The halogenated cations are analogous to the cation in the pentahalides of phosphorus, $\text{PCl}_4^+ \text{PCl}_6^-$, and $\text{PBr}_4^+ \text{Br}^-$. There is some evidence for the existence of all the cations listed in Table II. Reasoning by analogy with the phosphorus halides, one can expect many of their double halides to be ionized. Thus the 1:1 adducts of phosphorus pentachloride with AuCl_3 , AlCl_3 , TiCl_3 , SnCl_4 , TiCl_4 , ZrCl_4 , VCl_4 , NbCl_5 , TaCl_5 , SeCl_4 , TeCl_4 , MoCl_5 , WCl_5 , CrCl_3 , FeCl_3 , and PtCl_4 and the 2:1 adducts with SnCl_4 , ZrCl_4 , TeCl_4 , and PtCl_4 may contain these halides in anions (for references, see 286).

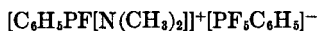
TABLE II
HALOGENATED CATIONS OF GROUP VB

$\text{PCl}_4^+ \text{BCl}_4^-$	$\text{PCl}_4^+ \text{PCl}_6^-$	$\text{PCl}_4^+ \text{SO}_2\text{Cl}^-$	$\text{PCl}_4^+ \text{F}^-$
$\text{PCl}_3\text{Br}^+ \text{BCl}_4^-$	$\text{PCl}_4^+ \text{PCl}_5\text{F}^-$	$\text{PCl}_4^+ \text{UCl}_6^-$	$\text{PCl}_4^+ \text{HCl}_2^-$
$\text{PCl}_4^+ \text{BF}_3\text{Cl}^-$	$\text{PCl}_4^+ \text{PF}_6^-$		$\text{PCl}_4^+ \text{ICl}_2^-$
$\text{PCl}_4^+ \text{AlCl}_4^-$	$\text{PCl}_4^+ \text{PCl}_5\text{Br}^-$		$\text{PBr}_4^+ \text{Br}^-$
$\text{PCl}_5\text{R}^+ \text{AlCl}_4^-$	$\text{PCl}_4^+ \text{PNCI}_3^-$		$\text{PBr}_4^+ \text{F}^-$
	$\text{PCl}_4^+ \text{SbCl}_6^-$		$\text{PCl}(\text{CF}_3)_3^+ \text{Cl}^-$
	$\text{PFCl}_3^+ \text{SbCl}_6^-$		$\text{PCl}(\text{CH}_3)_3^+ \text{Cl}^-$
	$\text{PCl}_n(\text{C}_6\text{H}_5)_{4-n}^+ \text{SbCl}_6^-$		
	$\text{PFC}_6\text{H}_5\{\text{N}(\text{CH}_3)_2\}_2^+ \text{PF}_6\text{C}_6\text{H}_5^-$		
$\text{AsCl}_4^+ \text{AlCl}_4^-$	$\text{AsCl}_4^+ \text{AsF}_6^-$		$\text{AsCl}_4^+ (2 \text{ solvent}) \text{Cl}^-$
$\text{AsCl}_4^+ \text{GaCl}_4^-$	$\text{AsCl}_4^+ \text{SbF}_6^-$		
	$\text{SbCl}_4^+ \text{SbF}_6^-$		$\text{SbCl}_4^+ \text{SO}_3\text{F}^-$
	$\text{SbCl}_4(\text{CH}_3\text{CN})_2^+ \text{SbCl}_6^-$		$(\text{SbF}_4\text{SO}_3\text{F})$
	$\text{SbCl}_4^+ \text{N}_3^-$		

Phosphorus pentachloride can exist in an ionic form in solid and solution, and a covalent form in vapor and melt. Many of the compounds listed also have such a chameleonic existence. The acylium ions described previously exhibit this tendency to a lesser extent, and are isolated in one or the other form with relatively small perturbations from an idealized structure. An extreme example of this type of "polarity isomerism" has been encountered in the substituted phosphorus pentafluoride $C_6H_5PF_5N(CH_3)_2$ (281). When freshly made by one of the following routes,

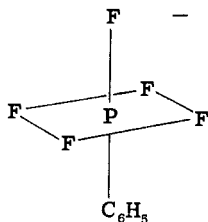


it is a liquid, boiling at 88° (6.5 torr), soluble in nonpolar solvents. The P^{31} n.m.r. spectrum consists of a doublet of triplets. This spectrum gradually alters and the liquid changes after a few weeks to a crystalline solid of the same empirical composition. The resulting solid forms conducting solutions in the polar solvent, acetonitrile. It is formulated in a dimeric ionic form,



to account for the following features of the n.m.r. spectra:

(1) P^{31} —A 1:1 doublet of the cation to the low field side of the phosphoric acid standard. On the high field side there is another doublet, caused by coupling of phosphorus to an axial fluorine atom, further split into quintets by coupling with four equatorial fluorine atoms. The similarity of coupling constant and chemical shift to that of the hexafluorophosphate anion confirms the anion structure as:



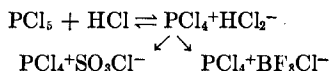
(2) F^{19} —A doublet appears for the cation, a doublet of doublets and a doublet of quintets for the anion.

(3) H^1 —A basic doublet appears in the aliphatic region caused by spin coupling of equivalent hydrogens in dimethylamino groups with phosphorus. Each component is further split by coupling to the fluorine in the cation.

The interpretation of these spectra provides an excellent example of the power of the method in structural determination. No other single method would give as much information.

Many workers have provided evidence for halogenated phosphonium, arsonium, and stibonium ions, based on conductivity, transport, and cryoscopic measurements as well as on chemical reactivity. Only a selection from this extensive work can be considered.

The ionization of phosphorus pentachloride itself has been measured in various solvents and the ions PCl_4^+ and PCl_6^- identified by transport measurements (240) and infrared spectra. A 1% solution in acetonitrile is completely ionized to unsolvated ions (325). If the PCl_4^+ ion is reasonably stable, its survival in chemical reactions in ionizing solvents could be expected. Some indication of stability is provided by the radioactive chlorine exchange between $\text{N}(\text{CH}_3)_4\text{Cl}$ containing Cl^{36} with compounds containing PCl_4^+ . The exchange is by a second order reaction of half reaction time from 1 to 19 minutes depending on concentration. The PCl_6^- ion is much less stable and exchanges too quickly to follow by a simple technique (i.e., less than 0.6 second) (179). Even in the relatively weak ionizing solvent, hydrogen chloride, neutralization reactions of phosphorus pentachloride, which is readily soluble and slightly ionized, indicate a certain cation stability (324):



The chlorosulfate is not stable enough to exist at room temperatures and resembles $\text{NO}_2\text{SO}_3\text{Cl}$ in this respect (123).

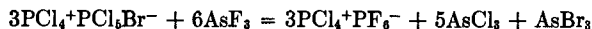
Phosphorus pentabromide dissociates in acetonitrile similarly to the pentachloride. The equivalent conductivity of these solutions varies in the normal linear way with the square root of concentration. Transport measurements show the solution ionization,



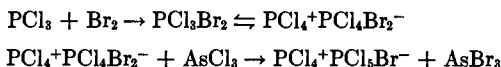
and not the ionization $\text{PBr}_4^+ \text{Br}^-$ of the solid pentabromide (140). Mixed halide systems are more complicated and the ionic species have yet to be fully delineated.

The $\text{PCl}_3\text{-Br}_2$ system forms compounds at 1:2 and 1:9 proportions. The latter has been equated with a polybromide $\text{PCl}_3\text{Br}^+[\text{Br}(\text{Br}_2)_8]^-$ by conductivity and transport measurements (141). However, Popov was unable to find simple phases and isolated a solid of composition $\text{PCl}_{4.67}\text{Br}_{0.33}$ which had a unit cell containing $\text{P}_{12}\text{Cl}_{56}\text{Br}_4$ (244). This suggested a packing of 8PCl_4^+ , 4PCl_6^- , and 4Br^- ions. Payne provided cryoscopic evidence for undissociated molecules $\text{PCl}_3(\text{Br}_2)$ and $\text{PCl}_3(2\text{Br}_2)$ in equilibrium with small amounts of unspecified ionic species. A simpler product was isolated by employing arsenic trichloride as an ionizing medium with equimolecular proportions of phosphorus trichloride and bromine (178). A yellow high

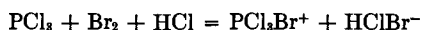
melting solid of composition $\text{PCl}_{4.5}\text{Br}_{0.5}$ was isolated which ionized in acetonitrile, and decomposed to pentahalides in carbon tetrachloride. The structure $\text{PCl}_4^+\text{PCl}_5\text{Br}^-$ was preferred to $\text{PCl}_3\text{Br}^+\text{PCl}_6^-$ because of the retention of the PCl_4^+ ion on fluorination with arsenic trifluoride:



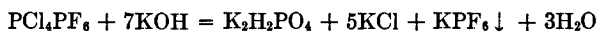
The suggested mechanism was:



The compound $\text{PCl}_{4.67}\text{Br}_{0.33}$ was believed to be a decomposition product of this salt. The heterocation PCl_3Br^+ has been isolated (323) as a tetrachloroborate by the addition of boron trichloride to the ion in liquid hydrogen chloride preformed according to:



The compound $\text{PCl}_4^+\text{PF}_6^-$, which appears in one of the above equations, was prepared quantitatively by the action of arsenic trifluoride on phosphorus pentachloride dissolved in arsenic trichloride (173). It is a white solid which sublimates at 135° and is sparingly soluble in arsenic trichloride. It is quite different in properties from the covalent isomer PCl_2F_3 (boiling point 8°) and the ionic nature is shown by its solubility and conductivity in acetonitrile. This is confirmed by the hydrolysis reaction,



in which the hexafluorophosphate ion in the precipitate could hardly be generated by an aqueous solution and must already exist in the compound. The compound $\text{AsCl}_4^+\text{PF}_6^-$, which can be prepared similarly, has an isomorphous structure according to the X-ray powder patterns (174). The simpler tetrachlorophosphonium fluoride is obtained impure when the hexafluorophosphate is decomposed thermally in suspension (176) in arsenic trichloride, or pure by thermal decomposition of the solid under reduced pressure. The reaction can be reversed with phosphorus pentafluoride:



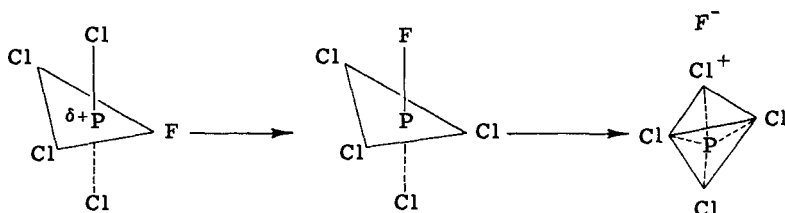
However, some PCl_2F_3 is also formed in the reverse reaction since equilibration between the forms is kinetically controlled. This is also illustrated by melting the ionic form to the covalent liquid which slowly reverts to the ionic solid, the rate being apparently dependent on the nucleating surface.

The kinetics of the exchange between covalent and polar forms has been followed quite simply by distilling off the volatile PCl_4F *in vacuo*

after holding at constant temperature for various times (176). The variation of the first order rate constant with temperature was given by

$$\log K = 4.37 - 10.6/RT$$

where the activation energy is in kcal/mole. At room temperatures the half-life of the covalent form is about 35 hours. The suggested reaction mechanism was by partial ionization of an apical chlorine, followed by exchange of the equatorial fluorine with the other apical chlorine and a simultaneous movement of phosphorus from equatorial plane to tetrahedral position:



The rate-determining step has not been deduced and there is only indirect evidence for the position of fluorine. Thus the apical position of chlorine atoms in PF_3Cl_2 has been shown by electron diffraction, and the reason suggested for its inability to transform to the $\text{PCl}_4^+\text{PF}_6^-$ isomer was the high activation energy which would be needed for the movement of three fluorine atoms to generate a PCl_4^+ cation. The corresponding trifluoromethyl derivatives behave similarly (see below). Thermochemical measurements on these and related systems would be interesting, especially if the activation energies can be related to energy differences between "polarity" isomers. The ionicity of the compound PCl_4^+F^- follows from the enhanced conductivity of solutions in acetonitrile, from a cryoscopic determination of molecular weight in acetic acid, and from the absence of hexafluorophosphate in the hydrolyzate. The corresponding PBr_4^+F^- is also known (177). It is made by keeping a mixture of PBr_2F and bromine below -30° when the molecular PBr_4F changes to the ionic form, a solid decomposing at 87° and forming a conducting solution in acetonitrile. The molecular form decomposed to a mixture of phosphorus pentachloride and pentabromide at room temperatures.

There is one other compound apart from the phosphorus pentahalides for which there is direct X-ray structural evidence for a tetrahalophosphonium salt. This is the compound IPCl_6 , which crystallizes from iodine monochloride and phosphorus pentachloride in carbon disulfide or tetrachloride. The structure consists of tetrahedral PCl_4^+ and linear ICl_2^- ions. The I-Cl distance of 2.36 Å can be compared with the distance 2.34 Å for

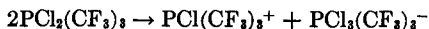
I-Cl in $N(CH_3)_4^+ICl_2^-$ (345). By analogy the other iodine monohalide adducts, $PCl_5 \cdot IBr$, $PBr_5 \cdot ICl$, and $PBr_5 \cdot IBr$, may also contain phosphonium ions.

There is evidence for the PCl_4^+ ion in solution when the double halide $UCl_5 \cdot PCl_5$ is dissolved in phosphorus oxychloride (234). On electrolysis phosphorus tri- and pentachlorides form at the cathode, and chlorine together with a material containing uranium ($2UCl_4 \cdot UCl_5 \cdot 6POCl_3$) at the anode. The low solubility of the compound in toluene (0.014 gm/100 ml) compared with phosphorus pentachloride (6.72 gm/100 ml), and the removal of phosphorus pentachloride in excess of the 1:1 compound from $UCl_5 \cdot 2PCl_5$ and $UCl_5 \cdot 3PCl_5$ by refluxing with toluene, indicate a stability compatible with an ionic salt.

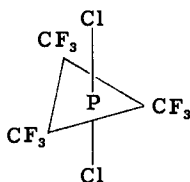
An ionic structure $PNCl_3^+PCl_4^-$ has been proposed for the compound P_2NCl_7 formed by the reactions $N_4S_4 + PCl_3$ or $(PNCl_2)_3 + PCl_5$ without compelling favorable evidence (132).

Later work has shown the compound to be a dimeric salt $\{PCl_2-(NPCl_2)Cl\}^+PCl_6^-$. The n.m.r. spectrum supports this conclusion (25). A similar compound P_3NCl_{12} , prepared from phosphorus pentachloride and ammonium chloride in polar solvents at low temperatures, has the structure $(PCl_3=N=PCl_3)^+PCl_6^-$ (26). These compounds are ionic intermediates in the polymerization of phosphonitrilic chlorides (233).

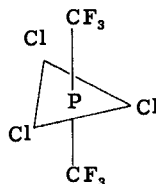
Trifluoromethyl-substituted phosphonium ions have been postulated to explain the conductivity of the substituted pentahalides $PCl_2(CF_3)_3$ and $PBr_2(CF_3)_3$ in acetonitrile or nitromethane (90):



The conductivities of these solutions slowly increase to a maximum, again illustrating kinetic control in the transformation. The corresponding disubstituted compound, $PCl_3(CF_3)_2$, is a nonconductor in solution. The possibility of ionicity in these compounds has been related to their configurations. If the chlorine is in an apical position of the trigonal bipyramidal structure it can ionize by heterolysis. The trifluoromethyl group in this position has no tendency to ionize as CF_3^- .



(a)



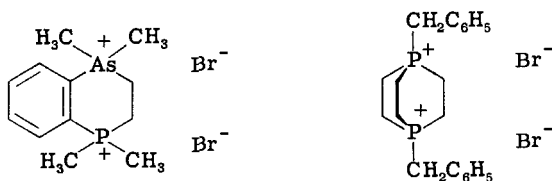
(b)

The C-F stretching frequency observed in the infrared spectrum provides some evidence for apical trifluoromethyl groups in structure (b) (91).

This type of argument is no longer convincing in view of the recently determined structure of $\text{PF}_3(\text{CH}_3)_2$ in which the methyl groups are in equatorial positions (19).

2. Other Phosphonium Cations

Alkyl- and aryl-substituted phosphonium ions have been known for many years. The synthesis of optically active compounds by differently substituting each tetrahedral position in a cation was the classical method of proving a tetrahedral configuration before X-ray structural analysis had been fully developed. A comprehensive summary of quaternary phos-



phonium salts should be consulted for details (222). Doubly charged cations in which phosphorus or phosphorus and arsenic are linked can be isolated, but salts such as $\text{PCl}_3\text{R}^+\text{AlCl}_4^-$ are more typical examples. They are made according to the reaction:



Their ionicity is evidenced by their high melting points, the hydrolyses $\text{PCl}_3\text{R}^+ + \text{OH}^- \rightarrow \text{RPOCl}_2 + \text{HCl}$, and the anodic transport of aluminum and cathodic formation of RPOCl_2 by electrolysis in methylene chloride solution (150).

A series of phosphonium salts, which span the halogen and organo-substituted salts, have recently been prepared (262) by employing antimony pentachloride simultaneously as a chlorinating agent and a Lewis acid:



The intermediate $\text{R}_3\text{P}^+\text{SbCl}_6^-$ was not always isolatable. Evidence for ionicity is provided by the high melting points of these compounds, and the equivalent conductivities in nitrobenzene solutions similar to those of quaternary ammonium salts. Spectral evidence for the structure $\text{PCl}_3\text{F}^+\text{SbCl}_6^-$ is provided by the F^{19} n.m.r. spectrum, for which the coupling constant $J_{\text{P-F}}$ interpolates in the expected position for tetrahedral hybridization in the series:

PF_3	PCl_3F^+	PF_5	PF_6	
1441	1294	916	710	cycles/sec

The infrared spectrum shows the resemblance of PCl_3F^+ to the isoelectronic molecule SiCl_3F .

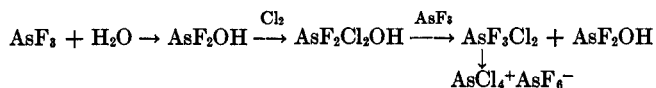
The simplest of the nonhalogenated ions is the tetrahydrophosphonium ion, for which a more complete assignment of infrared and Raman spectra is possible. This ion is the end member of the isoelectronic triad AlH_4^- , SiH_4 , PH_4^+ in which the stretching force constants are inversely related to the cube of the bond lengths (330). Tetrahalogenoborates of the same cation can be isolated from liquid hydrogen chloride. Their infrared spectra confirm the presence of a PH_4^+ ion (324). A less complete assignment is possible with the trimethylphosphine dihalides, which have C_{3v} symmetry and ionize as $(\text{CH}_3)_3\text{PX}^+\text{X}^-$ (126).

3. Arsonium Cations

The tetrachloroarsonium cation is stabilized in many compounds which can be formally represented as double halides with arsenic pentachloride. The latter has never been isolated so that the analogy with PCl_5 cannot be carried over to a salt $\text{AsCl}_4^+\text{AsCl}_6^-$. The patent instability of arsenic pentachloride, and the hexachloroarsenate ion, among Group Va pentahalides must arise from competing factors (300). In contrast, the salt with the hexafluoroarsenate ion is stable. It was first prepared by Kolditz, who passed chlorine through arsenic trifluoride (172). A compound of empirical composition AsCl_2F_3 separated after some hours from the saturated solution. The compound gave conducting solutions in arsenic trifluoride. The presence of the hexafluoroarsenate cation in the compound was inferred from the hydrolysis reaction,



since it could be separated as the well-known "nitron" salt. The slowness of the chlorination of arsenic trifluoride was explained subsequently when it was found that the dry trifluoride would not react with chlorine (78). At least 2.5% water was required in the trifluoride to initiate the reaction. The reaction time of 8–10 hours found at this level of water was about twice that encountered by Kolditz. The period decreased to 1/3–1/2 hour at 11% water content. The initiating species was believed to be AsF_2OH , which is susceptible to chlorination since the polarizing effect of the fluorine atoms on the arsenic "inert pair" is decreased:

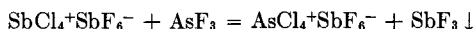


It is possible to prepare pure $\text{AsCl}_4\cdot\text{AsF}_6$ from the trifluoride and chlorine in arsenic trichloride as a solvent. The corresponding bromine compound $\text{AsBr}_4^+\text{AsF}_6^-$ could not be isolated. Again there was no reaction between

dry arsenic trifluoride and bromine. In the presence of water, reaction occurred with the formation of arsenic acid, arsenic tribromide, and hexafluoroarsenic acid. The explanation advanced was that further hydroxylation of the arsenic trifluoride was required before reaction took place with the weaker oxidant, bromine (77). The tetrachloroarsonium cation probably exists in the double halides made by passing chlorine into solutions of phosphorus or antimony pentachlorides dissolved in arsenic trichloride.

The double halides $\text{PCl}_5 \cdot \text{AsCl}_5$ and $\text{SbCl}_5 \cdot \text{AsCl}_5$ were believed to contain AsCl_4^+ cations rather than AsCl_6^- anions. This type of reaction was examined systematically with a series of halides in the expectation that the solution conductivity would increase sharply if a salt formed on chlorination, and would then level out when the solution was saturated. Such behavior was found with AuCl_3 , AlCl_3 , GaCl_3 , SnCl_4 , TaCl_5 , and FeCl_3 . The stability of the salts was judged by following the decrease in conductivity when molecular chlorine in equilibrium with the solution was displaced with nitrogen. The stability order was $\text{AlCl}_3 > \text{GaCl}_3 > \text{TaCl}_5 > \text{FeCl}_3 > \text{AuCl}_3$. Compounds of the first two were isolated and can be reasonably formulated as $\text{AsCl}_4^+ \text{AlCl}_4^-$ and $\text{AsCl}_4^+ \text{GaCl}_4^-$ (184).

The stable hexafluoroantimonate has been prepared by a displacement reaction:



The presence of the SbF_6^- ion was shown by precipitating the nitron salt of the acid HSbF_6OH from the hydrolyzate in the same way as from an aqueous solution of KSbF_6 (182). The conductivity in arsenic trifluoride and the cryoscopic molecular weight confirmed the dimeric ionic formula.

The stabilization and ionization of arsenic pentachloride with donor ligands have been suggested. Thus, chlorinating arsenic trichloride in the presence of triphenyl- or trimethylphosphine oxides produces $(\text{AsCl}_5)_2 \cdot \text{OP}(\text{C}_6\text{H}_5)_3$ and $\text{AsCl}_5 \cdot \text{OP}(\text{CH}_3)_3$ (277). The former slowly evolved chlorine. The ionization $\text{AsCl}_4[\text{OP}(\text{C}_6\text{H}_5)_3]_2^+ \text{Cl}^-$ was proposed, in which stabilization arose from the ligand bonding.

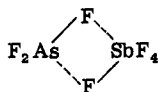
Quaternary organoarsonium salts are well known. The detailed structures of some tetraphenylarsonium salts have been determined by X-ray analysis. In the tetrachloroferrate (344), tetrahedral FeCl_4^- groups are packed together with cations in which the phenyl groups are rotated about the C-As axes, thus reducing D_{2d} symmetry encountered in $\text{As}(\text{C}_6\text{H}_5)_4^+ \text{I}^-$ (306). Tetrahydroarsonium ions have also been investigated (147).

4. Trivalent Arsenic Cations

Arsenic trichloride functions as an ionizing solvent for chlorides; the proposed self-ionization is



with the ionic product less than 10^{-9} . A conductometric titration of $\text{N}(\text{CH}_3)_4\text{Cl}$ with SbCl_5 to form $\text{N}(\text{CH}_3)_4^+\text{SbCl}_6^-$ provides some evidence for AsCl_2^+ in solution (135). Stabilization of this cation can be achieved by adding pyridine to arsenic trichloride. The moderately conducting solution that results can be titrated conductometrically with halides which behave as "acids" in this system, and this has been explained in terms of the ion pair $(\text{C}_5\text{H}_5\text{N})\text{AsCl}_2^+\text{AsCl}_4^-$. Similar evidence from conductometric and potentiometric titrations in arsenic tribromide has been advanced for the AsBr_2^+ cation (159). The self-ionization of arsenic trifluoride is of a higher order (338), and a number of stable salts M^+AsF_4^- , containing the anion formed on self-ionization, have been isolated (218). The existence of simple AsF_2^+ ions has yet to be proved conclusively in, for example, the compound $\text{AsF}_3\cdot\text{SbF}_5$ made from the conducting solution of SbF_5 in AsF_3 .

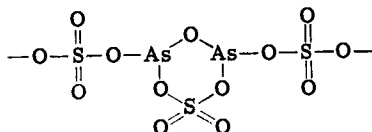


The F^{19} n.m.r. spectrum of this solution has one concentration-dependent peak between that of the component fluorides, indicating fluorine exchange between nonequivalent sets of fluorine atoms (218). On a statistical basis it seems that the As-F bond must ionize more frequently than an Sb-F one to obtain exchange equivalence via a bridged structure. This can be regarded as evidence for a short-lived AsF_2^+ ion in solution. Suitable ligand addition should stabilize this ion and enable stable salts of the cation to be isolated.

An oxycation may exist in dilute solutions of arsenious oxide in sulfuric acid. By analogy with nitrogen trioxide, it should form six particles according to:



A limiting value of 5.99 was obtained cryoscopically which decreased to 4.79 with increasing concentration, indicating a shift toward unionized AsOHSO_4 (118). This removal of bisulfate ions, the main current carrier, was shown by a drop in conductivity. The above measurements cannot distinguish the bare AsO^+ ion from its solvated forms such as $\text{HO}-\text{As}^+-\text{SO}_4\text{H}$ or $\text{H}_3\text{O}^+-\text{As}(\text{SO}_4\text{H})_2$. The species which finally separated from solution of empirical composition $(\text{AsO})_2\text{SO}_4$ were polymeric, possibly with six-membered rings as structural units:

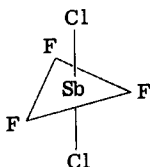


They cannot be regarded as simple arsenyl sulfates.

5. Stibonium Cations

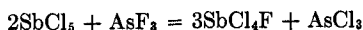
The SbCl_4^+ ion can be generated from antimony pentachloride by solvation or displacement reactions. Thus the pentachloride forms a conducting solution in acetonitrile. The infrared spectrum has a peak identical with that of pyridinium hexachloroantimonate in the same solvent which serves to identify the SbCl_6^- ion. The cation could not be identified. In the solid adduct $\text{SbCl}_5 \cdot 2\text{CH}_3\text{CN}$ there are bands which can be attributed to *trans*-(CH_3CN) $_2\text{SbCl}_4^+$ ions and these are the probable cations in solution (24, 181). It has been pointed out that the Raman spectrum of the pentachloride shows that the antimony is not exactly in the equatorial plane of the trigonal bipyramid, and this indicates an incipient ionization toward SbCl_4^+ .

Antimony trifluoride reacts with chlorine to form the solid SbF_3Cl_2 , which forms a conducting solution in arsenic trifluoride of the same order of conductivity as $\text{AsCl}_4^+\text{AsF}_6^-$ solutions. The molecular weight determined in the same solvent corresponded to the monomeric composition. The minute conductivity in the melt was associated with a reversion of ionic to a homopolar form (180). However, the infrared and Raman peaks of the same substance prepared from SbCl_5 and chlorine monofluoride (actually ClF_3 and excess Cl_2) show a close resemblance to the corresponding peaks of SbF_5 and SbCl_5 . The structure suggested was



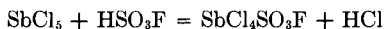
An ionic structure $\text{SbCl}_4^+\text{SbF}_6^-$ was rejected in both solid and liquid states (75). Presumably a small amount of ionization or even of asymmetry in the structure, not detectable in the above measurements, would lead to a fuller ionization in the solvent arsenic trifluoride. (Choice of solvents is restricted for this compound because of its reactivity.)

Fluorination of SbCl_5 with AsF_3 , a milder fluorinating agent than ClF , replaces a single chlorine (175):



The monofluoride sublimes *in vacuo* and melts with decomposition at 83° . The compound formulated as $\text{SbF}_5(\text{SbCl}_5)_3$ in the SbF_5 - SbCl_5 system is probably an impure form of $\text{SbCl}_4^+\text{F}^-$. The ionic nature of the compound was demonstrated by a molecular weight of 138 in arsenic trifluoride and the electrical conductivity in AsF_3 solutions. In contrast, solutions in sulfuryl chloride are nonconducting and the molecular weight is that for undissociated SbCl_4F .

Antimony pentachloride reacts with fluorosulfuric acid (146) analogously to the displacement reactions of alkali or alkali earth chlorides which form ionic fluorosulfates:



The ionization of the product has not been studied but it seems improbable that it should be a simple ionic salt. The corresponding fluorinated derivative $\text{SbF}_4\text{SO}_3\text{F}$ prepared from the pentafluoride and sulfur trioxide is a polymeric liquid in which SO_3F groups act as bridging elements. This was shown by n.m.r., infrared, and Raman spectra (120). The fluorosulfate group resembles the perchlorate and nitrate groups in the ability to behave as a bidentate ligand, and for this reason many compounds which appear to be ionic fluorosulfates are more likely homopolar compounds.

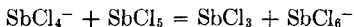
A sulfate has been prepared from SbCl_5 and SO_3 which, in spite of formulation as $(\text{SbCl}_4)_2\text{SO}_4$, may be polymeric (5).

6. Trivalent Antimony Cations

Antimony trichloride is an efficient solvent for many inorganic and organic compounds and in the usual way the self-ionization



is postulated, and supported by conductivity measurements and "neutralization" reactions (160). Thus certain Lewis acid chlorides such as AlCl_3 , SbCl_5 , or TeCl_4 are supposed to generate increased amounts of the SbCl_2^+ cation. However, the neutralization reactions can be interpreted by a direct chloride ion transfer from the highly ionized tetrachloroantimonate ion without postulating the SbCl_2^+ ion in appreciable amounts:



The SbCl_4^- ion is abnormally mobile compared with SbCl_6^- in the solvent (245). No solid compounds containing authenticated SbCl_2^+ ions are yet known.

The oxyocations of antimony are polymeric and simple SbO^+ ions exist only in the gas phase. For example, antimonyl chloride (SbOCl) consists of infinite puckered sheet cations $(\text{Sb}_6\text{O}_6\text{Cl}_4)_n^{2n+}$ held together by chloride ions (86). In other oxyhalides, layer and chain cations such as $(\text{Sb}_4\text{O}_5)_n^{2n+}$ and $[\text{Sb}_4\text{O}_5(\text{OH})]_n^{n+}$ appear (85).

7. Nitrosonium Ions

The nitrosonium and nitronium ions have been authenticated in solids and a variety of liquids during the period under review, but only a partial survey of the main lines of investigation can be presented here. Reviews on the chemistry of the nitrosyl group summarized evidence for the nitro-

sonium ion (2, 284). Spectroscopic and other evidence for the nitronium ion has been summarized more recently (227).

There are a number of general methods now available for generating nitrosonium ions either from nitrosyl halides or nitrogen oxides:

(1) Nitrosyl chloride reacts with Lewis acids chlorides to form double halides. The nitrosyl chloride is reactive enough to form many of the metal halides *in situ* from the metals, which then react further with excess of nitrosyl chloride (237). Nitrosyl chloride (47) or hydrogen chloride (323) can be used as ionizing solvent in these reactions. The compounds are listed in Table III [for references see (283)].

TABLE III
NITROSYL CHLORIDE ADDUCTS

MCl _n in MCl _n NOCl				
CuCl	ZnCl ₂	BCl ₃	AsCl ₃	UO ₂ Cl ₂
AuCl ₃	HgCl ₂	AlCl ₃	SbCl ₃	MnCl ₂
		GaCl ₃	SbCl ₅	FeCl ₃
		InCl ₃	BiCl ₃	
		TiCl ₃		
MCl _n in MCl _n 2NOCl				
SnCl ₄	TiCl ₄	FeCl ₃	PdCl ₂	
PbCl ₄	ThCl ₄		PtCl ₄	

(2) Double fluorides are formed in a similar fashion from the reaction of nitrosyl fluoride with metals (308), but a more convenient procedure is to generate the component fluorides in bromine trifluoride and allow them to interact in this solvent. Any material can be used as the starting material if it can be solvolyzed to a soluble fluoride in bromine trifluoride (331). Thus nitrosyl chloride or nitric oxide serves as a source of nitrosyl fluoride, and metals, oxides, oxyhalides, or halides as sources of other fluorides. The nitrosyl complex chlorides can also be fluorinated. The double fluorides listed in Table IV have been prepared via bromine trifluoride.

TABLE IV
NITROSYL FLUORIDE ADDUCTS PREPARED VIA BrF₃

MF _n in MF _n NOF					
AuF ₃	BF ₃	PF ₅	VOF ₃	MoF ₅	BrF ₃
		AsF ₅	VF ₅	MoF ₆	
		SbF ₅	NbF ₅	WF ₆	
			TaF ₅	UF ₆	
MF _n in MF _n 2NOF					
SiF ₄	SnF ₄	MnF ₄	IrF ₄		
GeF ₄	TiF ₄		PtF ₄		

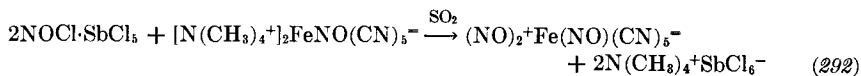
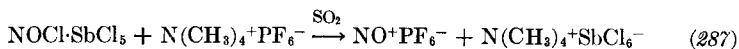
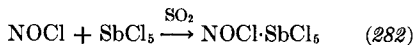
(3) The bromine trifluoride method is limited by displacement reactions when the fluoride is a weak acid in this solvent (see p. 272). Hydrogen fluoride is a more acidic and less oxidizing solvent. Solutions of nitrosyl chloride in this solvent provide another general route to double fluorides. A solvate $\text{NOF} \cdot 3\text{HF}$ (b.p. 94°) can be distilled from this solution; the solvation energy must be in excess of 13.5 kcal/mole, since this is the positive free energy change for $\text{NOCl} + \text{HF} \rightarrow \text{NOF} + \text{HCl}$ (285). Various chlorides and metals are converted to double fluorides by reaction with $\text{NOF} \cdot 3\text{HF}$ in the gas or liquid phase. Reported (285) adducts are listed in Table V.

TABLE V
NITROSYL FLUORIDE ADDUCTS PREPARED VIA HF

MF _n in MF _n NOF					
BeF ₂	BF ₃	AsF ₅	VF ₄	SeF ₄	IF ₅
		SbF ₅		TeF ₄	TeOF ₄
		NbF ₅		MoF ₆	MoOF ₄
		TaF ₅		WF ₆	
				UF ₆	
MF _n in MF _n 2NOF					
SiF ₄	TiF ₄	CrF ₃			
GeF ₄	ZrF ₄				
SnF ₄	VF ₄				

(4) Nitrosyl fluoride can also be stabilized with sulfur dioxide in a 1:1 compound which, although completely dissociated in the gas phase, can act as an effective fluorinating agent below -10° . Again, many metals and halides are converted to double fluorides (288). If these reactions are carried out in glass or silica vessels, attack on the containers produces some $2\text{NOF} \cdot \text{SiF}_4$. This resembles reactions in bromine trifluoride where there is a similar dissociation of a solvate to the reactive nitrosyl fluoride.

Sulfur dioxide can also be employed in a more conventional manner for metathesis leading to nitrosyl salts:



The last is an example of a compound containing both cationic and anionic NO groups.

(5) The nitrosonium ion can also be generated from nitrogen oxides or their hydrates by solution in strong protonic acids such as absolute sulfuric,

nitric, or hydrofluoric acid. Dinitrogen tetroxide, for example, behaves as nitrosonium nitrate. The nitrosyl salts listed in Table VI are derived from strong oxyacids. A simple sulfate has yet to be isolated.

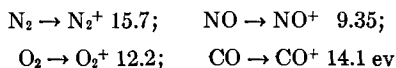
TABLE VI
NITROSYL OXYACID SALTS^a

NOP ₃ O ₈ (NO) ₂ P ₄ O ₁₁ (NO) ₂ P ₆ O ₁₇ NOSO ₃ Cl NOHSeO ₄ (NO) ₂ SeO ₄	NOHSO ₄ (NO) ₂ S ₂ O ₇ (NO) ₂ S ₃ O ₁₀ NOSO ₃ F	NOReO ₄	NOCIO ₄
--	--	--------------------	--------------------

^a From (291).

(6) The nitrosonium ion can be formed when some metals or their halides are dissolved in liquid nitrogen dioxide. The addition of organic solvents such as ethyl acetate facilitates reaction by increasing ionization. Thus, with zinc, the compound Zn(NO₃)₂·2N₂O₄ (3) and, with ferrous or ferric chloride, Fe(NO₃)₃·N₂O₄ (1) are formed. These compounds are electrolytes whose spectra accord with formulas (NO⁺)₂Zn(NO₃)₄ and NO⁺Fe(NO₃)₄⁻.

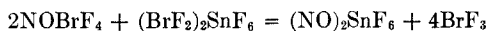
The existence of nitrosonium ions in all these substances is possible because of the relatively low ionization potential of the odd electron molecule NO, and the small size of the ion (N-O distance 1.062 Å). The ionization potential can be compared with that of similar diatomic molecules:



These two factors would be consistent with the formation of stable ionic lattices for nitrosonium salts, and indeed Hantzsch provided cryoscopic and spectral evidence for this many years ago (136). Other older evidence included the isomorphism of nitrosyl with ammonium salts as shown by X-ray diffraction (169), and the identification of a Raman frequency around 2310 cm⁻¹ with the NO⁺ ion since it was isoelectronic with nitrogen with a frequency of 2330 cm⁻¹ (4).

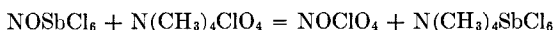
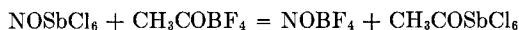
Modern evidence relies mainly on behavior in ionizing solvents together with spectral data. Some nitrosyl salts are strong electrolytes in liquid nitrosyl chloride, a solvent of medium dielectric constant (19.7 at -10°). Nitric oxide is generated at the cathode on electrolysis, indicating the nitrosyl cation. The latter has a high mobility according to transport measurements. This is also shown by the minimum in the conductivity when ferric chloride solutions are titrated with tetramethylammonium

chloride, the nitrosyl ion being replaced by the less mobile ammonium ion (47). Radioactive chlorine exchange between NOCl and chlorides in solution is compatible with ionic mechanisms (194). In bromine trifluoride the existence of NOBrF₄ was postulated as an intermediate to explain the production of other nitrosyl salts (331), and it has now been isolated as a solid (m.p. 225°) structurally similar to potassium tetrafluoroborate. The nitrosyl compound is an electrolyte in bromine trifluoride, and can be titrated with stannic or titanous fluoride solutions to a minimum conductance at half a molecule of the latter (41) according to the equation:

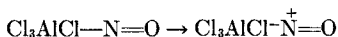


The structural similarity of (NO)₂SiF₆ to K₂TiF₆ was also indicated in this work.

Nitrosyl salts are also strong electrolytes in liquid sulfur dioxide. The equivalent conductivity of nitrosyl hexafluoroantimonate is only a little less than the potassium salt. Again, nitric oxide is liberated cathodically on electrolysis, and conductivity titrations of nitrosyl chloride with antimony pentachloride reach maximum values at the 1:1 composition (282). Double decomposition reactions in this solvent illustrate their ionic nature:



The spectral evidence for nitrosonium salts is convincing. Gerding and Houtgraaf compared the spectra of NaCl·AlCl₃ with those of NOCl·AlCl₃ in both the solid and liquid states. The former compound is a salt Na(AlCl₄) containing discrete tetrahedral AlCl₄ units as shown by an X-ray structure determination (108), and the Raman spectrum is reasonably consistent with a slightly distorted AlCl₄⁻ tetrahedron. The Raman spectrum for NOCl·AlCl₃ showed the shifts characteristic of the AlCl₄⁻ ion, together with an intense line at 2236 cm⁻¹ close to that in NOHSO₄ or NOClO₄ due to the stretching frequency of NO⁺. However, this frequency value is significantly lower than that for other nitrosyl salts or nitrogen itself, and suggests that the bonding is incompletely polar. A small contribution from a nonpolar adduct was proposed:



The nitrosonium ion was also identified by its Raman spectrum in N₂O₄·3SO₃, i.e., (NO⁺NO₂⁺)S₃O₁₀⁻ (107), and when the lower oxides of nitrogen N₂O₃ and N₂O₄ were dissolved in sulfuric or nitric acid (213). In the latter the NO⁺ frequency at 2240 cm⁻¹ was again lower than the 2300 value for most nitrosonium salts, and was explained by a more complex ion NONO₂⁺ held by a single electron bond (127). A similar ion N₂O₂⁺ was

obtained by passing nitric oxide into nitrosyl salt solutions in liquid sulfur dioxide or in strong acids. The ion is unstable, the equilibrium constant for $\text{NO} + \text{NO}^+ \rightleftharpoons \text{N}_2\text{O}_2^+$ being $6 \times 10^{-3} \text{ atm}^{-1}$ at 20° (290). An unstable solvated nitrosonium ion NONOCl^+ was also encountered in liquid nitrosyl chloride (47), and in general ions of the type,



where the ligand L contains an oxygen or nitrogen donor, are not uncommon. These ions account for the increased reaction rates when organic ligand molecules are added to metals dissolving in liquid nitrogen dioxide (2).

Finally, two recent extreme examples of nitrosonium salts prepared from chlorine fluorides and nitrosyl fluoride confirm the pattern of ionicity of other nitrosonium salts. These compounds are completely dissociated at room temperatures and can be examined only at low temperatures. Thus $\text{NOF} \cdot \text{ClF}$ dissolved in chlorine monofluoride at -79° has a low but significant equivalent conductivity. The solid has the usual infrared frequency at 2279 cm^{-1} of the NO^+ ion, and an asymmetrical stretching frequency at 635 cm^{-1} expected for a linear ClF_2^- ion (51, 329).

8. The Nitronium Ion

This ion is the reactive electrophilic entity in aromatic nitration, and there is sufficient evidence for its existence on mechanistic grounds alone. Its existence in salts is considered in the same order as for the corresponding nitrosonium ion. It can be generated by the same general methods:

(1) From nitryl chloride and Lewis acid chlorides. This method is restricted because of the instability of nitryl chloride. The hexachloroantimonate has been precipitated by mixing solutions of nitryl chloride and antimony pentachloride in liquid chlorine (289). At room temperature the salt begins to decompose irreversibly. This instability of nitryl salts compared with the corresponding nitrosyl salts is expected because of the much higher ionization potential $\text{NO}_2 \rightarrow \text{NO}_2^+$ (11.0 eV).

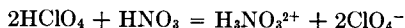
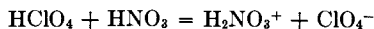
(2) Nitryl fluoride is more stable than the chloride, although the N-F bond is still weaker than in nitrosyl fluoride, and is able to attack elements and convert some to nitronium salts. Others can be obtained by direct combination with fluorides (11). Again, a more convenient procedure is to generate the component fluorides with bromine trifluoride and react them *in situ* (337). Nitrogen dioxide has been the source of nitryl fluoride but the nitrates would also serve. The method is limited to those "acids" in bromine

trifluoride which are not displaced by the BrF_4^- ion. Nitronium tetrafluorobromate has not been isolated at ordinary temperatures, in accord with the expected lower stability of nitronium salts. The complexes listed in Table VII have been obtained by the above methods.

TABLE VII
NITRONIUM COMPLEX FLUORIDES

NO_2BF_4	$(\text{NO}_2)_2\text{SiF}_6$	NO_2PF_6	NO_2SeF_5	NO_2IrF_5
	$(\text{NO}_2)_2\text{GeF}_6$	NO_2AsF_6	$\text{NO}_2\text{SO}_3\text{F}$	$(\text{NO}_2)_2\text{IrF}_6$
	$(\text{NO}_2)_2\text{SnF}_6$	NO_2SbF_6	NO_2IF_6	
		NO_2VF_6		NO_2AuF_4
		NO_2VOF_4		
		NO_2NbF_6		
		NO_2TaF_6		

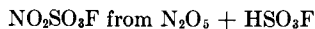
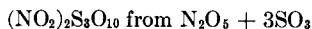
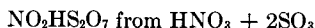
(3) Nitrogen oxides or nitric acid in protonic solvents have acted as sources of the nitronium ion. Hantzsch, who obtained crystalline compounds from nitric acid-perchloric acid mixtures, believed that acidium ions were formed by proton transfer,



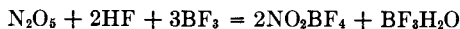
whereas it has been shown that a mixture of perchlorates is formed:



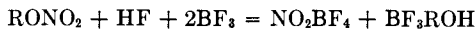
By working in nitromethane solutions it is possible to isolate single nitronium salts (123):



Similarly, from fluoro acids—generated *in situ* in nitromethane from hydrogen fluoride and a Lewis acid fluoride—and nitrogen pentoxide the salts NO_2BF_4 and $(\text{NO}_2)_2\text{SiF}_6$ were produced. Alternatively, the complex fluorides are obtained by using hydrogen fluoride as the solvent (271):

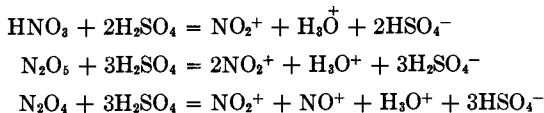


Alkyl nitrates can act as a source of NO_2^+ :

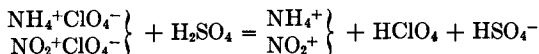


(4) Lewis acid fluorides can react directly with nitric acid or nitrogen oxides to form nitronium salts. It should be remembered that nitrogen pentoxide is nitronium nitrate in the solid state.

The experimental evidence for the nitronium ion in the above complexes is firmly based. Refined X-ray structures of $\text{NO}_2^+\text{ClO}_4^-$ and $\text{NO}_2^+\text{NO}_3^-$ show almost perfectly linear nitronium ions (319), and less precise structures show the same ions in $(\text{NO}_2)_2\text{S}_3\text{O}_{10}$ and $(\text{NO}_2)\text{HS}_2\text{O}_7$ (110). Ionization in sulfuric or nitric acid solutions has been demonstrated by cryoscopic measurements (115). The following are almost complete:



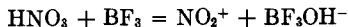
The similarity in cryoscopic behavior between nitronium and ammonium perchlorate in sulfuric acid is due to the liberation of the largely un-ionized perchloric acid from each salt (113):



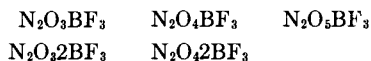
The Raman spectrum seems the most decisive identification for nitronium ions (158). In nitric acid the weak lines at 1400 and 1050 cm^{-1} are intensified by adding sulfuric acid or nitrogen pentoxide. Only the 1400 cm^{-1} line is obtained by adding perchloric acid or selenic acid and this highly polarized line is the NO_2^+ line. Such a line is expected for an A-A, A-B, or linear AAA or ABA molecule. In nitric acid the only possible species with this structure would be $\text{N}=\text{N}=\text{N}^-$ and $\text{O}-\text{N}-\text{O}^+$ (68). The former is excluded by the chemistry and its known spectra, and hence the 1400 cm^{-1} line is the totally symmetrical frequency for NO_2^+ . The 1050 cm^{-1} line is the strong Raman line for HSO_4^- and is not observed in sulfuric acid because the amount of ionization is too small. The nitrate ion has three fundamentals but only the 1047 cm^{-1} line is detectable. Using these criteria, the spectra of $\text{NO}_2^+\text{ClO}_4^-$, $\text{NO}_2^+\text{NO}_3^-$, and $\text{NO}_2^+\text{SO}_3\text{F}$ are explained:

	$\frac{\nu_{\text{NO}_2^+} (\text{cm}^{-1})}{1396.2}$
$(\text{NO}_2)\text{ClO}_4$	
$\text{NO}_2\text{HS}_2\text{O}_7$	1396
$(\text{NO}_2)_2\text{S}_2\text{O}_7$	1401
$\text{NO}_2\text{SO}_3\text{F}$	1405
NO_2NO_3	1394

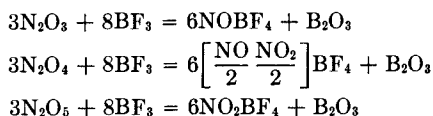
The generation of NO_2^+ by passage of boron fluoride or sulfur trioxide into nitric acid, e.g.,



is shown by the 1400 cm^{-1} Raman line (107). Spectral evidence enables the structures of the compounds



to be decided. Originally these were formulated as nitrosyl and nitronium salts of anions $\left[\text{N} \begin{array}{c} \diagup \text{OBF}_3 \\ \diagdown \text{OBF}_3 \end{array} \right]^-$ and $\left[\text{O}-\text{N} \begin{array}{c} \diagup \text{OBF}_3 \\ \diagdown \text{O} \end{array} \right]^-$, but the spectra are not complex enough for salts of these anions and they are now regarded as tetrafluoroborates formed as follows:



The boric oxide is present in only small amounts and, since it would be near the BF_4^- spectrum, has not been detected (93).

Finally, conductivity measurements on the nitronium complex fluorides in tetramethylene sulfone or nitromethane show the ionicity of these compounds (187). In these solvents the ion dissociation is incomplete and there is a minimum in the conductivity-dilution curve expected for the equilibrium between ions, ion pairs, and ion triplets. This is confirmed by cryoscopic measurements in the organic solvent.

D. GROUP VI

The pattern of heterocations in this group follows that in the previous group, except that the maximum valency is not exerted by elements in the nonmetallic subgroup and there is uncertainty concerning the status of oxyocations.

Oxygen itself is too electronegative to act as a core element in general. It can appear as a molecular ion in the gas phase, and more remarkably in stable salts. Although the dioxygenyl cation is not strictly a heterocation as originally defined, its importance as the precursor of rare gas chemistry, as well as the method employed in its generation and identification, merits some discussion. It was first encountered in the fluorination of platinum or platinum halides with elemental fluorine at 450° as a red sublimate of composition PtO_2F_6 , the oxygen arising fortuitously. It was produced subsequently by tensimetric titration of oxygen with platinum hexafluoride at ambient temperatures. Chemical evidence for its structure relies on displacement reactions in which the relatively unstable O_2^+ is replaced by more stable cations, as shown in Fig. 5. (The structures of the replacing cations are discussed later.)

More direct evidence was provided by X-ray analysis. Cubic and rhombohedral forms exist: the former isomorphous with the well-known $\text{NO}^+\text{SbF}_6^-$ and K^+SbF_6^- , and the latter with KPtF_6 , KRuF_6 , and KOsF_6 . Good agreement with X-ray intensity measurements was obtained with a

model based on packing of O_2 and PtF_6 units. The data were not precise enough to distinguish O_2^+ from O_2^- so that recourse was necessary to lattice energy considerations, which easily differentiate $O_2^+Pt^VF_6^-$ from $Pt^{VII}F_6+O_2^-$. The first ionization potential of platinum hexafluoride, obtained from a Born-Haber cycle with the lattice energy calculated by the usual approximation from interionic distances (166), would be less than 4.3 eV if the latter formulation were correct. This value is about the same as that for potassium and cannot be correct.

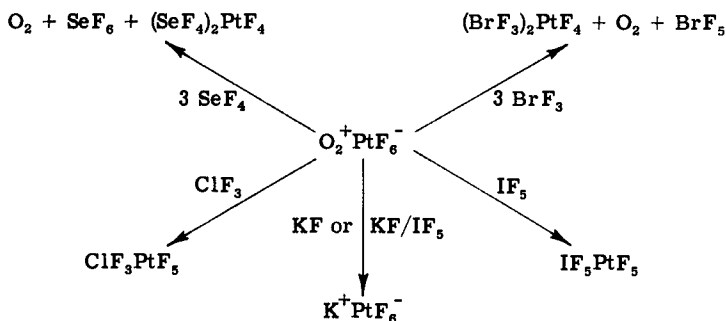
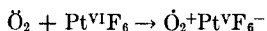
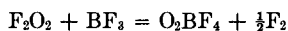


FIG. 5. Displacement reactions on O_2PtF_6 (20).

The minimum value of electron affinity for the hexafluoride calculated on the basis of the $O_2^+PtF_6^-$ formulation was -7.0 eV, a value well above that for the halogens and indicative of an extremely powerful oxidant. This is compatible with a direct abstraction of an electron from the oxygen molecule in a redox reaction:



The unpaired electron on the cation is shown directly by an e.s.r. spectral measurement on the tetrafluoroborate prepared by the reaction:



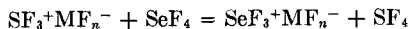
(Paramagnetic measurements on bulk samples of $O_2^+PtF_6^-$ are difficult to interpret because there are contributions from both ions, and assumptions about their interaction have to be made before a value can be ascribed to O_2^+ .) Other oxygenyl salts have also been prepared from difluorine dioxide and Group V pentafluorides (342).

1. Sulfur Cations

It has not proved possible to ionize hexavalent sulfur cationically; all examples of sulfonium ions contain S(IV) or S(II). Organosulfonium ions have been well established. Simple examples are the tetrachloroborate $(C_4H_9)S^+BCl_4^-$ (188) and the tetrafluoroborate $(C_2H_5)S^+BF_4^-$ (211).

2. Halogeno Sulfur Cations

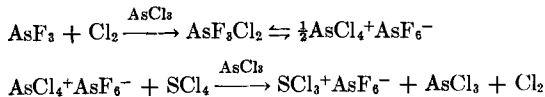
The halogenated cations are of more recent origin. They were first encountered during investigations into properties of sulfur and selenium fluorides. Boron trifluoride combines equimolecularly with sulfur tetrafluoride to form a colorless crystalline compound which dissociates into its components on heating. The heat of dissociation is close to that of the alkali fluoroborates and is consistent with a formulation $\text{SF}_3^+\text{BF}_4^-$. This is confirmed by the infrared spectrum in which the boron trifluoride peaks are replaced by those of BF_4^- as in the alkali salts, and a new peak, presumably of SF_3^+ , replaces the SF_4 bands (286). The compound is isomorphous with NH_4IO_3 (49). More stable binary compounds are formed with arsenic and antimony pentafluorides. The latter melts at 253° without decomposition. Its cubic unit cell is compatible with ionic $\text{SF}_3^+\text{SbF}_6^-$. These compounds undergo displacement reactions with selenium tetrafluoride, which acts as a stronger base than sulfur tetrafluoride toward the Lewis acid fluorides (21):



Selenium tetrafluoride can even displace bromine trifluoride from its adducts to give the isomorphous series $(\text{SeF}_4)_2\text{PtF}_4$, $(\text{SeF}_4)_2\text{GeF}_4$, $(\text{SeF}_4)_2\text{PdF}_4$, a series reasonably formulated as hexafluoro anion salts of SeF_3^+ . Another example of a displacement reaction has been given in Fig. 5, in which the similarity of SeF_4 to BrF_3 in the displacement reactions with the oxygenyl cation is illustrated.

Analogous chlorinated cations have also been made. Double halides, thermally much more stable than sulfur tetrachloride, include $\text{SnCl}_4 \cdot 2\text{SCl}_4$, $\text{SbCl}_5 \cdot \text{SCl}_4$, and $\text{FeCl}_3 \cdot \text{SCl}_4$ and presumably contain SCl_3^+ cations. Stable hexafluoroarsenates of this cation and of selenium and tellurium analogs have recently been characterized (183).

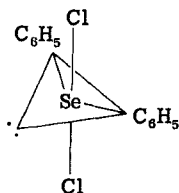
The elements S, Se, and Te can be chlorinated in arsenic trichloride and then arsenic trifluoride is added. This synthesis can be regarded as a displacement reaction by the chalcogen tetrahalides on an intermediate $\text{AsCl}_4^+\text{AsF}_6^-$ (p. 250):



Iodine trichloride is unable to displace the AsCl_4^+ ion, indicating the stability sequence $\left. \begin{matrix} \text{S} \\ \text{Se} \\ \text{Te} \end{matrix} \right\} \text{Cl}_3^+ > \text{AsCl}_4^+ > \text{ICl}_2^+$. The relative instability of ICl_2^+ is discussed in the next section.

The presence of hexafluoroarsenate anions is inferred from the precipitation of nitron hexafluoroarsenate from the alkaline hydrolyzate. The compounds form conducting solutions in nitromethane with equivalent conductivities similar to those of other binary electrolytes in this solvent. The extent of ionization increases in the expected order from the sulfur to the tellurium compound.

Raman spectroscopy provides confirmatory evidence for the SeCl_3^+ and TeCl_3^+ cations. In solid SeCl_4 and in solid or liquid TeCl_4 , the four stronger lines are close to those of the respective isoelectronic arsenic trichloride and antimony trichloride. These spectra together with the ionic conductivity of solid and liquid TeCl_4 constitute excellent evidence for $\text{Se}(\text{Te})\text{Cl}_3^+\text{Cl}^-$ ionizations (109). However, some weak lines in the spectra have not been explained. Perhaps these halides are other examples of a tendency to "polarity" isomerism by a distortion toward a nonpolar form. It should be noted that, if two of the chlorines are replaced by the less electronegative phenyl groups, the substituted compound has the symmetry shown in the solid state and not that of the pyramidal cation:



A similar pattern of lines is observed with the compounds $\text{SCl}_4\cdot\text{AlCl}_3$ and $\text{SeCl}_4\cdot\text{AlCl}_3$, although the higher frequency values indicate stronger interaction with the anion. The sulfur trioxide adducts of the tetrachlorides are also probably SeCl_3^+ and TeCl_3^+ chlorosulfates, but the apparent fluorosulfates $\text{SF}_5\text{SO}_3\text{F}$ and $\text{SF}_4(\text{SO}_3\text{F})_2$ are not simple salts (279). They are in all probability covalently linked compounds with fluorosulfate bridging.

Sulfur tetrafluoride has the same trigonal bipyramidal structure shown above with nonbonding electron pair in an equatorial position. The fluorine exchange between nonequivalent fluorine atoms (219), observed in the low temperature n.m.r. spectra, may proceed via an ionic intermediate in view of the ionization observed in selenium tetrachloride.

There is also evidence for ionization in the lower sulfur halides. A solvent system, based on the self-ionization of sulfur monochloride,



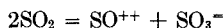
has been postulated and justified by conductometric titrations of "acids" with "bases." The amount of ionization of solvent and solutions is minute.

The value for solutions is 10^{-6} to 10^{-8} ohm $^{-1}$ cm $^{-1}$ and for the solvent 10^{-10} ohm $^{-1}$ cm $^{-1}$ (309).

The ionization of sulfur monochloride in compounds with Lewis acids has been examined (223).

3. Oxysulfur and Oxyselenium Cations

These have usually been postulated as participants in the self-ionization schemes used to correlate chemical reactions in sulfur and selenium oxides and oxychlorides. Thus, in sulfur dioxide an oxide ion transfer, and in sulfuryl, thionyl, and selenyl chlorines a chloride ion transfer, between molecules is assumed to produce hetero-oxyocations:

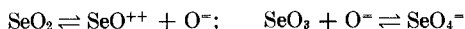


It is now generally accepted, for at least sulfur dioxide, that metathetical, "neutralization," and displacement reactions need not proceed via the solvent self-ionization. For example, the absence of sulfur or oxygen exchange between thionyl halides and sulfur dioxide precludes the SO^{++} ion. Also the structures of many oxyhalide adducts with Lewis acids, which are supposed to form acids in the oxyhalide systems by halogen abstraction, are in fact bonded via oxygen to the Lewis acid, e.g.,

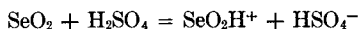


An extensive review of the evidence against SO^{++} has appeared recently and further comment is unnecessary (323).

The selenyl ion SeO^{++} has been postulated in the molten state. The conductivity of molten selenium trioxide initially 10^{-7} ohm $^{-1}$ cm $^{-1}$ increases to 5×10^{-3} ohm $^{-1}$ cm $^{-1}$ when the oxide is thermally decomposed at 175° . The conductivity in the supercooled residual Se_2O_5 is ascribed (161) to the ionizations:



Oxygen ion transfer in molten salts is the basis of Lux and Flood's interpretation of the reactivity of molten oxides (104), but the above evidence in a much less conducting medium is hardly definitive. The ionization of selenium dioxide in a particularly favorable medium, sulfuric acid, does not result in oxygen ion transfer to produce SeO^{2+} or SeOHSO_4^+ cations, but rather it acts as a base (105):



A planar cyclic ion $S_4N_3^+$ (see Fig. 6) has recently been verified by an X-ray structural determination of thiotrithiazyl nitrate (68, 326). Delocalization of ten electrons in a π system is proposed to account for the stability of the ion and its electronic spectrum (163).

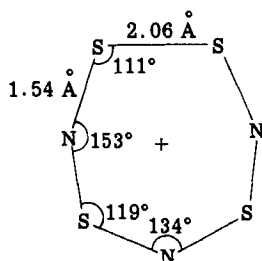
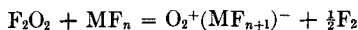


FIG. 6. Dimensions of $S_4N_3^+$ cation.

E. GROUP VII

The heterocations belonging to this group have been encountered during investigations into the reactivity of interhalogen compounds and halogen oxyfluorides. Some cations have been merely postulated in the self-ionization equilibrium of solvents without adequate physical characterization by, for example, spectral methods. However, structures proposed by analogy or extrapolation have generally been confirmed by later studies.

Fluoronium cations have not been prepared. The most feasible preparative route, by interaction of fluorine oxides and strong Lewis acid fluorides, has yielded with dioxygen difluorides the oxygenyl cation rather than an oxyfluoronium one,



where $M = B(III), P(V), As(V),$ and $Sb(V)$. These complexes have been recognized by identifying the complex anions, and also by showing their isomorphism with nitrosonium salts of the same anions (342).

The compound fluorine fluorosulfate is a covalent one. Similar insertions of sulfur trioxide between halogen atoms occur with halogen fluorides; again, there is no evidence of ionic structures (255). Fluorine invariably appears as a negative substituent in other halogen cations.

1. Difluorohalogen(III) Cations

The self-ionization in liquid bromine trifluoride is considered in more detail than in previous accounts, because it exemplifies the type of reasoning applied to other interhalogens. The extreme nature of this solvent leads to a simplification of its solution chemistry. Only fluorides, and a few oxyfluorides, of elements in high valency states exist in solution. The effect of

traces of moisture on conductivities in this solvent, the usual bane of the experimentalist, is unimportant, since they are eliminated as hydrogen fluoride and oxygen. The high conductivity of bromine trifluoride, which approaches that of sulfuric acid, has been independently confirmed in cells of different materials (Fig. 7) (16, 249). The possible trace impurities Br_2

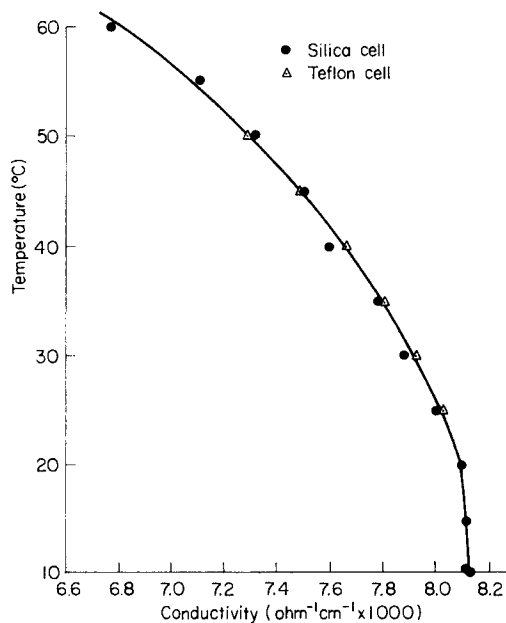
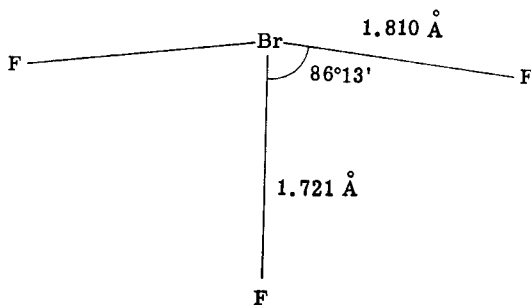


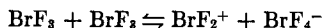
FIG. 7. Variation of conductivity of bromine trifluoride with temperature.

(or BrF), BrF_3 , and HF have been shown to lower the conductivity. The negative temperature coefficient is a sign of ionic instability rather than electronic conduction because of the large drop in conductivity on freezing. The liquid is an associated one, as evidenced by the high Trouton constant and high ratio of energy of evaporation to free energy of viscous flow (257).

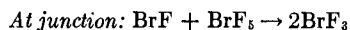
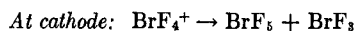
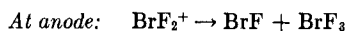


The molecular shape shows that a dipole is present in the direction of the shortest bond (207). It is reasonable to assume that in the liquid state the dipoles will orient with fluorine of one molecule close to the bromine of an adjacent molecule, possibly in chain configurations.

This arrangement will facilitate a fluoride ion transfer, which is the most reasonable postulate to explain the solvent conductivity, i.e.,



The ionization is regarded as a mobile one with a continuous but random breaking and remaking of Br-F bonds, so that an instantaneous picture would reveal a few ions in every thousand molecules or, alternatively, observation of a single bond would show it to be ionized for a correspondingly small fraction of the time. The self-ionization equation is only a partial representation of the overall ionization mechanism. The rapid exchange of radioactive fluorine between fluorides and bromine trifluoride agrees with the mobility of the fluoride ion in this solvent. The solvent on electrolysis behaves as an ohmic conductor, but the creation of a sharp color boundary, brown on the cathode side against unchanged yellow, shows that transport occurs. This is explicable as a redox reaction between products at the color junction regenerating solvent and preventing a build-up of products at the electrodes:



Bromine monofluoride is known to be in equilibrium with bromine and the solvent (310):



Thus the evidence of the high conductivity of the solvent and its behavior on electrolysis by itself requires one to postulate the fluoro-bromonium cation. The conductivities of fluorides in bromine trifluoride provide confirmatory evidence. In Fig. 8 it can be seen that fluorides divide into two classes (336):

(1) The alkali and alkaline earth fluorides, the conductivities of which if extrapolated to zero concentration intercept the conductivity axis below the value of the solvent conductivity.

(2) The fluorides of Groups IV and V, which intercept above the solvent value. Normally the equivalent conductivity is plotted against concentration, but this cannot be done for a highly conducting solvent unless the contribution of solvent ions toward the total conductivity, and how it is affected by solute ions, can be ascertained.

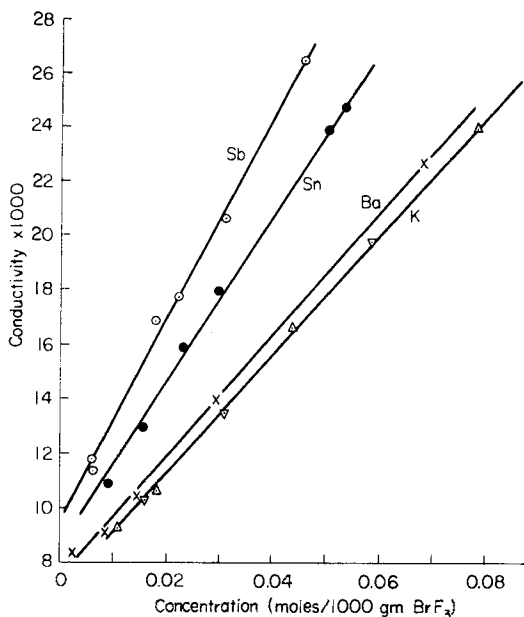
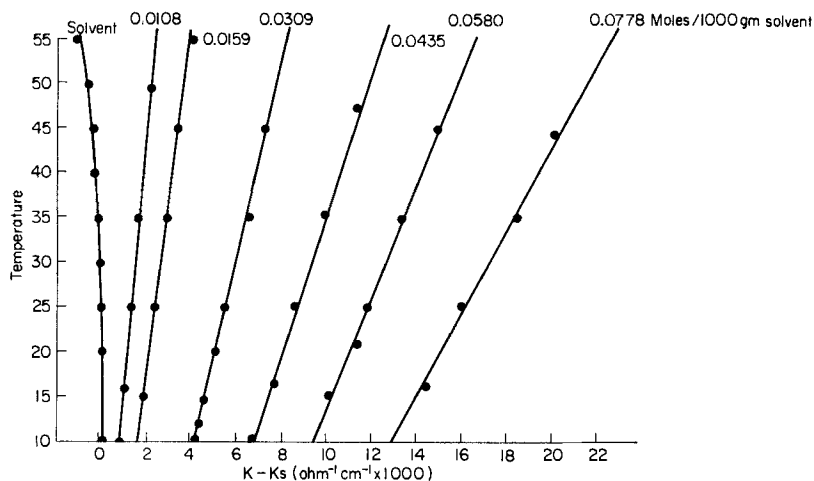
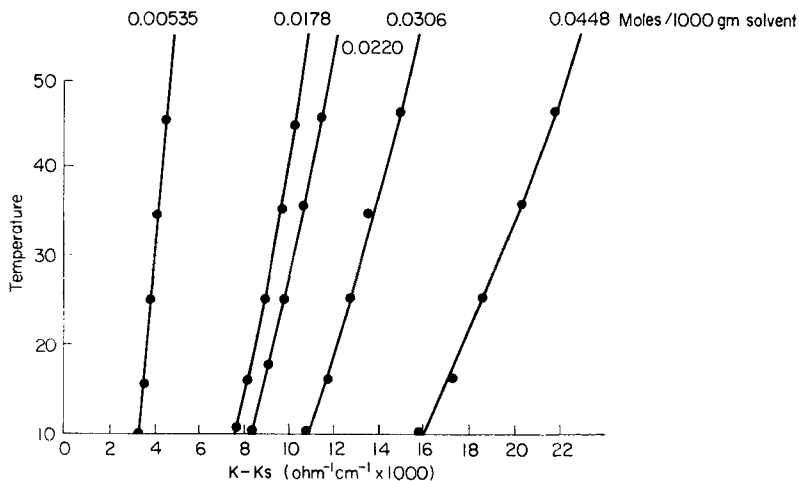


FIG. 8. Conductivity of acids and bases at 25°.

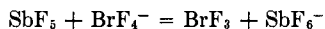
The latter effect is illustrated in Figs. 9a and 9b which show the temperature variation of conductivity for different solute concentrations. For potassium fluoride solutions it can be seen that the temperature variation is linear and positive from the lowest concentrations. (The temperature coefficient extrapolates to zero at just detectable concentration.) This behavior can be compared with the negative and nonlinear variation of the solvent conductivity.

It follows from this effect of the solute on the temperature coefficient, and from the extrapolated value of conductivity below that of the solvent (Fig. 8), that the solvent ionization is being repressed presumably by production of one of the solvent ions by the solute. Since an alkali salt can only ionize to form an alkali cation it follows that the fluoride ion, solvated by the solvent, must be the repressing ion, and indeed ionic salts of composition $MBrF_4$ (307) can be isolated from solution.

For antimony pentafluoride, however, although the temperature coefficient becomes positive, the curves remain nonlinear even at the highest concentrations. This fact together with the conductivity intercept above the solvent value (Fig. 8) indicates that the solvent ionization is being stabilized. Antimony pentafluoride is not ionizing as with the alkali fluorides, i.e., $SbF_5 \rightleftharpoons SbF_4^+ + F^-$, but is presumably removing the tetra-

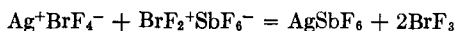
FIG. 9a. Temperature variation of conductivity of KBrF_4 solutions.FIG. 9b. Temperature variation of conductivity of BrF_3SbF_6 solutions.

fluorobromate ion from the solvent equilibrium and causing further solvent ionization to replace it:



Each solute anion must then be balanced by a BrF_2^+ cation. The detailed picture is obviously more complex because it is known that antimony pentafluoride, as well as bromine trifluoride, is associated with short chains of antimony octahedrally coordinated with fluorine (149). Thus it is not

surprising that compounds other than the least volatile $\text{BrF}_3 \cdot \text{SbF}_5$ (melting at 130°) exist in the $\text{BrF}_3 \cdot \text{SbF}_5$ system, namely, another congruently melting compound $\text{BrF}_3 \cdot 3\text{SbF}_5$ (33.5°) and the volatile incongruently melting compounds $3\text{BrF}_3 \cdot \text{SbF}_5$ (-16°) and $3\text{BrF}_3 \cdot 2\text{SbF}_5$ (31°) (102). Although the ionicity of these relatively reactive compounds in the solid or molten state has yet to be proven, it seems probable that the 1:1 compound ionizes as $\text{BrF}_2^+ \text{SbF}_6^-$. It certainly behaves in this way in solution because, when added to a solution of an alkali fluoride or silver fluoride, the conductivity falls until equimolecular amounts are present, i.e., a replacement of BrF_4^- by less mobile SbF_6^- , and then rises at the same rate as a solution with increasing concentration of antimony pentafluoride:



The unsolvated hexafluoroantimonates can be isolated from the resulting solutions.

The mobilities of ions in this solvent have not been measured directly but, by comparing solutions at 0.01 *M* concentration and assuming that the mobility of the potassium ion is about the same as in water, an assumption based on the validity of Walden's law in both solvents, it follows from the above conductivity measurements that BrF_2^+ and BrF_4^- are the most mobile ions, in that order. This would be expected if fluoride ion transfer proceeded by a chain mechanism. The ionic product $[\text{BrF}_2^+][\text{BrF}_4^-]$ is approximately 4×10^{-4} .

The description of the antimony pentafluoride ionization on the coordination model advocated by Drago (p. 226) differs from the above insofar as a coordinated intermediate would be the precursor of ionization. If it is accepted that the antimony becomes anionic, then, in the absence of kinetic or thermodynamic data on the intermediate, any difference between the two theories is more in the realm of semantics. The formation of the difluorobromonium ion follows according to the requirement of charge neutrality.

The behavior of other Lewis acid fluorides in this solvent have been studied similarly by conductivity methods or by neutralization and displacement reactions. The generation of extra BrF_2^+ ions, at least in solution, occurs with the addition of the fluorides which form the complex anions listed in Table VIII.

The acid strengths, i.e., the equilibrium constants, for

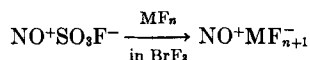


can be compared by consideration of solvolysis or displacement reactions. For example, hexafluorotitanates when made by neutralization reactions retain solvent because of the reversal of the neutralization $\text{BrF}_2^+ + \text{BrF}_4^-$

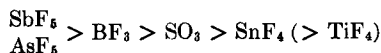
TABLE VIII
COMPLEX ANIONS ASSOCIATED WITH THE BrF_2^+ CATION

AuF_4^-	VF_6^-	GeF_6^-	VOF_4^-
BF_4^-	NbF_6^-	SnF_6^-	CrOF_4^-
	TaF_6^-	TiF_6^-	SO_3F^-
PF_6^-	RuF_6^-	MnF_6^-	ReOF_4^-
AsF_6^-	OsF_6^-	PtF_6^-	
SbF_6^-	IrF_6^-	PdF_6^-	
BiF_6^-			

$\rightarrow 2\text{BrF}_3$, whereas hexafluoroantimonates do not (298). Hence the titanium acid is much weaker than the antimony acid, in agreement with conductivity measurements. The displacement of the fluorosulfate anion from its nitrosonium salt by other Lewis acids,



indicates (331) the following order of acid strength:

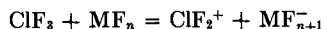


(The relative strength of the last two is indicated from conductivity data. The first pair is not differentiated since both displace SO_3F^- completely.)

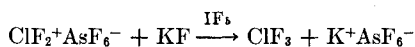
A wide range of fluorides has now been examined in bromine trifluoride, and since the majority form the BrF_2^+ ion it is reasonable to assume, even in the absence of quantitative equilibrium data, that the solvent is a basic one. This contrasts with the acid solvent sulfuric acid of the same order of ionization, in which most solutes generate the bisulfate ion.

Liquid chlorine trifluoride is quite different in physical properties from bromine trifluoride, even though the structures are geometrically similar in the gas phase. The solvent conductivity is of the order $10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$ and any self-ionization is minute (15). The solvating and ionizing ability must also be low because of the small dielectric constant ($\epsilon = 4.3$) and normal entropy of vaporization. The only evidence for association in the liquid state is from n.m.r. measurements, but the traces of hydrogen fluoride required for F^{19} exchange suggest that ionization is more important than association (217).

The minuteness of solvent ionization is also shown by the nonformation of tetrafluorochlorates M^+ClF_4^- in solution. These salts are made by fluorination of alkali chlorides with fluorine (6). It is therefore remarkable that strong Lewis acids can provoke ionization in solution to produce the difluorochloronium cation:



Thus passage of boron trifluoride increases the solvent conductivity and the 1:1 compound which can be isolated has a melt conductivity of $1.5 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$. The spectra of the solid show the broad peak characteristic of the BF_4^- anion and the symmetrical and asymmetrical stretching frequencies of the bent ClF_2^+ cation. Solutions of phosphorus, arsenic, and antimony pentafluorides behave similarly but the solution conductivities indicate much smaller ionizations than in bromine trifluoride (296). The solids which can be isolated from solution have infrared spectra characteristic of fluoro anions and bent ClF_2^+ cations. Solutions of these compounds in a more effective ionizing solvent, iodine pentafluoride, show their ionic nature. Thus the freezing point depression of $\text{ClF}_3 \cdot \text{AsF}_6$ is that for a dissociation into two particles in solution, and a conductometric titration with potassium fluoride is explained by (52):



The heat of dissociation of the $\text{ClF}_3 \cdot \text{BF}_3$ compound (23.6 kcal/mole) is also significant, being of the same order as for other fluoroborates, e.g., $\text{SF}_3 \cdot \text{BF}_4^-$ 25.1, RbBF_4 27.0 (286).

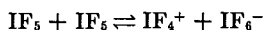
The corresponding platinum fluoride adduct $\text{ClF}_3 \cdot \text{PtF}_6$, which results from the displacement of the oxygenyl ion in $\text{O}_2^+ \text{PtF}_6^-$ by chlorine trifluoride, is presumably another salt of the ClF_2^+ cation (20). The stability of the ClF_2^+ ion is rather low in the order given by displacement reactions, i.e., $\text{K}^+ > \text{SF}_3^+ > \text{NO}^+ > \text{NO}_2^+ > \text{BrF}_2^+ > \text{ClF}_2^+ > \text{O}_2^+$. Such an order has not been established directly but can be reasonably deduced from partial series in the literature.

The difluoroiodonium cation IF_2^+ should be the most stable of the trivalent halogen ions but, since iodine trifluoride is an unstable solid which disproportionates to iodine and its pentafluoride, there is no direct route to its salts. It may be possible to prepare the IF_2^+ cation by reductive processes from iodine pentafluoride in a suitable solvent in the presence of Lewis acid fluorides, analogously to the formation of the IF_4^- anion (137). It should be noted that mixtures of halogens and higher halogen fluorides can behave as a lower halogen fluoride, i.e., $\text{Cl}_2 + \text{ClF}_3$ is equivalent to ClF , $\text{Br}_2 + \text{BrF}_3$ to BrF , $\text{I}_2 + \text{IF}_5$ to IF (145).

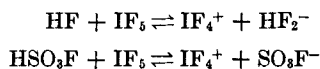
2. Other Fluoro Cations

Iodine pentafluoride is the most likely of the remaining interhalogen fluorides to exhibit an appreciable self-ionization. The dielectric constant is high and the liquid is associated. The conductivity, $5 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25° , is probably not the minimum value since it is easily affected by

traces of moisture (258). There is evidence from neutralization reactions for the self-ionization,



and the adduct $\text{IF}_5 \cdot \text{SbF}_5$ is a stable solid which ionizes in iodine pentafluoride. The compound $\text{IF}_5 \cdot \text{PtF}_5$, made by the displacement of the oxygenyl cation in $\text{O}_2^+ \text{PtF}_6^-$ by iodine fluoride, could be $\text{IF}_4^+ \text{PtF}_6^-$. However, the overall evidence for IF_4^+ is somewhat circumstantial. Spectral measurements are badly needed to confirm the postulated ionizations, as well as further investigations in other solvents to confirm equilibrium such as:



The basicity of iodine pentafluoride in these solvents has yet to be firmly established (332).

Other fluoro heterocations may exist in the adducts which form between iodine heptafluoride and Lewis acid fluorides (286):

(1) $\text{IF}_7 \cdot \text{BF}_3$ has been formulated as $\text{IF}_6^+ \text{BF}_4^-$ but its instability at room temperatures makes this less probable. The alternative formulation as a coordinate compound would require participation of $4d$ orbitals in a bonding scheme and would account for the instability of a covalent form.

(2) $\text{IF}_7 \cdot \text{AsF}_5$ is a solid with a low vapor pressure at room temperatures, again formulated as the hexafluoroiodine(VII) hexafluoroarsenate.

(3) $\text{IF}_7 \cdot 3\text{SbF}_5$ is the stablest of the three. It melts at 92° – 94° and at 100° the melt has a conductivity of $6.7 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$. The solid ionization $\text{IF}_4^{3+}(\text{SbF}_6^-)_3$ is suggested, which in the melt becomes a solution of $\text{IF}_6^+ \text{SbF}_6^-$ in antimony pentafluoride. A less labored explanation would be a partial ionization by fluoride ion transfer to produce $\text{IF}_6^+ \text{Sb}_3\text{F}_{16}^-$. The existence of corresponding polymeric fluoro anions of trivalent antimony with fluorine bridging, $(\text{SbF}_3)_n\text{F}^-$, with $n = 1$ – 4 , is well established (327). Other compounds in the IF_7 – SbF_5 system are indicated (cf. the BrF_3 – SbF_5 system, p. 272).

Fluoro cations derived from bromine pentafluoride, although less probable than those derived from iodine pentafluoride, should also exist in solution.

3. Cations Derived from Other Interhalogen Compounds and Halogens

The heterocation ICl_2^+ is derived from iodine trichloride. The compound IAlCl_6 was prepared by heating iodine and aluminum trichlorides in a chlorinated hydrocarbon, the compound ISbCl_8 from iodine trichloride

in liquid antimony pentachloride. Although the latter conducts in the melt, it is difficult to differentiate from the conductivity of molten iodine trichloride into which it could dissociate. In liquid sulfur dioxide the equivalent conductivity is only a small fraction of the values for hexachloroantimonates. The ultraviolet spectrum in carbon tetrachloride is a superposition of the spectra of ICl_3 and SbCl_5 .

In the solid the results of X-ray analysis indicate ionization to $\text{ICl}_2^+\text{SbCl}_6^-$ and $\text{ICl}_2^+\text{AlCl}_4^-$ but, as commented on in the introduction, there is a considerable interaction between the rectangular ICl_2 unit and pairs of chlorine in the supposed anions. The I-Cl distance between the units is much shorter than the sum of the van der Waals' radii (322). It is therefore not surprising that the molecule should revert to its constituents in a nonpolar solvent and only partially ionize in sulfur dioxide, a solvent of low polarity. The cation stability should be enhanced with donor molecules which are themselves stable to chlorination.

The possible occurrence of simple halogen cations X^+ has been discussed, and it appears that almost all the species designated as halogen cations are in fact solvated heterocations (8). Even for the conducting melt of iodine monochloride, it is more reasonable to write the self-ionization $3\text{ICl} \rightleftharpoons \text{I}_2\text{Cl}^+ + \text{ICl}_2^-$.

Indeed, phase studies of the systems ICl with AlCl_3 or SbCl_5 show 2:1 adducts and not 1:1, i.e., $\text{I}_2\text{Cl}^+\text{AlCl}_4^-$. When 1:1 adducts are encountered they may contain the ICl_2^- anion, e.g., PCl_5 . ICl is $\text{PCl}_4^+\text{ICl}_2^-$ (345). With organic donor molecules it is possible to isolate the solvated cations in the form of stable salts. A few recent examples are $\text{I}(\text{py})\text{F}$, $\text{I}(\text{py})_2\text{F}_3$, $\text{Br}(\text{py})_2\text{NO}_3$, and $\text{Br}(\text{SR}_2)^+\text{B}(\text{C}_6\text{H}_5)_4^-$, where py = pyridine, R = isopropyl (39, 274, 275).

Substituted iodonium cations can also be made by metathesis. Thus the diphenyl-substituted iodine(III) chloride and potassium tetrachloroplatinate(II) precipitate $(\text{C}_6\text{H}_5)_2\text{I}^+\text{PtCl}_4^-$ from aqueous solutions. The iodonium cation presumably has the same bent shape as in diphenyliodine monochloride (185).

4. Oxyhalogeno Cations

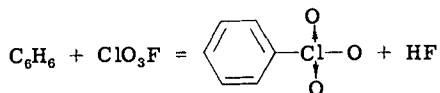
The presence of these ions in halogen oxides and as intermediates in reaction mechanisms has often been proposed. Only the solid compounds which may be salts are discussed here. A full series of chlorine oxyfluorides, ClOF , ClO_2F , ClO_3F , ClO_4F with chlorine in an increasingly higher valency state, is known. If the fluorine in these oxyfluorides could be ionized to a simple or complex fluoride ion, the expected order of stability of the resulting cations would be $\text{ClO}^+ > \text{ClO}_2^+ > \text{ClO}_3^+$.

The first of these ions has yet to be studied, presumably because a

reliable preparation of chlorosyl fluoride is not available. The first indication of a chloronium ion was the isolation of a red solid $\text{Cl}_2\text{O}_5 \cdot 3\text{SO}_3$, by reaction of sulfur trioxide with potassium chlorate, which is analogous in a formal sense to $\text{N}_2\text{O}_5 \cdot 3\text{SO}_3$ (190).

The structure of the latter established by X-ray analysis is that of a nitronium salt $(\text{NO}_2^+)_2\text{S}_3\text{O}_{10}^-$ (92). In later work the direct reaction of chloryl fluoride with Lewis acid fluorides (BF_3 , SF_4 , PF_5 , AsF_5 , SbF_5 , and SO_3) has yielded solid adducts which have been formulated as ClO_2^+ salts by analogy to nitronium salts of the same complex anions (270, 272, 334). The chloryl ion is isoelectronic with sulfur dioxide and should be a bent ion with a Cl-O distance of about 1.43 Å. This would give an ion of radius about 0.3 Å larger than the nitronium ion, and would result in a larger lattice energy for the chloronium salt of the same anion. The lattice energy difference is believed to be the main energy term which governs the relative stability of the two cations. The relative stabilities can be confirmed by carrying out displacement reactions in bromine trifluoride, which provide the stability sequence $\text{K}^+ > \text{NO}_2^+ > \text{BrF}_2^+ > \text{ClO}_2^+$.

Perchloryl fluoride, the most inert of the oxyfluorides, does not complex with the typical Lewis acids AlCl_3 or BF_3 , but with an active aromatic molecule and aluminum halides the following reaction occurs:



The transient existence of the ClO_3^+ cation in a ternary complex $\text{C}_6\text{H}_6\text{AlCl}_3\text{F} \cdot \text{ClO}_3^+$ is part of the suggested mechanism (228). It is possible that the formation of salts of the planar perchloryl cation is kinetically limited rather than thermodynamically prohibitive, and that more vigorous reaction conditions may yield stable salts. Fluorine perchlorate resembles the nitrate in being an unstable covalent compound. It would not be expected to act as a source of ClO_3^+ ions.

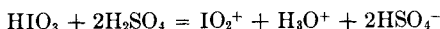
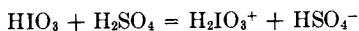
The evidence for oxyiodonium cations is inconclusive except for spectral evidence of a hexafluoroarsenate salt. The sulfur trioxide adducts of iodine oxides, $\text{I}_2\text{O}_3 \cdot 3\text{SO}_3$, $\text{I}_2\text{O}_4 \cdot 3\text{SO}_3$, $\text{I}_2\text{O}_5 \cdot 2\text{SO}_3$, have been formulated respectively as $(\text{IO}^+)_2\text{S}_3\text{O}_{10}^-$, $(\text{IO}^+\text{IO}_2^+)\text{S}_3\text{O}_{10}^-$, and $(\text{IO}_2^+)_2\text{S}_2\text{O}_7^-$, again by analogy to corresponding compounds of nitrogen oxides (191). The substitution reactions of aromatics with iodine oxides in sulfuric acid have also been advanced as evidence for iodonium ions in solution and possibly in the solid. However, the infrared spectra show that iodosyl cations are not present in $(\text{IO})_2\text{SO}_4$, $(\text{IO})_2\text{SeO}_4$, or IOIO_3 . These compounds, unlike the nitrosyl salts, are insoluble in nitromethane. They are diamagnetic, whereas the

iodosyl cation should be paramagnetic in the ground state. The cation should be isoelectronic with tellurium monoxide, but with a slightly higher vibration frequency because of the charge (72),

NO ₂ ⁺	CO ₂	NO ⁺	CO
2390	2349	2200	2144 cm ⁻¹

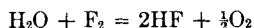
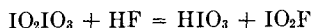
and hence one would expect the IO⁺ stretching frequency at above 800 cm⁻¹ compared with 796 cm⁻¹ for TeO. The observed absorptions are at much lower frequencies, 553–658 cm⁻¹. It is suggested that the tetrahedral symmetry of the sulfate is retained in iodosyl sulfate by bonding of each oxygen to a neighboring iodine. The yellow color of the compound argues against purely covalent bonding, and the color may be associated with partly charged —I—O—I— chains in a manner reminiscent of the fully ionic titanyl sulfate structure, which has —Ti—O—Ti— chains held together by sulfate ions.

The behavior of iodic acid in sulfuric acid, a solvent capable of stabilizing an iodonium cation, has been examined cryoscopically and conductometrically (121). Three modes of ionization were considered:



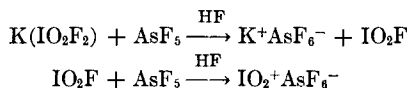
The results are consistent with the last ionization, in contradiction to an earlier report (7), but involve polymeric forms of iodyl hydrogen sulfate which depolymerize on dilution and are partially ionized.

More recently the existence of an iodonium cation in a complex fluoride has been established. The oxyfluoride IOF₃ made from the pentoxide and pentafluoride was originally considered as IO₂⁺IF₆⁻. Its thermal decomposition to IO₂F at 110° parallels that of alkali hexafluoroiodates and is consistent with its formulation as a hexafluoroiodate (122). Iodyl fluoride can be more conveniently made by passing fluorine through a solution of iodine pentoxide in hydrogen fluoride. The purpose of the fluorine is to dehydrate the intermediate iodic acid (273):

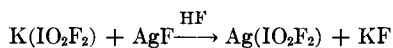


If the iodyl fluoride solution in hydrogen fluoride is treated with arsenic pentafluoride, the compound IO₂AsF₆ can be isolated. The alternative ionization AsF₄⁺IO₂F₂⁻ was suggested as being more probable in view of the existence of stable difluoroiodates (13), but it now appears that the ionization originally suggested was the correct one. Examination of the infrared

spectra shows the presence of absorptions characteristic of hexafluoroarsenates and the absence of those of difluoroiodates. Another quantitative preparation of the iodyl salt also demonstrates the structure (242):

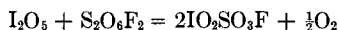


The iodyl fluoride in this instance behaves as a base toward a strong Lewis acid (or ansolvo acid in the hydrogen fluoride system). It can also function as an acid toward fluorides which are basic:



The behavior of the oxyfluoride IOF_3 in fluoride systems is of interest in view of possible amphoteric character (i.e., $\text{IF}_4^+\text{IO}_2\text{F}_2^-$ versus $\text{IO}_2^+\text{IF}_6^-$).

A substance which can be written in the form of an iodyl salt has been prepared by reaction of iodine pentoxide with peroxydisulfuryl fluoride at 150° when the latter dissociates to SO_3F radicals:



This compound is insoluble in fluorosulfuric acid and may be a polymeric substance with SO_3F acting as bidentate bonding groups. It is unlikely to be a simple ionic salt (9).

No mention has been made of the xenon fluorides and oxyfluorides which are analogous to the interhalogen compounds, but the resemblances between rare gas and halogen chemistry are such as to allow the possibilities of heterocations of xenon; no doubt this is being actively pursued (62, 295).

III. The Proton in Heterocations

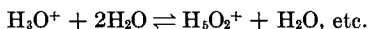
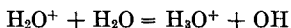
The isolated proton is unlikely to exist to any extent in solution because the ionization potential of elemental hydrogen (13.6 eV) is so much greater than that of other elements which form stable univalent ions in solution. The extreme charge-to-radius ratio for the proton will also encourage polarization of solvent molecules, so that acids in solution once formulated with bare protons are invariably solvated. (Protons can exist under special conditions in solids and liquids, for example during the diffusion of hydrogen in metals or in liquids exposed to intense radiation fields.) An illustrative cross section of the occurrence of complex protons is presented.

A. AQUEOUS SOLUTIONS

Evidence for the hydroxonium ion H_3O^+ and hydronium ion $\text{H}_3\text{O}^+ \cdot n\text{H}_2\text{O}$ in the commonest protonic solvent, water, has been comprehensively reviewed (38). X-ray examination of a number of oxyacid hydrates has shown

distinct anion units and oxygen atoms. By inference the latter are taken to be hydroxonium ions. Thus in $\text{HClO}_4 \cdot \text{H}_2\text{O}$, a substance isomorphous with ammonium perchlorate and isostructural with barium sulfate, the almost perfect tetrahedral ClO_4 unit is seen. The H_2O units are coordinated with twelve oxygens from surrounding ClO_4 groups. If molecular HClO_4 were present, one of the Cl-O bonds would differ from the others (189). In the structure of $\text{HCl} \cdot \text{H}_2\text{O}$ the oxygen and chlorine atoms alternate in parallel planes. Each atom is three-coordinate so the units are presumably H_3O^+ and Cl^- (341). The hydrogen atoms in these hydrates can be located by examining the shape of p.m.r. absorption curves. Isolated nuclei have narrow resonances, but in solids the resonance is broadened by interaction with fields of neighboring nuclei. These nuclei by exchanging energy levels reduce the time of occupancy of the levels and hence broaden the resonance. The width of the absorption can be related to internuclear distance. By assuming an equilateral triangle of protons of edge 1.72 Å, it is possible to calculate absorption curves in close agreement with experiment. In this way $\text{HNO}_3 \cdot \text{H}_2\text{O}$, $\text{HClO}_4 \cdot \text{H}_2\text{O}$, $\text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$, and $\text{H}_2\text{SeO}_4 \cdot \text{H}_2\text{O}$ were shown to be hydroxonium salts, whereas $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ contains water molecules (254). The p.m.r. spectra are consistent with a pyramidal shaped ion with an approximate O-H distance of 1.0 Å.

The third type of evidence is from infrared and Raman spectra. The spectra of solid $\text{HCl} \cdot \text{H}_2\text{O}$ and $\text{HBr} \cdot \text{H}_2\text{O}$ are explicable in terms of pyramidal H_3O^+ ions isoelectronic with NH_3 , but not in terms of water and hydrogen halide molecules (96). The vibrational-rotational bands of H_3O^+ in acid solutions are difficult to detect in the presence of the strong infrared absorption of water itself. Nevertheless the three broad bands at 1205, 1750, and 2900 cm^{-1} , whose intensity increases with acid concentration, can be associated with the hydroxonium ion. This is confirmed by the expected isotope shift which occurs for deuterated acids. There is a true bond between proton and water molecule which lasts long enough for normal vibrations to occur (97). More recently it has been shown that $\text{HNO}_3 \cdot \text{H}_2\text{O}$ contains traces of the covalent form (267). In fact this is also detectable from X-ray analysis in the slight asymmetry of the nitrate ion. The equilibrium between covalent and ionic forms in solution can be followed quite precisely by intensity measurements on suitable Raman lines. In aqueous perchloric acid, by using the perchlorate line at 931 cm^{-1} , it has been shown that the ionization is essentially complete from 0.3 to 10 *M* solutions. Above 10 *M* there is insufficient water to solvate the proton as H_9O_4^+ and ionization is incomplete (70). This ion has been detected directly in a glow discharge in water vapor by mass spectrometry. The suggested mechanism of formation is ionization of a water molecule by electron bombardment followed by reactions with other water molecules (170):



The forward reaction is faster than the reverse. There is a maximum stability at composition H_9O_4^+ . Further species up to $\text{H}_3\text{O}^+(\text{H}_2\text{O})_9$ have been observed with field emission sources (27). The existence of H_9O_4^+ in water follows indirectly from studies on the rate of proton transfer by relaxation methods (88). The neutralization represented by $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$ has a rate constant of $1.4 \times 10^{-11} \text{ mole}^{-1} \text{ sec}^{-1}$ at 25° , the maximum rate for an aqueous reaction which is diffusion-controlled. The distance of closest approach of ions which appears in the diffusion rate equation is 8 \AA , indicating that the proton is solvated as H_9O_4^+ , an ion of this diameter (87).

The presence of the hydroxonium ion in hydrates of mineral acids substituted by electronegative elements or groups such as F or CF_3 can be inferred from their behavior as strong acids in solution. The solid hydrate of trifluoromethylsulfuric acid would be $\text{H}_3\text{O}^+\text{SO}_3(\text{CF}_3)^-$. This acid is stronger than perchloric acid when dissolved in acetic acid (143). Another example is the solid hydrate of a substituted phosphoric acid, $(\text{H}_3\text{O})^+_2(\text{PO}_3\text{C}_3\text{F}_7)^-$ (91).

The ionization of halides or oxyhalides by Lewis acid halides is a general method for generating heterocations and many examples have been quoted. An analogous reaction with water would be the formation of boron trifluoride hydrates. The mono- and dihydrate are known; the latter in the solid state is isomorphous with ammonium tetrafluoroborate, and has been formulated as $\text{H}_3\text{O}^+\text{BF}_3\text{OH}^-$. The alternative $\text{H}_2\text{F}^+\text{BF}_2(\text{OH})_2^-$, possible because of the similar size of F^- and OH^- , was eliminated by examination of electrolysis products from the melt (128). The monohydrate was formulated as $\text{H}^+\text{BF}_3\text{OH}^-$ from electrolysis experiments. The extent of ionization was calculated as 20% for the dihydrate and 10% for the monohydrate (129). However, the presence of an unsolvated proton in the latter is incompatible with general views on this species.

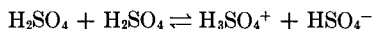
The p.m.r. spectra of the hydrates were examined subsequently (106). If samples were crystallized slowly, the resonances at 90°K had double maxima whose shape could be calculated on the basis of proton pairs separated by 1.62 \AA in the monohydrate, and 1.54 \AA in the dihydrate. The monohydrate structure was therefore consistent with a molecular hydrate containing water molecules little different from those in the gas phase. The fluorine resonance was consistent with this picture. In the dihydrate the shorter H-H distance was taken as indicative of different types of water molecule, one-coordinated to boron trifluoride as in the monohydrate, and the other possibly hydrogen-bonded in the lattice. If liquid samples were rapidly quenched the p.m.r. of the solids became single maxima, presumably

because the col between the above mentioned double maximum was obscured by new central maxima. For both hydrates a partial ionization to H_3O^+ and BF_3OH^- ions would explain the resonances. The quenched liquids can be regarded as supercooled melts which retain the melt structure. A recent X-ray structural investigation of the dihydrate provides confirmatory evidence (17). Although the solid is almost isomorphous with $\text{H}_3\text{O}^+\text{ClO}_4^-$, it is distinctly less symmetrical (monoclinic rather than orthorhombic). It is not possible to locate hydrogen or to distinguish oxygen from fluorine directly. However, the longest of the four bonds around boron must be the B-O bond, and the three shorter bonds B-F. The latter are shorter than in BF_4^- and close to B-F bonds in amine adducts with boron trifluoride. This suggests $\text{BF}_3\text{H}_2\text{O}$ units rather than BF_3OH^- ions. The remaining water is water of crystallization hydrogen-bonded in the structure. The X-ray and p.m.r. spectral evidence, although not decisive, seems to dispose of ionic structures in the solid. Even in the melt the amount of ionization may be less than measured because of the asymmetrical dissociation induced by the measuring field (339). This example has been quoted at some length because it demonstrates the uncertainty in transferring structural interpretations from one state of matter to another.

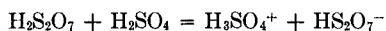
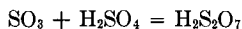
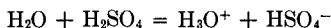
A stabilization of ionization can be achieved by adding a third component, namely, hydrogen fluoride, to the 1:1 system $\text{BF}_3\text{H}_2\text{O}$ when the ternary compound $\text{H}_2\text{O}\cdot\text{HF}\cdot\text{BF}_3$ can partly ionize as $\text{H}_3\text{O}^+\text{BF}_4^-$. Thus the hydroxonium ion can be detected by p.m.r. when water is present in a saturated solution of boron trifluoride in hydrogen fluoride at -75° (206). Similarly, addition of alcohol forms the solvated proton $\text{C}_2\text{H}_5\text{OH}_2^+$. The p.m.r. spectrum shows resolved peaks of CH_3 , CH_2 , and OH_2^+ groups.

B. SOLUTIONS IN SULFURIC ACID

The ionizations which occur in this solvent have been thoroughly reviewed by Gillespie and Robinson (119). The 100% acid has a conductivity at 25° of $1.04 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$. (This is not the minimum conductivity, which occurs at a slightly weaker composition containing 0.0019 mole of water/kg.) The conductivity is partly due to the proton transfer,



and partly to other solvated protons produced in a sequence of reactions,



which when summed are equivalent to the above solvent self-ionization and an ionic self-dehydration:



Sulfuric acid is an acid solvent, consequently the majority of solutes act as bases and the strengths of acids are leveled to a greater extent than in water. Hence few substances can increase the H_3SO_4^+ content of the solvent. The strong acids HClO_4 and HSO_3F in water are weak acids in sulfuric acid. Only the polysulfuric acids and complex hydrogen-sulfato acids such as $\text{HB}(\text{HSO}_4)_4$, derived from boric acid in oleum, are strong acids. Both ions produced in the solvent's self-ionization have high mobilities similar to those of H_3O^+ and OH^- in water. This suggests that proton transfer also occurs via hydrogen bonds without actual movement of H_3SO_4^+ units. The conductivities of strong acids in sulfuric acid are approximately equal because the H_3SO_4^+ ion, or rather the associated proton, is so mobile. Strong acid-base titrations give minimum conductivities at or near equivalence, because of removal of mobile ions as the self-ionization reaction is reversed.

More direct evidence for H_3SO_4^+ in sulfuric acid is sparse because the self-ionization, although large by water standards, is still difficult to detect spectroscopically. The detection of a similar ion H_5SO_5^+ ($\text{H}_3\text{O}^+ + \text{H}_2\text{SO}_4$) has been claimed in the infrared spectrum of the monohydrate and in more concentrated sulfuric acid solutions (343). The same unit may also occur in the crystal structure of the solid monohydrate in which five hydrogen bonds emerge from each sulfate group (40). The Raman spectra of concentrated $\text{H}[\text{B}(\text{HSO}_4)_4]$ solutions are quite complex but an assignment has been made for the H_3SO_4^+ and $[\text{B}(\text{HSO}_4)_4]^-$ species (117). A pure sample of the solid acid has not been isolated.

The main evidence for H_3SO_4^+ therefore relies on the internal self-consistency of a simple self-ionization scheme, and the ability to correlate a large body of cryoscopic and conductivity measurements on this basis.

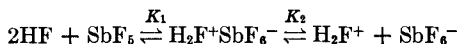
C. SOLUTIONS IN ANHYDROUS HYDROGEN FLUORIDE

The evidence adduced for a solvated proton in this solvent follows the familiar pattern for other ionizing solvents. The stabilization of protonated aromatic species in anhydrous hydrogen fluoride (A.H.F.) is a unique feature, since it is carried to a higher degree than in other solvents (e.g., H_2SO_4). The solvent itself is associated, as evidenced by a high entropy of vaporization and exceptional boiling point. The dielectric constant (84 at 0°) is higher than that of water at a corresponding temperature (i.e., fraction of boiling temperature). The solvent conductivity is particularly

affected by minute traces of water and values have lessened with increasing purification. The lowest values ($2.6\text{--}5.7 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 0°) are still two orders of magnitude greater than in water (263).

The postulated self-ionization, $3\text{HF} = \text{H}_2\text{F}^+ + \text{HF}_2^-$, is only a short-hand representation of a more complex situation. It is not believed that large molecular aggregates or ions are present in the liquid, but that ion transfer occurs via short chains and not through three-dimensional networks as in water. Approximate calculations based on an electrostatic model show a gain in stability on passing from HF_2^- to H_3F_4^- , and only small differences between H_2F_3^- , H_3F_4^- , and H_4F_5^- . Conductivity measurements show that the proton mobility in A.H.F. is less than that of alkali metal ions and that it is only the fluoride ion which has an exceptional mobility, but even for this ion differences in mobility are mitigated by the low solvent viscosity. The chain cations $\text{H}^+(\text{HF})_n$ with n large are improbable; angular H_2F^+ entities isoelectronic with water molecules should occur to some extent.

Protonic acids are unable to function as acids in A.H.F. Even the strong acids HClO_4 and HSO_3F are little ionized. The addition of Lewis acid fluorides, however, produces substantial ionization. Antimony pentafluoride in particular forms solutions more highly conducting than solutions of alkali fluorides. The $\text{HF}\text{--}\text{SbF}_5$ system has been examined in some detail, and two ionic equilibria are postulated to explain the conductivity and spectral data (156):



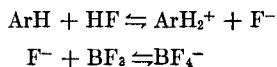
The ion dissociation equilibrium predominates at lower concentrations of the pentafluoride. For example, at 20 mole% SbF_5 , $K_1 \simeq 4.4 \times 10^{-4}$ and $K_2 \simeq 1.7 \times 10^{-2}$. The possibility of the SbF_6^- anion being formed from traces of water (i.e., $\text{H}_2\text{O} + \text{HF} = \text{H}_3\text{O}^+ + \text{F}^-$, $\text{SbF}_5 + \text{F}^- = \text{SbF}_6^-$) is no longer important at high concentrations of antimony pentafluoride, so that solvent purification is less critical than for dilute solutions. Addition of A.H.F. raises the very low conductivity of antimony pentafluoride until a maximum is reached at 90 mole% HF. At this point the equivalent conductivity is about 40% of its value at infinite dilution. The Raman spectra show the disappearance of molecular antimony pentafluoride lines at 20–30 mole% HF, and their replacement by the single line of the SbF_6^- anion. There are no HF_2^- lines and hence the solvated proton must accompany the SbF_6^- anion.

The functioning of other fluorides in the production of H_2F^+ or similar solvated protons has been demonstrated more qualitatively by salt formation and attack on metals by solutions of these fluorides (59, 61). The close analogy between fluoride solubilities, as well as acid strengths, in

A.H.F. and bromine trifluoride provides mutual support for the contention that fluoride ion transfer occurs in both solvents. In view of this similarity, the direction of transfer for halogen fluorides dissolved in A.H.F. is of interest. Some workers maintain that iodine pentafluoride is an acid because they isolated salts of the hexafluoroiodate anion (60); others were unable to isolate these salts and suggest that the products are bifluorides and that the ionization is $\text{IF}_4 + \text{HF}_2^-$ rather than $\text{H}_2\text{F} + \text{IF}_6^-$ (335). The extent of ionization is minute, however, and there is no evidence for a 1:1 adduct (259). It is also believed that bromine and chlorine trifluorides, which are more conducting, are bases in A.H.F. Xenon hexafluoride is readily soluble in A.H.F. to form highly conducting solutions with equivalent conductivities about a third of those of potassium fluoride solutions (208). From the trend with halogen fluorides one would expect the hexafluoride to become acidic in A.H.F. and to generate the solvated proton. Xenon tetrafluoride, the analog of iodine pentafluoride, does not form conducting solutions.

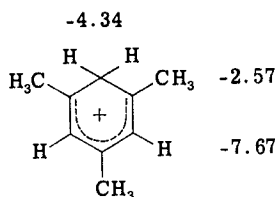
The solubility of aromatic hydrocarbons in A.H.F. has been known for many years and is attributed to the proton-accepting ability of the aromatic nucleus. The resulting arenonium ion can be further stabilized by addition of Lewis acid fluorides, or by increasing the electron availability in the aromatic circuit. The extraction of methylbenzenes with A.H.F. containing controlled amounts of boron trifluoride increases with the basicity of the hydrocarbon from toluene to hexamethylbenzene. The stoichiometry of the interaction can be followed tensimetrically. The vapor pressure of hydrogen fluoride increases with the addition of boron trifluoride, but in the presence of a strongly basic aromatic hydrocarbon the pressure decreases to a minimum at the 1:1 ratio of $\text{BF}_3:\text{ArH}$ (204).

There are similar inflections in the conductivity curves at 1:1 ratios (168). The conductivity, however, remains constant after this value is exceeded. The conductivities of the more basic hydrocarbons are similar and approach the potassium fluoride values. The reactions are summarized:



With excess of boron fluoride the first equation is displaced to the ionic side, so that conductivities of all the methyl-substituted hydrocarbons approach parity. Further information on the cation produced is provided by spectral methods. The ultraviolet spectra of methylbenzenes in the acid boron fluoride solutions show absorptions characteristic of arenonium ions, which can also be predicted theoretically (71). The p.m.r. spectra have been studied at low temperature to slow down proton exchange and separate the peaks. For example, with mesitylene solutions the broadened

solvent peak is observed to the low field side followed by that of the ring protons and "aliphatic" methylene group and finally the methyl protons. The chemical shifts relative to trimethylsilane are indicated in the formula:

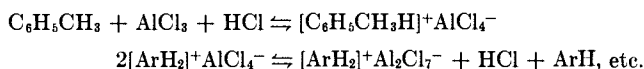


At higher temperatures the spectra show that the added proton remains attached to the complete ion, but exchanges its position with the other ring protons (206). These cations cannot be isolated as tetrafluoroborate salts except at low temperature, but many of the corresponding hexafluoroantimonates are stable at ordinary temperatures, e.g., symmetrical $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{H}^+\text{SbF}_6^-$ melts at 51° (229). The p.m.r. spectra of this salt and related hexafluoro anions measured in liquid sulfur dioxide agree with their formulation as σ -arenonium complexes. Thus, although the solvated proton in hydrogen fluoride has yet to be adequately characterized, there is no doubt about the stabilized protonic species which exist in solution or as salts.

D. SOLUTIONS IN LIQUID HYDROGEN CHLORIDE

The existence of H_2Cl^+ in the gas phase has been demonstrated (98), but its existence in liquid hydrogen chloride can only be inferred from reactions carried out in this solvent (323). It can be stabilized in the presence of Lewis acids and aromatics analogously to the systems just described (45).

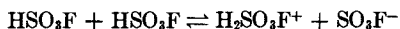
Brown and Pearsall showed by vapor pressure measurements that dry hydrogen chloride does not combine with aluminum chloride down to as low a temperature as -120° but, in the presence of toluene at -80° for each molecule of aluminum chloride dissolved, one molecule of hydrogen chloride enters the green solution. At higher temperatures, hydrogen chloride is evolved with another region of stability at $\text{AlCl}_3:\text{HCl}$ of 2:1 before all the hydrogen chloride is dissociated from the complex. The reactions are:



The increasing acid strength of the polymeric anions parallels that of polysulfates (89).

E. SOLUTIONS IN FLUOROSULFURIC ACID

This solvent has some properties in common with, and some intermediate between, hydrogen fluoride and sulfuric acid. The postulated self-ionization by proton transfer forms another solvated proton:

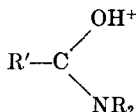


There is no complication from self-dehydration as in sulfuric acid. The acids which increase the solvated proton content are again the Lewis acid fluorides (18), e.g.,



Recent work has shown that the simple antimony acid is only a weak acid in fluorosulfuric acid, but that further substitution with sulfur trioxide forms the acids $\text{H}_2\text{SO}_3\text{F}^+[\text{SbF}_{5-n}(\text{SO}_3\text{F})_{1+n}]^-$ which increase in strength from $n = 1$ to $n = 3$. The protonated cation species has the abnormally high mobility expected for conduction processes controlled by proton transfers (317).

Protonated organic cations are stabilized in solution by these acids or even by the solvent itself. For example, the O-protonation has been shown by p.m.r. measurements on *N,N*-dimethylformamide and other amides (36, 114) to produce the cation:



The signal from the bound proton can be observed directly in fluorosulfuric acid solutions at low temperatures when proton exchange is not appreciable as it is in other solvents. Much quantitative work remains to be done with this solvent before an informed comparison can be drawn with hydrogen fluoride and sulfuric acid.

IV. Cations with Metal-Carbon and Metal-Metal Bonding

Although the sandwich-type structure of ferrocene has been well established by spectral and X-ray measurements, the bonding scheme in the compound is far less certain. A strong ligand-field model with ionic bonding to cyclopentadienyl anions is favored (210). Whatever the exact nature of the metal-to-carbon bonding, a convenient working rule is to regard the diamagnetism and the stability of ferrocene as arising from a noble gas configuration around the central atom. Appropriate electron contributions come from each type of ligand as this is varied, and in this way a whole series of charged or neutral compounds can be prepared with the same configuration. A selection of heteromononuclear cations is collected in

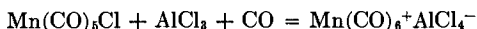
TABLE IX
ISOELECTRONIC CATIONS WITH METAL-CARBON BONDING^a

		Mn(hmbnz) ₂ ⁺	Fe·Cpd·Bzn ⁺	Co·Cpd·Bzn ²⁺	
		Tc(Bzn) ₂ ⁺	Fe(Mes) ₂ ²⁺	Co·(Cpd) ₂ ⁺	
		Re(Bzn) ₂ ⁺	Ru(Mes) ₂ ²⁺	Ir·(Cpd) ₂ ⁺	
			Ru(Bzn) ₂ ²⁺	Rh(Bzn) ₂ ³⁺	
		MnBzn(CO) ₃ ⁺	Fe(Cpd)(CO) ₃ ⁺		
	W(Cpd) ₂ H ₃ ⁺	Re(Cpd) ₂ H ₂ ⁺	FeH(CO) ₅ ⁺		
V(Cpd) ₂ (CO) ₂ ⁺	Cr(Cpd)(CO) ₄ ⁺	Re(Etn) ₂ (CO) ₄ ⁺	Fe(CO) ₆ ²⁺		Ag(Disn) ₂ ⁺
VBzn(CO) ₄ ⁺	CrCht(CO) ₃ ⁺	Mn(Etn)(CO) ₅ ⁺	Os(CO) ₆ ²⁺		Cu(PR ₃) ₄ ⁺
		Re(CO) ₆ ⁺			
	W(hmbnz)(CO) ₃ Cl ⁺	Mn(CO) ₆ ⁺	Fe(CNR) ₆ ²⁺	Co(CNR) ₅ ⁺	Cu(CNR) ₄ ⁺

^a Bzn = benzene (6); Cpd = cyclopentadiene (5); Cht = cycloheptatriene (7); Disn = diarsine (*o*-phenylenebis-dimethylarsine) (4); Etn = ethylene (2); hmbnz = hexamethylbenzene (6); Mes = mesitylene (6); CO (2); CNR (2); HCl (1). Numbers in parentheses indicate electrons contributed.

Table IX. (If the number of electrons in the outer orbitals of the metal, i.e., the group number, is added to the indicated electron contribution from the ligands less the charge number, it can be seen that all these ions have the same outer configuration of 18 electrons.) The stability of this arrangement is reflected in the variety of preparative methods available. A few illustrative examples are given.

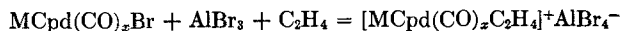
Metal carbonyl cations were isolated in the form of tetrahaloaluminates by reacting metal carbonyl halides directly with aluminum halides in the presence of carbon monoxide (101):



The compound was decomposed to dimanganese decacarbonyl with water. Its infrared spectra showed the single carbonyl frequency at 2090 cm^{-1} expected for the hexacarbonyl ion. The corresponding rhenium compound was stable to water so that its ionic nature could be demonstrated by precipitation of an insoluble perchlorate or tetraphenylborate from aqueous solutions (148). The carbonyl band of this regular octahedral ion appeared at 2083 cm^{-1} . Doubly charged iron and osmium hexacarbonyl cations were produced by analogous reactions:

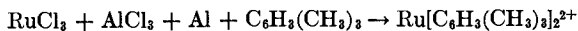


Ethylene can be used in place of carbon monoxide, or other carbonyl derivatives in place of halides, to make this a general reaction. Thus reactions of the type

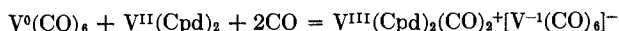


lead to ions such as FeCpd(CO)_3^+ , $\text{Mn(C}_2\text{H}_4)(\text{CO})_6^+$, WCpd(CO)_4^+ (100).

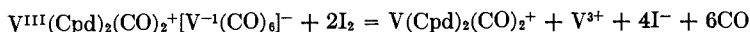
An example of direct synthesis for a purely hydrocarbon metal cation is provided by the ruthenium-mesitylene cation. Aluminum chloride was used in a reductive combination with aluminum at 130° and the cation isolated as the insoluble hexafluorophosphate or tetraphenylborate (99):



The combination of a carbonyl cation with a carbonyl anion in a single salt has been achieved in a recent synthesis (48):



Only the product was diamagnetic. The formal charges on the vanadium in the product were demonstrated by oxidation of the anion with iodine in potassium iodide:



The triiodide of the cation was precipitated with excess iodine.

Quite obviously the noble gas rule serves as a reliable guide to the preparation of these heterocations, as well as providing a convenient classification of the products.

A number of ionic halides of transition metals in lower valency states have structures containing polymeric units. The metal-metal bond lengths within the units approximate those in the metals. General reviews on this bonding are available for more detailed consideration (193, 268).

The lower molybdenum chloride of empirical composition MoCl_2 provides an example. It is extremely stable and can be heated to 800° *in vacuo*, or 300° in air, without change. Concentrated acids displace only a third of the chlorine. The chloro acid of empirical formula $\text{HMo}_3\text{Cl}_7 \cdot 4\text{H}_2\text{O}$ can be crystallized from solutions in hydrochloric acid. Part of the chlorine in this acid can be replaced on controlled hydrolysis to form products which include $\text{Mo}_3\text{Cl}_6 \cdot 4\text{H}_2\text{O}$ and $\text{Mo}_3\text{Cl}_4(\text{OH})_2 \cdot 7\text{H}_2\text{O}$. X-ray structural analyses of these products show the (Mo_6Cl_8) unit consisting of an octahedron of molybdenum atoms oriented at the face centers of an enclosing cube of chlorine atoms. The Mo_6Cl_8 unit is itself enclosed in a surrounding octahedron of six atoms or groups (44). The above compounds are now formulated $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]6\text{H}_2\text{O}$, $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_4(\text{H}_2\text{O})_2]6\text{H}_2\text{O}$, and $[\text{Mo}_6\text{Cl}_8(\text{OH})_4(\text{H}_2\text{O})_2]12\text{H}_2\text{O}$, respectively.

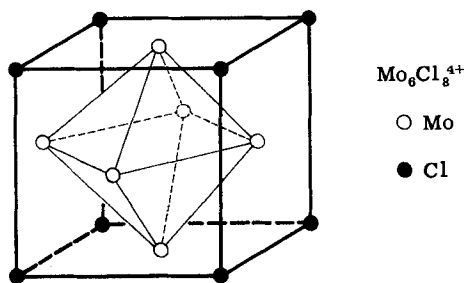


FIG. 10. The $\text{Mo}_6\text{Cl}_8^{4+}$ ion.

The integrity of the heterocation unit shown in Fig. 10 is evident in all its reactions. A variety of derivatives can be prepared such as $\text{MCl}_4(\text{C}_5\text{H}_5\text{N})_2$, $\text{MCl}_4(\text{C}_2\text{H}_5\text{OH})_2$, $\text{MBr}_4(\text{H}_2\text{O})_2$, $(\text{H}_3\text{O})_2\text{MI}_6$, and $\text{K}_2\text{MCl}_6 \cdot 6\text{H}_2\text{O}$ where $\text{M} = \text{Mo}_6\text{Cl}_8$. Exchange studies with Cl^{36} showed only six labile chlorine atoms in the last compound (299). It has been suggested on the basis of magnetic and spectral data that other lower halides of tungsten and molybdenum probably contain similar trinuclear cations, e.g., $\text{Mo}_3\text{Cl}_9^{3+}$, $\text{W}_3\text{Cl}_{12}^{3+}$, $\text{W}_3\text{Br}_{12}^{3+}$ (65).

The lower niobium and tantalum halides $\text{M}_6\text{X}_{14} \cdot x\text{H}_2\text{O}$, made by reduction of the pentahalides with metals, have been examined in concentrated

solutions by the X-ray scattering technique (321). The polynuclear cation in these substances is an octahedron of metal atoms bridged along each edge with halogen atoms, $M_6X_{12}^{2+}$ (Fig. 11). More recently other lower halide phases made by metal reduction in temperature gradients have

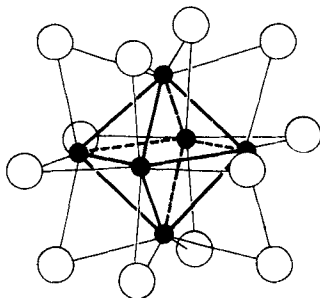
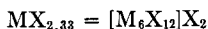
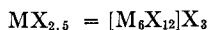
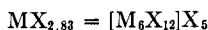


Fig. 11. The $M_6X_{12}^{2+}$ structure ($M = Nb, Ta$; $X = Cl, Br$).

been identified as salts of similar cations but in different oxidation states (202). The equilibrium diagrams of Ta-TaBr₅ and Ta-TaI₅ systems have established the phases TaBr_{2.33}, TaBr_{2.5}, TaBr_{2.33}, and TaI_{2.33} as well as the tetrahalides. The nonintegral phases are formulated as



The Ta₆Cl₁₂³⁺ ion is unstable in aqueous solution being reduced to Ta₆Cl₁₂²⁺, whereas the phases TaBr_{2.33} and TaI_{2.33} provide stable aqueous solutions of Ta₆X₁₂⁴⁺ (203).

The nature of the bonding in these ions is of special interest. Sheldon has given a valence-bond interpretation of the MCl₆⁻ structure in which the tetragonal pyramidal configuration around each Mo employs $d_{x^2-y^2}sp^3$ hybrid orbitals and the square planar Mo-Mo bonding utilizes d_{xz} , d_{yz} orbitals. The two remaining electrons from molybdenum are supposed to pair their spins and strengthen the metal-metal bonding.

A more general molecular orbital approach is favored by Cotton and Haas (69), who discuss the difficulties in treating these systems in terms of two center bonds. Thus in M₆Cl₁₂²⁺ the formal metal oxidation number is 2, or in Pauling's terminology the metal-metal links have a bond order of 2/3 (239). The similarity in the square planar environment around metal atoms in the ions M₆X₈⁴⁺, M₆X₁₂²⁺, and M₃X₁₂³⁻ encourages a common treatment of bonding rather than a special treatment for each species. Energy level diagrams were derived using appropriate L.C.A.O.-M.O. wave functions for each of the three systems. Robin and Kuebler (256)

relied on direct spectral evidence to obtain an order of energy levels different from that of Cotton and Haas. The spectral effects of metal-ligand bonding were distinguished from those of metal-metal bonding by comparing spectra of $\text{Nb}_6\text{Cl}_{12}^{2+}$ with $\text{Nb}_6\text{Br}_{12}^{2+}$, and of $\text{Nb}_6\text{Cl}_{12}^{2+}$ with $\text{Ta}_6\text{Br}_{12}^{2+}$. (A change of ligand has a large effect on metal-ligand bonding and little effect on metal-metal bonding.) A complicating factor in the interpretation was the splitting of some of the bands observed in spectra of niobium complexes into two components in the corresponding tantalum spectra. This was attributed to a tetrahedral elongation in the tantalum octahedra giving rise to a formal charge distribution, shown in Fig. 12a.

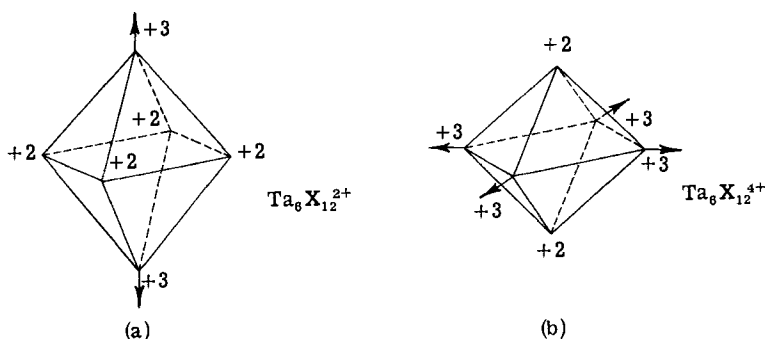


FIG. 12. Charge distribution in distorted octahedral ions. See text for explanation.

The expected alteration in charge distribution on a two-electron oxidation is shown in Fig. 12b, and this was again supported by the spectra obtained in solution. Distortions are supposed to occur in order to separate high charge entities as well as to produce integral valencies. This is feasible because it can be shown that coulombic repulsions between like ions are less if part of the charge from the equatorial plane of an equi-charged octahedron is transferred to the apical positions. The amount of charge transferred, and especially the absence of detectable transference in niobium compounds, is not explained, but certainly the avoidance of non-integral or unusual valencies by charge separation is in line with previous work on colored complexes ($[\text{Fe}_2(\text{CN})_6]^-$ contains Fe^{2+} and Fe^{3+} ; SbBr_6^{2-} contains Sb^{3+} and Sb^{5+}).

The nontransition metal complex $\text{Bi}_6(\text{OH})_{12}^{6+}$ has a structure similar to the M_6X_{12} units described above (see p. 291).

V. Ions in the Gas Phase

Mass spectrometry is the method most frequently employed for detecting such ions (205). The main interest has not been in the ions themselves

but rather in their neutral precursors, which in effect have been recognized by ionizing them. Nevertheless these studies have revealed a surprising complexity for many gaseous ions and have demonstrated the stability of structural units encountered in other phases. Certainly modern determinations of vapor pressure at high temperature cannot afford to ignore some of the vapor phase species if they are to be meaningful. Conversely, these studies imply that a number of structural entities in the gas phase may also exist in the solid or liquid state. For example, the species formed by surface ionization from rhenium, which had been treated with nitric acid, included considerable amounts of the primary ReO_4^+ in addition to ions derived from rhenium heptoxide and its fragmentation (313). The neutral tetroxide, which has been claimed to result from the oxidation of the metal, has not been taken seriously and is usually ascribed to traces of water forming anhydrous perhenic acid (318). From the mass spectral evidence it could well be a genuine species at ordinary temperatures. A selection of heterocations encountered during mass spectrometric observations is collected by Reed (252).

The primary aim of many studies has been to obtain thermochemical data such as dissociation energies and heats of evaporation. A common high temperature technique employs a Knudsen cell containing the specimen to be vaporized, with a small orifice area in comparison with its total internal surface in order to obtain equilibrium inside the cell. This is heated resistively, or by electron bombardment, at low pressures and the emerging molecular beam is ionized by a cross beam of electrons controlled at a voltage a little above the required ionization potentials. (A compromise voltage which gives a sufficient yield without undue fragmentation is needed.) The ion beam is then analyzed in a mass spectrometer of moderate resolution (1 in 600). It is important to distinguish ionization of the Knudsen cell beam from that of extraneous sources such as deposits or residual gases. This is possible if a plate with a defined aperture is inserted in the beam path under operating conditions, which can either stop the beam completely or allow through a cross section of the beam (55, 56). The beam intensity profile varies according to the place of origin of a particular ion. Photo-ionization of metal vapors by the cell acting as a light source must also be allowed for. The ion current, derived from neutral species and collected by a photomultiplier detector, is related to the concentration of neutral species in the ionizing region by

$$I_+ = \eta Q I_e n$$

where η is the collection efficiency, Q is the ionization cross section, I_e is the electron beam current, l is the active path length of electrons, and n is the concentration of neutral species. Substituting for n according to the

ideal gas law shows that the pressure $p = kI_+T$, where k is a combined constant usually determined with a standard element such as silver in the Knudsen cell. The variation of p with T for any particular species provides data for calculating the thermochemical quantities. Recent reviews on other ion sources (251), and on time-resolved spectrometry (251), serve to illustrate the potential of the method.

Much of the earlier work was concerned with the vapor of elements (301). In particular, the existence of polymeric ions derived from neutral species helped to resolve the controversy concerning the heat of sublimation of carbon. At the sublimation point of carbon the relative amounts of the species were (80):

C ⁺	C ₂ ⁺	C ₃ ⁺	C ₄ ⁺	C ₅ ⁺	C ₆ ⁺	C ₇ ⁺
1	2.8	4.5	0.35	0.5	<0.0005	

The heats of sublimation of the separate species were derived from

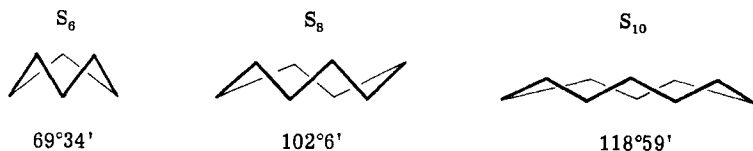
$$\frac{d \ln (I_+T)}{d(1/T)} = \frac{-\Delta H_s}{R}$$

and the overall value for carbon vapor was derived (55). Similar studies have been carried out on silicon, germanium, and their carbides (81, 82, 83, 153).

More recently the measurement of polymeric sulfur cations S_n^+ ($n = 2-8$) over a range of temperatures has reiterated their persistence outside the liquid phase (209). Their stability decreases with temperature so that only monomeric sulfur exists above 2500°. The species observed by electron impact on metal sulfide vapors, which give undersaturated sulfur vapor in the gas phase, are summarized:

Sulfide	Temperature (°K)	n for S_n^+ ions
FeS	1323	1,2
ZnS	1244	1,2,3,4
CdS	1014	1,2,3,4
HgS	581	1-8

By comparing the ions produced from pure sulfur with those from mercuric sulfide, it was shown that S_2^+ ions were in large part derived from S_8^+ ions. The mean degrees of polymerization obtained from these results are in close agreement with vapor pressure measurements. The mole fraction of all the species can be plotted as a function of temperature. Such a diagram demonstrates the unique stability of S_8^+ , which can be rationalized as the least strained of the puckered ring structures, being closest to the natural dihedral angle for the unit S—S—S (238):

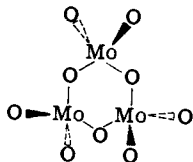


Mean angle in $(CH_3)_3S_3$, $(CF_3)_3S_3$, and BaS_3 is 104° .

Investigations of oxide vapors have also shown polymeric and presumably cyclic ions. Molybdenum trioxide at 850° gave the following relative yields of ions (32):

$Mo_3O_9^+$	$Mo_4O_{12}^+$	$Mo_5O_{15}^+$	MoO_3^+	$Mo_2O_6^+$
1	0.33	0.05	~ 0.01	~ 0.01

The low monomer and dimer yields resulted from fragmentation of higher polymers. Polymers higher than a pentamer, if present, were in less than 10^{-5} yield. The structure suggested for the trimer was a cyclic one with the d^{5s} hybridization of the molybdenum orbitals reinforced by π -bonding. The ring would be puckered if the molybdenum angles approached the tetrahedral values.



Similar results were obtained with tungsten trioxide vapor. The monomer and dimer ions arose by fragmentation. At $1492^\circ K$ the ion yields were:

$(WO_3)_3^+$	$(WO_3)_4^+$	$(WO_3)_5^+$	$(WO_3)^+$	$(WO_3)_2^+$
1	0.32	0.002		< 0.05

A rich spectral pattern was observed for each of the ions because of the number of tungsten isotopes. The trimer, for example, had twelve values ranging from 690 to 702 a.m.u. (28).

The refractory oxide of beryllium, when ionized in the vapor phase at 2000° – $2400^\circ K$, produced mainly $(BeO)_4^+$ and some trimer and pentamer (54). Only traces of monomer and dimer were detected. The polymeric ions derive from primary ionization of molecules since a low potential electron beam was employed. Apart from the dimer, these ions are believed to be cyclic by analogy to ions in solution or in solids. The trimeric ion would be a six-membered ring similar to the cation in $Be_3(OH)_3(H_2O)_6^+Hg_2I_7^-$ and consisting of beryllium tetrahedra linked at two of their apices. A tungsten container which held the sample became oxidized, presumably by the oxygen dissociating from the beryllium oxides, and a series of mixed oxides

was detected. The most abundant of these ions were $\text{WO}_2(\text{BeO})_2^+$ and $\text{WO}_3(\text{BeO})_2^+$, which can also be represented as hexagonal rings. The adventitious production of these mixed ions during primarily thermochemical investigations suggests that a more systematic approach could provide valuable information on a whole series of mixed complex ions.

Vanadium pentoxide was not investigated in detail because its ready decomposition prevented thermochemical measurements (29). The results obtained are of interest, however, for comparison with solid state structures. The monomer ion was not detected but only the dimer and dissociated products from this and the trimer: V_4O_8^+ , V_3O_6^+ , V_4O_9^+ , and $\text{V}_6\text{O}_{14}^+$, $\text{V}_6\text{O}_{12}^+$. Fragmentation ions from higher polymers V_2O_3^+ , V_3O_6^+ , V_4O_9^+ were also observed. The $\text{V}_4\text{O}_{10}^+$ peak diminished with time as the oxide dissociated. The oxide compositions encountered in the solid state range from $\text{VO}_{0.8}$ to $\text{VO}_{2.5}$ including a series $\text{V}_n\text{O}_{2n-1}$ ($n = 3-8$) and V_6O_{13} (328). These are infinite structures. The oxide V_6O_{13} consists of distorted oxygen octahedra around vanadium atoms, linked by some corners and edges into a rather complex double chain cum layer structure. The smaller units encountered in the gas phase are relatively oxygen-rich compared with the solid units, presumably because of unshared oxygen atoms at the surface of the finite units. Cyclic structures seem improbable for these ions. The actual structures would be of considerable interest in view of the range of vanadium coordinations which must exist in the series.

The ions of lower oxides, which may be unstable at lower temperatures, can be produced *in situ* by reduction of oxides with metals. Again the reduction may be unintentional if metal containers are used at high temperatures under reduced pressures. Tantalum pentoxide was reduced by tantalum to yield mainly TaO^+ and TaO_2^+ (157). The Ta-O bond strength is particularly high, almost as great as for the multiple-bonded carbon monoxide or nitrogen. Titanium dioxide reduced by titanium gave simple TiO^+ and TiO_2^+ ions (31). The polymeric nature of TiO units in titanyl salts, both solid and in solution, is not carried over to the vapor phase. Also in the reduction of alumina with tungsten the primary hetero-ions AlO^+ , Al_2O^+ , and Al_2O_2^+ are less complex than in some of the aluminum oxyhalides and basic salts (83). Reduction with aluminum gave Al_2O^+ almost exclusively. A silicon-silica mixture yielded SiO^+ and Si_2O_2^+ with SiO_2^+ at higher temperatures (246).

The ionization of oxyhalides has been examined in a cursory manner compared with oxides. One example is provided by the mass spectra of chromyl halides (103). Ions from the halide CrO_2ClF can be detected in an equimolecular mixture of chromyl chloride and fluoride, but even for a simple halide it has not been possible to ascertain the processes leading to the great variety of ions produced. Dimeric ions and fragment ions were

present (CrO_2F_2 , CrO_2F , CrO_2 , CrOF_2 , CrOF , CrO , CrF_2 , CrF , Cr , $\text{Cr}_2\text{O}_4\text{Cl}_3$, $\text{Cr}_2\text{O}_4\text{Cl}_2$, $\text{Cr}_2\text{O}_4\text{Cl}$, $\text{Cr}_2\text{O}_3\text{Cl}_3$, $\text{Cr}_2\text{O}_3\text{Cl}$, and CrOCl ions).

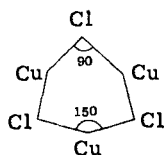
Halides, especially the alkali halides, have been examined in much greater detail. The alkali halide vapors contain appreciable amounts of dimers and trimers (Table X) and even traces of tetrameric molecules, which yield the ions M_2X^+ , M_3X_2^+ , and M_4X_3^+ by electron impact (30). The amount of MX^+ ion is low and decreases with increasing cation size. The degree of dimerization also follows a regular pattern, being greatest for lithium salts and for chlorides. The forces binding these structures are the same as in solid alkali halides, since it is possible to treat the gas molecules as ion pairs which polarize one another. The potential energy of the molecules is compounded of electrostatic and small van der Waals' attractions less an exponential repulsion energy. There is good agreement between experimental and calculated values. The dissociation energies can also be calculated on an ionic model (31). The polymers from which the ions derive can be recognized as fragments of the solid state structures.

TABLE X
IONIZATION OF THE ALKALI FLUORIDES

MF	Temperature (K°)	Relative ion intensities	
		$\text{M}_2\text{F}^+/\text{M}^+$	$\text{M}_3\text{F}_2/\text{M}^+$
LiF	954	3.3	0.31
NaF	1017	0.8	0.015
KF	1031	0.93	0.013
RbF	888	0.59	0.0055
CsF	764	0.29	0.0022

The vapors of alkali hydroxides resemble those of alkali fluorides and the main ions are MOH^+ and M_2OH^+ (278).

Polymeric structures have also been found in other halide vapors. The predominant ion from cuprous chloride is Cu_3Cl_3^+ , which is undoubtedly cyclic since electron diffraction of the molecular vapor has given the molecular shape shown (260). This ring is part of the solid state structure (zinc blende type).



The aluminum halide ions in the vapor are less directly related to solid state structures (247). The layer lattice of solid aluminum chloride

is converted to dimeric species in the vapor. Mass spectra show Al_2Cl_5^+ as the predominant ion followed by AlCl_2^+ . However, traces of trimeric species are also present and these are obviously not detectable by the electron diffraction technique used to examine the structure of the vapor species. (The relative ion intensities were Al_2Cl_5^+ , 187; AlCl_2^+ , 100; Al_3Cl_9^+ , Al_3Cl_8^+ , Al_3Cl_7^+ , total 0.86.) The bromide is dimeric in the solid, in nonpolar solvents, and in the vapor. The mass spectra show the expected main ions AlBr_2^+ and Al_2Br_5^+ and no trimeric species. Aluminum fluoride vapor is almost exclusively monomeric with predominance of AlF_2^+ ions and only traces of Al_2F_5^+ . A time-resolved study of the vaporization process might be more informative with respect to evaporation of units from the solid structures.

Ions derived from glow discharges in water vapor have been mentioned. An example of a monohydrated metal ion, $\text{K}\cdot\text{H}_2\text{O}^+$, has been observed when traces of water vapor contaminated alkali halides (53). This ion contrasts with the $\text{K}(\text{H}_2\text{O})_4^+$ ion in aqueous solutions where the potassium ions are inserted substitutionally in the water lattice (42).

Finally, to complete this brief survey of the types of ion investigated by mass spectrometry, mention should be made of ion-molecular reactions. If the pressure in a mass spectrometer is allowed to rise, the chance of ions interacting with molecules as they move from source to detector is correspondingly increased. The process has been considered theoretically and experimentally for rare gas-hydrogen molecule interactions (311). The ions ArH^+ and KrH^+ have been measured when the pressure in the ion source was higher than normal. The corresponding neutral molecules would not of course be stable.

VI. Heterocations in Aqueous Solution

Heterocations in aqueous solution have been studied intensively in recent years and a more detailed picture of the species qualitatively designated as solvated cations is beginning to emerge. The extent of this work is reflected in, for example, compilations of stability constants (37, 340) and texts devoted wholly or in part to the determination of stability constants (216, 261).

A. ION PAIRING

The concept of ion pairing in solution arose from deviations between experimentally determined activity coefficients of the more polarizing ions in dilute solutions, and the values calculated on the simple Debye-Hückel theory. Two methods have been proposed to remove the discrepancy. In one approach it was no longer assumed that the energy required to place an ion in the vicinity of another ion was negligibly small compared with

thermal energies, and hence a more accurate solution of the Poisson-Boltzmann expression was found (e.g., 134). The alternative approach was to assume that some of the ions became paired with ions of opposite charge and thereby lessened the energy needed to place ions in their ion atmospheres. The association constant for ion pairing, K , relative to the separate ions was evaluated by Bjerrum as

$$1/K = 4\pi \int_a^q \exp [Z_1 Z_2 e^2 / DKTr] r^2 dr$$

where r is the distance between ion centers of charge $Z_1 e$, $Z_2 e$, in a medium of dielectric constant D at temperature T , and K is Boltzmann's constant. The lower limit of the integral is the distance of closest approach of oppositely charged ions. Oppositely charged ions have been considered to pair and become nonelectrolytes when they approach closer than a distance $q = Z_1 Z_2 e^2 / 2DKT$. The sharp distinction between ions and ion pairs at distance q is of course a mathematical device without necessarily having a particular physical significance.

Other arbitrary choices of q and hence association constants are possible. For example, precise cryoscopic measurements with aqueous copper sulfate solutions showed negative deviations from the values expected for 1:1 electrolytes and hence suggested incomplete dissociation (46). The calculated minimum q value (13.9 Å) was much larger than Cu-S distances in solid $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ which vary from 3.6 to 5.5 Å. The latter would approximate the distance of closest approach for the ion pair (a), and the former distance (q) would allow insertion of five to six water molecules. It was found that almost constant values for an association constant were obtained from the data for values of q from 5 to 6.9 Å; the "constant" then increased with increase of the chosen q . These results could therefore be taken to indicate an intimate ion pair, although the theory allows longer-range attractions.

Other methods for detecting ion interaction may yield quite different results, depending on the range of interaction susceptible to the measurement; in particular, spectrophotometric investigations of ion pairing, when a new visible or ultraviolet absorption band is generated on addition of anions to a particular cation in solution. It is assumed on good evidence that the new bands arise when an electron is transferred from anion to cation, or at least to the aquated cation. Hence only ion pairs in fairly close proximity would be detectable by optical methods and the association constant could be less than that found as above. These indirect methods of measuring ion association depend on the model assumed and the derived theoretical equation used in computation (63).

It is therefore of considerable interest that ion pairing of a hydration

cation has now been observed directly in solution by the X-ray scattering technique. With solutions of erbium chloride at various concentrations the radial distribution curves peak first at 2.3 Å, corresponding to the sum of Er^{3+} and H_2O radii, and the area under the peak corresponds to octahedral coordination (43).

There is a further peak at 4.6 Å that corresponds to an $\text{Er}^{3+}\text{-Cl}^-$ distance which would place the chloride ions in the position shown (Fig. 13) with an overall D_{3h} symmetry, the same symmetry required to explain the visible spectra of the solution.

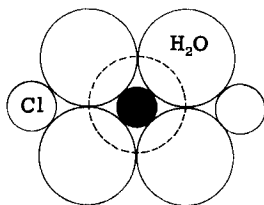


FIG. 13. $\text{Er}^{3+}(\text{Cl}^-)_2$ pairing.

The direct measurement of coordinated water in alkali cations has also been made by X-ray scattering from solutions (42). Another method which distinguishes the first coordination shell of water molecules around cations from the rest employs n.m.r. techniques (66). If cobalt perchlorate is added to solutions of diamagnetic salts in water enriched with O^{17} , it is possible to separate the O^{17} resonances arising from water molecules in the first coordination shell from those of unbound water molecules. The paramagnetic cobalt ion interacts much more strongly with O^{17} in the latter and shifts the resonance to lower field values. The sixfold coordination of $(\text{Al}\cdot 6\text{H}_2\text{O})^{3+}$ was found from the area under the resolved absorption curve. The absorption curves for beryllium solutions, besides showing the $(\text{Be}\cdot 4\text{H}_2\text{O})^{2+}$ ion, were slightly asymmetrical because of exchange of the free and coordinated water molecules. The lifetime of the coordinated water, determined from the temperature dependence of resonance, was about 3×10^{-4} second. This value can be compared with a lifetime of about 3×10^{-12} second for the proton in its hydrate complex $(\text{H}\cdot 3\text{H}_2\text{O})^+$.

B. HYDROLYTIC EQUILIBRIA

Many hydrated cations can interact further with water molecules and the nature of the hydrolytic equilibria has been the subject of numerous investigations, especially by Scandinavian chemists (303). In addition to mononuclear products, polynuclear ones containing two or more metal ions linked by ligand bridges can also form. It is not possible to formulate the resulting heterocations unambiguously because of the excess of solvent

molecules and salts added to provide a constant ionic medium. Their concentrations remain approximately constant during the formation of the complex cations and hence equilibrium equations convey no information about these species. The hydrolytic cations are formulated with OH^- as ligands, omitting solvent and electrolyte participation (302). Hydrolytic reactions are a special instance of a quite general formation of complexes in solution.

The thermodynamic equilibrium constant for complex formation would normally be expressed in terms of activities but, since these are readily accessible only for dilute solutions where activity coefficients can be calculated from the Debye-Hückel formula, it is usual to add large amounts of supporting electrolyte consisting of noncomplexing, or at most weakly complexing, ions. In such swamping media the ionic strength and activity coefficients remain constant as the complexes are formed. A stability constant can then be given in terms of concentrations which will be valid for the particular medium used. Complex formation involves the successive substitution of the originally solvated cation by ligands (anions or neutral molecules); the successive steps usually overlap and it is difficult to separate the participating equilibria.

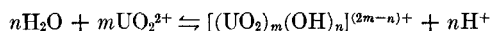
These would be disturbed if chemical methods were employed to follow them, so that only physical methods are practicable in these labile systems. It can be shown for mononuclear complexes that the average number of ligands (L) for each metal ion (M) is related to the stability constants β_n for $\text{ML}_{n-1} + L = \text{ML}_n$ by:

$$\bar{n} = \sum_{n=1}^{n=\infty} n\beta_n[\text{L}]^{n-1}/1 + \sum_{n=1}^{n=\infty} \beta_n[\text{L}]^n$$

For polynuclear complexes M_mL_n a new set of stability constants β_{nm} are defined, which are similarly related to the average ligand number. The latter is determined, and the problem is to find the values for m and n and the stability constants which fit the equation. Experimentally the free metal ion concentration is found potentiometrically or polarographically, the free ligand concentration by pH measurement if the ligand is the anion of a weak acid, or the complex by solvent extraction into a nonmiscible solvent. The pH method is the commonest; among others are solubility, cation exchange, and spectrophotometric and other spectral measurements (for details of which the cited references should be consulted).

The hydrolysis of the uranyl ion provides a good example, being one of the most thoroughly studied equilibria. A summarizing paper compares the complexes and their stability constants as determined in a number of ionic media (84). Solutions are made up with a constant concentration of

uranyl ion and supporting electrolyte, e.g., 3 *M* NaClO₄, but with varying amounts of acid or alkali. The solution pH is then measured and the average number of OH groups bound to the uranyl groups (\bar{n}), which is equivalent to the number of protons released on hydrolysis, is deduced from the measured hydrogen ion concentration and the number of protons introduced into the solution:



A series of curves of \bar{n} against pH at constant uranyl concentrations is plotted and values for m , n , and the stability constants chosen to fit the curves over the widest range. In earlier studies these values were obtained by graphical methods, but nowadays more accurate values are obtained by suitable computer programming shortened by using approximate graphical values (266, 304). Often there is no unique solution and with increasing accuracy of data the number of species tends to increase. The main species are not usually in dispute but the choice of minor species is more contentious. Since the interpretation can be no more accurate than the experimental data will allow, it is important that alternative methods be used to avoid undetectable systematic errors of a single method. In the work on uranyl ion hydrolysis it is interesting to follow the changing interpretation as the data become more precise or are reinterpreted by more accurate procedures. Originally the mononuclear ion $\text{UO}_2(\text{OH})^+$ was assumed, then the parallel \bar{n} -pH curves were interpreted as indicating an unlimited series $[(\text{UO}_2)_{n+1}(\text{OH})_{2n}]^{2+}$. More refined results in a variety of media showed deviations from parallelism in some of the media and the following assignments were made:

<u>Ionic medium</u>	<u>n, m for $(\text{UO}_2)_m(\text{OH})_n$</u>
SO_4^-	2,2; 4,3; 6,4; 8,5
NO_3^-	2,2; 4,3; 6,4; 5,3
Cl^-	2,2; 4,3; 6,4; 5,3; 7,4
ClO_4^-	2,2; 4,3; 6,4; 5,3

In addition, the mononuclear 1,2 complex was needed in the most concentrated uranyl solutions (about 0.1 *M* in U compared with 3 *M* perchlorate substrate), and the 1,1 complex at low uranium concentrations (down to 0.00025 *M*) to obtain a better fit with the data. Other authors fit their results with a smaller number of species. Thus in nitrate media only the 1,1, 2,2, and 5,3 species were used to explain the pH measurements. The increasing stability of the dimeric species with increasing temperature was noted (14). The difference in species produced in different media suggests additional complexing by the medium anions.

It is possible to compare the complexing tendency relative to the perchlorate medium, and this shows that sulfates are stronger complexing

media with nitrates approximately the same as perchlorates (84). Chloride ion complexing in sodium chloride media is also indicated by optical absorption measurements (265) for the 4,3 ion but not for the 2,2 and 5,3 ions, which have the same extinction coefficients in perchlorate as in chloride media. $(\text{UO}_2)_3(\text{OH})_4^{2+}$ is present in substantial amount in chloride but not in perchlorate media.

A more direct method for measuring polynuclear species is obviously desirable since the e.m.f. results do not give unique schemes. Ultracentrifugation provides such a method. This is a weight-sensitive technique in which sedimentation is followed by optical interferometry, and weight-average degrees of polymerization are obtained. The degree of polymerization is plotted against \bar{n} and the curve is fitted with species of the appropriate stability constants. Thus in sodium chloride media the e.m.f. results can be fitted to 2,2 and 5,3 species and with less certainty to 4,3 and 6,4 species. The agreement is just as good for 4,3 and 6,4 species alone, or together, or even with an unlimited series $2n, n + 1$. The ultracentrifugation data rule out the last possibility, and best agreement is obtained with only the three species 2,2, 4,3, and 5,3 (264).

C. STRUCTURES IN SOLUTION

The existence of polynuclear cations in solution, as indicated by the above work, led to the hypothesis that these cations were the precursors of the solids which precipitated when sufficient hydroxyl ion was added. The structures in solution were therefore regarded as related to solid structures. In uranyl salt solutions, for example, the series of polynuclear ions $\text{UO}_2[(\text{OH})_2\text{UO}_2]_n^{2+}$ was related to units in the sheetlike crystal structure of $\alpha\text{-UO}_2(\text{OH})_2$ and related salts (34, 303). This attractive hypothesis is no longer tenable and the relation between solution and solid structure in this particular instance has yet to be elucidated.

The relationship is more clearly indicated for aluminum ions. Alkali can be added to aluminum chloride solution to near the ratio $\text{OH}^-/\text{Al}^{3+}$ of 2.5 without forming a permanent precipitate. From these solutions it is possible to obtain well-crystallized salts. The structure of the selenate salt has been determined by X-ray analysis (162). The solid contains alkali ions, which seem essential to the structure, as well as a large amount of water, some of it zeolitic. The significant structural feature is the large discrete group of twelve AlO_6 octahedra surrounding a central AlO_4 tetrahedron, i.e., $\text{Al}_{13}\text{O}_{40}\text{H}_{48}^{7+}$. The salt can be written as:



The hydrogen atoms are located by inference in a hydrogen-bonding scheme based on Pauling's rules for packing of polyhedra. The $\text{PW}_{12}\text{O}_{40}^{3-}$ anion

has an analogous structure (167). The early e.m.f. results for hydrolysis in solution were fitted to an infinite series, $\text{Al}[(\text{OH})_5\text{Al}_2]_n^{(3+n)+}$, or preferably to a single species, $\text{Al}_6(\text{OH})_{18}^{3+}$. Only recently has more direct evidence been adduced for the higher polymeric species $\text{Al}_{18}(\text{OH})_{32}^{7+}$ as a result of ultracentrifugation studies which show mean degrees of polymerization up to about 12. The best fit to the degree of polymerization versus \bar{n} curve is obtained by assuming only the $\text{Al}_2(\text{OH})_4^{4+}$ and $\text{Al}_{18}(\text{OH})_{32}^{7+}$ species, and the stability constants derived for them from acidity measurements (10). Other species could be introduced at low \bar{n} values, but the activity coefficients alter most in this region and any improvement in curve fitting is not meaningful. The apparent discrepancy between the cation formulas in solid and solution arises from the nondetectability of complexed water molecules in solution. Evidence from X-ray scattering in solution also substantiates this hetero species (250).

The hydrolysis of bismuth solutions in perchlorate media has been followed by measuring the free bismuth ion concentration or the acidity, and also by ultracentrifugation (151, 232). The curves can best be fitted with the two species $\text{Bi}(\text{OH})^{2+}$ and $\text{Bi}_6(\text{OH})_{12}^{6+}$. The structure of the latter has been examined in concentrated solution (5.8 *M* $\text{BiO}(\text{ClO}_4)$ in 0.95 *M* HClO_4) by X-ray scattering (192). Maxima are observed at 3.71 and 5.25 Å due to Bi-Bi interactions. Excellent agreement with the intensity measurements are obtained with an octahedral distribution of bismuth atoms bridged by oxygens along the octahedral edges, in the same structure type encountered for $\text{Nb}_6\text{Cl}_{12}^{2+}$ (p. 291).

The hydrolyses of zirconium and hafnium halides apparently produce hydrated oxyhalides $\text{MOX}_2 \cdot 8\text{H}_2\text{O}$. The actual structures, confirmed by X-ray scattering in solution and by X-ray structural determination in the solid, are tetrameric with no metal-halogen bonds (53, 221). Ultracentrifuge studies also show this degree of polymerization (164). Zirconium atoms are bridged by pairs of OH and each zirconium is coordinated by a distorted antiprismatic arrangement of eight oxygen atoms (Fig. 14).

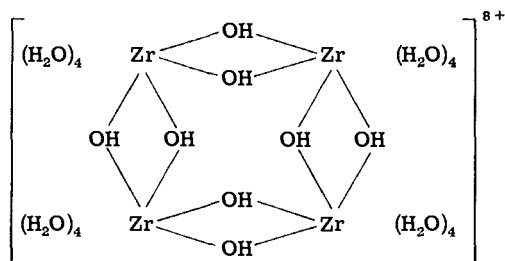


FIG. 14. The cation in zirconium oxyhalides.

The presence of a cyclic polymeric cation in hydrolyzed beryllium solutions has also been suggested. The acidity curves are fitted with $\text{Be}(\text{OH})_2$ and the cations $\text{Be}_2\text{OH}^{3+}$ and $\text{Be}_3(\text{OH})_3^{3+}$. The last is the predominant species and the proposed structure (Fig. 15) utilizes the tetrahedral coordination of beryllium, known for example in the $(\text{Be} \cdot 4\text{H}_2\text{O})^{2+}$ cation (165).

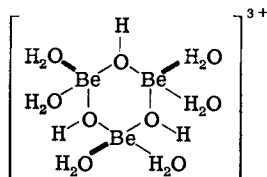


FIG. 15. The main cation in beryllium solutions.

The beryllium oxide trimer in the gas phase and the volatility of beryllium oxide in the presence of traces of water are explicable on the basis of similar cyclic structures.

It can be concluded that many of the species which emerge from a purely mathematical treatment of hydrolytic data have a truly physical significance.

VII. Concluding Remarks

Although the above account has been confined mainly to heterocations formed by the nontransition elements, there has been a corresponding large amount of work with transition metals, exemplified by review articles on a single species VO^{2+} (293), and oxycations in general (294). The emphasis of this work with transition elements has been the explanation of spectral and magnetic properties in terms of modern theories of bonding, the results of which are too extensive to consider here. With the nontransition elements one of the main aims has been to extend the range of heterocations, and consequently less attention has been paid to the detailed structure and configuration of the hetero-ions. One of the most interesting problems raised has been the relation between polar and homopolar forms of the simple and substituted Group V halides (152). The ionic form seems to be the thermodynamically stable form at room temperatures. With some solids, conversion to the covalent form occurs in the melt and reversion on cooling is slow; with others, the ionic form is the only stable form at room temperatures.

Equilibrium and kinetic data are badly needed on these compounds before a rational interpretation is possible. Interconversion of forms is unlikely to admit of a universal interpretation, as can be seen by comparing aluminum trichloride with iodine trichloride. The former ionic solid melts

to a nonconducting liquid, whereas the latter solid consists of I_2Cl_6 molecules which produce a conducting melt. It should also be noted that a low volatility is not a universal criterion of ionicity. Nitrogen pentoxide, for example, is nitronium nitrate in the solid with a sublimation pressure of 200 torr at 15° . The low heat of sublimation for this compound can be explained by the ionic lattice energy being nearly compensated with the formation energy of covalent N-O bonds (214).

The exact nature of the cation bonding in various double halides such as $NOSbCl_6$, $NOAlCl_4$ (108), and $CH_3COGaCl_4$ (67) is far from clear. There are additional lines in the infrared spectra which are incompatible with the simple ionic formulations. An X-ray structural investigation, preferably at low temperatures, should help resolve the cation-anion interaction in these substances. Even with $NO_2^+ClO_4^-$ the spectra are not consistent with a purely ionic structure held by electrostatic forces (225).

The bonding in many nitrates, sulfates, fluorosulfates, and iodates, in which these groups act as bidentate ligands rather than anions, is a more extreme deviation from conventional ionic bonding. Again, a precise description of the charge distribution in such polymeric structures has yet to be achieved.

Apart from these finer structural details, the broad relationship between structures in the different states of matter is also of great interest. There are various lines of evidence which have related the physical properties of liquid to solid structures in the region of the melting point (320). Supercooling phenomena in liquids or premelting effects in solids are examples. It is therefore attractive to consider certain common units which survive a phase change. The precipitation of basic salts in aqueous solution has been regarded as a build-up of the crystal structure by a stepwise succession of hydrolytic equilibria. Evidence for this has been controverted in part, but there are still examples of smaller cations of bismuth and aluminum which are common to both solids and aqueous solutions. Even in the gas phase there are polymeric ions which resemble those of cations in solution.

The isoelectronic principle has been widely applied in the recognition of cation spectra, but less attention has been paid to it as a guide to synthetic possibilities. The proliferation of "diamond-type" semiconductors in recent years (125) is an example of the systematic application of this principle. It would seem that a similar approach could provide substitutional series of polymeric cations with interesting electrical properties when incorporated in suitable salts.

REFERENCES

1. Addison, C. C., Boorman, P. M., and Logan, N., *J. Chem. Soc.* p. 4978 (1965).
2. Addison, C. C., and Lewis, J., *Quart. Rev. (London)* **9**, 115 (1955).

3. Addison, C. C., Lewis, J., and Thompson, R., *J. Chem. Soc.* p. 2829 (1951).
4. Angus, W. R., and Leckie, A. H., *Proc. Roy. Soc.* **A149**, 327 (1935).
5. Appel, R., *Z. Anorg. Allgem. Chem.* **285**, 114 (1956).
6. Asprey, L. B., Margrave, J. L., and Silverthorn, M. E., *J. Am. Chem. Soc.* **83**, 2955 (1961).
7. Arotzky, J., Mishra, H. C., and Symons, M. C. R., *J. Chem. Soc.* p. 2582 (1962).
8. Arotzky, J., and Symons, M. C. R., *Quart. Rev. (London)* **14**, 282 (1962).
9. Aubke, F., Cady, G. H., and Kennard, C. H. L., *Inorg. Chem.* **3**, 1799 (1964).
10. Aveston, J., *J. Chem. Soc.* p. 4438 (1965).
11. Aynsley, E. E., Hetherington, G., and Robinson, P. L., *J. Chem. Soc.* p. 1119 (1954).
12. Aynsley, E. E., Nichols, R., and Robinson, P. L., *J. Chem. Soc.* p. 623 (1953).
13. Aynsley, E. E., and Sampath, S., *J. Chem. Soc.* p. 3099 (1959).
14. Baes, C. F., Jr., and Meyer, N. J., *Inorg. Chem.* **1**, 780 (1962).
15. Banks, A. A., Davies, A., and Rudge, A. J., *J. Chem. Soc.* p. 732 (1953).
16. Banks, A. A., Emeléus, H. J., and Woolf, A. A., *J. Chem. Soc.* p. 2861 (1949).
17. Bang, W. B., and Carpenter, G. B., *Acta Cryst.* **17**, 742 (1964).
18. Barr, J., Gillespie, R. J., and Thompson, R. C., *Inorg. Chem.* **3**, 1149 (1964).
19. Bartell, L. S., and Hansen, K. W., *Inorg. Chem.* **4**, 1775 (1965).
20. Bartlett, N., and Lohmann, K. H., *J. Chem. Soc.* p. 5253 (1962).
21. Bartlett, N., and Robinson, P. L., *J. Chem. Soc.* p. 3417 and p. 3549 (1961).
22. Bayliss, J. W. A., Evans, A. G., and Ross, J. R., *J. Chem. Soc.* p. 206 (1955).
23. Beattie, I. R., and Gibson, T., *Nature* **193**, 1041 (1962).
24. Beattie, T. R., and Webster, M., *J. Chem. Soc.* p. 38 (1963).
25. Becke-Goehring, M., Fluck, E., and Lehr, W., *Z. Naturforsch.* **17b**, 126 (1962).
26. Becke-Goehring, M., and Fluck, E., *Chem. Ber.* **94**, 1591 (1961).
27. Beckey, H. D., *Z. Naturforsch.* **15a**, 822 (1960).
28. Berkowitz, J., and Chupka, W. A., *J. Chem. Phys.* **27**, 85 (1957).
29. Berkowitz, J., and Chupka, W. A., *J. Chem. Phys.* **27**, 87 (1957).
30. Berkowitz, J., and Chupka, W. A., *J. Chem. Phys.* **29**, 653 (1958).
31. Berkowitz, J., Chupka, W. A., and Inghram, M. G., *J. Phys. Chem.* **61**, 1569 (1957).
32. Berkowitz, J., Inghram, M. G., and Chupka, W. A., *J. Chem. Phys.* **26**, 842 (1957).
33. Berry, R. S., Dehl, R., and Vaughan, W. R., *J. Chem. Phys.* **34**, 1466 (1961).
34. Biedermann, G., *Acta Chem. Scand.* **10**, 1340 (1956).
35. Bijvoet, J. M., and Lonsdale, K., *Phil. Mag.* [7] **44**, 204 (1953).
36. Birchall, T., and Gillespie, R. J., *Can. J. Chem.* **41**, 2642 (1963).
37. Bjerrum, J., Schwarzenbach, G., and Sillén, L. G., "Stability Constants of Metal Ion Complexes," Pt. I. Organic Ligands. Chem. Soc., London, 1957; Pt. II. Inorganic Ligands, 1958.
38. Bockris, J. O. M., and Conway, B. E., *Mod. Aspects Electrochem.* **3**, 43 (1964).
39. Böhme, H., and Boll, E., *Z. Anorg. Allgem. Chem.* **291**, 160 (1957).
40. Bourrie-Malandière, P., *Compt. Rend.* **246**, 1063 (1958).
41. Bouy, P., *Ann. Chim. (Paris)* [13] **4**, 853 (1959).
42. Brady, G. W., *J. Chem. Phys.* **28**, 464 (1958).
43. Brady, G. W., *J. Chem. Phys.* **33**, 1079 (1960).
44. Brossett, C., *Arkiv Kemi* **1**, 353 (1949).
45. Brown, H. C., and Pearsall, H. W., *J. Am. Chem. Soc.* **73**, 4681 (1951).
46. Brown, P. G. M., and Prue, J. E., *Proc. Roy. Soc.* **A232**, 320 (1955).
47. Burg, A. B., and McKenzie, D. E., *J. Am. Chem. Soc.* **74**, 3143 (1952).
48. Calderazzo, F., *Inorg. Chem.* **3**, 1207 (1964); **4**, 223 (1965).

49. Calvert, L. D., and Morton, J. R., *Acta Cryst.* **17**, 613 (1964).
50. Chalandon, P., and Susz, B. P., *Helv. Chim. Acta* **41**, 1332 (1958).
51. Christie, K. O., and Guertin, J. P., *Inorg. Chem.* **4**, 905 (1965).
52. Christie, K. O., and Pavlath, A. E., *Z. Anorg. Allgem. Chem.* **335**, 210 (1965).
53. Chupka, W. A., *J. Chem. Phys.* **30**, 458 (1959).
54. Chupka, W. A., Berkowitz, J., and Giese, C. F., *J. Chem. Phys.* **30**, 827 (1959).
55. Chupka, W. A., and Inghram, M. G., *J. Phys. Chem.* **59**, 100 (1955).
56. Chupka, W. A., Inghram, M. G., and Porter, R. T., *J. Chem. Phys.* **23**, 2159 (1955).
57. Clark, H. C., and O'Brien, R. J., *Inorg. Chem.* **2**, 740 and 1020 (1963).
58. Clearfield, A., and Vaughan, P. A., *Acta Cryst.* **9**, 555 (1956).
59. Clifford, A. F., Beachell, H. C., and Jack, W. M., *J. Inorg. Nucl. Chem.* **5**, 57 (1957).
60. Clifford, A. F., and Morris, A. G., *J. Inorg. Nucl. Chem.* **5**, 71 (1957).
61. Clifford, A. F., and Sargent, J., *J. Am. Chem. Soc.* **79**, 4041 (1957).
62. Clifford, A. F., and Zeilenga, G. R., *Science* **143**, 1431 (1964).
63. Cohen, S. R., *J. Phys. Chem.* **61**, 1670 (1957).
64. Collinge, R. N., Nyholm, R. S., and Tobe, M. L., *Nature* **201**, 1322 (1964).
65. Colton, R., and Martin, R. L., *Nature* **207**, 141 (1965).
66. Connick, R. E., and Fiat, D. N., *J. Chem. Phys.* **39**, 1349 (1963).
67. Cook, D., *Can. J. Chem.* **40**, 480 (1962).
68. Cordes, A. W., Kruh, R. F., and Gordon, E. K., *Inorg. Chem.* **4**, 681 (1965).
69. Cotton, F. A., and Haas, T. E., *Inorg. Chem.* **3**, 10 (1964).
70. Covington, A. K., Tait, M. J., and Wynne-Jones, W. F. K., *Proc. Roy. Soc.* **286A**, 235 (1965).
71. Dallinger, G., Verijn-Stuart, A. A., Smit, P. J., and Mackor, E. L., *Mol. Phys.* **1**, 123 (1958).
72. Dasent, W. E., and Waddington, T. C., *J. Chem. Soc.* p. 3350 (1960).
73. Dauben, H. J., Honnen, L. R., and Harmon, K. M., *J. Org. Chem.* **25**, 1442 (1960).
74. Davidson, J. M., and French, C. M., *J. Chem. Soc.* p. 114 (1958).
75. Dehnicke, K., and Weidlein, J., *Z. Anorg. Allgem. Chem.* **323**, 267 (1963).
76. Deno, N. C., *Prog. Phys. Org. Chem.* **2**, 129 (1964).
77. Dess, H. M., and Parry, R. W., *J. Am. Chem. Soc.* **78**, 5735 (1956).
78. Dess, H. M., Parry, R. W., and Vidale, G. L., *J. Am. Chem. Soc.* **78**, 5730 (1956).
79. Drago, R. S., and Purcell, K. F., *Progr. Inorg. Chem.* **6**, 271 (1964).
80. Drowart, J., Barns, P. P., de Maria, G., and Inghram, M. G., *J. Chem. Phys.* **31**, 1131 (1959).
81. Drowart, J., de Maria, G., Boerboom, A. J. H., and Inghram, M. G., *J. Chem. Phys.* **30**, 308 (1959).
82. Drowart, J., de Maria, G., and Inghram, M. G., *J. Chem. Phys.* **29**, 1015 (1958).
83. Drowart, J., de Maria, G., and Inghram, M. G., *J. Chem. Phys.* **32**, 1373 (1960).
84. Dunsmore, H. S., Hietanen, S., and Sillén, L. G., *Acta Chem. Scand.* **17**, 2644 (1963).
85. Edstrand, M., *Acta Chem. Scand.* **1**, 178 (1947).
86. Edstrand, M., *Arkiv Kemi* **6**, 89 (1953).
87. Eigen, M., *Angew. Chem. Intern. Ed. English* **3**, 1 (1964).
88. Eigen, M., and de Maeyer, L., *Proc. Roy. Soc.* **A247**, 505 (1958).
89. Eley, D. D., and King, P. J., *J. Chem. Soc.* p. 2517 (1952).
90. Emeléus, H. J., and Harris, G. S., *J. Chem. Soc.* p. 1494 (1959).
91. Emeléus, H. J., and Smith, J. D., *J. Chem. Soc.* p. 375 (1959).
92. Eriks, H., and MacGillavry, C. H., *Acta Cryst.* **7**, 430 (1954).
93. Evans, J. C., Rinn, H. W., Kuhn, S. J., and Olah, G. A., *Inorg. Chem.* **3**, 857 (1964).

94. Fairbrother, F., *J. Chem. Soc.* p. 503 (1937).
95. Fairbrother, F., and Wright, B., *J. Chem. Soc.* p. 1058 (1949).
96. Falk, M., and Giguère, P. A., *Can. J. Chem.* **35**, 1195 (1957).
97. Ferriso, C. C., and Hornig, D. F., *J. Am. Chem. Soc.* **75**, 4113 (1953).
98. Field, F. H., and Lampe, T. W., *J. Am. Chem. Soc.* **80**, 5583 (1958).
99. Fischer, E. O., and Böttcher, R., *Z. Anorg. Allgem. Chem.* **291**, 305 (1957).
100. Fischer, E. O., and Fichtel, K., *Chem. Ber.* **94**, 1201 (1961); **95**, 249 (1962).
101. Fischer, E. O., and Öfele, K., *Angew. Chem.* **73**, 581 (1961).
102. Fischer, J., Liimatainen, R., and Bingle, J., *J. Am. Chem. Soc.* **77**, 5848 (1955).
103. Flesch, C. D., and Svec, H. J., *J. Am. Chem. Soc.* **81**, 1786 (1959).
104. Flood, H., and Forland, T., *Acta Chem. Scand.* **1**, 592 (1947).
105. Flowers, R. H., Gillespie, R. J., and Robinson, E. A., *J. Inorg. Nucl. Chem.* **9**, 155 (1959).
106. Ford, P. F., and Richards, R. E., *J. Chem. Soc.* p. 3870 (1956).
107. Gerding, H., Heertjes, P. M., Revaillier, L. J., and Steeman, J. W. M., *Rec. Trav. Chim.* **71**, 501 and 773 (1952).
108. Gerding, H., and Houtgraaf, H., *Rec. Trav. Chim.* **72**, 21 (1953).
109. Gerding, H., and Houtgraaf, H., *Rec. Trav. Chim.* **73**, 737 (1954).
110. Gerding, H., Steeman, J. W. M., and Revaillier, L. J., *Rec. Trav. Chim.* **69**, 944 (1950).
111. Germann, A. F. O., and Gagos, K., *J. Phys. Chem.* **28**, 965 (1924).
112. Gerrard, W., Mooney, E. T., and Willis, H. A., *J. Chem. Soc.* p. 4255 (1961).
113. Gillespie, R. J., *J. Chem. Soc.* p. 2537 (1950).
114. Gillespie, R. J., and Birchall, T., *Can. J. Chem.* **41**, 148 (1963).
115. Gillespie, R. J., Graham, J., Hughes, E. D., Ingold, C. K., and Peeling, E. R. A., *J. Chem. Soc.* p. 2504 (1950).
116. Gillespie, R. J., Hughes, E. D., and Ingold, C. K., *J. Chem. Soc.* p. 2473 (1950).
117. Gillespie, R. J., and Robinson, E. A., *Can. J. Chem.* **40**, 1009 (1962).
118. Gillespie, R. J., and Robinson, E. A., *Can. J. Chem.* **41**, 450 (1963).
119. Gillespie, R. J., and Robinson, E. A., in "Non-Aqueous Solvent Systems" (T. C. Waddington, ed.), p. 117. Academic Press, New York, 1965.
120. Gillespie, R. J., and Rothenbury, R. A., *Can. J. Chem.* **42**, 416 (1964).
121. Gillespie, R. J., and Senior, J. B., *Inorg. Chem.* **3**, 440 (1964).
122. Glick, R. E., and Zwickel, A., *J. Inorg. Nucl. Chem.* **16**, 149 (1961).
123. Goddard, D. R., Hughes, E. D., and Ingold, C. K., *J. Chem. Soc.* p. 2559 (1950).
124. Gordon, W. E., and Spinks, J. W. T., *Can. J. Res.* **18B**, 358 (1940).
125. Goryunova, N. A., "The Chemistry of Diamond-Like Semi-Conductors." Chapman & Hall, London, 1965 (translation).
126. Goubeau, J., and Baumgärtner, R., *Z. Elektrochem.* **64**, 598 (1960).
127. Goulden, J. D. S., and Millen, D. J., *J. Chem. Soc.* p. 2600 and p. 2620 (1950).
128. Greenwood, N. N., and Martin, R. L., *J. Chem. Soc.* p. 1915 (1951).
129. Greenwood, N. N., and Martin, R. L., *J. Chem. Soc.* p. 1427 (1953).
130. Greenwood, N. N., and Wade, K., *J. Chem. Soc.* p. 1663 and p. 1671 (1958).
131. Groenveld, W. L., *Rec. Trav. Chim.* **75**, 594 (1956).
132. Groenveld, W. L., Visser, J. N., and Seuter, A. M. J., *J. Inorg. Nucl. Chem.* **8**, 245 (1958).
133. Groenveld, W. L., and Zuur, A. P., *Rec. Trav. Chim.* **76**, 1005 (1957).
134. Guggenheim, E. A., *Trans. Faraday Soc.* **58**, 86 (1962).
135. Gutmann, V., *Z. Anorg. Allgem. Chem.* **266**, 331 (1951); *Monatsh. Chem.* **85**, 491 (1954).

136. Hantzsch, A., and Berger, K., *Z. Anorg. Allgem. Chem.* **190**, 321 (1930).
137. Hargreaves, G. B., and Peacock, R. D., *J. Chem. Soc.* p. 2 and p. 373 (1960).
138. Harmon, K. M., and Cummings, F. E., *J. Am. Chem. Soc.* **84**, 1751 (1962).
139. Harmon, K. M., and Harman, A. B., *J. Am. Chem. Soc.* **83**, 865 (1961).
140. Harris, G. S., and Payne, D. S., *J. Chem. Soc.* p. 4613 (1956).
141. Harris, G. S., and Payne, D. S., *J. Chem. Soc.* p. 4617 (1956).
142. Hass, D. J., Harris, D. R., and Mills, H. H., *Acta Cryst.* **19**, 676 (1965).
143. Haszeldine, R., and Kidd, J. M., *J. Chem. Soc.* p. 4228 (1954).
144. Hathaway, B. J., and Underhill, A. E., *J. Chem. Soc.* p. 3091 (1961).
145. Hauptschein, M., and Braid, M., *J. Am. Chem. Soc.* **83**, 2283 (1961).
146. Hayek, E., Puschmann, J., and Czaloun, A., *Monatsh. Chem.* **85**, 359 (1954).
147. Heinmann, A., *Naturwissenschaften* **17**, 568 (1961).
148. Hieber, W., and Kruck, T., *Angew. Chem.* **73**, 580 (1961).
149. Hoffman, C. J., Holder, B. E., and Jolly, W. L., *J. Phys. Chem.* **62**, 364 (1958).
150. Hoffman, F. W., Simmonds, T. C., and Glunz, L. J., *J. Am. Chem. Soc.* **79**, 3570 (1957).
151. Holmberg, R. W., Kraus, K. A., and Johnson, J. S., *J. Am. Chem. Soc.* **78**, 5506 (1956).
152. Holmes, R. R., *J. Chem. Educ.* **40**, 125 (1963).
153. Honig, R. E., *J. Chem. Phys.* **22**, 1610 (1954).
154. Hughes, E. D., Ingold, C. K., Mok, S. F., Patai, S., and Pocker, Y., *J. Chem. Soc.* p. 1265 (1957).
155. Hughes, E. D., Ingold, C. K., and Reed, R. J., *J. Chem. Soc.* p. 2400 (1950).
156. Hyman, H. H., Quarterman, L. A., Kilpatrick, M., and Katz, J. J., *J. Phys. Chem.* **65**, 123 (1961).
157. Inghram, M. G., Chupka, W. A., and Berkowitz, J., *J. Chem. Phys.* **27**, 564 (1957).
158. Ingold, C. K., Millen, D. J., and Poole, H. G., *J. Chem. Soc.* p. 2, 576 (1950).
159. Jander, G., and Gunther, K., *Z. Anorg. Allgem. Chem.* **298**, 241 (1959); **302**, 155 (1959).
160. Jander, G., and Swart, K. H., *Z. Anorg. Allgem. Chem.* **301**, 54 and 80 (1959).
161. Jerschke, H. G., and Mennig, K., *Z. Anorg. Allgem. Chem.* **319**, 82 (1962).
162. Johansson, G., *Acta Chem. Scand.* **14**, 769 (1960).
163. Johnson, D. A., Blyholder, G. D., and Cordes, A. W., *Inorg. Chem.* **4**, 1790 (1965).
164. Johnson, J. S., and Kraus, K. A., *J. Am. Chem. Soc.* **78**, 3937 (1956).
165. Kakahana, H., and Sillén, L. G., *Acta Chem. Scand.* **10**, 985 (1956).
166. Kapustinskii, A. F., *Quart. Rev. (London)* **10**, 283 (1956).
167. Keggins, J. F., *Proc. Roy. Soc.* **A144**, 75 (1934).
168. Kilpatrick, M., and Luborsky, F. E., *J. Am. Chem. Soc.* **75**, 577 (1953).
169. Klinkenberg, L. J., *Chem. Weekblad* **35**, 197 (1938).
170. Knewstubb, P. F., and Tickner, A. W., *J. Chem. Phys.* **36**, 674 (1962).
171. Kodama, G., and Parry, R. W., *J. Am. Chem. Soc.* **82**, 6250 (1960).
172. Kolditz, L., *Z. Anorg. Allgem. Chem.* **280**, 313 (1955).
173. Kolditz, L., *Z. Anorg. Allgem. Chem.* **284**, 144 (1956).
174. Kolditz, L., *Z. Anorg. Allgem. Chem.* **286**, 308 (1955).
175. Kolditz, L., *Z. Anorg. Allgem. Chem.* **289**, 128 (1957).
176. Kolditz, L., *Z. Anorg. Allgem. Chem.* **293**, 147 (1957).
177. Kolditz, L., and Bauer, K., *Z. Anorg. Allgem. Chem.* **302**, 241 (1959).
178. Kolditz, L., and Feltz, A., *Z. Anorg. Allgem. Chem.* **293**, 286 (1957).
179. Kolditz, L., and Hass, D., *Z. Anorg. Allgem. Chem.* **294**, 191 (1958).
180. Kolditz, L., and Lieth, W., *Z. Anorg. Allgem. Chem.* **310**, 237 (1961).

181. Kolditz, L., and Preiss, H., *Z. Anorg. Allgem. Chem.* **310**, 242 (1961).
182. Kolditz, L., and Sarrach, D., *Z. Anorg. Allgem. Chem.* **293**, 132 (1957).
183. Kolditz, L., and Schäfer, W., *Z. Anorg. Allgem. Chem.* **315**, 35 (1962).
184. Kolditz, L., and Schmidt, W., *Z. Anorg. Allgem. Chem.* **296**, 188 (1958).
185. Krause, R. A., *Inorg. Chem.* **4**, 1227 (1965).
186. Kriegsmann, H., and Pischtschan, S., *Z. Anorg. Allgem. Chem.* **308**, 212 (1961).
187. Kuhn, S. J., and Olah, G. A., *J. Am. Chem. Soc.* **83**, 4654 (1961).
188. Lappert, M. T., *J. Chem. Soc.* p. 2784 (1953).
189. Lee, F. S., and Carpenter, G. B., *J. Phys. Chem.* **63**, 279 (1959).
190. Lehmann, H. A., and Krueger, G., *Z. Anorg. Allgem. Chem.* **274**, 141 (1953).
191. Lehmann, H. A., and Hesselbarth, H., *Z. Anorg. Allgem. Chem.* **299**, 51 (1959).
192. Levey, H. A., Danford, M. D., and Agran, P. A., *J. Chem. Phys.* **31**, 1458 (1959).
193. Lewis, J., and Nyholm, R. S., *Sci. Progr. (London)* **51**, 557 (1964).
194. Lewis, J., and Sowerby, D. B., *J. Chem. Soc.* p. 336 and p. 1617 (1957).
195. Lewis, T. J., *Progr. Dielectrics* **1**, 97 (1959).
196. Lichtn, N., *Progr. Phys. Org. Chem.* **1**, 75 (1963).
197. Lippincott, E. R., and Welch, F. E., *Spectrochim. Acta* **17**, 123 (1961).
198. Lipscomb, W. N., *J. Phys. Chem.* **62**, 381 (1958).
199. Lundgren, G., *Arkiv. Kemi* **10**, 397 (1957).
200. Lustig, M., and Cady, G. H., *Inorg. Chem.* **2**, 388 (1963).
201. McCachran, G. E., and Shore, S. G., *Inorg. Chem.* **4**, 125 (1965).
202. McCarley, R. E., and Boatman, J. C., *Inorg. Chem.* **4**, 1486 (1965).
203. McCarley, R. E., Hughes, B. G., Cotton, F. A., and Zimmerman, R., *Inorg. Chem.* **4**, 1491 (1965).
204. McCauley, D. A., and Lien, A. P., *J. Am. Chem. Soc.* **73**, 2013 (1951).
205. McDowell, C. A., (ed.), "Mass Spectrometry," McGraw-Hill, New York, 1963.
206. MacLean, C., and Mackor, E. L., *J. Chem. Phys.* **34**, 2207 (1961).
207. Magnusson, D. W., *J. Chem. Phys.* **27**, 223 (1957).
208. Malm, J. G., Selig, H., Jortner, J., and Rice, S. A., *Chem. Rev.* **65**, 199 (1965).
209. Marquart, J. R., and Berkowitz, J., *J. Chem. Phys.* **39**, 275 (1963).
210. Matsen, F. A., *J. Am. Chem. Soc.* **81**, 2023 (1959); *J. Chem. Phys.* **34**, 517 (1961).
211. Meerwein, H., *Angew. Chem.* **63**, 480 (1951).
212. Milburn, R. M., *J. Am. Chem. Soc.* **79**, 537 (1957).
213. Millen, D. J., *J. Chem. Soc.* p. 2600 (1950).
214. Millen, D. J., *J. Chem. Soc.* p. 2606 (1950).
215. Miller, N. E., and Muettterties, E. L., *J. Am. Chem. Soc.* **86**, 1033 (1964).
216. Monk, C. B., "Electrolytic Dissociation." Academic Press, New York, 1961.
217. Muettterties, E. L., and Phillips, W. D., *J. Am. Chem. Soc.* **79**, 322 (1957).
218. Muettterties, E. L., and Phillips, W. D., *J. Am. Chem. Soc.* **79**, 3686 (1957).
219. Muettterties, E. L., and Phillips, W. D., *J. Am. Chem. Soc.* **81**, 1084 (1959).
220. Muettterties, E. L., and Phillips, W. D., *Advan. Inorg. Radiochem.* **4**, 231 (1962).
221. Muha, G. M., and Vaughan, P. A., *J. Chem. Phys.* **33**, 194 (1960).
222. Muller, E. S., (ed.), "Methoden der organischen chemie" (Houben-Weyl), Vol. 12, Pt. 1, p. 79. Thieme, Stuttgart, 1963.
223. Nabi, S. N., and Khaleque, M. A., *J. Chem. Soc.* p. 3626 (1965).
224. Nakamoto, K., "Infra-red Spectra of Inorganic and Co-ordination Compounds." Wiley, New York, 1963.
225. Nebgen, J. W., McElroy, A. D., and Klodowski, H. F., *Inorg. Chem.* **4**, 1796 (1965).
226. Nordman, C. E., and Peters, C. R., *J. Am. Chem. Soc.* **81**, 3551 (1959).

227. Olah, G. A., "Friedel Crafts and Related Reactions," Vol. 1, p. 767. Wiley (Interscience), New York, 1963; also Vol. 3 Pt. II, p. 1393 (1964).
228. Olah, G. A., "Friedel Crafts and Related Reactions," Vol. 3, Pt. II, pp. 1 and 507. (Interscience), New York, 1964.
229. Olah, G. A., "Friedel Crafts and Related Reactions," Vol. 1, p. 743. Wiley (Interscience), New York, 1963.
230. Olah, G. A., and Kuhn, S. J., *J. Am. Chem. Soc.* **80**, 6535 (1958).
231. Olah, G. A., Baker, E. B., Evans, J. C., Tolgyesei, W. S., McIntyre, J. S., and Bastien, T. J., *J. Am. Chem. Soc.* **86**, 1360 (1964); **85**, 1328 (1963).
232. Olin, A., *Acta Chem. Scand.* **11**, 1445 (1957).
233. Paddock, N. L., *Quart. Rev. (London)* **18**, 168 (1964).
234. Panzer, R. E., and Suttle, J. F., *J. Inorg. Nucl. Chem.* **20**, 229 (1961).
235. Parker, A. J., *Quart. Rev. (London)* **16**, 163 (1962).
236. Parry, R. W., Rudolph, R. W., and Schriver, D. T., *Inorg. Chem.* **3**, 1479 (1964).
237. Partington, J. R., and Whyne, A. L., *J. Chem. Soc.* p. 3135 (1949).
238. Pauling, L., *Proc. Natl. Acad. Sci. U.S.* **35**, 495 (1949).
239. Pauling, L., "Nature of the Chemical Bond," 3rd ed., p. 440. Cornell Univ. Press, Ithaca, New York, 1960.
240. Payne, D. S., *J. Chem. Soc.* p. 1052 (1953).
241. Peach, M. E., and Waddington, T. C., *J. Chem. Soc.* p. 3450 (1962).
242. Pitts, J. J., Kongpricha, S., and Jacke, A. W., *Inorg. Chem.* **4**, 257 (1965).
243. Pocker, Y., *J. Chem. Soc.* p. 240 (1958).
244. Popov, A. I., Geske, D. H., and Baenziger, N. C., *J. Am. Chem. Soc.* **78**, 1793 (1956).
245. Porter, G. B., and Baughan, E. C., *J. Chem. Soc.* p. 744 (1958).
246. Porter, R. F., Chupka, W. A., and Inghram, M. G., *J. Chem. Phys.* **23**, 216 (1955).
247. Porter, R. C., and Zeller, E. E., *J. Chem. Phys.* **33**, 858 (1960).
248. Pratt, L., and Richards, R. E., *Trans. Faraday Soc.* **49**, 744 (1953); **50**, 670 (1954).
249. Quarterman, L. A., Hyman, H. H., and Katz, J. J., *J. Phys. Chem.* **61**, 912 (1957).
250. Rausch, W. V., and Bale, H. D., *J. Chem. Phys.* **40**, 3391 (1964).
251. Reilly, C. N., *Advan. Anal. Chem. Instr.* **3**, 143 (1964); **4**, 371 (1965).
252. Reed, R. T., "Ion Production by Electron Impact," p. 100. Academic Press, New York, 1962.
253. Richards, R. E., *Quart. Rev. (London)* **10**, 480 (1956).
254. Richards, R. E., and Smith, J. A. S., *Trans. Faraday Soc.* **47**, 1261 (1951); **48**, 307 (1952).
255. Roberts, J. E., and Cady, G. H., *J. Am. Chem. Soc.* **78**, 290 (1956).
256. Robin, M. B., and Kuebler, N. A., *Inorg. Chem.* **4**, 978 (1965).
257. Rogers, M. T., and Garver, E. E., *J. Phys. Chem.* **62**, 952 (1958).
258. Rogers, M. T., Speirs, J. L., and Parish, M. B., *J. Phys. Chem.* **61**, 366 (1957).
259. Rogers, M. T., Speirs, J. L., Parish, M. B., and Thompson, H. B., *J. Am. Chem. Soc.* **78**, 936 (1956).
260. Rosenstock, H. M., *J. Chem. Phys.* **23**, 2442 (1955).
261. Rossotti, F. J. C., and Rossotti, H., "The Determination of Stability Constants." McGraw-Hill, New York, 1961.
262. Ruff, J. K., *Inorg. Chem.* **2**, 813 (1963).
263. Runner, M. E., Balog, G., and Kilpatrick, M., *J. Am. Chem. Soc.* **78**, 5183 (1956).
264. Rush, R. M., Johnson, J. S., and Kraus, K. A., *Inorg. Chem.* **1**, 378 (1962).
265. Rush, R. M., and Johnson, J. S., *J. Phys. Chem.* **67**, 821 (1963).
266. Rydberg, J., *Acta Chem. Scand.* **15**, 1723 (1961).

267. Savoie, R., and Giguère, P. A., *J. Chem. Phys.* **41**, 2699 (1964).
268. Schäfer, H., and Schnering, H. G., *Angew. Chem.* **76**, 833 (1964).
269. Schaeffer, R., Telbe, T., and Phillips, C., *Inorg. Chem.* **3**, 1475 (1964).
270. Schmeisser, M., and Ebenhöch, F. L., *Angew. Chem.* **66**, 230 (1954).
271. Schmeisser, M., and Elischer, S., *Z. Naturforsch.* **7b**, 583 (1952).
272. Schmeisser, M., and Fink, W., *Angew. Chem.* **69**, 780 (1957).
273. Schmeisser, M., and Lang, K., *Angew. Chem.* **67**, 156 (1955).
274. Schmeisser, M., and Scharf, E., *Angew. Chem.* **72**, 324 (1960).
275. Schmidt, H., and Meinert, H., *Angew. Chem.* **72**, 109 (1960).
276. Schmulbach, C. D., *J. Inorg. Nucl. Chem.* **26**, 745 (1964).
277. Schmulbach, C. D., *Inorg. Chem.* **4**, 1232 (1965).
278. Schoonmaker, R. C., and Porter, R. C., *J. Chem. Phys.* **31**, 830 (1959); **28**, 168 and 455 (1958).
279. Schreeve, J. M., and Cady, G. H., *J. Am. Chem. Soc.* **83**, 4521 (1961).
280. Schultz, D. R., Shore, S. G., and Parry, R. W., *J. Am. Chem. Soc.* **80**, 4-27 (1958).
281. Schutzler, R., *J. Am. Chem. Soc.* **86**, 4500 (1964).
282. Seel, F., *Z. Anorg. Chem.* **252**, 33 (1943).
283. Seel, F., *Z. Anorg. Chem.* **261**, 75 (1950).
284. Seel, F., *Angew. Chem.* **68**, 272 (1956).
285. Seel, F., *Angew. Chem. Intern. Ed. English* **4**, 635 (1965).
286. Seel, F., and Detmer, O., *Z. Anorg. Allgem. Chem.* **301**, 113 (1959).
287. Seel, F., and Gössl, T., *Z. Anorg. Allgem. Chem.* **263**, 253 (1950).
288. Seel, F., and Massat, H., *Z. Anorg. Allgem. Chem.* **280**, 186 (1955).
289. Seel, F., Nogradi, J., and Posse, R., *Z. Anorg. Allgem. Chem.* **269**, 197 (1952).
290. Seel, F., and Sauer, H., *Z. Anorg. Allgem. Chem.* **292**, 1 (1957).
291. Seel, F., Schmutzler, R., and Wasem, K., *Angew. Chem.* **71**, 340 (1959).
292. Seel, F., and Wallassis, N. H., *Z. Anorg. Chem.* **261**, 85 (1950).
293. Selbin, J., *Chem. Rev.* **65**, 153 (1965).
294. Selbin, J., *J. Chem. Educ.* **41**, 86 (1964).
295. Selig, H., *Science* **144**, 537 (1964).
296. Selig, H., and Shamir, J., *Inorg. Chem.* **3**, 294 (1964).
297. Sharp, D. W. A., and Sheppard, N., *J. Chem. Soc.* p. 674 (1957).
298. Sharpe, A. G., *J. Chem. Soc.* p. 2907 (1950).
299. Sheldon, J. C., *Nature* **184**, 1210 (1959).
300. Siebert, H., *Z. Anorg. Allgem. Chem.* **265**, 303 (1951).
301. Siegel, B., *Quart. Rev. (London)* **19**, 77 (1965).
302. Sillén, L. G., *J. Inorg. Nucl. Chem.* **8**, 176 (1958).
303. Sillén, L. G., *Quart. Rev. (London)* **13**, 146 (1959).
304. Sillén, L. G., *Acta Chem. Scand.* **15**, 1981 (1961); **16**, 159 and 173 (1962).
305. Singer, S., Kim, N. G., Merkel, A. W., and Farber, M., *J. Phys. Chem.* **69**, 799 (1965).
306. Slater, R. C. L., *Acta Cryst.* **12**, 187 (1959).
307. Sly, W. G., and Marsh, R. E., *Acta Cryst.* **10**, 378 (1957).
308. Sokolskii, G. A., and Knunyants, J. L., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 779 (1960).
309. Spandau, H., and Huttig, H., *Z. Anorg. Allgem. Chem.* **311**, 32 (1961).
310. Steunenbergh, R. K., Vogel, R. C., and Fischer, J., *J. Am. Chem. Soc.* **79**, 1320 (1957).
311. Stevenson, D. P., and Schissler, D. O., *J. Chem. Phys.* **29**, 282 and 294 (1958).
312. Stranks, D. R., and Wilkins, R. G., *Chem. Rev.* **57**, 746 (1957).

313. Studier, M. R., *J. Phys. Chem.* **66**, 189 (1962).
314. Susz, B. P., and Wuhrmann, J. J., *Helv. Chim. Acta* **40**, 722 (1957).
315. Sutton, G. J., *Australian J. Chem.* **11**, 120 (1958).
316. Thomas, A. B., and Rochow, E. G., *J. Inorg. Nucl. Chem.* **4**, 205 (1957).
317. Thompson, R. C., Barr, J., Gillespie, R. J., Milne, J. B., and Rothenbury, R. A., *Inorg. Chem.* **4**, 1641 (1965).
318. Tribalat, S., "Rhenium et Technetium." Gauthier-Villars, Paris, 1957.
319. Truter, M. R., Cruickshank, D. J., and Jeffrey, G. A., *Acta Cryst.* **13**, 855 (1960).
320. Ubbelohde, A. R., *Quart. Rev. (London)* **4**, 356 (1950); **11**, 246 (1957).
321. Vaughan, P. A., Sturdivant, J. H., and Pauling, L., *J. Am. Chem. Soc.* **72**, 5477 (1950).
322. Vonk, C. G., and Wiebenga, E. H., *Rec. Trav. Chim.* **78**, 913 (1959).
323. Waddington, T. C., (ed.), "Non-Aqueous Solvent Systems," p. 144. Academic Press, New York, 1965.
324. Waddington, T. C., and Klanberg, F., *J. Chem. Soc.* p. 2329 (1960).
325. Webster, M., and Beattie, I. R., *J. Chem. Soc.* p. 38 (1963).
326. Weiss, J., *Z. Anorg. Allgem. Chem.* **333**, 314 (1964).
327. Wells, A. F., "Structural Inorganic Chemistry," 3rd ed., p. 666. Oxford Univ. Press, London and New York, 1962.
328. Wells, A. F., "Structural Inorganic Chemistry" 3rd ed., p. 685. Oxford Univ. Press, London and New York, 1962.
329. Whitney, E. D., *J. Am. Chem. Soc.* **86**, 4340 (1964).
330. Woodward, L. A., and Roberts, H. L., *Trans. Faraday Soc.* **52**, 1458 (1956).
331. Woolf, A. A., *J. Chem. Soc.* p. 1053 (1950).
332. Woolf, A. A., *J. Chem. Soc.* p. 3678 (1950).
333. Woolf, A. A., *J. Chem. Soc.* p. 252 (1954).
334. Woolf, A. A., *J. Chem. Soc.* p. 4113 (1954).
335. Woolf, A. A., *J. Chem. Soc.* p. 433 (1955).
336. Woolf, A. A., and Emeléus, H. J., *J. Chem. Soc.* p. 2865 (1949).
337. Woolf, A. A., and Emeléus, H. J., *J. Chem. Soc.* p. 1050 (1950).
338. Woolf, A. A., and Greenwood, N. N., *J. Chem. Soc.* p. 2200 (1950).
339. Wyatt, P. A. H., *Trans. Faraday Soc.* **57**, 773 (1961).
340. Yatsimirskii, K. B., and Vasil'ev, V. P., "Instability Constants of Complex Compounds." Macmillan (Pergamon) New York, 1960.
341. Yoon, Y. K., and Carpenter, G. B., *Acta Cryst.* **12**, 17 (1959).
342. Young, A. R., Hirata, T., and Morrow, S. T., *J. Am. Chem. Soc.* **86**, 20 (1964).
343. Young, T. F., and Walrafen, G. E., *Trans. Faraday Soc.* **57**, 34 (1961).
344. Zaslow, B., and Rundle, R. E., *J. Phys. Chem.* **61**, 450 (1957).
345. Zelesny, W. F., and Baenziger, N. L., *J. Am. Chem. Soc.* **74**, 6151 (1952).

THE INORGANIC CHEMISTRY OF TUNGSTEN

R. V. Parish

Department of Chemistry, University of Manchester Institute of Science and Technology,
Manchester, England

I. Introduction	315
II. Halides, Oxyhalides, and Their Derivatives	316
A. Halides and Oxyhalides	316
B. Complex Anions and Adducts	325
III. Cyano Complexes	332
A. Octacyanotungstates and Their Derivatives	332
B. Cyanotungstates(II and III)	335
C. Carbonylcyno Complexes	335
IV. Thiocyanato Complexes	336
A. Tungsten(VI)	336
B. Tungsten(V)	336
C. Tungsten(III)	337
D. Tungsten(0)	337
V. Oxides and Tungstates	337
A. Oxides	337
B. Tungstates	338
VI. Aromatic and Carbonyl Complexes	338
A. Tungsten(−II and −I)	339
B. Tungsten(0)	339
C. Tungsten(I)	341
D. Tungsten(II)	342
E. Tungsten(III)	343
F. Tungsten(IV and V)	344
VII. Other Compounds	344
A. Dithiolates	344
B. Oxalates	345
C. Phenyl Derivatives	345
VIII. Metal-Metal Bonds	345
Acknowledgments.	347
References	347

I. Introduction

The chemistry of tungsten is very varied, covering nine oxidation states from -2 to $+6$. The history of its development parallels that of inorganic chemistry itself and accurately reflects the various phases of the subject. Tungsten has been studied since the characterization of tungstic acid by

Woulffe (1779) and Scheele (1781). Oxychlorides were obtained by Wohler (1824) but were not recognized as such until more fully characterized by Riche (1857), who also prepared the pure hexachloride and hexabromide. The nineteenth century saw the development of the chemistry of the tungstates and halides and their derivatives. The early twentieth century workers, notably Lindner, Collenberg (alias Olsson), and Rosenheim, extended the aqueous solution chemistry by the preparation of anionic halide and cyanide complexes, but were able to obtain only two types of compound in which the metal had an oxidation state less than +4 (the dihalides and the salts of $W_2Cl_9^{3-}$). The preparation of derivatives of the lower oxidation states had to await the discovery of the hexacarbonyl (1928) and the cyclopentadienyl compounds (1954). In fact this division is almost complete, the earlier workers (pre-1930) producing mostly compounds of the high oxidation states and the more modern workers almost entirely of the lower oxidation states. With the more extensive use of non-aqueous solvents some interest is now being shown in the hydrolytically unstable complexes of the higher halides.

Despite its long and interesting history, the chemistry of tungsten has developed very unevenly. The paucity of tungsten(III) derivatives is particularly striking. The aim of this review is to summarize the known inorganic chemistry of tungsten, in the hope that the deficiencies will become more apparent.

Previous reviews have dealt with isopolytungstates (157), structures of the oxides (13, 130), the carbonyls (1), and π -complexes (89, 98, 124, 129, 237, 289). The treatment of these topics will be curtailed accordingly.

II. Halides, Oxyhalides, and Their Derivatives

Binary halides are now known for tungsten in all oxidation states from +2 to +6 inclusive, and very recently some halides with apparent fractional oxidation states have been reported. Oxyhalides are restricted, with one exception, to tungsten(VI).^{*} The simple halides and their derivatives by substitution will be discussed first, followed by the complex anions and adducts. Some properties of the halides and oxyhalides are summarized in Table I.

A. HALIDES AND OXYHALIDES

1. Tungsten(VI)

The three hexahalides—fluoride, chloride, and bromide—are volatile, diamagnetic solids or liquids, but the hexabromide is unstable to loss of

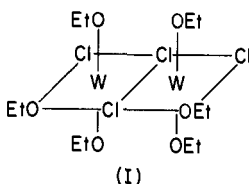
^{*} See Section II, A., 2, p. 319.

TABLE I
SOME PROPERTIES OF TUNGSTEN HALIDES AND OXYHALIDES

Compound		Trouton constant (e.u.)	$-\Delta H_f$ (kcal/mole) (287)	μ_{eff} (B.M./ W atom)
WF ₆	Colorless gas	21.8 (205)	416 (205)	diamag.
WCl ₆	Steel blue, volatile solid	25.0 (160)	97	diamag.
WBr ₆	Unstable, dark blue solid		44	diamag.
WF ₅ Cl	Unstable, yellow liquid		—	
WCl ₅	Green, volatile solid	22.8 (259)	82	1.1
WBr ₅	Black, volatile solid	23.1 (259)	43	1.0
WF ₄	Red-brown, involatile solid		—	
WCl ₄	Black, involatile solid		69	diamag.
WBr ₄	Black, involatile solid		35	diamag.
WI ₄	Black, involatile solid		0.5	
WBr ₃	—		—	0.45
WI ₃	—		—	ca. 4
WCl ₂	Gray, involatile solid		36	diamag.
WBr ₂	Yellow-gray, involatile solid		18.7	
WI ₂	Brown, involatile solid		1	
WOF ₄	White, volatile solid	31.0 (259)	—	
WOCl ₄	Scarlet, volatile solid	33.2 (259)	178	
WOBBr ₄	Brown-black, volatile solid		—	
WO ₂ Cl ₂	Unstable yellow, volatile solid		200	

bromine, giving the pentabromide. The hexahalides form regular octahedral molecules, as has been demonstrated by infrared and Raman (45, 112, 278), ¹⁹F nmr (46, 201), and ³⁵Cl nqr (131, 262) spectroscopy and by X-ray (159) and electron (37, 81) diffraction. Reaction of tungsten hexafluoride with titanium tetrachloride gives a volatile chloropentafluoride, WF₅Cl, together with other unidentified chlorofluorides. The ¹⁹F nmr and infrared spectra of the chloropentafluoride are compatible with an octahedral structure (58).

Ammonolysis of tungsten hexachloride gives products in which one or two chlorine atoms are replaced by NH₂ groups, WCl₅NH₂·2NH₃ and WCl₄(NH₂)₂·2NH₃; on heating, both these products give WCl₂(NH₂)₂ (99). Aminolysis with primary amines, however, yields tetraamido derivatives WCl₂(NHR)₄. The use of secondary or tertiary amines leads to reduction, giving WCl₆[—] which may then be aminolyzed, for example to WCl₃NR₂·2NHR₂ (38). Alcoholysis also leads to reduction, to the blue, paramagnetic trichloroalkoxides, WCl₃(OR)₂ (R = Me, Et). The ethyl compound undergoes further solvolysis to yield the red, diamagnetic dimer W₂Cl₄(OEt)₆ formulated as (I) on the basis of the ¹H nmr spectrum and the dipole moment (167). The green compound obtained by Fischer and



Michiels (85) by electroreduction of tungsten hexachloride in ethanol is now thought to be a tungsten(IV) derivative, $W_2Cl_4(OEt)_4 \cdot 2EtOH$ (167). Phenolysis of the hexachloride is also possible, to give the tetra- and hexaphenoxides, $WCl_2(OAr)_4$ and $W(OAr)_6$ (101, 228). Hexaphenoxides have also been obtained by the reaction of phenols with tungsten oxytetrachloride (199). These compounds are stable to hydrolysis and undergo phenol exchange in acid conditions. The rings may be brominated or nitrated without cleavage of the W—OC bonds (199). With dinitrogen pentoxide in carbon tetrachloride, tungsten hexachloride gives the volatile, highly reactive nitrate compound $WO_2(NO_3)_2$ (250).

Tungsten hexafluoride does not undergo substitution reactions with amines, the adducts being stable (54). With sulfur trioxide a product formulated as $WF_2(SO_3F)_4$ is obtained (54).

Oxyhalides are of two types: WOX_4 and WO_2X_2 ($X = F, Cl, Br$). A dioxydifluoride was claimed in 1907 but has never been mentioned since (243). The structure of neither type of oxyhalide is known, although preliminary crystallographic data have been reported (168). In the gas phase, WO_2X_2 would be expected to be tetrahedral, like $MoOCl_2$ (285). The insolubility of solid WO_2Cl_2 and its high Trouton constant suggest that the compound is polymeric. Similar considerations suggest that the oxytetrachloride is also associated in the condensed phases. For other MOX_4 systems, both oxygen bridging and halogen bridging have been suggested [see below and reference (277)]. In solution the W=O stretching frequency is normal (Table II, p. 000). This frequency could not be located for the solid, but for molybdenum oxytetrachloride there is a reduction in frequency from 1003 cm^{-1} (CS_2) to 958 cm^{-1} (solid) (79).

Infrared and mass spectroscopic measurements show that the dioxydihalides are monomeric in the gas phase. The mass spectrum shows a low concentration of a dimeric species, which also occurs in solution. The dimers must be halogen bridged, since W=O stretching frequencies are observed at about 980 cm^{-1} . For the solid, these frequencies do not appear and new bands are found at $750\text{--}800\text{ cm}^{-1}$, suggesting polymerization through oxygen bridges (20a).

On heating to $200^\circ\text{--}300^\circ\text{C}$, the dioxydihalides disproportionate into the trioxide and the oxytetrahalides.

Substitution of the chlorine atoms in the oxytetrachloride to give compounds of the type $\text{WO}(\text{OR})_4$ has been achieved with a wide variety of alcohols (108), phenols (230), and carboxylic acids (231). The alkoxy derivatives may be hydrolyzed to polytungstates (148). Partial substitution is also possible, to give $\text{WOCl}_3(\text{OR})$ (106).

Oxide ligands, such as triphenylphosphine oxide or pyridine *N*-oxide, will react with tungsten oxytetrachloride or the hexachloride to give oxygenated products of the type $\text{WO}_2\text{Cl}_2\text{L}_2$ ($\text{L} = \text{Ph}_3\text{PO}$, Me_2SO , $\text{C}_5\text{H}_5\text{NO}$) (84). Similar compounds have been obtained by the atmospheric hydrolysis of the products of halogenation of bis(tertiary-phosphine)tungsten tetracarbonyls (177).

2. Tungsten(V)

The only pentahalides known are the chloride and bromide. The pentafluoride may well be unstable to disproportionation like those of molybdenum, rhenium, and osmium (47), a process which would be favored by the high heat of formation of tungsten hexafluoride ($\Delta F^\circ_{298} = -397$ kcal/mole) (205).

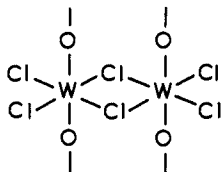
The structures of the pentahalides are not known, but are presumably similar to that of molybdenum pentachloride. In the vapor phase, molybdenum pentachloride consists of trigonal bipyramidal molecules (81), which dimerize in the solid (245). There is some evidence for dimerization of the tungsten compounds in the vapor phase, but the heat of dissociation is small and the Trouton constant normal (257). The magnetic moments of the solid pentahalides are low, 1.0–1.1 B.M., but independent of temperature (270) (cf. MoCl_5 : $\mu_{\text{eff}} = 1.67$ B.M., also temperature-independent) (65). Low values could arise from spin-orbit coupling or from metal-metal interaction, but the moment might then be expected to be temperature-dependent in both cases. The temperature independence has recently been confirmed by Colton and Tomkins (64), who pointed out that the magnetic moment corresponds to one third of an unpaired electron per tungsten atom. They suggested a trimeric structure, $[\text{W}_3\text{X}_{12}]\text{X}_3$, analogous to that of the rhenium(III) clusters.

Substitution of two or three halogen atoms may be achieved directly with phenols (107). The substitution of the third halogen atom is difficult, and completely substituted compounds, $\text{W}(\text{OAr})_5$, have been obtained only by reduction of the hexaphenoxides (105).

No oxyhalides of tungsten(V) were known until very recently, but a phase of composition $\text{WO}_2\cdot\text{WCl}_6$ appears in the WO_2/WCl_6 phase diagram (258).

Tungsten(V) oxytrichloride, WOCl_3 , has now been prepared by aluminium reduction of the oxytetrachloride. It is virtually diamagnetic

($\chi'_M = 60 \times 10^{-6}$ c.g.s.). The infrared spectrum and X-ray powder pattern suggest that the structure is analogous to that of NbOCl_3 (98a)



This structure is similar to that proposed for solid WO_2Cl_2 (see p. 318), which is obtained by replacing the bridging chlorine atoms by oxygen atoms.

3. Tungsten(IV)

Tetrahalides are known for all four halogens. They are dark, involatile, insoluble, diamagnetic solids, isomorphous with the corresponding niobium and tantalum tetrahalides (43). The latter compounds have structures in which MX_6 octahedra form linear chains by sharing edges. The diamagnetism arises through metal-metal bonds, which draw the metal atoms together in pairs (248).

The thermal stabilities of the tungsten tetrahalides are very dependent on the halogen. The tetraiodide is unstable to loss of iodine even at room temperature. The tetrabromide and tetrachloride disproportionate into the penta- and dihalides on heating to $450^\circ\text{--}500^\circ\text{C}$; this is a very convenient way of obtaining pure samples of these halides. The tetrahalides themselves are best prepared by reduction of the higher halides with aluminum in a controlled temperature gradient (43). A bromotrichloride, obtained by the action of bromine on $\text{K}_3\text{W}_2\text{Cl}_9$, is reported, surprisingly, to sublime in nitrogen at 135°C (293).

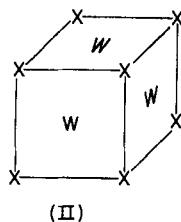
Tungsten tetrafluoride is obtained by reduction of the hexafluoride with benzene at 110°C (233). A similar method has been used to prepare molybdenum tetrachloride from the pentachloride (171), but tungsten hexachloride is not reduced at 80°C (127). The tetrafluoride has surprisingly high thermal stability, being unaffected up to about 800°C , above which temperature it dissociates into its elements (234).

The only known oxyhalide of tungsten(IV) is the oxydifluoride, WOF_2 , obtained by the action of hydrogen fluoride on tungsten dioxide at 500°C . It, too, is extremely inert (234).

4. Lower Halides

Until very recently (1962) the only lower tungsten halides known were the dihalides—chloride, bromide, and iodide. These, like the molybdenum

dihalides (42), are hexanuclear, containing the $W_6X_8^{4+}$ unit (265). This cluster may be envisaged as a cube of halogen atoms with a tungsten atom situated at the center of each of the cube faces (II). The cubes are linked



together in a two-dimensional lattice by bridging halogen atoms, the remaining two halogen atoms being situated above and below the cube, giving a $[W_6X_8]X_2X_{4/2}$ arrangement. Each tungsten atom is thus coordinated to a square pyramid of halogen atoms and is also bound to four other tungsten atoms, which are coplanar. The molecular orbital scheme for the $M_6X_8^{4+}$ cluster shows that these compounds should be diamagnetic, as observed (70).

The tungsten dihalides are markedly less stable than those of molybdenum, in that they are oxidized even by water (179). There is also a considerable difference in the ease with which substitution of the halogen atoms may be effected. To convert Mo_6Cl_{12} to Mo_6Br_{12} requires fusion in lithium bromide (261), whereas the corresponding conversion for the tungsten compound can apparently be achieved merely by warming with hydrobromic acid (179).

If W_6Br_{12} is allowed to react with liquid bromine at temperatures up to $110^\circ C$, an unstable tribromide is formed (43, 182, 265). At $140^\circ C$ an intermediate bromide of composition $WBr_{2.67}$ is obtained; this material is also produced by heating the tribromide under the same conditions. Above $160^\circ C$, both these compounds are oxidized to the hexabromide. Both WBr_3 and $WBr_{2.67}$ are unstable to loss of bromine, and on heating in a vacuum give a further bromide, $WBr_{2.33}$. The latter material has not been obtained directly from W_6Br_{12} . All these bromides revert to the W_6Br_{12} on strong heating (265). The ease with which these compounds are interconverted suggests that the W_6 unit is retained throughout the series, which is then formulated: W_6Br_{12} , W_6Br_{14} , W_6Br_{16} , W_6Br_{18} . The interrelations are shown in Fig. 1. This hexanuclear structure has been shown for W_6Br_{16} , in which $[W_6Br_8]Br_4$ units are linked in chains by linear Br_4^- ions (249). This behavior parallels that of the niobium and tantalum halides, $[M_6X_{12}]X_2$, which undergo two-electron oxidations without breakdown of the cluster (183). M_6X_8 clusters are also found in Ta_6I_{11} (249).

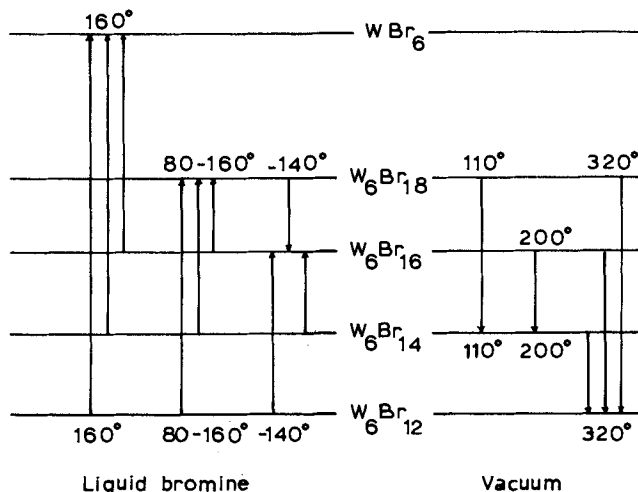


FIG. 1. Interconversions of the hexanuclear tungsten bromides [after Siepmann and Schäfer (265)].

Magnetic data are available only for W_6Br_{18} , which is antiferromagnetic with a Néel temperature above $355^\circ K$. The moment is low, being at room temperature 1.1 B.M. per W_6 unit (43). In marked contrast, the magnetic moment of WI_3 (which compound is obtained by reaction of tungsten hexacarbonyl with iodine at $120^\circ C$) is about 4 B.M. at room temperature and is field-dependent (77). The triiodide loses iodine on standing and reverts to the diiodide, WI_{12} . No trichloride has yet been reported.

These trihalides are thus very different from the molybdenum trihalides, which are stable to dissociation but unstable to disproportionation into the pentahalide and Mo_6X_{12} (200° – $400^\circ C$). These trihalides have TiI_3 -type chain structures (bromide, iodide) (17, 174) or $CrCl_3$ -type layer lattices (chloride) (254), both of which involve simple MoX_6 groups, although in the trichloride the metal atoms form pairs. These compounds are also antiferromagnetic (174, 248).

5. Thermodynamics

Thermodynamic data are available from many sources (19, 46, 201, 256, 259, 260, 287). For the halides the Russian enthalpy values are considerably higher than the American values, although there is agreement in the entropies. The relationship between the halides is shown in Fig. 2. The high stability of the hexafluoride and the instability of the hexabromide and the iodides are clearly shown. Tungsten pentachloride appears to be unstable to disproportionation at room temperature, but there is no evidence that such a reaction occurs. On raising the temperature the hexachloride

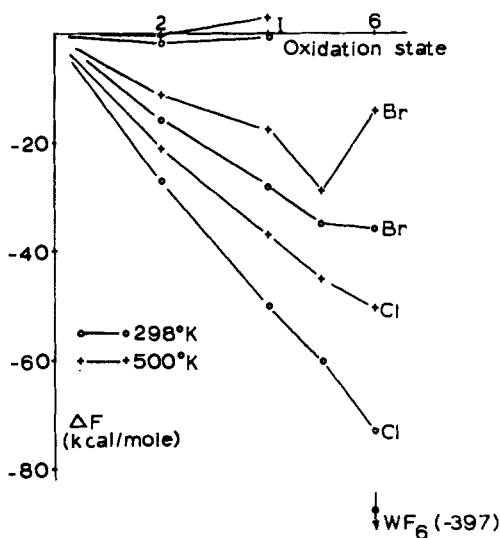


FIG. 2. Free energies of formation of tungsten halides at 298° and 500°K [data from (287)].

TABLE II
INFRARED DATA FOR HALIDE AND OXYHALIDE DERIVATIVES^a

Compound	$\nu_{\text{M-X}}$	$\delta_{\text{M-X}}$	$\nu_{\text{M=O}}$	$\delta_{\text{M=O}}$	Ref.
WOCl_4 (CS_2)			1030		(79)
(SOCl_2)			1019		(65)
$\text{WO}_2\text{Cl}_2(\text{OPPh}_3)_2$			960, 913		
$\text{WO}_2\text{Cl}_2(\text{dpO}_2)$			956, 909		(177)
$\text{WO}_2\text{Br}_2(\text{dpO}_2)$			954, 907		
Et_4NWCl_6	329				(4)
	305				(18)
Me_4NWCl_6	315				
Rb_2WOCl_5	339, 317	177, 164	930	229	
Cs_2WOCl_5	333, 309	174, 164	957	230	
Rb_2WOBr_5	224	142, 120	968	203	(244)
Cs_2WOBr_5	220	143, 119	960	202	
K_2WCl_6	324	164			
Rb_2WCl_6	306	160			
Cs_2WCl_6	308	166			
K_2WBr_6	229	74			(5)
Rb_2WBr_6	220	78			
Cs_2WBr_6	214	60			

^a All values are in cm^{-1} ; $\text{dpO}_2 = \text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2$.

TABLE III
COMPLEXES OF TUNGSTEN HALIDES AND OXYHALIDES^a

$[\text{WO}_2\text{F}_4]^-$	(31)	$\text{WF}_6 \cdot \text{ArH}$	(233)	$[\text{WO}_3\text{Cl}]^-$	(235)	$\text{WOCl}_4 \cdot 4\text{RNH}_2$	(229)
$[\text{WO}_3\text{F}_3]^{3-}$	(251)	$\text{WF}_6 \cdot 3\text{L}$	(54)	$[\text{WO}_2\text{Cl}_3]^-$	(63)	$\text{WO}_2\text{Cl}_2 \cdot 3\text{NH}_3$	(267)
$[\text{WO}_3\text{F}_2 \cdot \text{H}_2\text{O}]^-$	(252)	($\text{L} = \text{py}$, MeNH_2)		$\text{WCl}_6 \cdot \text{diars}$	(55)	$\text{WO}_2\text{Cl}_2\text{L}_2$	(84,177)
$[\text{WO}_4\text{F}]^{3-}$	(253)	$\text{WF}_6 \cdot 4\text{NH}_3$	(54)	$\text{WCl}_6 \cdot 6\text{L}$	(99,227)	($\text{L} = \text{Ph}_3\text{PO}$, Me_2SO , $\text{C}_6\text{H}_5\text{NO}$ diphosO_2)	
$[\text{WF}_8]^-$	(21,72, 132)	$\text{WOF}_4 \cdot \text{SeF}_4$	(22)	($\text{L} = \text{NH}_3$, ArNH_2)			
$[\text{WF}_7]^-$	(114, 132)	$\text{WOF}_4 \cdot \text{SeOF}_4$	(22)	$\text{WCl}_6 \cdot 4\text{NH}_3$	(99)		
$[\text{WOF}_5]^-$	(132, 204)			WOCl_4L	(106)		
				($\text{L} = \text{Et}_2\text{O}$, Me_2CO , RCN , bipy , 2py)			
$[\text{WF}_6]^-$	(133, 155)			$[\text{WCl}_6]^-$	(4,18)	$[\text{WCl}_4\text{bipy}]\text{Cl}$	(127)
$[\text{WF}_8]^-$	(132)			$[\text{WOCl}_5]^-$		$\text{WCl}_5 \cdot \text{PCl}_5$	(128)
				$[\text{WOCl}_4]^-$			$[\text{WOBBr}_5]^-$
				$[\text{WOCl}_4 \cdot \text{H}_2\text{O}]^-$	(63,59)		$[\text{WOBBr}_4]^-$
							$[\text{WOBBr}_4 \cdot \text{H}_2\text{O}]^-$
				$[\text{WCl}_6]^-$	(5,38,155)	WCl_4L_2	$\text{WBr}_5 \cdot 5\text{RNH}_2$
						($\text{L} = \text{py}$, RCN , diphos)	(232)
				$[\text{W}(\text{OH})\text{Cl}_5]^-$	(62,170)		$[\text{WBr}_6]^-$
							(156)
				$\text{WCl}_4 \cdot \text{S}_4\text{N}_4$	(75,209)		WBr_4L_2
				$[\text{W}_3\text{Cl}_9]^{3-}$	(62)		($\text{L} = \text{py}$, RCN)
				$\text{W}_2\text{Cl}_6\text{L}_3$	(36,152)		(10,43, 156)
				($\text{L} = \text{PhNH}_2$, py)			
				$[\text{W}_6\text{Cl}_{14}]^-$	(142,179)		$[\text{W}_3\text{Br}_9]^{3-}$
				$\text{W}_6\text{Cl}_{12} \cdot 2\text{EtOH}$	(203)		(292)
							$[\text{W}_6\text{Br}_{14}]^-$
							(142)

^a py = pyridine, bipy = bipyridyl, diars = $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$, diphos = $\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2$, $\text{diphosO}_2 = \text{Ph}_2\text{P}(\text{O})\text{C}_2\text{H}_4\text{P}(\text{O})\text{Ph}_2$.

and tetrachloride become relatively less stable, with the effect of stabilizing the pentachloride against disproportionation, and it is now the tetrachloride which is unstable with respect to decomposition into the dichloride and pentachloride.

B. COMPLEX ANIONS AND ADDUCTS

Large numbers of anionic halide and oxyhalide complexes are known, mostly for tungsten(V); this has been one of the major areas of study in the chemistry of tungsten. The other adducts have been only poorly characterized. The known complexes are summarized in Table III.

1. Tungsten(VI)

A variety of oxyfluoride anions is known, some at least of which contain octahedrally coordinated tungsten. This has been shown for $[\text{WOF}_5]^-$ (132), $[\text{WO}_2\text{F}_4]^-$ (143), and $[\text{WO}_3\text{F}_3]^{3-}$ (251). The fluoride and oxide ions have similar radii (1.36 and 1.40 Å, respectively) and are probably distributed randomly (222).

Salts of the octafluorotungstate(VI) anion, $[\text{WF}_8]^-$, have been reported as being formed by the reaction of alkali fluorides with tungsten hexafluoride (132), but it was later shown that no reaction occurs if the alkali fluoride is perfectly dry (72). These salts are best obtained by the reaction of the hexafluoride with an alkali iodide in iodine pentafluoride (132). Nitrosyl fluoride similarly gives $(\text{NO})_2\text{WF}_8$, which is isomorphous with the corresponding rhenium compound (2). In the alkali salts M_2ReF_8 , the anions have a square antiprismatic configuration (27), which may be retained in the nitrosyl compound.

If an excess of tungsten hexafluoride is used in these reactions, cubic heptafluoro complexes, MWF_7 , are obtained (132). Similarly, alkali and tetraethylammonium chlorides dissolve in phosphorus oxychloride solutions of tungsten hexachloride to give heptachlorotungstate(VI) ions (16).

The structures of the other adducts and of the oxyhalides are not known.

2. Tungsten(V)

The anionic complexes of tungsten(V) are all octahedral, with the possible exceptions of $[\text{WF}_6]^{3-}$ (132) and $[\text{WOX}_4]^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).

Salts of composition MWX_6 are known for $\text{X} = \text{F}, \text{Cl}, \text{Br}$. The fluorides are obtained from alkali iodides and tungsten hexafluoride in liquid sulfur dioxide (155). The chloro and bromo complexes are prepared either by reduction of the hexahalide, with an iodide at about 100°C (76) or with thionyl chloride (4, 18), or by direct addition of a chloride or bromide to the corresponding pentahalide in an inert solvent (39, 40, 76). The fluoro

compounds are isomorphous with the corresponding hexafluoroantimonates(V), MSbF_6 (155); the anions are therefore octahedral, with possibly a slight trigonal distortion for the cesium and rubidium salts and a definite tetragonal distortion for the potassium salt. The structure of the hexachlorotungstates(V) is not known, but the observation of a single W—Cl stretching frequency (see Table II) is indicative of octahedral coordination (4, 18).

All the hexahalogenotungstate(V) salts have low magnetic moments, 0.5–1.3 B.M. at room temperature, and the fluoro and chloro complexes are antiferromagnetic with Néel temperatures of 100°–150°K (Table IV).

TABLE IV
MAGNETIC PROPERTIES OF HEXAHALOGENOTUNGSTATES(V)

Compound	μ_{eff} (B.M., ca. 300°K)	Néel temperature (°K)	Ref.
NaWF_6	0.52	130	(133)
KWF_6	0.53	ca. 125	
RbWF_6	0.58	110	
CsWF_6	0.59	ca. 100	
NaWCl_6	0.88 ^a		(76)
KWCl_6	ca. 0.9 ^{a,b}		
RbWCl_6	ca. 0.9 ^{a,b}		
CsWCl_6	ca. 1.1 ^{a,b}		
CsWCl_6	0.95	105	(18)
Me_4NWCl_6	1.23	100	
Et_4NWCl_6	0.64	140	
Et_4NWCl_6	0.66 ^a		(76)
$\text{Ph}_4\text{AsWCl}_6$	1.21 ^a		
Et_4NWBr_6	1.28 ^a		(40)
$\text{Et}_3\text{NHWBr}_6$	1.23 ^a		

^a Measured at room temperature only.

^b Values varied for different preparations.

The antiferromagnetism presumably arises by exchange coupling through the halide ions, as in K_2IrCl_6 .

The colors of the salts are governed by charge-transfer bands, the fluorides being white, the chlorides green, and the bromides very dark green or black. The ligand-field bands probably occur at about 27,000 cm^{-1} (chloride) and 15,000–19,000 cm^{-1} (bromide) (Table V).

With the exception of the lithium salt, the fluoro complexes are stable up to 250°C (155), but the chlorides disproportionate at this temperature

TABLE V
ELECTRONIC SPECTRA OF TUNGSTEN COMPLEXES (147)

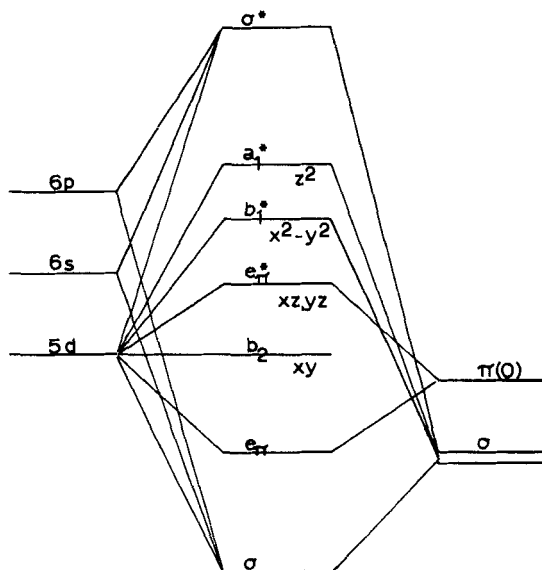
Anion	Absorption bands (cm ⁻¹)					
	Ligand-field		Charge-transfer			
WCl ₆ ⁻	27,400		32,260	35,700	39,200	42,800
WBr ₆ ⁻	14,900	18,900	23,500			
WCl ₆ ⁼	19,230		31,750	35,300	39,400	42,600
WBr ₆ ⁼	20,100	25,200	33,000			
WOCl ₅ ⁻	14,200	25,190	32,790	37,170		
WOBrs ⁻	14,290		25,640			
MoOCl ₅ ⁻	14,100	22,420	28,010	32,260	40,000	
MoOBrs ⁼	14,290	21,280	24,100	26,530		

into tungsten hexachloride and the hexachlorotungstates(IV). This reaction may be reversed by grinding the tungsten(IV) compound with the hexachloride (76).

When a solution of a tungstate in concentrated hydrochloric acid is reduced, chemically or electrolytically, an intensely blue solution is obtained from which several types of complex may be precipitated. The stoichiometry of the product seems to depend only on the precipitant: alkali chlorides give green M₂WOCl₅, quinoline or pyridine gives brown (AmH)WOCl₄, while tetraalkylammonium chlorides give the light blue R₄NWOCl₄·H₂O (59, 63). A similar series of bromo complexes results from reduction in hydrobromic acid and addition of the appropriate precipitant (223).

A molecular orbital scheme has been proposed (122) for the MO²⁺ systems in which significant π -bonding is restricted to the M=O bonds (Fig. 3). This scheme accounts satisfactorily for the major features of the absorption spectra of the [MOCl₅]⁻ ions (M = Mo, W; X = Cl, Br) (see Table V) (9). Thus the first *d-d* transition (²B₂ → ²E, *b*₂ → *e* _{π} ^{*}) occurs at about 14,000 cm⁻¹ for all the complexes, and there is a blue shift of about 4000 cm⁻¹ in the second band (²B₂ → ²B₁) on going from the molybdenum complexes to those of tungsten. Charge transfer from ligand to metal is indicated by a similar blue shift (ca. 5000 cm⁻¹) in the charge-transfer bands, but there is a shift in the opposite direction (ca. 4000 cm⁻¹) on changing the halide from chloride to bromide. This has been interpreted as implying the involvement of the halide π -system, which would be of higher energy than that of oxygen and would therefore be involved in the lowest charge-transfer transitions (147).

The magnetic susceptibilities follow the Curie-Weiss law in the range 90°–300°K with small values of θ (Table VI) (9). The asymmetry of the

FIG. 3. Molecular orbital scheme for $[\text{MOX}_5]^-$ [after Gray and Hare (122)].

metal environment effectively quenches the orbital contribution (2B_2 ground state) and the π -bonding results in a considerable diminution of the spin-orbit coupling constant; nevertheless the magnetic moments are appreciably below the spin-only value.

For the $[\text{WOX}_4]^-$ salts, the magnetic moments and θ values are similar to those for WOX_5^- (Table VI). The absorption spectra of $[\text{WOX}_4]^-$ have not been reported, but those of the corresponding molybdenum complexes

TABLE VI
MAGNETIC PROPERTIES OF TUNGSTEN(V) OXYHALIDE COMPLEXES (9)

Complex	μ_{eff} (B.M., ca. 300°K)	θ (°K)
Rb_2WOCl_5	1.55	20
Cs_2WOCl_5	1.49	16
$\text{Me}_3\text{NHWOCl}_5$	1.35	4
Rb_2WOBr_5	1.37 ^a	—
Cs_2WOBr_5	1.55	17
quinH WOCl_4	1.41	6
pyH WOCl_4	1.43 ^a	—
quinH WOBr_4	1.40 ^a	—
isoquinH WOBr_4	1.37 ^a	—

^a Measured at room temperature only.

show marked differences between measurements made on solutions (in liquid sulfur dioxide) and on the solid complexes, the frequency of the first ligand-field band being lower in the solid. It has been suggested that octahedral coordination of the metal is achieved either by solvation or by oxygen bridging. The latter effect would weaken the $M=O$ π -bonding and lead to a decrease in frequency of the first $d-d$ band (9). Dimerization by halogen bridging has also been postulated (11).

Although the presence of water in $[WOCl_4, H_2O]^-$ has never been explicitly demonstrated, these compounds differ markedly from the anhydrous ones both in color and in ease of hydrolysis.

The only other adducts of tungsten pentahalides appear to be $[WCl_4bipy]Cl$ (127), $WCl_5 \cdot PCl_5$ (128) ($[PCl_4]^+ [WCl_5]^-$?), and $[W(amine)_5Br_3]Br_2$ (232).

3. Tungsten(IV)

The only well-substantiated anionic complexes of tungsten(IV) are the hexahalogenotungstates(IV), $[WX_6]^-$ ($X = Cl, Br, I$), obtained by heating the higher tungsten halides with an alkali iodide (76, 156). The reaction proceeds by initial formation of the tungsten(V) complexes (see above). The tungsten(IV) chloro compounds also appear as intermediates in the aminolysis of tungsten hexachloride (38). The alkali salts have cubic, K_2PtCl_6 structures; the anions are therefore octahedral, with the exception of the potassium salt which is tetragonally distorted (156). The distortion is not enough to give a splitting of the ^{37}Cl nqr spectrum (206). This salt shows a higher $W-Cl$ stretching frequency than the cubic rubidium and cesium salts (Table II), although this difference has also been attributed to metal-ligand π -bonding (5). The values for the bromo compounds decrease more regularly. The magnetic moments of the salts are low and the θ values high (Table VII), suggesting antiferromagnetism; a Néel point was observed for K_2WCl_6 at 80°K (156).

These salts react with pyridine to give complexes of the type WX_4py_2 ($X = Cl, Br$) (156), which may also be obtained by direct reaction of pyridine with the tetra-, penta-, or hexahalides (43). The reduction proceeds with the formation of the 1-(4-pyridyl)pyridinium ion (43). Similar complexes are obtained with other heterocyclic amines (43) and with nitriles (9). The X-ray patterns of these derivatives are complicated, but the pyridine complexes are isomorphous with those of niobium and tantalum (43). The magnetic moments are again depressed, although less markedly than for the WX_6^- salts (Table VII). The majority of these compounds are soluble only in the parent ligand to give nonconducting solutions (9), although the conductivity of the pyridine complexes in pyridine slowly increases, with accompanying changes in the absorption

TABLE VII
 MAGNETIC PROPERTIES OF TUNGSTEN(IV) DERIVATIVES

Derivative	μ_{eff} (B.M., ca. 300°K)	θ (°K)	Reference
K ₂ WCl ₆	1.43	180	(5)
Rb ₂ WCl ₆	1.47	160	
Cs ₂ WCl ₆	1.47	122	
Tl ₂ WCl ₆	1.76	375	
BaWCl ₆	0.89	400	
K ₂ WBr ₆	1.42	200	
Rb ₂ WBr ₆	1.42	137	
Cs ₂ WBr ₆	1.72	148	
WCl ₄ py ₂	2.06	(antiferro)	(156)
	1.6		(43)
WBr ₄ py ₂	2.03	180	(156)
	2.1		(43)
WCl ₄ (MeCN) ₂	1.78	(9)	
WCl ₄ (EtCN) ₂	1.84		
WCl ₄ (Pr ⁿ CN) ₂	1.85		
WBr ₄ (MeCN) ₂	1.89		
WBr ₄ (EtCN) ₂	1.85		
WTr ₄ (Pr ⁿ CN) ₂	2.07		

spectrum, suggesting that further addition is possible (43). A molecular weight determination could be made only on the propyl cyanide derivative, which is monomeric in freezing benzene (9). The observation of two C≡N and two M—Cl stretching frequencies in MoCl₄(MeCN)₂ may be indicative of a *cis* octahedral configuration (9).

If a hydrochloric acid solution of a tungstate is reduced beyond the tungsten(V) stage, a dark red paramagnetic complex may be isolated, analyzing as K₂W(OH)Cl₅ (62). This compound apparently contains tungsten(IV) and the magnetic moment, 2.2 B.M. at room temperature (270), is not incompatible with this oxidation state. However, polarographic studies have shown that reduction occurs directly from tungsten(V) to tungsten(III), with no evidence for the intermediate tungsten(IV) stage (180). The complex has an intense absorption band in the visible region (19,900 cm⁻¹, $\epsilon_{\text{mol}} > 10^4$) (170), which may indicate a binuclear complex with tungsten atoms in two different oxidation states. In solution the complex decomposes rapidly, but is stabilized by high concentrations of chloride ions. One major product of the decomposition is [W₂Cl₉]³⁻, which has been taken to imply a disproportionation mechanism (170).

4. Tungsten(III)

The ultimate products of the reduction of tungstates in hydrohalic acid solution are the diamagnetic ions $[\text{W}_2\text{X}_9]^{3-}$ [$\text{X} = \text{Cl}$, green (62, 215), Br, brown (292)]. In these anions each tungsten atom is octahedrally surrounded by six halide ions, the two octahedra having a common face. The tungsten atoms are displaced slightly from the centers of the octahedra, forming a short tungsten-tungsten bond of length 2.41 Å (cf. 2.74 Å in the metal) (41, 283). The absorption spectrum shows two bands in the visible region, at 13,200 cm^{-1} (ϵ_{mol} ca. 25) and 16,300 cm^{-1} (ϵ_{mol} ca. 400). These bands were attributed to spin-forbidden transitions (154), but it is more likely that they are spin-allowed $d-d$ transitions between the orbitals of the metal-metal bond system.

Similar complexes exist for molybdenum, but no details have been published (173). There are no tungsten complexes corresponding to the readily prepared hexahalogenomolybdates(III), MoX_6^{3-} ($\text{X} = \text{Cl}$, Br, I). The preparation of $\text{KWF}_4 \cdot 9\text{H}_2\text{O}$ has been briefly reported (241).

Chloride exchange studies on $\text{W}_2\text{Cl}_9^{3-}$ suggest that complete exchange of all nine halide ions occurs (134). However, attempts to substitute the chloride with bromide or iodide lead to decomposition of the complex, with production of $\text{WO}_2 \cdot x\text{H}_2\text{O}$ (120). Similar oxidation occurs when the chloro complex is allowed to stand in water or alkali (292). The dimeric anion probably dissociates and is then oxidized by the solvent.

The salt $\text{K}_3\text{W}_2\text{Cl}_9$ reacts with refluxing pyridine or aniline to give brown, diamagnetic complexes $\text{W}_2\text{Cl}_6\text{L}_3$ (152). The same products may be obtained more conveniently by pyrolysis of, for example, $(\text{pyH})_3\text{W}_2\text{Cl}_9$ (36). The structures of these compounds are not known.

It has been suggested, on the basis of chloride exchange and spectroscopic studies, that other tungsten(III) species may exist in solution, but their nature is unknown (180). The reported "red tungsten(III)" (180) and the compound $\text{K}_5\text{W}_3\text{Cl}_{14}$ (172) both appear to contain $[\text{W}(\text{OH})\text{Cl}_5]^-$ (170).

5. Tungsten(II)

The $[\text{W}_6\text{X}_8]^{4+}$ group probably always has six ligands coordinated to it, as in the solid dihalides (265), $[\text{W}_6\text{Br}_8]\text{Br}_4 \cdot (\text{EtOH})_2$ (203), and the many salts of $[\text{W}_6\text{X}_8]\text{X}_6^-$ (142, 179).

The only known simple complex of tungsten(II) appears to be $\text{W}(\text{diars})_2\text{I}_2$ (diars = *o*-phenylenebisdimethylarsine), which has a magnetic moment of 2.70 B.M. (20°C) and is isomorphous with its molybdenum analog (77). All other monomeric tungsten(II) complexes involve carbonyl

or aromatic ligands and contain seven-coordinate, diamagnetic tungsten (see Section VI).

III. Cyano Complexes

The major class of tungsten cyano complexes is that of the octacyano-tungstates(IV and V). Until recently these were the only known tungsten complexes containing cyanide ligands only, but complexes of tungsten(II and III) are now known.

A. OCTACYANOTUNGSTATES AND THEIR DERIVATIVES

The octacyano complexes of molybdenum and tungsten are so similar in all respects (except properties such as oxidation potentials) that they may be discussed jointly and data for either may be applied to both. In this way a large body of information is available.

The $[M(CN)_8]^{4-}$ ions are obtained by reaction with aqueous cyanide ion of many other complexes containing the tri-, quadri-, or quinequevalent metal, e.g. halides (15, 44, 117, 137, 214, 215, 236, 239, 292), oxalates (20, 59), thiocyanates (240), hydroxides (192). Trivalent metal is oxidized by either the solvent or the atmosphere, while the pentavalent starting materials disproportionate, the other product being $[MO_4]^{2-}$ (292). It does not appear possible to obtain $[M(CN)_8]^{3-}$ directly, but only by oxidation of the quadrivalent complex. This oxidation occurs, as expected, more readily for tungsten than for molybdenum (61). The quadrivalent compounds are diamagnetic (d^2) (15, 32, 238), and the quinequevalent compounds show paramagnetism corresponding to a single unpaired electron ($\mu_{\text{eff}} = 1.76$ B.M. (W), d^1) (15).

Until recently the structure of these ions was not known with any certainty. An X-ray examination of $K_4[Mo(CN)_8] \cdot 2H_2O$ (with which the corresponding tungsten salt is isomorphous (15)) showed a slightly distorted dodecahedral configuration for the anion (144). However, the Raman spectrum of an aqueous solution of this salt appeared to be consistent with a square antiprismatic configuration (268). Stammreich and Sala took existing infrared data (141) and suggested that this configuration was maintained in the solid state. Other infrared spectra appeared to agree with neither the antiprismatic nor the dodecahedral structure (35, 82, 181). High resolution work has now clarified the situation for the solid, for which the spectrum is entirely consistent with the distorted dodecahedral structure found by X-ray examination (161, 217). The infrared spectra of salts with other cations are also consistent with a more or less distorted dodecahedral configuration (217).

Further refinement of the original X-ray data suggests that the distortion of the anion from D_{2d} symmetry is not very great and that the M—CN

bonds all have a similar length (145). In a dodecahedral structure four of the CN groups are better placed than the other four for π -bonding (with the $d_{x^2-y^2}$ orbital on the metal), and the ligand replacement reactions have been explained on this basis (216). Hoard and Silverton suggest that the bond shortening which such π -bonding would produce is offset by inhomogeneous repulsion due to the electron pair in $d_{x^2-y^2}$. However, such repulsions would be quite small since this orbital has its maxima between the ligands. This must mean that the π -bonding is weak and that the shape of the complex is determined by interligand repulsions and σ -bond strengths (145, 158, 219). Electron delocalization in $\text{Mo}(\text{CN})_8^{3-}$ is very small (see below).

For solutions, the position is less clear. The ^{13}C nmr spectrum of $[\text{Mo}(\text{CN})_8]^{4-}$ consists of a single line, which implies either that the groups are all very similar (antiprism) or that there is rapid intramolecular mixing of CN groups (200). (Intermolecular exchange may be ruled out since exchange with CN^- does not occur—see below.) It has been suggested that interconversions between dodecahedral and antiprismatic configurations could occur readily (145). The effect on the nmr spectrum of a decrease in temperature was not examined. The infrared spectra of aqueous solutions consist of a single, very broad line, in marked contrast to the spectrum of the solid. Such broadening could be caused, for example, by vibration or solvation of the anion, but the Raman spectrum does not appear to be unduly broadened (268). Cooling to -60°C had no effect on the infrared spectrum (161, 217). The electronic spectrum has been interpreted in terms of both models (169, 224). This spectrum, however, is very similar to the diffuse reflectance spectrum of the solid (169) and it seems unlikely that the actual configuration in solution is very different from that in the solid.

Oxidation of $[\text{M}(\text{CN})_8]^{4-}$ (for example with permanganate) gives the quinquevalent complexes which are stable in the absence of light. Little is known of the structure of these ions. The electronic spectra have been interpreted in terms of both dodecahedral and square antiprismatic configurations (169, 224). The esr spectrum has recently been redetermined. From the relative values of g_{\parallel} and g_{\perp} it was concluded that the anion had a square antiprismatic structure in solution but became dodecahedral when co-crystallized with $\text{K}_4\text{M}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$ (186). Analysis of the fine structure of the spectrum obtained with $[\text{Mo}(^{13}\text{CN})_8]^{4-}$ gave a spin density on the metal atom of 0.96, showing that π -delocalization is small (284).

Both the $[\text{M}(\text{CN})_8]^{4-}$ and $[\text{M}(\text{CN})_8]^{3-}$ ions are stable in solution in the dark and no exchange with $^{14}\text{CN}^-$ can be detected in either case (7, 15, 117). For $[\text{M}(\text{CN})_8]^{4-}$ this exchange is strongly photocatalyzed, the rate being dependent on the light intensity (7). The half-life of the reaction

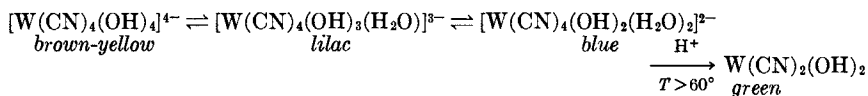
is independent of concentration, showing that the rate-determining step involves the photoexcited species (117). Ligand replacement reactions are similarly photoinduced although the detailed mechanism of these reactions is not clear. If the yellow solutions of $[M(CN)_8]^{4-}$ are exposed to light in the range 300–500 m μ , the color changes rapidly to red and then, more slowly, to violet (W) or blue (Mo) (49, 60, 150); these colors are due to the ions $[M(CN)_4(OH)_3H_2O]^{3-}$ (150, 178, 193). The color changes are accompanied by an increase in pH of the solution (7, 185). If the reaction is stopped at the red stage and the solution is allowed to stand in the dark or is heated, the yellow color is regained and the pH decreases (7, 151, 185). The color reversal can also be achieved by addition of base (150, 151). Adamson and Perumareddi have shown that the red color develops maximum intensity most rapidly at high light intensities and that there is concurrent production of free CN^- , approximately one g-ion of CN^- per g-ion of photolyzed complex (6). The rate of disappearance of the red color, after irradiation, is dependent on the concentration of CN^- , an excess of which also inhibits the formation of the final blue product. It is suggested that the red intermediate is $[M(CN)_7(OH)]^{4-}$, which may undergo thermal reactions either experiencing further (presumably stepwise) substitution or returning to $[M(CN)_8]^{4-}$ by reaction with CN^- or HCN (6). Similar conclusions were reached by Carassiti and his co-workers (49). The reversal of the yellow-red reaction by base suggests that CN^- is the reagent.

Jakob *et al.* find that in the presence of a base (e.g., NH_3 , N_2H_4) the reaction does not proceed beyond the red stage and is no longer reversible (150, 151). From this solution red salts can be isolated, such as $Cd_2W(CN)_8 \cdot 2NH_3$, and it is claimed that the two molecules of base are associated with the anion, even in solution (149–151). It is suggested that the $[M(CN)_8]^{4-}$ ion undergoes a change of configuration from dodecahedral to antiprismatic and that the two "extra" ligands are bound to the two square faces. Such an arrangement would be favored by polarizable ligands, the square faces being regions of negative charge density. Water molecules, being less polarizable than those of amines, would be bound less strongly, accounting for the greater lability of this system (151). Jakob further suggests that this is the initial stage in the photohydrolysis reaction, but it is difficult to see why the addition of other bases or of cyanide should reverse this stage if no substitution is occurring.

The $[M(CN)_8]^{3-}$ ions are also stable, in the dark, to CN^- exchange, hydrolysis, and reduction. On exposure to light, reduction occurs rather than solvolysis, and a chain mechanism involving OH radicals has been proposed to explain the observation of quantum yields greater than unity (48). By contrast, electron exchange between $[M(CN)_8]^{3-}$ and $[M(CN)_8]^{4-}$ is very fast, even in the dark (118).

As mentioned above, the ultimate product of photohydrolysis is

$[\text{M}(\text{CN})_4(\text{OH})_3(\text{H}_2\text{O})]^{3-}$. It is only possible to isolate tetrasubstituted species; an early report (60) of $[\text{M}(\text{CN})_5(\text{OH})_3]^{4-}$ has been shown to be incorrect (30, 48, 151). The form of the tetrasubstituted complex is dependent on the acidity of the medium, three protonation stages being possible before decomposition (178), e.g.,



Salts of each of the anions have been isolated (178). The color changes are due to a red shift in a ligand-field band as protonation proceeds. For example, the diffuse reflectance spectra of the potassium salts show maxima at $21,000 \text{ cm}^{-1}$ for $[\text{W}(\text{CN})_4(\text{OH})_4]^{4-}$ and $19,100 \text{ cm}^{-1}$ for $[\text{W}(\text{CN})_4(\text{OH})_3(\text{H}_2\text{O})]^{3-}$ (218). This shift is the opposite of that expected from the spectrochemical series and the "average environment" rule. These complexes undergo a reversible one-electron oxidation and the oxidation potential has been measured (195). The heats of combustion (194) and acidity constants have also been reported (178).

If the salts $\text{Ag}_4[\text{M}(\text{CN})_8]$ are allowed to react with alkyl iodides (methyl, ethyl, *t*-butyl, triphenylmethyl, allyl), reaction again occurs at four sites to give $\text{M}(\text{CN})_4(\text{CNR})_4$ (146, 220). The visible spectra of the solutions of these compounds are very similar to that of the parent ion, and they presumably have the same dodecahedral structure. An early report suggests that it may be possible to obtain ionic species containing only two alkyl groups (146).

B. CYANOTUNGSTATES(II AND III)

The reduction of anhydrous $\text{K}_4\text{M}(\text{CN})_8$ with hydrogen at $330^\circ\text{--}390^\circ\text{C}$ gives green or black products which analyze as $\text{K}_4\text{M}(\text{CN})_6$. Oxidation state determinations support their formulation as derivatives of the bivalent metals. Extraction of these products with methanol in the presence of air yields yellow-brown solids of composition $\text{K}_3\text{M}(\text{CN})_6$. The conductivities of solutions of these compounds are consistent with the presence of $\text{M}(\text{CN})_6^{3-}$ and $\text{M}(\text{CN})_6^{4-}$ ions. The solutions are very reducing and on standing develop a yellow color, presumably due to $[\text{M}(\text{CN})_5]^{4-}$. The infrared spectra of the solids are complex, suggesting nonoctahedral structures, which is also indicated by the magnetic data [magnetic moments (B.M.) at room temperature: $\text{K}_4\text{M}(\text{CN})_6$, 1.13 (Mo), 0.94 (W); $\text{K}_3\text{M}(\text{CN})_6$, 1.50 (Mo), 1.76 (W) (166)].

C. CARBONYLCYANO COMPLEXES

Cyanide ion may replace CO in $\text{W}(\text{CO})_6$, when up to three CN groups may be coordinated giving $[\text{W}(\text{CO})_{6-n}(\text{CN})_n]^{n-}$, in which the CN groups

are mutually *cis* (24, 25). The complexes $[\pi\text{-CpW}^{\text{II}}(\text{CO})_3\text{CN}]$ and $[\pi\text{-CpW}(\text{CO})_2(\text{CN})_2]^-$ and their methyl derivatives $[\pi\text{-CpW}(\text{CO})_n\text{-(CNCH}_3)_4-n]$ have been obtained (56).

IV. Thiocyanato Complexes

Many thiocyanato complexes are known, mostly for tungsten(V) (cf. the halides). The majority of these complexes are not well characterized, but it appears that the NCS group coordinates through nitrogen.

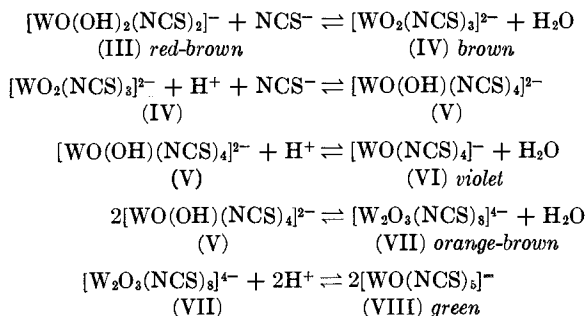
A. TUNGSTEN(VI)

Solutions of WCl_6 , WOCl_4 , or WO_2Cl_2 in acetone or similar solvents react with thiocyanate ion to give the substituted products $\text{W}(\text{NCS})_6$, $\text{WO}(\text{NCS})_4$, and $\text{WO}_2(\text{NCS})_2$, but these have never been obtained free of solvent, there usually being 2 moles of solvent per mole of compound, e.g. $\text{W}(\text{NCS})_6 \cdot 2(\text{CH}_3)_2\text{CO}$ (103).

Neutral or weakly acid aqueous solutions of tungstates react with thiocyanate to give condensed tungstates or thiocyanatotungstates, both of which are colorless (33). No further data have been reported.

B. TUNGSTEN(V)

Despite their long use in analysis (83), the nature of the colored species obtained by reduction of tungstate with thiocyanic acid has only recently been elucidated. The stoichiometry of these complexes is markedly dependent on the acidity of the solutions, and the following sequence of equilibria has been suggested on the basis of the amine salts which can be isolated (33, 102):



Anions (III), (IV), (VI), (VII), (VIII), and $[\text{W}(\text{OH})_3(\text{NCS})_3]^-$ (IX) (dark violet) give amine salts with the colors shown. No salt of (IV) appears to have been isolated.

Nothing is known of the structures of most of these complexes, but (VI) and (VIII) are presumably analogous to the corresponding halogeno

complexes. It has been suggested that the molybdenum complex corresponding to (IV) is dimeric, $[\text{Mo}_2\text{O}_4(\text{NCS})_6]^{4-}$, with a double oxygen bridge (196, 197). Infrared measurements on salts of (III) and (IX) are consistent with coordination of the thiocyanate through nitrogen [$\nu_{\text{C-N}} = 2058 \text{ cm}^{-1}$ (IX) (101); $\nu_{\text{C-S}} = 815 \text{ cm}^{-1}$ (III) (33)], and this may reasonably be assumed for the remainder. The spectrum of (III) also shows the presence of hydroxyl groups and indicates extensive hydrogen bonding (33). The position of the W=O stretching frequency was not recorded.

Complex (VIII), $[\text{WO}(\text{NCS})_6]^-$, is paramagnetic (no value given) and (VII), $[\text{W}_2\text{O}_3(\text{NCS})_6]^{4-}$, is diamagnetic (33). The latter presumably has a single oxygen bridge through which the unpaired electrons are coupled.

The species which is extracted into organic solvents from acidic aqueous solutions has been assigned the formula $[\text{W}(\text{NCS})_2\text{X}_4]^-$, where X was shown not to be halide (8). This complex must presumably be (III), $[\text{WO}(\text{OH})_2(\text{NCS})_2]^-$, although other compositions have been suggested (119, 225). The complex $\text{py}_2\text{WO}_2(\text{NCS})_3$ (240) is probably the pyridinium salt of (IV), although the color is different from that of Böhland's product (102).

C. TUNGSTEN(III)

Olsson found that reaction of aqueous $\text{K}_3\text{W}_2\text{Cl}_9$ with thiocyanic acid gave a deep red color which could be extracted into ether. This extract yielded a red oil which was found to contain tungsten(III) but was not further characterized (213). Böhland has also obtained evidence for reduction to tungsten(III) by polarography in methanol (33). No such complexes have yet been isolated (cf. $\text{Mo}(\text{NCS})_6^{3-}$).

D. TUNGSTEN(0)

A thiocyanato analog of $[\text{W}(\text{CO})_6\text{Hal}]^-$ has been obtained by reaction of $\text{W}(\text{CO})_6$ with $(\text{CH}_3)_4\text{NNCS}$ in diglyme. The product is a yellow solid with moderate air stability. The infrared spectrum shows C_{4v} symmetry and bonding of the NCS group through nitrogen ($\nu_{\text{C-S}} = 791 \text{ cm}^{-1}$). Similar compounds have been isolated from $\text{Cr}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ but the molybdenum compound is unstable (291).

V. Oxides and Tungstates

A. OXIDES

Tungsten trioxide has a slightly distorted ReO_3 -type structure in which WO_6 octahedra are linked in three dimensions by sharing corners in a $\text{WO}_{6/2}$ arrangement (130). The dioxide has a deformed rutile structure, in which the WO_6 units are linked in chains by common edges, the chains

being bound into two-dimensional layers by sharing the apical oxygens. Within the individual chains, the tungsten atoms are drawn together in pairs, alternate tungsten-tungsten distances being 2.49 and 3.08 Å (cf. 2.74 Å in the metal) (130). The dioxide is diamagnetic (264).

Several substoichiometric oxides also exist. When the trioxide is heated strongly *in vacuo*, oxygen is lost preferentially, giving a defect lattice. This process continues to a limiting composition of $\text{WO}_{2.98}$, beyond which several new phases begin to appear (113). These phases consist of blocks of the basic ReO_3 -type structure separated by shear planes or dislocations (110, 113, 130). In well-annealed samples the shear planes are parallel and regularly spaced, giving phases of well-defined but complex stoichiometry. Where the ReO_3 blocks are separated by shear planes, phases of composition $\text{W}_n\text{O}_{3n-1}$ are obtained, where n is a measure of the thickness of the block (130). The known phases are $\text{W}_{50}\text{O}_{148}$, $\text{W}_{40}\text{O}_{118}$, $\text{W}_{25}\text{O}_{74}$, $\text{W}_{20}\text{O}_{58}$, $\text{W}_{18}\text{O}_{49}$, and W_4O_8 . In samples prepared at low temperatures (less than 1000°C) the shear planes occur randomly (109).

When the trioxide vaporizes, polymeric species are formed, which have been detected mass spectrometrically. The major species are W_4O_{12} , W_3O_9 , W_5O_{15} , and W_2O_6 (3). The free energies of formation of these species and of the solids $\text{W}_{18}\text{O}_{49}$, $\text{W}_{20}\text{O}_{58}$, and $\text{W}_{50}\text{O}_{148}$ have been measured (3, 211).

The hydrated forms of the trioxide, the so-called tungstic acid, appear to contain only lattice water. Infrared and ^1H nmr studies gave no evidence of hydroxyl groups (255). However, the volatility of tungsten trioxide increases considerably in the presence of water vapor, owing to the formation of $\text{WO}_2(\text{OH})_2$ (115).

B. TUNGSTATES

The oxo anions of tungsten(VI) range from the simple $\text{WO}_4^{=}$ tetrahedra and WO_6^{6-} octahedra (271) to highly polymeric species such as $\text{W}_{24}\text{O}_{72}(\text{OH})_{12}^{12-}$ (116). These isopolytungstates consist of WO_6 octahedra linked by common corners, although in the early members WO_4 tetrahedra may also occur.

The chemistry of the isopolytungstates has been reviewed (157); more recent data are given by Aveston (14) and Glemser *et al.* (116).

VI. Aromatic and Carbonyl Complexes

The lowest oxidation states of tungsten, as of other metals, are stabilized by ligands which can accept electrons from the metal by π -back-donation. Outstanding among these ligands is carbon monoxide, which occurs in complexes in which tungsten has oxidation states of -2 to $+3$; tungsten hexacarbonyl has the highest metal—CO bond energy of those measured to date. Unsaturated organic molecules, and aromatic systems in particular,

are also effective electron acceptors; the cyclopentadienyl anion, for instance, forms complexes in which the formal oxidation state of the tungsten is in the range +1 to +5.

Complexes of both these types have recently been reviewed (1, 89, 124, 129, 140, 289); the present discussion will be condensed accordingly. Since both types of ligand frequently occur in the same complex and stabilize much the same oxidation states with similar stereochemistries, it is convenient to treat both together.

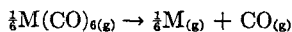
To facilitate discussion, oxidation states and coordination numbers will be assigned using the formalisms that radical ligands act as the corresponding anions and organic groups donate all their π -electron "pairs" to the metal. Thus in cyclopentadienyl complexes the ligand is formally "tridentate" $C_5H_5^-$, so that $[\pi-C_5H_5W(CO)_3]_2$ would be a derivative of seven-coordinate tungsten(I).

A. TUNGSTEN(−II AND −I)

Carbon monoxide provides the only complexes in which tungsten has a negative oxidation state, in the anions $[W(CO)_5]^-$, $[W_2(CO)_{10}]^-$, $[W_2(CO)_9]^{4-}$, and $[W_3(CO)_{14}]^-$ (23, 25, 26). The structure of none of these is known with certainty, but $[W(CO)_5]^-$ is presumably trigonal bipyramidal. The infrared spectrum of $[W_2(CO)_{10}]^-$ in the C=O stretching region (140) is compatible with a staggered structure as in the isoelectronic $Re_2(CO)_{10}$ (73). A protonated derivative, $[W_2(CO)_{10}H]^-$, has been described (25), the nmr and infrared spectra of which suggest that the hydrogen atom is bound equally to both metal atoms and that the D_{4d} symmetry is maintained (12).

B. TUNGSTEN(0)

Tungsten(0) occurs not only in the hexacarbonyl, $W(CO)_6$, and its multitudinous substitution products, but also in dibenzenetungsten, $(\pi-C_6H_5)_2W$ (97), hexakisisonitriletungsten, $(RNC)_6W$ (138, 188), and tris(1,2-bisdiphenylphosphinoethane)tungsten, $(Ph_2PC_2H_4PPh_2)_3W$ (53). All these compounds are diamagnetic and contain six-coordinate tungsten. Thermodynamic data are available only for the hexacarbonyl, which shows the solid tungsten compound to be slightly less stable than its chromium and molybdenum analogs, although the mean bond dissociation energies for the process



increase regularly (Cr, 27.1; Mo, 35.9; W, 42.1 kcal/bond) (69). The lower heat of formation of $W(CO)_6$ is presumably due mainly to the high heat of atomization of the metal (220 kcal/g-atom). A compound of com-

position $(\text{bipy})_3\text{W}$ is paramagnetic ($\mu_{\text{eff}} = 1.03$, 20°C) (138, 139) and may therefore not be a true tungsten(0) derivative.

The stability and ease of handling of tungsten hexacarbonyl (as of those of chromium and molybdenum) have made it the object of much study. In particular, the substitution reactions have been extensively investigated with ligands of all types; introductory references may be obtained from Abel's review (1). The types of reaction may be summarized as follows:

(i) Reaction with 1 mole (or less) of a monodentate ligand at 100° – 160°C gives monosubstitution.

(ii) Reaction with 2 moles of a monodentate ligand or 1 mole of a bidentate ligand at 100° – 160°C results in disubstitution.

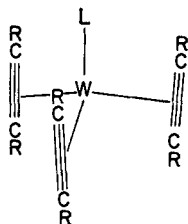
Both these reactions may be carried out at room temperature under ultraviolet radiation (273, 276), when reaction apparently occurs via an unstable pentacarbonyl, $\text{W}(\text{CO})_5$. The infrared spectrum of this intermediate suggests that it has a square pyramidal configuration at -180°C . The corresponding molybdenum species apparently isomerizes to a trigonal bipyramidal form above -155°C (274).

(iii) Reaction with excess ligand at higher temperature (180° – 240°C) gives trisubstitution. These derivatives can often be obtained more conveniently from the intermediates $(\text{CH}_3\text{CN})_3\text{W}(\text{CO})_3$ (280) or $(\pi\text{-mesitylene})\text{-W}(\text{CO})_3$ (96).

(iv) Substitution of more than three CO groups is difficult and has been achieved only with bidentate ligands at high temperatures. All the ligands used to date are capable of π -bonding with the metal (24, 52, 210).

Derivatives in which more than one CO group is replaced are usually obtained in the *cis* form; the *trans* complexes are seldom obtainable pure. This is consistent with the theory of $\text{M}-\text{CO}$ π -bonding. The major exception to this rule appears to be the trisubstituted acrylonitrile complex. In the mono- and disubstituted complexes the ligand is bound to the metal through the nitrogen atom, $(\text{CH}_2\text{:CHCN} \rightarrow)_n\text{W}(\text{CO})_{6-n}$ ($n = 1, 2$), while in the tricarbonyl coordination apparently occurs via the double bond and the complex is obtained entirely in the *trans* form (191, 242). This complex is also of interest since it is one of the few derivatives in which a monoolefin is bound to the metal by its double bond. A few other unstable compounds are known (273), but olefin coordination normally requires chelation as with dienes, aromatic systems, or in $(o\text{-Ph}_2\text{As}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CH}_3)\text{W}(\text{CO})_4$ (28).

Reaction of $\text{W}(\text{CO})_6$ or $(\text{CH}_3\text{CN})_3\text{W}(\text{CO})_3$ with acetylenes results in the formation of $(\text{RC}:\text{CR})_3\text{W}(\text{CO})$ ($\text{R} = \text{ethyl}$ (279), *phenyl* (275)), or $(\text{CF}_3\text{C}:\text{CCF}_3)_3\text{W}(\text{CH}_3\text{CN})$ (165), in which it is suggested that the four groups are situated tetrahedrally around the metal atom (X) (279).



(X)

σ -Bonded derivatives $K_3[(RC\equiv C)_3W(CO)_3]$ may be obtained by reaction of $(NH_3)_3W(CO)_3$ with the potassium alkynyl in liquid ammonia (207). The action of ethereal LiR on $W(CO)_6$ gives $[W(CO)_5COR]^-$ ($R = Me, Ph$) (93).

The high symmetry of the Group VI hexacarbonyls has made them the object of much theoretical discussion (121, 153). In particular, the force constants of the $C=O$ stretching vibrations have been correlated with the degree of $M-CO$ π -bonding. It has recently been suggested that in $M(CO)_6$ the three nonbonding electron pairs on the metal are fully utilized in π -bonding. The $M-C$ bond order would then be 1.5, rising to 2.0 when three of the CO groups are replaced with ligands which are incapable of π -bonding (68). This seems unrealistic in view of the fact that π -bonding is expected to increase in the isoelectronic series $[Mn(CO)_6]^+$, $Cr(CO)_6$, $[V(CO)_6]^-$ (78). Also, the π^* orbitals of CO , into which the metal electrons are donated, are probably of higher energy than the t_{2g} orbitals of the metal, and figures of 0.1 and 0.2 electron pair transferred per CO group have been proposed (78, 121).

C. TUNGSTEN(I)

There are only two monomeric representatives of tungsten(I): $[(C_6H_5)_2W]^+$ (97) and $[(diphos)_2W(CO)_2]I_3$ ($diphos = Ph_2PCH_2CH_2PPh_2$) (176). The single unpaired electron gives magnetic moments of 1.58 and 1.86 B.M., respectively.

The phosphine compound is remarkable in that the two CO groups are apparently *trans*. It has been suggested (176) that this configuration is adopted for steric reasons, which may also inhibit the dimerization expected for a low-valent heavy metal complex with an odd number of electrons. All other formal tungsten(I) derivatives are dimeric, and diamagnetic.

Treatment of tetramethyldiphosphine or -diarsine with $W(CO)_6$ gives the diamagnetic complexes $(CO)_5W(LMe_2)_2W(CO)_5$ ($L = P, As$) (50, 51, 136). The small dipole moment (ca. 1 D) of these compounds has been interpreted in terms of folding about the $L-L$ axis, which would enhance the metal-metal bond (51), but the nmr spectra suggest that the four

TABLE VIII
 X GROUPS REPORTED FOR $\pi\text{-CpW(CO)}_3\text{X}$

X Group	References
$\pi\text{-CpW(CO)}_3$	(91,288,290)
H, Me, Et	(91,226)
$\sigma\text{-CH}_2\text{:CH}_2\text{CH}_2\text{-}$, $\sigma\text{-Me}_2\text{CH-}$, $\pi\text{-CH}_2\text{:CHCH}_3$	(125)
$\text{CF}_3\text{-}$, $\text{C}_3\text{F}_7\text{-}$, $\sigma\text{-CH}_2\text{:CH-}$	(164)
$\sigma\text{-CHF}_2\text{CF}_2\text{-}$	(281)
$\pi\text{-CH}_2\text{:CH}_2$	(57)
$\text{C}_2\text{H}_5\text{CO-}$	(184)
CO	(88,90)
NO	(86)
Halogen	(87)
$\text{Cl}_3\text{Sn-}$	(34)
$\text{PhSnCl}_2\text{-}$, $\text{Ph}_3\text{Sn-}$, $\text{Ph}_3\text{Pb-}$, $[\pi\text{-CpW(CO)}_3]\text{SnPh}_2\text{-}$, $[\pi\text{-CpW(CO)}_3]\text{SnCl}_2\text{-}$ $[\pi\text{-CpW(CO)}_3]\text{PbPh}_2\text{-}$, $[\pi\text{-CpW(CO)}_3]\text{PbCl}_2\text{-}$ }	(208)
$[\text{Mn(CO)}_5]\text{SnMe}_2\text{-}$	(221)
$\text{Ph}_3\text{PAu-}$	(57)
NH_3 , N_2H_4	(94)
Other compounds:	
$\pi\text{-CpW(CO)}_2(\pi\text{-C}_3\text{H}_5)$	(125)
$[\pi\text{-CpW(CO)}_2\text{SMe}_2]_2$	(135,281)
$\pi\text{-CpW(CO)(Hal)(}\pi\text{-Ph}_4\text{C}_4\text{)}$	(187)
$[\pi\text{-CpW}(\pi\text{-C}_6\text{H}_6)\text{CO}]^+$	(90)

methyl groups are all equivalent, implying a planar WL_2W system (136).

In $[\pi\text{-CpW(CO)}_3]_2$ (Cp = cyclopentadienyl, C_5H_5) two $\pi\text{-CpW(CO)}_3$ groups are held together by a single, long (3.28 Å) tungsten-tungsten bond. The molecule has a center of symmetry and the axis of the ring is coincident with that of the W(CO)_3 system (290).

D. TUNGSTEN(II)

Several tungsten(II) compounds are known, all of which are diamagnetic and seven-coordinate. Of these, approximately half are of the type $\pi\text{-CpW(CO)}_3\text{X}$. The X groups reported to date are listed in Table VIII. It may reasonably be presumed that the structures of these complexes are analogous to that of $[\pi\text{-CpW(CO)}_3]_2$, the group X replacing one $\pi\text{-Cp(CO)}_3\text{W}$ unit.

The remaining tungsten(II) compounds have all been obtained by the halogenation of substituted carbonyls. Except for $[(\text{diphos})_2\text{W(CO)}_2]^+$ (see above) (176), smooth, two-electron oxidations occur. Reaction usually takes place without loss of carbon monoxide to give seven-coordinate complexes in which one halide ion is coordinated and the other is ionic, the

compounds being uniunivalent electrolytes. In other cases, 1 mole of carbon monoxide is lost during the oxidation and nonelectrolytes are obtained (Table IX). This is probably the more stable form, since $[(v\text{-triars})W(CO)_3X]X$ is converted to $[(v\text{-triars})W(CO)_2X_2]$ by heating to $200^\circ C$ (212). With the corresponding molybdenum complexes this conversion is easier (66, 212) and the nonelectrolytes are more often obtained directly (66, 175, 176, 190). The chromium compounds usually undergo complete loss of carbon monoxide, the exceptions being $[Cr(CO)_5I]^-$ and $(v\text{-triars})Cr(CO)_3$, which give $Cr(CO)_5I$ (164) and $[(v\text{-triars})Cr(CO)_2]^{+}$ (212), respectively.

TABLE IX
OXIDATION PRODUCTS OF SUBSTITUTED TUNGSTEN CARBONYLS^a

Starting material		Product	Ref.
$[W(CO)_5X]^-$		$[W(CO)_4X_3]^-$	(164)
diars $W(CO)_4$	$[diarsW(CO)_4I]I$	diars $W(CO)_3Br_2$	(175)
bipy $W(CO)_4$		bipy $W(CO)_3X_2^b$	(272)
diphos $W(CO)_4^c$		diphos $W(CO)_3I_2$	(176)
dithia $W(CO)_4$		dithia $W(CO)_3X_2$	(189)
ttas $W(CO)_3$	$[ttasW(CO)_3X]X$		(66)
tas $W(CO)_3$	$[tasW(CO)_3X]X$		(190)
v-triars $W(CO)_3$	$[v\text{-triars}W(CO)_3X]X$	v-triars $W(CO)_2X_2$	(212)
hmb $W(CO)_3$	$[hmbW(CO)_3X]X$		(266)
diars $_2W(CO)_2$	$[diars_2W(CO)_2X]X$		(175)

^a diars = $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$, bipy = bipyridyl, diphos = $\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2$, dithia = 2,5-dithiahexane, ttas = $\text{PhAs}(o\text{-C}_6\text{H}_4\text{AsPh}_2)_2$, tas = $\text{MeAs}(\text{CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2)_2$, v-triars = $\text{MeC}(\text{CH}_2\text{AsMe}_2)_3$, hmb = hexamethylbenzene, and X = Cl, Br, I.

^b X may also be HgCl (111).

^c Evidence was obtained for the product $[diphosW(CO)_4I]I_3$, but the complex could not be isolated (176).

The ion $[W(CO)_4I_3]^-$ (163) and its tungsten(0) precursors $[W(CO)_5X]^-$ (X = halogen) (2, 95, 198) are the only known carbonyl halides of tungsten. When $[W(CO)_5X]^-$ is treated with an allyl halide, $\text{C}_3\text{H}_5\text{Y}$, a halogen-bridged, dimeric anion is obtained, $[(\pi\text{-C}_3\text{H}_5)W(CO)_2Y_3(CO)_2W(\pi\text{-C}_3\text{H}_5)]^-$. The bridge may be cleaved by pyridine to give $(\pi\text{-C}_3\text{H}_5)W(CO)_2Y\text{-py}$ (202). Tungsten hexacarbonyl apparently does not react with allyl halides (98).

E. TUNGSTEN(III)

Further oxidation of $(diars)W(CO)_3Br_2$ gives $[(diars)W(CO)_3Br_2]Br$, in which the tungsten atom is still seven-coordinate but has a single unpaired electron, $\mu_{\text{eff}} = 1.54 \text{ B.M.}$ (175).

F. TUNGSTEN(IV AND V)

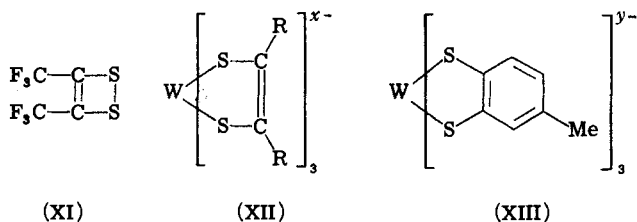
No carbonyl complex is known in which tungsten has an oxidation state higher than +3. The only aromatic group reported as coordinating to tungsten(IV) or tungsten(V) is cyclopentadienyl. Tungsten(IV) gives derivatives of the type $(\pi\text{-Cp})_2\text{WX}_2$, where X is H (92, 123) or halogen (67). In these compounds the two π -bonded rings are not parallel, the four groups forming a rough tetrahedron about the metal atom (29, 100, 123). The two π -bonded ligands are separated by a lone pair, which can be donated to a suitable acceptor, as in $[(\pi\text{-Cp})_2\text{WH}_3]^+$ and $(\pi\text{-Cp})_2\text{WH}_2\cdot\text{BF}_3$ (123, 126, 263). The halogen compounds may be oxidized to the tungsten(V) derivative $[(\pi\text{-Cp})_2\text{WX}_2]\text{X}$ (X = Cl, Br) (67, 71).

VII. Other Compounds

A few compounds do not fall readily into the above categories.

A. DITHIOLATES

The reaction of bis(trifluoromethyl)-1,2-dithietene (XI) with tungsten hexacarbonyl gives a monomeric, diamagnetic complex $\text{W}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_3$ (XII, R = CF_3 , $x = 0$) (74, 162). Similar derivatives of diphenyldithietene and toluenedithiol have been obtained [XII, R = Ph, $x = 0$ (282); XIII, $y = 0$ (269)]. These are formally complexes of tungsten(VI).



Anionic species may be obtained by reduction [XII, R = CF_3 , $x = 1$ (74); R = Ph, $x = 1, 2$ (269); XIII, $y = 1$ (282)]. The mononegative anions are paramagnetic, with a magnetic moment of 1.77 B.M. (XII, R = CF_3 , $x = 1$), while the dinegative anions are diamagnetic. The esr spectra of the paramagnetic species give g values very close to 2.00 and show little or no anisotropy (269). This cannot be explained in terms of a distorted octahedral ligand field (74), and it is probable that the configuration is that of a trigonal prism. This configuration has been found for $\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3$ (80), with which the corresponding tungsten compound is isomorphous (269).

B. OXALATES

When a tungstate solution is reduced in the presence of oxalic acid, a red solution is obtained containing tungsten(V), from which salts of the anion $[\text{WO}_2(\text{C}_2\text{O}_4)_2]^{3-}$ may be obtained (59). These salts have been little studied but are useful intermediates, as in the preparation of oxyhalide complexes (59) or octacyanotungstates (20). This seems to be the only isolated oxalato complex of tungsten, in contrast to the many derivatives known for molybdenum.

C. PHENYL DERIVATIVES

Reduction of tungsten hexachloride or pentabromide with phenyllithium gives a black, diamagnetic, air-sensitive solid which has been formulated both as $\text{Ph}_3\text{W}\cdot 3\text{LiPh}\cdot 3\text{Et}_2\text{O}$ (104) and as $\text{Ph}_4\text{W}\cdot 2\text{LiPh}\cdot 3\text{Et}_2\text{O}$ (246). This product may be hydrogenated, when 2 moles of hydrogen are taken up, and another reactive solid has been isolated which was formulated as $\text{WH}\cdot 2\text{LiPh}$ (247).

VIII. Metal-Metal Bonds

Compounds in which there are metal-metal bonds occur under two sets of circumstances:

(a) A wide variety of transition metals form metal-metal bonds when the metal is in a low oxidation state and the ligands are strongly π -bonding (57). The metal-metal bonding in these systems is a function more of the ligands than of the metal, since the ligands can, by delocalization of the metal electrons, make the metal more electronegative and reduce the repulsion between nonbonding electrons.

(b) Metals with high heats of atomization are prone to the formation of cluster compounds and their other compounds often exhibit metal-metal bonds (248). These properties presumably result from the occurrence of the optimum number of d electrons and available orbitals and of good overlap between these orbitals. Tungsten has the highest heat of atomization of all the transition metals (Table X).

Tungsten shows examples of both types of compound (Table XI). Many of the low oxidation state compounds are stabilized by metal-metal bonds, and the compounds are diamagnetic. The metal-metal bonds are not very strong unless reinforced by bridging ligands. Crystallographic data are available only for the cyclopentadienyltricarbonyl, $[\pi\text{-CpW}(\text{CO})_3]_2$, in which the two halves of the molecule are united only by a tungsten-tungsten bond of length 3.28 Å (cf. 2.74 Å in the metal) (290). This bond is readily cleaved, either by oxidation, e.g. with halogens to give $\pi\text{-CpW}(\text{CO})_3\text{X}$, or by reduction, e.g. with sodium to give $[\pi\text{-CpW}(\text{CO})_3]^-$.

Despite the formal changes in oxidation state, the total number of electrons associated with the tungsten atom is the same in all these compounds, all are "eighteen-electron" compounds. A similar tungsten-tungsten bond presumably occurs in $[\text{W}_2(\text{CO})_{10}]^-$.

Crystallographic data are available also for the dioxide, WO_2 (130), and for the enneachloride, $[\text{W}_2\text{Cl}_9]^{3-}$ (41, 283). In both these compounds

TABLE X
HEATS OF ATOMIZATION OF TRANSITION METALS
(kcal/g-atom) (248)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
80	113	123	95	69	100	102	102	81
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
102	146	175	158	155	155	133	84	68
La	Hf	Ta	W	Re	Os	Ir	Pt	Au
100	168	187	202	186	162	160	135	87

the metal-metal bonds are shorter than in the metal (metal, 2.74 Å; WO_2 , 2.49 Å; $\text{K}_3\text{W}_2\text{Cl}_9$, 2.41 Å) and are probably multiple bonds. The chloro complex provides a good example of the ease with which the heavier metals form metal-metal bonds compared to the lighter metals. The chromium complex, $\text{Cs}_3\text{Cr}_2\text{Cl}_9$, is paramagnetic, $\mu_{\text{eff}} = 3.82$ B.M. per chromium atom. The anion is symmetrical (D_{3h}) and the two chromium atoms repel each other to a distance of 3.12 Å (cf. 2.45 Å in chromium metal) (286). The

TABLE XI
COMPOUNDS IN WHICH METAL-METAL BONDING PROBABLY OCCURS

$[\pi\text{-Cp}(\text{CO})_5\text{W}]_2$	W_6X_{12} , W_6X_{14} , W_6X_{16} , W_6X_{18}
$[(\text{CO})_5\text{W}]_2^-$	WX_4
$[\text{W}_2(\text{CO})_9]^{4-}$	WX_5
$[\text{W}_3(\text{CO})_{14}]^-$	$[\text{W}_2\text{X}_9]^{3-}$
$[(\text{CO})_4(\text{LR}_2)\text{W}]_2$	$\text{W}_2\text{X}_6\text{L}_3$
	WO_2
	$\text{W}_2(\text{OEt})_6\text{Cl}_4$

corresponding titanium and vanadium complexes are isomorphous with the chromium compound (286). The molybdenum and tungsten derivatives are diamagnetic, however, and the structure of $\text{K}_3\text{W}_2\text{Cl}_9$ shows that the tungsten atoms are drawn together. The anion is slightly distorted by twisting of the triangle of bridging chlorine atoms about the trigonal axis. It would be of interest to determine whether this distortion occurs in salts with other cations.

ACKNOWLEDGMENTS

I am indebted to Professor N. N. Greenwood for encouraging the preparation of this review and to Dr. B. H. Robinson for helpful comments. Financial support during much of the preparation was provided by the General Electric Co., Schenectady, N.Y.

REFERENCES

1. Abel, E. W., *Quart. Rev. (London)* **17**, 133 (1963).
2. Abel, E. W., Butler, I. S., and Reid, J., *J. Chem. Soc.* p. 2068 (1963).
3. Ackermann, R. J., and Rauh, E. G., *J. Phys. Chem.* **67**, 2596 (1963).
4. Adams, D. M., Chatt, J., Davidson, J. M., and Gerratt, J., *J. Chem. Soc.* p. 2189 (1963).
5. Adams, D. M., Gebbie, H. A., and Peacock, R. D., *Nature* **199**, 278 (1963).
6. Adamson, A. W., and Perumareddi, J. R., *Inorg. Chem.* **4**, 247 (1965).
7. Adamson, A. W., Welker, J. P., and Volpe, M., *J. Am. Chem. Soc.* **72**, 4030 (1950).
8. Afsprung, H. E., and Murphy, J. W., *Anal. Chim. Acta* **32**, 381 (1965).
9. Allen, E. A., Brisdon, B. J., Edwards, D. A., Fowles, G. W. A., and Williams, R. G., *J. Chem. Soc.* p. 4649 (1963).
10. Allen, E. A., Brisdon, B. J., and Fowles, G. W. A., *J. Chem. Soc.* p. 4531 (1964).
11. Allen, J. F., and Neumann, H. M., *Inorg. Chem.* **3**, 1613 (1964).
12. Anders, U., and Graham, W. A. G., *Chem. Commun.* p. 499 (1965).
13. Anderson, J. S., *Proc. Chem. Soc.* p. 166 (1964).
14. Aveston, J., *Inorg. Chem.* **3**, 981 (1964).
15. Baadsgaard, H., and Treadwell, W. D., *Helv. Chim. Acta* **38**, 1669 (1955).
16. Baaz, M., Gutmann, V., and Talaat, M. Y. A., *Monatsh. Chem.* **92**, 707 (1961).
17. Babel, D., and Rüdorff, W., *Naturwissenschaften* **51**, 85 (1964).
18. Bagnall, K. W., Brown, D., and du Preez, J. G. H., *J. Chem. Soc.* p. 2603 (1964).
19. Barber, E. J., and Cady, G. H., *J. Phys. Chem.* **60**, 505 (1956).
20. Barbieri, G. A., and Fiano, E., *Atti Accad. Sci. Ist. Bologna* [11] **2**, 106 (1955).
- 20a. Barraclough, C. G., and Stals, J., *Australian J. Chem.*, **19**, 741 (1966).
21. Bartlett, N., Beaton, S. P., and Jha, N. K., *Chem. Commun.* p. 168 (1966).
22. Bartlett, N., and Robinson, P. L., *J. Chem. Soc.* p. 3549 (1961).
23. Behrens, H., and Haag, W., *Chem. Ber.* **94**, 320 (1961).
24. Behrens, H., and Harder, N., *Chem. Ber.* **97**, 426 (1964).
25. Behrens, H., and Vogl, J., *Chem. Ber.* **96**, 2220 (1963).
26. Behrens, H., and Weber, R., *Z. Anorg. Allgem. Chem.* **291**, 122 (1957).
27. Kozmin, P. A., *J. Struct. Chem. (USSR) (English Transl.)* **5**, 60 (1964).
28. Bennett, M. A., Interrante, L. V., and Nyholm, R. S., *Z. Naturforsch.* **20b**, 633 (1965).
29. Bennett, M. J., Gerloch, M., McCleverty, J. A., and Mason, R., *Proc. Chem. Soc.* p. 357 (1962).
30. Bertoluzza, A., Carassiti, V., and Marinangeli, A. M., *Ann. Chim. (Rome)* **50**, 806 (1960).
31. Berzelius, J. J., *Ann. Chim. Phys.* [2] **29**, 365 (1825).
32. Biltz, W., Eschweiler, W., and Bodensieck, A., *Z. Anorg. Allgem. Chem.* **170**, 161 (1928).
33. Böhlend, H., and Niemann, E., *Z. Anorg. Allgem. Chem.* **336**, 225 (1965).
34. Bonati, F., and Wilkinson, G., *J. Chem. Soc.* p. 179 (1964).
35. Bonino, G. B., and Fabbri, G., *Atti. Accad. Nazl. Lincei, Rend. Classe Sci. Fis. Mat. Nat.* [8] **20**, 566 (1956).

36. Boorman, P. M., Grant, A., Greenwood, N. N., and Parish, R. V., unpublished observations, 1965.
37. Braune, H., and Pinnow, P., *Z. Physik. Chem.* **B35**, 239 (1937).
38. Brisdon, B. J., Fowles, G. W. A., and Osborne, B. P., *J. Chem. Soc.* p. 1330 (1962).
39. Brisdon, B. J., and Walton, R. A., *J. Inorg. Nucl. Chem.* **27**, 1101 (1965).
40. Brisdon, B. J., and Walton, R. A., *J. Chem. Soc.* p. 2274 (1965).
41. Brossett, C., *Arkiv Kemi, Mineral. Geol.* **12A**, No. 4 (1935).
42. Brossett, C., *Arkiv Kemi* **1**, 353 (1950); Vaughan, P. A., *Proc. Natl. Acad. Sci. U.S.* **36**, 461 (1949).
43. Brown, T. M., and McCarley, R. E., *Inorg. Chem.* **3**, 1232 (1964); Brown, T. M., *U.S. At. Energy Comm.* **IS-741** (1964).
44. Bucknall, W. R., and Wardlaw, W., *J. Chem. Soc.* p. 2981 (1927).
45. Burke, T. G., Smith, D. F., and Nielsen, A. H., *J. Chem. Phys.* **20**, 447 (1952).
46. Cady, G. H., and Hargreaves, G. B., *J. Chem. Soc.* p. 1563 (1961).
47. Cady, G. H., and Hargreaves, G. B., *J. Chem. Soc.* p. 1568 (1961).
48. Carassiti, V., and Claudi, M., *Ann. Chim. (Rome)* **49**, 1697 (1959).
49. Carassiti, V., Marinangeli, A. M., and Balzani, V., *Ann. Chim. (Rome)* **50**, 630, 645 and 790 (1960).
50. Chatt, J., and Thompson, D. T., *J. Chem. Soc.* p. 2713 (1964).
51. Chatt, J., and Thornton, D. A., *J. Chem. Soc.* p. 1005 (1964).
52. Chatt, J., and Watson, H. R., *J. Chem. Soc.* p. 4980 (1961).
53. Chatt, J., and Watson, H. R., *J. Chem. Soc.* p. 2545 (1962).
54. Clark, H. C., and Emeléus, H. J., *J. Chem. Soc.* p. 4778 (1957).
55. Clark, R. J. H., Kepert, D. L., Nyholm, R. S., and Lewis, J., *Nature* **199**, 559 (1963).
56. Coffey, C. E., *J. Inorg. Nucl. Chem.* **25**, 179 (1963).
57. Coffey, C. E., Lewis, J., and Nyholm, R. S., *J. Chem. Soc.* p. 1741 (1964).
58. Cohen, B., Edwards, A. J., Mercer, M., and Peacock, R. D., *Chem. Commun.* p. 322 (1965).
59. Collenberg, O. O., *Z. Anorg. Allgem. Chem.* **102**, 247 (1918).
60. Collenberg, O. O., *Z. Anorg. Allgem. Chem.* **136**, 245 (1924).
61. Collenberg, O. O., *Z. Physik. Chem.* **109**, 353 (1924).
62. Collenberg, O. O., and Backer, J., *Z. Elektrochem.* **30**, 230 (1924).
63. Collenberg, O. O., and Guthe, A., *Z. Anorg. Allgem. Chem.* **134**, 317 (1924).
64. Colton, R., and Tomkins, I. B., *Australian J. Chem.* **19**, 759 (1966).
65. Colton, R., and Tomkins, I. B., *Australian J. Chem.* **18**, 447 (1965).
66. Cook, C. D., Nyholm, R. S., and Tobe, M. L., *J. Chem. Soc.* p. 4194 (1965).
67. Cooper, R. L., and Green, M. L. H., *Z. Naturforsch.* **19b**, 652 (1964).
68. Cotton, F. A., *Inorg. Chem.* **3**, 702 (1964).
69. Cotton, F. A., Fischer, A. K., and Wilkinson, G., *J. Am. Chem. Soc.* **78**, 5168 (1956); **81**, 800 (1959).
70. Cotton, F. A., and Haas, T. E., *Inorg. Chem.* **3**, 10 (1964).
71. Cotton, F. A., and Wilkinson, G., *Z. Naturforsch.* **9b**, 417 (1954).
72. Cox, B., Sharp, D. W. A., and Sharpe, A. G., *J. Chem. Soc.* p. 1242 (1956).
73. Dahl, L. F., Ishishi, E., and Rundle, R. E., *J. Chem. Phys.* **26**, 1750 (1957).
74. Davidson, A., Edelstein, N., Holm, R. H., and Maki, A. H., *J. Am. Chem. Soc.* **86**, 2799 (1964).
75. Davis, O. C. M., *J. Chem. Soc.* p. 1575 (1906).
76. Dickinson, R. N., Feil, S. E., Collier, E. N., Horner, W. W., Horner, S. M., and Tyree, S. Y., *Inorg. Chem.* **3**, 1600 (1964).

77. Djordjevic, C., Nyholm, R. S., Pande, C. S., and Stiddard, M. H. B., *J. Chem. Soc., A, Inorg., Phys., Theoret.*, p. 16 (1966).
78. Dobson, G. R., *Inorg. Chem.* **4**, 1673 (1965).
79. Edwards, D. A., and Woolf, A. A., *J. Chem. Soc. (A)*, p. 91 (1966).
80. Eisenberg, R., and Ibers, J. A., *J. Am. Chem. Soc.* **86**, 4198 (1964).
81. Ewens, R. V. G., and Lister, M. W., *Trans. Faraday Soc.* **34**, 1358 (1935).
82. Fabbri, G., and Capellina, F., *Atti. Accad. Nazl. Lincei, Rend. Classe Sci. Fis. Mat. Nat.* [8] **25**, 299 (1958).
83. Feigl, F., and Krumholz, P., *Angew. Chem.* **45**, 674 (1932).
84. Feil, S. E., *Dissertation Abstr.* **26**, 1338 (1965).
85. Fischer, A., and Michiels, L., *Z. Anorg. Chem.* **81**, 102 (1913).
86. Fischer, E. O., Beckert, O., Hafner, W., and Stahl, H. O., *Naturwissenschaften* **10b**, 598 (1955).
87. Fischer, E. O., and Fichtel, K., *Chem. Ber.* **94**, 1200 (1961).
88. Fischer, E. O., Fichtel, K., and Öfele, K., *Chem. Ber.* **95**, 249 (1962).
89. Fischer, E. O., and Fritz, H. P., *Advan. Inorg. Chem. Radiochem.* **1**, 55 (1959).
90. Fischer, E. O., and Kohl, F. J., *Z. Naturforsch.* **18b**, 504 (1963).
91. Fischer, E. O., Hafner, W., and Stahl, H. O., *Z. Anorg. Allgem. Chem.* **282**, 47 (1955).
92. Fischer, E. O., and Hristidu, Y., *Z. Naturforsch.* **15b**, 135 (1960).
93. Fischer, E. O., and Maasböl, A., *Angew. Chem.* **76**, 645 (1964).
94. Fischer, E. O., and Moser, E., *J. Organometal. Chem.* **2**, 230 (1964).
95. Fischer, E. O., and Öfele, K., *Chem. Ber.* **93**, 1156 (1960).
96. Fischer, E. O., Öfele, K., Essler, H., Fröhlich, W., Mortensen, J. P., and Semmlinger, W., *Chem. Ber.* **91**, 2763 (1958).
97. Fischer, E. O., Scherer, F., and Stahl, H. O., *Chem. Ber.* **93**, 2065 (1960).
98. Fischer, E. O., and Werner, H., *Z. Chem.* **2**, 181 (1962).
- 98a. Fowles, G. W. A., and Frost, J. L., *Chem. Commun.*, p. 252 (1966).
99. Fowles, G. W. A., and Osborne, B. P., *J. Chem. Soc.* p. 2275 (1959).
100. Fritz, H. P., Hristidu, Y., Hummel, H., and Schneider, R., *Z. Naturforsch.* **15b**, 419 (1960).
101. Funk, H., and Baumann, W., *Z. Anorg. Allgem. Chem.* **231**, 264 (1937).
102. Funk, H., and Böhländ, H., *Z. Anorg. Allgem. Chem.* **318**, 169 (1962).
103. Funk, H., and Böhländ, H., *Z. Anorg. Allgem. Chem.* **324**, 168 (1963).
104. Funk, H., and Hanke, W., *Z. Anorg. Allgem. Chem.* **307**, 157 (1960).
105. Funk, H., Matschiner, H., and Naumann, H., *Z. Anorg. Allgem. Chem.* **340**, 75 (1965).
106. Funk, H., and Mohaupt, G., *Z. Anorg. Allgem. Chem.* **315**, 204 (1962).
107. Funk, H., and Schauer, H., *Z. Anorg. Allgem. Chem.* **306**, 203 (1960).
108. Funk, H., Weiss, W., and Mohaupt, G., *Z. Anorg. Allgem. Chem.* **304**, 238 (1960).
109. Gado, P., *Acta Cryst.* **16**, A182 (1963).
110. Gado, P., and Magnéli, A., *Acta Chem. Scand.* **19**, 1514 (1965).
111. Ganorkar, M. C., and Stiddard, M. H. B., *Chem. Commun.* p. 22 (1965).
112. Gaunt, J., *Trans. Faraday Soc.* **49**, 1122 (1953).
113. Gebert, E., and Ackermann, R. J., *Inorg. Chem.* **5**, 136 (1966).
114. Geichmann, J. R., Smith, E. A., and Ogle, P. R., *Inorg. Chem.* **2**, 1012 (1963).
115. Glemser, O., and Ackermann, H., *Z. Anorg. Allgem. Chem.* **325**, 281 (1963).
116. Glemser, O., Holznagel, W., Holtje, W., and Schwarzmann, E., *Z. Naturforsch.* **20b**, 725 (1965).
117. Goodenow, E. L., and Garner, C. S., *J. Am. Chem. Soc.* **77**, 5268 (1955).

118. Goodenow, E. L., and Garner, C. S., *J. Am. Chem. Soc.* **77**, 5272 (1955).
119. Gottschalk, G., *Z. Anal. Chem.* **187**, 164 (1962).
120. Grant, A., Greenwood, N. N., and Parish, R. V., unpublished observations, 1964.
121. Gray, H. B., and Beach, N. A., *J. Am. Chem. Soc.* **85**, 2922 (1963).
122. Gray, H. B., and Hare, C. R., *Inorg. Chem.* **1**, 363 (1963).
123. Green, M. L. H., McCleverty, J. A., Pratt, L., and Wilkinson, G., *J. Chem. Soc.* p. 4854 (1961).
124. Green, M. L. H., and Nagy, P. L. I., *Advan. Organometal. Chem.* **2**, 235 (1964).
125. Green, M. L. H., and Stear, A. N., *J. Organometal. Chem.* **1**, 230 (1963).
126. Green, M. L. H., Street, C. N., and Wilkinson, G., *Z. Naturforsch.* **14b**, 738 (1959).
127. Greenwood, N. N., Boorman, P. M., Hildon, M. A., and Parish, R. V., unpublished observations, 1966.
128. Groenveld, W. L., *Rec. Trav. Chim.* **71**, 1152 (1952).
129. Guy, R. G., and Shaw, B. L., *Advan. Inorg. Chem. Radiochem.* **4**, 78 (1962).
130. Haag, G., and Magnéli, A., *Rev. Pure Appl. Chem.* **4**, 235 (1954); Magnéli, A., *J. Inorg. Nucl. Chem.* **2**, 330 (1956).
131. Hamlen, R. P., and Koski, W. S., *J. Chem. Phys.* **25**, 360 (1956).
132. Hargreaves, G. B., and Peacock, R. D., *J. Chem. Soc.* p. 2170 (1958).
133. Hargreaves, G. B., and Peacock, R. D., *J. Chem. Soc.* p. 3776 (1958).
134. Hawkins, G. L., and Garner, C. S., *J. Am. Chem. Soc.* **80**, 2946 (1958).
135. Hayter, R. G., *Inorg. Chem.* **2**, 1031 (1963).
136. Hayter, R. G., *Inorg. Chem.* **3**, 711 (1964).
137. Heintz, E. A., *Inorg. Syn.* **7**, 142 (1961).
138. Herzog, S., and Gutsche, E., *Z. Chem.* **3**, 393 (1963).
139. Herzog, S., and Kubetschek, E., *Z. Naturforsch.* **18b**, 162 (1963).
140. Hieber, W., Beck, W., and Braun, G., *Angew. Chem.* **72**, 795 (1960).
141. Hildago, A., and Matthieu, J.-P., *Compt. Rend.* **249**, 233 (1959).
142. Hill, J. B., *J. Am. Chem. Soc.* **38**, 2383 (1916).
143. Hoard, J. L., and Martin, W. J., *J. Am. Chem. Soc.* **63**, 11 (1941).
144. Hoard, J. L., and Nordsieck, H. H., *J. Am. Chem. Soc.* **61**, 2853 (1939).
145. Hoard, J. L., and Silverton, J. H., *Inorg. Chem.* **2**, 235 (1963).
146. Hölzl, F., *Sitzber. Akad. Wiss. Wien Abt. IIb* **137**, 953 (1929).
147. Horner, S. M., and Tyree, S. Y., *Inorg. Nucl. Chem. Letters* **1**, 43 (1966).
148. Jahr, K. E., Fuchs, J., Witte, P., and Flindt, E. P., *Chem. Ber.* **98**, 3588 (1965).
149. Jakob, W. F., and Jakob, Z. L., *Roczniki Chem.* **26**, 492 (1952).
150. Jakob, W., Samotus-Kosinska, A., and Stasicka, Z., *Proc. 7th Intern. Conf. Coord. Chem., Stockholm, 1962*, Almqvist and Wiksell, A. B., Uppsala p. 238 (1962).
151. Jakob, W., Samotus-Kosinska, A., and Stasicka, Z., *Roczniki Chem.* **36**, 165 (1962).
152. Jonassen, H. B., and Cantor, S., *Rec. Trav. Chim.* **75**, 609 (1956); Jonassen, H. B., Cantor, S., and Tarsey, H. R., *J. Am. Chem. Soc.* **78**, 271 (1956).
153. Jones, L. H., *J. Mol. Spectry.* **9**, 130 (1962).
154. Jorgensen, C. K., *Acta Chem. Scand.* **11**, 72 (1957).
155. Kemmitt, R. D. W., Russel, D. R., and Sharp, D. W. A., *J. Chem. Soc.* p. 4408 (1963).
156. Kennedy, C. D., and Peacock, R. D., *J. Chem. Soc.* p. 3392 (1963).
157. Kepert, D. L., *Progr. Inorg. Chem.* **4**, 199 (1962).
158. Kepert, D. L., *J. Chem. Soc.* p. 4736 (1965).
159. Ketelaar, J. A. A., and van Oosterhout, G. W., *Rec. Trav. Chim.* **62**, 197 (1943).
160. Ketelaar, J. A. A., van Oosterhout, G. W., and Braun, P. B., *Rec. Trav. Chim.* **62**, 597 (1943).

161. Kettle, S. F. A., and Parish, R. V., *Spectrochim. Acta* **21**, 1087 (1965).
162. King, R. B., *Inorg. Chem.* **2**, 641 (1963).
163. King, R. B., *Inorg. Chem.* **3**, 1039 (1964); Ganorkar, M. C., and Stiddard, M. H. B., *J. Chem. Soc.* p. 3494 (1965).
164. King, R. B., and Bisnette, M. B., *J. Organometal. Chem.* **2**, 15 (1964).
165. King, R. B., and Fronzaglia, A., *Chem. Commun.* p. 547 (1965).
166. Kleinberg, J., Griswold, E., and Yoo, S. J., *Inorg. Chem.* **4**, 365 (1965).
167. Klejnot, O. J., *Inorg. Chem.* **4**, 1669 (1965).
168. Kokovin, G. A., and Toropova, N. K., *Russ. J. Inorg. Chem. (English Transl.)* **10**, 304 (1965).
169. König, E., *Theoret. Chim. Acta* **1**, 23 (1962).
170. König, E., *Inorg. Chem.* **2**, 1238 (1963).
171. Larson, M. L., and Moore, E. W., *Inorg. Chem.* **3**, 285 (1964).
172. Laudise, R. A., and Young, R. C., *J. Am. Chem. Soc.* **77**, 5288 (1955).
173. Lewis, J., *Pure Appl. Chem.* **10**, 11 (1965).
174. Lewis, J., Machin, D. J., Nyholm, R. S., Pauling, P., and Smith, P. W., *Chem. Ind. (London)* p. 259 (1960).
175. Lewis, J., Nyholm, R. S., Pande, C. S., and Stiddard, M. H. B., *J. Chem. Soc.* p. 3600 (1963).
176. Lewis, J., and Whyman, R., *J. Chem. Soc.* p. 5486 (1965).
177. Lewis, J., and Whyman, R., *J. Chem. Soc.* p. 6027 (1965).
178. Litvinchuk, V. M., and Mikhalevich, K. N., *Ukr. Khim. Zh.* **25**, 563 (1959).
179. Lindner, K., and Köhler, A., *Z. Anorg. Allgem. Chem.* **140**, 364 (1924).
180. Lingane, J. J., and Small, L. A., *J. Am. Chem. Soc.* **71**, 973 (1949).
181. Lorenzelli, V., and Delorme, P., *Spectrochim. Acta* **19**, 2033 (1963).
182. McCarley, R. E., and Brown, T. M., *J. Am. Chem. Soc.* **84**, 3216 (1962).
183. McCarley, R. E., Hughes, B. G., Cotton, F. A., and Zimmerman, R., *Inorg. Chem.* **4**, 1491 (1965).
184. McCleverty, J. A., and Wilkinson, G., *J. Chem. Soc.* p. 4096 (1963).
185. McDiarmid, A. G., and Hall, N. F., *J. Am. Chem. Soc.* **75**, 5204 (1953).
186. McGarvey, B. R., *Inorg. Chem.* **5**, 476 (1966); Hayes, R. G., *J. Phys. Chem.* **44**, 2210 (1966).
187. Maitlis, P. M., and Efraty, A., *J. Organometal. Chem.* **4**, 172 (1965).
188. Malatesta, L., and Sacco, A., *Ann. Chim. (Rome)* **43**, 622 (1953).
189. Mannerskantz, H. C. E., and Wilkinson, G., *J. Chem. Soc.* p. 4454 (1962).
190. Masek, J., Nyholm, R. S., and Stiddard, M. H. B., *Collection Czech. Chem. Commun.* **29**, 1714 (1964).
191. Massey, A. G., *J. Inorg. Nucl. Chem.* **24**, 1172 (1962).
192. Mikhalevich, K. N., and Litvinchuk, V. M., *Zh. Neorgan. Khim.* **3**, 1846 (1958).
193. Mikhalevich, K. N., and Litvinchuk, V. M., *Russ. J. Inorg. Chem. (English Transl.)* **4**, 800 (1959).
194. Mikhalevich, K. N., and Litvinchuk, V. M., *Proc. 7th Intern. Conf. Coord. Chem., 1962 Stockholm*, p. 242, Almquist and Wiksell, A. B., Uppsala (1962).
195. Mikhalevich, K. N., and Litvinchuk, V. M., *Zh. Neorgan. Khim.* **9**, 2391 (1964).
196. Mitchell, P. C. H., and Williams, R. J. P., *J. Chem. Soc.* p. 1912 (1960).
197. Mitchell, P. C. H., and Williams, R. J. P., *J. Chem. Soc.* p. 4570 (1962).
198. Moore, B., and Wilkinson, G., *Proc. Chem. Soc.* p. 61 (1959).
199. Mortimer, P. I., and Strong, M. I., *Australian J. Chem.* **18**, 1579 (1965).
200. Muettterties, E. L., *Inorg. Chem.* **4**, 769 (1965).
201. Muettterties, E. L., and Phillips, W. D., *J. Am. Chem. Soc.* **81**, 1084 (1959).

202. Murdoch, H. D., *J. Organometal. Chem.* **4**, 119 (1965).
203. Murray, G. A., *U.S. At. Energy Comm.* **IS-T-5** (1965).
204. Musil, F. J., and Ralston, K., *U.S. At. Energy Comm.* **GAT-T-839** (1960).
205. Myers, O. E., and Brady, A. P., *J. Phys. Chem.* **64**, 591 (1960).
206. Nakamura, D., Ikeda, R., and Kubo, M., *Proc. 8th Intern. Conf. Coord. Chem., 1965 Vienna*, p. 57, Springer-Verlag, Wein and New York, (1965).
207. Nast, R., and Kohl, H., *Chem. Ber.* **97**, 207 (1964).
208. Nesmayanov, A. N., Anisimov, K. N., Kolobova, N. E., and Zakharova, M. Y., *Dokl. Akad. Nauk SSSR* **156**, 612 (1964).
209. Neubauer, D., and Weiss, J., *Z. Anorg. Allgem. Chem.* **303**, 28 (1960).
210. Nigam, H. L., Nyholm, R. S., and Stiddard, M. H. B., *J. Chem. Soc.* p. 1803 (1960).
211. Norman, J. H., and Staley, H. G., *J. Chem. Phys.* **43**, 3804 (1965).
212. Nyholm, R. S., Snow, M. R., and Stiddard, M. H. B., *J. Chem. Soc.* p. 6570 (1965).
213. Olsson, O. O., *Ber. Deut. Chem. Ges.* **46**, 566 (1913).
214. Olsson, O. O., *Ber. Deut. Chem. Ges.* **47**, 917 (1914).
215. Olsson, O. O., *Z. Anorg. Chem.* **88**, 49 (1914).
216. Orgel, L. E., *J. Inorg. Nucl. Chem.* **14**, 136 (1960).
217. Parish, R. V., *Spectrochim. Acta* **22**, 1191 (1966).
218. Parish, R. V., unpublished observations, 1964.
219. Parish, R. V., and Perkins, P. G., unpublished results, 1966.
220. Parish, R. V., and Simms, P. G., unpublished observations, 1965.
221. Patil, H. R. H., and Graham, W. A. G., *J. Am. Chem. Soc.* **87**, 673 (1965).
222. Pauling, L., *J. Am. Chem. Soc.* **46**, 2747 (1924).
223. Paulssen-v. Beck, H., *Z. Anorg. Allgem. Chem.* **196**, 85 (1931).
224. Perumareddi, J. R., Liehr, A. D., and Adamson, A. W., *J. Am. Chem. Soc.* **85**, 249 (1963).
225. Pfeiffer, V., *Mikrochim. Acta* 518, (1960).
226. Piper, T. S., and Wilkinson, G., *J. Inorg. Nucl. Chem.* **3**, 104 (1956).
227. Prasad, S., and Krishnaiah, K. R. S., *J. Indian Chem. Soc.* **37**, 588 (1960).
228. Prasad, S., and Krishnaiah, K. R. S., *J. Indian Chem. Soc.* **37**, 681 (1960).
229. Prasad, S., and Krishnaiah, K. R. S., *J. Indian Chem. Soc.* **38**, 352, 757, and 760 (1961).
230. Prasad, S., and Krishnaiah, K. R. S., *J. Indian Chem. Soc.* **38**, 400 (1961).
231. Prasad, S., and Krishnaiah, K. R. S., *J. Indian Chem. Soc.* **38**, 763 (1961).
232. Prasad, S., and Swarup, R., *J. Indian Chem. Soc.* **42**, 789 (1965).
233. Priest, H. F., and Schumb, W. C., *J. Am. Chem. Soc.* **70**, 2291 (1948).
234. Priest, H. F., and Schumb, W. C., *J. Am. Chem. Soc.* **70**, 3378 (1948).
235. Prigent, J., and Caillet, P., *Compt. Rend.* **256**, 2184 (1963).
236. Raines, M. M., *Compt. Rend. Acad. Sci. URSS* **18**, 339 (1938).
237. Rausch, M. D., *Can. J. Chem.* **41**, 1289 (1963).
238. Ray, P., and Bahr, H., *J. Indian Chem. Soc.* **5**, 497 (1928).
239. Rosenheim, A., and Dehn, E., *Ber. Deut. Chem. Ges.* **46**, 392, (1914).
240. Rosenheim, A., and Dehn, E., *Ber. Deut. Chem. Ges.* **48**, 1167 (1915).
241. Rosenheim, A., and Li, T. H., *Ber. Deut. Chem. Ges.* **56**, 2228 (1923).
242. Ross, B. L., Grasselli, J. G., Ritchey, W. M., and Kaesz, H. D., *Inorg. Chem.* **2**, 1023 (1963).
243. Ruff, O., *Z. Anorg. Chem.* **52**, 257 (1907).
244. Sabatini, A., and Bertini, I., *Inorg. Chem.* **5**, 204 (1966).
245. Sands, D. E., and Zalkin, A., *Acta Cryst.* **12**, 723 (1959).
246. Sarry, B., and Dettke, M., *Angew. Chem.* **75**, 1022 (1963).

247. Sarry, B., Dettke, M., and Grossmann, H., *Z. Anorg. Allgem. Chem.* **329**, 218 (1964).
248. Schäfer, H., and Schnering, H. G., *Angew. Chem.* **76**, 833 (1964).
249. Schäfer, H., Schnering, H. G., Simon, A., Giegling, D., Bauer, D., Siepmann, R., and Spreckelmeyer, B., *J. Less-Common Metals* **10**, 154 (1966).
250. Schmeisser, M., *Angew. Chem.* **67**, 493 (1955).
251. Schmitz-Dumont, O., Bruns, I., and Heckmann, I., *Z. Anorg. Allgem. Chem.* **271**, 347 (1953).
252. Schmitz-Dumont, O., and Opgenhof, P., *Z. Anorg. Allgem. Chem.* **275**, 21 (1954).
253. Schmitz-Dumont, O., and Weeg, E., *Z. Anorg. Allgem. Chem.* **265**, 139 (1951).
254. Schnering, H. G., and Wohrle, H., *Naturwissenschaften* **50**, 91 (1963).
255. Schwarzmann, E., and Glemser, O., *Z. Anorg. Allgem. Chem.* **312**, 45 (1961).
256. Shchukarev, S. A., and Kokovin, G. A., *Russ. J. Inorg. Chem. (English Transl.)* **5**, 241 (1960); **9**, 715 (1964).
257. Shchukarev, S. A., Novikov, G. I., and Andreeva, N. V., *Vestn. Leningr. Univ. Ser. Fiz. i Khim* **14**, No. 1, 120 (1959); *Chem. Abstr.* **53**, 14619h.
258. Shchukarev, S. A., Novikov, G. I., Suvorov, A. V., and Maksimov, V. K., *Zh. Neorgan. Khim.* **4**, 2062 (1959).
259. Shchukarev, S. A., Novikov, G. I., Vasilkova, N. V., Suvorov, A. V., Andreeva, N. V., Sharupin, B. N., and Baev, A. K., *Russ. J. Inorg. Chem. (English Transl.)* **5**, 802 (1960).
260. Shchukarev, S. A., Vasilkova, N. V., and Novikov, G. I., *Zh. Neorgan. Khim.* **3**, 2642 (1958).
261. Sheldon, J. C., *J. Chem. Soc.* p. 410 (1962).
262. Shimomura, K., *J. Sci. Hiroshima Univ., Ser. A* **21**, 241 (1958); *Chem. Abstr.* **52**, 19464a.
263. Shriver, D. F., *J. Am. Chem. Soc.* **85**, 3509 (1963); Johnson, M. P., and Shriver, D. F., *ibid.* **88**, 301, (1965); Brunner, H., Wailes, P. C., Kaesz, H. D., *J. Inorg. Nucl. Chem.* **1**, 125 (1965).
264. Sienko, M. J., and Banerjee, B., *J. Am. Chem. Soc.* **83**, 4149 (1961).
265. Siepmann, R., and Schäfer, H., *Naturwissenschaften* **52**, 344 (1965).
266. Snow, M. R., and Stiddard, M. H. B., *Chem. Commun.* p. 580 (1965).
267. Spacu, P. G., *Bull. Sect. Sci. Acad. Roumaine* **22**, 329 (1940); *Chem. Abstr.* **34**, 6894⁷.
268. Stammreich, H., and Sala, O., *Z. Elektrochem.* **64**, 741 (1960); **65**, 149 (1961).
269. Steifel, E. I., and Gray, H. B., *J. Am. Chem. Soc.* **87**, 4012 (1965).
270. Steinberg, H., and Klemm, W., *Z. Anorg. Allgem. Chem.* **227**, 193 (1936).
271. Steward, E. G., and Rooksby, H. P., *Acta Cryst.* **4**, 503 (1951).
272. Stiddard, M. H. B., *J. Chem. Soc.* p. 4712 (1962).
273. Stolz, I., Dobson, G. R., and Sheline, R. K., *Inorg. Chem.* **2**, 1264 (1963).
274. Stolz, I., Dobson, G. R., and Sheline, R. K., *J. Am. Chem. Soc.* **85**, 1013 (1963).
275. Strohmeier, W., *Z. Naturforsch.* **19b**, 959 (1964).
276. Strohmeier, W., and v. Hobe, D., *Chem. Ber.* **94**, 2031 (1961).
277. Szustorowicz, E. M., and Atowjan, L. O., *J. Struct. Chem. (USSR) (English Transl.)* **4**, 273 (1963); Hepworth, M. A., and Robinson, P. L., *J. Inorg. Nucl. Chem.* **4**, 24 (1957); quoted by B. Jezowska-Trzebiatowska, in "Essays in Coordination Chemistry" (W. Schneider, G. Anderegg, and R. Gut, eds.), p. 128. Birhäuser, Basel, (1964).
278. Tanner, K. N., and Duncan, A. B. F., *J. Am. Chem. Soc.* **73**, 1164 (1951).
279. Tate, D. P., and Augl, J. M., *J. Am. Chem. Soc.* **85**, 2174 (1963).

280. Tate, D. P., Knipple, W. R., and Augl, J. M., *Inorg. Chem.* **1**, 433 (1962).
281. Treichel, P. M., Morris, J. H., and Stone, F. G. A., *J. Chem. Soc.* p. 720 (1963).
282. Waters, J. H., Williams, R., Gray, H. B., Schrauzer, G. N., and Finck, H. W., *J. Am. Chem. Soc.* **86**, 4198 (1964).
283. Watson, W. H., and Waser, J., *Acta Cryst.* **11**, 689 (1958).
284. Weissmann, S. I., and Cohen, M., *J. Chem. Phys.* **27**, 1440 (1957).
285. Wells, A. F., "Structural Inorganic Chemistry," p. 387. Oxford Univ. Press, London and New York, 1962.
286. Wessel, G. J., and IJdo, D. J. W., *Acta Cryst.* **10**, 466 (1957).
287. Wicks, C. E., and Block, F. E., *U.S. Bur. Mines Bull.* **605** (1963).
288. Wilkinson, G., *J. Am. Chem. Soc.* **76**, 209 (1954).
289. Wilkinson, G., and Cotton, F. A., *Progr. Inorg. Chem.* **1**, 1 (1959).
290. Wilson, F. C., and Shoemaker, D. P., *J. Chem. Phys.* **27**, 809 (1957); *Naturwissenschaften* **43**, 57 (1956).
291. Wojcicki, A., and Farona, M. F., *J. Inorg. Nucl. Chem.* **26**, 2289 (1964).
292. Young, R. C., *J. Am. Chem. Soc.* **54**, 4515 (1932).
293. Young, R. C., and Laudise, R. A., *J. Am. Chem. Soc.* **78**, 4861 (1956).

AUTHOR INDEX

Numbers in parentheses are reference numbers and indicate that an author's work is referred to although his name is not cited in the text. Numbers in *italic* show the page on which the complete reference is listed.

A

- Abbattista, F., 86(19), 98(23), 99(23), *127*
 Abe, H., 106(4), *127*
 Abel, E. W., 316(1), 325(2), 339(1), 340
 343(2), *347*
 Abrosimowa, L. N., 86(135), 88(135), *130*
 Ackermann, H., 338(115), *349*
 Ackermann, R. J., 338(3, 113), *347*, *349*
 Adaev, D. P., 29(264), *79*
 Adams, D. M., 323(4, 5), 324(4, 5), 325(4),
 326(4), 329(5), 330(5), *347*
 Adamson, A. W., 333(7, 224), 334(6, 7),
 347, *352*
 Addison, C. C., 255(2), 257(1, 3), 259(2),
 306, *307*
 Affsprung, H. E., 337(8), *347*
 Aftandilian, V. D., 166(1), *178*
 Agran, P. A., 304(192), *311*
 Agte, C., 95(1), 98(1), 99(1), 112(1), *127*
 Ahrens, E. H., Jr., 3(51), *73*
 Ajiro, Y., 106(4), *127*
 Akatsu, E., 55(130), 71(130), *75*
 Akatsu, J., 71(131), *75*
 Akishin, P. A., 99(2, 3), *127*
 Alcock, K., 27(1, 2, 239), *72*, *78*
 Alders, L., 3, *72*
 Alderweireldt, F., 3, *79*
 Alimarin, I. P., 26(4), *72*, *72*
 Allen, E. A., 324(10), 327(9), 328(9), 329
 (9), 330(9), *347*
 Allen, J. F., 329(11), *347*
 Alleston, D. L., 172(2), 177(2), *178*
 Allred, A. L., 168(153), 177(153), *182*
 Alter, H. W., 27(304), 70(304), *80*
 Amaya, K., 106(4), *127*
 Anders, U., 339(12), *347*
 Anderson, H. H., 145(5, 16, 22, 24, 25, 26),
 146(22, 28), 147(12, 16, 22, 26), 148
 (3, 25, 28), 153(8, 9, 10, 11, 13, 14, 23,
 24, 26, 28, 71, 72, 77, 78), 154(71),
 155(3, 9, 10, 11, 23, 72, 73, 75, 78, 79),
 156(3, 8, 9, 10, 11, 15, 17, 21, 23, 25,
 26, 71, 72, 73, 75, 76, 78, 79), 157(8,
 20, 24, 28, 72, 74), 158(14, 17, 19, 20,
 (25, 27), 162(8, 71, 77, 79), 163(8), 164
 (79), 165(10, 76), 167(23, 24, 26), 168
 (14, 15, 17, 23, 26, 27), 169(10, 15, 18
 19, 20, 24, 25, 28), 170(25), 171(7, 9,
 76), 173(9, 19), 175(4, 5, 7, 9, 10, 23,
 26, 76), 176(6, 7, 9, 10, 11, 15, 19, 23,
 25, 26, 76), 177(12, 15, 18, 20, 24, 25,
 28), *178*, *179*, *180*
 Anderson, J. S., 316(13), *347*
 Andreeva, N. V., 317(259), 319(257), 322
 (259), *353*
 Andrejasich, C. M., 42(204), 46(203), *77*
 Andrianov, K. A., 155(214), 158(214),
 183
 Andrussow, L., 126(38), *128*
 Angus, W. R., 257(4), *307*
 Anisimov, K. N., 342(208), *352*
 Anschütz, E., 126(79), *129*
 Antikainen, P. J., 70, *72*
 Appel, R., 162(28b), *178*, 254(5), *307*
 Apraksin, I. A., 30(231), *78*
 Arbuzov, A. E., 30(6, 7), *72*
 Arnold, R. G., 162(28a), *178*
 Arnott, A. J., 104(178), 106(178), 120(5),
 131
 Arnott, R. J., 119(45), 120(45), *127*, *128*
 Arotzky, J., 276(8), 278(7), *307*
 Asprey, L. B., 24(8), *72*, 273(6), *307*
 Atherton, N. M., 212(1), *213*
 Atoji, M., 190(93), *215*
 Atowjan, L. O., 318(277), *353*
 Aubke, F., 279(9), *307*
 Audrieth, L. F., 134(29), 162(180a), *178*,
 183
 Auer, P. L., 19, *72*
 Augl, J. M., 340(279, 280), *353*, *354*

Auten, R. W., 213
 Aveston, J., 304(10), 307, 338, 347
 Aynsley, E. E., 229(11), 259(11), 278(12,
 13), 307

B

Baadsgaard, H., 332(15), 333(15), 347
 Baaz, M., 325(16), 347
 Babel, D., 322(17), 347
 Backer, J., 324(62), 330(62), 331(62), 348
 Baenziger, N. C., 245(244), 312
 Baenziger, N. L., 248(345), 276(345), 314
 Baes, C. F., Jr., 35, 36, 41(24), 42(24), 44
 (24), 65(24), 66(23), 72, 302(14), 307
 Baev, A. K., 317(259), 322(259), 353
 Bagnall, K. W., 323(18), 324(18), 325(18),
 326(18), 347
 Bahr, H., 332(238), 352
 Bailar, J. C., 188(8, 57), 189(15), 190(15),
 196, 197(79), 198(79), 199, 200(8, 70),
 201(8, 44, 57), 203(14), 204(6), 206(2),
 207(57), 212, 213, 214, 215
 Baker, E. B., 240(231), 312
 Baldwin, R. A., 141(194), 183
 Bale, H. D., 304(250), 312
 Ballard, R. E., 195(9), 213
 Ballou, N. E., 35, 36, 78
 Balog, G., 284(263), 312
 Balthis, J. H., 188(8), 200(8), 201(8), 213
 Balzani, V., 334(49), 348
 Banerjee, B., 338(264), 353
 Bang, W. B., 282(17), 307
 Banks, A. A., 268(16), 273(15), 307
 Banks, C. V., 33(190), 77
 Baratashvili, J. B., 101(6), 127
 Barker, E. J., 322(19), 347
 Barbien, R., 172(41a), 179
 Barbieri, G. A., 332(20), 345(20), 347
 Barns, P. P., 294(80), 308
 Baroncelli, F., 54, 72
 Barr, J., 287(18, 317), 307, 314
 Barraclough, C. G., 318(20a), 347
 Bartell, L. S., 249(19), 307
 Bartlett, N., 229(20), 263(20), 264(21),
 274(20), 307, 324(21, 22), 347
 Bastien, T. J., 240(231), 312
 Eate-Smith, E. C., 60(15), 72
 Bauer, D., 321(249), 353
 Bauer, K., 247(177), 310
 Bauer, S. H., 155(106b), 160(106b), 171
 (106b), 175(106b), 180
 Baughan, E. C., 254(245), 312
 Baumann, W., 318(101), 337(101), 349
 Baumgärtner, R., 250(126), 309
 Baybarz, R. D., 46, 52, 53, 54(160), 71,
 72, 76
 Bayliss, J. W. A., 239(22), 307
 Beach, N. A., 341(121), 350
 Beachell, H. C., 143(126, 127), 145(126,
 127), 149(126, 127), 151(126, 127),
 175(126), 181, 284(59), 308
 Beard, C. I., 171(30), 178
 Beaton, S. P., 324(21), 347
 Beattie, I. R., 240(23), 245(325), 307, 314
 Beattie, T. R., 228(24), 253(24), 307
 Beck, W., 339(140), 178, 350
 Becke-Goehring, M., 248(25, 26), 307
 Becker, K., 85(8), 86(8), 100(7), 127
 Becker, M., 135(155a), 182
 Beckert, O., 342(86), 349
 Beckey, H. D., 281(27), 307
 Bedford, F. C., 27(1), 72
 Behmel, K., 153(192), 156(192), 160(192),
 183
 Behrens, H., 336(24, 25), 339(23, 25, 26),
 340(24), 347
 Belcher, R., 3, 72
 Benesovsky, F., 86(127), 94(93), 117(128),
 121(73, 74, 75, 76), 122(73, 129), 129,
 130
 Bennett, M. A., 340(28), 347
 Bennett, M. J., 344(29), 347
 Bennett, W. E., 206(10), 208(10), 209(10),
 213
 Beranová, H., 59, 72
 Berethiani, J. B., 101(6), 127
 Berger, J. A., 87(176), 106(176), 119(176),
 131
 Berger, K., 257(136), 310
 Berkowitz, J., 294(209), 295(28, 32, 54),
 296(29, 31, 157), 297(30, 31), 307,
 308, 310, 311
 Bernier, R., 87(9), 104(9), 127
 Bernström, B., 28, 72
 Berry, R. S., 238(33), 307
 Bertini, I., 323(244), 352
 Bertoluzza, A., 335(30), 347
 Bertsch, C. R., 142(30b), 178
 Berzelius, J. J., 324(31), 347

- Best, G. F., 26(22), 27(2), 72
 Bever, M. B., 87(132), 95(132), 100(132), 130
 Beyer, G. H., 31(49), 73
 Biedermann, G., 303(34), 307
 Biesenberger, K., 2(85), 74
 Bijkerk, I., 189(55), 214
 Bijvoet, J. M., 186(11), 213, 221(35), 307
 Bille, H., 142(210), 144(210), 150(210), 183
 Biltz, W., 332(32), 347
 Bilz, H., 110, 111(10), 112(10), 127
 Bingle, J., 272(102), 309
 Birch, S. F., 143(31), 144(31), 178
 Birchall, T., 287(36, 114), 307, 309
 Birkenbach, L., 133(31a), 178
 Birkofer, L., 135(32, 33, 35, 36), 138(32), 141(35), 142(33, 36), 155(34), 158(34), 163(34), 178
 Bisnette, M. B., 342(164), 343(164), 351
 Bither, T. A., 143(37), 145(37), 146(37), 147(37), 148(37), 149(37), 178
 Bjerrum, J., 298(37), 307
 Blake, C. A., Jr., 41, 42, 44, 65, 66, 71(44), 72, 73
 Blix, R., 86(11), 88(11), 95(11), 127
 Block, F. E., 317(287), 322(287), 323(287), 354
 Bluestein, B. A., 158(38), 178
 Blum, A., 97(12), 127
 Blumendal, H. B., 189, 197, 198, 200(56), 202(56), 214
 Blyholder, G. D., 267(163), 310
 Boatman, J. C., 291(202), 311
 Bochinski, J., 31(25), 72
 Bockris, J. O. M., 279(38), 307
 Boden, R., 63, 76
 Bodensieck, A., 332(32), 347
 Böhland, H., 336(33, 102, 103), 337(33, 102), 347, 349
 Böhme, H., 276(39), 307
 Boerboom, A. J. H., 294(81), 308
 Böttcher, R., 289(99), 309
 Bogucki, R. F., 70, 72
 Bolander, B., 51(115), 75
 Boll, E., 276(39), 307
 Bolliger, A., 64, 72
 Bolliger, J. E., 64, 72
 Bonati, F., 342(34), 347
 Bonino, G. B., 332(35), 347
 Booman, G. L., 55(163), 76
 Boorman, P. M., 257(1), 306, 320(127), 324(36, 127), 329(127), 331(36), 348, 350
 Bouchaud, J. P., 118(13), 120(144), 121(144), 123(13), 127, 130
 Bourne-Maladière, P., 283(40), 307
 Bouy, P., 258(41), 307
 Boyd, G. E., 48, 72
 Boyer, J. H., 134(39), 178
 Bracken, N. C., 145(137), 149(137), 181
 Brady, A. P., 317(205), 319(205), 352
 Brady, G. W., 221(42), 298(42), 300(42, 43), 307
 Brager, A., 86(14), 88(14, 32), 96(14), 100(14), 103(14), 127, 128
 Braid, M., 274(145), 310
 Brandao, F. A. J. A., 27(212), 29(212), 37(212), 41(212), 77
 Brauer, G., 86(15), 88(15), 123(16), 127
 Braun, G., 339(140), 350
 Braun, P. B., 317(160), 350
 Braune, H., 317(37), 348
 Brennan, G. L., 142(40), 144(40), 167(40), 174(40), 179
 Brezhneva, N. E., 70, 78
 Bridelle, R., 87(17), 104(17), 106(17), 124(17), 127
 Brinkman, U. A. T., 64, 72
 Brisdon, B. J., 317(38), 324(10, 38), 325(39, 40), 326(40), 327(9), 328(9), 329(9, 38), 330(9), 347, 348
 Brisi, C., 86(18, 19), 89(19), 104(18), 127
 Britton, D., 136(157a), 146(157a), 151(157a), 182
 Brossett, C., 290(44), 321(42), 331(41), 346(41), 307, 348
 Brothers, J. A., 70, 72
 Brown, D., 323(18), 324(18), 325(18), 326(18), 347
 Brown, H. C., 286(45), 307
 Brown, K. B., 41(24), 42(24), 44(24), 51(45), 65(24), 66(23), 71(44, 116), 72, 73
 Brown, P. G. M., 299(46), 307
 Brown, T. M., 320(43), 321(43), 182), 322(43), 324(43), 329(43), 330(43), 348, 351
 Browne, A. W., 133(40a), 179

Brukl, C., 86(127), 130
 Brunauer, S., 100(31), 128
 Brunner, H., 344(263), 353
 Bruns, I., 324(251), 325(251), 353
 Bryan, S. E., 54, 73
 Bubnov, Y. N., 143(135), 144(135), 151(135), 181
 Bucknall, W. R., 332(44), 348
 Bürger, H., 153(192), 156(192), 160(192), 164(193), 173(193), 183
 Burdese, A., 87(20, 21), 96(21), 98(22, 23), 99(23), 127
 Burg, A. B., 255(47), 258(47), 259(47), 307
 Burger, L. L., 26(32), 28, 29, 73
 Burke, T. G., 317(45), 348
 Busch, D. H., 203(12), 204(12), 213
 Bush, M. T., 6(33), 19, 73
 Butler, I. S., 325(2), 343(2), 347

C

Cady, G. H., 229(200, 279), 265(279), 267(255), 279(9), 307, 311, 312, 313, 317(46), 319(47), 322(19, 46), 347, 348
 Cahours, A., 146(41, 42), 157(41), 177(41), 179
 Caillet, P., 324(235), 352
 Calderazzo, F., 289(48), 307
 Calvert, L. D., 264(49), 308
 Campbell, I. E., 96(24), 97(24), 127
 Canter, F. C., 134(39), 178
 Cantor, S., 324(152), 331(152), 350
 Capellina, F., 332(82), 349
 Carassiti, V., 334(48, 49), 335(30, 48), 347, 348
 Carlson, G. L., 153(136), 156(136), 157(136), 160(136), 171(40b), 176(40b), 179, 181
 Carpenter, G. B., 280(189, 341), 282(17), 307, 311, 314
 Cassol, A., 172(41a), 179
 Cerrai, E., 59, 60(40), 61, 63, 64(38), 73
 Chaigneau, M., 142(43), 144(43), 149(43, 94a), 179, 180
 Chakravorty, A., 206(46, 47), 208(47), 209(47), 214
 Chalandon, P., 241(50), 308
 Challenger, E., 143(44), 144(44), 167(44), 173(44), 175(44), 179
 Chang, C., 71(131), 75
 Charonnat, R., 194(16a), 213
 Chatt, J., 323(4), 324(4), 325(4), 326(4), 339(53), 340(52), 341(50, 51), 347, 348
 Chen, Y., 71(131), 75
 Cheng, W., 55(130), 71(130, 131), 75
 Chiu Fan Liu, 203(14), 213
 Chong Tan Liu, 207(13), 213
 Choppin, G. R., 70, 73
 Christeleit, W., 212(80), 215
 Christie, K. O., 259(51), 274(52), 308
 Chupka, W. A., 219(56), 293(55, 56), 294(55), 295(28, 32, 54), 296(29, 31, 157, 246), 297(30, 31), 298(53), 307, 308, 310, 312
 Churchill, L., 55(295), 80
 Clark, H. C., 240(57), 308, 318(54), 324(54), 348
 Clark, R. J. H., 324(55), 348
 Clarke, J., 87(25), 94(25), 125(25), 127
 Claudi, M., 334(48), 335(48), 348
 Clearfield, A., 304(58), 308
 Clifford, A. F., 279(62), 284(59, 61), 285(60), 308
 Coates, G. E., 143(45), 144(45), 149(45), 150(45), 151(45), 179
 Cocksedge, H. E., 166(46), 172(46), 174(46), 179
 Coffey, C. E., 336(56), 342(57), 345(57), 348
 Cohen, B., 317(58), 348
 Cohen, M., 87(132), 95(132), 100(132), 130, 333(284), 354
 Cohen, S. R., 299(63), 308
 Coleman, C. F., 36(13), 41(24), 42(24), 44(24), 51, 55, 65(24), 71, 72, 73
 Collenberg, O. O., 324(59, 62, 63), 327(59, 63), 330(62), 331(62), 332(59, 61), 334(60), 335(60), 345(59), 348
 Collier, E. N., 325(76), 326(76), 327(76), 329(76), 348
 Collinge, R. N., 240(64), 308
 Colton, R., 290(65), 308, 319(64, 65), 323(65), 348
 Compere, E. L., 19, 73
 Connick, R. E., 68, 69, 73, 300(66), 308
 Connolly, J. W., 135(47), 138(47), 141(47), 179
 Conway, B. E., 279(38), 307
 Cook, C. D., 343(66), 348
 Cook, D., 242(67), 306(67), 308

- Cooke, D. W., 203(12), 204(12), 213
 Cooley, W. E., 203(14), 213
 Cooper, R. L., 344(67), 348
 Cordes, A. W., 261(68), 267(68, 163), 308, 310
 Corey, E. J., 189(15), 190(15), 196, 197, 198, 199, 212, 213
 Corliss, L. M., 86(26), 88(26), 104(26), 105(26), 127
 Cotton, A., 209, 213
 Cotton, F. A., 291(203), 308, 311, 316 (289), 321(70, 183), 339(69, 289), 341 (68), 344(71), 348, 351, 354
 Covington, A. K., 223(70), 280(70), 308
 Cox, B., 324(72), 325(72), 348
 Cox, R. P., 31(49), 73
 Cragg, R. H., 154(47a), 165(47a), 179
 Craig, A. D., 143(48), 145(48), 147(48), 179
 Craig, L. C., 3, 8, 73
 Crandall, H. W., 35, 79
 Creveaux, H., 106(46), 128
 Crouse, D. J., 51(45), 71(116), 73, 75
 Cruickshank, D. J., 261(319), 314
 Cummings, F. E., 238(138), 310
 Cummins, R. A., 146(49), 150(49), 168 (49), 169(49), 170(49), 171(49), 172 (49), 177(49), 179
 Cuninghame, J. G., 64, 73
 Curtius, T., 134(50), 136(51), 175(51), 179
 Czaloun, A., 254(146), 310
- D**
- Daasch, L. W., 30(53), 73
 Dahl, G. H., 142(40, 52), 144(40, 52), 167 (40), 174(40), 179
 Dahl, L. F., 339(73), 348
 Dailey, B. P., 171(30), 178
 Dallinger, G., 285(71), 308
 Daneels, A., 63, 73
 Danford, M. D., 304(192), 311
 Dasent, W. E., 278(72), 308
 Dauben, H. J., 238(73), 308
 Davidson, A., 344(74), 348
 Davidson, J. M., 236, 308, 323(4), 324(4), 325(4), 326(4), 347
 Davies, A., 273(15), 307
 Davies, A. G., 172(2), 177(2), 178
 Davies, D. D., 94(173), 97(173), 131
 Davis, O. C. M., 324(75), 348
 Day, R. A., Jr., 27(55, 56), 69, 70, 73
 De, A. K., 31, 76
 Dean, J. A., 29, 30, 43, 74
 Deane, A. M., 66, 73, 76
 de Boer, J. H., 96(171a), 131
 Dehl, R., 238(33), 307
 Dehn, E., 332(239, 240), 337(240), 352
 Dehnicke, K., 135(140b), 136(53), 137 (140b), 138(53), 139(140b), 141(53), 179, 181, 253(75), 308
 Delepine, M., 194(16a), 213
 Delorme, P., 332(181), 351
 de Maeyer, L., 281(88), 308
 de Maria, G., 294(80, 81, 82, 83), 296(83), 308
 Deneke, K., 118(80), 119(80, 86), 129
 Deno, N. C., 237(76), 308
 Densen, P. M., 6(33), 19, 73
 Dess, H. M., 250(78), 251(77), 308
 Detmer, O., 229(286), 243(286), 264(286), 274(286), 275(286), 313
 Dettke, M., 345(246, 247), 352, 353
 de Vries, G., 64, 72
 Diamond, R. M., 2, 3, 25, 71, 73
 Dickinson, R. N., 325(76), 326(76), 327 (76), 329(76), 348
 Dijkgraaf, C., 196(17), 207, 213
 Dingley, D. P., 94(59), 98(59), 99(59), 128
 Di Pietro, H. R., 145(103), 147(103), 180
 Djordjevic, C., 322(77), 331(77), 349
 Doak, G. O., 30, 73
 Dobson, G. R., 340(273, 274), 341(78), 349, 353
 Dolgov, B. N., 172(190), 175(190), 176 (190), 183
 Douglas, B. E., 203(18), 207(13), 213
 Dousmanis, G. C., 171(54), 179
 Drago, R. S., 226(79), 308
 Dreze, P., 36(62, 63), 38, 73
 Driscoll, W. J., 16(199), 21(199), 22(217), 36(206, 217), 39(206), 40(205), 44 (206), 45(206), 46(205), 59(217), 60 (217), 77, 78
 Drowart, J., 294(80, 81, 82, 83), 296(83), 308
 Druce, J. G. F., 146(55), 148(55), 151(55), 179

Dudek, G. D., 206(46, 47), 208(47), 209(47), 214
 Dürr, F., 126(38), 128
 Duncan, A. B. F., 317(278), 353
 Dunlop, J. H., 186(19, 21), 194(19, 20, 21), 195(19, 21), 206(20), 207(20), 209(20), 210(20), 211(20), 212(1, 20), 213, 214
 Dunn, D., 146(49), 150(49), 168(49), 169(49), 170(49), 171(49), 172(49), 177(49), 179
 Dunsmore, H. S., 301(84), 303(84), 308
 du Preez, J. G. H., 323(18), 324(18), 325(18), 326(18), 347
 Duwez, P., 117(27), 123(27), 127
 Duyckaerts, G., 36(62), 38, 52(191), 73, 77
 Dwyer, F. P., 192(23, 25, 28), 193(22), 198(27), 199, 202(27), 203(29, 30), 204(24, 25a), 214
 Dyrssen, D., 3, 35(77), 36, 37, 38, 66, 68, 70, 71(66, 69, 70, 71, 246, 247), 72, 73, 74, 78

E

Eaborn, C., 143(56, 57), 145(56, 57), 148(57), 149(57), 153(57), 162(57), 164(57), 169(57), 172(57), 176(57), 179
 Ebenhöch, F. L., 277(270), 313
 Ebert, F., 85(8), 86(8), 127
 Ebsworth, E. A. V., 135(61), 138(61), 141(61), 145(58), 149(58), 153(60), 155(58, 60), 160(58), 164(60), 170(59), 171(58, 62), 175(58, 59, 62), 179
 Edelstein, N., 344(74), 348
 Edgington, D. N., 66(122), 67(123, 124, 125, 126), 75
 Edstrand, M., 254(85, 86), 308
 Edwards, A. J., 317(58), 348
 Edwards, D. A., 318(79), 323(79), 327(9), 328(9), 329(9), 347, 349
 Efraty, A., 342(187), 351
 Ehrlich, P., 86(28), 88(28), 95(28), 128
 Eigen, M., 218(87), 281(87, 88), 308
 Eisenberg, R., 344(80), 349
 Eisenhut, O., 91, 128
 Ekberg, S., 35(74), 68(73), 73
 Eley, D. D., 286(89), 308
 Elischer, S., 260(271), 313
 Ellenburg, J. Y., 50, 74
 Elliott, N., 86(26), 88(26), 103(103), 104(26), 105(26), 127, 128
 Elmore, D. T., 162(62a), 179
 Emeléus, H. J., 143(64), 145(64), 146(63), 148(63), 168(63), 177(63), 179, 248(90), 249(91), 259(337), 268(16), 269(336), 281(91), 307, 308, 314, 318(54), 324(54), 348
 Emmett, P. H., 100(31), 128
 Epelbaum, V., 86(33), 88(32, 33), 128
 Eremin, G. K., 58(175), 76
 Eriks, H., 277(92), 308
 Eriksson, S., 86(34), 88(34), 128
 Eschweiler, W., 332(32), 347
 Essler, H., 340(96), 349
 Ettmayer, P., 86(107), 89(107), 96(107), 129
 Evans, A. G., 239(22), 307
 Evans, D. A., 122(35), 128
 Evans, J. C., 240(231), 262(93), 308, 312
 Evans, P. R., 146(63), 148(63), 168(63), 177(63), 179
 Evers, E. C., 143(65a), 144(65, 65a), 145(65), 149(65a), 151(65a), 152(65, 65b), 179
 Ewens, R. V. G., 317(81), 319(81), 349

F

Fabbri, G., 332(35, 82), 347, 349
 Fairbrother, F., 239(95), 241(94), 309
 Falk, M., 280(96), 309
 Farber, M., 225(305), 313
 Faron, M. F., 337(291), 354
 Fast, J. D., 95(36), 128
 Fedotov, V. P., 101(6), 127
 Feigl, F., 336(83), 349
 Feil, S. E., 319(84), 324(84), 325(76), 326(76), 327(76), 329(76), 348, 349
 Feldl, K., 178
 Feltz, A., 245(178), 310
 Fernelius, W. C., 203(88), 215
 Ferraro, J. R., 35(82, 200), 38(83), 41(83), 44(82), 67, 68, 74, 77
 Ferriso, C. C., 280(97), 309
 Fiano, E., 332(20), 345(20), 347
 Fiat, D. N., 300(66), 308
 Fichtel, K., 289(100), 309, 342(87, 88), 349
 Fidelis, I., 58, 74, 79
 Field, F. H., 286(98), 309

- Fielding, H. C., 155(66), 164(66), 173(67), 179
 Fields, P. R., 31(129), 56(128), 75
 Finch, A., 167(68, 69), 171(69), 174(68, 69), 179
 Finck, H. W., 344(282), 354
 Fink, W., 277(272), 313
 Fischer, A., 317, 349
 Fischer, A. K., 339(69), 348
 Fischer, E. O., 289(99, 101), 289(100), 309, 316(89, 98), 339(89, 97), 340(96), 341(93, 97), 342(86, 87, 88, 90, 91, 94), 343(95, 98), 344(92), 349
 Fischer, J., 269(310), 272(102), 309, 313
 Fischer, W., 2, 74
 Fisher, B. E., 140(99), 180
 Flanary, J. R., 31(86), 74
 Flesch, C. D., 296(103), 309
 Fletcher, J. M., 3, 27(106, 239), 74, 78
 Flindt, E. P., 319(148), 350
 Flint, R. F., 63, 78
 Floe, C. F., 87(132), 95(132), 100(132), 180
 Flood, H., 266(104), 309
 Flowers, R. H., 266(105), 309
 Fluck, E., 248(25, 26), 307
 Flynn, K. F., 14(93), 74
 Foerster, W., 145(70), 149(70), 171(70), 175(70), 179
 Foldi, A., 196(31), 214
 Foldi, T., 196(31), 214
 Foldi, Z., 196(31), 214
 Fomin, V. V., 2, 27(90, 91), 70, 74
 Forbes, G. S., 153(71, 72, 77, 78), 154(71), 155(72, 73, 75, 78, 79), 156(71, 72, 73, 75, 76, 78, 79), 157(72, 74), 162(71, 77, 79), 164(79), 165(76), 171(76), 175(76), 176(76), 179, 180
 Ford, P. F., 281(106), 309
 Foreman, B. M., Jr., 71, 78
 Foreman, J. K., 28(173), 76
 Forland, T., 266(104), 309
 Foster, L. S., 96(37), 100(37), 128
 Fowles, G. W. A., 317(38, 99), 320(98a), 324(10, 38, 99), 327(9), 328(9), 329(9, 38), 330(9), 347, 348, 349
 Fraker, A. C., 120(162), 131
 Frankenburger, W., 126(38), 128
 Frankiss, S. G., 145(58), 149(58), 155(58), 160(58), 171(58), 175(58), 179
 Franks, A. W., 173(80), 180
 Frazer, B. C., 106, 107(167), 114(167), 118(167), 128, 131
 Fredlund, F., 51(115), 75
 Freedman, L. D., 30, 73
 Freeman, H. C., 207(32), 214
 Freiser, H., 2, 3, 74, 77
 Freitag, W. O., 143(65a), 144(65, 65a), 145(65), 149(65a), 151(65a), 152(65, 65b), 179
 French, C. M., 236, 308
 Fried, S., 56(102), 74
 Friederich, E., 95, 98(40), 99(40), 100(40), 102(40), 103(40), 128
 Friend, J. A., 200(33), 203(33), 214
 Fritz, H. P., 316(89), 339(89), 344(100), 349
 Fröhlich, W., 340(96), 349
 Froentjes, W., 210(66), 211(66), 215
 Fronzaglia, A., 340(165), 351
 Frost, J. L., 320(98a), 349
 Fruchart, R., 118(13), 120(144), 121(144), 123(13), 127, 130
 Fry, A., 101(41), 128
 Fuchs, J., 319(148), 350
 Fuger, J., 52(64, 191), 73, 77
 Fujino, T., 28(134), 31(139), 71(131), 75
 Fujita, Y., 208(89), 215
 Funk, H., 318(101), 319(105, 106, 107, 108), 324(106), 336(102, 103), 337(101, 102), 345(104), 349
- G**
- Gado, P., 338(109, 110), 349
 Gagos, K., 242(111), 309
 Gaidis, J. M., 135(80a), 141(80a), 180
 Ganorkar, M. C., 343(111, 163), 349, 351
 Garbett, K., 200(34), 214
 Gardner, C. S., 19, 72
 Gardner, P. J., 167(68), 174(68), 179
 Garner, C. S., 331(134), 332(117), 333(117), 334(117, 118), 349, 350
 Garvan, F. L., 192(23, 25), 204(24), 214
 Garver, E. E., 268(257), 312
 Gaunt, J., 317(112), 349
 Gayoso, M., 135(140b), 137(140b), 139(140b), 181

- Gebbie, H. A., 323(5), 324(5), 329(5), 330(5), 347
- Gebert, E., 338(113), 349
- Geichmann, J. R., 324(114), 349
- Gerber, H., 162(28b), 178
- Gerding, H., 241(108), 258(107, 108), 261(107, 110), 265(109), 306(108), 309
- Gergel, M. V., 11(207), 12(207), 30(207), 77
- Gerloch, M., 344(29), 347
- Germann, A. F. O., 242(111), 309
- Gerrard, W., 222(112), 309
- Gerratt, J., 323(4), 324(4), 325(4), 326(4), 347
- Geske, D. H., 245(244), 312
- Ghersini, G., 63, 73
- Gibson, T., 240(23), 307
- Giegling, D., 321(249), 353
- Gieren, W., 126(81), 129
- Giese, C. F., 295(54), 308
- Giffin, G., 16(208), 22(208), 41(208), 77
- Giguère, P. A., 280(96, 267), 309, 313
- Gillard, R. D., 186(19, 21, 43), 187(37), 189(38), 193(37), 194(19, 20, 21, 43), 195(19, 21), 196(38, 39), 199(43), 200(34, 43), 201(40), 202(38), 203(51), 204(35, 36, 49, 50), 205(35), 206(20, 39), 207(20, 42), 208(39), 209(20, 39), 210(20), 211(20, 42), 212(1, 20, 42a), 213(41), 213, 214
- Gillespie, R. J., 223(116, 119), 241(119), 252(118), 254(120), 261(113, 115), 266(105), 278(121), 282(117), 287(18, 36, 114, 317), 307, 309, 314
- Gillis, B. T., 213(61), 215
- Gilman, H., 146(116a), 153(81), 155(81), 158(81), 162(81), 163(81), 164(81), 170(81), 173(81), 175(81), 177(116a), 180, 181
- Gindler, J. E., 14, 74
- Gingold, K., 157(82), 180
- Girgis, R. K., 104(179), 131
- Glatte, J., 101(175), 131
- Glemser, O., 338(115, 116, 255), 349, 353
- Glick, R. E., 237, 309
- Gloaki, G. R., 176(83), 180
- Glunz, L. J., 249(150), 310
- Goble, A. G., 68, 74
- Goddard, A. E., 167(84), 175(84), 180
- Goddard, D. R., 245(123), 260(123), 309
- Gössl, T., 256(287), 313
- Goldfarb, T. D., 145(85, 175, 177), 147(175), 150(85, 175), 152(177), 180, 182
- Goldstein, G., 70, 74
- Golumbic, C., 19, 74
- Gonser, B. W., 96(24), 97(24), 127
- Good, M. L., 54, 55, 73, 74
- Goode, J. H., 31(86), 74
- Goodenough, J. B., 112, 113(43, 44), 114(42, 43, 44), 115(44), 119(45), 120(44, 45), 128
- Goodenow, E. L., 332(117), 333(117), 334(117, 118), 349, 350
- Gordon, E. K., 261(68), 267(68), 308
- Gordon, W. E., 229(124), 309
- Gorican, H., 48, 74
- Goryunova, N. A., 306(125), 309
- Gott, A. D., 201(44), 213, 214
- Gottschalk, G., 337(119), 350
- Goubeau, J., 149(91), 153(87), 154(87), 155(89, 90), 156(89), 158(90), 159(87), 160(86, 87, 89), 162(87, 88, 90), 163(87, 90), 164(87, 88), 171(92), 175(89, 92), 176(92), 180, 250(126), 309
- Goulden, J. D. S., 258(127), 309
- Gräbner, H., 153(87), 154(87), 159(87), 160(87), 162(87), 163(87), 164(87), 180
- Graf, P., 56(102), 74
- Graham, J., 261(115), 309
- Graham, W. A. G., 339(12), 342(221), 347, 352
- Grant, A., 324(36), 331(36, 120), 348, 350
- Grasselli, J. G., 340(242), 352
- Gray, H. B., 327(122), 328, 341(121), 344(269, 282), 350, 353, 354
- Gray, J., Jr., 14(93), 74
- Grdenic, D., 48, 74
- Green, B. S., 167(93), 168(93), 171(93), 174(93), 175(93), 176(93), 177(93), 180
- Green, H., 55, 71, 74
- Green, M. L. H., 316(124), 339(124), 342(125, 184), 344(67, 123, 126), 348, 350
- Greenwood, N. N., 237(130), 252(338), 281(128, 129), 309, 314, 320(127), 324(36, 127), 329(127), 331(36, 120), 348, 350

Griffiths, J. E., 145(171, 172), 147(171),
148(171), 153(171), 156(171, 172),
168(171), 169(171), 171(172), 172
(171), 176(171, 172), 182
Griswold, E., 335(166), 351
Groenveld, W. L., 226(131, 133), 248(132),
309, 324(128), 329(128), 350
Grossmann, H., 345(247), 353
Gruen, D. M., 56(128), 74, 75
Guertin, J. P., 259(51), 308
Guggenheim, E. A., 299(134), 309
Guillaud, C., 95(47), 106(46), 107(47), 128
Gunther, K., 252(159), 310
Guthe, A., 324(63), 327(63), 348
Gutmann, V., 143(94), 144(94), 180, 252
(135), 309, 325(16), 347
Gutsche, E., 339(138), 340(138), 350
Guy, R., 149(94a), 180
Guy, R. G., 316(129), 339(129), 350
Gyarfas, E. C., 204(25a), 214

H

Haag, G., 316(130), 337(130), 338(130),
346(130), 350
Haag, W., 339(23), 347
Haas, T. E., 291, 308, 321(70), 348
Haebler, H., 98(124), 130
Hägg, G., 82, 85(50, 51), 86(49, 50), 87
(48, 52), 89(49), 90(49), 128
Haffon, J. V., 144(94b), 175(94b), 180
Hafner, W., 342(86, 91), 349
Hahn, H., 86(53), 87(82), 88(53), 94(54,
82), 95(53), 98(54, 83), 99(53), 100
(53, 83), 128, 129
Hall, N. F., 334(185), 351
Halpern, M., 30, 76
Hamilton, F. D., 70(57), 73
Hamilton, N. H., 201(45), 214
Hamlen, R. P., 317(131), 350
Handley, T. H., 29, 30, 43, 74
Hanke, W., 345(104), 349
Hansen, K. W., 249(19), 307
Hansen, M., 85(55), 89(55), 90(55), 128
Hantzsch, A., 257(136), 310
Hara, R., 31(197), 77
Harder, N., 336(24), 340(24), 347
Hardy, C. J., 27, 74
Hardy, G. F., 102(56), 128
Hardwick, W. H., 27(1), 72
Hare, C. R., 327(122), 328, 350
Harfenist, E. J., 3(51), 73
Hargreaves, G. B., 274(137), 310, 317(46),
319(47), 322(46), 324(132, 133), 325
(132), 326(133), 348, 350
Harman, A. B., 238(139), 310
Harmon, K. M., 238(73, 138, 139), 308,
310
Harris, D. R., 240(142), 310
Harris, G. S., 245(140, 141), 248(90), 308,
310
Hart, R. G., 70(30), 72
Hass, D., 245(179), 310
Hass, D. J., 240(142), 310
Hasselbarth, H., 277(191), 311
Hastings, J. M., 86(26), 88(26), 104(26),
105(26), 127
Haszeldine, R., 281(143), 310
Hathaway, B. J., 240(144), 310
Haug, J., 126(81, 84), 129
Hauptschein, M., 274(145), 310
Hausmann, W., 3(51), 73
Hawkins, G. L., 331(134), 350
Hayek, E., 254(146), 310
Hayter, R. G., 341(136), 342(135, 136),
350
Healy, T. V., 26(110, 111), 67(108), 68,
74, 75
Heap, R., 146(95), 148(95), 157(95), 158
(95), 168(95), 177(95), 180
Heckmann, I., 324(251), 325(251), 353
Heertjes, P. M., 258(107), 261(107), 309
Heikes, R. R., 107(168), 114(168), 118
(168), 119(168), 131
Heinmann, A., 251(147), 310
Heintz, E. A., 332(137), 350
Henderson, F., 101(172), 131
Hendifar, A., 145(26), 147(26), 153(26),
156(26), 167(26), 168(26), 175(26),
176(26), 178
Hendra, P. J., 167(69), 171(69), 174(69),
179
Hendricks, S. B., 92, 100(31), 128
Heners, J., 127(85), 129
Heppner, J., 2(85), 74
Hepworth, M. A., 318(277), 353
Herber, R., 136(96a), 139(96a), 180
Herber, R. H., 136(96), 180
Herzog, S., 339(138), 340(138), 139), 350
Hesford, E., 16(113), 21(113), 27(2, 113,
239), 31, 72, 75, 78

- Hesse, T., 212(80), *215*
 Hetherington, G., 229(11), 259(11), *307*
 Heubach, E., 155(89), 156(89), 160(89),
 162(88), 164(88), 175(89), *180*
 Heumann, F. K., 27(304), 70(304), *80*
 Heying, T. L., 154(97), 165(97), 170(97),
 174(97), *180*
 Hicks, T. E., 34, 35, 36, *79*
 Hieber, W., 151(98), *180*, 289(148), *310*,
 339(140), *350*
 Hietanen, S., 301(84), 303(84), *308*
 Hildago, A., 332(141), *350*
 Hildon, M. A., 320(127), 324(127), 329
 (127), *350*
 Hill, J. B., 324(142), 331(142), *350*
 Hill, L., 135(138), 137(138), *181*
 Hilpert, R. S., 96(58), *128*
 Hirai, A., 106(4), *127*
 Hirata, T., 263(342), 267(342), *314*
 Hladký, E., 71, *79*
 Hoard, J. L., 325(143), 332(144), 333(145),
350
 Hobbs, R. S., 60(227), 62(227), *78*
 Hoch, M., 94(59), 98(59), 99(59), *128*
 Hodgman, C. D., 144(98a), *180*
 Högfelddt, E., 51, *75*
 Hoel, A. B., 133(40a), *179*
 Hölzl, F., 335(146), *350*
 Hofferth, B., 153(81), 155(81), 158(81),
 162(81), 163(81), 164(81), 170(81),
 173(81), 175(81), *180*
 Hoffman, C. J., 271(149), *310*
 Hoffman, F. W., 249(150), *310*
 Hoffmann, A., 96(58), *128*
 Holder, B. E., 271(149), *310*
 Holland, F. F., Jr., 55(97), *74*
 Holm, R. H., 206(46, 47), 208, 209, (47),
214, 344(74), *348*
 Holmberg, B., 86(60), 88(60), *128*
 Holmberg, R. W., 304(151), *310*
 Holmes, R. R., 305(152), *310*
 Holt, R. J. W., 2, *76*
 Holtje, W., 338(116), *349*
 Holznagel, W., 338(116), *349*
 Honig, R. E., 294(153), *310*
 Honnen, L. R., 238(73), *308*
 Horder, J. R., 165(98b), *180*
 Hori, K., 208(89), *215*
 Horner, D. E., 71, *75*
 Horner, S. M., 325(76), 326(76), 327(76),
 147), 329(76), *350*
 Horner, W. W., 325(76), 326(76), 327(76),
 329(76), *348*
 Hornig, D. F., 280(97), *309*
 Horowitz, J. P., 140(99), *180*
 Horwitz, E. P., 14(201), 38(201), 62(201),
77
 Hosoya, S., 103(103), 114(103), *129*
 Hoste, J., 63(54), *73*
 Houtgraaf, H., 241(108), 258(108), 265
 (109), 306(108), *309*
 Hovsepian, P., 55(295), *80*
 Hristidu, Y., 344(92, 100), *349*
 Huch, F. H., 96(58), *128*
 Hucher, I., 15(209), 16(209), 22(209), 27
 (212), 29(212), 37(212), 40(209, 210),
 41(211, 212), 53(209), 70(211), *77*
 Hüttig, G. F., 97, 120(64), *128*
 Huffman, E. H., 188(8, 57), 200(8), 201
 (8, 57), 207(57), *213*, *214*
 Hughes, B. G., 291(203), *311*, 321(183),
351
 Hughes, E. D., 223(116), 224(155), 239
 (154), 245(123), 260(123), 261(115),
309, *310*
 Huisgen, R., 135(100), 137(100), *180*
 Hulet, E. K., 63, *75*
 Hulm, D. K., 102(56), *128*
 Hume, D. N., 70, *79*
 Hume-Rothery, W., 109, 123(62), *128*
 Hummel, H., 344(100), *349*
 Humphrey, G. L., 98(63), *128*
 Hundecck, J., 145(100a), *180*
 Hunter, T. G., 19, *75*
 Hurlimann, H., 197, 198, *214*
 Huttig, H., 266(309), *313*
 Hyde, E. K., 24(120), *75*
 Hyman, H. H., 268(249), 284(156), *310*,
312
- I
- Ibers, J. A., 344(80), *349*
 IJdo, D. J. W., 346(286), *354*
 Ikeda, R., 329(206), *352*
 Imai, Y., 101(65), *128*
 Inghram, M. G., 219(56), 293(55, 56), 294
 (55, 80, 81, 82, 83), 295(32), 296(31,
 83, 157, 246), 297(31), *307*, *308*, *310*,
312

Ingold, C. K., 223(116), 224(155), 239
(154), 245(123), 260(123), 261(115,
158), 309, 310
Interrante, L. V., 340(28), 347
Irving, H., 2, 66(122), 67(123, 124, 125,
126), 75
Irving, H. M., 189(38), 196(38, 39), 202
(38), 203(51), 204(49, 50), 206(39),
208(39), 209(39), 214
Isaac, N. M., 31(129), 56, 75
Ishimori, T., 28, 31, 49, 55(130, 137), 71,
75
Ishishi, E., 339(73), 348
Ishizaki, T., 101(65), 128
Isumi, T., 71(131), 75
Ito, F., 117(66), 123(66), 128
Iwanaga, R., 86(126), 89(126), 130
Iwasaki, H., 189(86), 190(52, 86), 194 (86),
199(52a), 214, 215
Izumi, T., 55(137), 75

J

Jack, K. H., 87(25, 67, 69, 71, 72), 91(67,
70, 71, 72), 92(71), 93(67, 72), 94(25,
69), 98(70), 122(35), 123(68), 124(68),
125(25, 69), 127, 128, 129
Jack, W. M., 284(59), 308
Jacke, A. W., 279(242), 312
Jackson, E. E., 16(113), 21(113), 27(113),
31(113), 75
Jaeger, F. M., 189(55), 193, 197, 198, 200
(56), 202, 214
Jagodic, V., 48, 74
Jahr, K. E., 319(148), 350
Jakob, W., 334(150, 151), 335(151), 350
Jakob, W. F., 334(149), 350
Jakob, Z. L., 334(149), 350
Jander, G., 252(159), 254(160), 310
Janeff, W., 102(77), 129
Janssen, M. J., 136(123), 138(123), 139
(123), 141(123), 145(189), 181, 183
Jefferson, R., 173(100b), 175(100b), 180
Jeffrey, G. A., 261(319), 314
Jeitschko, W., 121(73, 74, 75, 76), 122(73,
129), 129, 130
Jenkins, D. R., 171(101, 102), 175(101,
102), 180
Jerschewitz, H. G., 266(161), 310

Jezowska-Trzebiatowska, B., 318(277),
353
Jha, N. K., 324(21), 347
Johansson, G., 303(162), 310
Johns, I. B., 145(103), 147(103), 180
Johnson, D. A., 267(163), 310
Johnson, F. D., 38(215), 78
Johnson, J. S., 303(264, 265), 304(151,
164), 310, 312
Johnson, O. H., 157(104), 180
Johnson, M. P., 344(263), 353
Johnston, L., 94(59), 98(59), 99(59), 128
Johnstone, S. T. M., 101(172), 131
Jolly, W. L., 271(149), 310
Jonassen, H. B., 188(57), 201(57), 207
(57), 213, 214, 324(152), 331(152),
350
Jonelis, F. G., 213
Jones, L. H., 341(153), 350
Jorgensen, C. K., 331(154), 350
Jortner, J., 285(208), 311
Joyner, T. B., 87(78), 94(78), 129
Juza, R., 86(87), 87(82, 89, 90), 89(87),
90(87), 94(82, 89, 90), 95(89, 90), 96
(89, 90), 97(89), 98(83), 100(83), 101
(87), 102(88), 107(86), 118 (80, 86),
119(80, 86), 123(86), 125(89), 126(79,
81, 84, 91, 143), 127(85), 129, 130

K

Kaczmarczyk, A., 143(105), 145(105), 180
Kaes, H. D., 340(242), 344(263), 352, 353
Kahlen, N., 145(162), 146(162), 147(161,
162), 148(161, 162), 149(162), 151
(161, 162), 152(162), 169(162), 176
(162), 177(162), 182
Kakihana, H., 305(165), 310
Kamenev, A. I., 58(175), 76
Kanaga, M., 210(74), 215
Kapustinskii, A. F., 263(166), 310
Karipides, A. G., 195(83), 215
Kartushova, R. E., 70(89), 74
Katada, K., 155(106b), 160(106b), 171
(106b), 175(106b), 180
Katz, I., 155(209), 163(209), 183
Katz, J. J., 268(249), 284(156), 310, 312
Katzin, L. I., 2, 75
Kaufmann, H. P., 170(106), 172(106), 180
Kaupp, E., 91, 128

- Kaverin, S. V., 86(137), 87(136), 88(137), 130
- Kawakami, K., 172(190b), 183
- Keane, F. M., 136(118, 119a), 139(118, 119a), 181
- Keder, W. E., 51, 52, 75, 76, 80
- Keggin, J. F., 304(167), 310
- Keith, J. N., 143(176), 144(65), 145(65, 176), 147(176), 150(176), 152(65, 176), 155(176), 179, 182
- Kellermann, K., 133(31a), 178
- Kelley, K. K., 98(92), 129
- Kelly, P., 70(293), 80
- Kemmitt, R. D. W., 324(155), 325(155), 326(155), 350
- Kennard, C. H. L., 279(9), 307
- Kennedy, C. D., 324(156), 329(156), 330(156), 350
- Kennedy, J., 26(110), 55, 59, 66(58), 73, 74, 76
- Keper, D. L., 316(157), 324(55, 157), 333(158), 338(157), 348, 350
- Kertes, A. S., 30, 60(159), 76
- Ketelaar, J. A. A., 317(159, 160), 350
- Kettle, S. F. A., 332(161), 333(161), 351
- Kewley, R., 171(101, 102), 175(101, 102), 180
- Khaleque, M. A., 266(223), 311
- Kharasch, N., 162(106a), 180
- Khazanova, N. E., 100(100), 129
- Khorana, H. G., 29(149, 150, 151), 76
- Kidd, J. M., 281(143), 310
- Kieffer, R., 94(93), 97, 129
- Kiessling, R., 122(95), 129
- Kilpatrick, M., 284(156, 263), 285(168), 310, 312
- Kiluk, K., 55(295), 80
- Kim, N. G., 225(305), 313
- Kim, S. M., 135(35), 141(35), 178
- Kimura, K., 55(137), 71(131), 75, 76, 155(106b), 160(106b), 171(106b), 175(106b), 180
- King, P. J., 286(89), 308
- King, R. B., 340(165), 342(164), 343(163, 164), 344(162), 351
- Kinser, H. B., 52(18), 53(18), 54(18), 72
- Kirsanov, A. V., 162(106c, 165a), 180, 182
- Kirschner, S., 204(6), 213
- Kirson, B., 135(138), 137(138), 181
- Kischkin, S. T., 101(96), 129
- Klanberg, F., 166(107, 108), 171(107), 175(107, 108), 180, 245(324), 250(324), 314
- Kleinberg, J., 335(166), 351
- Klejnot, O. J., 317(167), 318(167), 351
- Klemm, W., 104(97), 129, 319(270), 330(270), 353
- Klinkenberg, L. J., 257(169), 310
- Klodeev, Y. S., 99(2, 3), 127
- Klodowski, H. F., 306(225), 311
- Klotz, P., 68, 77
- Knewstubb, P. F., 225(170), 280(170), 310
- Knipe, W. W., 96(165), 131
- Knipple, W. R., 340(280), 354
- Knoth, W. N., 143(37), 145(37), 146(37), 147(37), 148(37), 149(37), 178
- Knunyants, J. L., 255(308), 313
- Kobune, T., 71(131), 75
- Kodama, G., 234(171), 310
- Kögler, F., 170(106), 172(106), 180
- Köhler, A., 321(179), 324(179), 331(179), 351
- Koehler, W. C., 106(161), 131
- König, E., 324(170), 330(170), 331(170), 333(169), 351
- Kohl, F. J., 342(90), 349
- Kohl, H., 341(207), 352
- Kokovin, G. A., 318(168), 322(256), 351, 353
- Kolditz, L., 228(181), 245(178, 179), 246(173, 174, 176), 247(176, 177), 250, 251(182, 184), 253(175, 180, 181), 264(183), 310, 311
- Kolobova, N. E., 342(208), 352
- Konarev, M. I., 29(264), 79
- Kongpricha, S., 279(242), 312
- Konrad, A., 94(54), 98(54), 100(54), 128
- Kontorowitsch, J. E., 101(98), 129
- Kooi, J., 63, 76
- Korovin, S. S., 30(231), 78
- Korpar, B., 48, 74
- Kortengraber, A., 95(153), 99(153), 131
- Koski, W. S., 317(131), 350
- Kosolapoff, G. M., 35, 76
- Kosolapova, T. Y., 85(147), 86(147), 130
- Kosting, P. K., 92, 128
- Kotlinska, B., 57, 79
- Kovaleva, T. V., 54(280), 79
- Kozmin, P. A., 325(27), 347
- Krasovec, F., 36, 74

- Kratzer, R. H., 141(109, 109a), 181
 Kraus, K. A., 55, 63(156), 76, 303(264),
 304(151, 164), 310, 312
 Krause, E., 135(109b), 181
 Krause, R. A., 276(185), 311
 Krebs, H., 110, 129
 Krichevskii, I. R., 160(100), 129
 Kriegsmann, H., 145(70), 149(70), 171
 (70), 175(70), 179, 240(186), 311
 Kriner, W. A., 143(65a), 144(65, 65a), 145
 (65), 149(65a), 151(65a), 152(65,
 65b), 179
 Krishna Pillai, M. G., 145(110), 150(110),
 181
 Krishnaiah, K. R. S., 318(228), 319(230,
 231), 324(227, 229), 352
 Kröger, C., 98(124, 125), 130
 Kruck, T., 289(148), 310
 Krueger, G., 277(190), 311
 Kruh, R. F., 261(68), 267(68), 308
 Krumholz, P., 336(83), 349
 Kubetschek, E., 340(139), 350
 Kubo, M., 329(206), 352
 Kuca, L., 66, 74
 Kuchen, W., 143(64, 111), 145(64, 111),
 172(111), 175(111), 179, 181
 Kudielka, H., 121(100), 129
 Kuebler, N. A., 291, 312
 Kuhn, S. J., 224(230), 262(93, 187), 308,
 311, 312
 Kume, K., 112, 129
 Kunz, H., 98(125), 130
 Kuriyama, M., 103(103), 114(103), 129
 Kuroya, H., 186(78), 189(78), 190(78),
 199(76), 215
 Kussy, M. E., 55(163), 76
 Kutzelnigg, A., 86(107), 89(107), 96(107),
 129
 Kyuno, E., 210(74), 215
- L**
- Lampe, T. W., 286(98), 309
 Landolt-Börnstein, 98(104), 99(104), 129
 Lang, K., 278(273), 313
 Lappert, M. F., 134(114), 149(114a), 151
 (114a), 153(112, 113, 114, 114a, 115),
 154(47a, 112, 113, 114, 115), 155(113),
 158(115), 159(113, 114, 114a, 115),
 160(112, 113, 114), 162(113, 114, 115),
 163(113, 114, 115), 164(112, 113, 114,
 114a, 115), 165(47a, 98b, 113, 114),
 166(112, 113, 114, 114a, 115), 167
 (114), 169(115), 170(112, 113, 114,
 114a, 115), 171(112, 114), 172(113,
 114, 114a, 115), 173(100b, 111a, 114),
 174(112, 113, 114, 115), 175(100b,
 112, 115), 179, 180, 181
 Lappert, M. T., 263(188), 311
 Laran, R., 71(300), 80
 Larson, M. L., 320(171), 351
 Laubengayer, A. W., 153(116), 157(116),
 181
 Laudise, R. A., 320(293), 331(172), 351,
 354
 Laxminarayanan, T. S., 70, 76
 Leckie, A. H., 257(4), 307
 Leddicotte, G. W., 50(80), 74, 76
 Lederer, M., 60(159), 76
 Lee, F. S., 280(189), 311
 Leeper, R. W., 146(116a), 177(116a), 181
 Leffler, J. E., 137(117), 181
 Lehmann, H. A., 277(190, 191), 311
 Lehr, W., 248(25), 307
 Lehrer, E., 91, 95(105), 105(106), 129
 Leonawa, L. G., 101(138), 130
 Leuze, R. E., 46, 54, 71, 72, 76
 Levey, H. A., 304(192), 311
 Lewey, S., 22(176, 213), 39(176), 40(213),
 41(213), 42(213), 76, 77
 Lewis, J., 187(58), 215, 255(2), 257(3),
 258(194), 259(2), 290(193), 306, 307,
 311, 319(177), 322(174), 323(177),
 324(55, 177), 331(173), 341(176), 342
 (57, 176), 343(175, 176), 345(57), 348,
 351
 Lewis, T. J., 219(195), 311
 Ley, H., 210(60), 215
 Li, N. C., 48(294), 49(294), 68, 70(293),
 79, 80, 213(61), 215
 Li, T. H., 331(241), 352
 Lichtin, N., 239(196), 311
 Lieber, E., 136(118, 119a), 139(118, 119a),
 140(119), 181
 Liehr, A. D., 333(224), 352
 Liem, D. H., 35(74, 77), 36, 37, 73, 74
 Lien, A. P., 285(204), 311
 Lieth, W., 253(180), 310
 Lifschitz, I., 206, 209, 210(63, 66), 211
 (65, 66), 212(65), 215
 Lihl, F., 86(107), 89(107), 96(107), 129

Liimatainen, R., 272(102), 309
 Lindenbaum, S., 48, 72
 Lindner, K., 321(179), 324(179), 331(179), 351
 Lindsey, R. V., 143(37), 145(37), 146(37), 147(37), 148(37), 149(37), 178
 Lingane, J. J., 330(180), 331(180), 351
 Linton, H. R., 145(120), 149(120, 121), 151(120), 181
 Lipovskii, A. A., 55(281), 79
 Lippincott, E. R., 239(197), 311
 Lipscomb, W. N., 236(198), 311
 Lister, M. W., 317(81), 319(81), 349
 Little, A. T., 123(62), 128
 Litvinchuk, V. M., 332(192), 334(178, 193), 335(178, 194, 195), 351
 Lloyd, P. J., 54, 76
 Lockhart, J. C., 167(68, 122), 174(68, 122), 179, 181
 Logan, N., 257(1), 306
 Lohmann, K. H., 229(20), 263(20), 274(20), 307
 Lonsdale, K., 221(35), 307
 Lorberch, J., 146(122a), 148(122a), 181
 Lorenzelli, V., 332(181), 351
 Louat, N., 101(172), 131
 Luborsky, F. E., 285(168), 310
 Lübke, K., 146(215), 148(215), 151(215), 183
 Luijten, J. G. A., 136(123), 138(123), 139(123), 141(123), 142(123a), 145(189), 146(124, 188), 148(124, 188), 151(124), 181, 183
 Lundgren, G., 218(199), 311
 Lustig, M., 229(200), 311
 L'vov, S. M., 112(108), 123(108), 125(150), 129, 131
 Lyutana, M. D., 85(147), 86(147), 130

M

Maasböl, A., 341(93), 349
 McAchrán, G. E., 234(201), 311
 McBeth, R. L., 56(102), 74
 McBride, J. J., 143(126, 127), 145(125, 126, 127), 149(126, 127), 151(125, 126, 127), 169(125), 175(126), 181
 McCaffery, A. J., 195(9, 67), 213, 215
 McCarley, R. E., 291(202, 203), 311, 320(43), 321(43, 182, 183), 322(43), 324(43), 329(43), 330(43), 348, 351
 McCarty, S., 16(177, 199), 21(199), 22(177), 37(214), 38(215), 40(205), 45(177), 46(177, 205), 66(177), 76, 77, 78
 McCauley, D. A., 285(204), 311
 McCleverty, J. A., 344(29, 123), 347, 350, 351
 McCloskey, A. L., 135(128), 137(128), 139(128), 175(128), 181
 McDermott, T. E., 192(28), 198(27, 28), 199, 202(27, 28), 214
 MacDiarmid, A. G., 143(48, 65a), 144(65, 65a), 145(48, 65, 187), 147(48), 149(65a), 151(65a), 152(65, 65b, 187), 153(131, 186), 155(186), 160(186), 168(130), 179, 181, 183, 334(185), 351
 McDonald, C. C., 206(68), 208, 209(68), 215
 McDowell, C. A., 219(205), 292(205), 311
 McElroy, A. D., 303(225), 311
 McGarvey, B. R., 333(186), 351
 McGee, S. W., 101(109), 129
 MacGillavry, C. H., 277(92), 308
 Machin, D. J., 322(174), 351
 McIntyre, J. S., 240(231), 312
 McKay, H. A. C., 3, 16(113), 21(113), 26(22, 111), 27(1, 2, 113, 239), 31(113), 72, 74, 75, 76, 78
 Mackay, K. M., 143(129), 145(129), 181
 McKenzie, D. E., 255(47), 258(47), 259(47), 307
 McKenzie, E. D., 201(40), 213(41), 214
 Mackor, E. L., 282(206), 285(71), 286(206), 308, 311
 MacLean, C., 282(206), 286(206), 311
 McReynolds, J. P., 197(79), 198(79), 200, 213, 215
 McVey, W. H., 68, 69, 73
 Maddock, A. G., 68, 74, 153(131), 181
 Maack, W. J., 55, 76
 Magnéli, A., 316(130), 337(130), 338(110, 130), 346(130), 349, 350
 Magnusson, D. W., 269(207), 311
 Mah, A. D., 98(110, 111, 112), 99(110, 111, 112), 129
 Maier, G., 135(141), 137(141), 140(141), 181

- Maier, J. L., 19(216), 22(217), 30(216), 36(217), 58(216), 59(217), 60(217), 78
- Maiorova, E. P., 27(90, 91), 70, 74
- Maitlis, P. M., 342(187), 351
- Majumdar, S. K., 31, 76
- Maki, A. H., 344(74), 348
- Maksimov, V. K., 319(258), 353
- Malatesta, L., 339(188), 351
- Malm, J. G., 285(208), 311
- Mandil, M. A., 41, 76
- Mannerskantz, H. C. E., 343(189), 351
- Manning, D. L., 70(95), 74
- Manning, P. G., 29(166), 68, 70, 76
- Maratray, F., 118(113), 129
- Marcus, Y., 2, 3, 76
- Marenets, M. S., 162(106c), 180
- Marenko, G. N., 85(147), 86(147), 130
- Margolin, H., 86(131), 97(131), 130
- Margolin, M., 123(166), 131
- Margrave, J. L., 273(6), 307
- Marinangeli, A. M., 334(49), 335(30), 347, 348
- Marquart, J. R., 294(209), 311
- Marsh, R. E., 270(307), 313
- Martell, A. E., 70(26), 72
- Martin, A. J. P., 64, 76
- Martin, B., 28, 76
- Martin, F. S., 2, 76
- Martin, R. L., 281(128, 129), 290(65), 308, 309
- Martin, W. J., 325(143), 350
- Martinette, M., 199, 200(69, 70), 215
- Martynenko, L. I., 58, 76
- Masek, J., 343(190), 351
- Mason, E. A., 54, 76
- Mason, G. W., 11(207), 12(207, 218), 13, (201, 218, 219), 15(209), 16(177, 208, 209), 19(216), 22(176, 177, 208, 209, 213, 217), 27(212), 29(212), 30(207, 216), 35(82, 200), 36(206, 217), 37(212, 214), 38(201, 215), 39(206), 40(205, 209, 210, 213, 220), 41(165, 178, 202, 208, 211, 212, 213), 42(204, 213), 44(82, 206), 45(177, 206), 46(178, 203, 205, 218), 47(230), 53(209), 58(216), 59(217), 60(217), 62(201), 66(112, 218), 70(211), 74, 75, 76, 77, 78
- Mason, R., 213(41), 214, 344(29), 347
- Mason, S. F., 195(9, 67, 71), 211(71a), 213, 215
- Massart, D. L., 63(54), 73
- Massat, H., 256(288), 313
- Massey, A. G., 340(191), 351
- Mathers, W. G., 70(30), 72
- Mathieu, J. P., 200, 206, 215
- Matschiner, H., 319(105), 349
- Matsen, F. A., 287(210), 311
- Matsuura, M., 106(4), 127
- Matthieu, J.-P., 332(141), 350
- Mayhew, S. J., 213(41), 214
- Mays, M. J., 135(61), 138(61), 141(61), 153(60), 155(60), 164(60), 170(59), 175(59), 179
- Meerwein, H., 263(211), 311
- Meinert, H., 276(275), 313
- Mekata, M., 114, 115(114), 119(114), 129
- Meller, A., 143(94), 144(94), 180
- Mellor, D. P., 204(25a), 214
- Melvin, H. W., 153(81), 155(81), 158(81), 162(81), 163(81), 164(81), 170(81), 173(81), 175(81), 180
- Menis, O., 70(95), 74
- Mennig, K., 266(161), 310
- Menschikow, A. Z., 104(122), 130
- Menyuk, N., 104(178), 106(178), 131
- Menzer, W., 146(132), 147(132), 181
- Mercer, M., 317(58), 348
- Merkel, A. W., 225(305), 313
- Meyer, N. J., 302(14), 307
- Meyer-Simon, E., 126(91), 129
- Michalowski, Z., 150(133), 151(133), 169(133), 172(133), 173(133), 181
- Michaud, H., 135(197, 199, 200, 201, 202), 136(199), 137(197, 200), 138(199, 201, 202), 140(198), 183
- Michiels, L., 317, 349
- Miguel, M., 168(134), 181
- Mikhail, H., 104(179), 131
- Mikhailov, B. M., 143(135), 144(135), 151(135), 181
- Mikhalevich, K. N., 332(192), 334(178, 193), 335(178, 194, 195), 351
- Milburn, R. M., 228(212), 311
- Miles, J. H., 3, 76
- Millen, D. J., 258(127, 213), 261(158), 306(214), 309, 310, 311
- Miller, F. A., 153(136), 156(136), 157(136), 160(136), 181

- Miller, G. W., 213(61), *215*
 Miller, H. C., 142(30b), 166(1), *178*
 Miller, N. E., 234(215), *311*
 Mills, H. H., 240(142), *310*
 Milne, J. B., 287(317), *314*
 Mishra, H. C., 278(7), *307*
 Mitchell, P. C. H., 337(196, 197), *351*
 Mizushima, S-I., 190(85), *215*
 Moers, K., 95(1), 96(115), 97(115), 98(1),
 99(1), 112(1), *127, 130*
 Mohaupt, G., 319(106, 108), 324(106), *349*
 Mok, S. F., 239(154), *310*
 Moline, S. W., 14(219), *78*
 Monk, C. B., 70, *76*, 298(216), *311*
 Mooney, E. T., 222(112), *309*
 Moore, B., 343(198), *351*
 Moore, E. W., 320(171), *351*
 Moore, F. L., 50(80), 52, 54, 55, 56, 71
 (185), *74, 76, 77*
 Moore, J. G., 51(45), *73*
 Moore, T. E., 71(300), *80*
 Morgunova, M. M., 155(214), 158(214),
 183
 Mori, M., 210(74), *215*
 Morris, A. G., 285(60), *308*
 Morris, J. H., 342(281), *354*
 Morrison, G. H., 2, 3(92), *74, 77*
 Morrow, S. T., 263(342), 267(342), *314*
 Mortensen, J. P., 340(96), *349*
 Mortimer, P. I., 318(199), *351*
 Morton, J. R., 264(49), *308*
 Moser, E., 342(94), *349*
 Moskvina, L. N., 62, 63, *77*
 Mostovaya, O. A., 29(299), *80*
 Mott, N. F., 112, *130*
 Mould, R., 171(62), 175(62), *179*
 Mrochek, J. E., 33, *77*
 Müller, W., 52(64), *73, 77*
 Münster, A., 86(117), 96(117, 118), 97
 (117), 99(119), 100(117), 102(117),
 103(117), 104(117), 125(117), *130*
 Muetterties, E. L., 166(1), *178*, 222(220),
 224(219), 234(215), 252(218), 265
 (219), 273(217), *311*, 317(201), 322
 (201), 333(200), *351*
 Mufti, A. S., 157(136a), 162(136a), *181*
 Muha, G. M., 304(221), *311*
 Mukherjee, R. N., 143(45), 144(45), 149
 (45), 150(45), 151(45), *179*
 Muller, E. S., 249(222), *311*
 Muller, N., 145(137), 149(137), *181*
 Murakami, H., 49(132, 133), 55(137), 71
 (131), *75*
 Murakami, M., 201(75), 207(75), *215*
 Murakami, Y., 70(26), *72*
 Murdoch, H. D., 343(202), *352*
 Murphy, J. W., 337(8), *347*
 Murray, G. A., 324(203), 331(203), *352*
 Musil, F. J., 324(204), *352*
 Muszkat, K. A., 135(138), 137(138), *181*
 Myers, O. E., 317(205), 319(205), *352*
- N**
- Nabi, S. N., 266(223), *311*
 Nadler, M. A., 155(209), 163(209), *183*
 Nagy, P. L. I., 316(124), 339(124), *350*
 Naito, K., 31, *77*
 Naito, M., 208(89), *215*
 Nakahara, A., 199(76), *215*
 Nakamoto, K., 222(224), *311*
 Nakamura, D., 329(206), *352*
 Nakamura, E., 49(132, 133), 71(131, 140),
 77
 Nakatsu, K., 186(78), 189(77, 78), 190
 (77, 78), *215*
 Nambodiri, M. N., 40(220), *78*
 Nambury, C. N. V., 140(119), *181*
 Nash, A. W., 19, *75*
 Nast, R., 341(207), *352*
 Naumann, H., 319(105), *349*
 Nebgen, J. W., 306(225), *311*
 Néel, L., 107, *130*
 Neitzel, U., 2(85), *74*
 Nelson, F., 55(156), 63(156), *76*
 Nelson, J. A., 162(28a), *178*
 Nemchenko, V. F., 112(108), 123(108), 125
 (150), *129, 131*
 Nemnonow, S. A., 104(122), *130*
 Nenarokomov, E. A., 29(194), *77*
 Neruda, B., *183*
 Neshpor, V. S., 103(123), 110(123, 148), *130*
 Nesmayanov, A. N., 342(208), *352*
 Neubauer, D., 324(209), *352*
 Neumann, B., 98(124, 125), *130*
 Neumann, H. M., 329(11), *347*
 Newman, L., 68, *77*
 Newsom, H. C., 135(138a), *181*
 Nichols, R., 278(12), *307*
 Nielsen, A. H., 317(45), *348*
 Nielsen, J. P., 86(131), 97(131), *130*

Niemann, E., 336(33), 337(33), 347
 Nigam, H. L., 340(210), 352
 Nikitina, S. A., 55(281), 79
 Nishimo, M., 172(190a), 183
 Nishiyama, Z., 86(126), 89(126), 130
 Nitta, I., 207(32), 214
 Nixon, E. R., 145(120), 149(120, 121), 151
 (120), 181
 Nogradi, J., 259(289), 313
 Nomura, S., 31(197), 77
 Nordman, C. E., 234(226), 311
 Nordsieck, H. H., 332(144), 350
 Norman, B. J., 195(67, 71), 215
 Norman, J. H., 338(211), 352
 Novák, M., 59, 72
 Novikov, G. I., 317(259), 319(257, 258),
 322(259, 260), 353
 Nowicki, D. H., 96(24), 97(24), 127
 Nowotny, H., 86(127), 117(128), 121(73,
 74, 75, 76), 122(73, 129), 129, 130
 Nunn, E. K., 200(33), 203(33), 214
 Nyholm, R. S., 240(64), 290(193), 308,
 311, 322(77, 174), 324(55), 331(77),
 340(28, 210), 342(57), 343(66, 175,
 190, 212), 345(57), 347, 348, 349, 351,
 352

O

O'Brien, R. J., 240(57), 308
 O'Brien, T. D., 197(79), 198(79), 215
 Ockenden, D. W., 28(173), 76
 Odell, F., 117(27), 123(27), 127
 Ōfele, K., 289(101), 309, 340(96), 342(88),
 343(95), 349
 Ogle, J. R., 162(62a), 179
 Ogle, P. R., 324(104), 349
 Oho, R. J. A., 162(180a), 183
 Okawana, R., 172(190a), 183
 Olah, G. A., 224(230), 240(231), 255(227),
 262(93, 187), 277(228), 286(229), 308,
 311, 312
 O'Laughlin, J. W., 33(190), 77
 Olin, A., 304(232), 312
 Olsson, O. O., 331(215), 332(214, 215),
 337(213), 352
 Ono, R., 71(131), 75
 Onyszechuk, M., 143(64), 145(64, 171, 172),
 147(171), 148(171), 153(171), 156
 (171, 172), 168(171), 169(171), 171

(172), 172(171), 176(171, 172), 179,
 182
 Opfermann, W., 96(130), 130
 Opgenhof, P., 324(252), 353
 Orgel, L. E., 333(216), 352
 Ormont, B., 86(33), 88(33), 128
 Osakabe, T., 55(130), 71(130, 131), 75
 Osborne, B. P., 317(38, 99), 324(38, 99),
 329(38), 348, 349
 Ota, H., 189(86), 190(86), 194(86), 215

P

Paciorek, K. L., 141(109, 109a), 181
 Paddock, N. L., 248(233), 312
 Paetzold, P. I., 135(139, 140, 140a, 140b,
 141), 137(139, 140, 140a, 140b, 141),
 139(139, 140, 140a, 140b), 140(139,
 140, 140a, 141), 181
 Page, J. E., 49, 79
 Palty, A. E., 86(131), 97(131), 130
 Panassjuk, J. O., 101(96), 129
 Pande, C. S., 322(77), 331(77), 343(175),
 349, 351
 Panzer, R. E., 248(234), 312
 Paranjpe, V. G., 87(132), 95(132), 100
 (132), 130
 Pâris, J. M., 125(140, 141), 130
 Parish, M. B., 275(258), 285(259), 312
 Parish, R. V., 320(127), 324(36, 127), 331
 (36, 120), 332(161, 217), 333(161, 217,
 219), 335(218, 220), 348, 350, 351,
 352
 Parker, A. J., 226(235), 312
 Parkins, R. M., 196(39), 206(39), 208(39),
 209(39), 214
 Parry, R. W., 233(280), 234(171), 235
 (236), 250(78), 251(77), 308, 310, 312,
 313
 Partington, J. R., 229(237), 255(237), 312
 Patai, S., 239(154), 310
 Patel, S. J., 167(141a), 175(141a), 181
 Patil, H. R. H., 342(221), 352
 Patil, S. K., 70(157), 76
 Paulin, D., 155(89, 90), 156(89), 158(90),
 160(89), 162(90), 163(90), 175(89),
 180
 Pauling, L., 108, 130, 291(239, 321), 294
 (238), 312, 314, 325(222), 352
 Pauling, P., 322(174), 351

- Paulssen-v. Beck, H., 324(223), 327(223), 352
- Pavlath, A. E., 274(52), 308
- Payne, D. S., 245(140, 141, 240), 310, 312
- Payne, N. C., 196(39), 206(39), 207(42), 208(39), 209(39), 211(42), 214
- Peach, M. E., 222(241), 312
- Peacock, R. D., 274(137), 310, 317(58), 323(5), 324(5, 132, 133, 156), 325(132), 326(133), 329(5, 156), 330(5, 156), 347, 348, 350
- Pearn, E. J., 167(68, 69), 171(69), 174(68, 69), 179
- Pearsall, H. W., 286(45), 307
- Peck, P. F., 59, 60(224, 226, 227), 62(227), 78
- Peel, J. L., 213(41), 214
- Peeling, E. R. A., 261(115), 309
- Peerdeman, A. F., 186(11), 213
- Peifer, J. J., 64, 77
- Penneman, R. A., 24(8, 267), 72, 79
- Peppard, D. F., 11(207), 12(207, 218), 13(201, 218, 219), 15(209), 16(177, 199, 208, 209), 19(221), 21(199), 22(176, 177, 208, 209, 213, 217), 27(212), 29(212), 30(207, 216), 35(82), 36(206), 37(214), 38(83, 201, 215), 39(176, 206), 40(205, 209, 210, 213, 220), 41(83, 165, 178, 202, 208, 211, 212, 213), 42(204), 44(82), 45(177), 46(177, 178, 203, 205, 218), 47(230), 53(209), 58(216), 59(217), 60(217), 62, 66(112, 177), 70, 74, 75, 76, 77, 78
- Peppard, M. A., 19(221), 78
- Perkins, P. G., 333(219), 352
- Perkins, R., 55, 76
- Perumal, A., 145(110), 150(110), 181
- Perumareddi, J. R., 333(224), 334(6), 347, 352
- Peshkova, V. M., 71, 80
- Peters, C. R., 234(226), 311
- Peterson, H. C., 31(49), 73
- Pettit, L. D., 196(39), 206(39), 208(39), 209(39), 214
- Pfeiffer, P., 146(195), 155(194a), 183, 212(80), 215
- Pfeiffer, V., 337(225), 352
- Pfitzner, H., 212(80), 215
- Philips, J. F., 192(81), 197(81), 215
- Phillips, C., 236(269), 313
- Phillips, W. D., 206(68), 208, 209(68), 215, 222(220), 224(219), 252(218), 265(219), 273(217), 311, 317(201), 322(201), 351
- Pierce, T. B., 59, 60(224, 226), 62, 63, 78
- Pigenot, D., 151(98), 180
- Pinnow, P., 317(37), 348
- Pinsker, Z. G., 86(135, 137), 87(136), 88(135, 137), 130
- Piper, T. S., 186(82), 195(83), 196(95), 215, 342(226), 352
- Pischtschan, S., 240(186), 311
- Pitts, J. J., 279(242), 312
- Pocker, Y., 239(154), 310, 312
- Pohland, E., 142(142), 144(142), 181
- Polis, A., 170(143), 177(143), 181
- Poller, R. C., 157(136a), 162(136a), 181
- Pollock, J. M., 155(66), 164(66), 173(67), 179
- Poole, H. G., 261(158), 310
- Popov, A. I., 245(244), 312
- Popov, K. K., 155(214), 158(214), 183
- Popplewell, D. S., 203, 215
- Portanova, R., 172(41a), 179
- Porter, G. B., 254(245), 312
- Porter, R. C., 297(247, 278), 312, 313
- Porter, R. F., 296(246), 312
- Porter, R. T., 219(56), 293(56), 308
- Poskanzer, A. M., 71, 78
- Posse, R., 259(289), 313
- Post, H. W., 176(83), 180
- Powell, C. F., 96(24), 97(24), 127
- Powell, J. S., 35, 76
- Powers, R. M., 27(55), 70, 73
- Pranowo, 68, 76
- Prasad, S., 318(228), 319(230, 231), 324(227, 229, 232), 329(232), 352
- Pratt, L., 222(248), 312, 344(123), 350
- Preiss, H., 222(181), 253(181), 311
- Priest, H. F., 320(233, 234), 324(233), 352
- Prigent, J., 324(235), 352
- Prince, M. I., 135(143a), 181
- Prober, M., 147(144, 145), 181
- Prokai, B., 149(114a), 151(114a), 153(114a), 159(114a), 164(114a), 166(114a), 170(114a), 172(114a), 173(111a), 181
- Prokhorova, N. P., 70, 78
- Prue, J. E., 299(46), 307

Puff, H., 86(87), 89(87), 90(87), 101(87), 107(86), 118(80, 86), 119(80, 86), 123(86), 126(79), *129*
 Pump, J., 147(147), 155(146, 148), 156(149), 157(146), 158(146, 148), 164(149, 193), 173(193), *182, 183*
 Purcell, K. F., 226(79), *308*
 Puschmann, J., 254(146), *310*
 Pyszora, H., 134(114, 150), 149(114a), 151(114a), 153(112, 113, 114, 114a, 115, 150), 154(112, 113, 114, 115, 150), 155(113, 150), 158(115), 159(113, 114, 114a, 115), 160(112, 113, 114, 150), 162(113, 114, 115, 150), 163(113, 114, 115, 150), 164(112, 113, 114, 114a, 115, 150), 165(113, 114, 150), 166(112, 113, 114, 114a, 115, 150), 167(114, 150), 168(115), 170(112, 113, 114, 114a, 115, 150), 171(112, 114, 150), 172(113, 114, 114a, 115, 150), 173(114, 150), 174(112, 113, 114, 115, 150), 175(112, 115, 150), *181, 182*

Q

Quagliano, J. V., 190(85), *215*
 Quarterman, L. A., 268(249), 284(156), *310, 312*

R

Rabenau, A., 102(88), *129*
 Raff, P., 142(211), 144(211, 212), *183*
 Raider, S., 145(177), 152(177), *182*
 Raines, M. M., 332(236), *352*
 Ralston, K., 324(204), *352*
 Rao, C. N. R., 136(119a), 139(119a), *181*
 Rao, G. S., 47, *78*
 Raschig, F., 135(203, 204, 205, 206), 138(203, 204, 205, 206), 139(203), 141(203, 204, 206), *183*
 Ratner, A. W., 101(138), *130*
 Rauh, E. G., 338(3), *347*
 Rausch, M. D., 316(237), *352*
 Rausch, W. V., 304(250), *312*
 Ray, P., 332(238), *352*
 Raynor, G. V., 123(62), *128*
 Reas, W. H., 69, *73*
 Reed, R. J., 224(155), *310*
 Reed, R. T., 293, *312*
 Reggel, L., 153(116), 157(116), *181*
 Reiche, A., 135(155a), *182*

Reichle, W. T., 135(151), 136(96a, 151, 151a), 138(151), 139(96a, 151a), 141(151), *180, 182*
 Reid, J., 325(2), 343(2), *347*
 Reilly, C. N., 294(251), *312*
 Rein, J. E., 55(163), *76*
 Revallier, L. J., 258(107), 261(107, 110), *309*
 Reyhling, J., 149(91), 171(92), 175(92), 176(92), *180*
 Reynold, J. E., 168(152), 173(152), 176(152), *182*
 Reznik, A. M., 30, *78*
 Rhee, C. T., 28(134), *75*
 Rice, S. A., 285(208), *311*
 Richards, O. V., 143(44), 144(44), 167(44), 173(44), 175(44), *179*
 Richards, R. E., 222(248, 253, 254), 280(254), 281(106), *309, 312*
 Richter, P., 135(32, 33), 138(32), 142(33), *178*
 Rieber, M., 153(115), 154(115), 158(115), 159(115), 162(115), 163(115), 164(115), 166(115), 169(115), 170(115), 172(115), 174(115), 175(115), *181*
 Rinn, H. W., 262(93), *308*
 Ritchey, W. M., 340(242), *352*
 Ritter, A., 135(32, 33, 36), 138(32), 142(33, 36), 155(34), 158(34), 163(34), *178*
 Robbins, M., 106, *130*
 Roberts, H. L., 250(330), *314*
 Roberts, J. E., 267(255), *312*
 Robin, M. B., 291, *312*
 Robinson, E. A., 223(119), 241(119), 252(118), 266(105), 282(117), *309*
 Robinson, P. L., 229(11), 259(11), 264(21), 278(12), *307, 318(277), 324(22), 347, 353*
 Rochow, E. G., 136(154), 147(147), 155(146), 157(82, 146, 154), 158(146), 168(153), 177(153, 163), *180, 182, 240(316), 314*
 Roebuck, P. J., 143(129), 145(129), *181*
 Rogers, M. T., 268(257), 275(258), 285(259), *312*
 Rohde, H., 121(101), *129*
 Rooksby, H. P., 338(271), *353*
 Rosenheim, A., 331(241), 332(239, 240), 337(240), *352*

Rosenstock, H. M., 297(260), 312
 Ross, B., 167(158), 175(158), 182
 Ross, B. L., 340(242), 352
 Ross, J. R., 239(22), 307
 Ross, W. J., 28(292), 80
 Rossotti, F. J. C., 298(261), 312
 Rossotti, H., 298(261), 312
 Rothenbury, R. A., 254(120), 287(317), 309, 314
 Roubin, M. P., 125(140, 141), 130
 Royer, D., 192(81), 197(81), 215
 Rozen, A. M., 30(231), 71, 78
 Ruby, S. L., 106(158), 131
 Rudenko, T. I., 70(89), 74
 Rudge, A. J., 273(15), 307
 Rudnicki, R. P. T., 158(27), 168(27), 178
 Rudolph, R. W., 235(236), 312
 Rudy, E., 117(128), 130
 Rüdorff, W., 322(17), 347
 Ruff, J. K., 249(262), 312
 Ruff, O., 318(243), 352
 Ruhlmann, K., 135(155a), 182
 Ruidisch, I., 135(155), 136(155), 138(155), 182
 Rundle, R. E., 109, 116, 130, 251(344), 314, 339(73), 348
 Runner, M. E., 284(263), 312
 Ruppert, W., 96(118), 130
 Rush, R. M., 303(264, 265), 312
 Russel, D. R., 324(155), 325(155), 326(155), 350
 Russel, J. H., 64, 78
 Ryan, J. L., 52(143), 76
 Ryazanov, I. A., 54(280), 79
 Rydberg, J., 28, 72, 302(266), 312
 Ryland, A. L., 19, 73

S

Sabaev, I. Y., 71(232), 78
 Sabatini, A., 323(244), 352
 Sacco, A., 339(188), 351
 Sachsze, W., 87(89, 90), 94(89, 90), 95(89, 90), 96(89, 90), 97(89), 125(89), 126(143), 129, 130
 Saisho, H., 28, 32, 78
 Saito, Y., 186(78), 189(78, 86), 190(52, 78, 86), 194(86), 199(52a, 76), 214, 215
 Sakurai, H., 33(190), 77
 Sala, O., 332(268), 333(268), 353

Samarin, A. M., 101(6), 127
 Sammes, P. G., 66(58), 73
 Sammour, H. M., 31, 55(137), 71(131), 75
 Samotus-Kosinska, A., 334(150, 151), 335(151), 350
 Sampath, S., 278(13), 307
 Samson, C., 120, 121(144), 130
 Samsonov, G. V., 85(147), 86(147), 101(149), 102(149), 110(145, 146, 148), 112(108), 123(108), 125(150), 129, 130, 131
 Sanders, T. M., 171(54), 179
 Sands, D. E., 319(245), 352
 Sano, K., 98(151), 131
 Sargent, J., 285(61), 308
 Sargeson, A. M., 192(28), 198(27, 28), 201, 202(27, 28, 87), 203(29, 30), 214, 215
 Sarrach, D., 251(182), 311
 Sarry, B., 345(246, 247), 352, 353
 Satô, S., 98(152), 131
 Sato, T., 36, 54, 78
 Sauer, H., 259(290), 313
 Saunders, B. C., 146(95, 156), 148(95, 156), 157(95), 158(95), 168(95), 177(95), 180, 182
 Savoie, R., 280(267), 313
 Scadden, E. M., 35, 36, 78
 Scargill, D., 27(106, 239), 74, 78
 Scargill, P., 64(52), 73
 Schäfer, H., 290(268), 313, 320(248), 321(249, 265), 322(248), 331(265), 345(248), 346(248), 353
 Schäfer, W., 264(183), 311
 Schaeffer, R., 142(40), 144(40), 167(40), 174(40), 179, 236(269), 313
 Scharf, E., 276(274), 313
 Schaschel, E., 143(94), 144(94), 180
 Schauer, H., 319(107), 349
 Scheibel, E. G., 19, 78
 Schenk, R., 95(153), 99(153), 131
 Scherer, F., 339(97), 341(97), 349
 Scherer, O. J., 135(157), 136(157), 138(157), 182
 Schissler, D. O., 298(311), 313
 Schlamp, C., 99(119), 130
 Schlemper, E. O., 136(157a), 146(157a), 151(157a), 182

- Schmeisser, M., 260(271), 276(274), 277
(270, 272), 278(273), 313, 318(250),
353
- Schmid, K. H., 135(207), 141(208), 183
- Schmidt, H., 276(275), 313
- Schmidt, M., 135(155, 157), 136(155, 157),
138(155, 157), 182
- Schmidt, W., 251(184), 311
- Schmitz-Dumont, O., 87(154), 94(154), 97
(154), 125(155), 131, 167(158), 175
(158), 182, 324(251, 252, 253), 325
(251), 353
- Schmulbach, C. D., 237(276), 251(277),
313
- Schmutzler, R., 257(291), 313
- Schneider, R., 344(100), 349
- Schnell, E., 172(159, 160), 176(159, 160),
182
- Schnell, W. D., 86(15), 123(16), 127
- Schnering, H. G., 320(248), 321(249), 322
(248, 254), 345(248), 346(248), 353
- Schob, O., 86(127), 130
- Schönberg, N., 117(157), 118(156), 131
- Schoonmaker, R. C., 297(278), 313
- Schramm, J., 155(34), 158(34), 163(34),
178
- Schrauzer, G. N., 344(282), 354
- Schreeve, J. M., 229(279), 265(279), 313
- Schriver, D. T., 235(236), 312
- Schuieler, E., 178
- Schüth, W., 104(97), 129
- Schultz, D. R., 233(280), 313
- Schumb, W. C., 320(233, 234), 324(233),
352
- Schutzler, R., 244(281), 313
- Schwarzenbach, G., 298(37), 307
- Schwarzkopf, P., 97, 129
- Schwarzmann, E., 338(116, 255), 349, 353
- Schweitzer, G. K., 71, 78
- Seibona, G., 54(14), 72
- Seaborg, G. T., 24(244), 78
- Seaton, D. L., 158(27), 168(27), 178
- Seel, F., 229(286), 243(286), 255(283, 284),
256(282, 285, 287, 288, 292), 257(291),
258(282), 259(289, 290), 264(286),
274(286), 275(286), 313
- Sekine, T., 70, 71(246, 247), 78
- Selbin, J., 305(293, 294), 313
- Selig, H., 274(296), 279(295), 285(208),
311, 313
- Semmlinger, W., 340(96), 349
- Sen, D. C., 203(88), 215
- Senior, J. B., 278(121), 309
- Seuter, A. M. J., 248(132), 309
- Seyferth, D., 136(154), 145(162), 146(162),
147(161, 162), 148(161, 162), 149
(162), 151(161, 162), 152(162), 157
(82, 154), 169(162), 176(162), 177
(162, 163, 164), 180, 182
- Shamir, J., 274(296), 313
- Sharkley, W. H., 143(37), 145(37), 146
(37), 147(37), 148(37), 149(37), 178
- Sharma, H. D., 70(157), 76
- Sharp, D. W. A., 238(297), 313, 324(72,
155), 325(72, 155), 326(155), 348, 350
- Sharpe, A. G., 273(298), 313, 324(72), 325
(72), 348
- Sharupin, B. N., 317(259), 322(259), 353
- Shaw, B. L., 316(129), 339(129), 350
- Shchukarev, S. A., 317(259), 319(257,
258), 322(256, 259, 260), 353
- Sheldon, J. C., 290(299), 313, 321(261),
353
- Sheline, R. K., 340(273, 274), 353
- Sheppard, N., 238(297), 313
- Sheridan, J., 149(165), 182
- Sherif, F. G., 162(180a), 183
- Shevchenko, V. B., 55, 70, 78
- Shevchenko, V. I., 162(165a), 182
- Shibata, M., 208(89), 210(74), 215
- Shibata, Y., 213(90), 215
- Shimomura, K., 317(262), 353
- Shimura, Y., 190(91), 215
- Shirane, G., 106(158), 107(167, 168), 114
(167, 168), 118(167, 168), 119(168),
131
- Shiro, M., 186(78), 189(78), 190(78), 215
- Shoemaker, D. P., 342(290), 345(290), 354
- Shokin, I. N., 71(232), 78
- Shomate, C. H., 98(159, 160), 131
- Shore, S. G., 233(280), 234(201), 311, 313
- Shriver, D. F., 344(263), 353
- Shtepanek, A. S., 162(165a), 182
- Shull, C. G., 106(161), 131
- Shulman, A., 192(25), 214
- Siddall, T. H., III, 29(250), 31(251), 32,
78, 79
- Sidgwick, N. V., 151(166), 182
- Siebert, H., 250(300), 313
- Siegel, B., 294(301), 313

- Siekierski, S., 31, 54, 57, 58, 59, 61, 62, 66,
72, 74, 79
- Sienko, M. J., 338(264), 353
- Siepmann, R., 321(249, 265), 322, 331
(265), 353
- Sillén, L. G., 298(37), 300(303), 301(84,
302), 302(304), 303(84, 303), 305
(165), 307, 308, 310, 313
- Silverton, J. H., 333(145), 350
- Silverthorn, M. E., 273(6), 307
- Simmonds, T. C., 249(150), 310
- Simms, P. G., 335(220), 352
- Simon, A., 36(63), 73, 321(249), 353
- Singer, S., 225(305), 313
- Sironen, R. J., 12(218), 13(218), 14(218),
16(199), 21(199), 36(206), 39(206),
44(206), 45(206), 46(218), 66(218),
77, 78
- Sittig, L., 95, 98(40), 99(40), 100(40), 102
(40), 103(40), 128
- Slater, R. C. L., 251(306), 313
- Slepchenko, I. G., 29(194), 77
- Sly, W. G., 270(307), 313
- Small, L. A., 330(180), 331(180), 351
- Smirnof, A. P., 189, 215
- Smit, P. J., 285(71), 308
- Smith, A. C., 136(154), 157(82, 154), 180,
182
- Smith, D. F., 317(45), 348
- Smith, E. A., 324(114), 349
- Smith, E. L., 49, 79
- Smith, G. B. L., 133(40a), 179
- Smith, H. D., 154(97), 165(97), 170(97),
174(97), 180
- Smith, J. A. S., 222(254), 280(254), 312
- Smith, J. D., 249(91), 281(91), 308
- Smith, P. W., 322(174), 351
- Smolinsky, G., 141(167, 168), 182
- Smulek, W., 54, 72, 79
- Smutz, M., 31(25), 72
- Snow, M. C., 207(32), 214
- Snow, M. R., 343(212, 266), 352, 353
- Sochacka, R. J., 59, 61, 62, 79
- Sokolov, W., 188(94), 215
- Sokolskii, G. A., 255(308), 313
- Solony, N., 213(61), 215
- Solovkin, A. S., 29(264), 70, 79
- Sowerby, D. B., 166(170), 167(93), 168
(93), 171(93, 170), 171(169), 172
(170), 174(93, 170), 175(93, 169), 176
(93, 169), 177(93), 180, 182, 258(194),
311
- Spacu, P. G., 324(267), 353
- Spandau, H., 266(309), 313
- Spedding, F. H., 31(25), 72
- Speirs, J. L., 275(258), 285(259), 312
- Spinks, J. W. T., 229(124), 309
- Spreckelmeyer, B., 321(249), 353
- Srivastava, S. C., 55(97), 74
- Srivastava, T. N., 145(171, 172), 147(171),
148(171), 153(171, 173), 156(171,
172), 157(173), 168(171, 173), 169
(171), 171(172), 172(171), 176(171,
172), 177(173), 182
- Ssowalow, G. A., 101(98), 129
- Stacey, G. J., 146(156), 148(156), 182
- Stadelmaier, H. H., 120(162, 163, 164),
121(163), 131
- Stahl, H. O., 339(97), 341(97), 342(86,
91), 349
- Staley, H. G., 338(211), 352
- Stals, J., 318(20a), 347
- Stamm, W., 157(173a), 159(173a), 182
- Stammreich, H., 332(268), 333(268), 353
- Stangroom, J., 213(41), 214
- Starý, J., 71, 79
- Stasicka, Z., 334(150, 151), 335(151), 350
- Stear, A. N., 342(125), 350
- Steemann, J. W. M., 258(107), 261(107,
110), 309
- Steifel, E. I., 344(269), 353
- Steinberg, H., 319(270), 330(270), 353
- Steinberg, K., 125(155), 131
- Stephanou, S. E., 24(8, 267), 72, 79
- Steunenberg, R. K., 269(310), 313
- Stevenson, D. P., 298(311), 313
- Steward, E. G., 338(271), 353
- Stewart, D. C., 34, 35, 36, 79
- Steyermark, P. R., 155(174), 156(174),
182
- Stiddard, M. H. B., 322(77), 331(77), 340
(210), 343(111, 163, 175, 190, 212,
266, 272), 349, 351, 352, 353
- Stiegmann, C. A., 188(8), 200(8), 201(8),
213

Stöckler, H., 136(96a), 139(96a), 180
 Stokes, C. S., 96(165), 131
 Stolz, I., 340(273, 274), 353
 Stone, F. G. A., 177(164), 182, 342(281), 354
 Stone, L., 123(166), 131
 Stoughton, R. W., 27(56), 69, 70, 73, 79
 Stranks, D. R., 224(312), 313
 Street, C. N., 342(184), 344(126), 350
 Strohmeier, W., 340(275, 276), 353
 Strommer, D. P., 135(180c), 136(180c), 139(180c), 155(180c), 156(180c), 157(180c), 159(180c), 160(180c), 171(180c), 175(180c), 176(180c), 177(180c), 183
 Strong, M. I., 318(199), 351
 Studier, M. R., 293(313), 314
 Sturdivant, J. H., 291(321), 314
 Sudgen, T. M., 171(101, 102), 175(101, 102), 180
 Sujishi, S., 143(176), 144(65), 145(65, 175, 176, 177), 147(175, 176), 150(175, 176), 152(65, 65b, 176, 177), 155(176), 179, 182
 Summers, L., 146(116a), 177(116a), 181
 Sump, C. H., 101(109), 129
 Sundermeyer, W., 135(178, 179a, 180), 138(178, 179a, 180), 145(179), 153(179), 155(179), 156(179), 168(179), 175(179), 176(179), 182
 Sustmann, R., 135(204, 205, 206), 138(204, 205, 206), 141(204, 206), 183
 Susz, B. P., 241(50, 314), 308, 314
 Suttle, J. F., 45, 80, 248(234), 312
 Sutton, G. J., 237(315), 314
 Suvorov, A. V., 317(259), 319(258), 322(259), 353
 Suzuki, T., 31, 77, 103(103), 114(103), 129
 Svec, H. J., 296(103), 309
 Swaminathan, K., 203(12), 204(12), 213
 Swart, K. H., 254(160), 310
 Swarup, R., 324(232), 329(232), 352
 Swezey, F. H., 133(40a), 179
 Swink, L. N., 190(93), 215
 Symons, M. C. R., 276(8), 278(7), 307
 Synge, R. L. M., 64, 76
 Szustorowicz, E. M., 318(277), 353

T

Tait, M. J., 223(70), 280(70), 308
 Takahashi, K., 201(75), 207(75), 215
 Takaki, H., 117(66), 123(66), 128
 Takei, W. J., 106(158), 107(167, 168), 114, 118(167, 168), 119(168), 131
 Talaat, M. Y. A., 325(16), 347
 Tandon, S. K., 153(173), 157(173), 168(173), 177(173), 182
 Tang, P., 48(294), 49(294), 80
 Tanner, K. N., 317(278), 353
 Tarsey, H. R., 324(152), 350
 Tate, D. P., 340(279, 280), 353, 354
 Taube, M., 26(270), 66, 71, 79
 Taylor, R., 171(62), 175(62), 179
 Tchugaev, L., 188(94), 215
 Telbe, T., 236(269), 313
 Temme, T., 210(59), 215
 Terao, N., 87(169, 170), 94(169, 170), 120(171), 181
 Tesi, G., 162(180a), 183
 Testa, C., 59, 60(40), 61(41), 63, 64(38), 73, 79
 Thayer, J. S., 134(180b), 135(180c, 181, 182, 196), 136(180c, 181, 182), 138(181, 182, 196), 139(180c), 141(181, 183, 196), 155(180c), 156(180c), 157(180c), 159(180c), 160(180c), 171(180c), 175(180c), 176(180c), 177(180c), 183
 Thielert, H., 212(80), 215
 Thomas, A. B., 240(316), 314
 Thomas, R. M., 153(194a), 156(194a), 183
 Thompson, D. T., 341(50), 348
 Thompson, R., 257(3), 307
 Thompson, R. C., 287(18, 317), 307, 314
 Thompson, U. B., 285(259), 312
 Thornton, D. A., 341(51), 348
 Tickner, A. W., 225(170), 280(170), 310
 Tilley, B. P., 154(47a), 165(47a), 179
 Timoshev, V. G., 70(248), 78
 Tobe, M. L., 240(64), 308, 343(66), 348
 Todd, A. R., 29(151), 76
 Todd, L. J., 137(117), 181
 Tolgyesi, W. S., 240(231), 312
 Tomasewski, A. J., 140(99), 180
 Tomita, K., 207(32), 214
 Tomkins, I. B., 319(64, 65), 323(65), 348
 Tong, S. Y., 120(164), 131

Toropova, N. K., 318(168), 351
 Townes, C. H., 171(54), 179
 Treadwell, W. D., 332(15), 333(15), 347
 Treichel, P. M., 342(281), 354
 Treybal, R. E., 3, 22(273, 274, 276, 277), 79
 Tribalat, S., 293(318), 314
 Triulzi, C., 61(41), 73
 Truter, M. R., 261(319), 314
 Tsuchida, T., 117(66), 123(66), 128
 Tsukuechi, K., 55(130), 71(130, 131), 75
 Tuck, D. G., 2, 3(59), 25, 71, 73, 167 (141a), 175(141a), 181
 Turner, A. C., 149(165), 182
 Turner, H. S., 135(185, 185a), 137(185, 185a), 155(185, 185a), 167(184, 185a), 174(184, 185, 185a), 183
 Tyree, S. Y., 325(76), 326(76), 327(76, 147), 329(76), 348, 350

U

Ubbelohde, A. R., 306(320), 314
 Ueno, K., 71(131), 75
 Ugi, I., 135(100), 137(100), 180
 Ugo, R., 212(42a), 214
 Uhlenbrauck, H., 135(36), 142(36), 178
 Umezawa, H., 28, 79
 Underhill, A. E., 240(144), 310
 Unrein, P. J., 70, 73
 Urenovitch, J. V., 143(48), 145(48, 187), 147(48), 152(187), 153(186), 155(186), 160(186), 179, 183
 Urry, G., 135(47), 138(47), 141(47), 143 (105), 145(105), 179, 180

V

van Arkel, A. E., 96(171a), 131
 van Bommel, A. J., 186(11), 213
 van der Kerk, G. J. N., 136(123), 138(123), 139(123), 141(123), 142(123a), 145 (189), 146(188), 148(188), 146(124), 148(124), 151(124), 181, 183
 van Oosterhout, G. W., 317(159, 160), 350
 Varga, L. P., 70, 79
 Vasil'ev, V. P., 298(340), 314
 Vasilkova, N. V., 317(259), 322(259, 260), 353
 Vasta, J. A., 146(28), 148(28), 153(28), 157(28), 169(28), 177(28), 178

Vaughan, P. A., 291(321), 304(58, 221), 308, 311, 314, 321(42), 348
 Vaughan, W. R., 238(33), 307
 Vdovenko, V. M., 54, 55, 79
 Verbane, J. J., 162(28a), 178
 Verhoek, F. H., 87(78), 94(78), 129
 Verijn-Stuart, A. A., 285(71), 308
 Verkhoglyadova, T. S., 101(149), 102 (149), 125(150), 131
 Verstegen, J. M. P. J., 54, 79
 Verzele, M., 3, 79
 Vidale, G. L., 250(78), 308
 Vink, H., 64, 79
 Visser, J. N., 248(132), 309
 Vogel, R. C., 269(310), 313
 Vogl, J., 336(25), 339(25), 347
 Volkova, A. A., 70(248), 78
 Volpe, M., 333(7), 334(7), 347
 v. Hobe, D., 340(276), 353
 Von Grosse, A., 135(109b), 181
 Vonk, C. G., 219(322), 276(322), 314
 von Metzsch, F. A., 2, 79
 Voronkov, M. G., 172(190), 175(190), 176 (190), 183

W

Wada, M., 172(190a, 190b), 183
 Waddington, T. C., 222(241), 245(324), 246(323), 250(324), 255(323), 266 (323), 278(72), 286(323), 308, 312, 314
 Wade, K., 237(130), 309
 Wagenknecht, F., 86(87), 89(87), 90(87), 101(87), 129
 Waggener, W. C., 70, 79
 Wagner, R. I., 142(191), 144(191), 155 (191), 167(191), 174(191), 183
 Wailes, P. C., 344(263), 353
 Wain, H. L., 101(172), 131
 Waind, G. M., 26(110), 74
 Walker, W. R., 68, 79
 Wallassie, N. H., 256(292), 313
 Walrafen, G. E., 283(343), 314
 Walti, A., 155(209), 163(209), 183
 Walton, R. A., 325(39, 40), 326(40), 348
 Wannagat, U., 153(192), 155(148), 156 (149, 192), 158(148), 160(192), 164 (149, 193), 173(193), 182, 183
 Ward, M., 24(289), 79
 Wardlaw, W., 332(44), 348
 Warf, J. C., 26, 80

- Warne, R. J., 135(185, 185a), 137(185, 185a), 155(185, 185a), 167(184, 185a), 174(184, 185, 185a), 183
 Warren, C. G., 45, 80
 Wasem, K., 257(291), 313
 Waser, J., 331(283), 346(283), 354
 Washburn, R. M., 141(194), 183
 Watanabe, K., 31(139), 71(131, 140), 75
 Waters, J. H., 344(282), 354
 Watson, H. R., 339(53), 340(52)
 Watson, W. H., 331(283), 346(283), 348, 354
 Watt, G. W., 94(173), 97(173), 131
 Weaver, B. S., 52(18), 53(18), 54(18), 54(160), 71(116), 72, 75, 76
 Weaver, C. W., 101(174), 131
 Weber, H. H., 126(91), 129
 Weber, R., 339(26), 347
 Webster, M., 228(24), 245(325), 253(24), 307, 314
 Weeg, E., 324(253), 353
 Wei, Y. K., 204(6), 213
 Weidlein, J., 253(75), 308
 Weiss, J., 267(326), 314, 324(209), 352
 Weiss, K., 135(143a), 181
 Weiss, W., 319(108), 349
 Weisse, G. K., 153(194a), 155(194a), 156(194a), 183
 Weissmann, S. I., 333(284), 354
 Welch, F. E., 239(197), 311
 Welch, G. A., 24(289), 79
 Welker, J. P., 333(7), 334(7), 347
 Wells, A. F., 275(327), 296(328), 314, 318(285), 354
 Wentworth, R. A. D., 196(95), 215
 Werner, A., 146(195), 183, 201, 215
 Werner, H., 316(98), 343(98), 349
 Wersin, G., 172(159, 160), 176(159, 160), 182
 Wessel, G. J., 346(286), 354
 West, R., 135(80a, 181, 182, 196), 136(181, 182), 138(181, 182, 196), 141(80a, 181, 183, 196), 157(82), 180, 183
 West, R. C., 144(98a), 180
 West, T. S., 3(19), 72
 Westall, R. G., 60(15), 72
 Westphal, R. C., 101(175), 131
 White, J. C., 28(292), 41(24), 42(24), 44(24), 65(24), 72, 80
 White, J. G., 106, 130
 White, J. M., 48, 49, 70, 80
 Whitney, E. D., 259(329), 314
 Whyman, R., 319(177), 323(177), 324(177), 341(176), 342(176), 343(176), 351
 Whynes, A. L., 229(237), 255(237), 312
 Wiberg, E., 135(197, 199, 200, 201, 202, 203, 204, 205, 206, 207), 136(199), 137(197, 200), 138(199, 201, 202, 202a, 203, 204, 205, 206), 139(203), 140(198), 141(203, 204, 206, 208), 183
 Wicks, C. E., 317(287), 322(287), 323(287), 354
 Widmaier, I., 155(89), 156(89), 160(89), 175(89), 180
 Wiebenga, E. H., 219(322), 276(322), 314
 Wiener, G. W., 87(176), 106(176), 119(176), 131
 Wihksne, K. Y., 167(93), 168(93), 171(93), 174(93), 175(93), 176(93), 177(93), 180
 Wilhite, R. N., 70(57), 73
 Wilkins, J. W., 31(129), 75
 Wilkins, R. G., 224(312), 313
 Wilkinson, G., 186(21, 43), 194(21, 43), 199(43), 200(43), 214, 316(289), 339(69, 289), 342(34, 184, 226, 288), 343(189, 198), 344(71, 123, 126), 347, 348, 350, 351, 352, 354
 Wilkinson, G. R., 171(62), 175(62), 179
 Williams, R., 344(282), 354
 Williams, R. E., 71(300), 80
 Williams, R. G., 327(9), 328(9), 329(9), 330(9), 347
 Williams, R. J. P., 2, 75, 337(196, 197), 351
 Willis, H. A., 222(112), 309
 Willis, H. H., 64(52), 73
 Wilson, A. M., 55, 80
 Wilson, A. S., 51, 52(143), 54, 76, 80
 Wilson, C. L., 3(19), 72
 Wilson, F. C., 342(290), 345(290), 354
 Wilson, J. C., 155(209), 163(209), 183
 Winchester, J. W., 61, 80
 Winkler, H., 210(60), 215
 Wilkins, R. G., 187(58), 215
 Witte, P., 319(148), 350
 Wittig, G., 142(210, 211), 144(210, 211, 212), 150(210), 183
 Wöhler, F., 122, 131
 Wohrle, H., 322(254), 353

Wojcicki, A., 337(291), 354
 Wold, A., 104(178), 106(178), 119(45), 120
 (5, 45), 127, 128, 131
 Woldbye, F., 195(97), 215
 Wollan, E. O., 106(161), 131
 Woodgate, P. R., 26(22), 72
 Woodward, L. A., 171(62), 175(62), 179,
 250(330), 314
 Woolf, A. A., 242(333), 243(333), 252
 (338), 255(331), 258(331), 259(337),
 268(16), 269(336), 273(331), 275(332),
 277(334), 285(335), 307, 314, 318(79),
 323(79), 349
 Wright, B., 239(95), 309
 Wuhrmann, J. J., 241(314), 314
 Wyart, J., 95(47), 107(47), 123
 Wyatt, P. A. H., 220, 282(339), 314
 Wynne-Jones, W. F. K., 223(70), 280(70),
 308

Y

Yagodin, G. A., 29(299), 80
 Yamagishi, H., 112, 129
 Yasuoka, H., 106(4), 127
 Yates, P. C., 71, 80
 Yatsimirskii, K. B., 298(340), 314
 Yoffe, A. D., 135(213), 183
 Yong, Ae Im, 203(12), 204(12), 213
 Yoo, S. J., 335(166), 351
 Yoon, Y. K., 280(341), 314
 Yoshida, H., 31, 80
 Young, A. R., 263(342), 267(342), 314
 Young, F. E., 98(160), 131
 Young, R. C., 320(293), 324(292), 331
 (172, 292), 332(292), 351, 354
 Young, T. F., 283(343), 314
 Yousef, Y. L., 104(179), 131

Z

Zafonte, B. P., 145(85), 150(85), 180
 Zakharova, M. Y., 342(208), 352
 Zalkin, A., 319(245), 352
 Zangen, M., 66, 80
 Zaslow, B., 251(344), 314
 Zebroski, E. L., 27(304), 70, 80
 Zeiger, H. J., 171(54), 179
 Zeilenga, G. R., 279(62), 308
 Zelesny, W. F., 248(345), 276(345), 314
 Zeller, E. E., 297(247), 312
 Zhdanov, Y. F., 55, 78
 Zhinkin, D. Y., 155(214), 158(214), 183
 Zifferero, M., 54(14), 72
 Zimmer, H., 146(215), 148(215), 151(215),
 183
 Zimmerman, R., 291(203), 311, 321(183),
 351
 Zingaro, R. A., 28, 36(13), 72, 80
 Zolotov, Y. A., 26(4), 72, 72
 Zozulya, A. P., 71, 80
 Zuur, A. P., 226(133), 309
 Zwickel, A., 237, 309
 Zwicker, U., 91(180), 101(180), 131

SUBJECT INDEX

A

- Acylium cation, 231, 241-243
- Alamine 336, in liquid-liquid extraction, 55
- D*-Alanine, coordination compounds, 206-207, 208, 209-210, 211, 213
- Alkali fluorides, ionization, 297
- Alkali halides, ionization, 297
- Aluminum, heterocations of, 236-237
- Aluminum azides, preparation, 137-138
 - properties, 135, 139, 140
- Aluminum chloride, ionization, 297-298, 303-304
- Aluminum cyanides, preparation, 143
 - properties, 144, 150
 - structure, 149
- Aluminum isothiocyanate, properties, 175
- Amine oxides, liquid-liquid extraction, 49-56
- Amines, liquid-liquid extraction using, 49-56
- Amino acid complexes, 204-211
- Amino alcohol complexes, 211
- Antiferromagnetism, in transition metal nitrides, 104-105
- Antimony cations, trivalent, 254
- Arsenic cations, trivalent, 251-252
- Arsonium cations, 250-251
- Arylium cations, 231, 241-243
- Aspartic acid, coordination complexes, 208-209, 210
- Azides, organometallic, 134-142
 - preparation, 136-139
 - properties, 135-136, 139-142
- Azidoborazocines, preparation, 137
- Azidochlorostannane, preparation, 138
- B*-Azido-*B'*,*B''*-dichloroborazines, preparation, 137
- Azidosilanes, preparation, 138
 - properties, 140-141

B

- Beryllium, solution, ionization, 305
- Beryllium oxide, ionization, 295-296
- Bis(di-*n*-hexyl phosphinyl)methane (HDPM), in liquid-liquid extraction, 33

- Bis(hexoxy-ethyl)phosphonic acid, in liquid-liquid extraction, 41
- Bishydroxymethylenecamphorpropylenediamine, 212
- Bismuth solutions, ionization, 304
- Boron, heterocations of, 231, 233-236
- Boron azides, preparation, 137
 - properties, 135, 139
- Boron cyanides, preparation, 143
 - properties, 144, 151, 152
 - structure, 149
- Boron isocyanates, preparation, 153, 157
 - properties, 154, 162, 163, 165
- Boron isothiocyanates, preparation, 166-167, 170
 - properties, 172, 174-175
 - structure, 170

C

- Carbidenitrides, transition metal, 122-125
- Carbon tetrachloride, ionization, 230-231
- Carbonium ions, 237-241
- Carbonylcyan tungsten complexes, 335-336
- Cations, generation of, 224-230
 - in the gas phase, 224-225
 - in the solid phase, 229-230
 - in solution, 225-229
 - with metal-carbon and metal-metal bonding, 287-292
 - of nontransition elements, 233-279
- Cermets, nitrides in, 81-82
- Chloryl ion, 277
- Chromium nitrides, 81, 88
 - bonding in, 113-114
 - properties, 99, 101
 - structural data, 86
- Chromyl halides, ionization, 296-297
- Cobalt nitrides, 94
 - properties, 100
 - structural data, 87
- Coordination compounds, stereoselectivity, 185-215
 - of amino acids, 204-211
 - Cotton effect, 186
 - of diamines, 188-204
 - nomenclature, 186-187

- Copper nitride, 94
 properties, 102
 structural data, 87
Cotton effect, 186
Countercurrent extraction of metal ions, 15-22
Cuprous chlorides, ionization, 297
Cyanides, organometallic, 142-152
 preparation, 142-148
 properties, 144-146, 150-152
 structures, 149-150
Cyanotungstates(II and III), 335
trans-1,2-Cyclopentanediamine complexes, 192-193, 196-199

D

- Dialkyl alkyl phosphonates, in liquid-liquid extraction, 29
Diamines, coordination complexes, 188-204
 conformational theory, 189-191
1,2-Diaminetetraacetic acid, as liquids in complexes, 203-204
Diaminotetracarboxylatocobaltates, circular dichroisms, 205
Dibutyl phosphonic acid (HDBP), in liquid-liquid extraction, 34-35, 36-37
Di-2-ethyl hexyl phosphoric acid (HDEHP), in liquid-liquid extraction, 36, 38, 39, 40, 41, 59-63
Difluorohalogen(III) cations, 267-274
Dimesitylazidoborane, preparation, 137
Dimethyldiazidosilane, preparation, 138
Dinonyl naphthalene sulfonic acid, in liquid-liquid extraction, 48
Di-*n*-octyl phosphinic acid, in liquid extraction, 40
Diol complexes, 211
Di[*p*-(1,1,3,3-tetramethyl butyl)phenyl]-phosphoric acid (HDO_4P), in liquid-liquid extraction, 37, 39, 40
Dodecyl benzene sulfonic acid, in liquid-liquid extraction, 49

E

- Ethylenediamine complexes, 192
2-Ethyl hexyl hydrogen chloromethyl phosphonate, in liquid-liquid extraction, 40

- 2-Ethyl hexyl hydrogen 2-ethyl hexyl phosphonate, in liquid-liquid extraction, 40
2-Ethyl hexyl hydrogen phenyl phosphonate, in liquid-liquid extraction, 40
Europium, liquid-liquid extraction, 14

F

- Ferredoxin, 213
Ferric chloride, ionization, 227-228
Ferrimagnetism, in transition metal nitrides, 107-108
Ferrocene, bonding of, 287
Ferromagnetism, in transition metal nitrides, 105-106
Formylium cation, 231

G

- Gallium, heterocations of, 237
Gallium azide, preparation, 138
 properties, 135
Gallium cyanides, preparation, 143
 properties, 144, 159
Germanium azides, preparation, 138
 properties, 135-136, 139, 141
Germanium cyanides, preparation, 147-148
 properties, 145-146, 152
 structure, 150
Germanium isocyanates, preparation, 153, 158
 properties, 156-157, 163, 165
Germanium isothiocyanate, preparation, 167-168, 169
Glycine, coordination compounds of, 206-207
L-Glutamic acid, coordination compounds of, 207, 210, 211

H

- Hafnium halides, ionization, 304-305
Halide, ionization, 297
Heterocations, 217-314
 in aqueous solution, 298-305
 hydrolytic equilibria, 300-303
 ion pairing in, 298-300
 structures in solution, 303-305
 classification, 230-233
 Periodic Table and, 230

- proton in, 279-287
 in aqueous solutions, 279-282
 in fluorosulfuric acid, 287
 in hydrogen chloride, 286
 in hydrogen fluoride, 283-286
 in sulfuric acid, 282-283
 (See also Cations, Ions)
Hexahalogenotungstates, magnetic properties, 326
"Hochofenwürfel," 122-123
Hydrazoic acid, 134
Hydronium ion, 279-282
Hydroxonium ion, 279-282
- I**
- Indium cyanides, preparation, 143
 properties, 144, 150
 structure, 149
Indium isothiocyanates, preparation, 167
 properties, 175
Iodine pentafluoride, ionization, 274-275
Iodonium cations, 276
Ions, definition, 218-219
 in gas phase, 292-298
 recognition of, 219-224
 by colligative behavior, 223
 by interaction with radiation, 220-223
 by ion transport, 219-220
 by kinetic behavior, 223-224
 (See also Cations, Heterocations)
Iron carbidinitrides, 123-125
Iron nitrides, 81, 90, 91-94
 bonding in, 114
 properties, 99-100
 structural data, 87
Isocyanates, organometallic, 152-165
 preparation, 152-159
 properties, 154-157, 160-165
 reaction with alcohols and amines, 162
 structures, 159-160
Isocyanides, organometallic, 142-152
 preparation, 142-148
 properties, 144-146, 150-152
 structures, 149-150
Isothiocyanates, organometallic, preparation, 165-177
 properties, 172-177
 reaction with alcohols and amines, 162
 structures, 170-171

L

- Lanthanides, countercurrent extraction of, 20-21
Lead azides, preparation, 138, 139
 properties, 136, 139
Lead cyanides, preparation, 148
 properties, 146
Lead isocyanates, preparation, 158
 properties, 157
Lead isothiocyanates, properties, 177
L-Leucine, coordination compounds, 206-207
Liquid-liquid extraction of metal ions, 1-80
 with acidic P-based extractants, 34-48
 dinuclear, 47-48
 mononuclear, 34-47
 with amines and amine oxides, 49-56
 complexes in, 68-71
 "countercurrent extraction" method, 15-25
 multiple type, 7-25
 with neutral P-based extractants, 25-33
 dinuclear, 32-34
 mononuclear, 25-32
 organic extractant vs. fused salt, 56-57
 by partition chromatography, 57-64
 "push-through" method, 8-15, 23-25
 single-stage, 4-7
 synergism and antisnergism in, 64-68
 with sulfonic acids, 48-49
Lithium cyanides, preparation, 142
Lithium isothiocyanates, preparation, 166

M

- Manganese carbidinitrides, 123
Manganese nitrides, 81, 88-91
 bonding in, 114-116
 properties, 99, 100
 structural data, 86, 87
Mesidine, 137
Metal ions, liquid-liquid extraction of, 1-80
Molybdenum chloride, heterocations of, 290, 291
Molybdenum trioxide, ions from, 295
Monobutyl phosphoric acid (H_2MBP), in liquid-liquid extraction, 34

Mono-2-ethyl hexyl phosphoric acid, in
liquid-liquid extraction, 44-47

N

Neptunium, liquid-liquid extraction, 13

Nickel nitride, 94

properties, 100

structural data, 87

Niobium halides, heterocations, bonding
in, 290-291

Nitride halides, transition metal, 126-127

Nitride oxides, transition metal, 125

Nitrides, of transition metals, *see* Transi-
tion metal nitrides

Nitrogen, heterocations of, 232

Nitrogen dioxide, ionization, 225

Nitronium cations, 243, 254, 259-262
preparation, 226

Nitronium complex fluorides, 260

Nitronium perchlorate, preparation, 229

Nitronium tetrafluoroaurate, preparation,
230

Nitrosonium cations, 243, 254-259

Nitrosonium salts, preparation, 229

Nitrosyl chloride, adducts of, 255

Nitrosyl fluoride, adducts of, 255, 256

Nitrosyl oxyacid salts, 257

O

Octacyanotungstates, 332-335

Oxygenyl ion, preparation of, 229

Oxyhalogeno cations, 276-279

Oxyiodonium cations, 277

Oxyselenium cations, 266-267

Oxysulfur cations, 266-267

P

Palladium, liquid-liquid extraction, 11, 29

Paramagnetism, in transition metal ni-
trides, 104

Partition chromatography, in metal sep-
aration, 57-64

Phenylazidosilanes, properties, 141

Phosphonium cations, 243-250
halogenated, 243-249

Phosphorus, heterocations of, 231-233

Platinum heterocations, 262-263

Propylenediamine complexes, 185-189

Proton, in heterocations, 279-287

Pseudohalides, 133-183

definition, 133-134

"Push-through" method of liquid-liquid
extraction, 8-15

Pyridine-azidodiphenylborane, prepara-
tion, 137

properties, 139-140

S

Scandium nitride, 85

properties, 100, 102

structural data, 86

Selenium cations, 265

Selenium oxycations, 232

Silicon, ions involving, 231

Silicon azides, properties, 135, 141

Silicon cyanides, preparation, 143, 147,
148

properties, 144-145, 151, 152

structure, 149

Silicon isocyanates, preparation, 153, 158-
159

properties, 155-156, 162, 163-165

Silicon isothiocyanates, preparation, 168,
170

properties, 172, 175-176

structures, 171

Stereoselectivity, of coordination com-
pounds, 185-215

Stibonium, cations, 253-254

Sulfonic acids, in liquid-liquid extraction,
48-49

Sulfur cations, 263

halogen, 264-266

Sulfur oxycations, 232

T

Tantalum halides, heterocations of, bond-
ing, 290-291

Tantalum pentoxide, ions of, 296

Tellurium cations, 265

Tetraazidosilane, properties, 139

Tetra-*n*-butyl ethylene diphosphonate
(TBEDP), in liquid-liquid extrac-
tion, 32

Tetrachlorostibonium ion, preparation,
228

Thallium, heterocations of, 237

Thallium azide, properties, 135

- Thallium cyanides, preparation, 143
 properties, 144-145
 structure, 149
Thallium isothiocyanates, preparation, 167
 properties, 175
Thenoyltrifluoroacetone, in liquid-liquid extraction, 64-68
Thorium, liquid-liquid extraction of, 11
Tin azides, preparation, 138
 properties, 136, 139
Tin cyanides, preparation, 148
 properties, 146, 151
 structure, 150
Tin isocyanates, preparation, 157
 properties, 162
Tin isothiocyanates, preparation, 168
 properties, 177
"Tiron," 70
Titanium carbidenitride, 123
Titanium dioxide, ions from, 296
Titanium nitride halides, 126-127
Titanium nitrides, 81, 85, 86, 88
 properties, 98-99, 102
 structural data, 86
Transition metal nitrides, 81-131
 binary compounds, 82-116
 phases, 82-94
 bonding in 108-116
 band model, 111-117
 covalent model, 108-111
 carbidenitrides, 122-125
 chemical properties, 98-100
 color of, 102-103
 electrical and optical properties, 102-103
 Hall coefficients, 102
 magnetic properties, 103-108
 mechanical properties, 100-102
 nitride halides, 126-127
 perovskite-type, 83, 84, 118, 124
 bonding in, 114
 preparation, 94-97
 growth processes, 96-97
 melting, 97
 nitriding of metallic compounds, 95-96
 nitriding of metals, 94-95
 solid-state reactions, 97
 thermal decomposition, 97
 properties, 98-99
 sodium chloride type, 83, 116-118
 superconductivity in, 102
 ternary compounds, 116-127
 phases, 116-125
 polar, 125-127
 thermal properties, 98-100
 X-ray emission spectra, 103
Transition metals, heats of atomization, 346
Triazidoborane, preparation, 136-137
Tribenzylamine, in liquid-liquid extraction, 50
Tributyl phosphate (TBP), in liquid-liquid extraction, 26, 30-31, 56, 57-59, 64-65, 70
Trichlorocarbonium cation, preparation, 230-231
Trifluorosulfonium salts, preparation, 229
Triisooctylamine, in liquid-liquid extraction, 50-51, 52, 54
Triisooctyl thiophosphate (TOTP), in liquid-liquid extraction, 30
Trilaurylamine, in liquid-liquid extraction, 51-52
Trimethylazidosilane, preparation, 138
Tri-*n*-octylamine, in liquid-liquid extraction, 51, 63-64
Tri-*n*-octylphosphine oxide (TOPO), in liquid-liquid extraction, 28-29
Trisethylenediaminecobalt, stereoselectivity of, 187-188
Trityl cation, 238-239
Tungsten, aromatic and carbonyl compounds of, 338-344
 chemistry of, 315-354
 cyano complexes of, 332-336
 dithiolates, 344
 halides and oxyhalides, 316-325
 complexes of, 324-332
 electronic spectra, 327
 infrared data, 323
 magnetic properties, 328, 330
 properties, 317
 thermodynamics, 322, 325
 tungsten(II), 331-332
 tungsten(III), 331
 tungsten(IV), 320, 329-330

tungsten(V), 319-320, 325-329
tungsten(VI), 316-319, 325
metal-metal bond formation, 345-346
oxalates, 345
oxides and tungstates of, 337-338
phenyl derivatives, 345
thiocyanate complexes of, 336-337
Tungsten oxide, ionization, 295-296
Tungsten trioxide, ionization, 295

U

Uranium, liquid-liquid extraction, 11
Uranyl ion, hydrolysis of, 301-302
structures in solution, 303

V

Vanadium carbide nitrides, 123
Vanadium nitrides, 88
properties, 99, 100-101
structural data, 86
Vanadium pentoxide, ionization, 296

W

Water, ionization, 225

Z

Zirconium halides, ionization, 304-305