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THE HALIDES OF BORON

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I. Introduction

It is now almost 150 years since Gay-Lussac and Thenard first isolated ammonia-boron trifluoride, H_3NBF_3 , and so initiated a study of the boron halides. Since that time, notably during the past 30 or so years, a tremendous volume of research has been carried out on the halides, ranging from their use in syntheses of hydrides and borohydrides required for rocketry and wartime atomic energy projects (279, 534) to the very extensive use of boron trifluoride as a catalyst in the petroleum industry, polymer production, and organic chemistry generally (817). This review will be concerned only with the chemistry of the boron halides, and will neglect studies of their catalytic activity and of their more physical properties except where the latter (e.g., structural studies) have a direct bearing on the chemistry.

Nomenclature is always a headache and never more so than in boron chemistry; thus B_2Cl_4 might be more correctly called tetrachloro-diborane-4, but few chemists would immediately recognize this as

diboron tetrachloride. For this reason I have elected to call compounds by what appears to be their most frequently used literature-name and so, while BCl_3 is boron trichloride, BMe_3 is written as trimethylborane; similarly diboron tetrachloride is used for B_2Cl_4 , whereas $\text{B}_2(\text{OMe})_4$ is called tetramethoxydiboron (97).

The review deals first with the preparation and molecular structures of the boron halides, and then an account is given of their main chemical

TABLE I
THE HALIDES OF BORON^a

B_nX_m	X = F	X = Cl	X = Br	X = I
BX_3	BF_3	BCl_3	BBr_3	BI_3
B_2X_4	B_2F_4	B_2Cl_4	B_2Br_4	B_2I_4
B_4X_4	—	B_4Cl_4	—	—
B_8X_8	—	B_8Cl_8	—	—
B_9X_9	—	B_9Cl_9	—	—
$\text{B}_{11}\text{X}_{11}$	—	$\text{B}_{11}\text{Cl}_{11}$	—	—
$\text{B}_{12}\text{X}_{11}$	—	$\text{B}_{12}\text{Cl}_{11}$	—	—
B_nX_n	$*(\text{BF})_x$	$(\text{BCl})_x$	$(\text{BBr})_x$	$(\text{BI})_x$
B_nX_m	B_3F_5	$*\text{BCl}_{0.6}$	$*\text{BBr}_{0.2}$	$*\text{BI}_{0.4}$
	B_8F_{12}		$*\text{BBr}_{0.4}$	
BX	BF	BCl	BBr	BI

^a x, y = unknown. Compounds marked with asterisk are known to be involatile in high vacuum. " $\text{B}_{11}\text{Cl}_{11}$ " and " $\text{B}_{12}\text{Cl}_{11}$ " appear, from their physical properties, to be the same compound, but it is not perfectly clear which formula is the correct one (see text).

properties; by far the most research has been carried out on the trihalides and, while attempting to cover the maximum number of references in the minimum of space, some have obviously had to be left out or given under a collective review reference. Table I lists by formulas the boron halides known to date (1966). As these compounds are all water-sensitive and one or two ignite spontaneously in air, they are best handled in a glass high-vacuum apparatus, preferably out of contact with hydrocarbon- or silicone-based stopcock lubricants. Most constructional metals appear to be unaffected by the halides at reasonable temperatures; although data are mainly lacking for the action of the halides on polymeric materials, a careful study on boron trifluoride (421) shows it

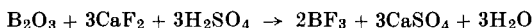
to be without action on Teflon, polystyrene, Araldite, and pure polyvinylchloride up to at least 80°, whereas rubber tubing, phenol-formaldehyde resins, Nylon, cellulose, and commercial polyvinylchloride are readily attacked.

The literature has been covered up to June 1966. [The reader is referred to Martin *et al.* (82, 330, 528, 817) for earlier accounts of the chemistry of boron trifluoride, Lappert *et al.* (288, 476, 528) for chemistry involving the other boron trihalides, and Holliday and Massey (410) for a discussion of the diboron tetrahalides. General articles in which the boron halides are frequently mentioned are to be found in references (187, 280, 378, 621, 793).]

II. Preparation of the Boron Halides

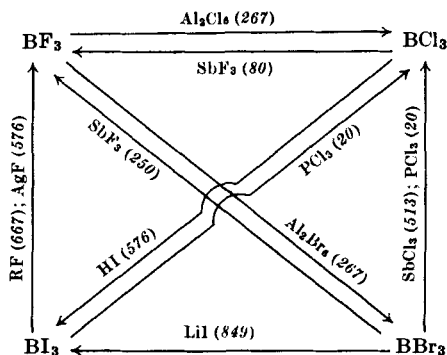
A. BORON TRIHALIDES

The trifluoride (430, 868), trichloride (250, 265), tribromide (849), and triiodide (549) can be prepared by treating elemental boron with the appropriate halogen. A better method for the trifluoride is to heat a mixture of fluospar, concentrated sulfuric acid, and boric oxide (86),



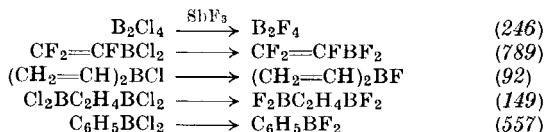
while the triiodide is formed in good yield by refluxing sodium borohydride and iodine in either hexane or benzene (452, 757).

Having obtained one boron trihalide it is possible to make the others from it by various halogen-exchange processes, of which the following are typical:

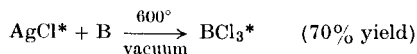


While these reactions are normally of little value to the preparative chemist (all four halides are now available commercially), they can be employed in making an isotopically labeled trihalide, e.g., $^{10}\text{BCl}_3$ from

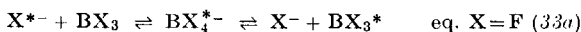
an available sample of $^{10}\text{BF}_3$ (439, 499, 506). Also, since some of the halogen-interchange reactions appear to be quite general in scope they can be of help in synthesizing new boron compounds, as in the fluorinations carried out with antimony trifluoride¹:



Sometimes it is necessary to prepare a boron trihalide labeled with radioactive halogen atoms for use in tracer experiments. Special synthetic methods can be devised, such as heating silver chloride with boron (504)



but exchange of halogen atoms between a suitable reagent and a boron trihalide is more convenient. Tetramethylammonium chloride, containing radioactive chlorine, exchanges rapidly with boron trichloride and this has been used to prepare specimens of the labeled trichloride (392-394); the method should be applicable to other trihalides:

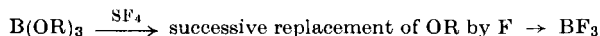


The rapid exchange between free bromine and boron tribromide (238) could also make a useful route to the labeled tribromide.

B. DIBORON TETRAHALIDES

Stock made the first compound of this series, diboron tetrachloride, in low yield (ca. 1%) by striking an arc between zinc electrodes immersed in liquid boron trichloride; the product contained about 12% of silicon tetrachloride impurity (800). Subsequently it was found better to carry out the reduction of the trichloride in the gaseous phase using an electrical discharge between either mercury (406, 545, 718, 751, 826, 843) or copper (845) electrodes, and about 1 mmole/hr can now be obtained relatively easily. Exact details of the synthesis can be found in references (545, 845); care has to be taken in the construction of the cell so that the hot discharge does not touch the glass walls at any point, otherwise silicon is etched away and contaminates the diboron tetrachloride with SiCl_4 , Si_2Cl_6 , Si_3Cl_8 , and $\text{Cl}_3\text{SiOSiCl}_3$ (535, 542).

¹ The stepwise fluorination of alkoxyboron compounds by sulfur tetrafluoride should also prove to be an extremely useful synthetic technique, e.g. (210):

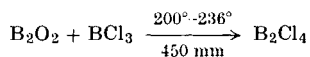


When boron trichloride vapor at 1–2 mm pressure is passed through a resonance cavity operating in the microwave region of the spectrum, a glow discharge is set up in the vapor and diboron tetrachloride is formed (256):

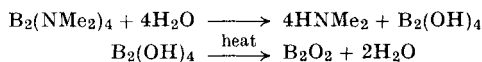


Since chlorine reacts with diboron tetrachloride (18), it must be removed rapidly by fractionation; the method is useful when small intermittent supplies of diboron tetrachloride are required, and can be made more efficient by passing the effluent gases from the cavity through a plug of copper wool that reacts with and removes the chlorine (88). The spectra of discharges through boron trichloride vapor have been shown to contain lines due only to BCl (419, 691), and it is thought that BCl, not BCl_2 , may actually be an intermediate in the preparation of diboron tetrachloride (419, 546).

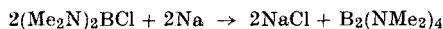
It is possible to make diboron tetrachloride without resorting to the use of electrical discharges. The simplest method in theory is to pass boron trichloride over boron at 1000°C but, in practice, attack of the reaction vessel at these temperatures makes the method very difficult to operate (633). When boron trichloride is passed over heated boron monoxide a 13% yield of diboron tetrachloride is obtained (552, 553):



The boron monoxide (which has a structure involving boron-to-boron bonds, eq. 626) can be made either by heating boric oxide with boron (425, 436, 744) or by first hydrolyzing tetrakis(dimethylamino)diboron carefully at low temperature (647) and then dehydrating the sub-boric acid so formed (841, 842):

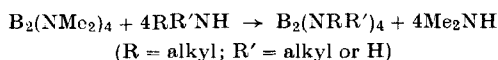


Tetrakis(dimethylamino)diboron is the only diboron compound commercially available, being prepared on a large scale by treating bis(dimethylamino)boron chloride or bromide with highly dispersed sodium (96, 647):

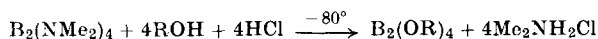


Much effort has been expended in trying to convert the rather unreactive tetrakis(dimethylamino)diboron to more useful diboron reagents. Transamination, which may involve some rupture of the boron-

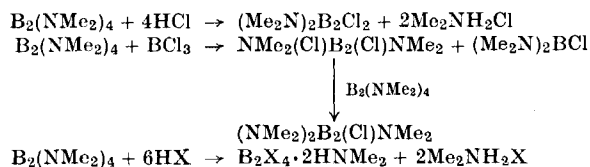
boron bond (650), takes place with primary and secondary amines (15, 96, 121, 638, 650),



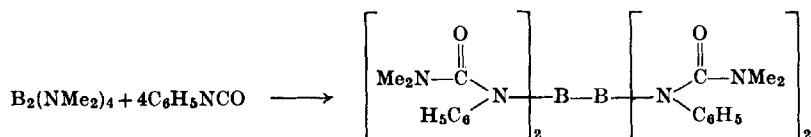
while alcohols, at low temperatures and in the presence of hydrogen chloride, produce the tetraalkoxydiborons in good yield (97, 615):



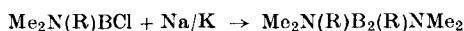
Although one, two, or four dimethylamino groups in tetrakis(dimethylamino)diboron can be replaced with halogen atoms on treatment with HCl, HBr, or HF (120, 524, 632, 648), BX_3 (X = F, Cl, or Br) (651), or $\text{BCl}_3 \cdot \text{NMe}_3$ (120), no free diboron tetrahalides can be isolated from the reaction mixtures; e.g.:



Addition of the B—NMe₂ groups in tetrakis(dimethylamino)diboron across the N=C bond of phenyl isocyanate occurs when the two are mixed in hexane solution at room temperature (74):



The corresponding symmetrical bis(dimethylamino)dialkyldiborons can be made by a Würtz-type coupling reaction, using sodium-potassium alloy (95, 638):



Diboron tetrafluoride is formed during the fluorination of boron monoxide, sub-boric acid, or tetraalkoxydiborons using sulfur tetrafluoride (98, 266), so that the production of the tetrafluoride is not now dependent on diboron tetrachloride from which it had been previously synthesized using antimony trifluoride (246) or allyl fluoride (149).

Attempts to fluorinate tetrakis(dimethylamino)diboron directly to diboron tetrafluoride with BF_3 (98, 651), SF_4 (98, 540), IF_5 (540), and SF_5Cl (540) were unsuccessful. Although boron trifluoride is not reduced by a mercury discharge (246), the absorption spectrum of BF can be detected when the trifluoride either flows through a silica tube connected to an oscillator operating at 2340 Mc/sec (722), or is subjected to an electrical discharge in helium gas (673); furthermore, when it is mixed with hydrogen and passed through a tungsten arc, a small amount of crystalline boron is formed (194).

Diboron tetrabromide has been synthesized by passing boron tribromide through a glow discharge maintained between nickel electrodes (208), or by treating the tetrachloride with boron tribromide at room temperature (826):



Neither the tetrabromide nor the tetraiodide (formed in about 30% yield when boron triiodide passes at low pressure through a radio-frequency discharge) (757) has been studied in detail and little is known of their properties.

C. TETRABORON TETRAHALIDES

The only known member of this group, the chloride, is one of the products when boron trichloride is reduced in a mercury arc (545, 827); the yield is very low and amounts to only 1 or 2 mg per day of discharge operation. Tetraboron tetrachloride is also probably formed in the thermal decomposition of diboron tetrachloride (545, 823), but it is difficult to judge if the very small amounts obtained from this source do not arise, at least in part, from imperfect separation of B_4Cl_4 from the original diboron tetrachloride.

One might predict that the other tetraboron tetrahalides would be formed by treating the tetrachloride with SbF_3 , BBr_3 , or BI_3 , although it has been suggested that tetraboron tetrafluoride might be thermally unstable (544). The stability of the partially methylated chloride, $\text{B}_4\text{Cl}_3\text{Me}$ (823), however, leaves little doubt that mixed halides (at least) should be capable of existence, even if only as participants in an equilibrium.

D. OTHER BORON HALIDES

During the thermal decomposition of the diboron tetrahalides, compounds of formulas $(\text{BX}_n)_x$ are formed. When X = fluorine, the

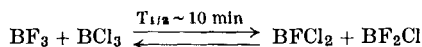
value of n is unity and the product is a yellow, involatile polymer (414). When the halogen is chlorine there are several polymers having the composition $(\text{BCl})_x$ [where x is equal to 8 (426), 9 (253, 541, 543), 10 (541), 11 (543), 12 (543), but see also (753, 825)], which can be separated by vacuum sublimation (545, 753). During the mercury discharge preparation of diboron tetrachloride a yellow polymeric film of $(\text{BCl})_x$ is formed on the apparatus walls, but it has yet to be studied; it may be similar to the yellow monochloride produced when diboron tetrachloride is subjected to a silent electric discharge (724). A colored boron monobromide, $(\text{BBr})_x$, is formed when diboron tetrabromide decomposes thermally or when boron tribromide is passed through a glow discharge or a silent electric discharge (208); at least two other products of empirical formulas $\text{BBr}_{0.2}$ and $\text{BBr}_{0.4}$ are also produced in the discharges. The position regarding the boron sub-iodides is obscure, but it appears that many dark-colored compounds having formulas B_xI_y arise during the preparation (and from the decomposition) of diboron tetraiodide (757); nothing is known about their chemistry or structures.

$\text{B}_{10}\text{X}_{10}^{2-}$ and $\text{B}_{12}\text{X}_{12}^{2-}$ Ions. The borohydride ions $\text{B}_{10}\text{H}_{10}^{2-}$ and $\text{B}_{12}\text{H}_{12}^{2-}$ (375, 376) have been shown to react with the halogens (and with HCl or HF) to give many substituted ions, such as $\text{B}_{10}\text{Br}_{10}^{2-}$, $\text{B}_{12}\text{I}_{12}^{2-}$, $\text{B}_{12}\text{F}_4\text{H}_8^{2-}$, $\text{B}_{12}\text{H}_3\text{Br}_6\text{Cl}_3^{2-}$ to mention but a few (454, 455).

E. MIXED BORON HALIDES

Although the existence of stable mixed halides, $\text{MX}_n\text{Y}_{4-n}$, of several Group IV elements has prompted a search for similar compounds of boron, the only successful isolation of mixed boron halides is that of the bromo-iodides, BBr_2I and BBrI_2 , described by Besson 75 years ago (73). A study of the chlorination of boron tribromide using a variety of inorganic chlorides (250, 513) gave no isolable boron chlorobromides, although Raman and infrared spectra of the reaction mixture (and of mixtures of pure boron trichloride and tribromide) showed that the chlorobromides were present (148, 321, 438, 439, 506, 513). Although the distribution of the halogens was almost random, the equilibrium is so mobile, even at -50° , that separation of the various species is impossible and the only end products of repeated distillation or low temperature fractionation are the pure trichloride and the pure tribromide (513).

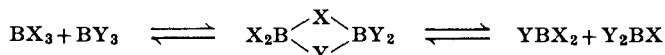
The interchange of halogen atoms in binary mixtures of boron trifluoride and trichloride has been the subject of both kinetic and equilibrium studies; the components of the equilibrium,



while not being separable by distillation, were estimated by quantitative infrared and mass spectral measurements (125, 359, 396, 625). Two slightly differing values for the equilibrium constant, K , were obtained: $K = 1.6$ (711a) and $K = 0.53$ (359, 396) at 27°–29°, the heat of reaction being about 1 kcal/mole (359).

In a ternary mixture the halide BClBrF has been detected by ^{19}F nuclear magnetic resonance (n.m.r.), its identity being verified by the chemical shift of the fluorine atom relative to those in BFCl_2 and BFBr_2 prepared from the respective binary mixtures (184). This technique suffers from the disadvantage that fluorine must be present in the species being studied; however, boron possesses a nuclear spin in both its natural isotopes: ^{11}B , 80% abundance, spin 1; and ^{10}B , 20% abundance, spin 3. Hence the ^{11}B isotope makes an ideal probe for investigating the mixed boron halides (471), and all ten components in a $\text{BCl}_3/\text{BBr}_3/\text{BI}_3$ mixture have been identified in this manner (271). Molecular orbital calculations on the system $\text{BCl}_3/\text{BBr}_3/\text{BF}_3$ have resulted in the evaluation of the ^{11}B n.m.r. shifts of the various mixed fluoroboron halides, the local paramagnetic effect being assumed the chief contributor to the shifts (22). The agreement with the experimental shifts is shown in Table II.

It is usually assumed that the mechanism for the halogen redistribution reaction involves boron-halogen bridges, either like those found in the aluminum chloride dimer or a close approximation to them found in favorably oriented collisions; cleavage of such bridges can then take place via two paths, one of which results in halogen exchange:



However, such dimers have not been detected in pure liquid boron trifluoride at low temperatures² (506, 795) (considering the combined effects of electronegativity and π -bonding on dimer formation, one might expect boron trifluoride to be the least favorable case for such a study) or in mixtures of the trichloride and tribromide (439).

Ogg (660) has shown that the ^{11}B n.m.r. spectrum of boron trifluoride exhibits no boron-fluorine coupling, which might suggest that the fluorine atoms are exchanging rapidly as expected if a monomer-dimer equilibrium exists similar to that given above. As the converse boron splitting of the fluorine resonance spectra in boron trifluoride and mixed chloro-bromo-fluorides is readily observed (see Table III),

² Infrared studies on crystalline boron trifluoride suggest that some intermolecular association occurs in the solid, perhaps via weak $\text{B} \cdots \text{F} \cdots \text{B}$ bridges (214).

TABLE II

¹¹B n.m.r. CHEMICAL SHIFTS OF MIXED BORON HALIDES (IN P.P.M.)^a

Halide	Observed (370)	Observed (271)	Calculated (22)
BF ₃	36.2	—	36.2
BF ₂ Cl	25.6	—	27.5
BFCl ₂	14.4	—	18.0
BCl ₃	0.0	0.0	—
BCl ₂ Br	1.4	1.2	—
BClBr ₂	3.7	3.9	—
BBr ₃	7.1	7.4	—
BF ₂ Br	26.1 $J_{B-F} = 56$ c/s	—	26.0
BFBBr ₂	16.0 $J_{B-F} = 107.5$ c/s	—	13.2
BCl ₂ I	10.2	10.3	—
BClI ₂	27.8	28.3	—
BI ₃	53.6	53.5	—
BFClBr	14.5 $J_{B-F} = 89$ c/s	—	15.7
BFBBrI	18.9 $J_{B-F} = 178$ c/s	—	—
BClBrI	14.3	14.5	—
BBr ₂ I	19.1	19.6	—
BBrI ₂	35.2	34.8	—

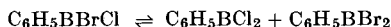
^a Boron trifluoride and triiodide do not exchange in heptane after 24 hours at room temperature, and because of this it is thought (370) that BFI₂ and BF₂I may be nonlabile and therefore isolable.

TABLE III

¹⁹F CHEMICAL SHIFTS AND ¹¹B-¹⁹F COUPLING CONSTANTS FOR MIXED BORON TRIHALIDES (184)

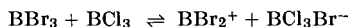
Halide	Chemical shift (p.p.m.)	$J_{^{11}\text{B}-^{19}\text{F}}$ (c.p.s.)
BF ₃	0	15 ± 2
BF ₂ Cl	- 51.5 ± 0.2	34 ± 1
BF ₂ Br	- 68.4 ± 0.3	56 ± 1
BFCl ₂	- 99.0 ± 0.6	74 ± 1
BFBBr	- 114.8 ± 0.6	92 ± 2
BFBBr ₂	- 130.4 ± 0.7	108 ± 3

the failure to detect the boron-fluorine coupling of 15 c.p.s. in the ^{11}B resonance may be due to other factors, including line width (471). In some cases, however, e.g. (245, 285, 509),



the exchange between the halides may be so rapid that the ^{11}B n.m.r. resonance lines due to the various species cannot be observed separately and only a single line intermediate between the pure halides results (245); equilibria involving B—F compounds are apparently slower, and in systems containing $\text{C}_6\text{H}_5\text{BF}_2$ the discrete resonance line of the mixed halide, $\text{C}_6\text{H}_5\text{BFX}$, can be observed. No substantial proportion of a dimer species could be detected.

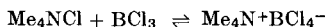
It has been pointed out (513) that halogen exchange, instead of involving dimers, might occur via a slight ionization process such as:



The rapid exchange (392) between labeled tetramethylammonium chloride and liquid boron trichloride is compatible with such an ionization:

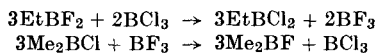


However, in view of the very low conductivity of boron trichloride, a simple exchange involving the tetrachloroborate anion is more likely,

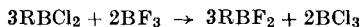


especially as several tetrachloroborates can be made directly in this manner (see page 98).

If the temperature is held low enough to stop their disproportionation, the alkylboron halides will also undergo ready exchange of halogen with the boron trihalides (91, 93):



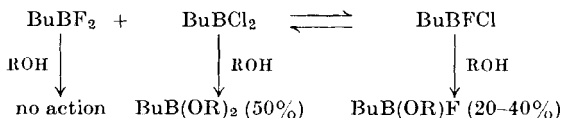
These systems are not too labile and all compounds shown in the equations can be separated by fractional distillation. A mass spectral study of these exchanges using $^{10}\text{BF}_3$ showed that reactions such as:



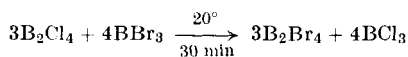
occur only via exchange of halogen, which supports a mechanism involving halogen-bridged dimers. The same work indicated the existence of the labile mixed halides RBFCl and RBFBr in these mixtures (93).

A particularly novel chemical method has been devised for detecting the presence of $\text{C}_4\text{H}_7\text{BFCl}$ in mixtures of butylboron dichloride and butylboron difluoride (126). BuBF_2 does not react with alcohols to give

alkoxyboron derivatives whereas butylboron dichloride readily forms BuB(OR)_2 . Hence, although no mixed-halogen product could be distilled from a $\text{BuBF}_2/\text{BuBCl}_2$ mixture, treatment with an alcohol, ROH ($\text{R} = \text{cyclohexyl}$ or isopropyl), gave good yields of BuB(OR)F :

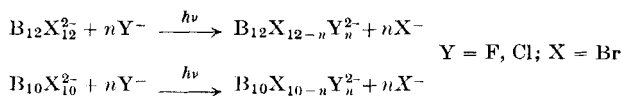


The first report of halogen interchange involving the diboron tetrahalides did not record the formation of mixed diboron halides (826):



Later work using ^{19}F n.m.r. and infrared spectroscopy (89, 90) has shown that small amounts of mixed halides are slowly formed when diboron tetrafluoride and tetrachloride are held together at 0° or during the controlled fluorination of the tetrachloride using antimony trifluoride. Whereas boron trichloride and diboron tetrafluoride over a period of 16 hours give the trifluoride and tetrachloride, a similar reaction using dimethylboron fluoride and the tetrachloride shows that the fluorine ends up almost wholly in the diboron compound (i.e., as B_2F_4); boron trifluoride and the tetrachloride do not react. All the scrambling reactions studied using the diboron tetrahalides were very much slower than the corresponding ones involving the trihalides alone.

In the case of the ions $\text{B}_{10}\text{X}_{10}^{2-}$ and $\text{B}_{12}\text{X}_{12}^{2-}$, any halogen can apparently be substituted at will during the preparation; this makes the number of theoretically possible mixed halides enormous. The mixed-halogen ions are very stable toward disproportionation, while their exchange with other boron halides has not yet been reported (454, 455). An exchange of halogen can be accomplished by irradiating these ions, in aqueous solution, in the presence of halide (827):



III. Structures of the Boron Halides

A. BORON TRIHALIDES

The boron trihalides are symmetrical planar molecules (26, 495, 503, 720, 848, 849) in which the angle XBX is 120° and the boron atom is assumed to be sp^2 hybridized. In such a configuration the boron atom

has only a sextet of electrons, the vacant $2p_z$ orbital being at 90° to the plane of the molecule. Therefore, as would be expected, the trihalides are electrophilic and behave as strong Lewis acids.

TABLE IV
THE B—X BOND LENGTHS IN THE TRIHALIDES AND THEIR ADDUCTS^a

Trihalide, BX_3	B—X distance in BX_3 (in Å)	B—X distance in BX_3D (in Å)
BF_3	1.295 ^b (624, 848)	1.43 ^c BF_4^- (705)
	1.30 ^d (503)	1.38 BF_3NH_3 (399)
		1.39 $\text{BF}_3\text{NH}_2\text{Me}$ (400)
		1.39 BF_3NMe_3 (277)
		1.33 BF_3NCMe (400)
		1.41 $\text{BF}_3\text{NC}_5\text{H}_5$ (879)
BCl_3 ; boron covalent radius 0.82 Å (720)	1.75 (26, 848)	1.43 ^d BF_3OMe_2 (49)
	1.72 ^d (503)	
BBr_3 ; boron covalent radius 0.83 Å (720)	1.87 ^d (503, 848)	
BI_3 ; boron covalent radius 0.84 Å (720)	2.10 ^e (720)	

^a Unless noted otherwise, the structures were determined by X-ray diffraction studies on single crystals. The early literature on B—X bond lengths in general is summarized in Bauer and Beach (48).

^b Infrared study of gas phase.

^d Electron diffraction.

^c N.m.r. study of single crystal.

^e Powder X-ray determination.

Table IV compares the boron-halogen bond lengths in the trihalides with those found in the halide adducts, BX_3D , where the boron atom is tetracoordinate and approximately sp^3 hybridized. The short B—X distance in the case of the trihalides has been taken as partial proof of $p_\pi-p_\pi$ bonding (back-bonding) caused by overlap of filled halogen p orbitals with the boron $2p_z$ orbital, although other factors no doubt operate simultaneously. For example, the electronegativity difference between X and B causes an electrostatic contribution $\text{B}^{\delta+}-\text{X}^{\delta-}$ to the bonding, which will be greater for the trihalides than for their adducts. There has been considerable effort recently to obtain other physical evidence for this π -bonding, since it has important consequences when one attempts to correlate the relative Lewis acid strengths of the trihalides (417).

TABLE V
SOME REFERENCES^a TO PHYSICAL DATA FOR THE BORON TRIHALIDES

Data	BF ₃	BCl ₃	BBr ₃	BI ₃	Mixed trihalides
Melting point (°C)	− 127.6 (310a)	− 107 (310a)	− 45.8 (39)	49.9 (757)	—
Boiling point (°C)	− 100.0 (310a)	12.1/752 mm (310a)	89.9 (39)	212	—
Vapor pressure	(85, 443)	—	19 mm at 0° (39)	1 mm at 90°	—
Infrared and Raman spectra	(215, 310a) (216)	(216, 310a)	(242, 310a) (216)	(242, 310a) (216)	(148); also see text
Mass spectrum	(443, 526)	(457)	(457)	(457)	—
nmr spectra	(657)	(657)	(657)	(657)	(184, 271, 370); also see text
Calculation of thermodynamic functions from infrared data	(605)	(605)	—	—	(604)
Force field calculations from infrared data	(500a)	(500a)	(500a)	(500a)	—
Heat of formation	(355, 868)	(355, 356)	(783)	(239)	(531)
Heat of hydrolysis	(355)	(782)	(783)	(239)	—
Nuclear quadrupole resonance	—	(495, 508)	(495)	(495)	—
Force constants	(468, 565, 777)	(468, 777)	(468, 777)	(468, 777)	—

^a Nöth and Vahrenkamp (657) have given a catalog of both old and new ¹¹B n.m.r. data for boron compounds in general and boron halide derivatives and adducts in particular. The thesis of Laurent (494) contains, in addition to the details of preparation, a useful collection of melting points, boiling points, and refractive indices of many adducts of boron trifluoride and trichloride with amines, ethers, ketones, esters, carboxylic acids, alcohols, and dialkyl sulfides; ditto refs. 330 and 528.

Using molecular orbital theory, the amount of π -bonding in the trihalides has been calculated to be in the order $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3$ (177, 706), which is the exact order of the constant K_D/l^2 ($l = \text{B—X}$ bond length, and K_D is the restoring force of the vibration) for the out-of-plane bending mode in BX_3 . The restoring force of such a vibration will be strongly influenced by B—X π -bonding, since this will be greatest when the molecules are planar.

If a halogen is replaced by a group R that is incapable of π -bonding to the boron atom (e.g., R = alkyl), then in the series BX_3 , RBX_2 , R_2BX there should be an increase in the amount of π -bonding in the remaining B—X bonds, which should be manifested by an increase in the force constant of the B—X stretching frequency. This was apparently verified for the case R = methyl and X = chlorine (59), but the method has since been criticized (506) on the grounds that calculation of the correct force constant can be difficult.

The presence of π -bonding between the boron atom and the $\text{C}=\text{C}$ bond in tricoordinate vinyl- and perfluorovinylboron derivatives has been demonstrated by infrared and ultraviolet spectroscopy (182, 311). However, in $\text{CH}_2=\text{CHBF}_2$ and $\text{CF}_2=\text{CFBF}_2$ the $\text{C}=\text{C}$ stretching frequency attains its maximum value for such compounds (showing a marked increase, for example, compared to the corresponding dichloro derivatives), the carbon-carbon double bond interacting only weakly with the boron $2p_z$ orbital. Although strong B—F π -bonding has made the $2p_z$ orbital less available for bonding with the $\text{C}=\text{C}$ bond than when the other halogens are linked to the boron (182, 183, 790), electron impact studies show that the B—C bond in vinylboron difluoride is still significantly stronger than that found in the alkylboron difluorides (791).

^{19}F and ^{11}B n.m.r. chemical shifts have been considered to reflect the electron densities (shielding) at these atoms (e.g., 671, 672, 709, 737), and using this concept it is possible to follow, qualitatively or semi-quantitatively, changes in the electron distribution that take place on substitution. For example, as fluorine is progressively replaced by chlorine or by bromine in the mixed trihalides, the ^{19}F n.m.r. resonance moves downfield due to deshielding of (removal of electrons from) the remaining atoms by increased π -bonding to the boron (185); see Table III. Similar deshielding of the fluorine atoms occurs on substitution of alkyl, aryl, vinyl, and perfluorovinyl for fluorine in the tricoordinate compounds RBF_2 and R_2BF . In the tetracoordinate trimethylamine adducts of BF_3 , EtBF_2 , and $\text{CH}_2=\text{CHBF}_2$, however, the ^{19}F chemical shift stays relatively constant since little or no B—F π -bonding can occur to alter the shielding of the fluorine atoms (182).

It is of interest to note that an almost linear relationship exists between the ^{19}F chemical shift and the boron-fluorine coupling constant, $J_{\text{B-F}}$, in the mixed trihalides (see Table III), the coupling constant being largest for FBBr_2 where most B-F π -bonding is expected to occur. This suggests that, for the mixed halides, $J_{\text{B-F}}$ may also be some measure of the boron-fluorine interaction; outside this series, however, the value of $J_{\text{B-F}}$ varies widely, being well over 50 c.p.s. even in the tetracoordinate RBF_3^- ions (788) where one might have been tempted to predict a value close to zero.

The chemical shifts of the ^{11}B n.m.r. spectra of the trihalides (Table II) are in agreement with the assumption that the shielding of the boron atom is in the order $\text{F} > \text{Cl} > \text{Br} > \text{I}$ (271, 311, 671, 709). However, in the tetrahalogenoborates the shifts are 1.8, -6.6, 23.9, and 128 p.p.m. for BF_4^- , BCl_4^- , BBr_4^- , and BI_4^- , respectively, as measured relative to boron trifluoride etherate (813). Thus, although the opportunity for π -bonding between the halogen and boron atoms has been removed by making the boron atom tetracoordinate, the resonance due to BF_4^- (and BF_3 adducts) (709) occupies an anomalous position, the boron atom still being "too shielded" if judged purely on electronegativity (671, 709) grounds.

B. DIBORON TETRAHALIDES

The first compound of this series to be made was the tetrachloride isolated by Stock in 1925 (800). Vapor density measurements and a study of the hydrolysis of diboron tetrachloride (800, 826, 843) suggested that the molecule probably contained a boron-to-boron bond; this was verified by Lipscomb (27, 28), who worked out the structure using X-ray diffraction on a single crystal held at -165° . In the crystal at this temperature the diboron tetrachloride molecule is planar (I). The B-Cl



distance is shorter than that found in the tetracoordinate boron trichloride adducts, and probably manifests B-Cl π -bonding of the type found in the boron trihalides. The boron-boron bond is rather longer than one would expect for a single bond³ (ca. 1.60 Å) (122, 384) and may be

³ The boron-boron bond length in the B_2 molecule is 1.59 Å (211).

almost 0.1 Å longer than the same bond in diboron tetrafluoride. The two ^{35}Cl resonances at 38.65 and 40.38 Mc/sec noted in the nuclear quadrupole resonance spectrum of solid diboron tetrachloride are thought to arise from the nonequivalence of the halogen lattice positions (774).

In the liquid and gaseous states, diboron tetrachloride has Raman and infrared spectra that suggest that the molecule is in a staggered configuration with the two BCl_2 units mutually at right angles (525);

TABLE VI
DISTANCES (IN Å) AND ANGLES BETWEEN THE ATOMS IN B_2X_4 MOLECULES

	B_2Cl_4		B_2F_4
	D_{2h} (27, 28)	D_{2d} (385)	D_{2h} (820)
B—B	1.75 ● 0.05	1.74 ± 0.05	1.67
B—X	1.73 ± 0.02	1.74 ± 0.05	1.32
X—X in BX_2	—	3.02 ± 0.06	—
B—X in BX_2 —B	—	3.02 ± 0.06	—
X—X in different BX_2	—	4.06 ± 0.2	—
Angle XBX	—	120°	—

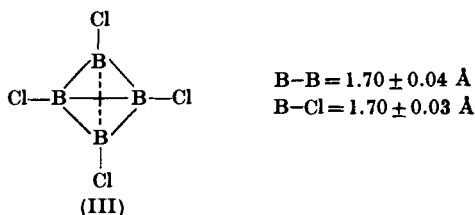
this symmetry is supported by electron diffraction data on the vapor (383, 385), which show that, although free rotation about the boron-boron bond does not take place, there is a large torsional vibration of the two BCl_2 groups. The barrier to rotation is approximately 2 kcal/mole (385, 525).

Diboron tetrafluoride has also been found to be planar in the solid state at -120° (820), and to be either staggered (266) or undergoing essentially free rotation (243) in the gaseous state; see Table VI. The two remaining tetrahalides have yet to be studied structurally. Tetramethoxydiboron is thought to be planar in the liquid state, but to satisfy steric requirements the NC_2 and BN_2 groups in liquid tetrakis(dimethylamino)diboron are twisted against the molecular plane (65).

C. TETRABORON TETRACHLORIDE

Tetraboron tetrachloride was the first electron-deficient boron halide to be discovered. (The term electron-deficient is used here to describe a

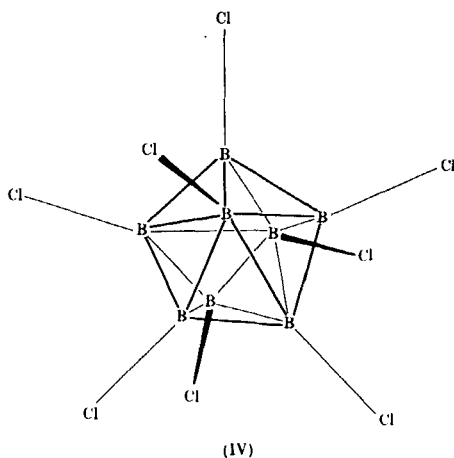
molecule with insufficient bonding electrons to form 2-electron, 2-center bonds throughout the molecule.) The structure in the solid state is that of an almost regular tetrahedron of boron atoms (III), to each of which is bonded a single terminal chlorine in such a manner that the four chlorine



atoms also form a tetrahedron (25). The electronic structure of tetraboron tetrachloride has been discussed (544) in terms of multicentered bonds involving all four boron atoms, the boron framework being strengthened by π -donation from p -orbitals of suitable symmetry on the chlorine atoms. No other tetraboron tetrahalides are known to date (1966) and, indeed, it has been suggested (544) that the fluoride might be unstable.

D. OCTABORON OCTACHLORIDE, B_8Cl_8

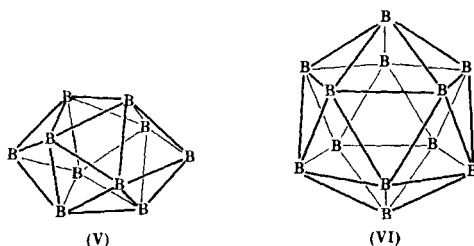
This red compound was isolated from among the decomposition products of diboron tetrachloride and crystals grown from boron trichloride for the X-ray diffraction measurements (426). Recent attempts to isolate the molecule from the same source but under very stringent conditions of moisture and air exclusion have failed (543, 753). The molecule has a boron-cage structure, IV, containing the eight boron atoms in the shape of a dodecahedron (426).



Several other boron chlorides have been isolated that probably have boron-cage structures [e.g., B_9Cl_8H (253); B_9Cl_9 (541); $B_{12}Cl_{11}$ (753, 825); $B_{11}Cl_{11}$ (543)] but none has yet been studied structurally.

E. $B_{10}X_{10}^{2-}$ AND $B_{12}X_{12}^{2-}$ IONS

The borohydride ions $B_{10}H_{10}^{2-}$ (375) and $B_{12}H_{12}^{2-}$ (376) have been shown to have the boron-cage structures V and VI; the hydrogen atoms, attached one to each boron, can be substituted either partially or wholly by the respective halogen or halogens (454, 455).

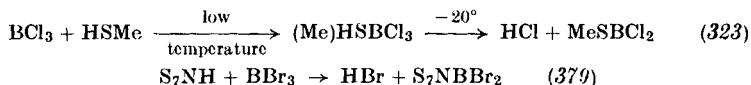


IV. Chemistry of the Boron Halides

A. BORON TRIHALIDES

As we have seen, in the trihalides the boron atom is hybridized to the sp^2 planar configuration and shares only six valency electrons. The trihalides are therefore coordinatively unsaturated, and their chemistry in the main is the satisfying of this unsaturation by the formation of adducts with suitable Lewis bases; many hundreds of boron halide adducts are now known and vary greatly in thermal stability. However, it is possible to make two general rules that are followed by the majority of adducts, and therefore help to predict the chemistry of new compounds.

(1) In the main, the donor atom of the Lewis base is a member of Group V (N, P, As) or Group VI (O, S) of the Periodic Table. If the base contains a hydrogen atom directly bonded to the donor atom, the adduct with a boron trihalide is susceptible to an intramolecular decomposition in which HX is eliminated:



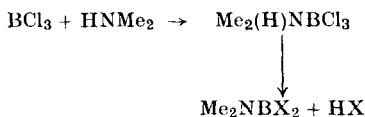
The adducts of boron trifluoride with this type of donor molecule are much more stable toward intramolecular decomposition than are those of the other trihalides due to the very much greater strength (738) of the

TABLE VII
BOND ENERGIES OF THE BORON TRIHALIDES (239)

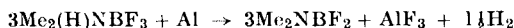
BX_3	$E(\text{B—X})^a$ in kcal
BF_3	154 ± 2
BCl_3	106 ± 1.5
BBr_3	88 ± 1.5
BI_3	68 ± 2

$^a E(\text{B—X}) = \frac{1}{3}[\Delta H_f^\circ \text{B}(g) + 3\Delta H_f^\circ \text{X}(g) - \Delta H_f^\circ \text{BX}_3(\text{ss}) - \Delta H(\text{BX}_3; \text{ss} \rightarrow g)]$ (where g = gaseous state, ss = standard state)

B—F bond; see Table VII. This is exemplified by the adduct dimethylamine-boron trifluoride, which is stable at room temperature in the presence of excess dimethylamine, while the other boron trihalides react vigorously at low temperatures to release HX (which combines with excess of amine to give $\text{H}_2\text{NMe}_2^+\text{X}^-$), e.g.:

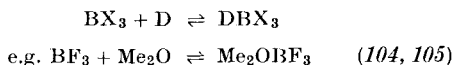


However, the loss of hydrogen fluoride from dimethylamino-boron trifluoride can be accelerated by treatment of the adduct with a reactive metal such as aluminum when a good yield of dimethylamino-boron difluoride is obtained (773):



The reaction of lithium with various amine complexes of boron trifluoride is similar (459). Substitution of a boron halide by an amine can sometimes take place via an $\text{S}_{\text{N}}2$ process (e.g., phenylboron dichloride and 2,4-dinitronaphthylamine, 510) instead of via the more usual Lewis adduct formation (509).

(2) If the donor atom is attached only to alkyl or aryl groups (e.g., R_3N , R_2S , or R_2O), the adducts formed with the trihalides are comparatively stable to intramolecular decomposition (e.g., 582, 684, 688), although in certain cases thermal instability of the adduct is due to dissociation:



The adducts with ethers decompose (often only slowly at room temperature) with the evolution of RX . Again the strength of the $B-F$ bond influences the stability of the trifluoride etherates and, for example, boron trifluoride diethyletherate is a well-known laboratory reagent whereas boron trichloride etherate readily evolves ethyl chloride:

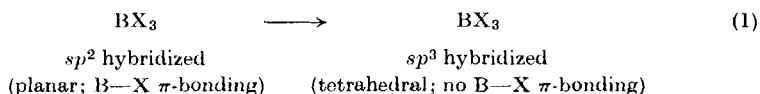


However, it may be significant that diborane prepared by the reaction of Et_2OBF_3 with lithium borohydride or lithium aluminum borohydride has been shown to contain small quantities of ethyl fluoride (197).

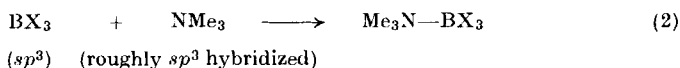
For many years it was considered that the acceptor power of the boron trihalides would be governed by electronegativity and steric effects, so that the acceptor strength series would be $BF_3 > BCl_3 > BBr_3 > BI_3$. However, evidence slowly accumulated that did not agree with this order. Thus the heat of formation of BCl_3MeCN was found to be greater than that of BF_3MeCN (491); also boron trichloride (792) and tribromide (798) complex with arsine, whereas boron trifluoride does not form an adduct even at low temperatures (529). The diphenyl ether adduct of boron trifluoride is unknown (330) while the trichloride, contrary to earlier reports, forms a rather unstable complex (m.p. ca. 4°), which loses boron trichloride quantitatively on heating (380). Phosphoryl chloride forms a reasonably stable adduct with boron trichloride (138) but only a very unstable one (83, 138) with the trifluoride. Phosphorus trichloride and tribromide do not interact with boron trifluoride but both give adducts with boron tribromide (416). The now classic work of H. C. Brown on the calorimetric determination of the heats of reaction between BF_3 , BCl_3 , and BBr_3 with nitrobenzene and pyridine finally showed in a quantitative manner that the acceptor strength of the three halides was in the reverse order of the electronegativities of the halogens, namely, $BBr_3 > BCl_3 > BF_3$ (108).

It was suggested (108) that this new order of acceptor strengths was due to the internal π -bonding between the boron and halogen atoms previously proposed by Pauling (699) to account for the rather short

B—X bond lengths found in the boron trihalides. When a boron halide and a donor molecule like trimethylamine enter into 1:1 adduct formation, several factors must be taken into account when attempting to compute the stability of the resulting complex:



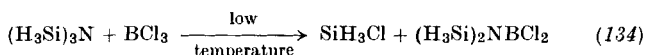
Step (1) involves a radical change in shape of the BX_3 entity, and energy will be required for (a) the orbital rehybridization to the reaction state, (b) overcoming any π -bonding in the original BX_3 molecule, (c) overcoming increased electron pair repulsions as the B—X bond angle decreases from 120° to about 109° , and (d) overcoming possible steric overcrowding due to the decreasing X—B—X angle (this will be partially offset by an increase in the B—X distance as the π -bonding is removed).



In step (2), little steric *change* will be experienced by the $\text{BX}_3(\text{\textit{sp}^3})$ or the donor molecule, since the initial and final state of rehybridization is close to the $\text{\textit{sp}^3}$ tetrahedral configuration (in some cases, if the donor molecule has very bulky groups, steric *hindrance* may cause a lowering of the stability of the adduct). This means that the donor molecule will suffer roughly the same readjustment whichever boron trihalide is used for adduct formation; an inductive effect due to the halogen atoms in $\text{BX}_3(\text{\textit{sp}^3})$ will also presumably influence the strength of the donor-acceptor bond at this point, the effect paralleling the electronegativities of the halogen atoms, $\text{F} > \text{Cl} > \text{Br} > \text{I}$. [It is assumed that the 1:1 adducts are monomeric; trimethylamine-boron trifluoride, once thought to be associated in the vapor state (133), is now known to be monomeric (137).] Hence any large variations in heats of reaction of the boron trihalides with a particular base will be due almost entirely to the acceptor molecules, and not the donor. Theoretical calculations (177, 706) show that the main contribution to the total reorganization energies of the boron trihalides is caused by loss of the boron-halogen π -bonding; these π -bond energies are approximately 48 (BF_3), 30 (BCl_3), and 26 (BBr_3) kcal/mole, while the $\text{\textit{sp}^2} \rightarrow \text{\textit{sp}^3}$ reorganization energy makes a much smaller contribution (177). Hence if the reorganized boron trifluoride molecule forms a donor-acceptor bond with a particular Lewis base without releasing 18 kcal/mole more energy than when boron trichloride makes a bond with the same donor, it will be the weaker

Lewis acid. The relative acceptor strengths of the trihalides are therefore expected to be in the order $\text{BBr}_3 > \text{BCl}_3 > \text{BF}_3$.

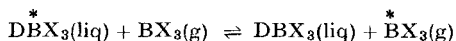
We have supposed above that the donor undergoes little steric or electronic change on coordination to the boron trihalide molecule. It is interesting therefore to compare the reactions of trimethylamine and trisilylamine, $(\text{H}_3\text{Si})_3\text{N}$, with the boron halides. Since trimethylamine readily forms stable adducts with many tricoordinate boron compounds, it might be expected on electronegativity grounds ($\text{N} > \text{C} > \text{Si}$) that trisilylamine would be an even stronger donor molecule; however, it has been demonstrated that trisilylamine does not form adducts with either borane (BH_3) or trimethylborane (134) while boron trifluoride reacts only at low temperatures (134, 805). Unfortunately the reactions between trisilylamine and the boron halides are complicated by a ready cleavage of silyl groups from the nitrogen atom,



but the indications are that trisilylamine is a much weaker base than is trimethylamine. This is probably due in the main to the substantial $d_{\pi}-p_{\pi}$ bonding between Si and N that holds the molecule in a planar configuration (220). On reaction with an acceptor molecule, therefore, the trisilylamine has to undergo considerable steric and electronic change and its adducts correspondingly suffer in stability. Similar results were obtained using the two series of amines $\text{Me}_n(\text{SiH}_3)_{3-n}\text{N}$ (804, 805) and $\text{Me}_n(\text{MeSiH}_2)_{3-n}\text{N}$ (221). The π -bonding that is thought to occur in silyl (and in alkylsilyl) analogs of ethers and sulfides may help to account for the inertness of disilyl sulfide toward boron trifluoride (674), but attempts to measure the stability of adducts formed with the silyl ethers and boron halides have been largely unsuccessful owing to cleavage of silyl groups from the oxygen atom (2, 219, 229, 674, 797).

As the strength of a donor-acceptor bond depends, in part, on the availability of electrons at the donor atom (cf. the work on the silyl compounds described above), the presence of electronegative substituents on the donor atom should reduce the stability of the adduct. Thus phosphine complexes with boron trifluoride (107) but the phosphorus trihalides PF_3 and PCl_3 do not (416). A similar trend of decreasing stability is noted when hydrogen is progressively replaced by chlorine in the acetic acid complex of boron trifluoride (572). The bis(1-chloroalkyl) ethers are so reduced in basic strength that no adduct formation was observed with boron trichloride (258, 288) while the bis(2-chloroethyl) ether complex $(\text{ClCH}_2\text{CH}_2)_2\text{OBCl}_3$ undergoes dissociation as well as irreversible decomposition (258).

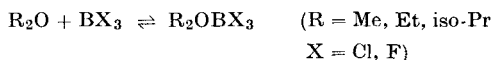
The substitution of phenyl groups for alkyl bound to oxygen markedly affects the stability of boron trifluoride etherates; the diethyletherate is a general laboratory reagent and can be distilled unchanged, but phenylmethyl ether-boron trifluoride readily loses BF_3 on warming (86, 571) and diphenyl ether forms no compound with boron trifluoride at all (86, 380, 571). Such considerations are of help when searching for a suitable system to use in the separation of the boron isotopes; an equilibrium such as



must be rapid, and also the isotopically enriched boron trihalide should be capable of 100% recovery from its adduct, DBX_3 , on heating. These requirements are met when D is not too powerful a donor molecule (as are pyridine and trimethylamine), and a typical system studied is that of phenylmethylether-boron trifluoride (380, 685, 689, 690), the donor properties of the ether having been depressed to a suitable extent by introduction of the phenyl group. Boron trifluoride is used mainly in such equilibrium studies because it undergoes only slight irreversible decomposition with donor molecules; the other trihalides are much more reactive and, for example, readily cleave many ethers. Phenyl groups also decrease the Lewis basicity of a nitrogen donor, as shown by the fact that triphenylamine does not react with boron trifluoride (770).

The effect of steric strain on boron complexes in general has been studied calorimetrically by H. C. Brown (103), but only the adducts of the trifluoride were so studied. Pyridine is a weaker base (proton acceptor) in aqueous solution than is 2,6-dimethylpyridine, but pyridine-boron trifluoride is a more stable adduct than 2,6-dimethylpyridine-boron trifluoride owing to the steric effect of the two methyl groups (114); as expected, there is virtually no difference in the stability of adducts formed by 4-substituted pyridines and boron trifluoride (109) or diborane (106). The relative order of strain introduced by alkyl groups on the base appears to be in the order *tert*-Bu > iso-Pr > Et > Me. For example, in a series of boron trifluoride etherates the order of stabilities is $\text{Me}_2\text{O} > \text{Et}_2\text{O} > (\text{iso-Pr})_2\text{O}$; if the ether is cyclic (e.g., tetrahydrofuran) the alkyl groups are effectively "tied back" so that steric interference is greatly reduced, and the tetrahydrofuran-boron trifluoride adduct is found to be more stable than the other three etherates (104). This relative order of base strengths for the ethers has been supported by gas phase dissociation studies (566), proton n.m.r. equilibrium measurements (190), and infrared distribution studies (867) using boron trifluoride as the reference acid; similarly it is found that $\text{NMe}_3 > \text{NEt}_3$ (388). Recently

Gore and Danyluk have shown by calculating the equilibrium constants for the reaction



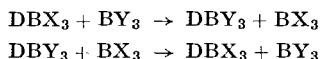
using proton n.m.r. chemical shift-concentration data, that the order of basicity is $\text{Et}_2\text{O} > (\text{iso-Pr})_2\text{O} > \text{Me}_2\text{O}$ when the reaction is carried out in dichloromethane solvent (312); they also cite electrical conductivity and vapor pressure measurements as evidence for their order.

Owing to the linear structure of nitrile compounds, $\text{R}-\text{C}\equiv\text{N}$, steric changes in R do not affect the stability of adducts with boron trifluoride to a significant degree (110), and this can be exploited when studying other effects connected with the donor-acceptor bond (808).

In the boron trihalide series there is an increase in steric requirements from F to I, which will tend to mask some of the effects discussed above and make boron triiodide, for example, a somewhat weaker Lewis acid than might be anticipated; Harmon (366) has calculated the I—I distance in boron triiodide to be 3.64 Å, which is considerably less than the value of twice the van der Waals radius of iodine, 4.30 Å. This steric overcrowding, being the greatest for the triiodide, may account for the comparatively low stability of BI_3 (757).

It will now be appreciated that the acceptor strength series of the boron halides depends on many factors (which can act in different directions). The considerable effort recently expended on this problem has shown that the series is the same as that found by Brown (108) and predicted by Cotton and Leto (177), namely, $\text{BI}_3 > \text{BBr}_3 > \text{BCl}_3 > \text{BF}_3$.

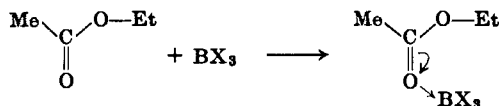
Displacement studies involving reactions such as



can show, clearly and in a dramatic way, the relative acceptor strengths of BX_3 and BY_3 toward the donor molecule D. An underlying assumption in such experiments is that the compounds being investigated should be closely related and have similar entropies and lattice energies (217, 582, 801). The technique has also been used to compare the acceptor strengths of other tricoordinate boron compounds with those of the trihalides (324, 325, 582). An interesting study of the above reactions, when $\text{D} = \text{NEt}_3$, $\text{X} = \text{F}$, and $\text{Y} = \text{Cl}$, showed that below 60° the “displacement” took place without rupture of the B—N bond; above 60°, B—N bond cleavage could be detected (179a).

Bases in which the donor atom is connected to the rest of the molecule by a bond having a characteristic vibrational frequency in the infrared

(e.g., ketones, aldehydes, carboxylic acids, esters, and nitriles) can be used in infrared spectral studies for comparing Lewis acidities (171, 481). For example, in complexes of esters with the boron halides (480, 481) the decrease in stretching frequency of the C=O bond is considered to be a measure of the O—B bond strength:



In a study of the infrared spectra of acetonitrile adducts, however, it was shown that the C—N stretching frequency was very insensitive to changes in the B—N bond, making this system unfavorable for a study of acceptor strengths (57).

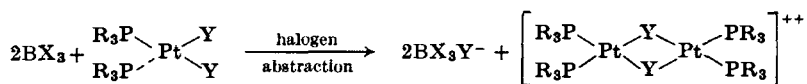
Nuclear magnetic resonance chemical shifts of the protons in trimethylamine adducts of the boron trihalides have been correlated (581) with the heats of formation of the corresponding pyridine complexes (108, 340). It was therefore suggested that the shifts were a measure of the acceptor strengths of the trihalides, the loss of electron density at the nitrogen atom being compensated by electron release from the methyl groups, resulting in a deshielding of the protons; the stronger the acceptor, the greater will be the deshielding of the protons and will result in a larger chemical shift (539, 581). Similar work has been carried out using methyl cyanide (583) and polycyclic phosphites (829) as the ligands. The internal chemical shifts (i.e., $\Delta = |\delta\text{CH}_2 - \delta\text{CH}_3|$) for triethylamine adducts have also been taken as a measure of the acceptor strength of the boron halides (270, 539), but the chemical shifts of the ring protons in pyridine adducts could not be measured with sufficient accuracy (270). The *para* fluorine atom in 4-fluorobenzonitrile is sensitive to changes in electronic structure of the molecule on coordination to a boron halide, and the chemical shift of it has been used to give a quantitative scale of acceptor strengths (808); the shape of the nitrile donor virtually rules out any steric interference in these adducts.

The ^{11}B chemical shifts show marked changes in shielding when the boron halides are complexed with various Lewis bases (672) and the value $\Delta\delta = (^{11}\text{B} \text{ shift of complex} - ^{11}\text{B} \text{ shift of the free halide})$ gives information about both the relative acceptor strengths of the halides and the donor abilities of various ligands (270). The almost constant variation in $\Delta\delta$ noted for the tetrahaloborate ions BX_4^- (366) must have been due to fortuitously chosen solute concentrations, because the ^{11}B chemical shifts of these ions are very concentration-dependent (813).

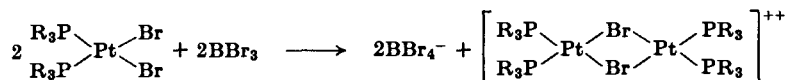
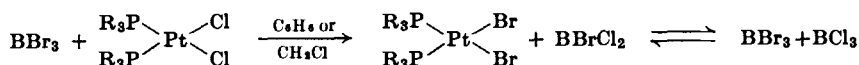
A more direct approach to the problem would be to calculate the moment of the $B^-—N^+$ bond in a series of adducts from observations of the dipole moments of the adducts; this is difficult to do in practice since it is not possible to measure the contribution of the tetrahedral BX_3 group. However, by assuming that the dipole moment of $H CX_3$ is a suitable approximation for BX_3 (tetrahedral) a rough measure of the $B—N$ moment can be obtained and, using trimethylamine or pyridine as the donor molecules, the relative acceptor strengths of the boron halides have been obtained (56).

1. Reactions with the Transition Elements and Their Compounds

Comparatively little has been reported concerning reactions of the transition elements and their compounds with the boron trihalides, although many transition metals form ionic tetrafluoroborates in which the metal ion is often aquated or ammoniated, e.g., $Mn(H_2O)_6(BF_4)_2$, $Cu(H_2O)_6(BF_4)_2$, $Ag(NH_3)_4BF_4$, and $Co(NH_3)_6(BF_4)_3$ (769, 817). The readiness of the trihalides to accept a halide ion and form the tetrahaloborates has been exploited in the synthesis of binuclear halogen-bridged platinum(II) cations, starting from the *cis*-diphosphine platinum halides (487):

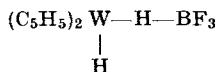


Halogen exchange may also take place before the halogen abstraction reaction if X and Y are different halogens:



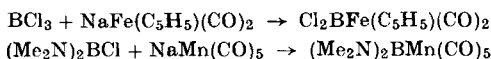
Several organometallic derivatives of the transition elements have a lone pair of electrons in a low energy orbital, which make them potential donor molecules. Dicyclopentadienyltungsten dihydride, $(C_5H_5)_2WH_2$, is such a molecule and readily adds on 1 mole of boron trifluoride (431, 780); the $W—H$ stretching frequency in the infrared spectrum of the

adduct is found to be virtually unchanged compared to that in the parent hydride, thus ruling out a singly hydrogen-bridged species

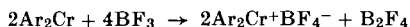


Furthermore, since $\text{C}_5\text{H}_5\text{Ti}$ (178) and $[\text{C}_5\text{H}_5\text{M}(\text{CO})_3]_2$ ($\text{M} = \text{Mo}$ or W) (431) do not react with boron trifluoride or trichloride, it is unlikely that the cyclopentadienyl rings in $(\text{C}_5\text{H}_5)_2\text{WH}_2$ are directly involved in bonding with the boron trifluoride, and so a tungsten-to-boron bond was considered to be the most likely possibility; other hydrides that form adducts with boron trifluoride and trichloride are $(\text{C}_5\text{H}_5)_2\text{MoH}_2$ and $(\text{C}_5\text{H}_5)_2\text{ReH}$ (431).

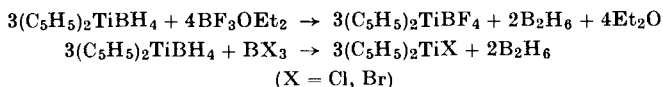
Although the pentacarbonylmanganate(−1) and similar anions show basic properties toward borane (692), no addition occurs when the ions $\text{C}_5\text{H}_5\text{W}(\text{CO})_3^-$ and $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3^-$ are treated with boron trifluoride (431); in certain cases, however, coupling products have been obtained when sodium carbonylmetallates are added to boron trichloride or substituted boron chlorides (652):



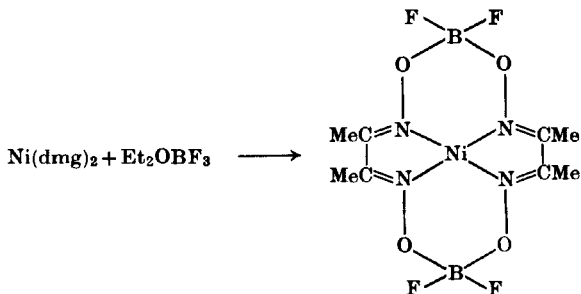
The reaction of boron trifluoride with a diarylchromium is considered to give diboron tetrafluoride (386),



whereas dicyclopentadienyltitanium(III) borohydride reduces the boron trihalides to diborane (643):



When boron trifluoride etherate is heated with nickel dimethylglyoxime or diphenylglyoxime, hydrogen fluoride is eliminated and the boron is incorporated into the metal chelate system:



These new chelate compounds will add on 2 moles of Lewis base (e.g., pyridine, phosphines, ammonia, piperidine), the acceptor site being the nickel atom (754).

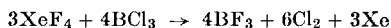
The free transition elements are mostly inactive toward the boron trihalides and, for example, tungsten and tantalum surfaces can be used in the high temperature pyrolysis of the tribromide and triiodide to crystalline boron (16, 66, 201, 550). Under the conditions of an electrical discharge other metals, such as copper (845), nickel (208), and mercury (826), can be made to reduce the trihalides to subhalides but, in the case of the more unstable boron triiodide, heating with silver at 185° is sufficient to produce boron monoiodide, (BI)_x (757). Mercury is not attacked by any of the trihalides at room temperature and can therefore be used in vacuum lines for manometers and float-valves; traces of water must be removed completely by baking out any vacuum apparatus used for handling boron tribromide or triiodide, otherwise hydrolysis will produce hydrogen bromide or hydrogen iodide, both of which readily attack mercury.

Several refractory oxides used in apparatus construction (e.g., TiO₂, Fe₂O₃, ZrO₂, SiO₂, Al₂O₃) are attacked at high temperatures (29, 50, 51), producing the metal halide and boric oxide. It has been suggested that, using boron trichloride, this may be a convenient way of preparing anhydrous metal chlorides on a small scale (29).

2. Reactions with Noble Gas Compounds

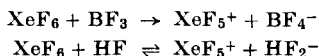
The noble gases contain several lone pairs of electrons that might conceivably be used in bonding to strong acceptor molecules like the boron halides. However, a careful search using argon and xenon (855) has shown that no adducts are formed, disproving the earlier claim (84) that argon and boron trifluoride give rise to several unstable compounds.

Xenon tetrafluoride does not combine with boron trifluoride up to 200° (42, 222), although at low temperatures (ca. -100°) a blue-violet solid of unknown structure may be formed (756). Attempts to use a stronger acceptor than the trifluoride results only in complete fluorination of the boron halide (43):



On the other hand, xenon hexafluoride and boron trifluoride react in a 1:1 ratio to give a white solid that melts at 90° to a pale yellow viscous liquid (766). The infrared spectrum of the vapor shows extensive dissociation while that of the solid indicates the presence of the BF₄⁻ ion; the Raman spectrum of the solid is similar to that obtained from xenon

hexafluoride dissolved in anhydrous hydrogen fluoride and could be due to XeF_5^+ ions:



If the solid, which reacts with sodium fluoride at 100° to give sodium tetrafluoroborate

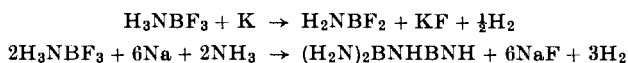


does contain XeF_5^+ ions, it might be considered as the acid analog of a nonaqueous solvent system based on liquid xenon hexafluoride (704):



3. Reactions with Compounds of Group I and II Elements

The boron trihalides react on heating with the alkali and alkaline earth metals, boron and the metal halides being the principal products (e.g., 200, 202, 213, 273, 445, 614, 711, 716, 751, 785); in the presence of hydrogen the reduction produces diborane (398, 422) and HBX_2 (520). Becher has also shown that the boron halides can be reduced by some metallic borides to give elemental boron of high purity (64). The only boron trihalide not ammonolyzed in liquid ammonia is the fluoride, which dissolves as the adduct ammonia-boron trifluoride. Attempted reduction of this adduct with solutions of the alkali metals in ammonia leads to ammonolysis and the production of boron amides and imides (428, 563), e.g.:

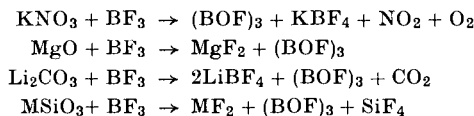


Alkali metal sulfates and phosphates form coordination compounds with boron trifluoride having compositions such as $\text{M}_2\text{SO}_4\cdot\text{BF}_3$; $\text{M}_2\text{SO}_4\cdot 2\text{BF}_3$; $\text{M}_3\text{PO}_4\cdot 3\text{BF}_3$; and $\text{M}_3\text{P}_2\text{O}_7\cdot 4\text{BF}_3$ (53, 54, 168); they are considered to be adducts in which the oxygen atoms of the anions are acting as donors:

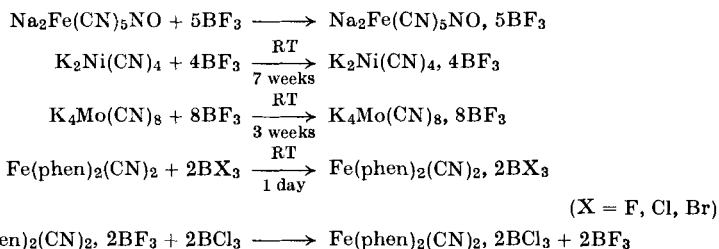


On heating to 300° or higher the complexes decompose with the evolution of boron trifluoride. The oxide and hydroxide ions can also be donors, as shown by the formation of BaOBF_3 (150) and NaHOBF_3 (453, 593, 732, 838). Other oxysalts and oxides, however, give no adducts but produce

the metal fluoride (or fluoroborate) and boron oxyfluoride (BOF)₃, on heating with boron trifluoride (50, 51):

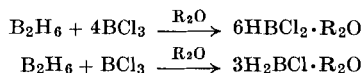


The complex cyanometallates of the alkali metals react in a similar way to sulfates and phosphates in that they slowly absorb 1 mole of boron trifluoride for each cyanide group in the complex, the bonding taking place between the nitrogen atom and boron to give a cyano bridge, M—C—N—B (778, 779, 781). Thus, where *RT* = room temperature,

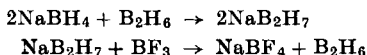


The cyanometallates have to be dehydrated before use, and it is thought that this may leave the crystals in an activated form because those cyanides that do not form hydrates (K₃Fe(CN)₆, K₃Cr(CN)₆) react much more sluggishly with boron trifluoride.

Alkali and alkaline earth metal hydrides react with a deficiency of boron halide or boron halide adduct in several solvents (usually ethers) to produce good yields of diborane (11, 116, 236, 315, 347, 387, 501, 579, 747–749), but if a reaction ratio (MH:BF₃) of 1:1 is used the hydrido-trifluoroborate anion, HBF₃[−], can be isolated as its sodium salt (315). If the NaH/BCl₃ reaction is carried out in benzene, addition of aluminum chloride to the solvent facilitates removal of sodium chloride from the surface of the sodium hydride as the soluble NaAlCl₄, and almost theoretical yields of diborane result (47). However, at 300° in the absence of a solvent, calcium hydride reduces boron trifluoride directly to boron (363). Complex hydrides of the alkali metals (MAIH₄, MBH₄, MHB(OMe)₃) also reduce the boron halides to diborane (11, 113, 116, 247, 631, 747–749, 876) but an excess of boron trichloride must be avoided, otherwise diborane is lost due to side reactions:



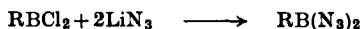
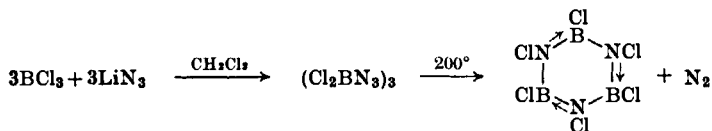
An excess of trifluoride, on the other hand, is beneficial to diborane production because it decomposes any $B_2H_7^-$ ions formed in a side reaction between diborane and the metal borohydride (116):



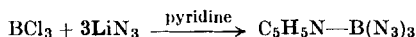
The commercial preparation of diborane in ether solvents using lithium hydride (227, 395) or sodium borohydride and boron trifluoride (41) has been described.

Tetrafluoroborates or tetrachloroborates result when alkali metal fluorides and chlorides are stirred, heated under pressure, or cold-milled with the corresponding boron trihalide (595, 599, 748, 813), while substituted boron fluorides, RBF_2 (R = vinyl, methyl, or pentafluorophenyl), react with potassium fluoride to give $K[RBF_3]$ (154, 788). Potassium fluoride will even extract boron trifluoride from the compound $SF_3^+BF_4^-$ to produce the tetrafluoroborate anion and pure sulfur tetrafluoride (762); boron trifluoride used in the formation of tetrafluoroborates may be prepared *in situ* by heating a stoichiometric mixture of, for example, boric oxide and potassium fluoride, with sulfur tetrafluoride (442). Halogen exchange occurs on heating calcium fluoride with boron trichloride (80).

Exchange of halogen for a pseudohalogen group is possible by treating a boron trihalide with the corresponding metal (often alkali metal) pseudohalide. Boron trichloride (or a substituted boron chloride) reacts with sodium and lithium azides in dichloromethane or benzene to give boron azide derivatives (678-681, 683):

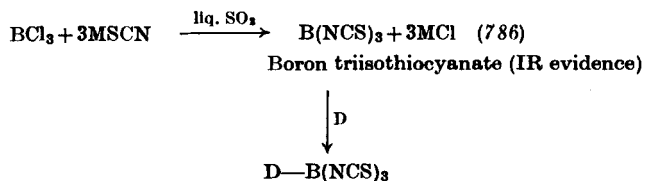


By carrying out the reaction in pyridine, all three chlorine atoms can be replaced by azide to give pyridine-boron triazide (681):



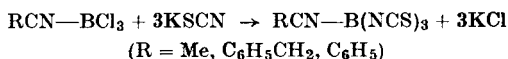
Boron triazide had previously been described by Wiberg (859), who prepared it by reacting hydrazoic acid with alkali metal borohydrides.

Boron trichloride reacts only very slowly with sulfur dioxide (381) [although the reaction is catalyzed by chloride ion (132)], making this a useful solvent for these exchanges:



(M = K, Na; D = NEt₃, pyridine, acetonitrile, phenylacetonitrile)

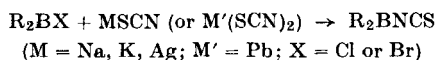
Nitrile adducts of boron trichloride also react with potassium thiocyanate in liquid sulfur dioxide (786):



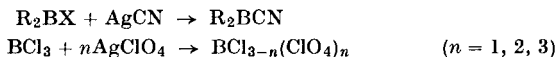
The analogous treatment of boron tribromide with silver thiocyanate in benzene was reported (165) to give boron trithiocyanate, but later work apparently failed to confirm the reaction (710); silver isocyanate, on the other hand, reacts readily (250):



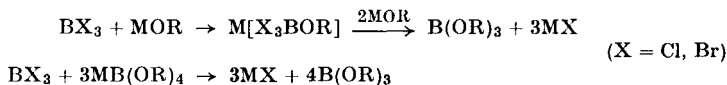
However, the work of Lappert (485, 486) shows that the products claimed previously to be boron cyanates and thiocyanates are probably the isomeric iso compounds (see also 316, 451):



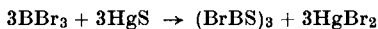
With boron tribromide the remarkable mixed halide-pseudohalide BBr(NCS)₂ was isolated and proved to be stable to distillation at low pressure (486) (cf. the mixed halides, page 8). Similar reactions between silver cyanide (151, 482) or perchlorate (592) and the boron halides give boron cyanides and boron perchlorates (although the reaction between silver cyanide and boron trichloride is rather slow!):



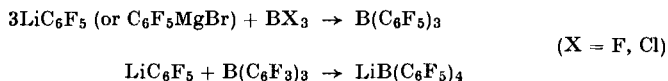
Alkali metal alkoxides or their complexes with trialkoxyboranes react with boron trifluoride, trichloride, and tribromide to give the trialkoxyborane (427, 572, 793):



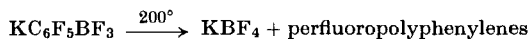
The corresponding thioboranes may be prepared either by reacting the sodium mercaptide with boron tribromide in the absence of solvent (140) or by carrying out the reaction in benzene or pentane using silver or lead mercaptide (323, 478). Mercuric sulfide and boron tribromide, however, give the borthiin (thioboroxine) and not boron sulfide (188):



The substitution of alkyl or aryl groups for halide by the use of Grignard or lithio reagents has been practised for many years in the preparation of BR_3 or LiBR_4 derivatives (82, 280, 288, 476, 817), but sometimes isomerization can take place during reaction as in the formation of triisobutylborane from *tert*-butylmagnesium chloride and a boron trihalide (390). More recently the method has been used to prepare tris(pentafluorophenyl)boron and several of its derivatives (538, 539):

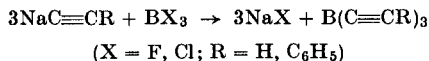


The high thermal stability of tris(pentafluorophenyl)boron is in direct contrast to the perfluoroalkyl derivatives of tricoordinate boron, which readily decompose by forming B—F bonds (45, 693, 802). The only reported instance of a fluorine shift to boron in the pentafluorophenyl-boron series is the thermal decomposition of $\text{KC}_6\text{F}_5\text{BF}_3$ (154):



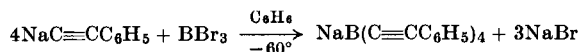
It may well be that the present nonexistence of tris(perfluoroalkyl)boron compounds ($\text{R}_{\text{F}3}\text{B}$ or $\text{R}_{\text{F}3}\text{B}$ —ligand) is more closely related to difficulties of preparing suitable Grignard or lithio reagents than to their thermal instability.

Sodium acetylide and phenylacetylide react with boron trihalides to give the rather unstable compounds, triethynylborane and triphenylethynylborane (24):

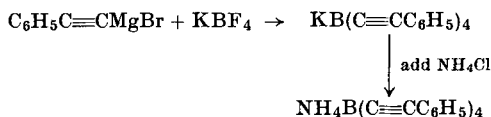


Similar reactions have been described for substituted boron halides, RBX_2 and R_2BX [see Lappert and Prokai (484) and references therein].

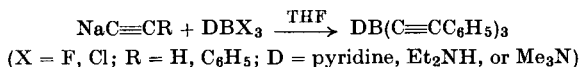
If an excess of sodium phenylacetylide is added to boron tribromide, the more stable tetraphenylethynylborate anion results (461),



which has also been prepared by heating potassium tetrafluoroborate with phenylethynylmagnesium bromide (740):

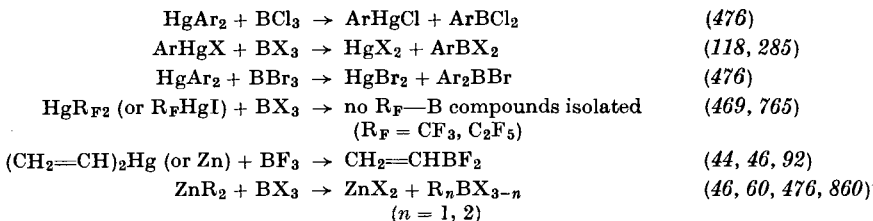


The triethynylboranes can be stabilized by forming tetracoordinate complexes using pyridine and amines, which is best accomplished by treating the corresponding boron trihalide adducts with $\text{NaC}\equiv\text{CR}$ (24):



A paramagnetic species, possibly $\text{B}(\text{C}_{10}\text{H}_8\text{N}_2)_2$, is formed when a mixture of the mono- and dilithium salts of 2,2'-dipyridyl reacts with boron trichloride in cyclopentane solvent (463).

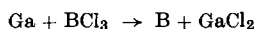
Other organometallic compounds of Group II elements used to form partially substituted boron halides include the alkyls and aryls of mercury and zinc (615a), but the sample of phenylboron difluoride, thought to be obtained from boron trifluoride using diphenylzinc (819), may be only a decomposition product of boron trifluoride etherate (557):



Although the hydrolysis of products obtained by treatment of boron trihalides with a deficiency of Grignard reagent yields alkyl/arylboric acids, the method is normally not well suited to preparation of the alkyl/arylboron halides (554, 557, 562); in some cases (e.g., RBCl_2) the difficulties may arise from complex formation between the solvent ether and the alkyl/arylboron halide (562).

4. Reaction with Compounds of Group III Elements

Reduction of boron trichloride with either aluminum or gallium produces elemental boron (272):



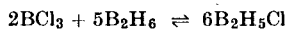
In the presence of hydrogen, reduction of boron trifluoride, trichloride, or tribromide gives good yields of diborane (252, 398, 422, 578); aluminum

can also be used to initiate the decomposition of dimethylamine-boron trifluoride (773):

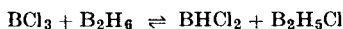


When the reduction of a trihalide is carried out using elemental boron at high temperature the boron monohalide, BX, is formed (78, 249, 350, 351). It is also possible to isolate small quantities of diboron tetrachloride when boron trichloride vapor is passed over heated boron (633).

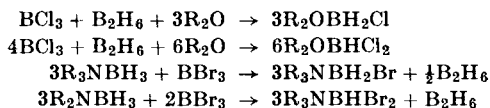
The many facile exchange reactions that take place between boron compounds have proved very useful in synthetic boron chemistry. One of the first to be studied, that between diborane and boron trichloride (128, 750, 799), was thought to be a simple equilibrium:



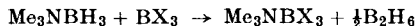
More recent evidence from spectroscopic studies shows the reaction (which does not take place at room temperature or below in a clean apparatus free of boric oxide) to be more complex,



with the added possibility of intermediates such as monochloroborane, BH_2Cl , and asymmetrical dichlorodiborane, $\text{B}_2\text{H}_4\text{Cl}_2$, also being present (444, 518, 603, 719); the main products, BHCl_2 and $\text{B}_2\text{H}_5\text{Cl}$, can be isolated by low temperature vacuum fractionation (719, 750) or by vapor phase chromatography (601, 602). A similar exchange between diborane and boron tribromide has been reported on briefly (719) and used to prepare pure bromodiborane; a structure determination on bromodiborane has shown the bromine atom to be in a terminal position (175). In the presence of ethers or amines, the equilibria in the $\text{B}_2\text{H}_6/\text{BCl}_3$ exchange are disturbed due to removal of one or more species by complex formation (115, 117, 635), e.g.:

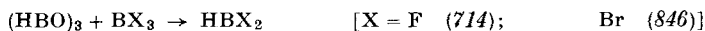


Diborane and boron trifluoride apparently do not undergo an exchange reaction at room temperature, but the pyrolysis of diborane at 100° in the presence of boron trifluoride (181) or subjecting a mixture of the two to an electrical discharge (517) results in the formation of small amounts of difluoroborane, F_2BH ; dialkoxyboranes, e.g. $(\text{MeO})_2\text{BH}$, may be used in place of the diborane (181). The addition of an excess of boron trihalide to trimethylamine-borane results in the displacement of borane (458, 582, 635):

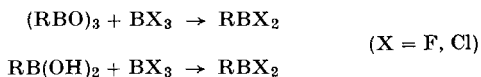


Similarly, gallane is displaced from trimethylamine gallane, Me_3NGaH_3 , by the stronger Lewis acid, boron trifluoride (345).

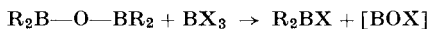
A more general method for preparation of the dihaloboranes is the reaction between boroxine and a boron trihalide:



The dihaloboranes (and the deuterated species) have been studied spectroscopically by ^1H , ^{19}F , and ^{11}B n.m.r. (181, 235, 851) and infrared (517, 519, 521, 714, 846) techniques. In analogous reactions, alkyl- and aryl-boroxines or -boric acids can be used to prepare the dihaloboron alkyls and aryls (6, 8, 129, 226a, 293, 554, 557, 561, 562, 623),



while the dialkyl- or diaryl-boric anhydrides react readily with boron trihalides, giving R_2BX (6, 7, 129, 680):



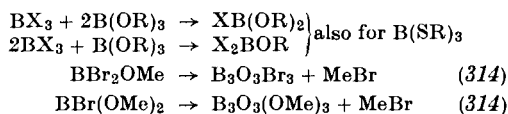
Aluminum trichloride may also be used to provide the chlorine atoms for these reactions (554).

At room temperature and low pressure (ca. 10^{-6} mm), boron trifluoride and boric acid have been observed, mass spectrometrically, to give hydroxyboron difluoride, $(\text{HO})\text{BF}_2$; at higher temperatures a further fluorine is substituted to give $(\text{HO})_2\text{BF}$ (711a). When boron trifluoride and boric oxide are heated together at 130° – 800° , trifluoroboroxine is the major product (77, 234, 248, 318, 397, 711a) unless hydrogen is added to the system when $\text{B}_3\text{O}_3\text{HF}_2$, $\text{B}_3\text{O}_3\text{H}_2\text{F}$, and $\text{B}_3\text{O}_3\text{H}_3$ are also formed (713). All the haloboroxines may be made in this way, but are unstable toward disproportionation back to BX_3 and B_2O_3 below about 250° and 1 atmosphere pressure (317–319). It has proved possible to trap trifluoroboroxine trimer at very low temperatures and to study its infrared spectrum (248) because the disproportionation becomes rapid only above -135° ; it is only at low pressures and about 1000° that the equilibrium $3\text{BOX} \rightleftharpoons (\text{BOX})_3$ lies well to the left-hand side⁴ [77, 233, 234, 397; see also Hofmeister and van Wazer (402)]. Tracer experiments using ^{10}B showed that boron trifluoride reacts more quickly with silica than with boric oxide and, apparently, trifluoroboroxine is best prepared by passing boron trifluoride over silica at 500° (248). Although aluminum oxide is said to be impervious to boron

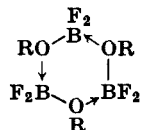
⁴ A tetramer $\text{B}_4\text{O}_4\text{Cl}_4$ of unknown structure has also been observed mass spectrometrically (712).

trifluoride up to about 1200° [(78); see, however, Baumgarten and Bruns (50)], boron trichloride (29) and boron triiodide (549) attack it on heating to between 500° and 1000°; conversely, a mixture of aluminum trichloride and boric oxide gives some boron trichloride on heating (423).

Mutual replacement of alkoxy and halide groups between trialkoxy- or triaryloxyboranes and boron trihalides leads usually to the alkoxy-boron halide (169, 260, 280, 288, 314, 403, 477, 793), unless the latter happens to be unstable (288, 314),



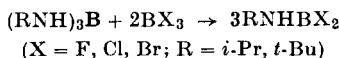
but in the case of the trifluoride a compound of empirical formula $\text{B(OR)}_3 \cdot 2\text{BF}_3$ ($\text{R} = \text{alkyl}$) is produced. The structure of this compound has received much discussion in the literature but the dispute appears to have been settled by a careful n.m.r. investigation of the system, which showed that all three boron atoms were equivalent (471). The proposed cyclic structure,



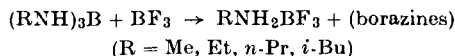
is in accord with the earlier chemical evidence summarized in (556). *n*-Butoxyboron difluoride and dichloride may also be prepared by treating *n*-butoxyboroxine with either boron trifluoride or trichloride (479).

Aluminum alkoxides react with boron trifluoride to give trialkoxyboranes and aluminum trifluoride (793).

Tris(primary-amino)boranes, $(\text{RNH})_3\text{B}$, can sometimes undergo group exchange when treated with the boron trihalides (328):

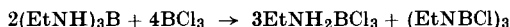


However, in the case of the trifluoride, mixtures of B-alkylamino- and B-fluoroborazines are the more usual products (328):

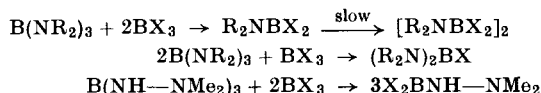


The low stability of sterically hindered aminoborazines may account for the formation of RNHBF_2 only in those cases where branching of the

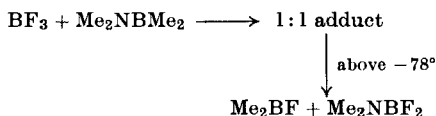
alkyl group, R, occurs at the carbon atom joined to nitrogen. A quantitative yield of ethylamine-boron trichloride is formed when boron trichloride and tris(ethylamino)borane are mixed (328):



Tris(dialkylamino)boranes give dialkylaminoboron dihalides or bis(dialkylamino)boron halides when treated with the stoichiometric amount of the boron trihalide (38, 96, 290, 320, 642, 645, 650):



The dialkylaminoboron dihalides, which slowly dimerize when allowed to stand, have been studied by infrared spectroscopy in the gas phase and by X-ray diffraction in the solid (38). Dimethylaminoboron difluoride is also one of the products when boron trifluoride reacts with tetramethylaminoborane at low temperature (130):

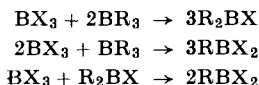


The same compound is obtained on mixing boron trifluoride and bis(dimethylamino)boron fluoride (130):

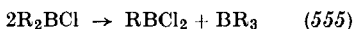


Borazine and boron trichloride react to give B-monochloro- and B-dichloroborazines (742); similarly, trichloroborazine exchanges halogen with boron trifluoride but the method is not suitable for large-scale preparation of trifluoroborazine (492).

The exchange of alkyl (or aryl) groups for halide has proved useful for preparation of alkyl/arylboron halides (8, 59, 125, 280, 288, 515, 555, 613, 615a, 616, 623, 741):



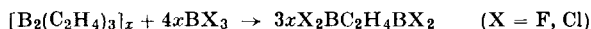
The alkylboron halides can often be distilled unchanged in a vacuum below 100°, but at higher temperatures disproportionation may take place, e.g.:



Alkylaluminum halides and aluminum trialkyls give trialkylboranes or alkylboron halides on reaction with the boron trihalides (40, 500, 852),

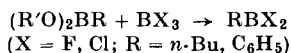
but, when lithium borohydride is added to the mixture, alkylated diboranes result (514). A mixture of hydrogen chloride, aluminum carbide Al_4C_3 , and boron trichloride gave the two methylboron chlorides when heated at 400° for 3 hours (40).

A remarkable boron alkyl $[\text{B}_2(\text{C}_2\text{H}_4)_3]_x$ results when an excess of acetylene reacts with diborane in dimethoxyethane solvent; this alkyl generates the 1,2-bis(dihaloboryl)ethanes on treatment with boron trihalides (162):

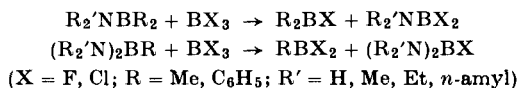


These compounds had previously been accessible only by using diboron tetrahalides. The reaction of boron trihalides with boron monoxide and tetrakis(dimethylamino)diboron have been discussed previously (pp. 5-6).

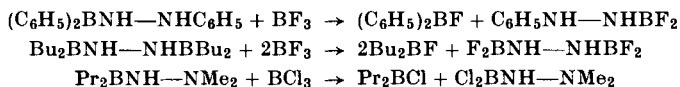
More complicated reactions involving the redistribution of three different groups have been attempted; thus Gerrard (94) prepared RBX_2 compounds by the route,



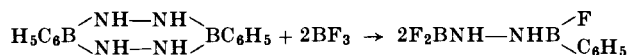
while Becher (61) and Niedenzu (616, 623) studied the interaction of the trihalides with aminoborane derivatives:



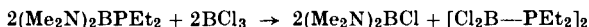
Substituted hydrazinoboranes react in the same manner (650):



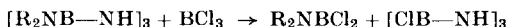
The hydrazinoboron halides formed as products in these reactions have yet to be made by treating the corresponding hydrazine with a boron halide, thus, this exchange constitutes a useful synthetic method. The heterocyclic compound, $(\text{C}_6\text{H}_5\text{BNH—NH})_2$, adds on 2 moles of boron trifluoride to form what is possibly $\text{C}_6\text{H}_5\text{FBNH—NHBF}_2$ (650):



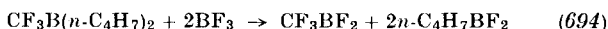
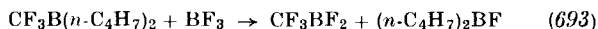
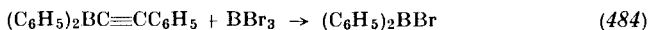
Mixed phosphine-aminoboranes are cleaved by boron trichloride (653),



as are the aminoborazines (622):



It has also been demonstrated that, for some asymmetrically substituted alkyl or aryl boranes $R'BR_2$, treatment with a boron halide results in cleavage of one alkyl (or aryl) group from the original borane:



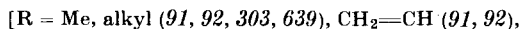
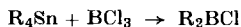
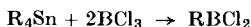
5. Reactions with Compounds of Group IV Elements

Little has been reported on the reaction of the free Group IV elements with the boron trihalides; silicon reduces the halides to boron (614) (or gives low yields of boron-silicon fluorides) (816), but graphite can be used to make the filaments used in the high-temperature hydrogen reduction of the trichloride to boron (796) and is apparently not attacked up to about 1000°.

The saturated hydrocarbons show little affinity for the boron halides, although boron trifluoride has been used in the catalytic isomerization of certain paraffins [see Chapter Nine of Topchiev *et al.* (817)].

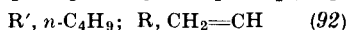
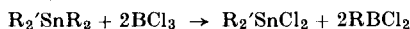
Monosilane has been stated (226) to react with boron trichloride to give silicon tetrachloride and dichloroborane, Cl_2BH (which disproportionated to diborane), but later work (218) has shown that reduction of the trichloride to diborane is possible with disilane but not monosilane. However, diborane is formed when methyl radicals are generated (from azomethane) in a mixture of monosilane and boron trichloride (743).

Tetraorgano-substituted stannanes have proved valuable synthetic reagents in the preparation of alkyl/arylboron halides; since many such stannanes are now commercially available, this method of preparing alkyl/arylboron halides is more useful than one employing poisonous mercury reagents or spontaneously inflammable zinc alkyls. Boron trichloride reacts smoothly with R_4Sn at room temperature or on slight heating, the products depending on the reaction ratios:

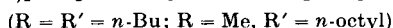
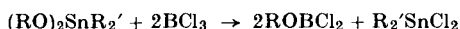


The method is suitable both for small-scale vacuum line procedure and for large-scale bench use. The tetraalkyl and tetravinyl stannanes lose only half the possible number of R groups during reaction, the tin ending

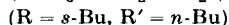
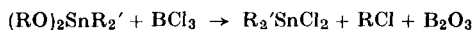
up as R_2SnCl_2 . As this is rather wasteful if R_4Sn is expensive or difficult to make, then, by making use of the known series for cleavage of groups from tin by boron trichloride, it is possible to use mixed stannanes, $R_2'SnR_2$, in the synthesis:



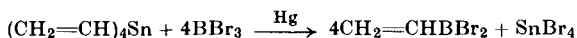
In the latter case, an added advantage of using $Me_2Sn(C_6F_5)_2$ is that tetrakis(pentafluorophenyl)tin has proved very unreactive and difficult to cleave. When mixed alkylalkoxystannanes are treated with boron trichloride, it is found that the alkyl groups remain attached to tin (305):



However, sometimes the alkoxyboron dichloride proves to be unstable and in such a case the alkyl halide corresponding to the alkoxy group is formed (305):

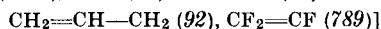
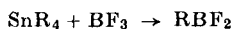


Similar reactions occur (92, 264, 639) when boron tribromide reacts with alkylstannanes, except that RBR_2 , R_2BBr , and R_3B tend to be produced simultaneously, making purification difficult. Mercury has been found to be a catalyst when tetravinyltin is treated with boron tribromide, since it ensures that all the vinyl groups are cleaved from the tin and that vinylboron dibromide is the only product (264):



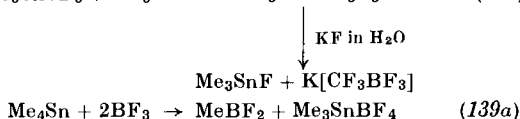
Apparently mercury is a specific catalyst for the tetravinyltin reaction because cleavage of tetraalkyltin compounds stops at the stage R_2SnX_2 even in the presence of mercury.

Boron trifluoride produces only RBF_2 even when an excess of tin reagent is employed:



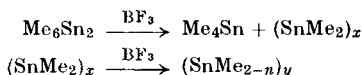
When mixed tin derivatives such as $R_3'SnR$ are treated with boron trifluoride, exchange of R and F does take place but sometimes a side

reaction can take place between $R_3'SnF$ and either RBF_2 or BF_3 (depending on which is the stronger Lewis acid):



Tetraorganolead compounds, e.g., $(C_6H_5)_4Pb$ (620), react similarly with the boron halides but RBX_2 and R_2BX are produced in somewhat lower yields.

Hexamethylditin is catalytically decomposed by boron trifluoride (139a):

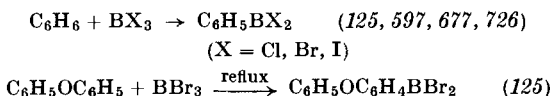


The tetramethyltin produced in the first stages of the reaction leads to the formation of methylboron difluoride and Me_3SnBF_4 (see above).

An attempt to couple tin and boron using trimethylstannylsodium and boron trifluoride resulted only in the catalytic decomposition of the sodium compound to hexamethylditin, which then reacted with the boron trifluoride in the usual manner (139a). However, it has proved possible to couple metals and nonmetals to the substituted boron halides using similar metal-salt reactions (e.g., 632, 644, 652, 653).

Only benzene of the unsaturated hydrocarbons has been shown to form (weak) adducts with the trihalides at room temperature (241). Although phase diagrams of benzene- BBr_3 and benzene- BI_3 mixtures showed no definite compound formation, intensity measurements on the symmetrical boron-halogen stretching frequency and a study of the ^{11}B n.m.r. spectra of solutions of the two trihalides in benzene indicated the formation of 1:1 complexes.

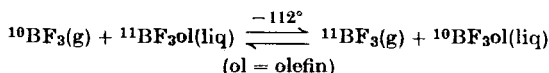
Much effort has been expended in efforts to synthesize arylboron compounds directly and thus, under forcing conditions, benzene and substituted benzenes have been shown to react with the boron halides in the presence of suitable catalysts (aluminum halides or palladium):



There is also some evidence that, during preparation of phenylboron dichloride from tetraphenyltin in benzene solution, some attack of the solvent occurs to give higher than theoretical yields of $C_6H_5BCl_2$ (616).

The boron halides (especially the trifluoride in the presence of a

promoter) are effective catalysts in the polymerization of olefins [see Chapter Six of Topchiev *et al.* (817)]. Only recently has it proved possible to detect the presence of unstable complexes between polar olefins and boron halides at very low temperatures; by measurements on the isotopic exchange reaction,

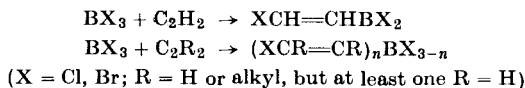


it was concluded that propylene, 1-butene, and *cis*-2-butene (but not ethylene) complexed with boron trifluoride (609–611). The absorption spectra of olefin solutions of boron trifluoride also indicated complex formation at -112° .

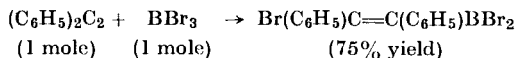
Brief mention (433, 434) has been made of the chloroboration of norbornadiene and bicyclo[4,2,0]octatriene using boron trichloride, the products being given the following structures:



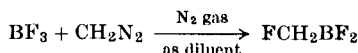
In the presence of suitable catalysts such as active carbon (310) or mixtures of mercuric chloride and active carbon (23), acetylene and alkyl-substituted acetylenes also undergo haloboration to give halovinylboron halides in good yields:



Diphenylacetylene reacts exothermally with boron tribromide to give 2-bromo-1,2-diphenylvinylboron dibromide (484):



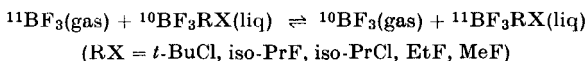
The somewhat similar reaction of diazomethane with boron trifluoride gives fluoromethylboron difluoride (322):



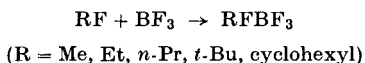
In ether solution, polymethylene is produced, but no proof could be obtained that the insertion of CH_2 proceeded further than FCH_2BF_2 (although it could be achieved with other groups in place of fluorine on the boron) (198). Boron trichloride catalyzes the polymerization of diazomethane to polymethylene (874).

Cycloheptatriene readily undergoes hydride abstraction in the presence of the boron halides and produces tropenium (i.e., cycloheptatrienylium) tetrahaloborates, the yields of which are very low in the case of the fluoride (365–369). Similar reactions occur when trianisylmethane, (*p*-MeOC₆H₄)₃CH, and triphenylmethane are treated with the boron halides, the trianisylmethyl or triphenylmethyl tetrahaloborates being formed (367–369). Under the conditions of reflux of the neat liquids, cycloheptatriene and boron trichloride apparently undergo a different reaction and give benzylboron dichloride (433).

Several alkyl halides form 1:1 complexes with boron trifluoride at low temperatures. The composition of the complexes was deduced by measuring the isotopic exchange between ¹⁰B and ¹¹B at various concentrations for the system (606–608),



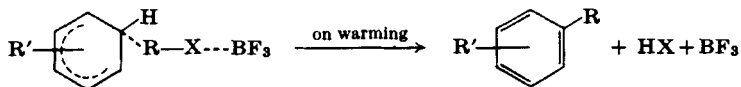
or by studying the electrical conductivity of RF/BF₃ mixtures (670):



The complexes are thought to have the structure $\text{RX}^{\delta+} \cdots \text{BF}_3^{\delta-}$, although the electrical conductivities of the complexes with certain alkyl fluorides (R = Pr, Bu, cyclohexyl) were rather high (ca. $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$) and this may be due to the formation of some carbonium ions, R^+BF_4^- (670). Prolonged contact of ethyl fluoride with boron trifluoride at room temperature produces a brown polymer (606) while methyl and ethyl chloride, when passed over heated aluminum or zinc in the presence of the boron halides, form boron trialkyls (424):

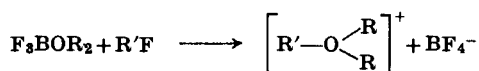


The adducts of boron trifluoride and alkyl halides mentioned above form brightly colored, isolable complexes (1:1:1) with aromatic hydrocarbons at low temperatures (1, 606, 607, 666), which are intermediates in Friedel-Crafts alkylation reactions. Since the infrared spectra of these complexes do not show absorption bands that can be assigned to free BF₄⁻ (or BF₃X⁻) ions, they have been assumed to have structures such as:



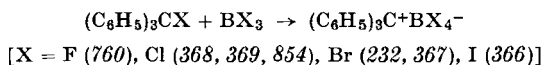
When a fluoroalkane is used for the alkylation reaction, the ease of catalytic activity of the boron trihalides is $\text{BI}_3 > \text{BBr}_3 > \text{BCl}_3 > \text{BF}_3$ (667). A halide RX that contains a phenyl group has been shown to eliminate HX on being heated with a boron trihalide [e.g., BCl_3 (288)], due possibly to a Friedel-Crafts reaction. Somewhat related to these studies are the reports that 1:1:1 complexes can be obtained with alkylbenzenes, anhydrous hydrogen fluoride, and boron trifluoride (330, 551, 661), in which the aromatic ring is protonated to give the tetrafluoroborate, RH^+BF_4^- . This might, at first sight, have been considered as a protonation by tetrafluoroboric acid, but it has been shown (551, 769) that boron trifluoride obeys Henry's law on dissolution in liquid hydrogen fluoride and hence cannot form a strong complex with the solvent.

If boron trifluoride etherate is treated with an alkyl fluoride, oxonium tetrafluoroborates are formed (570, 817):

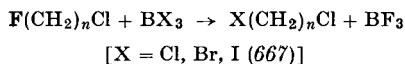


Similar ionic complexes are formed with certain sulfur (e.g., Et_2S) or nitrogen (e.g., pyridine) systems (330, 817).

The triphenylmethyl halides react readily with the corresponding boron halides to give 1:1 adducts now known to be tetrahaloborates (although the earlier workers did not recognize them as such):



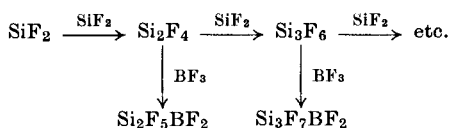
Triphenylmethyl fluoride and boron trichloride also form a 1:1 complex (440, 832, 854) that may be a mixed-halogen tetrahaloborate, $(\text{C}_6\text{H}_5)_3\text{C}^+\text{BFCl}_3^-$, but the fluoroalkanes undergo halogen exchange with the boron trihalides, e.g.:



Trimethylsilyl fluoride forms only a weak complex with boron trifluoride, for which no structure was proposed (231); trimethyltin fluoride, on the other hand, forms trimethyltin tetrafluoroborate (139a), which in the solid state is thought to contain bidentate tetrafluoroborate groups (373).

Carbon tetrachloride undergoes a complete halogen interchange when heated with boron tribromide (360) or boron triiodide (587), but

CClF_3 , CCl_2F_2 , and CF_4 are without action on boron trifluoride (83). Silicon difluoride, SiF_2 (made by heating silicon with silicon tetrafluoride at 1150°), interacts with boron trifluoride at low temperatures to give compounds of formulas $\text{F}_3\text{Si}(\text{SiF}_2)_n\text{BF}_2$ where $n = 1, 2, 3$, or 4 (816); no trifluorosilylboron difluoride, F_3SiBF_2 , could be detected (mass spectrometrically) in the reaction products. This was thought to be due to the initial step in the reaction being the production of a Si_2F_4 biradical to which the boron trifluoride or silicon difluoride may add:

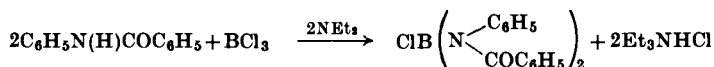
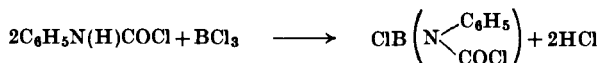


Less clearly defined products were obtained when boron trichloride was used in place of the trifluoride (816), although mixed fluoride-chloride was probably present. Trichlorosilylboron dichloride results when boron trichloride and silicon tetrachloride are passed through a mercury discharge (542), but no chemical reaction takes place in the SiX_4/BX_3 systems under normal conditions of temperature and pressure (21, 392, 584, 627). Germanium tetrachloride and tetrabromide (584) and tin tetrabromide and tetraiodide (12) have been shown to form no compounds with boron tribromide, whereas tin tetrachloride (and titanium tetrachloride) undergoes a quantitative halogen exchange (250).

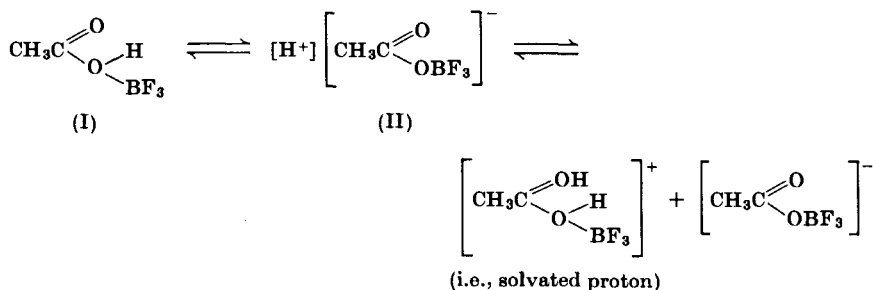
Formyl fluoride and acetyl fluoride both form 1:1 compounds with boron trifluoride, the infrared spectra and electrical conductivity of which suggests that they contain the tetrafluoroborate anion (665, 666, 763, 807, 872). Acetyl chloride forms rather low-melting, unstable complexes with boron trifluoride (112, 571, 763) and trichloride (339, 344, 702), but it is not clear whether these are tetrahaloborates; no complex results when benzoyl chloride is treated with boron trichloride (344).

Phase diagrams indicate that carbonyl chloride gives two unstable complexes with boron trifluoride, COCl_2BF_3 and $(\text{COCl}_2)_2\text{BF}_3$ (530); on heating in a sealed tube, carbonyl chloride and boron tribromide exchange halogen (576). Carbon monoxide under normal conditions shows no affinity for the boron trihalides but, when mixtures of carbon monoxide and either boron trifluoride or boron trichloride are subjected to a silent electric discharge, a slow reaction takes place to give polymers of unknown structure having the approximate composition $\text{BX}_3\text{}_2\text{CO}$ (844); although some carbonyl chloride is produced when the trichloride is used, diboron tetrachloride (which might have been expected as the

other product) could not be detected. Carbamoyl chloride and benz-anilide both lose hydrogen chloride to give bis(amido)chloroboranes when treated with boron trichloride (483):



Carboxylic acids form two series of compounds with boron trifluoride: $\text{RCOOH} \cdot \text{BF}_3$ and $(\text{RCOOH})_2\text{BF}_3$ (330, 572, 817). The acetic acid complex $\text{CH}_3\text{COOH} \cdot \text{BF}_3$, a typical member of the series, has a fairly high electrical conductivity at its melting point (ca. $2.2 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 37.5°), which suggests that it may ionize as acetoxyltrifluoroboric acid (71, 331, 338):



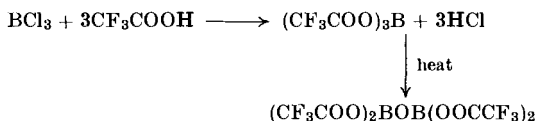
The second mole of acetic acid in the 2:1 acetic acid-boron trifluoride complex may then be attached to (I) by hydrogen bonding [as in $(\text{H}_2\text{O})_2\text{BF}_3$, page 79], or may solvate the proton in (II). The 1:1 acetic acid complex is rather unstable and begins to lose boron trifluoride a few degrees above its melting point. Electrolysis of the pure liquid produces 1 mole of hydrogen at the cathode per Faraday, together with variable amounts of boron trifluoride, while the anode gas consists of a mixture of oxygen, carbon dioxide, ethane, and boron trifluoride. A rather unusual method of preparing $(\text{CH}_3\text{COOH})_2\text{BF}_3$ in good yield is to treat a mixture of boric oxide and acetic anhydride with hydrogen fluoride (596).

The other boron halides react differently with carboxylic acids and evolve hydrogen halide in a complex sequence of reactions. With excess

of acid, the tetraacyldiborates are usually formed (280, 288, 307, 377, 476, 793),

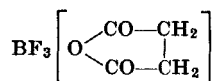


although trifluoroacetic acid produces the expected tris(trifluoroacetyl)-borate on treatment with boron trichloride (294):

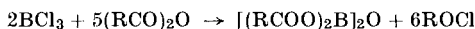
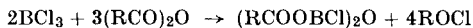


A deficiency of carboxylic acid leads to the formation of haloacyldiborates [e.g., $\text{Cl}(\text{RCOO})\text{BOB}(\text{OOCR})\text{ClCl}$] together with the acyl halide and carboxylic anhydride, both of which react further with boron trihalides. Attempts to make triacetylborate, using the reaction of silver acetate with boron trichloride in dioxan solution, gave only acetic anhydride, silver chloride, and small amounts of tetraacetyldiborate; sodium acetate did not react (159). Thus, the apparently low thermal stability of triacylborates would suggest that the triacylborates, reputedly formed in the reaction of boron tribromide with acetic, propionic, and butyric acids (793), were incorrectly analyzed.

Boron trifluoride normally does not give simple addition compounds with carboxylic acid anhydrides, although succinic anhydride, as an exception, gives a 1:1 complex (571):

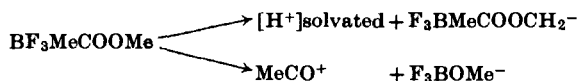


With acetic acid anhydride, the product of the reaction, which takes place readily in the cold, is an adduct of diacetic anhydride $(\text{BF}_3)_3[(\text{MeCO})_2\text{CHCO}]_2\text{O}$ (569, 573). The other boron halides cleave anhydrides to give the acyl halide, as for example in the case of acetic anhydride and boron trichloride (288):

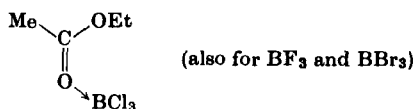


Boron trifluoride and trichloride react with carboxylic esters to form rather unstable 1:1 complexes. The trifluoride complexes tend to dissociate on slight warming and, when left in the liquid state, slowly form brown-colored decomposition products (335); the conductivities of the pure liquids (333–355) are very much higher than those of the parent

esters or boron trifluoride, which may be due to possible self-ionization reactions such as (330):

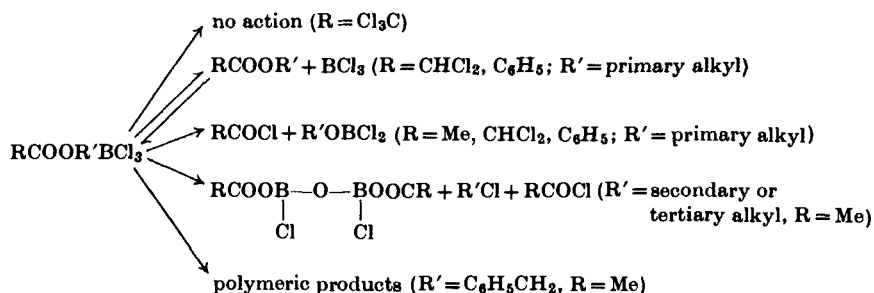


The ethyl acetate-boron trichloride compound is only a simple adduct at, or below, room temperature since treatment of it with *n*-octyl alcohol produces high yields of *n*-octyl borate, a result expected if the adduct has not undergone any internal rearrangement (257). With this established it was then proved, spectroscopically, that the donor site was the acyl oxygen atom (480):



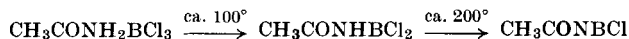
By assuming that the magnitude of the shift, Δ , of the carbonyl stretching frequency in a complex, $\text{EtOOCCH}_3\text{MX}_3$ ($\Delta = \nu_{\text{ligand}} - \nu_{\text{complex}}$), was a measure of the acceptor strength of the trihalide MX_3 , Lappert showed that the acceptor strength series for the boron halides was in the order $\text{BBr}_3 > \text{BCl}_3 > \text{BF}_3$. Similarly, the acceptor series for the Group III halides (toward ethyl acetate) is apparently $\text{BCl}_3 > \text{GaCl}_3 > \text{AlCl}_3 > \text{InCl}_3$ and $\text{BBr}_3 > \text{AlBr}_3 > \text{InBr}_3$ ($\text{GaBr}_3\text{EtOOCCH}_3$ was not studied), which is in accord with the Pauling electronegativity values for these elements (481).

The boron trichloride-ester complexes can decompose in several ways on warming, and all the following possibilities have been realized by changing the group R' in a series of esters, RCOOR' (257, 308):

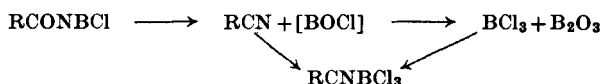


Hydroxy esters (e.g., ethyl glycolate, β -hydroxypropionate, malate, or lactate) act purely as expected of an alcohol and form borates, $(\text{RO})_3\text{B}$ (257).

Carboxylic acid amides form 1:1 complexes with the boron halides, in which the nitrogen atom provides the donor site [(291, 297, 599a, 702, 817; see, however, Gore *et al.* (312a)]. Boron trichloride-acetamide, a fairly typical member of the series, slowly loses hydrogen chloride on heating,

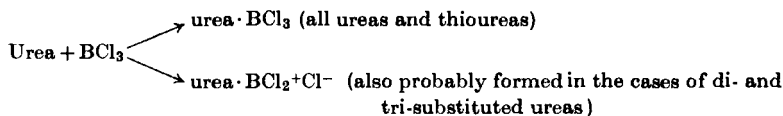


but the structures of the various products are unknown; in certain cases, further heating produces nitrile complexes of boron trichloride:

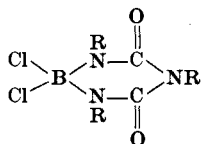


Triamidoboranes can be isolated from the reaction of amides with boron trichloride in the presence of triethylamine, the latter removing hydrogen chloride from the reaction zone as triethylamine hydrochloride (483).

Ureas and thioureas also form 1:1 complexes with the boron trihalides (62, 721) and, although strong intermolecular association in solution made spectral interpretation difficult for the urea $\cdot \text{BF}_3$ complexes, it was possible to show that a nitrogen atom was the donor in the thiourea $\cdot \text{BF}_3$ adducts; the n.m.r. spectra were consistent with a rapid exchange of boron trifluoride among the thiourea ligand molecules (721). Chemical evidence suggests that, in the urea adduct, the boron trifluoride is also attached to a nitrogen atom (62); this contradicts earlier work summarized, for example, in reference (187). The position regarding the other boron trihalide-urea complexes is more complicated, since the type of adduct formed depends upon the substituents on the nitrogen atoms (721):

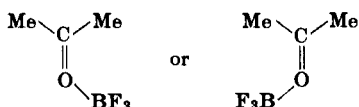


On standing in certain solvents the nonionic complexes give compounds of probable structure:

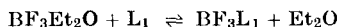


Boron tribromide-urea complexes are very unstable and have only a transitory existence, decomposing to insoluble solids of empirical composition $\text{urea} \cdot \text{BBr}_{2.5}$ (721).

Both aldehydes and ketones form fairly stable 1:1 complexes with boron trifluoride (112, 511, 817); the infrared spectra of the latter indicate that their structure is $\text{R}_2\text{C}=\text{O} \rightarrow \text{BF}_3$ (R = alkyl, aryl) (152, 153). The proton n.m.r. spectrum of $(\text{CH}_3)_2\text{COBF}_3$ exhibits only a single sharp line even at -70° (480) although two possible donor sites are available on the oxygen atom,

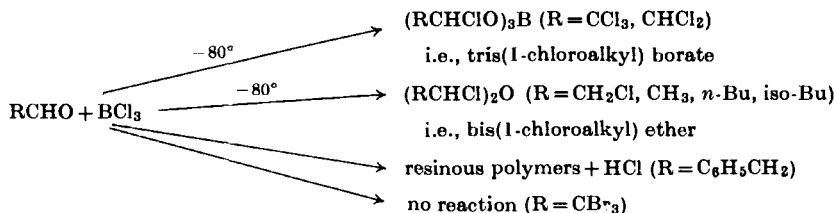


which should make the methyl groups inequivalent in the complexes. This suggests that the boron trifluoride is undergoing a rapid exchange between the two donor sites and/or between acetone molecules. By carrying out a spectroscopic study of equilibria, such as:



for ligands L_1 , L_2 , L_3 , it was deduced that the donor strength of a series of ketones was in the order *p*-methoxyacetophenone > *p*-methylacetophenone > acetophenone (588), in agreement with the expected order of electron release by the phenyl rings in these ketones.

The reactions of boron trichloride (and no doubt the tribromide and triiodide also) with aldehydes and ketones are more complex. Only in a few cases (e.g., crotonaldehyde) does an aldehyde give a 1:1 complex with boron trichloride (258). Gerrard has treated a series of aldehydes with the trichloride and a summary of his findings is (258):



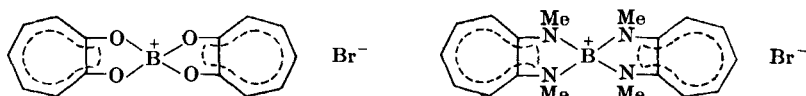
Aliphatic ketones are similarly very reactive toward boron trichloride and evolve hydrogen chloride while forming polymers⁵ (339,

⁵ Hexafluorocyclobutanone reacts differently and adds to boron trichloride, giving esters of 1-chlorohexafluorocyclobutanol (692a).

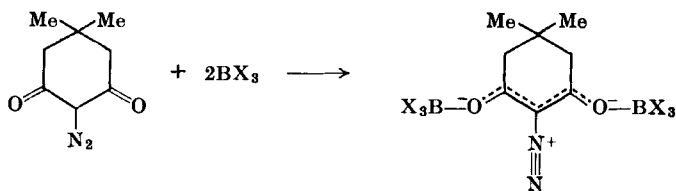
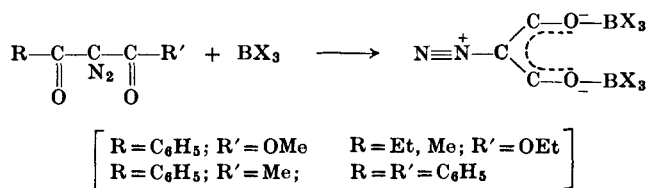
533, 702). The aromatic ketones on the other hand, give stable adducts, xanthone and benzophenone having been used in n.m.r. and infrared spectral studies to deduce the relative acceptor strengths of the boron trihalides (171, 270) (the latter workers also demonstrated that the ^{11}B chemical shifts of adducts can be used to compare the strengths of chemically unrelated bases). Certain diketones and epoxyketones form chelates with boron trifluoride (35, 374, 420, 590, 818),



which are rather similar to the ionic species formed between either tropolone or aminotroponimine and boron tribromide (600):

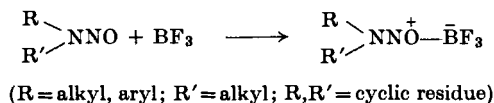


Boron trifluoride and trichloride react in benzene solution with α -carbonyldiazo compounds and with diazodimedone to form complexes containing 2 moles of trihalide, the donor sites being the carbonyl oxygen atoms (231a):



The 1:1 compounds formed between boron trifluoride and nitrosamines release the unchanged nitrosamine on treatment with alkali, demonstrating that no rearrangement takes place during preparation,

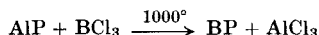
while spectroscopic studies show that the boron trifluoride is bonded to the oxygen atom (450):



Nitrobenzene forms 1:1 complexes with the trihalides (boron triiodide has yet to be studied), the structure of which are unknown (108, 446, 686); the boron tribromide adduct is rather unstable and just above its melting point (63°–64°C) rapidly decomposes (108). Neither 4-methylnitrobenzene nor 4-methoxynitrobenzene forms complexes with boron trifluoride but both give rather unstable adducts, which slowly lose hydrogen chloride at room temperature when treated with boron trichloride at –30° (364).

6. Reactions with Compounds of Group V Elements

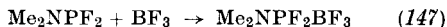
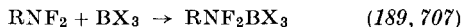
The free elements of Group V are inactive toward the trihalides under normal conditions, but active nitrogen is thought to give diboron tetrachloride on reaction with the trichloride (803), while trace amounts of boron trichloride and nitrogen in a helium electrical discharge produce the spectrum of BN (212). A mixture of hydrogen with either boron trichloride (863) or tribromide (568) gives boron phosphide when passed over heated phosphorus; aluminum phosphide gives the same product (863):



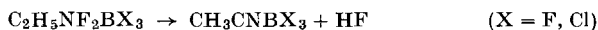
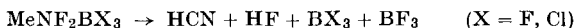
In the absence of hydrogen, phosphorus and boron trichloride apparently give elemental boron (614) but it should be noted that boron and phosphorus can react together to give boron phosphide (863). White phosphorus reacts with boron tribromide or triiodide (but not BCl_3) in chloroform solution to give polymers, P_2BX_3 , of unknown structure (275).

The Group V halides have received considerable attention regarding their possible Lewis basicity; some of the earlier work with phosphorus trichloride has been found misleading since the adducts described are not those of phosphorus trichloride but are formed from an impurity, phosphoryl chloride. The trifluorides of nitrogen (189) and phosphorus (83, 147) do not form isolable adducts with boron trifluoride or trichloride even at low temperatures; tetrafluorohydrazine and chloro- and tri-

fluoromethyl-difluoramine similarly show only a weak association below about -80° (189). The substitution of a fluorine atom by a less electro-negative group allows solid adducts to be isolated:

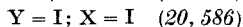
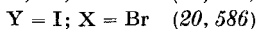
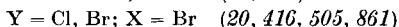
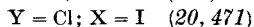
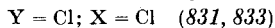
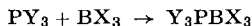


The difluoramine adducts, which have infrared spectra consistent with their being covalently bonded, are thermally unstable (189):

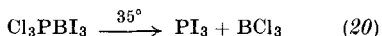
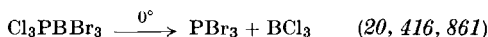


A study of the reactions of several chloroamines with boron trifluoride revealed that the basic properties decreased as $\text{NMe}_2\text{Cl} > \text{NMeCl}_2 > \text{NCl}_3$, no adduct being formed at all with nitrogen trichloride (14).

The other phosphorus halides form complexes with boron trichloride, tribromide, and triiodide but not with the trifluoride, this presumably being a manifestation of the relative Lewis acidities of the boron halides:



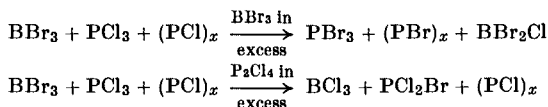
Exchange of halogen also occurs in these systems, when phosphorus trichloride is used as the donor molecule:



The trichlorides or tribromides of arsenic and antimony do not react with the boron trihalides to give adducts (12, 416, 528, 811) but, as indicated (page 4), the halides of antimony are valuable synthetic reagents in that they readily undergo halogen exchange with the boron trihalides (or substituted boron halides) (e.g., 512), the lighter halogen being transferred from antimony to boron. Halogen exchange also occurs when diphosphorus tetrachloride (which does not react with either BF_3 or BCl_3) is treated with boron tribromide; the reaction is complicated due to the quantitative disproportionation of diphosphorus tetrachloride to phosphorus trichloride and $(\text{PCl})_x$ that occurs initially (505),



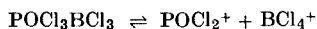
to be followed by halogen exchange:



However, an adduct $\text{P}_2\text{I}_4 \cdot 2\text{BBr}_3$ is formed when boron tribromide and diphosphorus tetraiodide react together (586). Phosphorus-boron coupling does not occur when a mixture of boron trichloride and phosphorus trichloride is passed through a mercury discharge (268).

Phosphorus pentachloride and pentabromide form 1:1 compounds with the boron trihalides, which probably contain the tetrahaloborate anions $\text{PCl}_4^+\text{BCl}_4^-$ (349, 833), $\text{PBr}_4^+\text{BBr}_4^-$ (809, 837), and $\text{PCl}_4^+\text{BF}_3\text{Cl}^-$ (833, 834). Phosphorus pentachloride is also capable of adding on a second mole of boron trichloride (833) or of boron tribromide (810) to give $\text{PCl}_5 \cdot 2\text{BX}_3$. Although the mode of bonding in these comparatively weak complexes is not understood, it is possible that monohalogen bridges are formed either between two boron atoms $[\text{X}_3\text{BX}-\text{BX}_3]$ or between boron and phosphorus $[\text{X}_3\text{PX}-\text{BX}_3]$, as in known adducts $\text{L} \cdot 2\text{BX}_3$ discussed later (page 68).

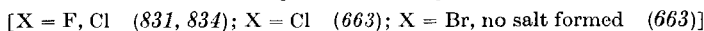
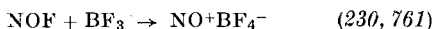
Phosphoryl chloride and bromide⁶ react readily in 1:1 ratios with boron trifluoride, trichloride, and tribromide to give white solids that sublime at room temperature (138, 361, 362, 576, 628, 833, 834, 840). Two possible structures have been proposed for the solid $\text{POCl}_3\text{BCl}_3$; the ionic form $\text{POCl}_2^+\text{BCl}_4^-$ was suggested on the basis of the infrared spectrum (304), but other workers argued that the spectrum supported a covalent structure $\text{Cl}_3\text{PO} \rightarrow \text{BCl}_3$ (393, 834, 840). A halogen exchange study of the $\text{BCl}_3/\text{POCl}_3$ system was also interpreted in terms of the covalent structure (393). By using substituted phosphorus oxychlorides such as $\text{R}_2\text{P}(\text{Cl})\text{O}$ or $\text{C}_6\text{H}_5\text{P}(\text{X}_2)\text{O}$, it was shown (362, 703) that the complex $\text{R}_2\text{P}(\text{Cl})\text{OBCl}_3$ still exhibited a P—Cl stretching frequency in the infrared spectrum so that the ionic structure, involving chlorine transfer, can probably be ruled out in these complexes, and hence the bonding is most likely via the oxygen atom (in keeping with all other known phosphoryl chloride complexes that have been studied structurally). Furthermore, conductivity measurements on $\text{POCl}_3\text{BCl}_3$ dissolved in liquid phosphoryl chloride show that the dissociation constant for the equilibrium,



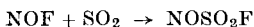
is only about 3×10^{-7} (34). Phosphoryl fluoride (703) and thiophosphoryl chloride (840) do not react with boron trichloride.

⁶ Thermal analysis suggests that phosphoryl fluoride and boron trifluoride may also form a 1:1 adduct (83).

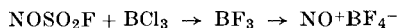
Nitrosyl fluoride and chloride react with the boron halides to form the nitrosyl cation, NO^+ :



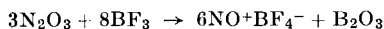
If the nitrosyl halide reaction is carried out in liquid sulfur dioxide, nitrosyl fluorosulfinate is formed initially:



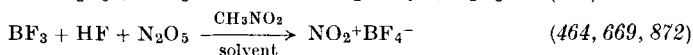
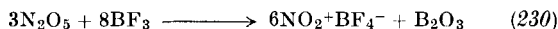
Boron trichloride is converted to the trifluoride under these conditions, and so the product is again nitrosyl tetrafluoroborate (763):



The same cation is formed when nitrogen trioxide is treated with boron trifluoride in liquid sulfur dioxide (230):



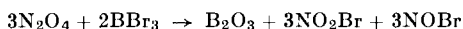
Sublimation of nitrosyl tetrafluoroborate in an atmosphere of ozone gives nitryl tetrafluoroborate (787), which can also be made by treating boron trifluoride with either nitryl fluoride (172, 464, 669) or nitrogen pentoxide (230, 872),



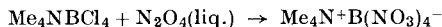
while dinitrogen tetroxide gives a mixture of both these cations (230):



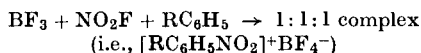
This work, involving a study of the reaction products by Raman and infrared spectroscopy and X-ray powder diffraction, apparently disproves earlier reports (e.g., 787), which suggested that the complexes formed between the nitrogen oxides and boron trifluoride involved the bonding of the trifluoride to nitrite and nitrate ions; however, boron trifluoride reacts with both sodium nitrate and nitrite to give mainly nitrosyl and sodium tetrafluoroborates [(759); see Evans *et al.* (230) for a discussion of the subject]. Boron tribromide reacts with dinitrogen tetroxide to give nitryl and nitrosyl bromides and not the tetrabromoborates⁷ (464):



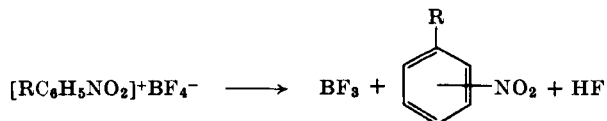
⁷ The tetranitratoborate anion is formed when tetramethylammonium tetrachloroborate is dissolved in an excess of liquid dinitrogen tetroxide (354):



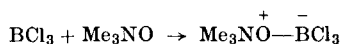
When nitryl fluoride and boron trifluoride are mixed in the presence of a substituted benzene, a colored 1:1:1 complex is formed (662, 668),



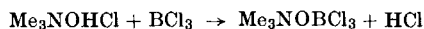
which on decomposing at low temperature gives good yields of the aromatic nitro compound:



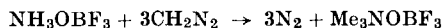
Trimethylamine oxide, trimethylphosphine oxide, triphenylphosphine oxide, and pyridine oxide all form 1:1 complexes on direct reaction with the boron trihalides in a suitable solvent, such as chloroform (131, 136, 262, 465, 703, 735, 817, 839), e.g.:



The latter complex also results when hydrogen chloride is displaced from trimethylamine oxide hydrochloride by boron trichloride (262, 703),



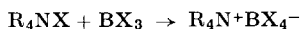
while the trifluoride adduct results from the treatment of hydroxylamine-boron trifluoride with diazomethane (839):



The hydroxylamine-boron trifluoride can be made by suspending the amine in ether cooled to -10° and then adding boron trifluoride (313, 839) or by displacing hydrogen chloride from hydroxylamine hydrochloride using boron trifluoride etherate (594, 734); the donor site was originally considered to be the nitrogen atom, but it is now thought (734) that the boron atom is bonded to oxygen. Hydroxylamine hydrochloride reacts further on heating with boron trichloride until *N*-hydroxy-*B*-trichloroborazine is produced (622). This is an extension of the well-known method of borazine synthesis in which an ammonium (or mono-substituted ammonium) halide is heated with a boron trihalide (usually the trichloride is used but never the trifluoride) (100, 128, 228, 574, 618, 775).

However, by suitably altering such reaction conditions as the

temperature and the solvent, substituted ammonium halides (and also phosphonium halides) (831, 833) can be made to form tetrahaloborates:

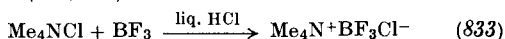


X = F; in methyl ether (850); many other solvents can be used, see (769)

X = Cl; in liquid HCl (833); in boiling $CHCl_3$ (466, 467); in liquid BCl_3 at -78° (813)

X = Br; in liquid HBr (835, 837)

X = I; in liquid HI (836, 837)



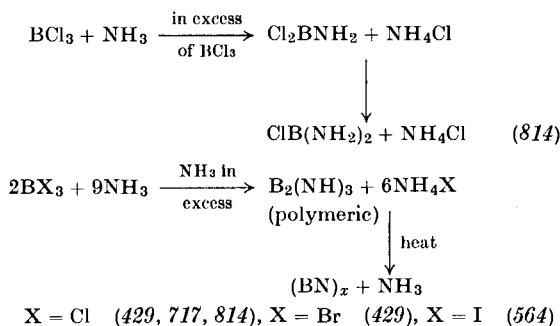
The pyridinium halides react in a similar manner (475). A useful collection of preparative methods covering all the tetrahaloborates, together with a discussion of their n.m.r. spectra, may be found in reference (813).

The reaction of ammonia and free amines with the boron halides has become one of the most extensively studied branches of boron chemistry since ammonia-boron trifluoride was first reported in 1808 by Gay-Lussac. The latter adduct can be sublimed in a vacuum but decomposes above 125° to give ammonium tetrafluoroborate and boron nitride (490); it also dissolves in liquid ammonia without change, unless an alkali metal is present (428, 563), e.g.:



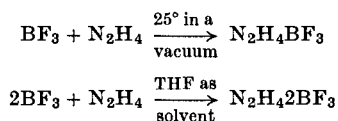
The kinetics of the ammonia/boron trifluoride reaction have been studied by a modification of Polanyi's spherical diffusion flame (447). The equilibrium constant for the formation of ammonia-boron trifluoride is greater than $5 \times 10^9 \text{ cm}^3/\text{mole}$, while the unusually large ratio between the rates for NH_3 and ND_3 was explained by assigning to the transition state a large degree of charge transfer stabilization and a negligible activation energy.

The other boron trihalides react vigorously with ammonia and lose hydrogen halide in a condensation process until boron imide remains:



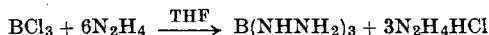
The weaker base, phosphine, forms a complex with boron trifluoride only at low temperatures (529, 801) whereas arsine does not complex even below -100°C (529). With the other trihalides, which are stronger Lewis acids than boron trifluoride, both phosphine and arsine form 1:1 complexes (792, 798) but on strong heating phosphine and boron trichloride react further to give boron phosphide (863).

With the bidentate ligand, hydrazine, boron trifluoride forms both a 1:1 and a 1:2 adduct, depending on the conditions employed (79, 695a, 696):



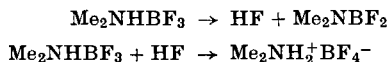
The thermal decomposition of the 1:1 adduct above 190° is complex; nitrogen, ammonia, ammonium tetrafluoroborate, and boron nitride are formed. The hydrazine is not replaced by ammonia at -80° , but a diammoniate $\text{N}_2\text{H}_4\text{BF}_3\cdot 2\text{NH}_3$ is formed in which the ammonia is thought to be held by dipole-dipole forces; on warming to room temperature the ammonia is lost (695a). Boron trifluoride displaces silicon tetrafluoride from the adduct $\text{SiF}_4 \cdot 2\text{N}_2\text{H}_4$ (13).

When either boron trichloride or tribromide is treated with hydrazine, hydrogen halide is eliminated that reacts with excess of hydrazine to give $\text{N}_2\text{H}_4\text{HX}$; thus with boron trichloride in tetrahydrofuran the combining ratio was 1:6 ($\text{BCl}_3:\text{N}_2\text{H}_4$), suggesting the reaction (697):

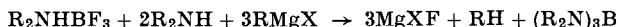


Diphosphine gives a 1:2 adduct with boron trifluoride at very low temperatures but above -118° this slowly decomposes to give phosphine; at -78° the evolution of phosphine and boron trifluoride becomes rapid (70).

Primary and secondary aliphatic amines complex readily with boron trifluoride to form 1:1 compounds (330, 817). However, Russian work apparently casts doubt on some of the earlier reports of simple adducts by showing that a white solid, thought for many years to be Et_2NHBf_3 , is in fact $\text{Et}_2\text{NH}_2^+\text{BF}_4^-$; the true 1:1 adduct is a viscous, colorless liquid that rapidly decomposes at room temperature (732). Dimethylamine forms a more stable adduct, which begins to decompose only above 240° (119):



Owing to the strong B—F bonds, loss of hydrogen fluoride from amine-boron trifluoride adducts can usually be accomplished only at elevated temperatures, which may cause pyrolysis of the desired end products; the hydrogen fluoride can be removed at much lower temperatures by employing a “getter,” such as a reactive metal (459, 773) or a Grignard reagent (209):

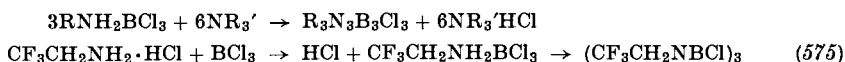


Heating an amine-boron trifluoride adduct with a tertiary amine does not remove hydrogen fluoride (119), although this technique has been found useful in the cases of the other trihalides (see below).

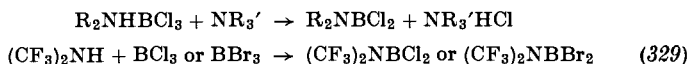
From kinetic measurements on the reactions of boron trifluoride with a series of amines in the gas phase, it has been deduced that about one collision in thirty is fruitful and, surprisingly in view of the steric changes and strains that occur on complex formation, the activation energies for the reactions are very small (269, 449); the reaction rates are $Me_3N > Me_2NH > MeNH_2$ (196).

Primary aromatic amine complexes with boron trifluoride have been reported to have infrared spectra and chemical properties that are in agreement with their formulation as hydrohalides of the arylaminoboron halides, $[C_6H_5NHBX_2]HX$ (301). This formulation has been questioned (739) since, on reexamination, the spectra were shown to support simple adduct formation of the type $R(H)_2N \rightarrow BF_3$; the rapid decomposition of solutions of these adducts during spectral studies may account for the different conclusions reached by the previous workers.

A ready loss of hydrogen halide is observed when the other boron trihalides are treated with an excess of a primary or secondary amine (288, 476). By careful use of stoichiometric amounts (1:1) of amine, however, it is possible to isolate the addition compounds in many cases (143, 144, 286, 618, 621, 656); a quantitative yield of ethylamine-boron trichloride is obtained by mixing boron trichloride and tris(ethylamino) borane (328). On being refluxed with a tertiary amine in a suitable solvent or on heating alone, these complexes readily lose hydrogen halide as $R_3NH^+X^-$, leaving either an N-substituted borazine (119, 143, 144, 195, 618, 621, 775, 822),

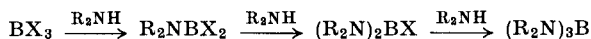


or an aminoboron dichloride (63, 119, 617–619, 656), e.g.:

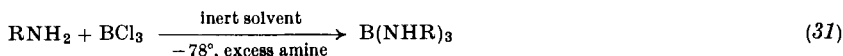


Pyridine cannot be used in these latter HX-abstraction reactions since Nöth has shown that a salt, $[\text{R}_2\text{NHB}(\text{Cl})_2\text{Py}]^+\text{Cl}^-$, is formed (636, 656).

When using secondary amines it is sometimes possible, by a suitable alteration of reaction ratios, to obtain several aminoborane derivatives (32, 288, 476, 621).



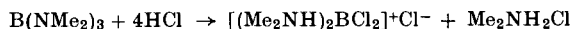
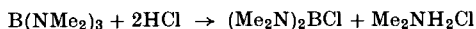
the amine often removing hydrogen halide from the reaction zone as $\text{R}_2\text{NH}^+\text{X}^-$, although when $\text{R} = \text{ethyl}$ the quaternary ammonium salt reacts further with boron trihalide to give diethylammonium tetrahaloborate (286). If the alkyl group of the secondary amine is branched in the α -position (30) or if diphenylamine is used (32), the above reaction sequence proceeds only as far as $(\text{R}_2\text{N})_2\text{BCl}$ due to steric interactions. Branching in the β -position allows the formation of $(\text{R}_2\text{N})_3\text{B}$, but substitution of the last chlorine atom is slow (30). Analogous reactions are observed when primary amines are used (621):



It has been demonstrated that the reaction



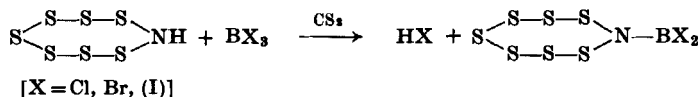
is reversible, since the treatment of aminoboron dichlorides with hydrogen chloride results in the reformation of 1:1 adducts (288, 476, 621, 637, 645). Tris(dialkylamino)boranes also react with hydrogen chloride (645), the products depending on the reaction ratios:



but substituted dialkylamino boranes give ionic complexes, containing the boron in the cation, when treated with hydrogen chloride (646).

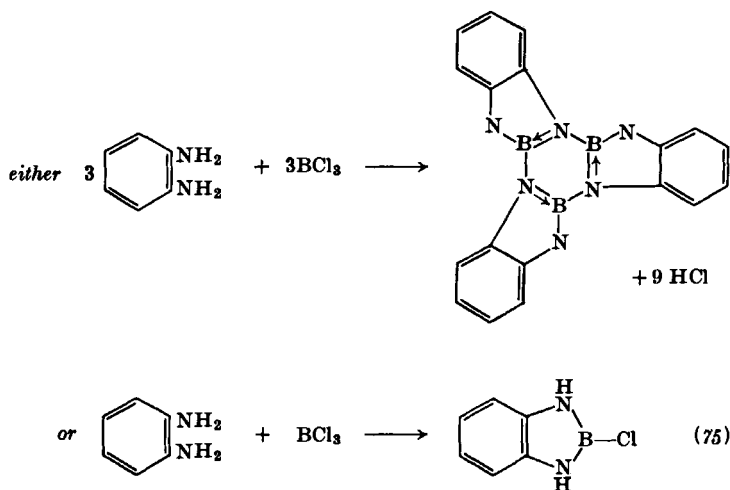
Cyclic secondary amines, such as piperidine, react as typical members of the amine series. A 1:1 complex is formed with boron trifluoride (86, 671, 817), whereas the other trihalide complexes (340, 344) undergo a ready loss of hydrogen halide (especially in the presence of triethylamine) to give aminoboron dihalides (e.g., 288). Heptasulfurimide is rather similar, except that no adduct is formed with boron trifluoride

between 80° and -78° (379); evolution of hydrogen halide occurs when the trichloride and tribromide are treated with heptasulfurimide in carbon disulfide solution, but the products of the boron triiodide reaction were too unstable to isolate (379):



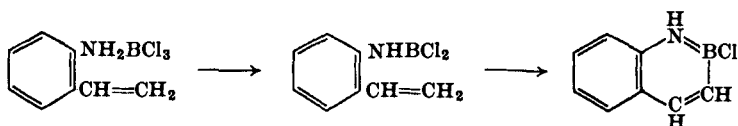
Sulphur tetranitride gives 1:1 complexes, only, when treated with boron trifluoride or trichloride, the bonding site being one of the nitrogen atoms (873a).

Typical aromatic amines such as aniline, pentafluoroaniline, *p*-toluidine, and *p*-anisidine form 1:1 complexes with boron trichloride and tribromide when the two are mixed in a suitable solvent; on heating the solutions, hydrogen halide is evolved until finally the *N*-triaryl-*B*-trihaloborazines are formed (288, 302, 575, 612, 621, 725, 775). The three phenylenediamines also give 1:1 complexes with boron trichloride, which lose hydrogen chloride on heating (758) as in the case of *o*-phenylenediamine (99, 725, 758):

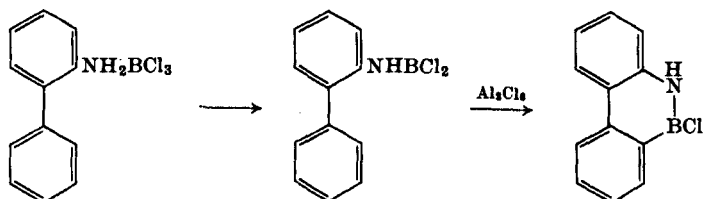


The ready loss of hydrogen chloride from aromatic amine-boron trichloride complexes has been used to advantage in the synthesis of heterocyclic molecules containing boron-nitrogen bonds (which are isoelectronic to C—C bonds). Ring closure is effected, after loss of

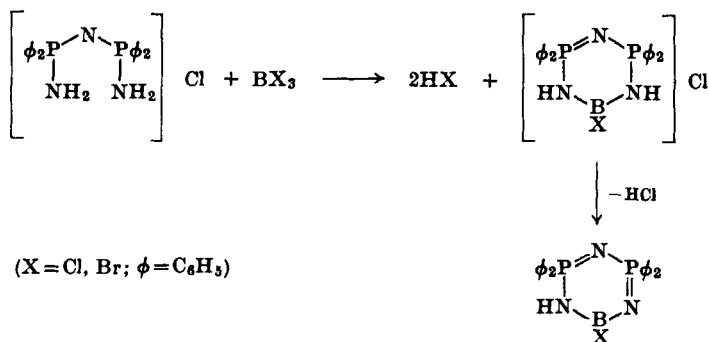
hydrogen chloride, either by placing reactive groups in suitable positions (203, 523),



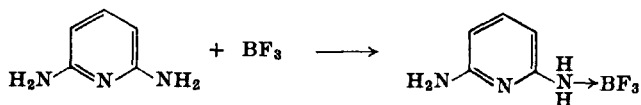
or by a Friedel-Crafts addition of the boron to the aromatic nucleus (205, 523):



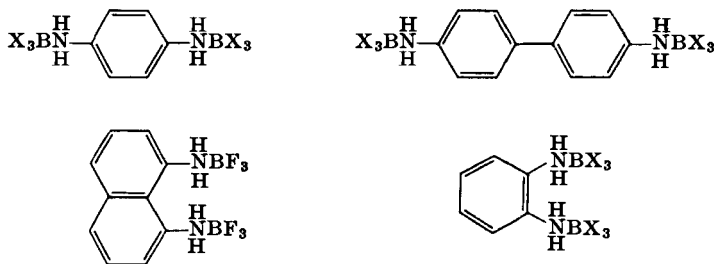
Boraphosphazenes, which are heterocycles containing boron, phosphorus, and nitrogen in the same ring, have been synthesized by a somewhat similar series of reactions (776):



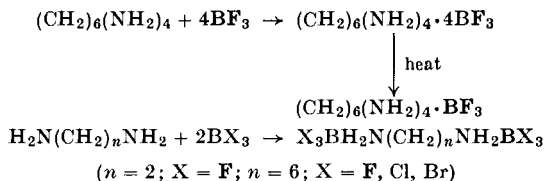
Heterocyclic polyamines usually give only a 1:1 adduct when treated with boron trifluoride, the donor site being provided by an exocyclic nitrogen atom; the addition of one boron trifluoride molecule appears to decrease the electron availability on the other possible donor atoms (460),



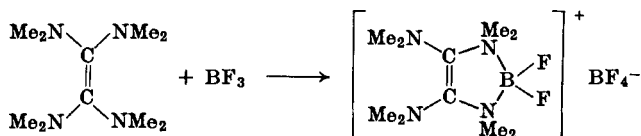
but polyamines in benzenoid systems are able to act as multicenter donor molecules toward all the boron trihalides, as shown by the following examples (281, 460):



The boron trihalides will also displace hydrogen halide from the phenylenediamine hydrohalides to give the 2:1 adducts of the corresponding diamines (281). Hexamethylenetetramine (135) and the polymethylenediamines (101, 281) react readily with boron trifluoride, trichloride, or tribromide to form adducts:

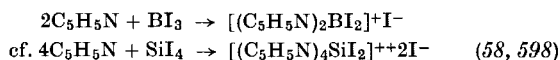


An ionic complex is formed, however, in similar reactions involving tetrakis(dimethylamino)ethylene (853):



Tertiary amines as a general rule form stable 1:1 complexes with the boron trihalides, an exception being that tertiary aromatic amines are usually too feebly basic (or too sterically hindered) to react. Thus triphenylamine does not form an adduct with boron trifluoride (770), although *N,N*-dimethylaniline and diphenylmethylaniline react quite readily (87, 686). Boron triiodide, the least studied halide, reacts as a typical Lewis acid toward trialkylamines and *N,N*-dimethylformamide in giving 1:1 adducts (471, 598), but in the reaction with pyridine its behavior is anomalous and further work with other amines seems

warranted. Two moles of pyridine react with each mole of triiodide to give what is considered to be a boronium salt (598):



Although addition of iodine to a solution of this solid gave rise to the triiodide ion, I_3^- (identified by its spectrum), no tetraiodoborate anion was produced in the presence of excess boron triiodide. The trichloride and tribromide react normally in a 1:1 ratio with pyridine forming simple adducts (56, 598), the solutions of which do not conduct electricity and

TABLE VIII
BOND DISTANCES (IN Å) AND ANGLES (IN DEGREES) IN BORON TRIFLUORIDE
ADDUCTS

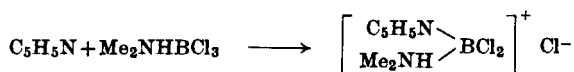
Compound	B—N	B—F	N—C _{CH₃}	F—B—F	F—B—N	B—N—C	Reference
H ₃ NBF ₃	1.60	1.38	—	111	107	—	(399, 400)
MeNH ₂ BF ₃	1.57	1.39	1.50	110.5	108.5	114	(277, 400)
Me ₃ NBF ₃	1.585	1.39	1.50	107	112	105	(277, 400)
MeCNBF ₃	1.635	1.33	—	114	103	—	(400, 401)
C ₅ H ₅ NBF ₃	1.53	1.41	1.36	109.5	108.5	—	(879)

show only a single ^{11}B n.m.r. peak in the region expected for BX_3 adducts. In the molten state, pyridine-boron trichloride behaves as if there is some dissociation into kinetically free ions, thought to be $(\text{C}_5\text{H}_5\text{N})_2\text{BCl}_2^+\text{BCl}_4^-$ (344), but certainly, in benzene solution, molecular weight determinations show the compound to be monomeric (56) —if it was present as the above salt, ion-pair formation under these conditions would result in a molecular weight closely corresponding to a dimer.

Very few amine adducts of boron trifluoride have been studied structurally by X-ray diffraction on single crystals, the results being summarized in Table VIII. In those adducts with strong donor molecules (ammonia and the amines), it can be seen that the disposition of groups around the boron atom is reasonably close to the tetrahedral, as expected if the boron were to use pure sp^3 orbitals for bond formation. Probably because of the inductive effect of the methyl group, the strengths of amine-boron trifluoride adducts are in the order $\text{NMe}_3 > \text{NHMe}_2 > \text{NH}_3\text{Me} > \text{NH}_3$, as deduced from the ^{19}F n.m.r. chemical shifts (388); this would be expected to cause a slight elongation of the B—N bond

length along the series $\text{NMe}_3 \rightarrow \text{NH}_3$, but unfortunately the errors in the X-ray measurements (between ± 0.015 and ± 0.03 Å) tend to conceal subtle changes of this nature. The B—F bond distance is virtually constant in the amine adducts; however, if a weak donor molecule such as methyl cyanide is used, marked changes occur in the geometry of the boron trifluoride adduct. The angle F—B—F increases to 114° and so makes the boron lie closer to the plane of the three fluorine atoms (indicating a smaller deformation of the original boron trifluoride molecule); the decreased B—F distance no doubt signifies a certain amount of π -bonding between boron and fluorine, while another significant factor is the increased B—N bond length. In keeping with these structural properties, which suggest a weak complex, methyl cyanide-boron trifluoride is partially dissociated in nitrobenzene solution at room temperature (583) and completely dissociated in the vapor state at 50° ; the methyl cyanide is also readily displaced by several amines. The short B—N bond length (1.53 Å) in pyridine-boron trifluoride is apparently at variance with n.m.r. data (123), which suggests that trialkylamines form stronger complexes with boron trifluoride than does pyridine.

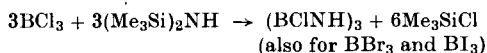
A boronium salt is thought to be formed when pyridine is added to a solution of dimethylamine-boron trichloride (636, 656),



but the evidence (102) put forward to suggest, although the authors agreed it did not prove, that dimethylamine-boron trichloride is ionic (either as $\text{Me}_2\text{NHBCl}_2^+\text{Cl}^-$ or $(\text{Me}_2\text{NH})_2\text{BCl}_2^+\text{BCl}_4^-$) would seem to be less convincing now that the compound $\text{Et}_2\text{NHBCl}_3$ has been shown (290) to closely resemble the simple adduct triethylamine-boron trichloride in its chemical properties and, like $\text{Me}_2\text{NHBCl}_3$ (320), to have a very low electrical conductivity in solution.

The substitution of silyl, disilanyl, or methylsilyl groups (i.e., SiH_3 , SiH_2SiH_3 , MeSiH_2 or Me_3Si) onto nitrogen in place of alkyl drastically alters the chemistry of the ensuing reactions from that expected by a study of the organoamines. Unlike the organoamines, which do not undergo N—C bond cleavage on reaction with the boron halides, the silylamines undergo a very facile N—Si cleavage often with such rapidity that the initial complexes (should they be formed) cannot be isolated except in a few cases (2, 67, 134, 167, 221, 630, 676, 805). An excellent example is the reaction of bis(trimethylsilyl)amine, $(\text{Me}_3\text{Si})_2\text{NH}$, with

boron trichloride, which can give a 30% yield of *B*-trichloroborazine (630),



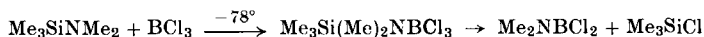
while under other conditions only one trimethylsilyl group is cleaved from the nitrogen (67),



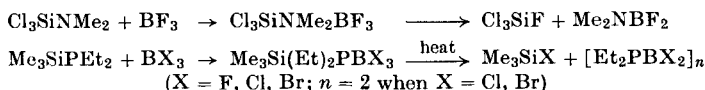
neither case resembling the analogous dialkylamine/boron trichloride reaction:



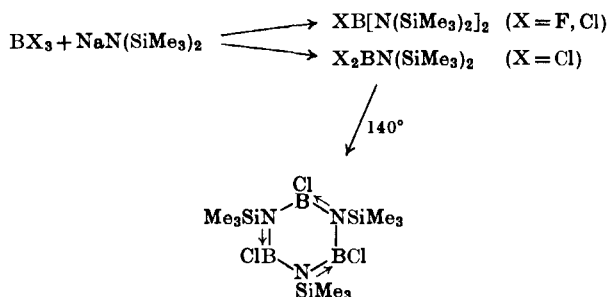
Trimethylsilyldialkylamines, Me_3SiNR_2 , also undergo N—Si cleavage when treated with boron trichloride, tribromide, or triiodide, a 1:1 adduct being formed at -78° when the trichloride is used (5, 630), e.g.:



Similar reactions occur when trichlorosilyldimethylamine (352, 353) and trimethylsilyldiethylphosphine (655) are employed:



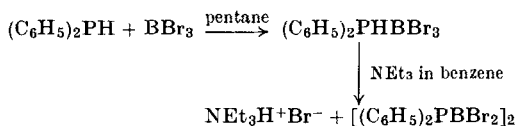
It is possible to make several of the silylaminoboron halides by employing a sodium salt coupling reaction in diethyl ether (309):



Some tertiary amine ligands, notably pyridine and triethylamine, will add 2 moles of a boron trihalide at low temperatures to form unstable solids, $\text{base} \cdot 2\text{BX}_3$ (115), which are considered to contain a single halogen bridge between the boron atoms: $\text{base} \cdot \text{X}_2\text{B—X—BX}_3$. Indirect evidence from n.m.r. studies on boron trifluoride/pyridine mixtures in toluene also indicates the formation of these 1:2 adducts (123). An alternative explanation of the bonding in the case of similar ether $\cdot 2\text{BX}_3$ adducts is

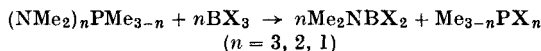
that the two trihalide molecules *may* be accommodated by the two lone pairs on the oxygen atom; however, this fails to account for $\text{Et}_2\text{O} \cdot 3\text{BF}_3$ in which at least one of the second and third boron trifluoride molecules must be assumed to bond in the same way as the above amine $\cdot 2\text{BX}_3$ adducts (865). Several examples are known in which an adduct contains more than 1 mole of base per mole of boron trihalide; thus ammonia and boron trifluoride have been shown to form BF_3NH_3 , $\text{BF}_3(\text{NH}_3)_2$, $\text{BF}_3(\text{NH}_3)_3$, and $\text{BF}_3(\text{NH}_3)_4$ at low temperatures (111). In almost every case it is possible to assume that the excess of ligand is held to the 1:1 adduct via hydrogen-bond formation. Such behavior has been shown to occur, for example, in the alcoholates, hydrates, and carboxylic acid derivatives of boron trifluoride [(330, 817); see also page 79 and Bang and Carpenter (37)].

The alkyl-substituted phosphines react with boron trifluoride in a similar fashion to the corresponding amines, except that the complexes formed are less stable (103) and tend to dissociate readily; the base strength of a series of phosphines toward boron trifluoride has been shown to be $\text{Me}_3\text{P} > \text{Me}_2\text{PH} > \text{MePH}_2$ (103). A gas phase kinetic study of the reaction between boron trifluoride and trimethylphosphine indicated that about one collision in fifteen is fruitful in giving the adduct Me_3PBF_3 (448). Diphenylphosphine forms 1:1 complexes with boron tribromide and triiodide, which readily lose hydrogen halide when refluxed with a tertiary amine (274, 276),

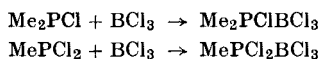


while triphenylphosphine gives a stable 1:1 adduct with boron trifluoride (671), trichloride (708), tribromide (274, 276), and triiodide (274, 598). Nitrogen compounds form more stable adducts with the boron trihalides than the corresponding phosphorus derivatives because of the decreasing electronegativity of the elements down Group V. Hence, the nonexistence of triphenylamine-boron trifluoride (770) must be due to steric interaction involving the phenyl groups; a similar effect is found in Group VI where the diphenylsulfide complex of boron trichloride is found to be more stable than the diphenyletherate (686). As expected, the base strength of the trimethyl derivatives of Group V decreases down the group, so that trimethylarsine forms a comparatively weak complex with boron trifluoride whereas trimethylstibine does not give a complex even at -78° (187). With the stronger Lewis acid boron trichloride, trimethylphosphine forms a very stable adduct (708).

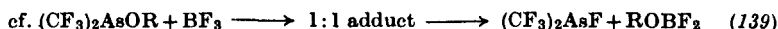
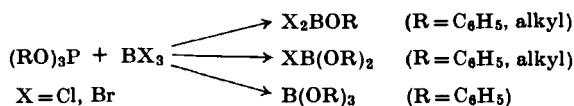
Dimethylaminophosphines, $(\text{Me}_2\text{N})_n\text{PMe}_{3-n}$, undergo a slow reaction with boron trifluoride and trichloride in which the dimethylamino groups are cleaved from the phosphorus:



When the chloride is used, side reactions also occur due to the formation of rather unstable 1:1 complexes between methylchlorophosphines and boron trichloride (418):

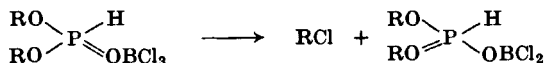


Alkoxy and aryloxy groups bound to phosphorus in the alkyl/aryl phosphites are similarly transferred to boron when the phosphite and boron trihalide are mixed (259, 260, 299):



Cleavage reactions apparently also occur when boron trifluoride and phosphites are mixed together, but the products were not studied (829).

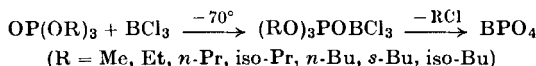
The dialkylhydrogen phosphites (68) form 1:1 complexes when treated with boron trichloride, the donor site being the oxygen atom; decomposition of these complexes occurs by loss of alkyl chloride:



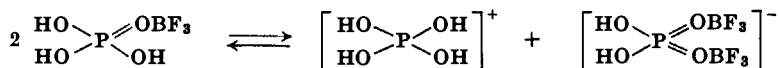
When diphenylhydrogen phosphite is used, hydrogen chloride is evolved from the complex instead of chlorobenzene (68):



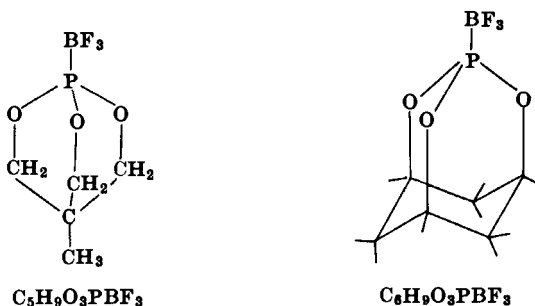
Trialkyl phosphates, after first forming 1:1 adducts at low temperatures, readily eliminate alkyl chloride, hydrogen chloride, and olefin when treated with boron trichloride; strong heating toward the end of the reaction gives a product resembling boron phosphate (261, 282–284):



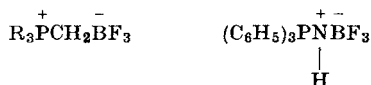
Free phosphoric acid reacts in a 1:1 ratio with boron trifluoride to form a complex that conductance measurements have shown to be highly ionized in the liquid state (342):



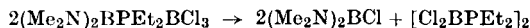
Triaryl phosphates form 1:1 complexes, $(\text{RO})_3\text{PO}-\text{BX}_3$, when treated with boron trifluoride, trichloride, and tribromide. The substitution of one, or two, chlorine atoms in group R (e.g., $\text{R} = 4\text{-ClC}_6\text{H}_4$ or $2,4\text{-Cl}_2\text{C}_6\text{H}_3$) is sufficient to depress the basicity of the phosphate below that required for complex formation with the trifluoride, although adducts are formed with the two stronger acceptors (261). Boron trifluoride forms 1:1 complexes with the two polycyclic phosphites $\text{C}_5\text{H}_9\text{O}_3\text{P}$ and $\text{C}_6\text{H}_9\text{O}_3\text{O}$ (389, 828, 829):



The acid strength for several Lewis acids toward these cyclic phosphites was deduced to be $\text{BH}_3 > \text{BMe}_3 \cong \text{BF}_3$ from proton n.m.r. chemical shift measurements on the corresponding adducts (829). Methylenephosphoranes, R_3PCH_2 (348), and triphenylphosphinimine, $(\text{C}_6\text{H}_5)_3\text{PNH}$ (17), also give 1:1 adducts when reacted with boron trifluoride or boron trifluoride etherate:



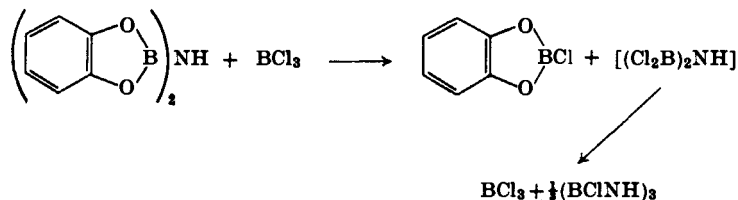
An adduct is first formed when bis(dimethylamino)diethylphosphinoborane, $(\text{Me}_2\text{N})_2\text{BPEt}_3$, is treated with boron trichloride (653), but this readily decomposes at room temperature:



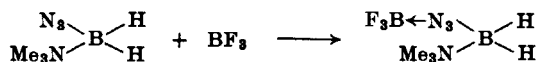
The reaction is reminiscent both of Burg's work on the dimethylamino-dimethylborane/boron trifluoride system (130),



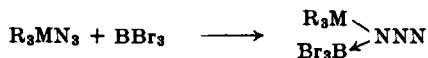
and of Lappert's on the reaction of boron trichloride with a borylamine (489):



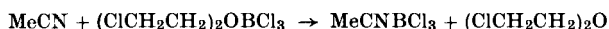
Another boron compound able to complex with a boron trihalide is trimethylamine-azidodihydridoborane, which adds on 1 mole of boron trifluoride, the azide group providing the donor site (585):



Similar adducts are formed between certain Group IV azides and boron tribromide (812):

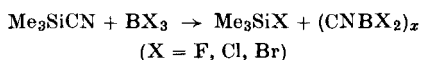


The nitrogen atom of the cyanide group is an effective donor site; the addition of boron trifluoride to complex metal cyanides (330) (page 31) has already been discussed. Hydrogen cyanide and silver cyanide (710) may also be used as donor molecules for example toward boron tribromide, while the organonitriles form many complexes with the boron trihalides (see Table X). The complexes formed are rather weak, as shown by the fact that pyridine, tetrahydrofuran, and di-*n*-butyl sulfide will displace boron trichloride from its methyl cyanide adduct (298); however, methyl cyanide is a stronger base than 2-chloroethyl ether:



The complexes formed by pentafluorophenyl cyanide are much weaker than the corresponding phenyl derivatives, the boron trifluoride complex being highly dissociated at room temperature while the trichloride complex exhibits a dissociation pressure of a few mm at 18° (496).

Silyl cyanide and trimethylsilyl cyanide give very unstable complexes with the boron trihalides, which readily eliminate the silyl halide (231)

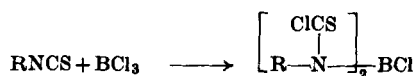
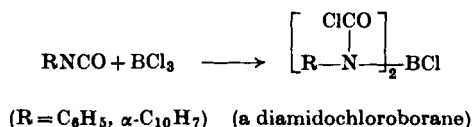


Due to a spontaneous decomposition, only in the case of X=F was it possible to isolate a specimen of pure $(\text{CNBF}_2)_x$:

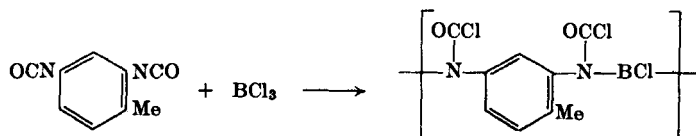


These solid chlorocyanides may well be related to the polymeric product $(\text{CN})_3\text{BCl}$ formed during the reaction between cyanogen and diboron tetrachloride (19).

Methyl isocyanide reacts with boron trifluoride to form a black tar with complete disruption of the organic molecule (686). Although phenyl isocyanate forms a weak complex with boron trifluoride (483), aryl isocyanates, and isothiocyanates generally undergo chloroboration when treated with boron trichloride (483):



When a diisocyanate is used, a polymeric product is formed (483):



7. Reactions with Compounds of Group VI Elements

At normal temperatures the free Group VI elements are inactive toward the boron trihalides, but oxygen and boron trifluoride in a discharge give the spectrum of the planar molecule OBF_2 (548) and, when mixtures of oxygen and boron trichloride are irradiated with ultraviolet light (456) or sparked (576), boric oxide and chlorine are produced. Trichloroboroxine was an intermediate in the irradiation experiments and found to be fairly stable in the gas phase at room

TABLE IX
TERTIARY AMINE ADDUCTS OF THE BORON TRIHALIDES^a

Amine	Reference to BF ₃	Reference to BCl ₃	Reference to BBr ₃	Reference to BI ₃	Reference when all trihalides studied
NMe ₃	IR (437); NMR (388); NMR (581); Gen (582); Dip (56); Kin (269); Kin (196); X (277, 400); Gen (133)	NMR (581); IR (437); Dip (56); Gen (582)	IR (437); NMR (581); Dip (56); Gen (582)	—	NMR (539)
NEt ₃	NMR (388); NMR (123); Gen (731); Gen (688, 689)	Gen (290)	Gen (528)	—	NMR (270)
NR ₃ (R = aryl)	Gen (441)	Gen (441)	Gen (441)	—	—
MeNR ₂ (R = aryl)	Gen (686)	—	—	—	—
(R = alkyl)	NMR (186)	—	—	—	—
Me ₂ NR (R = aryl)	Gen (686); Gen (87)	Gen (87)	Gen (528)	—	—
Pyridine	IR (437); IR, RAM (516); NMR (123); NMR (270); Dip (56); X (879); Cal (114); Cal (108); Kin (449)	IR (437); Dip (56); IR (341); NMR (270); NMR (598); Cal (108); Cal (340)	Cal (340); NMR (270); NMR (598); IR (437); Dip (56); Cal (108); Gen (391)	Gen (598)	—
4-R-pyridine	Cal (109)	IR (437); Dip (56) Dip (55)	IR (437); Gen (170)	—	—
2,6-R ₂ -pyridine	Cal (114); Cal (107)	—	—	—	—
2-R-pyridine	Cal (107)	—	—	—	—
3-R-pyridine	—	IR (437)	Gen (391)	—	—

^a Cal = calorimetric study
IR = infrared spectral study
Ram = Raman spectral study
Kin = gas phase kinetics study

NMR = n.m.r. study
Dip = dipole moment study
X = X-ray crystal structure determination
Gen = general study

TABLE X
NITRILE ADDUCTS OF THE BORON TRIHALIDES^a

R in RCN	Reference to BF ₃	Reference to BCl ₃	Reference to BBr ₃	Reference to BI ₃
Me	IR (166); IR (57); Cal, Dip (491); NMR (583); Gen (702)	IR (166); IR (57); IR (292); NMR (583); Cal, Dip (491); Gen (298, 702)	IR (57); NMR (583); Cal (583); Gen (528)	Gen (598)
Et	IR (166)	IR (166)	—	—
C ₆ H ₅	IR (166); Cal (110); Gen (364)	Gen (702)	—	—
4-FC ₆ H ₄	NMR (808)	NMR (808)	NMR (808)	—
MeC ₆ H ₄ (2-, 3-, or 4-substituted)	Cal (110)	—	—	—
2,4,6-Me ₃ C ₆ H ₂	Cal (110)	—	—	—
4-ClC ₆ H ₄	Gen (364)	Gen (364)	—	—

^a IR = infrared spectral study

NMR = proton or ¹⁹F n.m.r. study

Cal = calorimetric or gas phase dissociation study

Dip = dipole moment study

Gen = general study

TABLE XI
PHYSICAL PROPERTIES OF THE DIBORON TETRAHALIDES

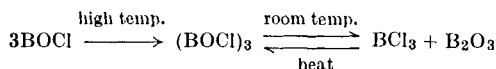
	B ₂ F ₄	B ₂ Cl ₄	B ₂ Br ₄	B ₂ I ₄
Melting point (°C)	− 56.0 (246)	− 92.6 (826) − 92.95 (507)	0.5–1.5 (208)	—
Boiling point (°C)	− 34 (246)	65.5 (826)	—	—
Vapor pressure relation for solid: $\log p_{\text{mm}} = A - \frac{B}{T}$ (T in °Abs)	$A = 10.82$ $B = 1856$ } (246)	—	—	Vapor pressure at 60°–70° is 10 ^{−3} mm (757)
Vapor pressure relation for liquid: $\log p_{\text{mm}} = A - \frac{B}{T}$ (T in °Abs)	$A = 9.009$ $B = 1446$ } (246)	$A = 8.057$ $B = 1753$ } (826)	Vapor pressure at 22.5° is 5.5 mm (826)	—
Trouton constant	28 (246)	23.7 (826)	—	—
Heat of evaporation (cal mole ^{−1})	6700 (246)	8029 (826)	—	—
Infrared spectrum	(243, 266)	(525)	—	—
Raman spectrum	—	(525)	—	—
Heat capacity	—	Normal from 20° to 220° Abs (507)	—	—
Heat of fusion (cal mole ^{−1})	—	2579 ± 4 (507)	—	—

TABLE XII
OLEFIN AND ACETYLENE ADDITION COMPOUNDS OF DIBORON TETRAFLUORIDE AND TETRACHLORIDE^a

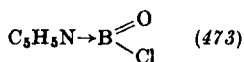
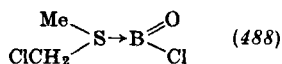
Olefin or acetylene used	Compound formed	M.P. (°C)	B.P. (°C)	<i>A</i>	<i>B</i>	<i>H</i>	Trouton constant	Ref.
C ₂ H ₄	B ₂ F ₄ C ₂ H ₄	-31.5	35	8.259	1656	7,550	24.4	(149)
C ₂ H ₄	B ₂ Cl ₄ C ₂ H ₄	-28.5	142	8.230	2220	10,140	24.4	(149, 824)
CH ₃ CH=CHCH ₃	B ₂ F ₄ (CH ₃ CH) ₂	—	68	7.770	1667	7,600	22.3	(149)
CH ₃ CH=CHCH ₃	B ₂ Cl ₄ (CH ₃ CH) ₂	(variable)	171	8.147	2339	10,700	24.1	(149, 237)
CH ₃ CH=CH ₂	B ₂ Cl ₄ CH ₃ CHCH ₂	-130	165	7.701	2105	9,600	22.1	(149)
1,3-Cyclohexadiene	—	—	—	—	—	—	—	(878)
<i>trans</i> -Di(<i>tert</i> -butyl)- ethylene	1:1 with B ₂ Cl ₄	(liquid at room temp.)	—	—	—	—	—	(878)
Norbornalene	—	1-1.5	—	—	—	—	—	(878)
HC≡CH	B ₂ F ₄ C ₂ H ₂	-81.7 to -82.6	15	8.565	1635	7,450	25	(149)
HC≡CH	B ₂ Cl ₄ C ₂ H ₂	-129 to -130	144	7.666	1995	9,100	21.8	(158, 184)
HC≡CH	(B ₂ Cl ₄) ₂ C ₂ H ₂	29-30	—	—	—	—	—	(158)
C ₁₀ H ₈	—	46.5-47.5	—	—	—	—	—	(255, 877, 878)

^a Vapor pressure equation: $\log_{10} p(\text{mm}) = A - \frac{B}{T}$; *H* = heat of vaporization in cal mole⁻¹.

temperature but, on contact with glass, it decayed rapidly giving boric oxide, chlorine, and possibly boron trichloride. This mode of decomposition is in direct contrast to that described (page 37) for trichloroboroxine made from boric oxide and boron trichloride:

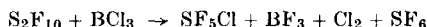


Several other papers are to be found in the literature that describe boron oxyhalides having considerable thermal stability. Thus boron trifluoride, when passed over heated boric oxide or silica, gave a solid product that was stable for days at room temperature but melted at about 80° with decomposition to boric oxide and boron trifluoride; the solid did not analyze accurately to $(\text{BOF})_x$ and always contained more boric oxide than required (522). A similar stable boron oxyfluoride, approximating to $\text{B}_2\text{O}_3\text{F}$, has been obtained from the reaction of oxygen with diboron tetrafluoride (414), and a compound given the formula $\text{B}_3\text{O}_4\text{Br}$ has been mentioned as appearing among the decomposition products of methoxyboron dibromide (314). The true position is far from clear; BOX and $(\text{BOX})_3$ are definite, unstable entities that can be studied only by mass spectrometry or by infrared spectroscopy at low temperature, but apparently there are other $\text{B}-\text{O}-\text{X}$ species (containing less halogen than oxygen) that have radically different properties and appear to be fairly stable at room temperature. Obviously further work is required on the problem to determine if these latter substances are more than solutions of boron trihalide in boric oxide [see Hofmeister and van Wazer (402)]. It has been shown to be possible to stabilize the BOCl monomer by complex formation:



Boron triiodide burns on heating in air or oxygen, forming copious clouds of iodine, and with sulfur, either molten or in solution, boron sulfide is produced (576).

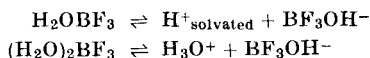
Dioxygen difluoride, O_2F_2 , reacts with boron trifluoride to give dioxygenyl tetrafluoroborate, $\text{O}_2^+\text{BF}_4^-$ (784), while sulfur tetrafluoride forms a 1:1 compound recently shown, by an X-ray structure determination, to be a salt $\text{SF}_3^+\text{BF}_4^-$ (145); neither the corresponding chloro compound SCl_4BCl_3 nor SCl_2BCl_3 can be isolated (649). Disulfur decafluoride fluorinates boron trichloride (167):



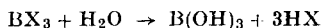
but sulfur chloride-pentafluoride at room temperature (536) and the hexafluoride at 200° (146) are without reaction. Halogen interchange also occurs on heating sulfur monochloride and boron tribromide together (250).

When disulfur monoxide and boron trifluoride are mixed below -160°, a wine-colored complex is formed having the composition $S_2O \cdot nBF_3$ where $n = 2$ or 3, but on raising the temperature to -140°, to release any trapped boron trifluoride, the complex decomposes (745). By thermal analysis a 1:1 compound (m.p. -96°) has been shown to be formed when sulfur dioxide is mixed with boron trifluoride (81), but there is no evidence for the analogous SO_2BCl_3 (527) (contrary to earlier reports). This is one of the rare examples of a complex being known for boron trifluoride but not for the stronger Lewis acid boron trichloride (neglecting those cases where the latter undergoes cleavage reactions with the ligand without a complex being isolated), and it is noteworthy that these complexes [e.g., $NOBF_3$ (409) and SO_2BF_3] are extremely unstable and may not, therefore, contain "normal" donor-acceptor bonds; liquid sulfur trioxide and boron trifluoride give the compound $S_3O_8F_2$ (498). Sulfuryl fluoride (83) and thionyl tetrafluoride, SOF_4 (762), give unstable 1:1 compounds with boron trifluoride, but sulfuryl chloride and thionyl chloride gave no isolable adducts with either boron trifluoride or trichloride (138, 833).

Boron trifluoride undergoes a certain amount of hydrolysis when dissolved in water (378) and an ^{19}F n.m.r. study of the solution showed that the following ions were probably present: BF_4^- , BF_3OH^- , $BF_2(OH)_2^-$, and $BF(OH)_3^-$ (206). With controlled amounts of water it is possible to isolate two hydrates, H_2OBF_3 and $(H_2O)_2BF_3$ (332, 700) or D_2OBF_3 and $(D_2O)_2BF_3$ (327); conductance measurements on and electrolysis of the liquid hydrates suggest that some ionization occurs (332),

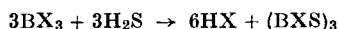


but an X-ray crystal structure determination (37) and an n.m.r. study (251) on the slowly crystallized solid dihydrate both support the presence of a molecular complex H_2OBF_3 , the second water molecule being held by hydrogen bonds. It is only the 1:1 adducts of boron trifluoride that can add a second molecule of ligand by hydrogen bonding (e.g., ligand = $MeCOOH$, ROH , H_2O), since the other boron trihalides readily undergo a loss of hydrogen halide with ligand hydrogen atoms polar enough to form hydrogen bonds. Thus, water causes the rapid hydrolysis of the other trihalides,

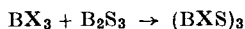


and an excess of water added rapidly to, say, boron trichloride held at room temperature in a confined apparatus can cause an explosion due to the violence of the hydrolysis.⁸

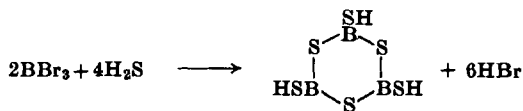
Hydrogen sulfide forms a 1:1 adduct with boron trifluoride that is considerably dissociated at its melting point, -137° (81, 278), this being a reflection of the greatly decreased Lewis basicity of hydrogen sulfide compared to water. The less reactive nature of the hydrogen atoms in hydrogen sulfide allows the formation at low temperature of a 1:1 complex (m.p. -35.3°) with boron trichloride (527), but at higher temperatures hydrogen chloride is evolved; boron tribromide reacts in a similar way (862):



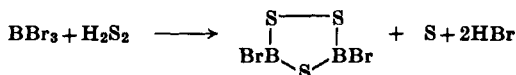
As with the oxygen analogs (page 37), the thioboroxines can be made by mixing trisulfide with a boron trihalide (528, 842):



If an excess of hydrogen sulfide is used, all the halogen is removed from boron (862):

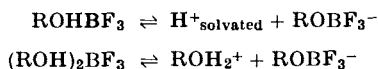


Hydrogen disulfide reacts with boron tribromide in carbon disulfide to form a five-membered sulfur-boron ring system (752):



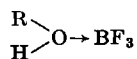
(a 1,2,4-trithia-3,5-diborolane)

Alcohols form 1:1 and 2:1 ($\text{ROH}:\text{BF}_3$) adducts with boron trifluoride (877), which conductivity and electrolytic studies suggest are ionized (at least partially) in the liquid state (330, 336),



⁸ An account has recently been given in the daily newspapers (see, for example, *The Guardian*, June 2, 1966) of a physicist being killed in a severe explosion resulting from the hydrolysis of boron tribromide.

although n.m.r. studies suggest that a molecular complex,



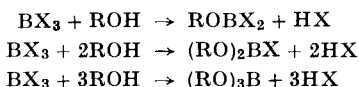
is formed to which the second alcohol molecule is bound via hydrogen bonds (206, 207). In a mixture of two alcohols at low temperature, two sharp ^{19}F n.m.r. signals can be observed due to ROHBF_3 and $\text{R}'\text{OHBF}_3$, and measurements of the respective peak areas allow a calculation of the equilibrium constant. As the temperature is raised, the signals broaden and begin to merge into one peak due to exchange of the boron trifluoride between the alcohol molecules. From a series of equilibrium studies using pairs of alcohols, it is possible to establish the donor strength series $\text{H}_2\text{O} > \text{MeOH} > \text{EtOH} > n\text{-PrOH} > n\text{-BuOH}$ toward boron trifluoride (207), which is the order of steric requirements of the various alcohols.

Two methyl proton resonances occur in the n.m.r. spectrum of sulfur dioxide solutions of boron trifluoride containing an excess of methyl alcohol, due to exchange processes between MeOHBF_3 and MeOH and between $(\text{MeOH})_2\text{BF}_3$ and MeOH . Using the stoichiometry of the reaction mixtures and the relative areas under these two peaks, it proved possible to calculate an equilibrium constant of roughly 3 for the reaction:



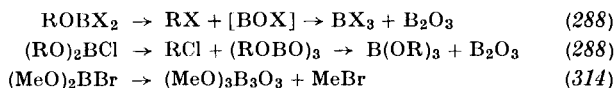
When an excess of boron trifluoride was used, all the methyl alcohol was shown to be present as the 1:1 complex (695).

The other trihalides react readily with alcohols and evolve hydrogen halide at low temperature (223, 280, 288, 295, 476, 477, 793):

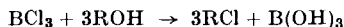


(R = primary or secondary alkyl; allyl; methallyl; ω -chloroalkyl)

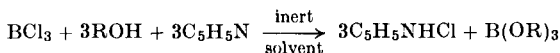
The alkoxyboron halides are sometimes unstable (e.g., ROBX_2 where R = secondary or tertiary alkyl, X = Cl; and $(\text{RO})_2\text{BX}$ where R = electron-releasing group, X = Cl) and in such cases the products are the alkyl halides and a boroxine:



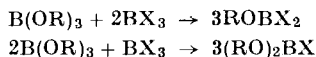
Tertiary alcohols (and $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ or $\text{C}_6\text{H}_5(\text{CH}_3)\text{CHOH}$) give the alkyl chloride and boric acid when treated with boron trichloride (288),



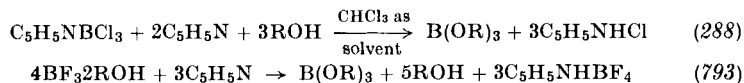
but in the presence of pyridine it is possible to form the borates of these and other alcohols (288, 473):



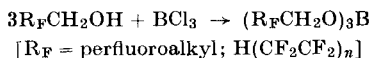
Group exchange reactions may be used to obtain alkoxyboron dihalides and dialkoxyboron halides (288):



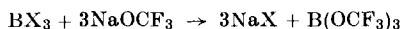
Under forcing conditions, using heat and pyridine to remove the hydrogen halide formed, it is possible to obtain alkyl borates from boron trihalide adducts:



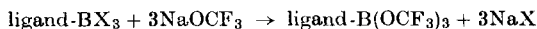
Polyfluoroalkyl-substituted methyl alcohols have also been used to prepare borates (9, 470, 755),



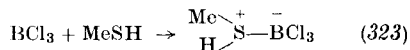
but the fully fluorinated borates cannot be made in this manner because the corresponding alcohols, $\text{R}_\text{F}\text{OH}$, are unknown. The recently obtained sodium perfluoromethoxide may prove to be of value in the preparation of perfluoromethoxyboron compounds using reactions such as:



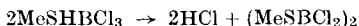
or



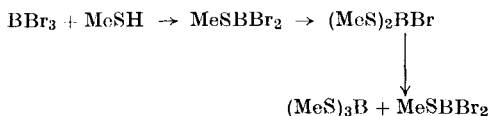
The decreased reactivity of the proton in the alkyl mercaptans, RSH , allows the formation of a boron trichloride adduct at low temperature,



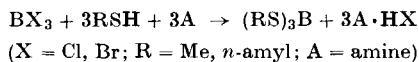
but above about -20° hydrogen chloride is eliminated:



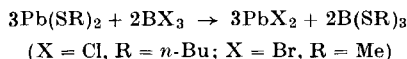
Even in the presence of excess methylmercaptan the remaining $\text{B}-\text{Cl}$ bonds are not substituted (323). The reaction proceeds further, however, if the tribromide is used (323):



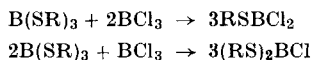
Better yields of the alkylthioborates are obtained if an amine is used to remove the hydrogen halide (698),



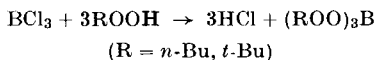
or if the corresponding lead mercaptide is added to a boron trihalide:



Again, group exchange reactions have been used to form mercaptoboron chlorides (288):

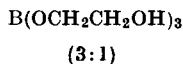
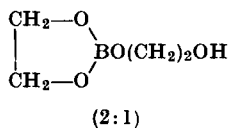
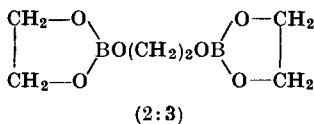
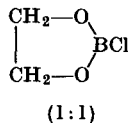
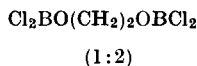


Hydroperoxides react with boron trichloride in a similar manner to alcohols, eliminating hydrogen chloride to give peroxyborates (199):

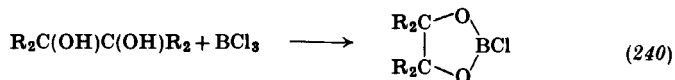
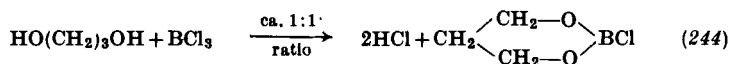


However, peroxy acids do not form peracylboron compounds and peroxy-caprylic acid, for example, gives caprylic acid, boric oxide and chlorine (199). Dialkyl peroxides, in contrast to ethers, undergo a vigorous and complex reaction when added to boron trichloride, producing hydrogen chloride, boric acid, and olefin (199).

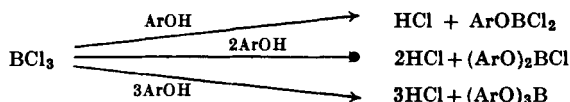
Polyhydroxy alcohols form stable complexes with boron trifluoride (817) but evolve hydrogen chloride on reaction with boron trichloride (288). Thus the reaction of ethylene glycol with the trichloride can be made to produce all the expected borates and alkoxyboron chloride by a suitable manipulation of the reaction ratios (glycol:BCl₃):



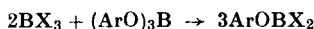
Similar boron heterocycles are formed when trimethylene glycol and the pinacols are mixed with boron trichloride:



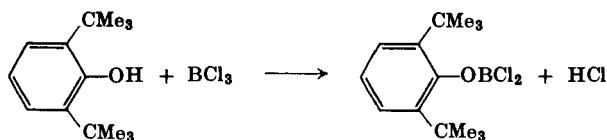
Both a 1:1 and a 2:1 complex (phenol:BF₃) are formed when boron trifluoride and phenol interact (687, 817), but boron trichloride readily loses hydrogen chloride when treated with most phenols (169, 288, 793):



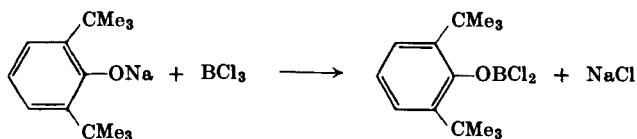
The usual group exchange reactions are also applicable to the formation of aryloxyboron halides (169, 288, 403):



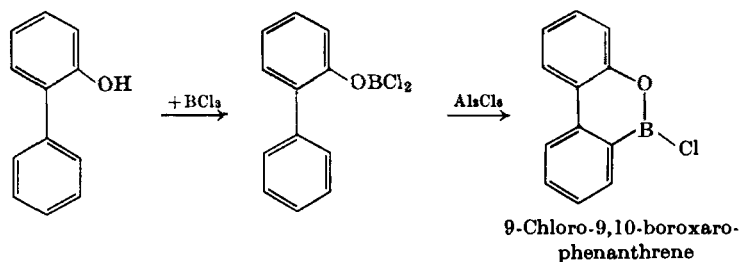
The use of metallic alkoxides or phenoxides in the production of borates has been referred to previously (page 33). In certain cases this has proved a superior method to the straight reaction of alcohols or phenols with boron trichloride. Thus the reaction



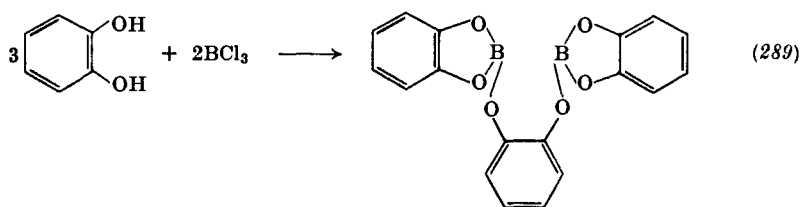
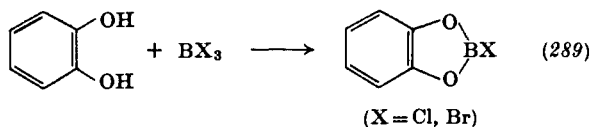
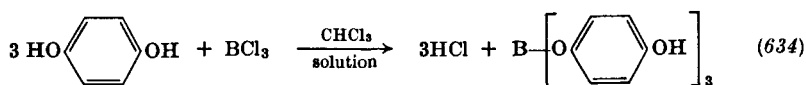
does not take place, probably due to steric interaction, but the sodium salt reacts smoothly in toluene at -60° (794):



Formation of an aryloxyboron dichloride followed by a Friedel-Crafts reaction has resulted in the successful isolation of several boron heterocycles, e.g. (204, 523):

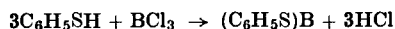


Polyhydroxyphenols can react to give monomeric aryl borates or aryloxyboron halides when treated with boron trichloride or tribromine,

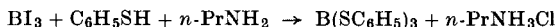


but polymeric products have been obtained under other conditions when mixtures of boron trichloride with resorcinol, quinol, or pyrogallol are used (288, 793).

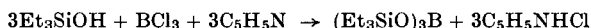
Thiophenol is a weaker Lewis base than phenol and forms no adducts with boron trifluoride (686), whereas boron trichloride gives a weak 1:1 complex that is fully dissociated at 25° (509, 686). On refluxing a mixture of this phenol and boron trichloride in benzene, a smooth evolution of hydrogen chloride occurs and the thioborate is produced (509, 875):



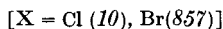
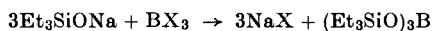
Boron tribromide may also be used in this reaction (793). The use of an amine to remove hydrogen halide has been suggested when making the thioborate from boron triiodide (698),



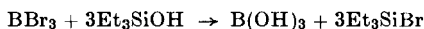
or triethylsilyl borates from boron trichloride (10):



Better yields of the silyl borate are obtained if the sodium salt of triethylsilanol is used,



but only boric acid is produced when triethylsilanol reacts with boron tribromide in the absence of an amine (857):



Many ethers complex readily with boron trifluoride to give 1:1 adducts (330, 817), but the substitution of fluorine in the alkyl chain, as in perfluoroethyl ether and cyclo- $\text{C}_4\text{F}_8\text{O}$ (866), or the substitution of two aryl groups for alkyl, as in diphenyl ether (380), so reduces the base strength of the ether that no complexes can be formed. Normally the 1:1 adducts are stable toward an ether-cleavage reaction to give the alkoxy-boron difluoride, but isopropyl ether-boron trifluoride has been shown to decompose in this manner above 50° (104),



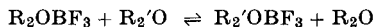
and diborane made from diethyl ether-boron trifluoride contains small amounts of ethyl fluoride (although it was suggested that the ethyl fluoride arose from attack of active fluorine or fluorine atoms on the ether solvent) (197); irreversible decompositions of the adducts Me_2OBF_3 and Et_2OBF_3 have also been mentioned (380, 689) but no details were given. Conductivity measurements and electrolytic studies on liquid diethyl ether-boron trifluoride indicate that the complex may partially ionize either as ethyl ethoxytrifluoroborate, $\text{Et}^+\text{EtOBF}_3^-$ (337), or as $[\text{BX}_2\text{OEt}_2]^+$ with BF_4^- and F^- as the anions (772).

Cyclic ethers also form 1:1 complexes with boron trifluoride (69, 123, 567, 865), but with the small-ring ethers (ethylene oxide, trimethylene oxide, furan, and tetrahydrofuran) there is also a tendency toward polymerization in the presence of boron fluoride; for example, a mixture of 0.5 mole of boron trifluoride and 1.0 mole of tetrahydrofuran has been

found to gel within a few minutes at room temperature (686). The glymes (dimethyl ethers of polyethylene glycols) form stable adducts with boron trifluoride that show no signs of cleavage even after 6 months at room temperature (115).

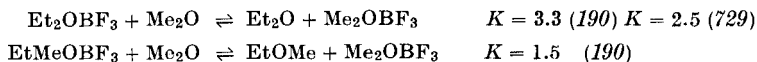
At low temperatures the 1:1 etherates will absorb a further one (or, in the case of $\text{Et}_2\text{O} \cdot \text{BF}_3$, two) mole of boron trifluoride (865) to form complexes that probably contain single fluorine bridges: $\text{R}_2\text{OBF}_2\text{—F—BF}_3$ (see page 68); the excess boron trifluoride is readily lost at temperatures well below 0° to leave the original 1:1 adducts.

It has been shown by ^{19}F and ^1H n.m.r. studies that, when boron trifluoride is dissolved in a mixture of two ethers (190, 728–730) or is dissolved in an inert solvent containing a single ether (123, 312), a rapid exchange of the trifluoride between the ether molecules occurs, the mean lifetime of an ether complex at room temperature being of the order of 10^{-4} second. When the temperature in the mixed-ether system is lowered the exchange rate slows down, and the ^{19}F n.m.r. peak (which was originally sharp) begins to broaden and then to separate into two peaks due to R_2OBF_3 and $\text{R}_2'\text{OBF}_3$ (728, 729). The equilibrium constant of the reaction



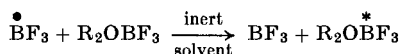
can then be calculated from the areas under the two n.m.r. peaks (the area under a peak being proportional to the amount of the species in the mixture that is responsible for that particular absorption peak) and a knowledge of the original mixture composition. In this way it was shown that dimethyl ether forms a more stable etherate with boron trifluoride than does diethyl ether (729).

At room temperature, measurements on the chemical shifts of either the single ^{19}F resonance or the protons in the ether molecules can also be used to calculate the equilibrium constant of the above reaction (the chemical shift of a nucleus in molecules involved in a rapid exchange reaction occurs at a position that is the weighted mean of the shifts in the two free molecules). From studies on several pairs of ethers, the following base strength series can be drawn up (190, 729, 730): $\text{Me}_2\text{O} > \text{MeOE} > \text{Et}_2\text{O} > \text{C}_6\text{H}_5\text{OMe}$. Typical values for some equilibrium constants are (at 26°):



The mechanism of these exchange reactions is believed not to involve an initial dissociation of the complex, since the energy of activation is less than the heat of formation of either of the complexes (729, 730); the

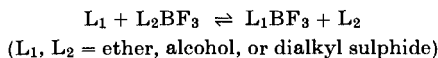
analogous boron trifluoride exchange taking place in solution of a single ether (69),



is also considered to be a displacement reaction (123). The values of the equilibrium constant for the $\text{Et}_2\text{OBF}_3/\text{Me}_2\text{O}$ exchange quoted above are close to that of 4.2, which can be calculated (190) from the *gas phase* dissociation data given by McLaughlin and Tamres for Me_2OBF_3 and Et_2OBF_3 (566).

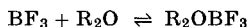
The order of base strengths of ethers can also be deduced from pressure measurements on the reversible gas phase dissociation of the complexes, R_2OBF_3 (since the measurements allow the calculation of the heats of formation of the complexes). Thus tetrahydrofuran forms stronger complexes with boron trifluoride than tetrahydropyran (567), and an increase in alkyl chain length in acyclic ethers decreases the base strength probably due to steric influence, i.e., $\text{Me}_2\text{O} > \text{Et}_2\text{O} > (\text{iso-Pr})_2\text{O}$ (104, 566).

Calculation of the equilibrium constants for the reaction



has been carried out, using known initial concentrations of reactants and obtaining a measure of the equilibrium concentration of both adducts from infrared spectral studies using Beer's law; the series obtained by this method is (867) $\text{THF} > \text{EtOH} > \text{tetrahydrofuran} > \text{MeOH} > \text{Me}_2\text{O} > \text{EtOMe} > \text{propylene oxide} > \text{Et}_2\text{O} > (n\text{-Pr})_2\text{O} > (\text{iso-Pr})_2\text{O} > \text{tetrahydrothiophene} > \text{Et}_2\text{S}$. This is in agreement with the n.m.r. studies as far as the ethers are concerned, but the position $\text{EtOH} > \text{MeOH}$ is in direct contrast to Diehl's n.m.r. work (206, 207) on boron trifluoride dissolved in EtOH/MeOH mixtures; sulfur donors are weaker than the oxygen analogs, as expected from the electronegativity values $\text{O} > \text{S}$.

When the reaction

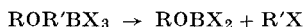


was studied in methylene dichloride solution by n.m.r., the ether basicities were found to be in the order $\text{Et}_2\text{O} > (\text{iso-Pr})_2\text{O} > \text{Me}_2\text{O}$ (312). As it is known that chloroform interacts strongly with boron trifluoride (123), the methylene dichloride may not have been as inert a solvent toward the trifluoride as was assumed by Gore and Danyluk, although Henry's law appears to be obeyed when the two compounds are mixed (124); however, this should not give rise to a different base strength series. These workers suggested that weak hydrogen bonding of the

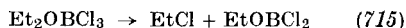
solvent to the alcohols may explain why their series was different from those obtained in other systems. (Solute-solvent interaction may account for the anomalous position of methyl and ethyl alcohols when the series given above was obtained from infrared measurements taken in benzene solution, as this might be expected to affect methyl alcohol to the greater extent.)

On coordination of an ether with boron trifluoride to form R_2OBF_3 , simple n.m.r. theory suggests that the ^{19}F resonance of the adduct should move to higher field compared to boron trifluoride, since there is additional shielding due to the increased electron density on the boron atom; the stronger the donor molecule the greater will be the observed shift. This has been confirmed for the acyclic ethers and the dialkyl sulfides where the shifts are in agreement with the base strength series (190, 728). Similarly, the hydrogen atoms attached to the α -carbon atom should experience a decreased shielding, and their resonance will move to lower field compared to the same protons in the free ether; the more basic the ether molecule, the more deshielded will be these protons and the greater should be the observed shift. In practice it is found that the shifts are in the order $Me_2O > MeOEt > Et_2O$ as predicted (190).

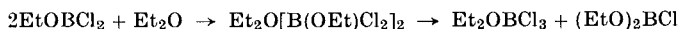
The 1:1 adducts formed by many ethers with boron trichloride and tribromide are unstable with respect to an ether-cleavage reaction:



For example, boron trichloride readily forms a solid 1:1 adduct with diethyl ether at -80° that regenerates ether on hydrolysis, indicating that the structure is $Et_2O \rightarrow BCl_3$ (280, 715). The rather large n.m.r. chemical shift noted for the protons in diethyl ether-boron trichloride dissolved in methylene dichloride has been interpreted as evidence for an ionic formulation $Et^+[EtOBCl_3]^-$ (312), which receives some support from the high value of the equivalent conductance measured in the same solvent (being higher than that observed for liquid Et_2OBF_3) (337). However, the hydrolysis experiment appears to rule out the possibility of the ion $EtOBCl_3^-$ being present in large amounts, since this would be expected to produce ethyl alcohol on contact with water. Russian work (772) involving cryoscopy and conductivity measurements suggests that the species present in solutions of ether and boron trichloride (also BF_3 and BBr_3) are BCl_3OEt_2 , $BCl_2OEt_2^+BCl_4^-$, and $BCl_2OEt_2^+Cl^-$, which could explain the large n.m.r. chemical shift and still be consistent with the hydrolysis experiments. The ionic forms of the adduct $Et^+EtOBCl_3^-$ may possibly be an intermediate (288) in the ether-cleavage reaction that takes place when the solid etherate melts at 56° :



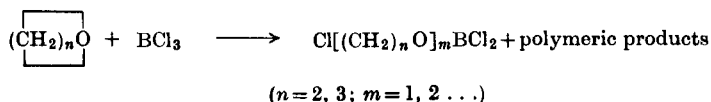
If the decomposition is carried out in the presence of an excess of ether, the ethoxyboron dichloride forms an unstable 2:1 etherate and then disproportionates (715):



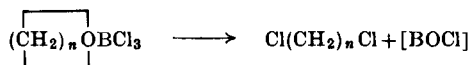
In ether (671) or methylene dichloride (312) solution, the slow ether cleavage can be followed at room temperature by observing the build-up and decay of the various species by proton n.m.r.; the rapid disproportionation of ethoxyboron dichloride in the presence of ether was also confirmed by this method (671).

The presence of electron-attracting groups in an ether molecule reduces its basicity so that diphenyl ether gives only a very unstable etherate with boron trichloride (380) (contrary to earlier reports), and bis(chloromethyl) ether gives no adduct at all (225). However, chloromethylmethyl ether forms a 1:1 adduct, from which the ether can be displaced by pyridine and which gives butyl borate on treatment with *n*-butyl alcohol (225). When a mixed ether is cleaved on heating with boron trichloride (225, 287, 295, 296) or tribromide (72), the more electron-releasing group is found in the alkyl halide; similarly, boron trichloride dissolved in monoglyme (364, 536) or diglyme (116) causes a slow ether cleavage at room temperature, giving methyl chloride.

Boron trichloride reacts rapidly with cyclic ethers,⁹ the products depending on the ring size. With tetrahydrofuran and tetrahydropyran, 1:1 adducts can be isolated (223, 288) but, with ethers having smaller rings, ring fission occurs even at -80° to form chloroalkoxyboron dichlorides when 1:1 ratios are used (224, 288),

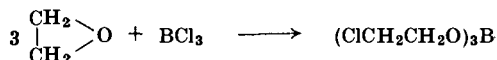


Ring fission in the cases of the 1:1 adducts of tetrahydrofuran and tetrahydropyran with boron trichloride produces the α,ω -dichloroalkane (288), presumably due to the instability of the chloroalkoxyboron dichloride:

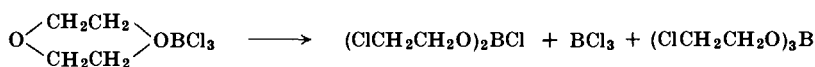


⁹ However, the basicity of some ethers is so reduced by substituents that no reaction occurs with boron trichloride even on heating, e.g., perfluoro-1-butyl-tetrahydrofuran, $\text{C}_8\text{F}_{16}\text{O}$ (815).

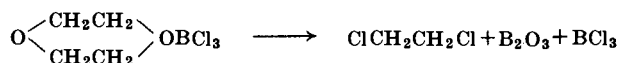
With an excess of cyclic ether, the chloroalkyl borates are formed (288), e.g., with ethylene oxide:



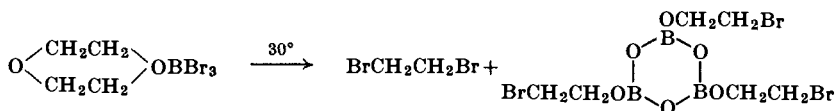
Cyclic diethers react in a similar manner with boron trichloride and tribromide. Dioxan forms a 1:1 complex with the trichloride, which undergoes ring fission when heated just above its melting point (174, 472),



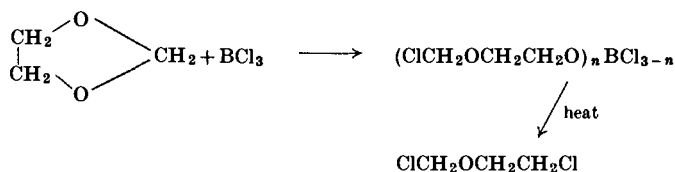
but, at higher temperatures (180°), 1,2-dichloroethane is produced (174):



The boron tribromide complex decomposes in a different manner, giving an alkoxyboroxine (174):



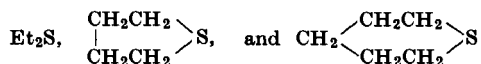
Ring fission and chlorine migration also occur when 1,3-dioxolan is treated with boron trichloride (174):



The expected 2:1 adducts of these two diethers with the boron trihalides could not be obtained, although at low temperature dioxan and boron trichloride formed a complex, $(\text{C}_4\text{H}_8\text{O}_2)_2\text{3BCl}_3$, of unknown structure (288).

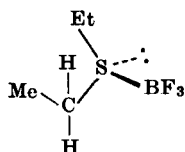
The dialkyls of the other members of Group VI are much less basic than the ethers, as shown by the fact that Me_2OBF_3 is 20% dissociated into its components at room temperature and 65 mm pressure while Me_2SBF_3 is more than 95% dissociated under the same conditions;

dimethyl selenide-boron trifluoride, although formed as a solid at -78° , is completely dissociated in the vapor at room temperature (324). This gives the base strength series as $\text{Me}_2\text{O} > \text{Me}_2\text{S} > \text{Me}_2\text{Se}$ toward boron trifluoride. Similarly, the adducts of boron trifluoride with



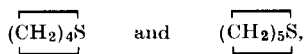
have been shown to be extensively dissociated at room temperature (180, 591, 689); $(\text{CH}_2)_2\text{S}$ is polymerized in the presence of either boron trifluoride or trichloride (591). Diphenyl sulfide, like diphenyl ether, is too weak a base to react with boron trifluoride (686).

The distribution of groups around the sulfur atom in diethylsulfide-boron trifluoride can be assumed to be close to tetrahedral,



which will make the two protons in the methylene groups inequivalent; a similar inequivalence can be detected, for example, in the proton n.m.r. spectrum of the related complex Et_2SBH_3 (186). However, the proton n.m.r. of Et_2SBF_3 shows only a single quartet in the methylene region of the spectrum (186), which shows that the boron trifluoride, unlike the borane group, is rapidly exchanging between the two donor sites on the sulfur atom (186, 190) or between different diethyl sulfide molecules; the lack of ^{19}F - ^{11}B coupling also supports this conclusion.

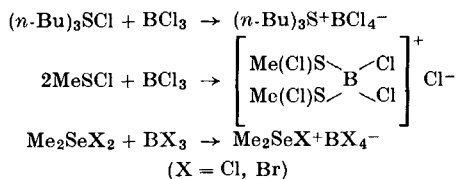
The dialkyl sulfides and the two cyclic sulfides,



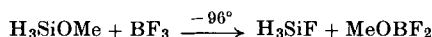
complex readily with boron trichloride to form 1:1 adducts that are stable toward irreversible decomposition (288, 474, 591, 708); the trichloride and tribromide also give 1:1 adducts with dimethyl selenide (873). Diphenyl sulfide gives a more stable 1:1 complex than diphenyl ether when treated with boron trichloride ($\Delta H_f, (\text{C}_6\text{H}_5)_2\text{SBCl}_3 = -8.7$ kcal/mole; $\Delta H_f, (\text{C}_6\text{H}_5)_2\text{OBCl}_3 = -5.3$ kcal/mole) (380, 686). Although this is the reverse of the stabilities predicted from electronegativity values, $\text{O} > \text{S}$, it can be explained by assuming a higher steric interaction in the

case of the diphenyl ether complex. The presence of an α -chlorine atom in the alkyl chain of a sulfide decreases the stability of the boron trichloride adduct; thus chloromethylmethyl sulfide-boron trichloride has a dissociation pressure of 10 mm at 20° (488).

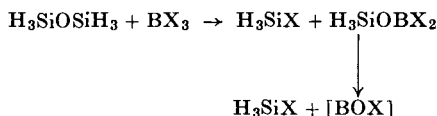
Ionic complexes are thought to be formed when tributylsulfonium chloride (288, 474), methylsulfur chloride (649), and dimethylselenium dihalides (873) react with boron trichloride or tribromide:



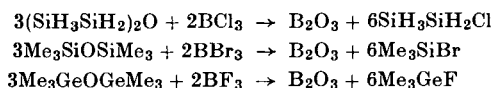
The reaction of silylmethyl ether with the boron trihalides at low temperature gives the silyl halide and methoxyboron dihalide (797):



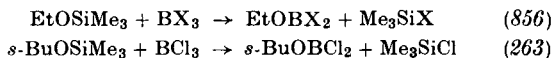
Disiloxane (disilyl ether) undergoes a typical ether-splitting reaction at low temperature when treated with boron trifluoride or trichloride (674) without an addition compound being isolated:



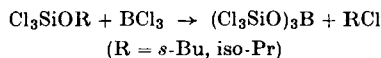
Similar reactions occur when $(\text{SiH}_3\text{SiH}_2)_2\text{O}$ (219), $(\text{MeH}_2\text{Si})_2\text{O}$ (229), $(\text{Me}_3\text{Si})_2\text{O}$ (352, 858), and $(\text{Me}_3\text{Ge})_2\text{O}$ (346) are used:



Trimethylsilylalkyl ethers (i.e., alkoxytrimethylsilanes) react with boron trichloride and tribromide, giving the trimethylsilyl halide,

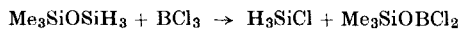


but a halogen on the silicon atom (e.g., Cl_3SiOR or $\text{ClSi}(\text{Me})_2\text{OR}$) causes the reaction to proceed via C—O fission (263):

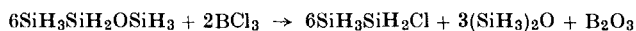


Trimethylsilyl (4) and trimethylstannyl (3) thioethers ($\text{R}_3\text{MSR}'$) cleave readily at the M—S bond, giving thioborate derivatives when treated with boron trichloride.

Trimethylgermylmethyl ether (methoxytrimethylgermane) forms a 1:1 adduct with boron trifluoride, which sublimates at 25° without irreversible decomposition (346). The products (93% SiH₃Cl and 7% Me₃SiCl) formed when trimethylsilylsilyl ether is treated with boron trichloride indicated that the main cleavage reaction was (219):

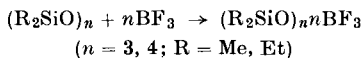


Disilanylsilyl ether, SiH₃SiH₂OSiH₃, was cleaved by boron trichloride to give mainly SiH₃SiH₂Cl,

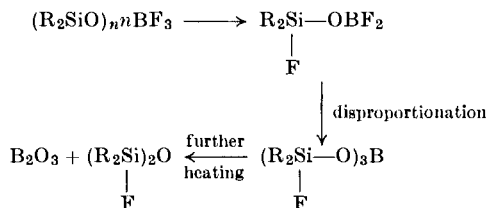


although the isolation of small quantities of silyl chloride showed that the opposite cleavage probably occurred to some extent (219).

The cyclic dialkylpolysiloxanes react to form adducts with boron trifluoride (560),

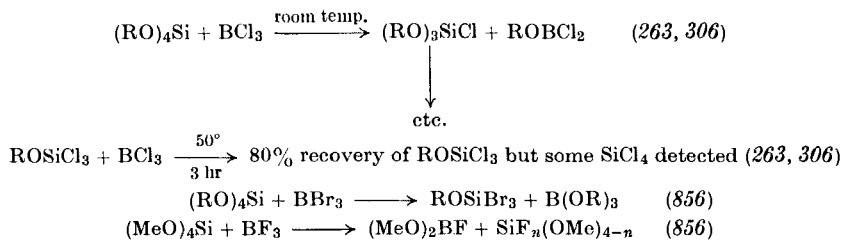


which decompose on heating to give dialkylfluorosiloxyboron derivatives (560):



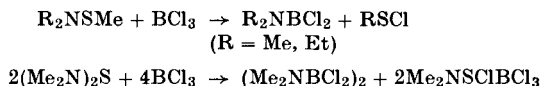
Similar dialkylhalosiloxyboron compounds are obtained when either boron trichloride (559) or tribromide (558) is substituted for the trifluoride. Boron trifluoride will also attack some silicone vacuum greases to form dimethylsilicon difluoride.

Tetraalkoxysilanes undergo a group exchange when treated with a boron trihalide, there being a noticeable fall in rate as each alkoxy group is removed from the silicon atom:

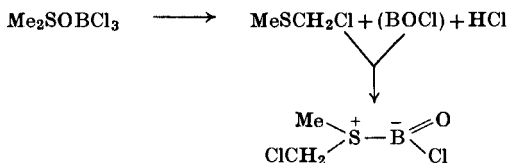


A steady replacement of alkoxy groups for chlorine also occurs, below 0° , when titanium alkoxides are treated with boron trichloride (173).

Bis(dimethylamino) sulfide, $(\text{Me}_2\text{N})_2\text{S}$, forms a very stable 2:1 (sulfide: BF_3) adduct when treated with an excess of boron trifluoride at 100° ; heating to 169° in a vacuum fails to dislodge the boron trifluoride, both molecules of which are considered to be bound to the nitrogen atoms (141). Attachment of oxygen atoms to the sulfur results in a lower stability of the trifluoride adducts, and it is found impossible to complex 2 moles of boron trifluoride to either $(\text{Me}_2\text{N})_2\text{SO}$ or $(\text{Me}_2\text{N})_2\text{SO}_2$, although 1:1 adducts can be isolated (141). Thionylmethylamine, MeSNO , forms a 1:1 adduct with boron trifluoride, which is highly dissociated at 50° (141). When boron trichloride is treated with amino-sulfur compounds, a group exchange occurs (649):

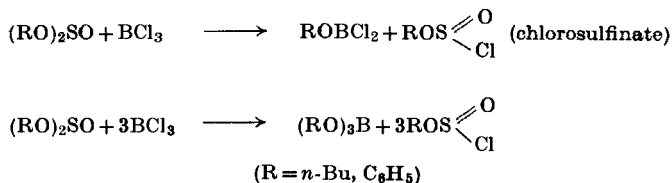


The dialkyl sulfoxides, R_2SO , form 1:1 adducts when treated with boron trifluoride (176, 488, 493) or trichloride (488, 703): infrared spectra of the trifluoride adducts suggest that the boron is bonded to the oxygen atom (176), which is in keeping with the order of stability of the trifluoride complexes, $\text{R}_2\text{SO} > \text{R}_2\text{S}$, R_2SO_2 (493). The adduct, dimethyl sulfoxide-boron trichloride, is unstable (703) and rapidly decomposes to give chloromethylmethyl sulfide (488):



Diphenyl sulfoxide forms a stable 1:1 adduct with boron trichloride (488, 703), but the dialkyl and diaryl sulfone complexes were unstable (703); the decomposition products were not, however, identified.

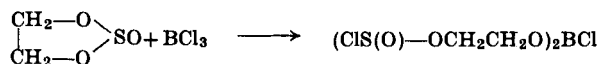
Borates and alkoxyboron chlorides result when alkyl or aryl sulfites are added to boron trichloride (160):



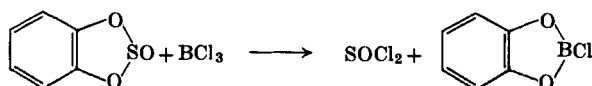
The alkyl chlorosulfonates do not react with boron trichloride but phenyl chlorosulfonate forms thionyl chloride (160):



Ethylene sulfite undergoes ring fission with boron trichloride (160),

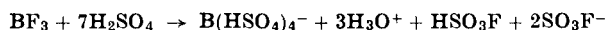


while *o*-phenylenesulfite gives thionyl chloride (160):

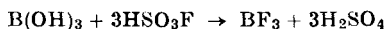


Dialkyl sulfates react with boron trichloride in an inert solvent to give alkyl chloride and a yellow solid approximating to a mixed anhydride ($\text{B}_2\text{S}_3\text{O}_{12}$); (160); in the absence of a solvent the reaction is vigorous at 20°, hydrogen chloride and sulfur dioxide being evolved with the formation of ill-defined solid products (160). Esters of sulfonic acid give sulfonylboron dichloride (161).

Boron trifluoride (382) and trichloride (337) are solvolyzed in pure sulfuric acid, giving the tetra(hydrogen sulfato)borate ion, $\text{B}(\text{HSO}_4)_4^-$; the reactions are rather complex for boron trifluoride:



This reaction probably does not go to completion, since boron trifluoride can be manufactured commercially by heating boric acid with fluoro-sulfonic acid (382),

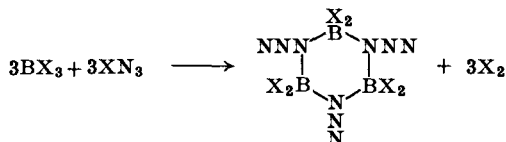


while a further complicating factor is that intermediate species $\text{BF}(\text{HSO}_4)_3^-$, $\text{BF}_2(\text{HSO}_4)_2^-$, and $\text{BF}_3(\text{HSO}_4)^-$ may be present in solution. It is possible to isolate the intermediate white solid, boron tri(hydrogen sulfate), when boron trichloride is treated with sulfuric acid (343).

8. Reactions with Compounds of Group VII Elements

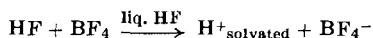
Displacement of halogen from a boron trihalide by a halogen of lower atomic weight is to be expected and, for example, chlorine ousts bromine from boron tribromide (250). The free halogens do not behave as strong Lewis bases toward the boron trihalides, as shown by the fact that iodine

does not react with boron trifluoride (52, 817), nor bromine with the tribromide (193), and iodine dissolves in boron triiodide to give only a purple-colored solution. Radioactive bromine, on the other hand, undergoes a rapid exchange when mixed with boron tribromide (238), indicative of at least a slight mutual interaction. Chlorine and bromine azides react with boron trichloride or tribromide to form the respective trimeric boron dihaloazide (682):

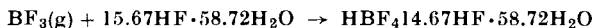


Cyanogen gives colored adducts with boron trichloride and tribromide (19) but hydrogen cyanide reacts only with the tribromide (710).

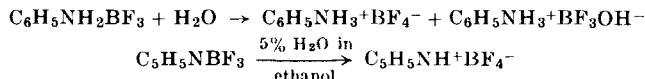
Although Henry's law is obeyed when boron trifluoride dissolves in anhydrous liquid hydrogen fluoride (551, 769) (strongly suggesting that no reaction occurs between the two), the ^{11}B n.m.r. chemical shift of the solution is exceedingly close to the value observed for the tetrafluoroborate ion (813), i.e.:



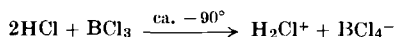
In aqueous solution, however, hydrogen fluoride and boron trifluoride definitely react to give fluoroboric acid (700) and the heat of the reaction



has been measured as -28.29 ± 0.07 kcal/mole (355). With the more dilute aqueous solutions of hydrogen fluoride formed during its partial hydrolysis, boron trifluoride forms the hydroxyfluoroborate anions HOBf_3^- , $(\text{HO})_2\text{BF}_2^-$, and $(\text{HO})_3\text{BF}^-$, which can be detected by ^{19}F n.m.r. techniques (206, 547, 769), but a partial hydrolysis in the presence of an amine [e.g., triphenylamine (770), aniline (733), or pyridine (659)] yields the quaternary tetrafluoroborate:

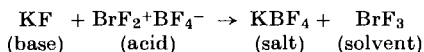


Thermal analysis shows that hydrogen chloride forms no compounds with boron trifluoride (81), but the molar conductivities of boron trifluoride and trichloride dissolved in liquid hydrogen chloride are reasonably high (ca. 10^{-4}) (832), indicative of a slight ionization, e.g.:



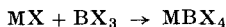
The exchange of radioactive chlorine noted between hydrogen chloride and boron trichloride in the gas phase at 24° is thought to be an atom-transfer process (392), which may involve the formation of an intermediate "HClBCl₃" species. The relatively weak interaction of the hydrogen halides (HCl, HBr, and HI) with their respective boron trihalides makes them useful solvents in which to study reactions of the trihalides (830), but halogen exchange occurs in the mixed systems HCl/BBr₃ (250), HF/BCl₃ (310a), HBr/BCl₃ (830).

Iodine pentoxide and boron trifluoride do not react together (52), but chloryl fluoride, ClO₂F, and chlorine trifluoride give 1:1 solid complexes regarded as ClO₂⁺BF₄⁻ (870) and ClF₂⁺BF₄⁻ (767). Similarly, solutions of boron trifluoride in bromine trifluoride may contain bromonium tetrafluoroborate, BrF₂⁺BF₄⁻, which would be an "acid" in the liquid bromine trifluoride system (411, 830):



Other nonaqueous solvents used for the preparation of tetrafluoroborates include liquid hydrogen fluoride (869), liquid arsenic trifluoride (871), liquid sulfur dioxide (727, 764), and liquid iodine pentafluoride (869).

The simplest method by which to prepare the tetrahaloborates is to add a suitable halide (preferably containing a large cation when the chloride, bromide, or iodide is used) to the corresponding boron trihalides, with or without an inert solvent:



M = alkali metal, NR₄⁺, H₃NR⁺, Ar₂MeC⁺, Ar₃C⁺, diazonium (ArN₂⁺)

X = F (769)

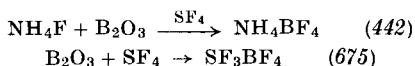
X = Cl (144, 368, 466, 467, 475, 595, 599, 663, 702, 813, 833)

X = Br (367, 471, 475, 663, 813, 835, 837)

X = I (144, 366, 813, 836)



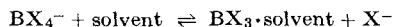
For the tetrafluoroborates, the boron trifluoride can be prepared *in situ* by using the reaction between sulfur tetrafluoride and boric oxide:



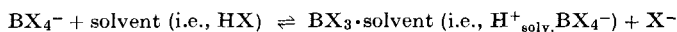
Another useful tetrahaloborate synthesis involves the addition of cycloheptatriene (either neat or in an organic solvent) to a boron trihalide, and gives good yields of the tropenium tetrahaloborates, C₇H₇⁺BX₄⁻ (X = Cl, Br, I) (365–369). The solubilities of sodium and potassium chlorides in liquid sulfur dioxide are low, but have been found to increase greatly on addition of boron trichloride; conductance measurements on

MCl/BCl₃ mixtures indicate a sharp break at ratios of 1:1, as expected if the tetrachloroborate ion was produced. However, on evaporation of the solvent and boron trichloride, only the metal chloride remains behind (142), which may indicate that an unstable ion such as Cl₃BSO₂Cl⁻, and not BCl₄⁻, is synthesized under these conditions [(132), see, however, Creighton (191)]. There are one or two discrepancies concerning the stability of tetrachloroborates, and the above experiment may be another; Herber has shown (392) that exchange of radioactive chlorine between tetramethylammonium chloride and pure boron trichloride occurs at 0° and, although he argued that this was evidence for the BCl₄⁻ ion, he did not isolate Me₄NBCl₄ on evaporation of the boron trichloride; yet later workers (813) obtained a 100% yield of tetramethylammonium tetrachloroborate by using almost the same procedure.

The ¹¹B n.m.r. chemical shifts of BX₄⁻ anions (except BF₄⁻) show a marked dependence upon halide ion concentration when they are measured in organic solvents (471, 813); this is probably due to an exchange equilibrium such as



occurring in these solvents. There is no dependence on halide concentration when the ¹¹B chemical shifts are measured for solutions in the corresponding hydrogen halides (813), lending further support to the idea that slight ionization takes place when the boron trihalides dissolve in a liquid hydrogen halide:



As no fluoride ion concentration dependence is observed for the ¹¹B chemical shift of tetrafluoroborates dissolved in organic solvents and no exchange occurs between F⁻ and BF₄⁻ in water (442), the BF₄⁻ ion must be virtually undissociated in solution; in other words, the stability series for tetrahaloborates is BF₄⁻ > BCl₄⁻ [> BBr₄⁻ > BI₄⁻], assuming that the magnitude of the chemical shift dependence on the concentration of X⁻ is inversely proportional to the stability of BX₄⁻. This stability relationship is probably a manifestation of several factors, including the strong Lewis basicity of F⁻ and adverse steric conditions operating for BCl₄⁻, BBr₄⁻, and BI₄⁻. The hydrolytic instability (and other chemical properties) of tetrachloro-, tetrabromo-, and tetraiodoborates can be explained in terms of the above dissociation equilibrium, but the solubility of tetramethylammonium tetrachloroborate in dimethyl sulfoxide is rather remarkable considering the vigor with which boron trichloride and the sulfoxide react together; however, such solutions become gelatinous during several hours at room temperature (813). The thermal

decomposition of many alkylammonium tetrachloroborates has been closely studied and shown to proceed via the 1:1 amine-boron trichloride adducts to the *N*-trialkyl-*B*-trichloroborazines (143, 144, 195):



Mixed tetrahaloborates, $\text{MBX}_n\text{Y}_{4-n}$, may be formed when boron trifluoride reacts with triphenylmethyl chloride (442, 701), phosphonium chloride (833), tetraalkylammonium chlorides (833), phosphorus pentachloride (834), nitrosyl chloride (834), and when boron trichloride reacts with triphenylmethyl fluoride (442, 701, 854). The infrared spectrum of $(\text{C}_6\text{H}_5)_3\text{CClBCl}_3$ in the solid state shows that the ions $(\text{C}_6\text{H}_5)_3\text{C}^+$ and BCl_4^- are present, but owing to an overlap of absorption bands it is impossible to judge from infrared spectra whether BF_3Cl^- and BFCl_3^- are present in $(\text{C}_6\text{H}_5)_3\text{CClBF}_3$ and $(\text{C}_6\text{H}_5)_3\text{CFBCl}_3$ or whether disproportionation to BF_4^- and BCl_4^- took place on crystallization (442); however, the spectra of several other solid salts, thought definitely to contain the chlorotrifluoroborate ion, have been described (834).

The mixing together of methylene dichloride solutions of triphenylmethyl tetrafluoroborate and tetrachloroborate produces an evolution of heat, and both the ^{19}F and ^{11}B n.m.r. spectra of the resulting solutions shows a single resonance line, the chemical shift of which varies systematically with the concentration of either BF_4^- or BCl_4^- . This is the expected behavior if a series of mixed tetrahaloborates were formed in the solution; the n.m.r. spectra of $(\text{C}_6\text{H}_5)_3\text{CFBCl}_3$ and $(\text{C}_6\text{H}_5)_3\text{CClBF}_3$ show single peaks having shifts corresponding to the relative amounts of fluorine and chlorine, and cannot be used to deduce whether discrete BFCl_3^- or BF_3Cl^- ions are present. Mixed tetrahaloborates are formed when boron tribromide is mixed with chloride ions in nitrobenzene or when either the trichloride or tribromide reacts with a tetrafluoroborate (442); however, fluorine-bridged complex ions such as B_2F_7^- and $\text{B}_3\text{F}_{10}^-$ may be formed when boron trifluoride reacts with various tetrafluoroborates in methylene dichloride solution (124). An attempt to isolate tetramethylammonium trifluorochloroborate using the reaction

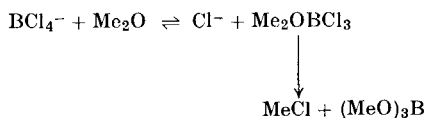


failed (850). The observed products

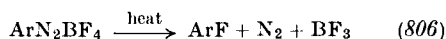


can be explained if it is assumed that the ion BF_3Cl^- was formed initially and that under the experimental conditions it disproportionated to give the series of mixed tetrahaloborates, the tetrafluoroborate, and the tetrachloroborate; the latter, in the presence of dimethyl ether, will

dissociate slightly (see above) giving the unstable dimethylether-boron trichloride:



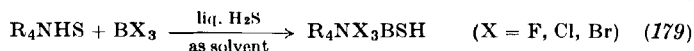
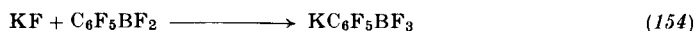
Tetraalkylammonium halides (593, 850) and diazonium chlorides (658, 723, 806) produce the corresponding tetrafluoroborates when added to aqueous tetrafluoroboric or trifluorohydroxyboric acid. A useful property of the tetrafluoroborates of silver and copper(II) is that they are soluble in organic solvents such as diethyl ether, benzene, and nitromethane (36), while the diazonium tetrafluoroborates are used in the Balz-Shiemann reaction, e.g.,



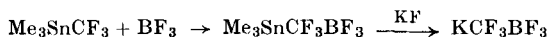
and in the presence of nickel carbonyl form ArH , Ar_2CO , or ArCO_2R when the reaction conditions are suitably manipulated (163).

Somewhat surprisingly, the ^{11}B n.m.r. chemical shifts of the tetrahaloborates, as measured in the corresponding liquid hydrogen halides, do not show a linear dependence on the electronegativity of the halogen, the boron atom in the BF_4^- ion being more highly shielded than expected (813). A similar trend is found in the boron trihalides, where ^{11}B chemical shifts of BCl_3 , BBr_3 , and BI_3 show a direct correlation with the electronegativity of the halogen, but in the trifluoride the boron atom is "too shielded" (311); this was explained by assuming that the chemical shift, δ , was composed of two components, one arising from the electronegativity of the halogen, the other being proportional to the π -electron density on the boron atom due to "back donation," i.e., $\delta = \delta_E + \delta_\pi$. In the case of the tetrahaloborates, however, π -bonding cannot reasonably be assumed, and some interaction between the halogen and low lying antibonding orbitals on the boron may be involved to affect the tetrafluoroborate ^{11}B shift to the greatest extent.

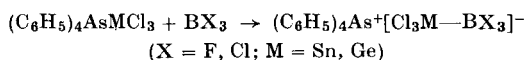
In contrast to the rather poorly characterized, mixed tetrahaloborates, several substituted trihaloborates have been isolated:



The trifluoromethyltrifluoroborate anion, the first boron compound to be isolated that contained a perfluoroalkyl group, results when trimethyltrifluoromethyltin is mixed with boron trifluoride (156, 157):



This is somewhat reminiscent of the preparation of the triphenylfluoroborate ion, $(\text{C}_6\text{H}_5)_3\text{BF}^-$, by addition of boron triphenyl to a fluoride in a suitable solvent (254), whereas an ionic pseudohalide (cyanide, cyanate, thiocyanate, or azide) when added to boron trichloride in nitrobenzene gives mixed ions such as BCl_3CN^- , $\text{BCl}_2(\text{CN})_2^-$, $\text{BCl}(\text{CN})_3^-$, and $\text{B}(\text{CN})_5^-$ (471). More recently this type of reaction has led to some interesting substituted tetrahaloborates containing tin-boron and germanium-boron bonds being isolated from addition of boron trichloride or trifluoride to the tetraphenylarsonium and tetramethylammonium salts of the trichlorostannate(II) and trichlorogermanate(II) ions (432), e.g.:



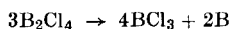
B. DIBORON TETRAHALIDES

Although Stock first made minute quantities of the tetrachloride in 1925 (800), the chemistry of the diboron tetrahalides did not begin to unfold until the late 1940's when Schlesinger considerably modified the tetrachloride synthesis (843) and was able to obtain about 10 gm per week by his new procedure. Even at the present time only a few laboratories are actively engaged in the study of the diboron halides, since it is commonly assumed that they are very difficult to prepare; it is hoped that the recent publication of the exact details involved in the synthesis of diboron tetrachloride (545, 845) will encourage more workers to enter the field.

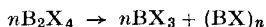
The diboron tetrahalides (see Table XI) are of interest to the chemist mainly because they are the simplest boron derivatives that contain a boron-to-boron bond (see page 16); similar bonds of course occur in certain of the boranes and carboranes, but a chemical study of them in such an environment is greatly complicated by the simultaneous presence of relatively large numbers of reactive boron-hydrogen bonds. In the tetrahalides the only complicating factor is the presence of the halogens; however, as was seen from the first part of this review, the chemistry of boron-halogen bonds has been extensively worked out, and it is thus possible to predict fairly accurately that part of a reaction that involves attack on the boron-halogen bonds. The chemistry of the diboron tetrahalides will therefore be governed by two factors: the reactivity of

the boron-halogen bonds on the one hand, and the boron-boron bonds on the other.

The thermal stability of the tetrahalides is very much less than the corresponding trihalides, and diboron tetrafluoride, the most stable member of the series, decomposes to the extent of about 8% in 1 day at room temperature (414). It was originally thought that decomposition involved disproportionation to elemental boron (800), e.g.,



but subsequent studies on many diboron compounds, including the halides, show that no boron is formed; instead polymers of empirical formula BX are often produced (641):



[X = F (246, 414), Cl (545, 546, 753, 825, 826), Br (208), I (757), OMe (97), OEt (97), $\text{ClCH}_2\text{CH}_2\text{O}$ (537), $\text{B}_2\text{R}_2(\text{NMe}_2)_2$ (640)]

The decomposition of the tetrachloride has been intensively studied and is in fact more complicated than is shown by the general equation above. The polymeric $(\text{BCl})_n$, e.g., is not a single compound and, by fractional sublimation under vacuum conditions, it is possible to resolve the solid mixture into its several (often highly colored) components, all of which have empirical formulas either equal or at least close to BCl . The major volatile polymeric product is a dark red solid of melting point 115° [incorrectly stated by Massey (410) to be octaboron octachloride], which classical analyses and molecular weight determinations indicate to be $\text{B}_{12}\text{Cl}_{11}$ (753, 825) whereas the mass spectrum gives a molecular weight corresponding to $\text{B}_{11}\text{Cl}_{11}$ (543, 545); at the present time it is not possible to choose between these two formulations but, should $\text{B}_{12}\text{Cl}_{11}$ be later proved the correct one, the mass spectrum shows, by the lack of a parent ion, the presence of a remarkably labile boron atom. Another red solid isolated from the decomposition products of diboron tetrachloride was shown by X-ray diffraction to be octaboron octachloride (426), but other workers (545, 753) have been unable to isolate this chloride when very stringent precautions were taken to prevent access of air and moisture to the apparatus. Mass spectral evidence has also been obtained for B_9Cl_9 (541, 545), while the same work suggests that minute quantities of $\text{B}_{10}\text{Cl}_{10}$ and $\text{B}_{12}\text{Cl}_{12}$ may also occur in the decomposition mixture. As well as the volatile polymers a white involatile solid is also formed (826), which analyzes as $\text{BCl}_{0.6}$, but nothing further is known of its properties or indeed if it is a single compound. Small amounts of tetraboron tetrachloride may also occur among the decomposition products of diboron tetrachloride, but the quantities obtained make this a very unattractive source of B_4Cl_4 .

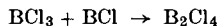
The structures of these curious polyboron halides [except B_4Cl_4 (25) and B_8Cl_8 (426)] are not yet known, but probably involve cages of boron atoms; liquid diboron tetrachloride, which has been held at room temperature for some time, exhibits an electron-spin resonance spectrum. Urry (753, 825) has traced this paramagnetism to the red $B_{12}Cl_{11}$ and to a purple polyboron chloride of unknown formulation, which suggests that intriguing molecular structures and bonding are involved in these halides; structure determinations are therefore awaited with great interest.

Although diboron tetrachloride is at present the only source of many of these polyboron chlorides (and for this reason alone B_2Cl_4 will no doubt be actively studied in the future), a new approach to the synthesis of boron-cage halides involves the thermal decomposition of the acid $H_2B_{10}Cl_{10} \cdot xH_2O$ (253) since at about 260° a 5% yield of the red volatile solid octachlorononaborane B_9Cl_8H can be isolated. It is interesting to note that this compound apparently exhibits an electron-spin resonance spectrum, but after several vacuum sublimations the paramagnetism decreases markedly without change in the analysis of the borane and may therefore be associated with an impurity. This suggests caution in the interpretation of the e.s.r. spectrum of $B_{12}Cl_{11}$, especially as liquid diboron tetrachloride does not develop an e.s.r. spectrum until it has remained at room temperature for many hours, even though the liquid chloride is previously colored deep red presumably due to dissolved $B_{12}Cl_{11}$ or $B_{11}Cl_{11}$ (536).

Since several BCl polymers are formed during the thermal decomposition of diboron tetrachloride, the first step may well involve the production of a BCl species,



and strong evidence in support of this comes from flash photolysis experiments on diboron tetrachloride carried out under essentially adiabatic conditions (546). The action of a silent electric discharge accelerates the decomposition of the tetrachloride (724) and a new boron polymer, a yellow solid of formula $(BCl)_x$ but unknown structure, is formed along with boron trichloride. During the microwave synthesis of diboron tetrachloride the spectrum of the ensuing discharge shows only those lines attributable to BCl (419), which, coupled to the fact that B_4Cl_4 and a yellow boron monochloride polymer are produced simultaneously with the B_2Cl_4 when boron trichloride is passed through a mercury discharge, suggests that BCl is a precursor in the formation of diboron tetrachloride,

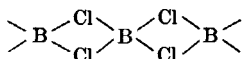


and not BCl_2 radicals as might have been expected; under some conditions the spectrum of the B_2 molecule is also observed (212). Since this equation is the exact opposite to that postulated for the thermal decomposition of the tetrachloride, it would appear that the reaction is reversible under certain conditions,



and that during decomposition the equilibrium is shifted to the right by the formation of BCl polymers. Diboron tetrafluoride is not formed when boron trifluoride is passed through an electric discharge (246), and this may be due to the fact that boron trifluoride will not react with BF since this species is readily detected spectroscopically in discharges passed through boron trifluoride vapor (673, 722); the other tetrahalides are formed when the respective trihalides are subjected to an electric discharge (208, 757). Again, unlike the other halogens, fluorine apparently forms only a single, involatile, lower fluoride with boron (246, 414), whereas several bromides (208) and iodides (757) have been isolated although not identified.

A study of the fragmentation pattern obtained in the mass spectra of the above volatile polyboron chlorides suggests that the chlorine atoms are terminally bonded one to each boron; however, tentative evidence (502) has been advanced for the formation of a white $(\text{BCl}_2)_x$ polymer when mixtures of boron trichloride and hydrogen are subjected to γ -radiation, in which the possibility of boron-chlorine bridges was recognized:



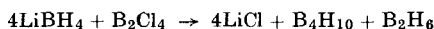
If this compound does indeed possess such bridging chlorine atoms, it will represent the first example in boron chemistry, although such halogen bridges are of course well known among the halides of other members of the Group III elements.

Not only do difficulties arise in handling the diboron tetrahalides owing to their thermal instability (which requires that most reactions be studied below room temperature), but the halides attack stopcock grease, hydrolyze readily with even traces of water, and are extremely oxygen-sensitive—the tetrafluoride in fact explodes on contact with dry oxygen (414, 820). Since the tetrafluoride, tetrachloride, and their hydrolysis products do not attack metallic mercury, they may conveniently be handled in vacuum lines equipped with mercury float-valves and mercury manometers; in recent years, however, increasing use has

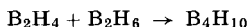
been made of greaseless stopcocks manufactured from polytetrafluoroethylene.

1. Reduction Reactions

Schlesinger, having managed to prepare reasonable quantities of diboron tetrachloride, was interested in its possible reduction to give the unknown hydride diborane-4, B_2H_4 . He found that lithium aluminum hydride would not react either in the presence or in the absence of an ether solvent; calcium aluminum hydride also failed to react in tetrahydrofuran solution (826). However, both lithium and aluminum borohydrides react rapidly, even in the absence of solvents and at temperatures as low as -45° , to produce mixtures of diborane-6, tetraborane-10, pentaborane-9, and traces of decaborane-14. The ratios of the hydrides formed varied somewhat with temperature, but the initial reaction appeared to be, e.g.:



The other boranes arose in the products due to the thermal decomposition of the unstable tetraborane. This suggests that diborane-4 may indeed have been formed in the reduction but that it quickly reacted with diborane-6 to form tetraborane-10 (826):



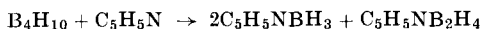
There have been two recent claims to have isolated stabilized adducts of diborane-4, both of which involve what amounts to the reverse of the above equation. Tetraborane-10 on treatment with 2 moles of trimethylamine produces trimethylamine-borane and trimethylamine-triborane-7:



Triphenylphosphine is then used to displace trimethylamine-borane from the triborane-7 adduct to give what was considered to be bis(triphenylphosphine)-diborane-4 (326):

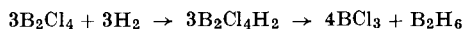


By using pyridine at 0° it is possible to remove the elements of diborane, as pyridine-borane, from tetraborane in a single step to form the monopyridine adduct of diborane-4 (580):

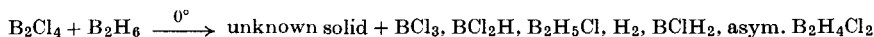


The reduction of diboron tetrachloride using hydrogen yields diborane and boron trichloride, the reaction being assumed to proceed via the initial addition of hydrogen across the boron-boron bond to give tetrachlorodiborane-6 [the monomer, BCl_2H , has actually been detected

among the products (719)], which would be expected to disproportionate readily to diborane and boron trichloride (826):



However, the position is considerably more complex than this, since side reactions occur between the diborane and both boron trichloride (see page 36) and diboron tetrachloride (719, 826):

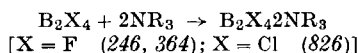


A different reaction occurs in the presence of diethyl ether when, at -23° , 1 mole of diboron tetrachloride absorbs 1 mole of diborane; removal of the excess of ether at room temperature was accompanied by loss of some diborane and the formation of a crystalline compound (melting point just above -80°), which analyzed to $(\text{B}_2\text{Cl}_4\text{BH}_3)_2\text{Et}_2\text{O}$ (826). Although nothing is known about this intriguing compound except that treatment with methanol liberates *four* moles of hydrogen suggesting that the boron-boron bond is still intact), it is possibly a tetrachloro derivative of the borane fragment, triborane-7, stabilized in some manner by the presence of the ether. The reaction obviously warrants further study.

2. Reactions Involving Compounds Containing Nitrogen or Phosphorus

Gaseous nitrogen and white phosphorus are inactive toward diboron tetrachloride at room temperature (18).

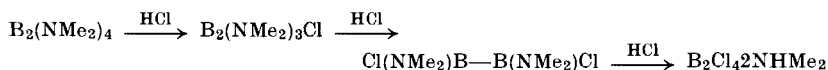
The diboron tetrahalides contain two tricoordinate boron atoms (see page 16), and typically the tetrafluoride and tetrachloride both add 2 moles of donor molecules like trimethylamine and triethylamine:



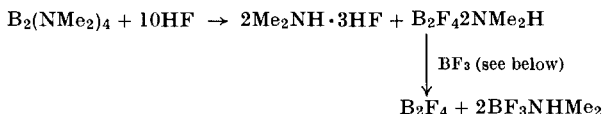
As often happens in boron chemistry, the addition of a donor molecule greatly increases the thermal stability of the tetrahalides and, for example, $\text{B}_2\text{Cl}_4\cdot 2\text{NMe}_3$ may be sublimed in a vacuum and melts at 228° without appreciable decomposition (826). Therefore a possibility was that on reduction of $\text{B}_2\text{Cl}_4 \cdot 2\text{NMe}_3$ by lithium borohydride the resulting diborane-4 would be stabilized by the 2 moles of trimethylamine; however, the only major product isolated from this reaction was diborane-6 (746); neither hydrogen nor diborane reacts with $\text{B}_2\text{Cl}_4\cdot 2\text{NMe}_3$ (826). The trimethylamine adducts of both diboron tetrafluoride and tetrachloride have been shown to be tetrameric in benzene solution and may not be simple adducts (246, 826); since both sublime on heating, it

would be interesting to determine (e.g., mass spectrometrically) their degree of polymerization in the vapor phase.

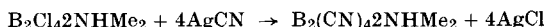
Probably one of the easiest derivatives of diboron tetrachloride to obtain is the monomeric $B_2Cl_4 \cdot 2NHMe_2$, which can be prepared by treating the commercially available tetrakis(dimethylamino)diboron with an excess of hydrogen chloride (120, 524, 632, 648):



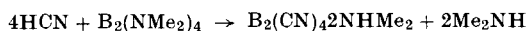
The formation of the dimethylamine adducts of diboron tetrafluoride and tetrabromide in a similar manner (524) could possibly open up another method for synthesis of free diboron tetrafluoride:



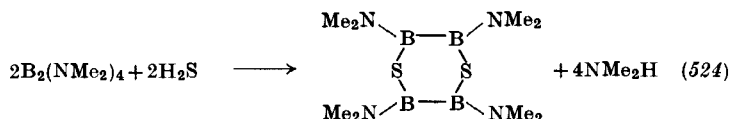
The dimethylamine adduct of diboron tetrachloride is reasonably reactive: thus acid hydrolysis gives sub-boric acid, while the halogen atoms are capable of substitution, for example, by silver cyanide (524):



The tetracyanodiboron derivative is identical to that formed when hydrogen cyanide reacts with tetrakis(dimethylamino)diboron (524):



The removal of dimethylamino groups from tetrakis(dimethylamino)-diboron by protonation has also been used in preparation of sulfur derivatives containing boron-boron bonds, e.g.:



The free amine formed in the latter reaction is removed by the slow addition of hydrogen chloride dissolved in ether. With diboron tetrachloride, tetramethylaminoborane, Me_2NBMe_2 , reacts in ratios that suggest the initial addition of 2 moles of borane via the nitrogen atoms to the diboron tetrachloride, but the adduct breaks up rapidly to evolve dimethylaminoboron dichloride (412).

A question of theoretical importance is how the Lewis acidity of a diboron tetrahalide compares with that of the corresponding trihalide. Obviously in the tetrahalides less overall π -bonding can occur than in the trihalides, since there is one less halogen atom to form a π -bond to the boron (unless there is considerable π -bonding in the boron-boron bond, and this is unlikely considering both the B—B distance in these compounds and the fact that almost free rotation has been shown to occur in B_2F_4 and B_2Cl_4); as a result, less energy will be required to reorganize the boron atoms in B_2X_4 molecules to the tetrahedral state, and simple theory predicts that the diboron compounds would form stronger adducts than the corresponding trihalides.

In a study on diboron tetrafluoride (364) the reverse was found to be true, and boron trifluoride displaced diboron tetrafluoride from its adducts with trimethylamine, triethylamine, and dimethoxyethane; furthermore, boron trifluoride forms a weak compound with *p*-chlorobenzonitrile whereas the tetrafluoride does not react at all. The difference between the observed and expected behavior of diboron tetrafluoride was assumed to be due to adverse steric interactions. When diboron tetrafluoride is bonded to a chelating ligand, such as *N,N,N',N'*-tetramethylethylenediamine, boron trifluoride or trichloride cannot displace the diboron tetrafluoride, and it appears that ring formation gives the adduct an increased stability (364).

Boron trifluoride and trichloride, on the other hand, are without action on the trimethylamine adduct of diboron tetrachloride (826), which appears to support the expected order of Lewis acidities although the n.m.r. chemical shift of the protons in this adduct indicates little difference between the acceptor strengths of the tetrachloride and trichloride (539). However, a complicating issue in all these studies is the apparently tetrameric nature of the $B_2X_4 \cdot 2NMe_3$ adducts, which may invalidate some of the conclusions drawn from the experimental results.

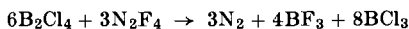
Bidentate donor molecules are to be expected to form 1:1 adducts with diboron tetrahalides, and a typical complex of this type is formed when tetramethyldiphosphine reacts with diboron tetrachloride (268):



Addition of trimethylamine to this adduct results in the production of $B_2Cl_4P_2Me_4NMe_3$; the isolation of this compound, coupled with the fact that only traces of $B_2Cl_4 \cdot 2NMe_3$ could be detected in the products, shows that trimethylamine is a stronger base than the diphosphine when the latter is acting as a bidentate donor, whereas the position is reversed when the diphosphine interacts with only one boron atom. The

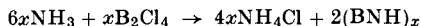
1:1 diphosphine adduct undergoes a transformation reaction when heated in a sealed tube at 250° to give a crystalline solid, which, from infrared evidence, was given the ionic structure $[(B \leftarrow PMe_2)_2]^+ BCl_4^-$ (268).

Substitution of the methyl groups in the diphosphine for chlorine, as in P_2Cl_4 , reduces the basicity of the phosphorus atoms and no compound is formed with diboron tetrachloride, although phosphorus trichloride gives a weak adduct, $B_2Cl_4 \cdot 2PCl_3$ (268); nor does tetrafluorohydrazine form an adduct with diboron tetrachloride, but in this case a slow reaction occurs as fluorine is transferred to boron (268):

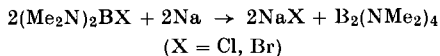


No reaction occurs between diboron tetrachloride and bis(trifluoromethyl)diazine, $(CF_3)_2N_2$ (545). Bidentate ligands such as ethylenediamine, hydrazine, and 1,2-dimethylhydrazine, which contain reactive hydrogen atoms, evolve hydrogen chloride on treatment with diboron tetrachloride and form the amine hydrochlorides as by-products (405).

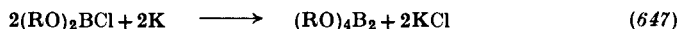
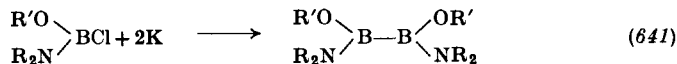
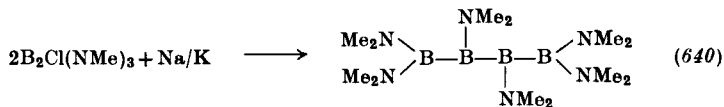
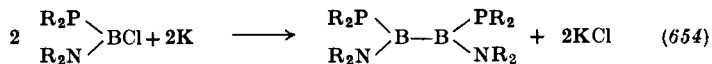
Similar loss of hydrogen chloride occurs when an excess of either ammonia or dimethylamine reacts with diboron tetrachloride (826):



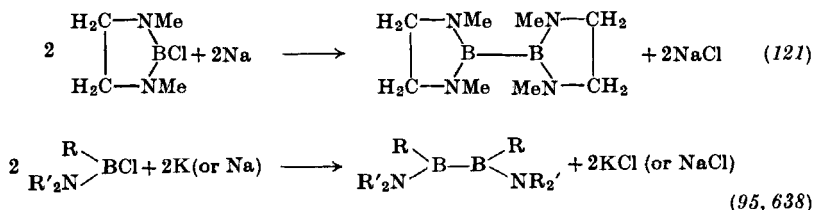
The product of this last reaction, tetrakis(dimethylamino)diboron, is identical to that formed in the Würtz-type synthesis (96, 647):



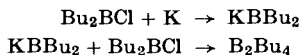
Nöth and others have shown that this type of coupling reaction can be extremely useful for the general synthesis of diboron derivatives, e.g.:



(In the latter reaction there is also a considerable amount of the normal borate, $B(OR)_3$, formed.)

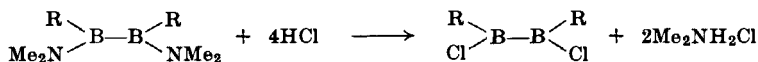


The formation of this latter series of diboron compounds is interesting since they are the only definitely known derivatives that contain boron-carbon bonds.¹⁰ Any attempt to alkylate diboron tetrachloride using, for example, zinc dimethyl (826) results in the rupture of the boron-boron bond and the formation of the corresponding boron trialkyl; the same product is obtained if dialkyl boron halides are treated with alkali metals (860). However, if the reduction of dibutylboron chloride (33) is carried out in ether, a solution is obtained that may contain tetrabutylboron stabilized by ether-coordination:

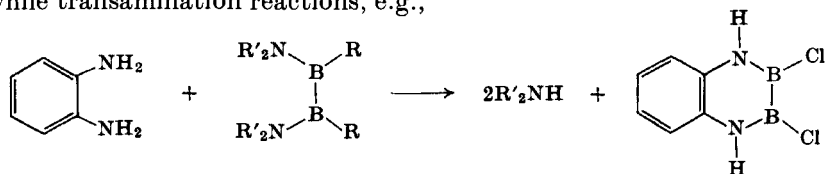


An electron-spin resonance study (497) of the reaction between dimesitylboron fluoride and sodium-potassium alloy shows (847) that the main radical produced is not the $\text{Ar}_2\text{B}-\text{BAR}_2^-$ ion as might be expected, but is the trimesitylborane negative ion, Ar_3B^- , presumably formed from trimesitylborane derived from the disproportionation of B_2Ar_4 .

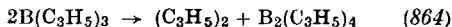
Although the bis(dialkylamino)dialkyldiborons react in a complex manner with hydrogen chloride, under the correct conditions dialkyl-dichlorodiborons can be isolated (638),



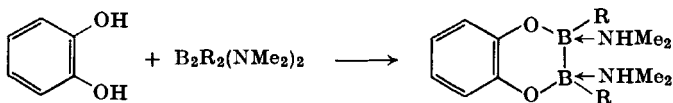
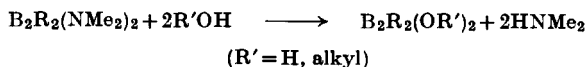
while transamination reactions, e.g.,



¹⁰ The thermal decomposition of triallylborane yields diallyl and a compound that analyzes as tetraallyldiboron:

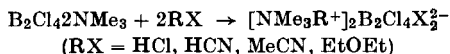


and treatment with hydroxy derivatives, e.g.,



can be used for the production of many other diboron compounds (638).

When dissolved in anhydrous liquid hydrogen chloride at low temperature,¹¹ diboron tetrachloride reacts with both tetramethylammonium chloride and phosphorus pentachloride to give the hexachlorodiborate anion, $\text{B}_2\text{Cl}_6^{2-}$; no evidence was obtained for the corresponding pentachlorodiborate ion (413). Attempts to remove trimethylamine from the adduct $\text{B}_2\text{Cl}_4\cdot 2\text{NMe}_3$ by treatment with dry hydrogen chloride failed, but 2 moles of hydrogen chloride were taken up by the adduct (405); similarly, $\text{B}_2\text{Cl}_4\cdot 2\text{NMe}_3$ will absorb about 2 moles of hydrogen cyanide (405), methyl cyanide (405), and diethyl ether (826). It is possible, although evidence is lacking, that these products may be ionic and contain derivatives of the hexachlorodiborate anion:

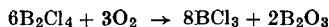


The salts $\text{Na}_2\text{B}_2(\text{C}_6\text{H}_5)_6$ and $\text{Na}_2\text{B}_2\text{Me}_5\text{H}$ (410) may contain fully substituted derivatives of the same ion.

Phosphine (unlike ammonia) when treated with diboron tetrachloride gives a 2:1 adduct ($\text{PH}_3:\text{B}_2\text{Cl}_4$), which is stable at room temperature in a vacuum; at about 65°, cleavage of boron-chlorine bonds becomes apparent as phosphonium chloride begins to be evolved (842). Stable, white 2:1 adducts are also formed when hydrogen cyanide and methyl cyanide react with diboron tetrachloride (405).

3. Reactions Involving Compounds Containing Oxygen or Sulfur

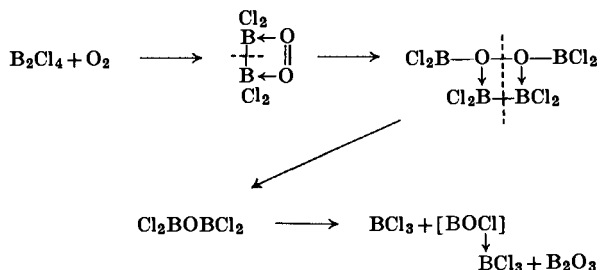
Although being inactive toward sulfur (18) or sulfur dioxide (415) at room temperature, diboron tetrachloride ignites when exposed to oxygen or air, producing boric oxide and boron trichloride (18); the amount of oxygen consumed suggests that the following reaction occurs:



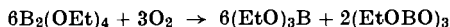
For this the postulated mechanism (409) involves, initially, the addition of 1 mole of diboron tetrachloride to an oxygen molecule followed by

¹¹ Hydrogen chloride and hydrogen iodide have no action on diboron tetrachloride even at 0° (842).

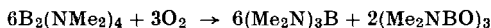
rupture of the B—B bond to give $\text{Cl}_2\text{B—O—O—BCl}_2$; this peroxy compound is then considered able to add on a further molecule of diboron tetrachloride:



When diboron tetrafluoride reacts with oxygen the position is complicated by the formation of a solid residue containing boron, oxygen, and varying amounts of fluorine (414). Other diboron compounds are also sensitive to dry oxygen, but only at temperatures much higher than -78° . At 25° tetraethoxydiboron and oxygen give triethyl borate and a compound thought to be triethoxyboroxine (97):

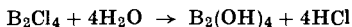


Tetrakis(dimethylamino)diboron does not react with oxygen at 100° (97), but at 200° tris(dimethylamino)borane and tris(dimethylamino)-boroxine are formed (540),

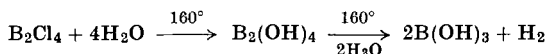


although the reaction is complicated by the concurrent oxidation of the methyl groups.

The careful treatment of diboron tetrachloride with an excess of distilled water at, or below, room temperature produces sub-boric acid (841, 842):

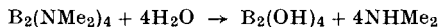


At higher temperatures some cleavage of the boron-boron bond in the sub-boric acid occurs simultaneously, and hydrogen is evolved; at 160° the cleavage is complete within a few hours (841, 842):

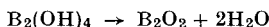


The presence of alkali catalyzes this cleavage, and in ca. 10% sodium hydroxide the evolution of 1 mole of hydrogen is essentially complete

after 3 hours at 70° (826); this alkaline hydrolysis has since been used extensively as a convenient method for the quantitative analysis of boron-boron bonds in general. A more useful source of sub-boric acid is the readily hydrolyzable tetrakis(dimethylamino)diboron (553, 647):



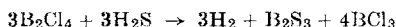
Sub-boric acid is stable for weeks at room temperature if stored in a vacuum, but begins to lose water on heating to 90°–100° (647, 841, 842); the loss of water is quantitative after 4 hours at 250°, the white solid, boron monoxide, being formed (841, 842):



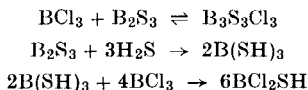
This monoxide is of some interest since it is possible to synthesize diboron tetrafluoride and tetrachloride directly from it either by heating with boron trichloride (552) or by the action of sulfur tetrafluoride at –78° (98). Other methods of preparing boron monoxide involve strong heating of boric oxide/boron mixtures at low pressure (436, 744) or by reducing a metal oxide, such as zirconium dioxide, with elemental boron (410); under the low pressure involved in these processes the boron monoxide can be made to sublime away from the other reaction products. The major component of “boron monoxide” in the vapor phase at 1500°K is actually the dimer, B_2O_2 (744).

Although the reaction of water with diboron tetrafluoride has yet to be studied, it has been stated that small amounts of silicon tetrafluoride are formed when diboron tetrafluoride is allowed to stand for some time in a Pyrex apparatus (414); this suggests that hydrolysis to hydrogen fluoride (which would then attack the glassware) occurs readily even with water adsorbed on the vessel walls. Hydrogen is quantitatively evolved when diboron tetrafluoride and tetrabromide are heated with sodium hydroxide solution (246, 826). Diboron tetraiodide reacts vigorously with pure water, and in alkaline solution hydrogen is produced (757).

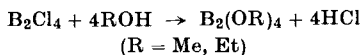
Hydrogen sulfide forms two adducts, $\text{B}_2\text{Cl}_4\text{H}_2\text{S}$ and $\text{B}_2\text{Cl}_4\text{2H}_2\text{S}$, when allowed to react with diboron tetrachloride at –78°; however, above –78° cleavage of the boron-boron bond occurs (842),



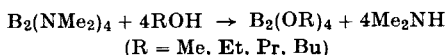
together with several concurrent side reactions:



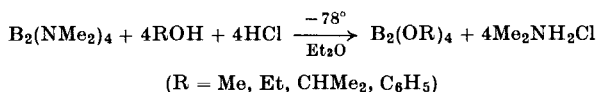
The boron-chlorine bonds in diboron tetrachloride are susceptible to attack by alcohols, giving hydrogen chloride and the corresponding tetraalkoxydiboron (826):



Again, tetrakis(dimethylamino)diboron is a more convenient source of the tetraalkoxydiborons (647):

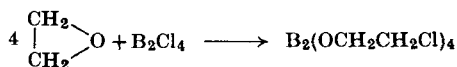


Hydrogen chloride has been used in large-scale preparations to remove the dimethylamine as it is formed (97):



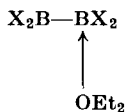
The tetraalkoxydiborons, unlike the tetraaminodiborons, will react with sulfur tetrafluoride to give diboron tetrafluoride (98). Some loss of diboron tetrafluoride occurs in this synthesis owing to the formation of a 1:1 adduct, B₂F₄SF₄, which slowly decomposes via the elimination of boron trifluoride.

Tetrakis(2-chloroethoxy)diboron is formed as the major product when ethylene oxide reacts with diboron tetrachloride (537):

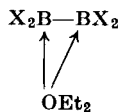


Like the other tetraalkoxydiborons, this compound is more thermally stable than the tetrahalides, hydrolyzes readily to lose the alkyl group as HOCH₂CH₂Cl, and does not react with dry oxygen at room temperature.

Diethyl ether forms a solid 2:1 etherate, B₂X₄2Et₂O, with both diboron tetrafluoride (246) and tetrachloride (826). On pumping at room temperature the 2:1 adducts lose ether, finally giving 1:1 adducts (246, 826). The structures of the 1:1 etherates is not known but at least two modes of bonding are possible for the ether:

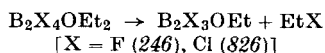


(oxygen using a single lone pair)



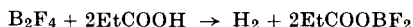
(oxygen using both available lone pairs)

On standing at room temperature the monoetherates lose ethyl halide as the B—X bonds are attacked¹²:

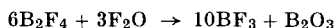


Dimethyl ether (826) and dimethyl sulfide (842) both form a 2:1 and a 1:1 complex with diboron tetrachloride; in the case of dimethyl sulfide, adduct formation is accompanied by the loss of some methyl chloride. 1,2-Dimethoxyethane gives a stable 1:1 complex on treatment with diboron tetrafluoride (364).

Acetone, like diethyl ether, yields a 2:1 adduct with diboron tetrachloride, which loses acetone in a vacuum at room temperature; however, decomposition via hydrogen chloride evolution takes place before the 1:1 adducts can be isolated (533). No adduct formation occurs when diboron tetrafluoride and propionic acid are mixed at 20°, instead an almost quantitative cleavage of the boron-boron bond occurs, resulting in the isolation of propionyloxyboron difluoride (404):



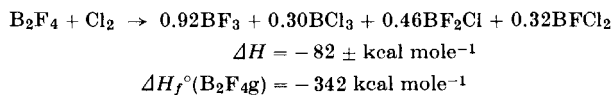
Mixtures of oxygen difluoride and diboron tetrafluoride ignite at temperatures as low as -78°, forming boron trifluoride and boric oxide (415):



Similar vigorous reactions, giving the same products, occur when certain metal oxides are in contact with diboron tetrafluoride, the vigor of reaction being in the same order as the ease of oxygen evolution on heating the oxides alone, e.g., $\text{HgO} > \text{MnO}_2 > \text{CuO}$ (415). As the metal oxide/ B_2F_4 mixtures often ignited, reaction would obviously be accompanied by some thermal decomposition of the diboron tetrafluoride to give $(\text{BF})_n$ and, in separate experiments, it was shown that the above metal oxides react with boron monofluoride to give oxygen (415).

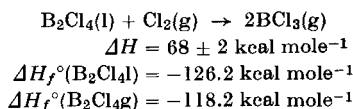
4. Other Reactions Involving Rupture of the Boron-Boron Bond

Chlorine reacts readily with diboron tetrafluoride to form a mixture of boron trifluoride, trichloride, and the two chlorofluorides (357):



¹² It is not yet established whether the adduct F_3BOEt_2 loses ethyl fluoride under the same conditions (see page 86).

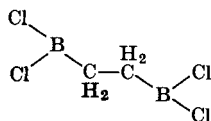
A more simple reaction occurs at -45° when diboron tetrachloride is used (18, 358):



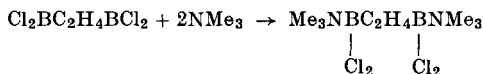
The thermochemical data from these two reactions allow the derivation of the bond energy for the B—B bond in B_2F_4 as 72.4 kcal (357) and in B_2Cl_4 as 79 kcal (358); these values are close to the B—B bond energy obtained from calorimetric data for sub-boric acid of 84 ± 5 kcal (239). By assuming the B—B bond energy in all the diboron compounds to be constant within about ± 5 kcal of 78 kcal,¹³ Finch has been able to estimate the heats of formation in the gas phase of diboron tetrabromide to be ca. -50 kcal and of the tetraiodide to be ca. $+20$ kcal mole⁻¹ (239).

Bromine reacts smoothly with diboron tetrachloride at -23° to give a mixture of boron trichloride, tribromide, and the two chloro-bromides (18); iodine has no action on diboron tetrachloride even at room temperature (18).

One of the most interesting reactions involving the cleavage of the boron-boron bond in the diboron tetrahalides is the reaction that occurs between the tetrafluoride or tetrachloride and C—C multiple bonds. Thus, ethylene reacts with diboron tetrachloride even at -78° to form a virtually quantitative yield of the adduct $\text{B}_2\text{Cl}_4\text{C}_2\text{H}_4$ (824). Schlesinger found that this adduct, a volatile liquid having a vapor pressure of a few mm at room temperature, did not yield hydrogen on alkaline hydrolysis, and therefore suggested that it was 1,2-bis(dichloroboryl)ethane. This has been verified by X-ray diffraction studies on single crystals, which also show that the molecule has a planar *trans* configuration in the solid state (589):



This molecule, being essentially an alkylboron dichloride, has properties intermediate between triethylborane and boron trichloride (see Fig. 1). Trimethylamine will add quantitatively to the boron atoms (407),



¹³ This value is considerably higher than the dissociation of the B_2 molecule, which has been calculated to be ca. 69 kcal mole⁻¹ (358).

while ammonia (407) attacks the boron-chlorine bonds, forming hydrogen chloride; alcohols give the corresponding 1,2-bis(dialkoxyboryl)ethanes (824), and zinc dimethyl substitutes methyl groups for the chlorine atoms (824). Ignition occurs in dry oxygen (cf. the lower members of the trialkyl-borane series), one of the products being free ethylene (407). Although boron-carbon bonds are normally stable to the action of water even at

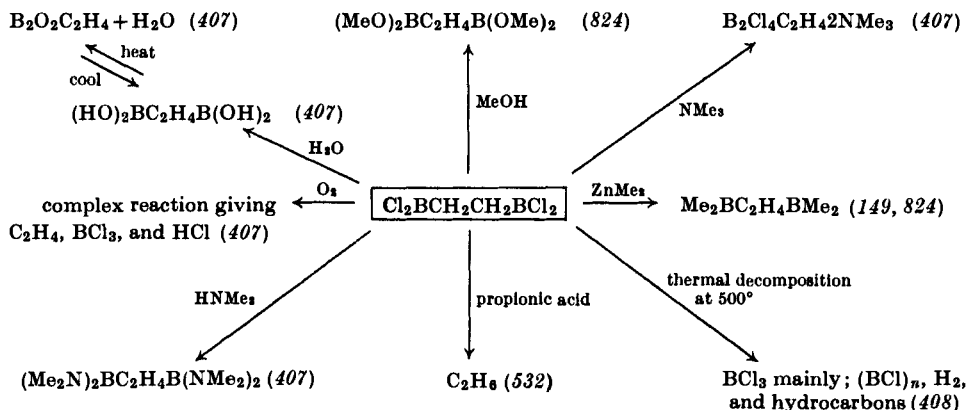
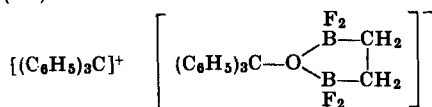


FIG. 1. Some reactions of 1,2-bis(dichloroboryl)ethane.

100° , carboxylic acids cleave the alkyl groups from boron and give the corresponding alkane; the case of 1,2-bis(dichloroboryl)ethane is no exception, since ethane (together with a trace of ethylene) is produced when the compound is heated for some hours in a sealed tube with propionic acid (192, 532). Antimony trifluoride undergoes fluorine exchange with 1,2-bis(dichloroboryl)ethane (149) to give 1,2-bis(difluoroboryl)ethane, which can also be made by allowing ethylene to react with diboron tetrafluoride, although this reaction is slower than the addition to B_2Cl_4 (149):

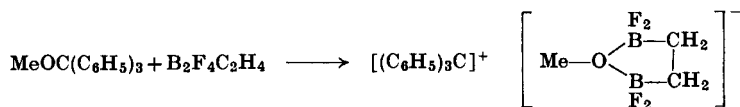


1,2-Bis(difluoroboryl)ethane forms the normal 1:2 adducts when treated with either dimethyl ether or tetrahydrofuran (76), but when bis(triphenylmethyl) ether is used only a 1:1 compound can be obtained, which has the structure (76):



In the corresponding case of methyl(triphenylmethyl) ether, it is possible to prepare the expected 1:2 adduct, but when an excess of

1,2-bis(difluoroboryl)ethane is used a similar chelated product is formed (76):

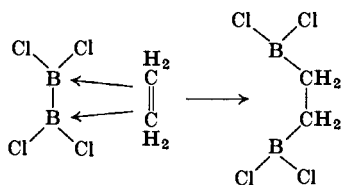


The olefin addition reaction seems to be fairly general; thus the use of butadiene gives either 1:1 addition (diene: B_2Cl_4) or 1:2 addition, depending on the reaction ratios, on treatment with diboron tetrachloride (149). However, allyl fluoride exchanges fluorine for chlorine when allowed to react with diboron tetrachloride:



More usually the presence of halogen in the olefin greatly interferes with the addition of diboron tetrachloride. One chlorine on a carbon atom forming the double bond is sufficient to stop the addition of diboron tetrachloride even at room temperature; if the halogen is on a carbon not involved in the olefinic double bond, then the addition of diboron tetrachloride can take place (e.g., in the cases of allyl chloride or 4-chlorobutene-1) (149) but even so it is found that the allyl chloride adduct is very thermally unstable.

The mechanism suggested (409) for this olefin addition reaction involves the initial formation of an adduct by overlap of the vacant boron orbitals with the olefinic π -bond, the diboron tetrachloride taking up the planar configuration followed by rupture of the boron-boron bond and

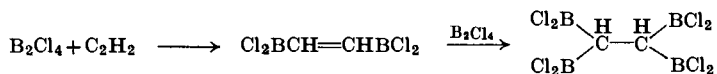


the simultaneous formation of two normal boron-carbon bonds. Deactivation of the olefinic π -bond by electron withdrawal in the case of halo-olefins would explain why such olefins do not undergo the addition reaction. However, it is interesting to point out that, whereas diboron tetrachloride will decompose rapidly above 0° , in the presence of the unreactive olefins the decomposition of the tetrachloride is inhibited even at temperatures well above 25° (149); this phenomenon has since

been confirmed in several laboratories. It is natural to assume that some weak interaction does occur between the halo-olefins and diboron tetrachloride, but all efforts so far to detect changes in the proton n.m.r. spectra of the olefins due to such an interaction have failed (90). The availability of the vacant orbitals on the boron atoms for attack by the olefin will also be an important factor in governing the kinetics of the addition reaction; and possibly the much slower reactions of diboron tetrafluoride with the olefins, compared to the tetrachloride, are a reflection of the stronger π -bonding that occurs between boron and fluorine than between boron and chlorine. The unreactivity of tetrakis(dimethylamino)-diboron toward ethylene can probably be explained by considerable B—N π -bonding (540), but there is also a complicating steric factor operating in this case when the diboron molecule attempts to adopt the planar configuration required for the initial stage of the reaction [see Becher *et al.* (65) for a discussion on the structures of tetramethoxydiboron and tetrakis(dimethylamino)diboron].

Cyclopropane will also add across the boron-boron bond of diboron tetrachloride at about 0° and, in this case, a three-membered carbon chain separates the boron atoms in the product, 1,3-bis(dichloroboryl)-propane (149). It might be an interesting experiment to attempt the synthesis of the yet unknown bis(dichloroboryl)methane by treating diazomethane with diboron tetrachloride.

When acetylene reacts with diboron tetrachloride, the 1:1 addition compound 1,2-bis(dichloroboryl)ethylene is initially formed (149, 158). The presence of the carbon-carbon double bond is shown by the fact that bromine will add quantitatively, while treatment of 1,2-bis(dichloroboryl)ethylene with propionic acid releases 1 mole of ethylene (158). Thus, as might be expected, it is possible to add a further mole of diboron tetrachloride to the double bond, giving 1,1,2,2-tetrakis(dichloroboryl)-ethane (158):



Although the 1,2-bis(dihaloboryl)alkanes are readily prepared from the diboron tetrahalides, syntheses not involving the use of the rather inaccessible tetrahalides would obviously be welcome to the preparative chemist. The first attempt at such a synthesis involved the treatment of the di-Grignard reagent $\text{BrMgC}\equiv\text{CMgBr}$ with dialkylboron iodides (372):



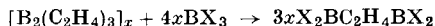
The products are 1,2-bis(dialkylboryl)acetylene derivatives; the action of oxygen will convert these compounds to the corresponding alkoxides:



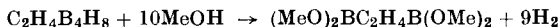
However, this method of synthesis, when applied to the bis(dialkylboryl)alkanes, results only in the formation of boron heterocycles (164):



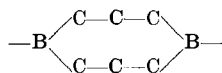
The addition of diborane to an excess of acetylene in 1,2-dimethoxyethane resulted in the formation of a white solid of approximate composition $(C_2H_2)_3B_2H_6$, which gave no hydrogen on hydrolysis but yielded ethane quantitatively on treatment with propionic acid; these properties suggest a polymeric structure made up of $>BC_2H_4B<$ links, and in accord with this it was found that the solid reacted with either boron trifluoride or trichloride to give good yields of the corresponding 1,2-bis(dihaloboryl)ethane (162):



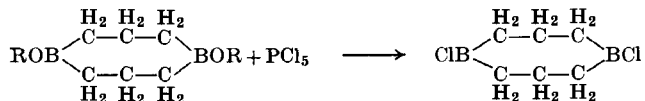
Similarly, dimethylenetetra-borane, formed from ethylene and tetra-borane-10 (768) produces 1,2-bis(dimethoxyboryl)ethane on methanolysis (371):



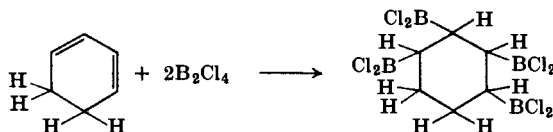
A somewhat related series of heterocycles involving



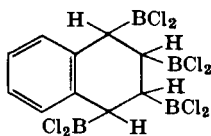
bridges have been made by heating triallylborane with triisobutylborane at 130–140° (410); butene is evolved and the resulting polymer, on boiling with an alcohol, gives the dialkoxy-1,5-diborocanes, which can be treated with phosphorus pentachloride to give the dichloro derivatives:



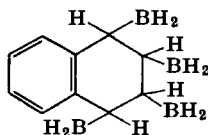
Cyclo-olefins will add on diboron tetrachloride quite readily; thus 1,3-cyclohexadiene reacts to give a 2:1 adduct when the temperature is allowed to rise from -78° to 20° over a period of 10 days (878).



Benzene and diboron tetrachloride appear to react at room temperature but an olefin-type addition product is not isolated, instead a high yield of phenylboron dichloride is obtained (255). However, if naphthalene is used, 2 moles of diboron tetrachloride are taken up at room temperature over about 2 weeks to give the yellow liquid, $C_{10}H_8B_2Cl_4$, for which chemical and 1H n.m.r. evidence suggest the structure:

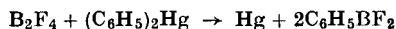


By treatment of this chloride with lithium borohydride it is possible to reduce it to the corresponding borane (877, 878):

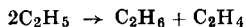


A similar reduction of 1,2-bis(dichloroboryl)ethane, however, gives only an unstable colorless oil, which on decomposition at about -20° produces diborane (878).

Although the boron-boron bond is broken when diboron tetrafluoride is treated with diphenylmercury, a different reaction takes place, in which phenylboron difluoride is the principal product (415):



Diethylmercury reacts similarly, ethylboron difluoride being formed; the presence of ethane among the by-products might suggest that some ethyl radicals were liberated:

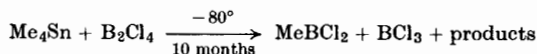


However, only traces of ethylene were isolated while no 1,2-bis(difluoroboryl)ethane could be detected (415).

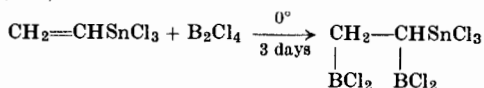
Tetravinylstannane produces a red viscous oil, tin, ethylene, and vinylboron difluoride when allowed to stand in contact with diboron tetrafluoride at -80° ; again, although ethylene was among the products, no 1,2-bis(difluoroboryl)ethane was detected (415). This is somewhat similar to the reactions that take place between either tetramethylstannane and diboron tetrafluoride (90),



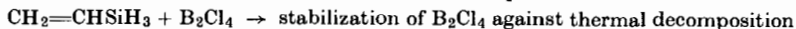
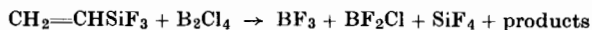
or between tetramethylstannane and diboron tetrachloride (90):



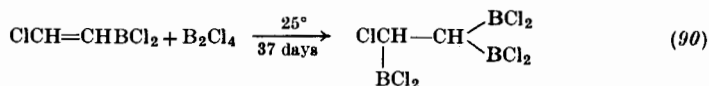
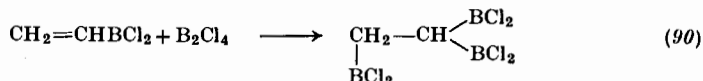
If vinyltrichlorostannane is treated with diboron tetrachloride, it is found that slow addition of the diboron compound to the olefinic double bond occurs (89, 90):



A similar addition occurs over a period of days when diboron tetrachloride and vinyltrichlorosilane are mixed together, the reaction being conveniently monitored by proton n.m.r. spectroscopy (90); rotational isomers complicate the n.m.r. spectrum of the products, as was found to be the case in the adduct formed by either *cis*- or *trans*-butene and diboron tetrachloride (237). However, no addition occurred between either vinyltrifluorosilane or vinylsilane and diboron tetrachloride (90):

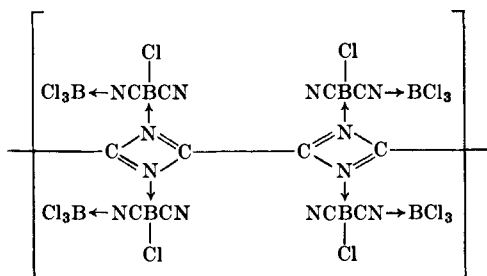


Vinylboron dichloride and chlorovinylboron dichloride both undergo a smooth, although slow, addition of diboron tetrachloride, the latter being presumably stabilized for many days before the reaction is complete:

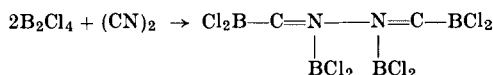


However, no adduct is formed when diboron tetrafluoride and vinylboron dichloride are heated to 100° (90).

Diboron tetrachloride readily absorbs 1.5 moles of cyanogen to form a dark brown solid, which evolves no hydrogen on alkaline hydrolysis (showing the absence of B—B bonds), and adds 2 moles of trimethylamine without loss of cyanogen; strong heating to 400° causes the solid to lose 1 mole of boron trichloride, leaving a residue of composition $\text{BCl}(\text{CN})_3$ (19). On the basis of these properties the following polymeric structure was proposed for the solid:

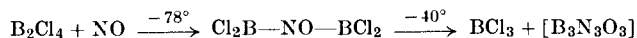


However, since cyanogen contains a triple carbon-nitrogen bond, it appears more attractive to assume that the molecule adds across the boron-boron bond in the same way as acetylene,



while a further mole of cyanogen might be used for forming donor-acceptor bonds with the tricovalent boron atoms [cyanogen has been shown to react quite readily with boron trichloride to form $(\text{CN})_22\text{BCl}_3$ (19)], and in this way a polymeric structure would be built up.

Nitric oxide, while interacting only weakly with the boron trihalides, readily reacts in a 1:1 ratio with diboron tetrachloride even at temperatures below -78° , giving a green solid; unfortunately this solid is unstable thermally and at -40° decomposes with the evolution of about 1 mole of boron trichloride, so that it was impossible to discern the presence or absence of a boron-boron bond by alkaline hydrolysis. Neither ethylene nor oxygen reacted with the adduct at -78° , although both readily attack diboron tetrachloride at that temperature. Attempts to stabilize the solid by treatment with trimethylamine resulted only in the loss of the boron trichloride (recovered as Me_3NBCl_3) at -78° . On this rather meager evidence it was suggested that addition of the nitric oxide across the boron-boron bond had occurred (409):



Ignition occurs if diboron tetrachloride and nitric oxide are mixed rapidly at room temperature. When the tetrafluoride is used, ignition sometimes occurs even at -78° , the products including boron trifluoride, nitrous oxide, and nitrogen (414); again a green colored unstable solid is formed at low temperatures. Neither carbon monoxide nor carbon dioxide reacts with diboron tetrachloride at room temperature (409).

C. OTHER BORON HALIDES

1. *Tetraboron Tetrachloride, B_4Cl_4*

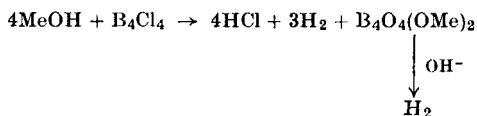
Probably little more than 1 or 2 grams of this rare, slightly yellow, solid chloride has ever been obtained, and in consequence comparatively little is known concerning its properties. The vapor pressure of the solid is suitably summarized by the equation:

$$\log p \text{ (mm)} = -\frac{2719}{T} + 9.464$$

At room temperature, p is about 2 mm (823, 827). The vapor density is normal at 70° (823, 827) and the mass spectrum of the vapor shows a strong group of peaks around mass 184 due to the parent ion $B_4Cl_4^+$ (543, 545).

Tetraboron tetrachloride is spontaneously inflammable in dry air (823), producing boron trichloride as was found in the combustion of diboron tetrachloride. However, in general, the chemistry of the two tetrachlorides is quite widely dissimilar. Hydrogen apparently produces traces of hydrogen chloride when heated with tetraboron tetrachloride to 70° (the decomposition point of the tetrachloride), but even after 18 hours at this temperature 95% of the starting material was recovered unchanged (823). A complex reaction occurs between diborane and tetraboron tetrachloride at 55° giving boron trichloride, $(BH)_x$, and possibly a compound of formula $B_4Cl_4B_2H_6$ (823); the reaction is being studied further in the hope of ascertaining if this latter compound is a tetrachloro derivative of the little known hexaborane-10.

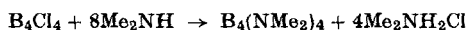
At room temperature the boron-boron bonds in tetraboron tetrachloride are cleaved by water to product 3 moles of hydrogen in 12 hours; a further mole of hydrogen is generated in the presence of alkali (823). A similar reaction occurs during the methanolysis of tetraboron tetrachloride:



The compound $B_4O_4(OMe)_2$ was not suitably identified and may well be a mixture (823). Ethylene did not cleave the boron-boron bonds even at 70° (823).

Attempts to form adducts of tetraboron tetrachloride with either phosphorus trichloride or diethyl ether failed; in diethyl ether solution at room temperature, the tetrachloride slowly evolves ethyl chloride in an ether-splitting reaction (823).

Substitution of the chlorine atoms is apparently possible in certain cases; dimethylzinc gives the monomethyl derivative B_4Cl_3Me at room temperature, which has a normal vapor density at 63° (823). Dimethylamine, on the other hand, removes all four of the chlorine atoms from tetraboron tetrachloride as hydrogen chloride (which then reacts with excess of the amine to give dimethylamine hydrochloride):

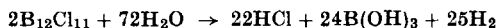


It was thought (823) that the nonexistence of a strong infrared band close to 1010 cm^{-1} in the spectrum of $B_4(NMe_2)_4$ indicated the loss of the boron-cage structure in this dimethylamino compound; however, the intense band at 1010 cm^{-1} in tetraboron tetrachloride is more likely to be associated with the B—Cl vibrations (in line with several other boron chlorides) than solely with a boron-cage absorption, and thus there is no evidence to suggest that the tetrahedral B_4 cage of tetraboron tetrachloride did not survive reaction with dimethylamine and so still exist in $B_4(NMe_2)_4$.

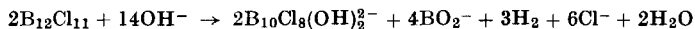
2. Dodecaboron Undecachloride, $B_{12}Cl_{11}$

This dark red solid is, next to boron trichloride, the major product formed during thermal decomposition of diboron tetrachloride; it melts at $115 \pm 1^\circ$ (753, 825) and sublimes in a vacuum above room temperature. There is some dispute as to the correct formulation since mass spectral studies suggest a molecular formula of $B_{11}Cl_{11}$ (543, 545), but, for a discussion of the few exploratory experiments carried out on the compound, it will be assumed to be $B_{12}Cl_{11}$. The most interesting physical property of the solid is its apparent paramagnetism, which gives rise to a broad, featureless peak in the electron-spin resonance spectrum of g value 2.011 and peak width 25 gauss (753, 825).

In contrast to diboron tetrachloride and tetraboron tetrachloride, $B_{12}Cl_{11}$ hydrolyzed more rapidly in acid solution than in alkali, but in neither case was the amount of hydrogen evolved equal to that required for the complete decomposition of the solid to boric acid:



The optimum amount of hydrogen was about 80% over a period of 27 days in acid solution (753). In the alkaline solution the extreme slowness of hydrolysis was assumed to be due to the formation of very stable derivatives of the $B_{10}X_{10}^{2-}$ ions, e.g.:

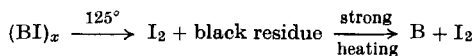


Trimethylamine discharged the red color of $B_{12}Cl_{11}$ when the two were mixed at -78° and a light tan-colored solid of composition $B_{12}Cl_{11} \cdot 2NMe_3$ was formed, which decomposed at 75° by evolving trimethylamine-boron trichloride; it was suggested that the loss of color may have been due to the loss of paramagnetism via dimerization (753).

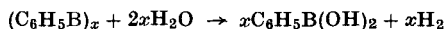
$B_{12}Cl_{11}$ on ethanolysis gave a mixture of triethyl borate, hydrogen chloride, ethyl chloride, diethyl ether, and an uncharacterized brown solid (753). The complex reaction with trimethylaluminum gave methane, boron trimethyl, and a series of volatile, highly colored, interesting, but uncharacterized solids (753), which obviously warrant further study. Nitric oxide did not react with $B_{12}Cl_{11}$, even though both molecules have an unpaired electron and nitric oxide attacked the boron-boron bond in diboron tetrachloride (753).

3. $(BX)_x$

Comparatively little is known about the chemistry of the other boron monohalides; the involatile yellow solid, $(BF)_x$, releases oxygen when treated with manganese dioxide, cupric oxide, or mercuric oxide (415), while $(BBr)_x$ (208) and $(BI)_x$ (757) evolve a little hydrogen during hydrolysis, giving rise to solutions with strong reducing properties. Ammonolysis of $(BBr)_x$ gives a white compound of composition $(B_2NH)_x$ (208). Both boron monobromide (208) and monoiodide (757) appear to sublime above room temperature in a good vacuum (a mass spectrometric study of the vapor may give useful information concerning the identity of these halides) but, on strong heating, decomposition occurs (757), e.g.:



Although not prepared from the monohalides, some substituted derivatives are known such as $(BH)_x$ (410), $(BC_4H_9)_x$ (33), $(BC_6H_{13})_x$ (864), and $(BC_6H_5)_x$ (462); the latter phenyl compound, the most studied of these, has a value of x lying between 9 and 12. It is an amorphous powder, readily oxidized by air and soluble in benzene, dioxan, and toluene to give a yellowish brown solution; hydrolysis gives some phenylboric acid, but only about 10% of the hydrogen required by the equation:



Ammonia, when passed into a benzene solution of $(C_6H_5B)_x$, gives a colorless compound, $[(C_6H_5B)NH_3]$.

V. Conclusion

There is little on which to comment concerning the boron trihalides, as their chemistry is comparatively well worked out, and advances in the main appear to center around new potential Lewis bases (e.g., 329) or the use of different reactive organic compounds (e.g., 433, 434). As in most other branches of chemistry, X-ray structural determinations on boron halide derivatives lag far behind preparative investigations, and one hopes that some of the many structural queries raised in this review will shortly be settled. This is especially so in the case of the many intriguing compounds arising from the study of the diboron tetrahalides.

Although it is now possible to obtain reasonable quantities of diboron tetrachloride, the search for good nondischarge routes to its synthesis should continue, as success in this direction would open up the chemistry not only of diboron tetrachloride itself but also of the polyboron chlorides that arise from it by thermal degradation. An exploration of halogen exchange reactions using these polyboron chlorides should prove rewarding and, for example, extend the number of known boron monofluorides from the single $(BF)_x$ to B_4F_4 (although it has been suggested that this compound may be unstable thermally) (544), B_9F_9 , and $B_{11}F_{11}$.

Many of the reactions described in this review, especially those involving the diboron tetrahalides, were carried out in the absence of a solvent, whereas in many cases it may well prove better to use a solvent provided that no reaction occurs between solvent and solute either by formation of stable adducts or by loss of hydrogen halide; for example, little advantage has yet been taken of the fact that halo-olefin solutions of diboron tetrachloride are quite stable thermally even at temperatures well above 20° . Such solvents should prove ideal media for studying the chemistry of diboron tetrachloride above 0° , while a study of such a system by several physical methods may reveal the nature of the solute-solvent interaction.

The difficulties experienced in the analysis and molecular weight determinations of several B—X polymers and of certain amine adducts of the diboron tetrahalides (often due to their air and moisture sensitivity) may well be overcome by the use of mass spectrometry, since these compounds are often quite volatile in high vacuum. Mass spectrometry should also be of great help in mapping out certain areas of the chemistry of tetraboron tetrachloride and $B_{12}Cl_{11}$, where the air sensitivity of the compounds augments the practical difficulties experienced

when working with the extremely small quantities of starting materials available; a particular area for such a study might be the reaction of $B_{12}Cl_{11}$ with aluminum trimethyl, where several highly colored, volatile species were detected, but in amounts too small to permit conventional analyses (753).

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NOTE ADDED IN PROOF

 B_3F_5 AND B_8F_{12}

When boron trifluoride is passed over boron at 2000°C and 0.1 to 1.0 mm Hg, a high yield of BF is obtained which can be condensed onto a surface, cooled to liquid temperatures. The resulting greenish-white polymeric deposit, on warming to room temperature, gives off three major fractions besides boron trifluoride: B_2F_4 , B_3F_5 and colorless, slightly-volatile boron fluorides containing up to 14 boron atoms. At least some of the diboron tetrafluoride is thought to be formed from the direct combination of BF and BF_3 .

The colorless triboron pentafluoride is probably the first compound to be isolated which has a simple B_3 chain structure; it melts at -50° to -55° C and above -30° rapidly decomposes to BF_3 , B_2F_4 and B_8F_{12} . The latter compound is a yellow oil with a vapor pressure at 0° of 2.3 cm. Hg. and is unstable above -10° .

P. L. Tims, *Chem. Eng. News*, **44**, 50 (Sept. 19, 1966).

FURTHER ADVANCES IN THE STUDY OF MECHANISMS OF REDOX REACTIONS

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I. Introduction

Since the first review in this series by Taube (377), and in part no doubt as a direct result of it, there has been considerable interest in the field of oxidation-reduction reactions. Some attempt is made here to present an up-to-date account of the subject with particular reference to work reported during the last eight years. Other reviews concerned with various aspects of the field are by Stranks (346), Halpern (181), Sutin (359, 361), Marcus (253), and Strehlow (350).

The present review is concerned with reactions of metal ions in which the oxidation state of the metal ion changes as a result of the reaction. Such reactions are believed to occur by an electron-transfer process, although in some cases at least atom transfer may be a possibility. Some of the questions which arise are, first of all, if the reaction is other than a straightforward single-stage process, what are the elementary steps which together account for the overall reaction? At the time of electron transfer, how close together are the two reactants, and is the reaction of the inner- or outer-sphere type? If a reaction is of the inner-sphere type

(the metal ions have a ligand in common in the activated complex), what effect do different bridging groups have, and is the same reactivity pattern observed with other metal ion reactants? What effect do non-bridging ligands have? Is there any evidence for the interpenetration of coordination spheres in outer-sphere reactions? Do the rate constants observed agree with calculated values, and is the simultaneous or near-simultaneous transfer of two electrons possible?

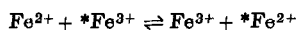
A wide range of experimental techniques has been used to study redox reactions. For exchange reactions isotopic labeling techniques are used whenever possible, and in a few special cases it has been possible to follow the exchange by measuring the change in optical rotation. The faster exchange reactions can in some cases be studied by NMR and ESR methods. For the slower reactions in which there is a net chemical change conventional spectrophotometric techniques are generally preferred, but volumetric and electrometric methods have also been used. The faster reactions may be studied by polarographic, stopped-flow, and relaxation techniques. The latter finds less use for redox reactions, since (if spectrophotometric techniques are to be used) an essential requirement is that the reaction should have a measurable equilibrium position, and in only relatively few instances is this possible. Further details of these various methods can be found elsewhere (346, 366). For a comprehensive survey of the methods used for fast reactions, the reader is referred the recent text on "Fast Reactions in Solution" by Caldin (72).

Abbreviations which are used are of the standard type. Thus for the ferric ion the formula Fe^{III} is generally used to refer to the total ferric present, i.e., $\text{Fe}^{3+} + \text{FeOH}^{2+}$, etc., it being understood that Fe^{3+} is in fact the hexaquo ion $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and that FeOH^{2+} is $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$, etc.

II. One-Equivalent Exchange Reactions

One-equivalent electron-exchange reactions constitute a relatively simple class of chemical reaction in that the reactants and products are identical, there is no free energy change, and in the case of outer-sphere reactions no chemical bonds are made or broken. As in other reactions, however, activation free energy requirements must be met for the reaction to proceed, and these requirements vary appreciably from one reaction to another.

The exchange is generally studied by isotopic labeling of one of the reactants, e.g.,



the approach of an equilibrium, $K = 1$, being measured. Rate constants are evaluated, using the McKay equation,

$$\log_{10} (1 - F) = - \frac{kt}{2.303} (a + b) \quad (1)$$

where a and b are the reactant concentrations, and F is the fraction of exchange at a time t .

A. TRANSITION METAL IONS

Exchange reactions between the II and III oxidation states of iron, chromium, and cobalt have been extensively studied, and provide much of the material for this section. Other reactions which have been studied include the exchange of vanadium(II) with vanadium(III), vanadium(III) with vanadium(IV), manganese(VI) with manganese(VII), and silver(I) with silver(II). The systematic study of other reactions which are referred to has, for a variety of reasons, proved more difficult.

Although the reaction of iron(II) with iron(III) was one of the first isotopic exchange reactions to be studied, details of the mechanism, whether inner- or outer-sphere, remain for the most part uncertain. This is largely because the inner-coordination spheres of both Fe^{II} and Fe^{III} aquo ions are labile, so that the exact composition of these immediately before and after the exchange is difficult to determine.

When the exchange is studied in aqueous perchloric acid solutions in the absence of catalytic anions,¹ the rate may be expressed as

$$\text{Rate} = k_{obs} [\text{Fe}^{\text{II}}] [\text{Fe}^{\text{III}}] \quad (2)$$

where k_{obs} shows an inverse dependence on the hydrogen-ion concentration (341):

$$k_{obs} = a + b[\text{H}^+]^{-1} \quad (3)$$

This expression suggests that there are two paths for exchange:



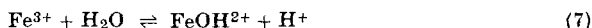
If reaction (5) is of the inner-sphere type (with symmetrical OH⁻ bridging), then it can be assumed that the Fe^{2+} – FeOH^{2+} path is relevant

¹ The perchlorate ion is a poor donor group and is the least complexing of common anions. With transition metal ions at least interactions with ClO_4^- are probably of the outer-sphere type, as in the case of Fe^{3+} (373), and it is unlikely that these play an important part in redox reactions. In more concentrated perchlorate solutions ($> 3 M$ say), inner-sphere complexes may well be formed and may be important. In 5–10 M perchloric acid, for example, there is evidence for the formation of a perchloratochromium(III) complex (224).

rather than the $\text{FeOH}^+-\text{Fe}^{3+}$ path since the acid dissociation constant for Fe^{3+} ($K_a \sim 10^{-3}$) is much greater than that for Fe^{2+} ($K_a \sim 10^{-6}$). The product of the concentration terms $[\text{Fe}^{2+}][\text{FeOH}^{2+}]$ is therefore much larger than the product $[\text{FeOH}^+][\text{Fe}^{3+}]$, and as long as the rate constants for the two paths are not widely different the $\text{Fe}^{2+}-\text{FeOH}^{2+}$ path will predominate. If anything, the rate constant for the $\text{FeOH}^+-\text{Fe}^{3+}$ path is probably smaller since the FeOH^+ ion has first to substitute into the coordination sphere of the Fe^{3+} ion, and ΔG^\ddagger is probably > 10 kcal mole $^{-1}$ for such a reaction. If, on the other hand, the reaction is of the outer-sphere type, then using the principle of balanced states (324, p. 32) it is possible that the rates $k[\text{Fe}^{2+}][\text{FeOH}^{2+}]$ and $k'[\text{FeOH}^+][\text{Fe}^{3+}]$ will be equal (i.e., $k' \gg k$). In short, although the $\text{Fe}^{2+}-\text{FeOH}^{2+}$ path is generally assumed relevant, the possibility that under certain conditions the $\text{FeOH}^+-\text{Fe}^{3+}$ path may make a significant contribution should not be overlooked. Similar reasoning applies to other reactions and to reactions studied in the presence of anions X^- . In Eq. (3) the rate constant k_{obs} may be expressed as

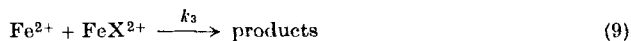
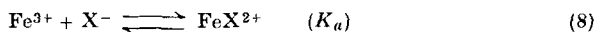
$$k_{obs} = k_1 + k_2 K_a [\text{H}^+]^{-1} \quad (6)$$

where K_a is the acid dissociation constant for Fe^{3+} :



If K_a is known, both the *true* rate constants k_1 and k_2 may be evaluated.

When the exchange is studied in the presence of anions other than ClO_4^- , there is almost invariably an increase in rate and further terms in $[\text{X}^-]$ are obtained in the rate equation. If other than small quantities of X^- are used, terms in $[\text{X}^-]^2$ and higher powers of $[\text{X}^-]$ have to be considered, and under these conditions the Fe^{II} may play some part in bringing anions into the activated complex. Reaction paths having a first-order dependence in $[\text{X}^-]$ can be interpreted in terms of FeX^{2+} participation, where the reaction sequence is believed to be:



If the equilibrium in Eq. (8) is rapid, the expression for k_{obs} is:

$$k_{obs} = \frac{k_1 + k_2 K_a [\text{H}^+]^{-1} + k_3 K_a [\text{X}^-]}{1 + K_a [\text{X}^-]} \quad (10)$$

In the fluoride-catalyzed reaction, Menashi *et al.* (261) have obtained evidence for a reaction sequence as in Eqs. (8) and (9). By using a large excess of ferrous it was possible to make the isotopic exchange rate comparable to the rate of formation of the inner-sphere complex FeF^{2+} .

Under these conditions the exchange rate was found to be dependent on the rate of formation of FeF^{2+} , as is to be expected if the reactants are Fe^{2+} and FeF^{2+} , but not if the fluoride is brought into the activated complex by the ferrous, or in the form of an ion-pair complex $\text{Fe}(\text{H}_2\text{O})_6^{3+} \cdot \text{F}^-$. This does not mean that the reaction is necessarily of the inner-sphere type, however, or that the fluoride is a bridging ligand.

TABLE I
KINETIC DATA FOR $\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}$ EXCHANGE REACTIONS
(AT 0° AND $\mu = 0.55\text{ }M$)

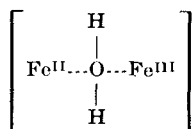
Reaction	k ($\text{l} \cdot \text{mole}^{-1} \text{sec}^{-1}$)	ΔH^\ddagger (kcal mole^{-1})	ΔS^\ddagger (eu)	Reference
$\text{Fe}^{2+} + \text{Fe}^{3+}$ ^a	0.87	9.3	-25	(341)
$\text{Fe}^{2+} + \text{FeOH}^{2+}$ ^a	1.1×10^3	6.9	-18	(341)
$\text{Fe}^{2+} + \text{FeF}^{2+}$	9.7	8.6	-21	(213)
$\text{Fe}^{2+} + \text{FeCl}^{2+}$ ^b	5.4	11.0	-15	(362)
$\text{Fe}^{2+} + \text{FeBr}^{2+}$	4.9	8.0	-25	(204)
$\text{Fe}^{2+} + \text{FeNCS}^{2+}$ ^c	4.2	9.2	-21	(205)
$\text{Fe}^{2+} + \text{FeN}_3^{2+}$	1.9×10^3	13.3	7	(68)
$\text{Fe}^{2+} + \text{FeF}_2^+$	2.5	9.0	-22	(213)
$\text{Fe}^{2+} + \text{FeCl}_2^+$	15	9.7	-20	(341)

^a Fukushima and Reynolds (144) have redetermined kinetic data for these reactions and there is essentially good agreement.

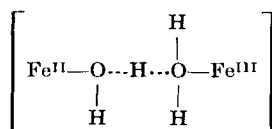
^b More than one activated complex is involved (73).

^c Previous data of Laurence (247) may be less precise (209).

Rate constants and activation parameters for a number of $\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}$ reactions are shown in Table I. Because there is so little variation in rate constants for $\text{X}^- = \text{F}^-$, Cl^- , Br^- , and NCS^- , compared to reactions of Cr^{2+} with CrX^{2+} , which are known to be inner-sphere with X^- the bridging ligand, it has been argued that some or all of the $\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}$ reactions must proceed by an alternative mechanism. One possibility is that water molecules bridge the two reactants as in either (I) or (II), and that X^- plays a relatively minor role as a nonbridging ligand. The



(I)



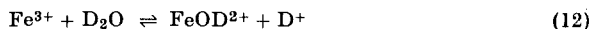
(II)

first of these, at least, now seems unlikely, since in recent work (56, 300) it has been shown that nonbridging anions can have a marked effect on rate constants. The suggestion that in (II) there is H-atom transfer between the Fe^{2+} and Fe^{3+} coordination spheres, with the formation of FeOH^{2+} and $\text{FeH}_3\text{O}^{3+}$, is unlikely on energetic grounds (higher activation energies of ~ 20 kcal mole $^{-1}$ would be expected) (181), but that there is H-atom bridging as in (II) is not unreasonable (213).

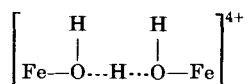
That the rate constants for the $\text{Fe}^{2+}\text{--Fe}^{3+}$ and $\text{Fe}^{2+}\text{--FeOH}^{2+}$ reactions are lowered by a factor of about 2 in D_2O (212) was thought to be evidence supporting a hydrogen-atom bridging mechanism. A similar effect has been observed for the $\text{Fe}^{2+}\text{--FeCl}^{2+}$ reaction (362). Doubts were expressed about this approach when a $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$ ratio of 1.3 was found for the $\text{Cr}^{2+}\text{--Co}(\text{NH}_3)_5\text{Cl}^{2+}$ reaction (414), which is known to proceed by an inner-sphere mechanism with chloride bridging. Since, moreover, the D_2O isotope effect on the equilibrium



is of the same order of magnitude (362), clearly this type of evidence is not conclusive. The acid dissociation constant for the reaction



also differs from that in H_2O , and activation parameters for the reaction between Fe^{2+} and FeOD^{2+} have been shown to be $\Delta H^\ddagger = 11.5 \pm 0.5$ kcal mole $^{-1}$ and $\Delta S^\ddagger = -4.0 \pm 1.8$ eu (144). Since these values differ significantly from those for the reaction between Fe^{2+} and FeOH^{2+} , it might in this one instance be argued that they provide evidence for a H-atom bridging mechanism with an activated complex:



Until more is known of D_2O and H_2O solvent effects the importance of these results is difficult to assess. Other redox reactions which have been studied in D_2O are listed in Halpern's review (181).

The use which Sutin and co-workers in particular have made of the stopped-flow method to demonstrate inner-sphere mechanisms is illustrated by their work on the $\text{Fe}^{2+}\text{--Fe}^{3+}\text{--Cl}^-$ system (73). In the first series of experiments the ferrous-catalyzed dissociation (i.e., aquation) of FeCl^{2+} was studied. The rate equation is

$$k_d = k_1 + k_2[\text{H}^+]^{-1} + k_3[\text{Fe}^{2+}] \quad (13)$$

where k_1 and k_2 correspond to substitution processes, and k_3 to an electron-transfer process which results in the dissociation of the chloride.

At 25° and ionic strength $\mu = 3.0 M$, $k_1 = 1.1 \text{ sec}^{-1}$, $k_2 = 3.4 \text{ sec}^{-1}$, and $k_3 = 12.1 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$. For k_3 the activated complex $[\text{FeClFe}]^{4+}$ cannot be effective, since it would almost certainly result in the transfer of the chloride to the newly formed ferric and there would be no dissociation. In the second series of experiments the isotopic exchange reaction

TABLE II

A COMPARISON OF DATA FOR THE $\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}$ EXCHANGE CATALYZED BY SULPHATE AT 25°

μM	k_1 ($\text{l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$)	k_2 ($\text{l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$)	Reference
0.25	693	19,400	(322)
0.50	346	—	(403)
0.75	586	20,700	(322)
1.00	295	17,500	(33)
1.00	360	—	(403)
1.00	515 ^a (760)	—	(337)
1.00	540 ^b	—	(322)

^a Recalculated by Reynolds and Lumry (324) using improved values of K_1 and K_a .

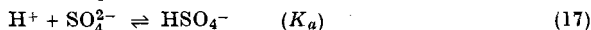
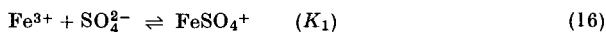
^b Extrapolated by Reynolds and Lumry (324) from data obtained by Reynolds and Fukushima (322) at various μ values.

was studied under identical conditions and in the presence of chloride, and k_4 for the chloride-dependent exchange was found to be $57.6 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$. From the difference between k_4 and k_3 it can be concluded that $\sim 65\%$ of the exchange is by the inner-sphere mechanism with an activated complex $[\text{FeClFe}]^{4+}$. The other 35% of the reaction (which corresponds to the Fe^{2+} -catalyzed dissociation of FeCl^{2+}) may be accounted for by either inner- or outer-sphere paths. Other inner-sphere activated complexes which are probably relevant are $[\text{FeH}_2\text{OFeCl}]^{4+}$ and $[\text{FeOHFeCl}]^{3+}$ (423). A similar study has been made of the Fe^{2+} -catalyzed dissociation of FeNCS^{2+} (418).

In 1963 four independent studies of the sulfate-catalyzed exchange between Fe^{II} and Fe^{III} were reported (33, 322, 337, 403). Terms in $[\text{SO}_4^{2-}]$ and $[\text{SO}_4^{2-}]^2$ were identified and these are believed to correspond to the reaction paths:



That k_1 values show considerable variation (Table II) would seem to be in some part due to the different values of the association constants for the reactions

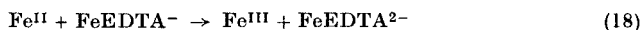


which were used, and those used by Sheppard and Brown (337) would seem to be particularly suspect. Because Willix (403) neglects contributions to the exchange from the $[\text{SO}_4^{2-}]^2$ path, his activation parameters for k_1 ($\Delta H^\ddagger = 9.0$ kcal mole⁻¹ and $\Delta S^\ddagger = -19$ eu) are probably less reliable than these of Bächmann and Leiser (33) ($\Delta H^\ddagger = 13.8$ kcal mole⁻¹ and $\Delta S^\ddagger = -1.2$ eu). Reynolds and Fukushima (322) have identified a further term in the rate equation which is dependent on $[\text{SO}_4^{2-}]$ and the inverse hydrogen-ion concentration. They suggest that the reaction is between FeSO_4 and FeOH^{2+} , but the reaction of Fe^{2+} with $\text{Fe}(\text{OH})\text{SO}_4$ is also a possibility.

The exchange in the presence of azide is of particular interest, and at present quite unique in that the Arrhenius plot is curved at temperatures greater than 13° (68). Below 13° the rate-determining step may be the substitution process leading to the formation of an inner-sphere complex $[\text{Fe}-\text{N}=\text{N}=\text{N}-\text{Fe}]^{4+}$ from Fe^{2+} and FeN_3^{2+} , while above this temperature the rate of decomposition of the complex and electron exchange may be comparable. Halpern and Orgel (188) and Wilkins and Eigen (401) have considered the possibility that in some reactions the formation of a bridged intermediate (rather than electron transfer within the intermediate) may be rate-determining.

Oxalate ions have a strong catalytic effect, the rate constant for the $\text{Fe}^{2+}-\text{FeC}_2\text{O}_4^+$ exchange being of the order of 2×10^3 l·mole⁻¹ sec⁻¹ at 20°, but again there is a lack of agreement between two sets of activation parameters (206, 337). With tartrate ions the reaction between Fe^{2+} and $\text{Fe}(\text{HTar})_2^+$, and not Fe^{2+} and $\text{Fe}(\text{HTar})^{2+}$, has been shown to predominate (258). Phosphate (337), acetate, succinate, and phenolate ions and silver foil also catalyze the exchange (206), but benzoic and *o*-phthalic acids have little effect probably because they are only weakly ionized (206). Fumaric acid has no catalytic effect when present in concentrations equivalent to those of the Fe^{II} and Fe^{III} (258).

The exchange between FeEDTA^{2-} and FeEDTA^- is fast (6), and an outer-sphere mechanism seems likely, although partial dissociation of the complexes cannot be excluded since both ions are spin-free. In the exchange of Fe^{2+} with FeEDTA^- a carboxyl group of the EDTA may act as a bridging group, although it is not transferred to the newly formed ferric ion:



The slow rate $k \leq 4.0 \times 10^{-4} \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ reflects the unfavorable free energy change of 15 kcal mole^{-1} for this reaction (323).

The hexacyano, tris(1,10-phenanthroline), and tris(bipyridyl) complexes of iron(II) and iron(III) are all spin-paired, and as a result are inert to substitution. Since electron transfer between such reactants is generally rapid, and the coordination spheres remain intact, it can be concluded that reactions are of the outer-sphere type. That the reactions are rapid is probably related to the fairly extensive delocalization of electrons from the central metal atom. The kinetics of the isotopic-exchange reaction between ferrocyanide and ferricyanide ions have been studied in potassium hydroxide and tetraphenylarsonium hydroxide ($\phi_4\text{AsOH}$) solutions (234). In the latter the reaction is first order in $\text{Fe}(\text{CN})_6^{3-}$, but the dependence of the rate on the concentration of $\text{Fe}(\text{CN})_6^{4-}$ is affected by the nature and concentrations of cations present. In the presence of $2.5 \times 10^{-4} M$ EDTA (to complex cationic impurities) and with $0.01 M$ $\phi_4\text{AsOH}$, the expression

$$\text{Rate} = k[\text{Fe}(\text{CN})_6^{4-}][\text{Fe}(\text{CN})_6^{3-}] \quad (19)$$

is obeyed and $k = 28 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ at 0.1° . The rate has been shown to increase with the first power of $[\phi_4\text{As}^+]$,

$$\text{Rate} = k'[\text{Fe}(\text{CN})_6^{4-}][\text{Fe}(\text{CN})_6^{3-}][\phi_4\text{As}^+] \quad (20)$$

k' having a value of $2800 \text{ l}^2 \cdot \text{mole}^{-2} \text{ sec}^{-1}$ at 0.1° . In $0.01 M$ KOH rates are much faster than in $0.01 M$ $\phi_4\text{AsOH}$, and, at 0.1° , k as defined in Eq. 19 is $3561 \cdot \text{mole}^{-1} \text{ sec}^{-1}$. On varying the concentration of potassium ions, the rate equation has been shown to be of the form:

$$\text{Rate} = [\text{Fe}(\text{CN})_6^{3-}][\text{Fe}(\text{CN})_6^{4-}] \frac{k_1 K_1 [\text{K}^+] + k_2 K_1 K_2 [\text{K}^+]^2}{1 + K_1 [\text{K}^+] + K_1 K_2 [\text{K}^+]^2} \quad (21)$$

The terms in $[\text{K}^+]$ and $[\text{K}^+]^2$ correspond to reactions of $\text{KFe}(\text{CN})_6^{3-}$ and, in all probability, $\text{K}_2\text{Fe}(\text{CN})_6^{2-}$. Further details of these various studies have now been published (417). The rate of exchange has also been determined by measuring the nitrogen-14 NMR line width (339). With the addition of cations the rate increases in going from H^+ to Cs^+ and from Mg^{2+} to Sr^{2+} (339).

Isotopic exchange and NMR line-broadening techniques have also been used to determine the lower limit of the rate constant for the exchange between $\text{Fe}(\text{phen})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{3+}$ ($k > 1 \times 10^5 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ at 0°) (105), and a similar high value is expected for the reaction between $\text{Fe}(\text{bipy})_3^{2+}$ and $\text{Fe}(\text{bipy})_3^{3+}$. With four complexes having methyl substituted 1,10-phenanthroline ligands the rate constants are all $> 10^5$

$1 \cdot \text{mole}^{-1} \text{sec}^{-1}$ at 25° (246), and there is no suggestion of steric hindrance by the methyl groups.

The $\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}$ exchange has been studied in a number of non-aqueous solvents. In nitromethane (250) and anhydrous alcohols (207, 358) exchange is extremely slow, which suggests that water may play a specific role in the reaction. Horne (207) has also studied the exchange in mixed water-acetone, water-methanol, and water-ethanol media, and finds the activation energy for exchange to be the same as in aqueous solutions. The decrease in rate with the decrease in concentration of water is consistent with the H-atom bridging mechanism. In dioxane and allyl alcohol the iron(II) component is rapidly oxidized by the solvent (207).

In dimethyl sulfoxide (DMSO), Menashi *et al.* (262) report a fairly rapid rate of exchange. In the absence of added water the reaction is independent of the hydrogen-ion concentration, and only when the mole fraction of water is greater than 0.05 is there a decrease in rate constants with the addition of increasing amounts of acid. This suggests that, in the absence of water, exchange is between iron(II) and iron(III) species containing only DMSO in their coordination spheres. Hydrogen-atom bridging is hardly a possibility, since it would involve hydrogen atoms of the methyl groups, and the mechanism is probably outer-sphere or inner-sphere with a sulfur-oxygen bridge between the two metal ions (262). It is surprising (and possibly a coincidence) that the activation parameters for the reaction in DMSO are approximately equal to those in water. Chloride ions catalyze the exchange (391) and, since there is evidence for inner-sphere complexing of the chloride to the ferric, the most likely paths for exchange are of $\text{Fe}(\text{DMSO})_6^{2+}$ with $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ and $\text{Fe}(\text{DMSO})_4\text{Cl}_2^+$, respectively. In the first of these the rate is the same as in water (suggesting a similar mechanism), but with $\text{Fe}(\text{DMSO})_4\text{Cl}_2^+$ the rate is approximately 3.5 times faster in DMSO.

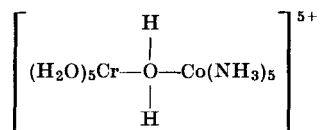
An exchange which proceeds rapidly in nonaqueous solvent is that between $\text{Fe}(\text{C}_5\text{H}_5)_2$ and $\text{Fe}(\text{C}_5\text{H}_5)_2^+$. In acetone the rate constant is $> 1 \times 10^5 \text{ l} \cdot \text{mole}^{-1} \text{sec}^{-1}$ at 26° (105), while in methyl alcohol k is $> 7 \times 10^6$ at 25° and 9×10^5 at -75° (347).

Recent work on the $\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}$ exchange in a solid ice matrix (205, 208) is more difficult to explain in terms of compact inner- or outer-sphere mechanisms, since the Fe^{2+} and Fe^{3+} ions are rigidly held in the lattice. Exchange occurs even when the reactants are on an average 100 Å apart, and H-atom transfer by a Grotthus mechanism would seem to be a possible explanation. Because the Arrhenius plot is a continuation of that observed in the liquid phase, it can be argued that a similar mechanism must be effective in the liquid phase. The same behavior is

observed in 7.5 *N* perchloric acid over the temperature range 0° to -84° (47) and, since the latter is a perchloric acid/water eutectic mixture, a phase separation seems unlikely. Chloride ions have no effect on the rate of exchange in ice (208). In a further study (424) some difficulty was experienced in obtaining reproducible results.

Information regarding the closeness of approach of the reactants in the exchange between chromium(II) and chromium(III) species is generally easier to obtain, because the chromium(III), but not the chromium(II), is inert to substitution. For the exchange in aqueous perchloric acid solutions there is an inverse hydrogen-ion dependence (22), which is consistent with a reaction of Cr^{2+} with CrOH^{2+} . The hydrogen ion-independent path makes little or no contribution ($k \leq 2 \times 10^{-5} \text{ l. mole}^{-1} \text{ sec}^{-1}$ at 25°). Although it has yet to be demonstrated that the hydroxide ion is transferred to the newly formed chromium(III), there seems little doubt that this is so, as in the reaction of Cr^{2+} with $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$ (244).

It is not easy to explain why the reaction of the two hexaquo ions should not be more effective, as it is in the exchange of iron(II) with iron(III) (341), cobalt(II) with cobalt(III) (171), and vanadium(II) with vanadium(III) (242). Reactions between two hexaquo ions are often assumed to be of the outer-sphere type, in which case it may simply be a reluctance of the Cr^{2+} and Cr^{3+} to react by an outer-sphere mechanism. In the reaction of Cr^{2+} with $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$, the water molecule is known to bridge the two metal ions in the intermediate (244),



and there seems at first no obvious reason for excluding the inner-sphere path in the case of the Cr^{2+} - Cr^{3+} reaction. Once an intermediate of the above type has formed, it might be expected to lose a proton fairly rapidly, to give a hydroxo-bridged intermediate which is more stable. If this is the case a possible explanation for the absence of a significant Cr^{2+} - Cr^{3+} path is that the binuclear intermediate (with a water molecule as a bridging group) might tend (a) to revert to mononuclear ions or (b) to lose a proton before electron transfer can occur. The former would seem to be a particularly strong possibility with Cr^{2+} since this ion is so very labile (103, 263). In the reaction of Cr^{2+} with $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$, electron transfer may be more rapid once a binuclear intermediate has formed (with H_2O or OH^- as a bridging group) due to the more favorable overall free energy change.

In the exchange between Cr^{2+} and CrX^{2+} species (Table III), transfer of the X^- to the newly formed chromium(III) has been demonstrated:



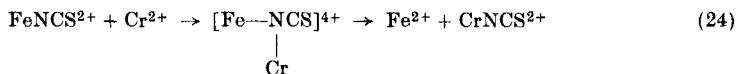
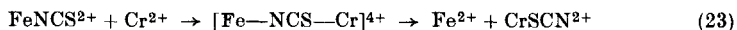
Since the net effect of exchange is the transfer of an X atom, these reactions are sometimes referred to as atom-transfer reactions. This term is perhaps best avoided, however, because the function of the bridging

TABLE III
KINETIC DATA FOR $\text{Cr}^{\text{II}}\text{-Cr}^{\text{III}}$ EXCHANGE REACTIONS

Reaction	Temp. (°C)	k ($\text{l} \cdot \text{mole}^{-1} \text{sec}^{-1}$)	ΔH^\ddagger (kcal mole^{-1})	ΔS^\ddagger (eu)	Ref.
$\text{Cr}^{2+} + \text{Cr}^{3+}$	25	$\leq 2 \times 10^{-5}$	—	—	(22)
$\text{Cr}^{2+} + \text{CrOH}^{2+}$	25	0.7	12.8	-16.4	(22)
$\text{Cr}^{2+} + \text{CrF}^{2+}$	0	2.4×10^{-3}	13.7	-20	(40)
$\text{Cr}^{2+} + \text{cis-CrF}_2^+$	0	1.2×10^{-3}	13.0	-24	(86)
$\text{Cr}^{2+} + \text{CrCl}^{2+}$	0	9	—	—	(40, 343)
$\text{Cr}^{2+} + \text{trans-CrCl}_2^+$	2	$\sim 1.7 \times 10^2$	—	—	(233)
$\text{Cr}^{2+} + \text{CrBr}^{2+}$	0	> 60	—	—	(40)
$\text{Cr}^{2+} + \text{CrNCS}^{2+}$	25	1.4×10^{-4}	—	—	(40)
$\text{Cr}^{2+} + \text{CrN}_3^{2+}$	0	1.23	9.6	-22.8	(343)
$\text{Cr}^{2+} + \text{CrSCN}^{2+}$	25	42	—	—	(176)
$\text{Cr}^{2+} + \text{cis-(CrN}_3)_2^+$	0	60	—	—	(342)

group is uncertain. Possibilities which have been considered by Halpern and Orgel (188) are that the bridging group (a) helps to bring the metal ions closer together so that a direct exchange between overlapping metal orbitals can occur (*direct exchange*), (b) provides vacant orbitals which serve to delocalize electrons on the metal ions and hence help in their migration (*superexchange*), (c) assists in electron transfer by accepting an electron from the reductant and at the same time losing an electron to the oxidant (*double exchange*), and (d) assists electron transfer by being temporarily oxidized or reduced (*chemical mechanism for exchange*). Transfer of the bridging group need not necessarily accompany electron transfer, however, and in one case at least it has been reported that the bridging group remains attached to the same metal ion throughout. The case in point is in the reaction of Cr^{2+} with IrCl_6^{3-} (272). An intermediate IrCl_6^{2-} is believed to be formed but Cr^{3+} and IrCl_6^{3-} are the final products.

Details of the chromium(II) attack on complexes CrNCS^{2+} , CrSCN^{2+} , and CrN_3^{3+} , whether adjacent or remote from the chromium(III) atom, are of considerable interest. In a very thorough study of the Cr^{2+} - Fe^{3+} - SCN^- system, using stopped-flow techniques, Haim and Sutin (176) have obtained information regarding the nature of these reactions. On mixing a solution of Fe^{III} and SCN^- with one containing excess Cr^{2+} , three distinct changes in absorbance are observed. These suggest that the Cr^{2+} attacks both the remote and adjacent positions of the thiocyanate, which is assumed to be nitrogen-bonded to the ferric. The first stage, which is believed to be due to the reaction of Cr^{2+} with FeNCS^{2+} , is too rapid to be followed ($k \geq 2 \times 10^7 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$). The second, of which only the tail is observed, is associated with the Cr^{2+} - Fe^{3+} , Cr^{2+} - FeOH^{2+} , and Fe^{3+} - Cr^{2+} - SCN^- reactions, and the third corresponds to the chromium(II)-catalyzed isomerization of the complex CrSCN^{2+} which is formed in the first stage. The rates of the Cr^{2+} - Fe^{3+} and Cr^{2+} - FeOH^{2+} reactions are known, and that for the Fe^{3+} - Cr^{2+} - SCN^- reaction, which does not involve FeNCS^{2+} as a reactant, can be obtained by mixing a solution containing Cr^{2+} and SCN^- with a solution of Fe^{3+} . These studies show that approximately 35% of the product from the Cr^{2+} - FeNCS^{2+} reaction is in the form CrSCN^{2+} , and that there is both remote and adjacent attack by the Cr^{2+} :



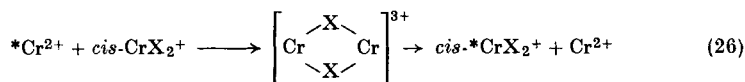
From the third stage of this study it was possible to determine the rate constant for the reaction of Cr^{2+} with CrSCN^{2+} ($k = 42 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$). If it is assumed that the exchange of chromium between Cr^{2+} and CrNCS^{2+} is slow ($k = 1.4 \times 10^{-4} \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$), because the less stable sulfur-bonded isomer is first formed, then the equilibrium constant for the reaction



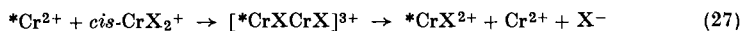
is simply the ratio of the rate constants for the Cr^{2+} - CrNCS^{2+} and Cr^{2+} - CrSCN^{2+} reactions (i.e., 3×10^5 at 25° and $\mu = 1.0 M$). Using this approach the nitrogen-bonded isomer is about $7.5 \text{ kcal mole}^{-1}$ more stable than the sulfur-bonded isomer. It is not surprising therefore that the reaction of Cr^{2+} with CrSCN^{2+} is faster than the reaction of CrN_3^{3+} (there is a favorable free energy change in the former), or that the reaction of Cr^{2+} with CrNCS^{2+} is slower (the free energy change is unfavorable). What is perhaps surprising is that there should be both remote and adjacent attack in the Cr^{2+} - FeNCS^{2+} reaction, but only remote attack

in the $\text{Cr}^{2+}\text{-CrNCS}^{2+}$ reaction. This point has been considered by Haim and Sutin (177). It can also be argued that remote attack of chromium(II) on CrN_3^{2+} is about 10^3 times more favorable than adjacent attack.

Reactions between chromium(II) and (*cis*)- CrX_2^+ complexes can proceed by two mechanisms, one of which leads to exchange via a double-bridged activated complex:



The other leads to a dissociation of one of the X^- ligands via a single-bridged activated complex:



The double-bridged activated complex is formed in the reaction of Cr^{2+} with *cis*- $\text{Cr}(\text{N}_3)_2^+$ (342), the rate being about 45 times faster than in the corresponding reaction with CrN_3^{2+} . In contrast, *cis*- CrF_2^+ reacts by the single-bridged activated complex (86), and *cis*- CrF_2^+ and CrF^{2+} react at about the same rate. More recently Haim (174) has shown that the reactions of Cr^{2+} with *cis*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$ and *cis*- $\text{Co}(\text{en})_2(\text{N}_3)_2^+$ proceed concurrently by both single- and double-bridged paths (the ratios of single- to double-bridged paths are 1.6:1 and 5:1, respectively), and that there is a small contribution from a single-bridged path in the reaction of *cis*- $\text{Cr}(\text{N}_3)_2^+$ with Cr^{2+} . Johnson and Reynolds (223) report that Cr^{2+} reacts with *cis*- CrCl_2^+ at about the same rate as *trans*- CrCl_2^+ , and this has now been confirmed (420). The single-bridged activated complex appears to be formed in both instances.

The rate equation for the reaction of Cr^{2+} with CrCl^{2+} , which results in a net dissociation of the chloride from the chromium(III), is of the form:

$$\text{Rate} = k[\text{CrCl}^{2+}][\text{Cr}^{2+}][\text{H}^+]^{-1} \quad (28)$$

The latter is consistent with the formation of an activated complex $[\text{CrOHCrCl}]^{3+}$ (11). The reaction is most likely between Cr^{2+} and $\text{Cr}(\text{Cl})\text{OH}^+$, in which case the true rate constant is $20 \pm 2.5 \cdot \text{mole}^{-1} \text{sec}^{-1}$ at 20° . The ratio of the rate constants for the reaction of Cr^{2+} with *trans*- CrCl_2^+ and $\text{Cr}(\text{Cl})\text{OH}^+$ is about the same as for the reactions of Cr^{2+} with CrCl^{2+} and CrOH^{2+} . For the series of reactions with different CrX^{2+} complexes, where X^- is a halide ion, the relative efficiency of X^- as a nonbridging ligand is $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$ (12, 300). This order is the reverse of the order of thermodynamic stability of the CrX^{2+} complexes, CrF^{2+} being more stable than Cr^{3+} . Orgel (292) and Taube (376, 377) have considered the effect which nonbridging ligands can have on

the rates of redox reactions. Electron transfer to the vacant d_{z^2} orbital on the chromium(III) will take place more readily the lower the energy of the d_{z^2} orbital. For the *trans*-Cr(X)OH⁺ complexes the energy of the d_{z^2} orbital is lowered (a) by X⁻ having a weak ligand field (292), and (b) by movement of the ligands in the d_{z^2} direction away from the metal atom (376, 377). The order of decreasing ligand-field strength is

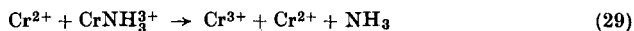
TABLE IV

DATA FOR THE CHROMIUM(II)-INDUCED DISSOCIATION OF Cr(NH₃)₅X²⁺ COMPLEXES (AT 25° AND $\mu = 1.0 M$) (291)

Reaction	k (l·mole ⁻¹ sec ⁻¹)	ΔH^\ddagger (kcal mole)	ΔS^\ddagger (eu)
Cr ²⁺ + Cr(NH ₃) ₅ F ²⁺	2.7×10^{-4}	13.4	-30
Cr ²⁺ + Cr(NH ₃) ₅ Cl ²⁺	5.1×10^{-2}	11.1	-23
Cr ²⁺ + Cr(NH ₃) ₅ Br ²⁺	0.32	8.5	-33
Cr ²⁺ + Cr(NH ₃) ₅ I ²⁺	5.5	—	—

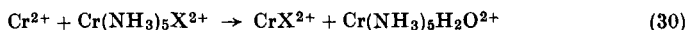
F⁻ > Cl⁻ > Br⁻ > I⁻, so that on this basis the order of reactivity should be I⁻ > Br⁻ > Cl⁻ > F⁻, which is as observed. The ease with which the Cr—X bond is stretched is probably related to the ease with which the X⁻ ligand in CrX²⁺ complexes is replaced by a water molecule (56), in which case the order of effectiveness should again be I⁻ > Br⁻ > Cl⁻ > F⁻. The halide ions are probably much less effective in the *cis*-Cr(X)OH⁺ complexes, although a significant contribution from this path cannot be excluded. The relative effectiveness of the nonbridging halide ions in these reactions (I⁻ is $\sim 10^4$ times more effective than F⁻) is of the same order of magnitude as is observed for similar series of reactions in which the halide ion is the bridging ligand (see Tables III and IV).

In the reaction of Cr²⁺ with Cr(H₂O)₆NH₃³⁺ (130),

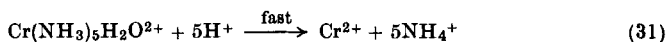


there is no evidence for bridging by the ammonia ligand, and the dominant path is again the inverse hydrogen ion-dependent path.

The apparent lability of Cr(NH₃)₅X²⁺ complexes in the presence of Cr²⁺ (291) can be accounted for by the reaction



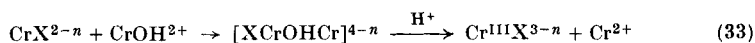
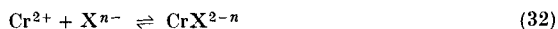
in which an electron and the X⁻ ligand are transferred to the newly formed chromium(III). This is followed by the rapid aquation of the labile chromium(II) complex:



Rate constants increase, $F^- < Cl^- < Br^- < I^-$ (Table IV), as the ligand field of the bridging group decreases, and as the polarizability of the bridging group increases.

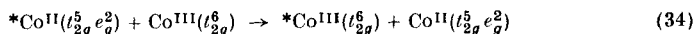
A similar Cr^{2+} -induced solution of anhydrous $CrCl_3$ has been observed (272). The solid is insoluble in aqueous solution but quickly dissolves (within a few minutes) when Cr^{2+} is added. Electron transfer between $CrCl_3$ and the Cr^{2+} results in the formation of $CrCl^{2+}$ in solution.

Exchange between Cr^{II} and Cr^{III} can also be accelerated by the addition of anions which are not initially complexed to the chromium(III) (215). The order of effectiveness is $EDTA > \text{pyrophosphate} > \text{citrate} \sim PO_4^{3-} > F^- > \text{tartrate} > SCN^- > SO_4^{2-}$, and since the chromium(III) ion is inert, the most likely mechanism is



the chromium(II) bringing the anion into the activated complex. The inverse hydrogen-ion dependence assumed for Eq. (33) has yet to be confirmed, and some of the reactions (with EDTA, for example) may be of the outer-sphere type, when Eq. (33) will not be applicable.

Exchange reactions between high-spin cobalt(II) and low-spin cobalt(III) are expected to be slow because of spin restrictions. The exchange may be represented by the equation,

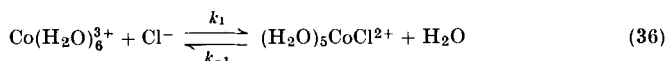


from which it can be seen that changes in electronic configuration of the two ions must take place in addition to electron transfer between the two ions. While many of the reactions are in fact slow (Table V), there are a number of exceptions. In particular, the rate constant for the Co^{2+} - Co^{3+} exchange (171) is only half that for the Fe^{2+} + Fe^{3+} exchange at 25°. The most likely explanation is that a small fraction of the Co^{3+} is present in the high-spin state:



This is not unreasonable since H_2O does not have a particularly strong ligand field, and CoF_6^{3-} is known to be a high-spin complex. Magnetic susceptibility measurements do not exclude this possibility, but accurate measurements are difficult since Co^{3+} slowly oxidizes water, and solutions are never completely free from Co^{2+} . Providing the interconversion is rapid and non-rate-determining, the above explanation is in no way contrary to the second-order kinetics which are observed.

The kinetics of the formation and dissociation of monochloro-cobalt(III)



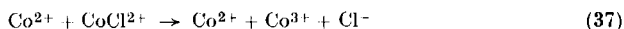
have been studied ($k_1 < 2 \cdot \text{l} \cdot \text{mole}^{-1} \text{sec}^{-1}$ and $k_{-1} < 0.05 \text{ sec}^{-1}$ at 25° and $\mu = 3.0 \text{ M}$) (95). From these values it can be concluded that $\text{Co}(\text{H}_2\text{O})_6^{3+}$

TABLE V
KINETIC DATA FOR $\text{Co}^{\text{II}}\text{--Co}^{\text{III}}$ EXCHANGE REACTIONS

Reaction	Temp. ($^\circ\text{C}$)	k ($\text{l} \cdot \text{mole}^{-1} \text{sec}^{-1}$)	ΔH^\ddagger (kcal mole $^{-1}$)	ΔS^\ddagger (eu)	Ref.
$\text{Co}^{2+} + \text{Co}^{3+}$ ($\mu = 0.5 \text{ M}$)	18.4	1.2	10.4	-22	(171)
$\text{Co}^{2+} + \text{CoOH}^{2+}$ ($\mu = 0.5 \text{ M}$)	18.4	6.6×10^3 ^a	—	—	(171)
$\text{Co}(\text{phen})_3^{2+} + \text{Co}(\text{phen})_3^{3+}$	0	1.1	16.5	+4	(35)
$\text{Co}(\text{NH}_3)_n^{2+} + \text{Co}(\text{NH}_3)_6^{3+}$	64.5	$< 10^{-9}$	—	—	(347)
$\text{Co}(\text{NH}_3)_n^{2+} + \text{Co}(\text{NH}_3)_6^{3+}, \text{OH}^-$	64.5	56.7×10^{-4}	12.6	-35	(59)
$\text{Co}(\text{NH}_3)_n^{2+} + \text{Co}(\text{NH}_3)_6^{3+}, \text{Cl}^-$	64.5	7.3×10^{-4}	—	—	(59)
$\text{Co}(\text{en})_n^{2+} + \text{Co}(\text{en})_3^{3+}$	50	1.4×10^{-4}	13.2	-31	(348)
$\text{Co}(\text{EDTA})^{2-} + \text{Co}(\text{EDTA})^-$	100	1.4×10^{-4}	20	-21	(6, 219)
$\text{Co}(\text{H--EDTA})^- + \text{Co}(\text{EDTA})^-$	100	8.0×10^{-4}	24.0	-9	(6, 219)
$\text{Co}(\text{PDTA})^{2-} + \text{Co}(\text{PDTA})^-$	100	2×10^{-4}	—	—	(118)
$\text{Co}(\text{H--PDTA})^- + \text{Co}(\text{PDTA})^-$	100	7×10^{-4}	—	—	(118)

^a Other k values can be obtained using more recent values for the acid dissociation constant for Co^{3+} (K_a). These are $k = 35 \text{ l} \cdot \text{mole}^{-1} \text{sec}^{-1}$, using $K_a = 1.8 \times 10^{-2} \text{ mole liter}^{-1}$ (357), and $k = 2.9 \text{ l} \cdot \text{mole}^{-1} \text{sec}^{-1}$, using $K_a = 0.22 \text{ mole liter}^{-1}$ (95).

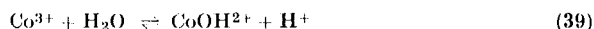
undergoes water exchange only relatively slowly, and that the stable state of $\text{Co}(\text{H}_2\text{O})_6^{3+}$ is therefore the low-spin form. It has also been shown (95) that the rate constant for the cobalt(II)-catalyzed dissociation of CoCl^{2+}



is $1.0 \text{ l} \cdot \text{mole}^{-1} \text{sec}^{-1}$ at 25° and $\mu = 2.0 \text{ M}$. In this reaction the chloride is a nonbridging ligand. Habib and Hunt (171) have found that, for the $\text{Co}^{\text{II}}\text{--Co}^{\text{III}}$ exchange in perchlorate solutions ($\mu = 0.5 \text{ M}$),

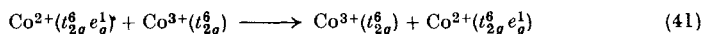
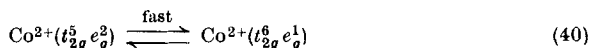
$$k_{obs} = k_1 + k_2 K_d [\text{H}^+]^{-1} \quad (38)$$

and, at 25° , $k_1 = 1.97 \text{ l} \cdot \text{mole}^{-1} \text{sec}^{-1}$ and $k_2 K_d = 1.517 \text{ sec}^{-1}$. A variety of K_d values have been obtained for the acid dissociation:



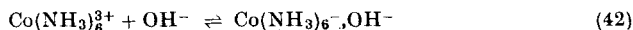
The most recent is 0.22 mole liter⁻¹ (95), but other values ranging from 1.8×10^{-2} to 1.0×10^{-4} (357) have been reported. The latter has been used by Habib and Hunt (171) to evaluate k_2 (Eq. 38). Fluoride and sulfate ions produce a marked catalysis of the Co^{II}-Co^{III} exchange (171).

The relatively high values of the rate constant for the Co(phen)₃²⁺-Co(phen)₃³⁺ exchange can be accounted for if a small fraction of the Co(phen)₃²⁺ is present in the ($t_{2g}^6 e_g^1$) spin-paired form (35):

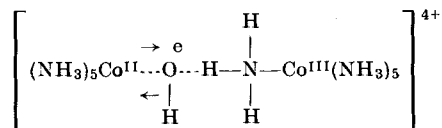


The large difference in the observed rate constant for this and the Fe(phen)₃²⁺-Fe(phen)₃³⁺ exchange (105) ($k > 1 \times 10^5$ l·mole⁻¹ sec⁻¹ at 25°) suggests that the equilibrium concentration of Co²⁺($t_{2g}^6 e_g^1$) is small. The rate law and rate constants depend upon the anions present, and results have been discussed in terms of ion associations (35).

Reactions between Co^{II} and Co^{III} complexes in which the ligands are of intermediate ligand-field strength (i.e., between those of 1,10-phenanthroline and water) are invariably slow (Table V). The direct exchange between Co(NH₃)_n²⁺ and Co(NH₃)₆³⁺, for example, where n has values ranging from 3 to 6, is extremely slow (59). The difference in the Co—N bond lengths in the cobalt(II) and cobalt(III) hexammines has been shown to be 0.15 Å (45), and not ~ 0.6 Å as was formerly supposed. Since the difference is no greater than the Fe—O bond distances in the hexaquo Fe²⁺ and Fe³⁺ ions, this factor can no longer be of first importance in explaining the slow rate of exchange between Co(NH₃)₃²⁺ and Co(NH₃)₆³⁺. The most favorable path for exchange appears to be one involving ion-pair complexes, for example Co(NH₃)₆³⁺, OH⁻ (59). Since K for the formation of such ion-pairs



is known (84), rate constants for the exchange between Co(NH₃)_n²⁺ and Co(NH₃)₆³⁺, OH⁻ can be obtained. The activated complex is believed to be of the type



an electron and the hydroxide ion being transferred as indicated. Evidence for such a path is as follows. First, the initial distribution of labile cobalt(II) complexes Co(NH₃)₆²⁺, Co(NH₃)₅H₂O²⁺, Co(NH₃)₄

(H_2O) $_2^{2+}$, etc. (60), is different from that of the cobalt(III) ammines produced. The difference suggests that conversion of Co^{II} to Co^{III} is accompanied by substitution into the inner sphere of the newly formed cobalt(III) complex. Second, the exchange shows an inverse hydrogen-ion dependence, which is in accordance with hydroxide ion participation. In the presence of chloride ions (concentration up to 0.75 *M*), ion pairs $\text{Co}(\text{NH}_3)_6^{3+} \cdot \text{Cl}^-$ are similarly effective. A consistent interpretation is possible if it is assumed that $\text{Co}(\text{NH}_3)_n^{2+}$ complexes from $n = 3-6$ react at the same rate (59).

TABLE VI

A COMPARISON OF DATA FOR $\text{M}^{\text{II}}-\text{M}^{\text{III}}$ EXCHANGE REACTIONS AT 25°

Reaction	k_1 ($\text{l} \cdot \text{mole}^{-1} \text{sec}^{-1}$)	k_2 ($\text{l} \cdot \text{mole}^{-1} \text{sec}^{-1}$)	Reference
$\text{Fe}^{\text{II}} + \text{Fe}^{\text{III}}$	4.0	3×10^3	(144)
$\text{Cr}^{\text{II}} + \text{Cr}^{\text{III}}$	$\leq 2 \times 10^{-5}$	0.7	(22)
$\text{Co}^{\text{II}} + \text{Co}^{\text{III}}$	1.97 ^a	6.3×10^3 ^{a,b}	(171)
$\text{V}^{\text{II}} + \text{V}^{\text{III}}$	0.01	~ 1.8	(242)

^a Temperature 18.4°.

^b Other possible values are 35 and $2.9 \text{ l} \cdot \text{mole}^{-1} \text{sec}^{-1}$ (see footnote to Table V).

Exchange between the tetrahedral 12-tungstocobaltate(II), $\text{Co}^{\text{II}}\text{O}_4\text{W}_{12}\text{O}_{36}^{6-}$, and 12-tungstocobaltate(III), $\text{Co}^{\text{III}}\text{O}_4\text{W}_{12}\text{O}_{36}^{5-}$ ions, has been studied in aqueous solutions (320). At 0° and $\mu = 0.6 \text{ M}$ the rate constant is $0.63 \text{ l} \cdot \text{mole}^{-1} \text{sec}^{-1}$. The mechanism is almost certainly of the outer-sphere type.

Exchange between the vanadium(II) and vanadium(III) aquo ions is first order in both reactants (242), the hydrogen-ion dependence being of the form:

$$k_{\text{obs}} = k_1 + k_2 K_d [\text{H}^+]^{-1} \quad (43)$$

Rate constants k_1 and k_2 have been determined and are shown in Table VI alongside data for other $\text{M}^{\text{II}}-\text{M}^{\text{III}}$ reactions. The wide range of rate constants observed for these reactions, all of which have zero free energy change, is surprising. For reactions which proceed by an inner-sphere mechanism there are three possible rate-controlling factors:

- The rate of formation of the activated complex.
- The rate of electron transfer within the activated complex.
- The rate of breakdown of the activated complex.

The slowness of the V^{2+} - V^{3+} exchange *may* be due to the slow rate of formation of the activated complex, since it is known that substitution of water molecules in the V^{2+} and V^{3+} coordination spheres is relatively

TABLE VII
CHARACTERISTIC RATE CONSTANTS FOR THE REPLACEMENT OF A
WATER MOLECULE IN THE INNER-COORDINATION SPHERE OF
METAL IONS^a

Metal ions ^b	<i>k</i> (sec ⁻¹)	Electronic configuration	References
Ti ³⁺ <i>c</i>	~ 10 ⁴	<i>d</i> ¹	(103)
VO ²⁺ <i>d, e</i>	5 × 10 ²	<i>d</i> ¹	(408)
V ³⁺ <i>c</i>	10 ² -10 ³	<i>d</i> ²	(52, 103, 243)
V ²⁺ <i>c</i>	10 ¹ -10 ²	<i>d</i> ³	(103, 243)
Cr ³⁺	3 × 10 ⁻⁶	<i>d</i> ³	(216)
Cr ²⁺ <i>d, f</i>	10 ⁸ -10 ⁹	<i>d</i> ⁴	(103, 263)
Mn ³⁺ <i>g</i>	> 10 ⁴	<i>d</i> ⁴	(103)
Mn ²⁺ <i>d</i>	3 × 10 ⁷	<i>d</i> ⁵	(364)
Fe ³⁺ <i>d</i>	3 × 10 ³	<i>d</i> ⁵	(91)
Fe ²⁺ <i>d</i>	3 × 10 ⁶	<i>d</i> ⁶	(364)
Co ³⁺	≤ 10 ³	<i>d</i> ⁶	(90, 95)
Co ²⁺ <i>d</i>	10 ⁶	<i>d</i> ⁷	(364)

^a For inner-sphere reactions the rate of formation of the activated complex (a substitution process) may be rate-determining. Alternatively, an electron-transfer process may be too rapid for an inner-sphere mechanism to be possible.

^b In the case of Cu²⁺, Hg²⁺, and Ti³⁺, rate constants are probably ~ 10⁹ sec⁻¹ [see, for example, Sutin (361) and references therein].

^c The incoming ligand is SCN⁻. The rate constant refers to the formation of an inner-sphere complex from an outer-sphere complex. The rate constant should be about the same (to within a power of ten) as for water exchange.

^d Determined by the NMR method. The rate constant refers to the replacement of a particular water molecule, i.e., 1/*k* is equal to the lifetime of a given water molecule in the inner-coordination sphere of the metal ion.

^e Assuming that four water molecules take part in the exchange (409).

^f With bipyridine as the incoming ligand (103).

^g With fluoride (either F⁻ or HF) as the incoming ligand.

slow (Table VII). Because of this an outer-sphere mechanism may in this case be the more favorable path. For both inner-sphere and outer-sphere reactions, the ease of electron transfer is determined by the electronic configuration of the reactants (i.e., whether *t*_{2g} or *e*_g electrons are involved) and the energy required to reorganize solvation spheres. For

outer-sphere reactions, it can be reasoned that the lowest energy path is the one in which solvation spheres adjust their size to an intermediate value, before electron transfer occurs (181).

The rate equation for the exchange between vanadium(III) and vanadium(IV) (145) has one term only:

$$\text{Rate} = [\text{V}^{3+}][\text{VO}^{2+}][\text{H}^+]^{-1} \quad (44)$$

This is consistent with reaction of VOH^{2+} with VO^{2+} ($k = 1.0 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ at 25° , $\Delta H^\ddagger = 10.7 \text{ kcal mole}^{-1}$ and $\Delta S^\ddagger = -24 \text{ eu}$), since V^{3+} ($K_d = 2 \times 10^{-3} \text{ mole liter}^{-1}$) is more extensively hydrolyzed than VO^{2+} ($K_d = 4.4 \times 10^{-6} \text{ mole liter}^{-1}$). Prior hydrolysis of the V^{3+} will obviously favor its conversion to VO^{2+} . The corresponding exchange of titanium(III) with titanium(IV) has not yet been studied.

Exchange between vanadium(IV) and vanadium(V) is too fast to be followed by conventional techniques. Nuclear magnetic resonance line-broadening techniques have indicated a rate equation of the form

$$\text{Rate} = k[\text{V}^{\text{IV}}][\text{V}^{\text{V}}]^2 \quad (45)$$

and exchange of vanadium(IV) with a dimeric form of vanadium(V) seems likely (170).

Reactions of manganese(III) are difficult to study because the disproportionation reaction



readily occurs with the precipitation of manganese dioxide. This tendency can be countered by having a high hydrogen-ion concentration ($[\text{H}^+] \sim 3.0 \text{ N}$) and a high concentration of manganese(II) (326). In the most recent attempt to study the exchange of manganese(II) with manganese(III), the rapid exchange was probably induced by the separation procedure (104). Application of the Marcus theory to the reaction of manganese(III) with iron(II) and various substituted iron(II)-phenanthroline complexes, and to the reaction of cobalt(III) with manganese(II), leads to an estimate of $\sim 10^{-4} \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ for the rate constant for the manganese(II)-manganese(III) exchange at 25° (104). Disproportionation of manganese(III) with the intermediate formation of manganese(II) and manganese(IV) may provide an alternative path for exchange which is energetically more favorable than the direct exchange (2).

The rapid exchange between manganate and permanganate ions has been studied by using radioactive tracers (150, 338), and by NMR spin-echo (63) and NMR line-broadening (273) techniques. The results show good agreement. As in the reaction of $\text{Fe}(\text{CN})_6^{4-}$ with $\text{Fe}(\text{CN})_6^{3-}$, cationic

effects, in this case $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ \sim \text{Li}^+$, have been demonstrated (Table VIII). Since MnO_4^{2-} and MnO_4^- are substitution inert (there is only slow exchange of oxygen atoms in H_2^{18}O), formation of the inner-sphere activated complex $[\text{O}_3\text{Mn}-\text{O}-\text{MnO}_3]^-$ is not possible. The various cationic effects are consistent with the formation of outer-sphere

TABLE VIII
RATE CONSTANTS FOR EXCHANGE OF MnO_4^{2-} AND MnO_4^- AT 0°
(150, 338)

Medium	k (l·mole ⁻¹ sec ⁻¹)
0.16 <i>M</i> LiOH	700
0.16 <i>M</i> NaOH	710 ± 30
0.16 <i>M</i> KOH	800
0.16 <i>M</i> CsOH	2470
0.08 <i>M</i> NaOH and 0.08 <i>M</i> CsOH	1730
0.16 <i>M</i> NaOH and 10 ⁻³ <i>M</i> $\text{Co}(\text{NH}_3)_6\cdot\text{Cl}_3$	1860

bridged activated complexes, for example $[\text{O}_3\text{MnOCsOMnO}_3]^{2-}$. The activation parameters are $\Delta H^\ddagger = 10.5$ kcal mole⁻¹ and $\Delta S^\ddagger = -9$ eu in 0.16 *M* NaOH. Exchange between the ruthenate and perruthenate ions in basic solutions is too rapid ($k > 3.3 \times 10^4$ l·mole⁻¹ sec⁻¹) to be measured by conventional techniques (249). There is no suitable ESR signal which can be used to determine the rate.

A rate law

$$\text{Rate} = k[\text{Ag}^{\text{II}}]^2 \quad (47)$$

has been obtained for the exchange between silver(I) and silver(II) (151). This is consistent with a disproportionation mechanism



the rate of exchange being equal to the rate of disproportionation at equilibrium. The fast exchange between copper(I) and copper(II) in 12 *N* hydrochloric acid has been studied by NMR line-broadening techniques ($k = 0.5 \times 10^8$ l·mole⁻¹ sec⁻¹). Chloride bridging is no doubt effective in the activated complex (259).

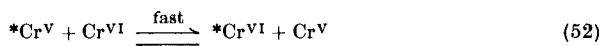
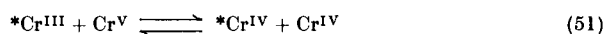
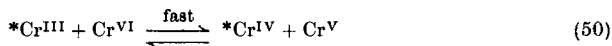
Two other reactions which it is convenient to consider in this section are both multistage processes. The first is the exchange of chromium(III) with monomeric chromium(VI) (13), which in acidic aqueous solutions at 94.8° is governed by the rate law,

$$\text{Rate} = [\text{Cr}^{\text{III}}]^{4/3}[\text{Cr}^{\text{VI}}]^{2/3}(k[\text{H}^+]^{-2} + k')$$

On the basis of this rate law it can be concluded that the rate-determining step is the reaction of chromium(III) with chromium(V), the concentration of the latter being determined by the equilibrium



The reaction sequence leading to exchange is, in full,



there being kinetic evidence only for the existence of the Cr^{IV} and Cr^{V} states in solution. The slow step (Eq. 51) is believed to correspond to a change in coordination number. Thus the chromium(V) ion is probably tetrahedral and chromium(IV) octahedral.

Adamson (2) has reported a similar sort of dependence

$$\text{Rate} = k[\text{Mn}^{2+}]^{3/2}[\text{MnO}_4^-]^{1/2} \quad (53)$$

for the exchange of manganese(II) with manganese(VII). This is consistent with a rapid equilibrium step



followed by a rate-determining step involving Mn^{III} and Mn^{IV} . Rosseinsky and Nicol (328) report a net chemical change for the reaction of manganese(II) with manganese(VII),



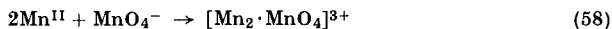
and a rate equation,

$$\text{Rate} = k[\text{Mn}^{\text{II}}]^2[\text{Mn}^{\text{VII}}] \quad (56)$$

The hydrogen-ion dependence of k is of the form :

$$k = k_1[\text{H}^+] + k_2 \quad (57)$$

Since the activated complex is tri-ionic in manganese,



they believe the $\text{Mn}^{2+} \cdot \text{MnO}_4^-$ ion pair to be a possible precursor to the activated complex. The contradiction which appears to exist in these two studies is at present under investigation (329).

B. LANTHANIDE IONS

The lanthanides form stable $3+$ ions, but the II and IV oxidation states, if they exist, tend to be highly reactive. Thus europium(II) and

ytterbium(II) are the most stable of the II states, while cerium(IV) is the most readily available of the ions in the IV oxidation state. Reactions of lanthanides are generally expected to be slow because the f orbitals are members of an inner shell of electrons, and these are shielded by other electrons. An initial $f \rightarrow d$ electronic excitation, which might lead to faster reactions, is more difficult for the lanthanides than for the actinides. Coordination numbers in aqueous solutions are almost certainly greater than six, and in the case of cerium(IV) a coordination number of eight seems likely [see, for example, Wiberg (399, p. 246)].

Exchange between europium(II) and europium(III) in aqueous perchloric acid solutions is extremely slow (260). Using the Marcus theory (253), and rate constants for the $\text{Eu}^{2+}\text{--V}^{3+}$ and $\text{V}^{2+}\text{--V}^{3+}$ reactions, the rate constant for the $\text{Eu}^{2+}\text{--Eu}^{3+}$ exchange is $\sim 10^{-6} \text{ l}\cdot\text{mole}^{-1} \text{ sec}^{-1}$ (10). The reaction is catalyzed by chloride (260), and at 22° the rate constant for the reaction of Eu^{2+} with EuCl^{2+} is $\sim 2.6 \times 10^{-4} \text{ l}\cdot\text{mole}^{-1} \text{ sec}^{-1}$.

Ytterbium(II) (standard electrode potential -1.15 volts) is an even stronger reducing ion than europium(II). Adamson (8) has studied factors affecting the stability of ytterbium(II) with a view to studying the $\text{Yb}^{\text{II}}\text{--Yb}^{\text{III}}$ exchange, and concludes that ytterbium(II) is probably reacting with both perchlorate and hydrogen ions. Solutions in hydrochloric acid of $\text{pH} > 2$ were found to be reasonably stable (decay half-times of an hour or more), but a satisfactory study of the exchange was not possible.

The kinetics of cerium(IV) reactions are complicated by the extensive hydrolysis of Ce^{4+} , the first hydrolysis constant being ca. 0.5 at 0° . The CeOH^{3+} ions are further hydrolyzed and also combine to form polynuclear ions. In the exchange between cerium(III) and cerium(IV) (III), the rate equation and relevant exchanging species are believed to be

$$\begin{aligned} \text{Rate} = & k_1[\text{Ce}^{3+}][\text{Ce}(\text{OH})_2^{2+}] + k_2[\text{Ce}^{3+}][\text{Ce}(\text{OH})_3^+] \\ & + k_3[\text{Ce}^{3+}][\text{CeO}(\text{CeOH})_5^{5+}] \end{aligned} \quad (59)$$

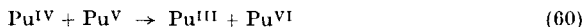
with smaller contributions from less hydrolyzed forms. The reaction is strongly catalyzed by fluoride and sulfate ions (340), but the effect of chloride is only slight and over long periods the chloride is oxidized to chlorine. A feature of the exchange in the presence of sulfate ions (0.5 and 0.0025 M sulfuric acid) is the reaction path which is first order in Ce^{3+} (34). This path is in addition to the sulfate-independent exchange, and the sulfate-dependent paths $\text{CeSO}_4^{2+}/\text{Ce}^{3+}$, $\text{Ce}(\text{SO}_4)_2/\text{Ce}^{3+}$, and $\text{Ce}(\text{SO}_4)_3^{2-}/\text{Ce}^{3+}$. The most likely explanation (167) is that excited Ce^{III}

ions are formed in the rate-determining step, possibly by collision with water molecules. The excited Ce^{III} ions react rapidly with Ce^{IV} .

C. ACTINIDE IONS

An important factor to be taken into account in considering the reaction of actinide ions is the degree of hydrolysis of the reactants. In acid solutions, $\text{pH} < 1$, the uranium (IV), (V), and (VI) and neptunium and plutonium (III), (IV), (V), and (VI) oxidation states are present at least predominantly as M^{3+} , M^{4+} , MO_2^+ , and MO_2^{2+} , respectively. The ions UO_2^{2+} (156), NpO_2^{2+} (312), and PuO_2^{2+} (256) exchange their oxygen atoms with water only very slowly (rate constants 10^{-7} – 10^{-9} sec^{-1}). The corresponding rate constants for UO_2^+ (157), NpO_2^+ (312), and PuO_2^+ (318) are somewhat faster and are of the order of magnitude 10^2 , 1, and 10^{-5} sec^{-1} , respectively. In other words, exchange rates vary with charge type, and the trends observed are such as to suggest that both AmO_2^+ and AmO_2^{2+} should exchange their oxygen atoms with water at a slow rate (312).

Electron-exchange reactions between M^{III} and M^{IV} and between M^{V} and M^{VI} ions are generally much faster than reactions between M^{IV} and M^{VI} ions. This is as might be expected since in the one case the two reactants are simple aquo ions or are both oxyocations of the type MO_2^+ and MO_2^{2+} , and in the other the reactants are one of each type. The extensive rearrangements required for the latter provide a barrier which tends to restrict reaction. Thus the exchange of UO_2^+ and UO_2^{2+} is fast, and the rate constant is of the order of 10^2 – $10^3 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ (257), while direct exchange between Np^{4+} and NpO_2^+ is slow (354). The various indirect paths possible in this system have been considered by Reynolds and Lumry (324). Exchange between Pu^{4+} and PuO_2^+ is slow, but there is a fairly rapid redox reaction (313):



The second-order rate constant for the latter is $37.3 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ at 25° .

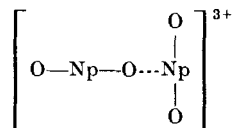
The reaction between NpO_2^+ and NpO_2^{2+} has been extensively studied (354). The rate may be expressed as

$$\text{Rate} = k_1[\text{NpO}_2^+][\text{NpO}_2^{2+}] + k_2[\text{NpO}_2^+][\text{NpO}_2^{2+}][\text{H}^+] \quad (61)$$

and at 4.5° $k_1 = 74 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ and $k_2 = 151^2 \cdot \text{mole}^{-2} \text{ sec}^{-1}$. The second term is thought to correspond to the reaction of protonated NpO_2^+ :



Since the solvent D_2O effect $k_{H_2O}/k_{D_2O} = 1.4$ (355) is about the same as that observed for the reaction of Cr^{2+} with $Co(NH_3)_5Cl^{2+}$, an inner-sphere activated complex of the type



is not unreasonable. With chloride ions there are further terms in $[Cl^-]$ and $[Cl^-]^2$ (87). Recently Amis (14) has studied the rates, orders, and temperature coefficients of exchange reactions involving uranium and neptunium ions, and in particular the reaction of NpO_2^+ with NpO_2^{2+} in pure and mixed solvents and in the presence of inert salts.

In view of the charges involved, the hydrogen-ion dependence of the reaction between Pu^{III} and Pu^{IV} is not as marked as might have been expected (230):

$$\text{Rate} = k_1[Pu^{3+}][Pu^{4+}] + k_2[Pu^{3+}][Pu^{4+}][H^+]^{-1} \quad (63)$$

In this equation, $k_1 = 20.0 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ and $k_2 = 1.1 \times 10^3 \text{ sec}^{-1}$ at 25° . That k_1 is some 10^2 times larger than the rate observed for the $Fe^{2+}-Fe^{3+}$ reaction supports the belief that charge repulsions are not of first importance in electron-transfer reactions.

III. Two-Equivalent Exchange Reactions

The main concern of this section is with exchange reactions between ions (and molecules) of subgroup B elements. These are generally two-equivalent overall reactions since, with the exception of mercury(I) and mercury(II), stable oxidation states differ by two electrons. The two-equivalent exchange between platinum(II) and platinum(IV) complexes is also considered.

The only reaction between aquo ions which it has been possible to study in a perchloric acid medium is that between thallium(I) and thallium(III). The rate equation is of the form

$$\text{Rate} = k_1[Tl^+][Tl^{3+}] + k_2[Tl^+][TlOH^{2+}] \quad (64)$$

and at 25° and $\mu = 3.0 \text{ M}$, $k_1 = 7.03 \times 10^{-5} \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ and $k_2 = 2.47 \times 10^{-5} \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ (325). Although in 6 M perchlorate media k_2 is slightly bigger than k_1 , hydroxide ions clearly do not have the strong catalytic effect which they have in many other reactions.

On the other hand, hydroxide ions do not have the even stronger inhibitory effect which chloride (191, 392), bromide (81), and cyanide

(299) ions have on the exchange. For a series of runs with the addition of increasing amounts of chloride, the experimental second-order rate constants first decrease to a minimum and then increase (148). By using association constants for thallic chloride species, this variation can be accounted for by a rate equation

$$\begin{aligned} \text{Rate} = & k_0[\text{Tl}^+][\text{Tl}^{3+}] + k_3[\text{Tl}^+][\text{TlCl}^{2+}] + k_4[\text{Tl}^+][\text{TlCl}_4^-] \\ & + k_5[\text{TlCl}_2^-][\text{TlCl}_4^-] + k_6[\text{TlCl}_3][\text{TlCl}_4^-] \end{aligned} \quad (65)$$

where k_0 is the rate constant for the exchange in 1.0 *M* perchloric acid in the absence of chloride (392). In Eq. (65) $k_0 = 6.6 \times 10^{-5}$, $k_3 = 0.28 \times 10^{-5}$, $k_4 = 4.58 \times 10^{-5}$, $k_5 = 1.32$, and $k_6 = 18.9 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ at 25°. Electron exchange occurs therefore only when the activated complex contains zero, one, four, six, and seven chloride ions. The reaction paths with one and four chlorides are actually slower than with zero chloride, while TlCl_2^+ is within experimental accuracy quite unreactive. Since at the higher chloride ion concentrations a D_2O solvent effect becomes negligible (148), some of the chloride-dependent paths at least are probably of the inner-sphere type.

For a similar series of experiments in which bromide ions are added (81), the rate first decreases, increases to a maximum, falls to a second minimum, and then increases again. The rate equation is of the form

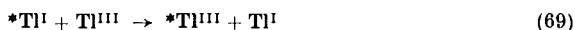
$$\begin{aligned} \text{Rate} = & k_0[\text{Tl}^+][\text{Tl}^{3+}] + k_3[\text{TlBr}_2^+] + k_4[\text{TlBr}_3] + k_5[\text{Tl}^+][\text{TlBr}_4^-] \\ & + k_6[\text{TlBr}_2^-][\text{TlBr}_4^-] \end{aligned} \quad (66)$$

a feature of the reaction being the first-order terms in k_3 and k_4 . Such terms are consistent with thallium(III) oxidation of bromide:

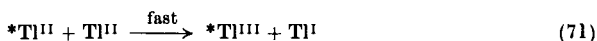


With the addition of cyanide there is a similar sort of decrease and then increase in rates (299). With sulfate (67, 400) and nitrate (304), however, the catalysis is more straightforward and in the expected manner. It has been concluded from spectroscopic observation (147) that, whereas chloride and bromide form inner-sphere complexes with thallium(III), complexing with sulfate is of the outer-sphere type, $\text{Tl}(\text{H}_2\text{O})_n^{3+}$, SO_4^{2-} . Unlike TlCl^{2+} and TlBr^{2+} , the sulfate complex reacts faster with Tl^+ than does Tl^{3+} , which suggests that the activated complex may be of the outer-sphere type. A term in $[\text{SO}_4^{2-}]^3$ is also effective in the rate equation (66), but there is a no term in $[\text{SO}_4^{2-}]^2$. The symmetry of the activated complex may be important in determining which paths are effective (65), but it is difficult to see how symmetry could be important unless inner-sphere activated complexes are involved.

Whether or not there is a simultaneous or near-simultaneous transfer of two electrons between thallium(I) and thallium(III) has been the subject of much discussion (359). The kinetics give no information as to whether the reaction proceeds directly,



or indirectly,



since both possibilities would be expected to give a rate equation which is first order in $[Tl^I]$ and $[Tl^{III}]$. Thallium(II) is known to be formed as a highly reactive intermediate in a number of noncomplementary reactions, for example that of iron(II) with thallium(III) (30). Following their study of the thallium(I)–cerium(IV) reaction in 6.18 *N* nitric acid at 53.9°, Gryder and Dorfman (168) conclude that either the Tl^I – Tl^{III} exchange or the Tl^I – Ce^{IV} reaction, or both, must involve a two-electron transfer. Since a two-electron transfer is unlikely for the reaction of thallium(I) with cerium(IV), it is probable that the thallium(I)–thallium(III) exchange is a single-stage two-equivalent process. Similar conclusions were possible following a study of the vanadium(IV)–thallium(III) reaction at 80° (367):



When vanadium(V) is added initially it produces a marked retardation, but the rate is unaffected by the addition of an excess of thallium(I) up to 0.13 *M*. This is consistent with the mechanism:



A full kinetic treatment is difficult, however, as the thallium(III) slowly decomposes to thallium(I) and molecular oxygen (197). Since the thallium(I)–thallium(III) exchange is known to proceed at an appreciable rate under the conditions of these experiments, it is unlikely that Tl^{II} is formed as an intermediate. If it were, then the progress of the reaction of vanadium(IV) with thallium(III) in Eqs. (73) and (74) would be affected by the addition of Tl^I .

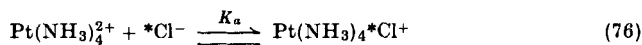
Using pulse radiolysis techniques, Cercek *et al.* (84a) have been able to measure the rate of the Tl^{II} disproportionation and, in view of the fast rate ($k = 2.3 \times 10^9$ l·mole⁻¹ sec⁻¹), the formation of Tl^{II} as an intermediate in the thermal exchange, where the Tl^{II} ions do not have time to escape from a solvent cage, cannot be excluded. Platinum black produces a marked catalysis of the exchange, but the activation energy

is surprisingly large (11.7 kcal mole⁻¹) (349). In the photo-induced Tl^I-Tl^{III} exchange, thallium(II) is formed as an intermediate but, since this system is extremely sensitive to the presence of added or accidental impurities, it again seems unlikely that thallium(II) is important in the thermal exchange (349).

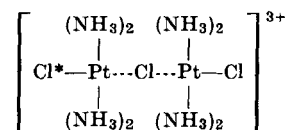
Complexing anions play an important and essential role in the exchange between platinum(II) and platinum(IV) (46). For the reactions so far studied the rate law is of the form :

$$\text{Rate} = k_{obs}[\text{Pt}^{\text{II}}][\text{Pt}^{\text{IV}}][\text{X}^-] \quad (75)$$

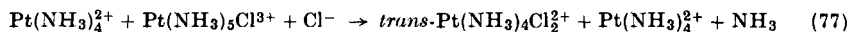
In the reaction of $\text{Pt}(\text{NH}_3)_4^{2+}$ with *trans*- $\text{Pt}(\text{NH}_3)_4\text{Cl}_2^+$ in the presence of free (and labeled) chloride, small equilibrium concentrations of a penta-coordinated platinum(II) complex are believed to be formed in a rapid first step :



These subsequently interact with the platinum(IV) with the formation of a symmetrical activated complex :



Two electrons are transferred and when the activated complex breaks down the chloride bridge remains, attached to the newly formed platinum(IV). The net effect of the exchange therefore is the substitution of a labeled chloride ion into the coordination sphere of the Pt^{IV}. The experimental rate constant k_{obs} is equal to kK_a (where K_a is as defined in Eq. 76). Values for k_{obs} vary a good deal depending on the ligands present (Table IX). That there is no detectable exchange between *trans*-Pt(tetrameen)₂Cl₂²⁺ and Pt(tetrameen)₂²⁺ over 14 days seems reasonable in view of the bulky nature of the tetramethylethylenediamine ligand, which prevents a sufficiently close approach of the two reactants. In the reaction of $\text{Pt}(\text{NH}_3)_4^{2+}$ with $\text{Pt}(\text{NH}_3)_5\text{Cl}^{3+}$, slower rates are to be expected since a Pt—NH₃ bond has to be broken :



Although the chloride forms a bridging group the transfer of two electrons cannot be accounted for by a mechanism involving chlorine-atom transfer. The transfer of Cl⁺ would seem even less likely. The exchange of $\text{Pt}(\text{NH}_3)_4^{2+}$ with *trans*- $\text{Pt}(\text{NH}_3)_4\text{Cl}_2^+$ in the presence of thiocyanate ions provides a useful method for the preparation of *trans*- $\text{Pt}(\text{NH}_3)_4(\text{SCN})_2^+$.

The exchange between tin(II) and tin(IV) has to be studied in a complexing medium to avoid precipitation of hydroxotin(IV) species. In dilute hydrochloric acid a variety of complexed ions are present, but in the concentrated acid the exchanging species are probably SnCl_4^{2-} and SnCl_6^{2-} . At 25° the rate constants in 9.0, 10.0, and 11.0 *N* acid are

TABLE IX

RATE OF EXCHANGE BETWEEN PLATINUM(II) AND PLATINUM(IV)
COMPLEXES IN THE PRESENCE OF CHLORIDE AT 25°

Reaction	k_{obs} ($l^2 \cdot \text{mole}^{-2} \text{ sec}^{-1}$)
$\text{Pt}(\text{NH}_3)_4^{2+} + \text{trans-Pt}(\text{NH}_3)_4\text{Cl}_2^{2+} + \text{Cl}^-$	6.5
$\text{Pt}(\text{en})_2^{2+} + \text{trans-Pt}(\text{en})_2\text{Cl}_2^{2+} + \text{Cl}^-$	15.0
$\text{Pt}(\text{NH}_3)_4^{2+} + \text{trans-Pt}(\text{en})_2\text{Cl}_2^{2+} + \text{Cl}^-$	3.3
$\text{Pt}(\text{NH}_3)_4^{2+} + \text{cis-Pt}(\text{NH}_3)_4\text{Cl}_2^{2+} + \text{Cl}^-$	2.7×10^{-3}
$\text{Pt}(\text{NH}_3)_4^{2+} + \text{Pt}(\text{NH}_3)_5\text{Cl}^{3+} + \text{Cl}^-$	6.5×10^{-4}
$\text{Pt}(\text{NH}_3)_4^{2+} + \text{trans-Pt}(\text{NH}_3)_3\text{Cl}_3^+ + \text{Cl}^-$	21.7

0.38, 0.55, and 0.73 $l \cdot \text{mole}^{-1} \text{ sec}^{-1}$, respectively (64). The activation energy of 10.8 kcal mole^{-1} in 10 *N* HCl is some 10 kcal mole^{-1} less than values obtained for the exchange between SnCl_2 and SnCl_4 in ethyl (264) and methyl (265) alcohol, and a different mechanism seems likely. Unlike other systems which are considered below, the exchange remains first order in both the reactants. The exchange has also been studied in sulfuric acid (155).

The rate of exchange of antimony(III) with antimony(V) increases steadily with increasing hydrochloric acid concentrations to a maximum value in approximately 9.3 *N* HCl and then decreases again between 9.3 *N* and 12.0 *N* (61, 85, 275). The complexity of the system can be explained in terms of slow interconversion among two or more forms of Sb^V which exchange at different rates (85). In 9.5 *N* hydrochloric acid the predominant form of Sb^V is SbCl_6^- (or possibly HSbCl_6), while the most likely form of Sb^{III} over a wide range of hydrochloric acid concentrations is thought to be SbCl_4^- (62). In concentrated HCl the activation energy is 17.2 kcal mole^{-1} . Over a lower range of hydrochloric acid concentrations, Kambara *et al.* (229) report a maximum rate at about 2.0 *N* hydrochloric acid. There is no exchange in aqueous sulfuric acid solutions but this can be initiated by the addition of chloride ions. In carbon tetrachloride there are two paths for exchange (44), one involving the dissociation and subsequent recombination of SbCl_5 ,



and the other having an activated complex containing one SbCl_3 and two SbCl_5 molecules. With the addition of anhydrous hydrochloric acid as catalyst (305) there is a third term which appears to involve SbCl_3 and HSbCl_6 or SbCl_6^- . In the full rate law,

$$\text{Rate (sec}^{-1}\text{)} = 1.6 \times 10^{-3}[\text{SbCl}_5] + 1.8 \times 10^{-4}[\text{SbCl}_3][\text{SbCl}_5]^2 + 2.1 \times 10^{-5}[\text{SbCl}_3][\text{HSbCl}_6] \quad (79)$$

the third term becomes dominant for conditions $[\text{HCl}] > [\text{SbCl}_5]$.

Other exchange reactions which have been studied include that of arsenic(III) with arsenic(V) in 10.8 *N* hydrochloric acid (24), and that of PCl_3 with PCl_5 in carbon tetrachloride (51). The latter is first order in PCl_5 and zero order in PCl_3 , which suggests a dissociation mechanism:



The exchange between $[\text{Hg}^{\text{I}}]_2$ and Hg^{II} is too fast to study by normal techniques (404). The most likely path is the disproportionation reaction

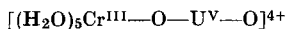


but a dissociation $\text{Hg}_2^{2+} \rightarrow 2\text{Hg}^+$ followed by the rapid exchange of Hg^+ and Hg^{2+} ions is also possible.

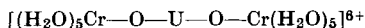
IV. Reactions in Which Binuclear Complexes Are Formed

Binuclear complexes have been identified as intermediates or final products in a number of redox reactions, and provide evidence for inner-sphere mechanisms. Typical cases are with chromium(II) or cobalt(II) complexes as the reducing agent, the chromium(III) or cobalt(III) ions which are formed capturing a nonlabile group attached to the other reactant in their inner-coordination spheres.

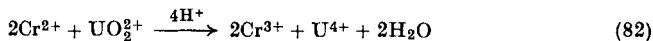
Newton and Baker (279) obtained evidence for the formation of at least one binuclear intermediate in the reaction of chromium(II) with uranium(VI). The intermediate reacts with thallium(III) and vanadium(IV) at rates which are first order in the intermediate but zero order in the concentration of oxidizing agent. In the absence of other reactants the intermediate decomposes to give U^{IV} , U^{VI} , and Cr^{III} ions with half-lives ranging from 4 to 8 minutes at 0°. Gordon (153) has shown that the intermediate,



which is first formed, undergoes a much slower reaction with a second Cr^{2+} with the formation of a second intermediate,

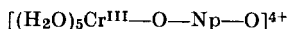


The latter then decomposes to give mononuclear products, the net reaction being



Experiments in which the UO_2^{2+} was labeled with oxygen-18 have shown that there is oxygen-atom transfer to the hexaquo chromium(III) product.

In the reaction of chromium(II) with neptunium(VI) a binuclear complex,



is formed, and this has been separated by ion-exchange techniques (351). The specific rate of decomposition for the complex is $2.32 \times 10^{-6} \text{ sec}^{-1}$ at 25° and in 1.0 *M* perchloric acid. A value of the equilibrium constant

$$K = \frac{[\text{Cr}^{\text{III}} \cdot \text{Np}^{\text{V}}]}{[\text{Cr}^{\text{III}}][\text{Np}^{\text{V}}]} \quad (83)$$

of $2.62 \pm 0.48 \text{ l} \cdot \text{mole}^{-1}$ has been determined at 25° by a spectrophotometric method (352).

The reaction of VO^{2+} and Cr^{2+} proceeds by way of a binuclear intermediate VOCr^{2+} , which has been identified spectroscopically (124). The binuclear ion is formed rapidly ($k > 3 \times 10^3 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ at 5°) and in relatively high concentrations providing $[\text{Cr}^{\text{II}}] \leq [\text{V}^{\text{IV}}]$. The green intermediate decays to vanadium(III) and chromium(III) in a pseudo-first-order reaction with a hydrogen-ion dependence indicating the presence of protonated and unprotonated forms of the intermediate. There is also evidence for the formation of a binuclear ion in the reaction of Cr^{2+} with VO_2^+ (279), but details of this reaction have not yet been studied. In Table X a list of data for the decomposition of various binuclear complexes is given.

When vanadium(II) and vanadium(IV) are mixed in acid perchlorate solutions a brown colored intermediate is observed, which has been shown to be a dimeric form of vanadium(III) (282). It has been possible to assign a formula VOV^{4+} to this intermediate (282). The rates of formation and decomposition of the dimer have been studied at the $425 \text{ m}\mu$ maxima ($\epsilon = 6.8 \pm 0.8 \times 10^3$). The rate of formation is given by $k_1[\text{V}^{2+}][\text{VO}^{2+}]$ and its rate of decomposition by the two terms $(k_2 + k_3[\text{H}^+])[\text{VOV}^{4+}]$. At 0° and ionic strength $\mu = 1.0 \text{ M}$, k_1 is about $0.067 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$, k_2 is very small and of the order of 0.003 sec^{-1} , and k_3 is $0.330 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$. The reaction can also be studied by following the disappearance of vanadium(IV) at $760 \text{ m}\mu$ (281), since the

dimeric species does not absorb at this wavelength. The rate law is of the form

$$-d[\text{V}^{\text{IV}}]/dt = (k_4 + k_5[\text{H}^+])[\text{V}^{\text{II}}][\text{V}^{\text{IV}}] \quad (84)$$

and k_4 ($0.106 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ at 0°) accounts for nearly all of the rate. By comparing k_1 and k_4 it can be concluded that about 65% of the overall reaction involves the intermediate, and the rest of the reaction proceeds

TABLE X

A COMPARISON OF DATA FOR THE DECOMPOSITION OF BINUCLEAR COMPLEXES (124)

Mode of formation	Binuclear ion ^a	k_{obs} (sec ⁻¹) at 25°	Reference
$\text{Cr}^{\text{II}} + \text{V}^{\text{IV}}$	CrOV^{4+}	$0.018 + 0.645[\text{H}^+]$	(124)
$\text{V}^{\text{II}} + \text{V}^{\text{IV}}$	VOV^{4+}	$0.03 + 1.54[\text{H}^+]$	(282)
$\text{Fe}^{\text{II}} + \text{Fe}^{\text{IV}}$	FeOFe^{4+}	$0.35 + 3.5[\text{H}^+]$	(93)
$\text{Cr}^{\text{II}} + \text{Cr}^{\text{IV}}$	CrOHCr^{5+b}	1.5×10^{-6}	(92)
$\text{Cr}^{\text{II}} + \text{Np}^{\text{VI}}$	CrONpO^{4+}	2.3×10^{-6}	(351)

^a In a number of cases the formula of the binuclear complexes is uncertain. Possibilities are $\text{M}(\text{OH})_2\text{M}'$, $\text{M}(\text{OH})\text{M}'$, and MOM' .

^b The double-bridged complex $\text{Cr}(\text{OH})_2\text{Cr}^{4+}$ is known to be formed by the direct reaction of Cr^{II} with Cr^{IV} (228). In the decomposition of this dimer the monobridged complex, CrOHCr^{5+} , is the immediate precursor of Cr^{3+} (92, 332).

directly to the final products, probably by way of an outer-sphere activated complex. Values of ΔH^\ddagger and ΔS^\ddagger corresponding to k_4 are $12.3 \text{ kcal mole}^{-1}$ and -16.5 eu , respectively.

In the reaction of chromium(II) with thallium(III) the chromium(III) product is in the form of a binuclear complex (27), which suggests that chromium(IV) is formed in the first step:



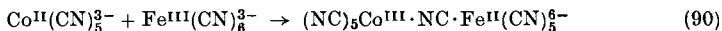
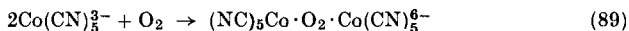
The binuclear complex has been shown to have the formula $(\text{H}_2\text{O})_4\text{Cr}(\text{OH})_2\text{Cr}(\text{H}_2\text{O})_4^{++}$ (228). A single-bridged dimer, $(\text{H}_2\text{O})_5\text{Cr} \cdot \text{OH} \cdot \text{Cr}(\text{H}_2\text{O})_5^{5+}$, is formed as an intermediate in the slow decomposition of the double-bridged complex (92).

A binuclear iron(III) complex (266) is also formed in the two-equivalent oxidation of iron(II) with HOCl and O_3 (93). Again this suggests that iron(IV) is being formed and the kinetic data are consistent with a reaction sequence:

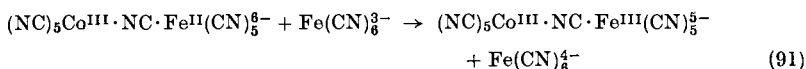


Decomposition of the dimer is rapid and has to be studied by flow techniques.

The binuclear ions $(\text{NC})_5\text{Co} \cdot \text{O}_2 \cdot \text{Co}(\text{CN})_5^{6-}$ and $(\text{NC})_5\text{Co} \cdot \text{NC} \cdot \text{Fe}(\text{CN})_5^{6-}$ have been prepared (179) by oxidation of the pentacyano complex of cobalt(II) with O_2 and $\text{Fe}(\text{CN})_6^{3-}$, respectively:



That small amounts of $\text{Fe}(\text{CN})_6^{4-}$ are formed in reaction (90) suggests that a second path occurring by an outer-sphere mechanism may be effective. Alternatively, significant amounts of $(\text{NC})_5\text{Co}^{\text{III}} \cdot \text{NC} \cdot \text{Fe}^{\text{III}}(\text{CN})_5^{6-}$ and $\text{Fe}(\text{CN})_6^{4-}$ may be formed in the reaction:



The $\text{Co}^{\text{III}} \cdot \text{Fe}^{\text{II}}$ complex can be oxidized to the $\text{Co}^{\text{III}} \cdot \text{Fe}^{\text{III}}$ complex with iodine. Taube and Myers (379) have suggested that the reaction between Cr^{2+} and $\text{Fe}(\text{CN})_6^{3-}$ occurs via a bridged activated complex with the cyanide bridge persisting in the insoluble product. The oxidation of $\text{Co}^{\text{II}}(\text{EDTA})^{2-}$ by $\text{Fe}(\text{CN})_6^{3-}$ (5), while giving $\text{Co}^{\text{III}}(\text{EDTA})^-$ and $\text{Fe}(\text{CN})_6^{4-}$ as the final products, also occurs with the formation of an intermediate $(\text{EDTA})\text{Co}^{\text{III}} \cdot \text{NC} \cdot \text{Fe}^{\text{II}}(\text{CN})_5^{5-}$. Wilkins and Hutchinal (402) have determined the rates of the various processes involved, using temperature-jump and stopped-flow techniques. Another intermediate, $(\text{EDTA})\text{Co}^{\text{III}} \cdot \text{NC} \cdot \text{Fe}^{\text{III}}(\text{CN})_5^{5-}$, which is formed as a result of the rapid oxidation of the first intermediate with $\text{Fe}(\text{CN})_6^{3-}$, must also be considered for a full description of the system (422). The reaction of $\text{Co}^{\text{II}}(\text{EDTA})^{2-}$ with IrCl_6^{3-} has also been studied (119), but as yet there is no evidence for an intermediate.

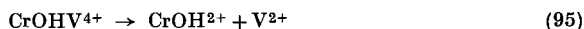
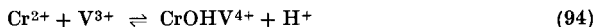
In a number of reactions a more complex hydrogen-ion dependence is the only evidence for the formation of a binuclear intermediate. In such cases the intermediate is of transitory nature and cannot be identified by spectrophotometric methods. A good example is the chromium(II) reduction of vanadium(III) (125, 174a, 370). The reaction is first order in both reactants,

$$\text{Rate} = k_{\text{obs}}[\text{Cr}^{\text{II}}][\text{V}^{\text{III}}] \quad (92)$$

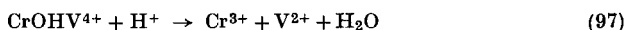
where k_{obs} shows a hydrogen-ion dependence of the form

$$k_{\text{obs}} = a/(c + [\text{H}^+]) \quad (93)$$

To fit this equation a mechanism of the type

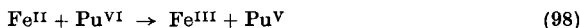


was suggested (125). This was unsatisfactory however because it appeared to exclude reactions of VOH^{2+} (370). Haim (174a) has considered a number of alternative mechanisms and one of these



seems more satisfactory, particularly as recent work (371) has confirmed Eq. (93). Other reactions of chromium(II) show a strong preference for paths involving a hydroxide ion, and although it is perhaps surprising that the reaction of Cr^{2+} with V^{3+} appears to make no contribution, this is more reasonable than the alternative in which the Cr^{2+} — VOH^{2+} reaction makes no contribution.

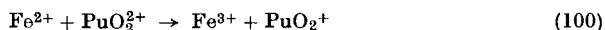
The kinetics of the reaction



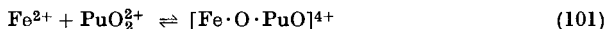
have been studied in 0.05–2.0 *N* perchloric acid solution, $\mu = 2.0$ *M* (280). The rate conforms to an empirical equation

$$\frac{-d[\text{Pu}^{\text{VI}}]}{dt} = [\text{Pu}^{\text{VI}}][\text{Fe}^{\text{II}}] \left(A + \frac{1}{B + C[\text{H}^+]} \right) \quad (99)$$

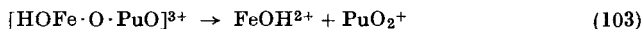
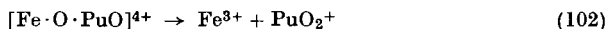
which can only be accounted for by considering the formation of a metastable binuclear intermediate $\text{Pu}^{\text{V}} \cdot \text{Fe}^{\text{III}}$ having the same composition as the activated complex. Thus reaction can occur in the normal way,



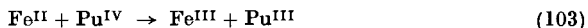
but in addition a binuclear intermediate is formed:



The latter (and its hydrolyzed form) subsequently decomposes to give products:

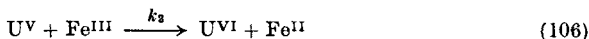
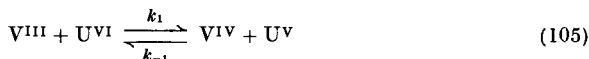


Using the steady-state approximation for the concentration of the intermediate, a hydrogen-ion dependence of the required form is obtained. The reaction of iron(II) with plutonium(IV) has also been studied (286),



and is relatively straightforward. The most important path is the one having an inverse hydrogen-ion dependence, which is consistent with a reaction of Fe^{2+} with PuOH^{3+} .

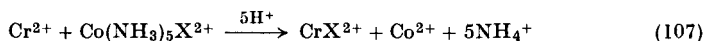
The reaction between vanadium(III) and uranium(VI) has also been studied (285), using the catalysis of the vanadium(III)-iron(III) reaction by uranium(VI). Without regard to the hydrogen-ion concentration, the mechanism is:



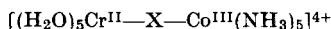
The hydrogen-ion dependence of k_1 is not consistent with a single rate-determining step or with a set of such steps occurring in parallel. The dependence is consistent with consecutive reactions and the formation of a binuclear intermediate which is present as $[\text{HOV} \cdot \text{O} \cdot \text{UO}]^{4+}$ and $[\text{OV} \cdot \text{O} \cdot \text{UO}]^{3+}$. In the analogous reaction between vanadium(III) and plutonium(VI), (310), there is as yet no evidence for an intermediate.

V. Other One-Equivalent Reactions between Metal Ions

For the series of reactions of Cr^{2+} with $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}^{2+}$ complexes, there is transfer of the X^- ligand to the newly formed chromium(III) (272):



As in the reactions of Cr^{2+} with $\text{Cr}^{\text{III}}\text{X}^{2+}$, the only satisfactory explanation is that inner-sphere activated complexes



are formed. Some of the results obtained for such reactions are shown in Table XI.² The order of effectiveness of the halide ions, $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$, is of particular interest (76). The same order is found with $\text{Co}(\text{CN})_5^{3-}$ (78) and H-atoms (20, 189, 274) as the reducing agent [and also in the outer-sphere reactions with V^{2+} (79, 104a), $\text{Cr}(\text{bipy})_3^{2+}$ (76, 413), $\text{Ru}(\text{NH}_3)_6^{2+}$ (122)], and may be termed the "normal" order of bridging efficiency. In the reactions with Fe^{2+} (104a, 126) and Eu^{2+} (79) (which are of uncertain mechanism), an inverted order, $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$, is observed (Fig. 1). The normal order is also found in the reactions of Cr^{2+} with $\text{Cr}(\text{NH}_3)_5\text{X}^{2+}$ (291) and CrX^{2+} (40), and the inverted order when Fe^{2+} reacts with FeX^{2+} complexes. The bridging

² Here and elsewhere, for convenience, X^- is used to denote ligands which in most cases have a unit negative charge, but which may also be H_2O , SO_4^{2-} , etc.

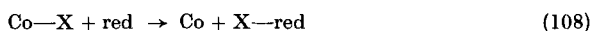
efficiency thus seems to depend primarily upon the nature of the reducing agent and to a lesser extent on the nature of the oxidizing agent. Sutin has pointed out (361) that the ratio of stability constants K_F-/K_I- is about 2×10^2 for the pentamminecobalt(III) complexes, and, since

TABLE XI
KINETIC DATA FOR Cr^{2+} - $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ REACTIONS AT 25°

Cobalt complex	k ($\text{l} \cdot \text{mole}^{-1} \text{sec}^{-1}$)	ΔH^\ddagger (kcal mole^{-1})	ΔS^\ddagger (eu)	Ref.
$\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ (20°)	0.5	2.9	-52	(412)
$\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$ (20°)	1.5×10^6	4.6	-18	(412)
$\text{Co}(\text{NH}_3)_5\text{F}^{2+}$	2.5×10^5	—	—	(76)
$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	6×10^5	—	—	(76)
$\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$	1.4×10^6	—	—	(76)
$\text{Co}(\text{NH}_3)_5\text{I}^{2+}$	3×10^6	—	—	(76)
$\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$	$\sim 3 \times 10^5$	—	—	(79)
$\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$	19	6.9	-29	(79)
$\text{Co}(\text{NH}_3)_5\text{SO}_4^+$	18	6.2	-32	(79)
	22	8.3	-25	(301)
$\text{Co}(\text{NH}_3)_5\text{SO}_3^+$	18.6	8.3	-26	(301)
$\text{Co}(\text{NH}_3)_5\text{S}_2\text{O}_3^+$ (O)	13.3	4.2	-39	(301)
$\text{Co}(\text{NH}_3)_5\text{S}_2\text{O}_3^+$ (S)	0.18	24.6	-3	(301)
$\text{Co}(\text{NH}_3)_5\text{SeO}_3^+$	> 100	—	—	(270)
$\text{Co}(\text{NH}_3)_5\text{SeO}_4^+$	360	—	—	(270)
$\text{Co}(\text{NH}_3)_5\text{NO}_3^{2+}$	~ 90	—	—	(79)
$\text{Co}(\text{NH}_3)_5\text{PO}_4$	5×10^9	—	—	(79)
$\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ (15°)	61	—	—	(129)

K_F-/K_{Br-} is 6×10^6 and 3×10^5 for the aquochromium(III) and aquo-iron(III) complexes, respectively, the standard free energy change is consistent with the inverted order for the reactions of both Cr^{2+} and Fe^{2+} with $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$. The polarizabilities of the halide ions favor the normal order, and the observed order might therefore reflect some compromise between these two factors. Free energy considerations are not able to explain why the normal order is observed for the exchange of Cr^{2+} with CrX^{2+} , and the inverted order for the exchange of Fe^{2+} with FeX^{2+} .

Halpern and Rābani (189) have suggested that for reactions



the reactivity order is determined by the strength of the bond being broken ($\text{Co}-\text{X}$), and the bond being formed ($\text{X}-\text{red}$). For the oxidants and reductants in question the trend is almost certainly for bond

strengths to increase in the order, $I^- < Br^- < Cl^- < F^-$. Since the influence of bond making is expected to be of less importance than bond breaking for highly reactive reductants, the reactivity order should follow the sequence $Co(NH_3)_5I^{2+} > Co(NH_3)_5Br^{2+} > Co(NH_3)_5Cl^{2+} > Co(NH_3)_5F^{2+}$. For reductants of low reactivity, on the other hand,

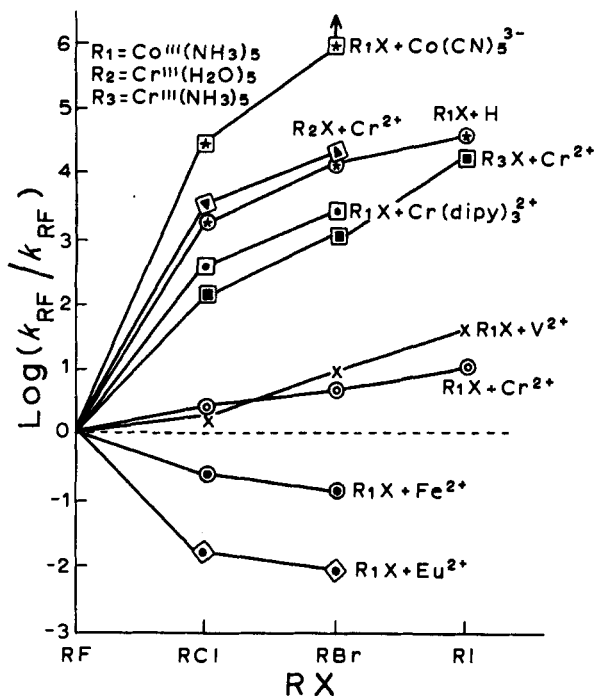
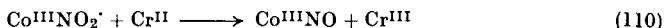
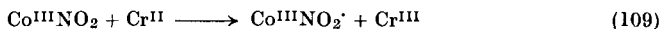


FIG. 1. Showing the trend in rate constants, $\log(k_{RX}/k_{RF})$, for reactions of fluoro, chloro, bromo, and iodo complexes. [Reproduced with permission from Halpern (182) with additional data from Halpern and Rabani (189).]

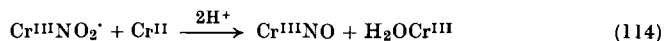
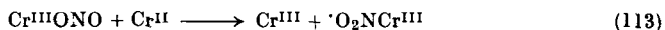
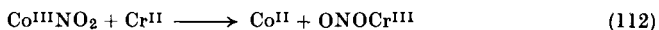
stabilization of the transition state by bond making to the reductant is expected to assume greater importance, and the reactivity order should thus be influenced to a greater degree by the strength of the bond being formed, i.e., $F^- > Cl^- > Br^- > I^-$. The observed reactivity orders are consistent with this interpretation; thus the rate constants for the reactions with $Co(NH_3)_5Cl^{2+}$ are H (1.6×10^9) $> Co(CN)_5^{3-}$ (2×10^7) $> Cr^{2+}$ (2.6×10^6) $> Eu^{2+}$ (3.9×10^2) $> Fe^{2+}$ (1.4×10^{-3}), the values in parentheses being the rate constants in $l \cdot mole^{-1} sec^{-1}$ at 25° . Diebler and Taube (104a) have suggested that electron transfer may proceed by means of σ -interactions when chromium(II) is the reducing agent, and

that π -interactions may be more important than σ -interactions when iron(II) is involved.

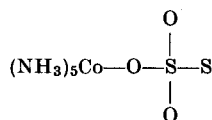
The relative rates observed with azide and thiocyanate ions as bridging groups are important. As in the corresponding Cr^{2+} - CrX^{2+} reactions, electron transfer is believed to proceed through a polyatomic bridged activated complex $[\text{Cr}-\text{N}=\text{N}=\text{N}-\text{Co}]^{4+}$, the much lower rate observed with $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ being attributed to the unsymmetrical nature of the NCS-bridged intermediate, which results in the formation of the less stable CrSCN^{2+} . As a general rule, provided transfer of the bridging group occurs in the inner-sphere activated complex and provided the nitrogen-bonded thiocyanate is the stable isomer, the inner-sphere reaction should proceed faster when the bridging group is azide than when it is thiocyanate. Using this criterion, the reactions of Fe^{2+} with FeN_3^{2+} and FeNCS^{2+} are probably inner-sphere reactions, while the similarity in rates for the reaction of V^{2+} with $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ suggests that these reactions are outer-sphere (79, 361). The absence of a discrimination between azide and thiocyanate in the reductions of $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ by $\text{Co}(\text{CN})_6^{3-}$ (78) (which are inner-sphere) is due to the fact that the sulfur-bonded form $\text{Co}(\text{CN})_5\text{SCN}^{3-}$ is the more stable form (182). With $\text{Cr}(\text{bipy})_3^{2+}$, which reacts via an outer-sphere path, the rates with $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ are comparable (79). The reactions of $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ with Cr^{2+} (129) and $\text{Co}(\text{CN})_6^{3-}$ (186) result in the formation of CrNC^{2+} and $\text{Co}(\text{CN})_5\text{NC}^{3-}$, respectively. The latter undergoes first-order decay to $\text{Co}(\text{CN})_6^{3-}$ with a half-life of 1.6 sec (186). The reduction of pentammine cobalt(III) complexes $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$, $\text{Co}(\text{NH}_3)_5\text{ONO}^{2+}$, and $(\text{NH}_3)_5\text{Co} \cdot (\text{NO})_2 \cdot \text{Co}(\text{NH}_3)_5^{4+}$ (containing nitro, nitrito, and hypoxynitrito ligands) with Cr^{2+} , and of $\text{Cr}(\text{NH}_3)_5\text{NO}_2^{2+}$ with Cr^{2+} , has been studied (137). In all cases the first step is the reduction of the cobalt(III) center and not the ligand. If ligand reduction were the first step, the reaction scheme, with for example nitropentammine cobalt(III) complex, would be



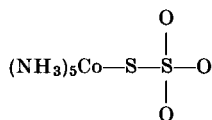
but this is inconsistent with experimental observations. The suggested mechanism is:



Peters and Fraser (301) find that both isomers of thiosulfatopentamminecobalt(III) are stable, the usual method of preparation yielding mainly the oxygen-bonded species (I). In the reactions with chromium(II) the oxygen-bonded isomer reacts about 70 times faster than



(I)

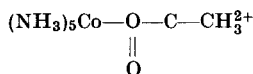


(II)

the sulfur-bonded form. The rate constant for the former is comparable to those observed for the sulfato and sulfito complexes. The similarity of the rate constants and activation parameters for the sulfato and sulfito reactions can be explained by considering the bonding of the ligands. Since the bonding in the sulfito complex is $\text{Co}-\text{S}$ and that of the sulfato complex $\text{Co}-\text{O}-\text{S}$, both ligands possess three oxygens which are not bound to the cobalt.

Fraser and colleagues have also studied the effect which different oxyanion complexes of pentammine and tetramminecobalt(III) have on rate constants of reactions with chromium(II), vanadium(II), europium(II), and titanium(III) (270). The complexes studied include the metaborato, carbonato, nitro, nitrito, nitrato, selenito, selenato, and phosphate complexes. Rates are found to increase when the sulfur atom is replaced by selenium. Candlin *et al.* (79) have also studied the reduction of the phosphatopentamminecobalt(III) complex with chromium(II), vanadium(II), and europium(II). In these reactions $\text{Co}(\text{NH}_3)_5\text{PO}_4$ and the protonated species $\text{Co}(\text{NH}_3)_5\text{PO}_4\text{H}^+$, $\text{Co}(\text{NH}_3)_5\text{PO}_4\text{H}_2^{2+}$, and $\text{Co}(\text{NH}_3)_5\text{PO}_4\text{H}_3^{3+}$ are effective.

Reactions of Cr^{2+} with pentamminecobalt(III) complexes $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$, where X^- is a carboxylate group, have been extensively studied. In the case in which X^- is an acetate group (333)



the product is $\text{Cr}^{\text{III}}\text{OOCCH}_3^{2+}$, and attack must therefore be at one of the oxygen atoms [contrary to one report (138), the two oxygens are not equivalent (134)]. It is not known whether Cr^{2+} attacks the carbonyl or the $\text{Co}-\text{O}-\text{C}$ oxygen, although the former would seem the most likely since it is sterically less hindered. As Taube has suggested, it is possible that in one series of complexes, those of the simple carboxylate ions for example, attack is at one of these positions, but when a chelate function

is introduced the position of attack changes (378). The reactions are not very rapid unless the bridging ligand contains (a) a conjugate bond system, or (b) a second group capable of binding the reducing agent. There are three types of reaction to consider: first, *adjacent attack*; second, *adjacent attack with chelation*; and third, *remote attack*.

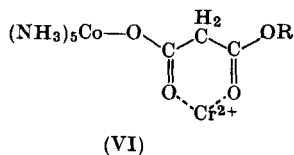
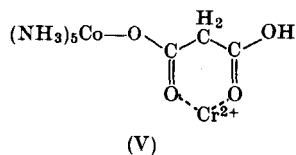
Table XII summarizes kinetic data for the reactions of chromium(II) with carboxylatopentammine complexes containing ligands which do not chelate the reducing agent or favor reaction by remote attack. That

TABLE XII
DATA (AT 25°) FOR Cr^{2+} - $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ REACTIONS INVOLVING ADJACENT
ATTACK OF THE Cr^{2+}

Ligand	k ($\text{l} \cdot \text{mole}^{-1} \text{sec}^{-1}$)	ΔH^\ddagger (kcal mole^{-1})	ΔS^\ddagger (eu)	ΔG^\ddagger (kcal mole^{-1})	Ref.
Acetate	0.18	3.5	-50	18.5	(333)
Monochloroacetate	0.10	7.9	-37	19.0	(139)
Dichloroacetate	0.074	2.5	-55	19.0	(139)
Trifluoroacetate	0.052	—	—	—	(164)
Benzoate	0.14	4.9	-46	18.7	(139)
<i>o</i> -Chlorobenzoate	0.074	6.0	-43	18.9	(139)
<i>p</i> -Chlorobenzoate	0.21	10.0	-28	18.4	(139)
<i>m</i> -Phthalate	0.13	2.1	-56	18.9	(333)
Propionate	0.081	—	—	—	(376)
Cyclo- $\text{C}_3\text{H}_5\text{COO}^-$	0.125	7.3	-38	19.0	(140)
Cyclo- $\text{C}_5\text{H}_9\text{COO}^-$	0.072	9.2	-33	19.0	(140)
Cyclo- $\text{C}_6\text{H}_{11}\text{COO}^-$	0.040	12.4	-23	19.0	(140)
Formate	7.0	—	—	—	(70)

the rate constants vary so little (if the formate complex is excluded, they all lie within the range 0.04 – $0.21 \text{ l} \cdot \text{mole}^{-1} \text{sec}^{-1}$) (70, 140, 333) deserves further comment. The ligands differ markedly in physical properties, and there is a large variation of 10^4 – 10^5 for the dissociation constants of the corresponding organic acids (378). Since the Cr^{2+} attacks an oxygen of the carboxyl group, the rates might be expected to reflect the availability of unshared electrons on the oxygen atoms (i.e., the basicity of the organic acids). A decrease in rate constants is in fact noted for the series CH_3COO^- , $\text{ClCH}_2\text{COO}^-$, and $\text{Cl}_2\text{CHCOO}^-$, but the ΔH^\ddagger and ΔS^\ddagger values are such that at a higher temperature the rate constants will not lie in this same order (378). Furthermore, the formate ion is less basic than acetate and yet the reduction of the formate complex is much faster (70). Fraser (141) had indicated the importance of steric effects in these

reactant. When the bridging ligand is malonate as in (V), the reaction rate is approximately twice that when it is acetate. Analysis of the reaction mixture by an ion-exchange technique (210) has shown that



well over 85% of the product is in the chelate form. The hydrogen-ion dependence is:

$$k_{obs} = k_1 + k_2[\text{H}^+]^{-1} + k_3[\text{H}^+] \quad (115)$$

With ethyl malonate and other derivatives obtained by substitution at the methylene center, there is no k_3 term. With methyl and ethyl half-

TABLE XIII
DATA (25°) FOR $\text{Cr}^{2+}-\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ REACTIONS BELIEVED TO INVOLVE
CHELATION

Ligand	k (l·mole ⁻¹ sec ⁻¹)	ΔH^\ddagger (kcal mole ⁻¹)	ΔS^\ddagger (eu)	Ref.
Glycolate	3.06	9.0	-26	(70)
Methoxyacetate	0.42	11.3	-23	(70)
Lactate	6.65	—	—	(70)
Methyl lactate	11.5	9.1	-24	(70)
<i>d</i> -Tartrate ^a	1.49	—	—	(70)
α -Malate ^a	2.7	—	—	(70)
β -Malate ^a	0.36	—	—	(70)
Malonate ^{a,b}	0.29	—	—	(70)
Ethyl malonate ^a	0.18	—	—	(70)
Benzyl malonate ^a	0.99	—	—	(70)
Dimethyl malonate ^a	0.070	—	—	(70)
Methyl malonate (half-ester) ^b	0.41	10.1	-26	(211)
Ethyl malonate (half-ester) ^b	0.50	9.6	-27.5	(211)

^a There is also an inverse hydrogen ion-dependent path.

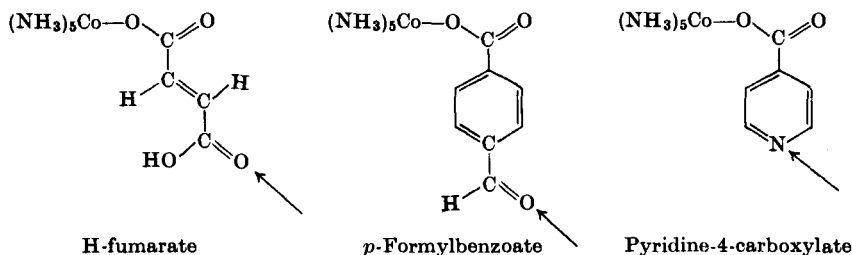
^b There is also a direct hydrogen ion-dependent path.

ester derivatives (VI), on the other hand, there appears to be a k_3 term but no k_2 term (211). Alternative explanations are possible to account for this variation (70, 211).

An investigation has been made of the product distribution in the reactions with the methyl and ethyl malonate complexes. In each case, ester hydrolysis accompanies the oxidation-reduction process (211). For the former complex about 50% of the bridging ligand appears as the

chelated product and for the latter about 67%. The alcohol corresponding to the amount of chelated product formed is found free in solution. The remainder of the ligand appears as the unchelated ester malonato complex of chromium(III). This suggests that there are parallel paths for the reaction, one corresponding to the simple adjacent attack leading to the monodentate half-ester complex, and the other to an intermediate in which both ends of the ligand are trapped in the chromium (III) coordination sphere. With vanadium(II) and europium (II) no hydrolysis results, and (contrary to a previous report) ester hydrolysis does not occur in the reaction of the succinate half-ester complex with any of the three reducing agents, Cr^{2+} , V^{2+} , and Eu^{2+} (211). The implication may be that there is no chelation in the case of the succinate half-ester. The effectiveness of *o*-phthalate (333) and salicylate ligands (139, 164, 363) has also been studied. Chelation can also occur through a sulfur atom (162), and appears to be important in the reduction of some pyridine- and pyrazine-carboxylato complexes (162).

Remote attack occurs when complexes having a ligand with a conjugate-bond system extending from a remote polar group (e.g., carboxyl, carbonyl, or the nitrogen of an aromatic ring system) are reduced. The reducing agent attacks the bridging ligand at the polar group remote from the coordinated carboxyl group, the continuous pathway of double bonds providing an efficient means of electron transport between the two metal ions. For most systems the evidence for



remote attack is simply that rates are larger than those observed for normal adjacent attack, and that chelation is absent. A feature of the reactions (Table XIV) is a term first order in hydrogen-ion concentration:

$$k_{obs} = k_1 + k_2[\text{H}^+] \quad (116)$$

It has been suggested that the addition of a proton to the carboxyl group adjacent to the cobalt(III) may improve conjugation between the two polar groups. In addition, the complexes of pyridine-4-carboxylate and pyridine-2-carboxylate (and possibly cinnoline-4-carboxylate) are rapidly reduced by Cr^{2+} , at least in the forms which present nitrogen

without an associated proton. The *p*-phthalate complex has now been shown to be reduced at the normal rate of $0.20 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ (which is of the same order as for the *ortho* and *meta* derivatives), thus ruling out any appreciable contribution by remote attack (162). Earlier evidence, which suggested that ester hydrolysis accompanies remote attack of the methyl fumarate complex, has recently been questioned (378). The

TABLE XIV

RATE CONSTANTS (AT 25°) FOR Cr^{2+} - $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ REACTIONS BELIEVED TO PROCEED BY REMOTE ATTACK

Ligand	k_1 ($\text{l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$)	k_2 ($\text{l}^2 \cdot \text{mole}^{-1} \text{ sec}^{-1}$)	References
H-fumarate	1.3	3.5	(333)
H-chlorofumarate ^a	1.3	1.2	(252)
	0.09	0.5	(252)
H-maleate	200	100	(143)
H-butadienedicarboxylate	2.2	15.0	(162)
<i>p</i> -Formylbenzoate	40	4×10^2	(142, 162)
Pyruvate	2.1×10^3	?	(70)
	($[\text{H}^+] = 0.1 \text{ N}$)		
Cinnoline-4-carboxylate	> 1100	?	(162)
Pyridine-4-carboxylate	1.5×10^3	1.3	(164)

^a Isomeric forms, see text.

specific rates for the methyl fumarate (333) and phenyl fumarate (143) half-ester complexes (1.4 and $1.3 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$, respectively) are not very different from the rate of the reaction with the fumarate complex ($1.3 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$) (333). Manning *et al.* (252) have concluded that the chlorofumarate isomer, which reacts the more rapidly (Table XIV), has the halogen remote from the carboxyl group attached to the cobalt atom. The halogen is thought to interfere more with the coplanarity of the carboxyl group when it is in the β position than when it is in the α position. It would now seem that remote attack may occur (with conjugate systems) only when the ligand is reducible (162, 164). For example, uncomplexed malic, oxalic, and pyruvic acids are readily reduced to a radical ion by Cr^{2+} , but phthalic acid is not. The maleato complex is partially isomerized to fumarate when the maleato complex is reduced (143). In the case of the *p*-formylbenzoate complex, the ligand is not bound to the chromium(III) product. This provides additional evidence for remote attack in this instance since, when the chromium(III) complex coordinated to *p*-formylbenzoate through the carboxylate group is

prepared, the rate of dissociation is slow (142, 162). It is reasonable to suppose that the position of attack is at the carbonyl group, since such a group attached to chromium(III) is expected to be lost rapidly by aquation.

More recently Gould (163) has extended his work on electron transfer through organic structural units to include the effect of chain branching and nitro and thia substituents. As in earlier studies, the enhancement of rates through remote attack of ligands having conjugate bonding is confined to those ligands which are readily reducible. Jordan *et al.* (226) have studied the Cr^{2+} reduction of nitrilo and related pentammine complexes $\text{Co}(\text{NH}_3)_5\text{NCCH}_3^{3+}$, $\text{Co}(\text{NH}_3)_5\text{NCCH}=\text{CH}_2^{3+}$, $\text{Co}(\text{NH}_3)_5\text{NCCH}_2\text{CN}^{3+}$, and $\text{Co}(\text{NH}_3)_5\text{NC}_5\text{H}_5^{3+}$.

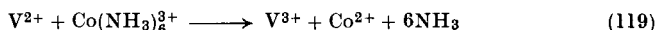
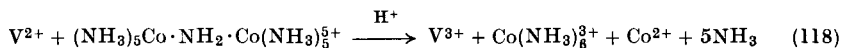
The reaction of chromium(II) with the hexammine complex $\text{Co}(\text{NH}_3)_6^{3+}$ is believed to be an outer-sphere reaction, since there is no inverse hydrogen-ion dependence (thus excluding amide bridging) (414). Manning and Jarnagin (251) have studied the catalysis by chloride and bromide,

$$k_{obs} = k_1 + k_2[\text{X}^-] \quad (117)$$

using relatively large ($> 0.1 M$) concentrations of the halide ions. They compare k_1 and k_2 values with those obtained for the Cr^{2+} - $\text{Co}(\text{NH}_3)_5\text{OAc}^{2+}$ and Cr^{2+} - $\text{Co}(\text{NH}_3)_5\text{FuH}^{2+}$ reactions (333) (where Fu = fumarate). These reactions are known to be inner-sphere and, since both the halide and organic ligand have been detected in the inner-coordination sphere of the chromium(III) produced, it can be concluded that the activated complexes are $[(\text{NH}_3)_5\text{Co} \cdot \text{OAc} \cdot \text{CrX}(\text{H}_2\text{O})_4]^{3+}$ and $[(\text{NH}_3)_5\text{Co} \cdot \text{FuH} \cdot \text{CrX}(\text{H}_2\text{O})_4]^{3+}$, respectively. They find that Cl^- is about 2.5 times more effective than Br^- in all three cases. It seems likely that in both inner- and outer-sphere reactions the Cr^{2+} reactant brings the halide into the transition complex. The role of the halide ion would appear to be either or both (a) to make the relaxation time of the ligand vibrations more rapid and (b) to raise the energy of the electron which is to be transferred, as Zwickel and Taube have suggested (414). Pyrophosphate accelerates the reduction of $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ by Cr^{2+} and the chromium(III) product contains both the chloride and pyrophosphate in its inner-coordination sphere (120, 375). Chloride ions accelerate the Cr^{2+} reduction of $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ presumably by a similar nonbridging mechanism (244).

While outer-sphere reactions are the exception with chromium(II), the converse may be the case with vanadium(II). It is perhaps significant that the reaction of V^{2+} with $\text{Co}(\text{NH}_3)_6^{3+}$ ($k = 4.4 \times 10^{-3} \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ at 25°) is faster than that of Cr^{2+} with $\text{Co}(\text{NH}_3)_6^{3+}$ ($k = 9 \times 10^{-5} \text{ l} \cdot \text{mole}^{-1}$

sec⁻¹), although the redox potential is much more favorable for Cr²⁺ (414). The reaction of V²⁺ with the binuclear complex (NH₃)₅Co·NH₂·Co(NH₃)₅⁵⁺ takes place in one-equivalent steps (109),



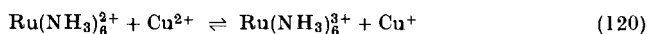
and not with intermediate formation of vanadium(IV). That reaction (118) is some 30 times faster than reaction (119) is due to the difference in activation entropies. Similar results have been obtained with Cr²⁺ as the reducing ion. In the reaction of V²⁺ with Co(NH₃)₅H₂O³⁺, rate constants are independent of hydrogen-ion concentrations over the range 10⁻⁴ to 1.0 *N* (107), and the path involving Co(NH₃)₅OH²⁺ appears to play no significant role as it does in the Cr²⁺ reaction. Dodel and Taube (107) have also studied the effect of Cl⁻, SO₄²⁻, and F⁻ on the rates of the V²⁺-Co(NH₃)₆³⁺ and V²⁺-Co(NH₃)₅H₂O³⁺ reactions, and find the ratios of *k*₂ (for the catalyzed reaction) to *k*₁ (for the uncatalyzed reaction) to be 8.0, 1930, and 21,000, respectively, in the one case, and 8.5, 1830, and 18,300 in the second case. They conclude that the V²⁺-Co(NH₃)₅H₂O³⁺ reaction, like the V²⁺-Co(NH₃)₆³⁺ reaction, is outer-sphere. The similarity of the rates for the vanadium(II) reduction of Co(NH₃)₅N₃²⁺ (18.0 l·mole⁻¹ sec⁻¹) and Co(NH₃)₅NCS²⁺ (0.3 l·mole⁻¹ sec⁻¹) suggests that these reactions are outer-sphere (79), but similar rates might also be expected here if substitution into the V²⁺ coordination sphere were rate determining. Other reasoning suggests that the reaction of V²⁺ with FeNCS²⁺ and FeCl²⁺ are outer-sphere (36). Thus the two rates are similar and are more rapid than rates which are generally observed for the replacement of a water molecule in the inner-coordination sphere of V²⁺. Other related studies have been reported (416, 419).

Candlin *et al.* (79) have compared kinetic data for the reduction of a wide range of pentamminecobalt(III) complexes with Cr²⁺, V²⁺, Eu²⁺, and Cr(bipy)₃²⁺. The variation in rate with V²⁺ as the reductant was found to be much smaller than with Cr²⁺, and to show sufficient similarity to the variation in rates observed with Cr(bipy)₃²⁺ to suggest that V²⁺ and Cr(bipy)₃²⁺ react by an outer-sphere mechanism. In contrast, the reactivity of Eu²⁺ toward the halopentamminecobalt(III) complexes (79) was found to decrease: Co(NH₃)₅F²⁺ > Co(NH₃)₅Cl²⁺ > Co(NH₃)₅Br²⁺ > Co(NH₃)₅I²⁺, a trend which has been interpreted in terms of an inner-sphere mechanism. A similar trend is observed in the reactions of Fe²⁺ with Co(NH₃)₅X²⁺ complexes (Fig. 1).

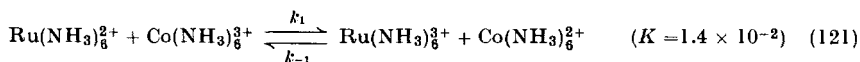
Candlin and Halpern (77) have examined volumes of activation for a number of Fe²⁺ reactions with cobalt(III) complexes as a possible means

of distinguishing between inner- and outer-sphere mechanisms. In the inner-sphere reaction, but not in the outer-sphere reaction, a coordinated water molecule is set free. Since the effective volume of the water molecule in the liquid is almost certainly larger than that when coordinated, more positive ΔV^\ddagger values should be observed for the inner-sphere process. The ΔV^\ddagger values observed range from 2.2 to 14 cc/mole and are consistent with inner-sphere mechanisms. Until a number of reactions of known mechanisms have been examined, however, this conclusion must be considered tentative.

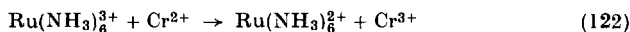
Endicott and Taube (122) have studied the reactions of $\text{Ru}(\text{NH}_3)_6^{2+}$ with pentammine and tetrammine cobalt(III) complexes. Since $\text{Ru}(\text{NH}_3)_6^{2+}$ undergoes substitution very slowly compared to the rate at which it is oxidized, and the product is $\text{Ru}(\text{NH}_3)_6^{3+}$ (121), there can be little doubt that these reactions are of the outer-sphere type. The redox potential for the $\text{Ru}(\text{NH}_3)_6^{2+}/\text{Ru}(\text{NH}_3)_6^{3+}$ couple was found to be 0.214 volt by measuring the position of the equilibrium (122, 123):



It is of interest that the $\text{Co}(\text{NH}_3)_6^{2+}/\text{Co}(\text{NH}_3)_6^{3+}$ couple (0.055 volt), but not the $\text{Co}^{2+}/\text{Co}^{3+}$ couple (1.95 volts), is less than this value. The reaction of $\text{Ru}(\text{NH}_3)_6^{2+}$ with $\text{Co}(\text{NH}_3)_6^{3+}$ is effective therefore only because $\text{Co}(\text{NH}_3)_6^{2+}$ is labile and is in effect removed from the equilibrium:



(Similar considerations also apply for other reactions in which cobalt(III) amines are reduced, e.g., with Fe^{2+} .) In view of the unfavorable free energy change it is surprising that this reaction is as rapid as it is ($k_1 = 1 \times 10^{-2} \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ at 25°). The reaction does not conform to the equation derived by Marcus for outer-sphere reactions (122). In the reaction of $\text{Ru}(\text{NH}_3)_6^{2+}$ with $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ complicated behavior is observed, the most likely explanation being that uncomplexed azide ion can also oxidize $\text{Ru}(\text{NH}_3)_6^{2+}$. The complex $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ ($k = 3.0 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$) reacts faster than the hydroxy complex $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$ ($k = 0.04 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$). It should be noted that for reactions in which $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$ does not react appreciably faster than $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$, i.e., with V^{2+} , $\text{Cr}(\text{bipy})_3^{3+}$, and $\text{Ru}(\text{NH}_3)_6^{2+}$, outer-sphere mechanisms are involved. In the reduction of $\text{Ru}(\text{NH}_3)_6^{3+}$, $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$, and $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ by Cr^{2+} (123), the net changes are



where in Eqs. (123) and (124) a water molecule probably completes the coordination sphere of $\text{Ru}(\text{NH}_3)_5^{2+}$.

The pentacyanocobalt(II) complex is a strong reducing agent (183) which is now thought to have a square pyramidal (415), or octahedral $\text{Co}(\text{CN})_5\text{H}_2\text{O}^{3-}$ structure (425). In the oxidation of $\text{Co}^{\text{II}}(\text{CN})_5^{3-}$ by pentamminecobalt(III) complexes in the presence of free cyanide ions, there is evidence for both inner- and outer-sphere mechanisms (78, 187). With $\text{X}^- = \text{Cl}^-$, N_3^- , NCS^- , and OH^- , the rate law is of the form

$$\text{Rate} = k_i[\text{Co}^{\text{II}}(\text{CN})_5^{3-}][\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}^{2+}] \quad (125)$$

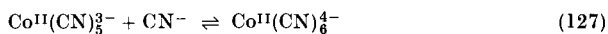
and, since $\text{Co}^{\text{III}}(\text{CN})_5\text{X}^{3-}$ ions are formed, it is concluded that the reactions proceed with the formation of an inner-sphere activated complex:



With $\text{X}^- = \text{PO}_4^{3-}$, CO_3^{2-} , SO_4^{2-} , NH_3 , and OAc^- , on the other hand, the reaction follows a different course and $\text{Co}^{\text{III}}(\text{CN})_6^{3-}$ is formed. The rate law shows a direct dependence on the concentration of cyanide ions,

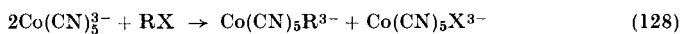
$$\text{Rate} = k_o[\text{Co}^{\text{II}}(\text{CN})_5^{3-}][\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}^{2+}][\text{CN}^-] \quad (126)$$

and reactions are thought to proceed by an outer-sphere mechanism involving $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}^{2+}$ and $\text{Co}^{\text{II}}(\text{CN})_6^{4-}$, where the latter is presumed to exist in equilibrium with $\text{Co}^{\text{II}}(\text{CN})_5^{3-}$:

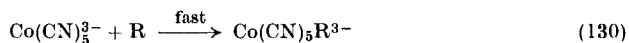
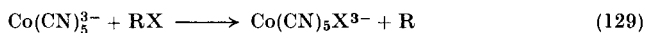


In two cases, with $\text{X}^- = \text{F}^-$ and NO_3^- , both inner- and outer-sphere paths are observed, and these can be made to predominate in turn by varying the concentration of cyanide ions. From the data in Table XV it can be seen that, for the outer-sphere reactions, there is only a relatively small variation in rate constants as X^- is varied.

Pentacyanocobalt(II) also reacts with organic halides in aqueous solution to form pentacyanoorganocobaltate(III) compounds according to the reaction:



Halpern and Maher (185) have studied the kinetics of such reactions with a number of organic halides, and in each case found the reaction to be first order in $\text{Co}(\text{CN})_5^{3-}$ and the halide. The results are interpreted in terms of the stepwise mechanism:



Second-order rate constants at 25° range from $2.5 \times 10^{-4} \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ for $\text{ClCH}_2\text{CO}_2^-$ to $9 \times 10^4 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ for $\text{ICH}_2\text{CO}_2\text{CH}_3$, the general trend reflecting an inverse dependence of the rate constant on the carbon-halogen bond strength.

TABLE XV
KINETIC DATA FOR INNER-SPHERE (k_i) AND OUTER-SPHERE (k_o)
 $\text{Co}^{\text{II}}(\text{CN})_5^{3-} - \text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}^{2+}$ REACTIONS (AT 25°, $\mu = 0.2$)
(78, 187)

X ⁻	k_i ($\text{l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$)	k_o ($\text{l}^2 \cdot \text{mole}^{-2} \text{ sec}^{-1}$)
Br ⁻	$> 2 \times 10^9$	—
Cl ⁻	$\sim 5 \times 10^7$	—
N ₃ ⁻	1.6×10^6	—
NCS ⁻	1.1×10^6	—
ONO ^{- a}	4.2×10^5	—
OH ⁻	9.3×10^4	—
NO ₂ ^{- a}	3.4×10^4	—
NH ₃	—	9×10^4
SO ₃ ²⁻	—	3.6×10^4
OAc ⁻	—	1.1×10^4
Fumarate ²⁻	—	1.2×10^4
Oxalate ²⁻	—	1.0×10^4
Malate ²⁻	—	7.5×10^3
Succinate ²⁻	—	6×10^3
CO ₃ ²⁻	—	$\sim 1 \times 10^3$
PO ₄ ³⁻	—	5.2×10^2
F ⁻	1.8×10^3	1.7×10^4
NO ₃ ⁻	$\leq 1.0 \times 10^4$	2.4×10^5

^a The nitro and nitrito complexes both give $\text{Co}(\text{CN})_5\text{NO}_2^{3-}$ as the final product. In the former, $\text{Co}(\text{CN})_5\text{ONO}^{3-}$ has been detected as an intermediate (186).

In the reactions of H-atoms with a variety of cobalt(III) ammine complexes, the ligands of the complex are inert toward the H-atoms with the possible exception of the complexes $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$, $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$, $\text{Co}(\text{NH}_3)_5(\text{O}_2\text{CCH}=\text{CHCO}_2\text{H})^{2+}$, and $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$, and reactions proceed with the reduction of cobalt(III) to cobalt(II). There is only general agreement between the rate constants determined by Halpern and Rabani (189), Anbar and Meyerstein (20), and Navon and Stein (274), and numerical values for any one reaction differ by as much as two powers of ten. The nature of the reductant, its low reactivity toward $\text{Co}(\text{NH}_3)_6^{3+}$, and the very drastic solvation change associated

with the direct outer-sphere oxidation of H-atoms to H_3O^+ (which will be more extensively solvated), tend to favor attack of the H-atom on the anionic ligand (189):



The reactivity pattern, $\text{Co}(\text{NH}_3)_5\text{I}^{2+} > \text{Co}(\text{NH}_3)_5\text{Br}^{2+} > \text{Co}(\text{NH}_3)_5\text{Cl}^{2+} > \text{Co}(\text{NH}_3)_5^{2+}$, is the same as that observed with Cr^{2+} and $\text{Co}(\text{CN})_5^{3-}$ as reductant, but the reverse of that observed for Eu^{2+} and Fe^{2+} (Fig. 1).

Recent studies of the reduction of $\text{Co}(\text{en})_2\text{NCSX}^+$ complexes by chromium(II) (177) and of $\text{Co}(\text{en})_2\text{ClX}^+$ complexes by iron(II) (56) ($\text{X}^- = \text{H}_2\text{O}$, NH_3 , Cl^- , and SCN^-) have shown that *cis* and *trans* isomers differ considerably in reactivity. Although the chromium(II) reactions proceed via thiocyanate-bridged activated complexes, while the iron(II) reactions are believed to proceed via chloride-bridged activated complexes (with the possible exception of $\text{Co}(\text{en})_2\text{ClN}_3^+$), the same sort of general pattern emerges in both series of reactions. First of all, for $\text{X}^- = \text{NH}_3$ or NCS^- , only minor differences between the rates of the *cis* and *trans* isomers are observed. Second, replacement of NH_3 by NCS^- in either the *cis* or *trans* position results in a modest increase in rate. Third, replacement of NH_3 by H_2O results in a large increase in rate, especially for the *trans* compound. The observed nonbridging ligand effects have been discussed (56) in terms of the models proposed by Orgel (292) and Taube (376, 377) (see also page 166). Green *et al.* (165) have investigated the extent to which the stretching of $\text{Co}-\text{NH}_3$ bonds is important in the reactions of $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$, $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, $\text{Co}(\text{en})_2\text{NH}_3\text{Cl}^{2+}$, and $\text{Co}(\text{en})_2(\text{NH}_3)\text{H}_2\text{O}^{2+}$ with Cr^{2+} . The kinetic fractionation factors $d(\ln[^{14}\text{N}])/d(\ln[^{15}\text{N}])$ are very small (1.002 and 1.001) for the first two complexes, and identical with NH_3 *cis* or *trans* to the bridging group in the ethylenediamine complexes. It is concluded that in these reactions at least there is little change in $\text{Co}-\text{NH}_3$ bond lengths attendant on electron transfer.

Kruse and Taube (245) have shown that, in the reaction of Cr^{2+} with *cis*- $\text{Co}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$, only one oxygen atom is transferred to the chromium atom. This demonstrates that electron transfer proceeds via a singly bridged activated complex. The reductions of *cis*- and *trans*-diaquo and aquoamminebis(ethylenediamine)cobalt(III) complexes by Cr^{2+} have been studied by Cannon and Earley (80) and found to obey the rate law:

$$\text{Rate} = k[\text{Co}^{\text{III}}][\text{Cr}^{\text{II}}][\text{H}^+]^{-1} \quad (132)$$

At 25° second-order rate constants $\times 10^{-6}$ ($\text{l} \cdot \text{mole}^{-1} \text{sec}^{-1}$) and activation energies (kcal mole^{-1}) for the reduction of the hydroxo complexes are: aquo complexes, *cis* 0.79, 6.4; *trans* 2.6, 2.6; ammine complexes, *cis* 0.20,

6.2; *trans* 0.22, 2.4. Outward motion of the ligand *trans* to the bridging group at the time of electron transfer is probably much less important in these reactions. The variation in activation energies may be due to reorganization requirements within the binuclear complex, or enthalpy requirements for the formation of the binuclear complex.

Haim (172) has compared the rates of reduction of *cis*- and *trans*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$ and $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ by Fe^{2+} (Table XVI). All three

TABLE XVI
RATE CONSTANTS k_1 AND k_2 FOR THE REACTION OF Fe^{2+} WITH AZIDE
COMPLEXES OF Co^{III} (AT 25°)

Co^{III} complex	k_1 ($l \cdot \text{mole}^{-1} \text{ sec}^{-1}$)	k_2 ($l^2 \cdot \text{mole}^{-2} \text{ sec}^{-1}$)
$\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$	0.009	—
<i>trans</i> - $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$	0.073	1.36
<i>cis</i> - $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$	0.186	—
<i>trans</i> - $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{N}_3^{2+}$	24.0	—
<i>cis</i> - $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{N}_3^{2+}$	0.355	—

reactions show a first-order dependence on each of the reactants, but, whereas the reactions of $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ and *cis*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$ are independent of the hydrogen-ion concentration, that of *trans*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$ shows a strong direct dependence:

$$k_{\text{obs}} = k_1 + k_2[\text{H}^+] \quad (133)$$

Because of the substitution lability of the Fe^{III} product, it cannot be ascertained whether these reactions proceed *via* a bridged or outer-sphere activated complex. Assuming that bridged activated complexes are formed, reasonable explanations can be advanced for the relative rates of these reactions. The increased reactivity of *trans*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$ as compared to $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ is as expected, but the reaction of the *cis* complex is faster still. In the latter case the most probable explanation is that both azide ligands bridge the reactants in the activated complex. With the *trans* isomer, one of the azide ions is non-bridging and protonation of this ligand facilitates electron transfer. Haim (173) has also studied the reduction of *cis*- and *trans*- $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{N}_3^{2+}$ with iron(II). The enhanced rate with a water molecule in the *trans* position is again noted.

Kopple and Miller (240) have determined the rates of reaction of a number of tetramminecobalt(III) complexes with chromium(II). With *trans*- $\text{Co}(\text{NH}_3)_4(\text{OAc})_2^+$ there is a direct hydrogen-ion dependence

($k = 15 + 50[\text{H}^+] \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ at 25°) and the reaction is appreciably faster than the reaction of $\text{Co}(\text{NH}_3)_5\text{OAc}^{2+}$ ($k = 0.18 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$), which has no hydrogen-ion dependence. In the case of the *cis*- $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{OAc}^{2+}$ complex there is an inverse hydrogen-ion dependence ($k = 47 + 2.8[\text{H}^+]^{-1} \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$), and since CoOAc^{2+} is the product a part of the reaction at least probably proceeds by a di-bridged activated complex with bridging hydroxo and acetato ligands. Similar reasoning applies in the reaction of *cis*- $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{SO}_4^+$ with Cr^{2+} (269), although in this instance the hydrogen-ion dependence is more complex:

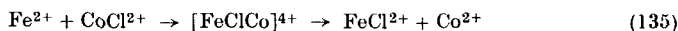
$$k_{obs} = 1.1[\text{H}^+]^{-1} + 3.0 + 8.5[\text{H}^+]$$

In the reduction of $\text{Co}^{\text{III}}\text{EDTA}^-$ (which may be written CoY^-) and related complexes with Fe^{2+} (303, 406) and Cr^{2+} (405), it is concluded that both series of reactions are of the inner-sphere type. One or two carboxylate groups of the chelate ligand are believed to form bridging groups, except in the case of $\text{Co}^{\text{III}}(\text{HY})\text{Cl}^-$ and $\text{Co}^{\text{III}}(\text{YOH})\text{OH}$. In the latter the bridging ligands are the chloro and hydroxo groups, respectively. In the reduction of CoY^- and $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ in weak acid solutions, some of the chromium(III) product is coordinated to three carboxylato groups (405). It now seems doubtful whether more than two carboxylate groups are transferred in the initial step (407).

At 0° the rate equation for the reaction of iron(II) and cobalt(III) aquo ions (53) is of the form:

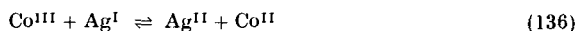
$$\text{Rate (sec}^{-1}\text{)} = 10[\text{Fe}^{2+}][\text{Co}^{3+}] + 6500[\text{Fe}^{2+}][\text{CoOH}^{2+}] \quad (134)$$

That the rate is some 10^5 times slower than that predicted by the Marcus theory is probably due to spin restrictions of the cobalt(III) reactant. With CoCl^{2+} as the oxidant it has been established that the reaction is of the inner-sphere type (94),



and high intermediate concentrations of FeCl^{2+} have been detected. Other $\text{Fe}^{\text{II}}\text{-Co}^{\text{III}}$ reactions are of the inner-sphere type (421).

Kirwin *et al.* (238) find that the reaction of cobalt(III) with silver(I) consists of a rapid equilibrium,



followed by the reaction of Ag^{II} with water. The latter reaction has been studied separately (237) and the rate law is of the form,

$$\text{Rate} = k[\text{Ag}^{\text{II}}]^2[\text{Ag}^{\text{I}}]^{-1} \quad (137)$$

which is consistent with a mechanism:



It can be concluded therefore that the Ag^{III} and not the Ag^{II} oxidizes water.

Dulz and Sutin (116) have used flow techniques to study the kinetics of the reaction of Cr^{2+} with Fe^{3+} in the presence of chloride ions. The rate equation is

$$\text{Rate} = k_1[\text{Cr}^{2+}][\text{Fe}^{3+}] + k_2[\text{Cr}^{2+}][\text{FeOH}^{2+}] + k_3[\text{Cr}^{2+}][\text{FeCl}^{2+}] + k_4[\text{Cr}^{2+}][\text{Fe}_3^{+}][\text{Cl}^{-}] \quad (140)$$

and, at 25° and $\mu = 1.0 M$, $k_1 = 2.3 \times 10^3 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$, $k_2 = 3.3 \times 10^6 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$, $k_3 = 2.0 \times 10^7 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$, and $k_4 = 2.0 \times 10^4 \text{ l}^2 \cdot \text{mole}^{-2} \text{ sec}^{-1}$. It is possible to identify the two chloride paths since observed rates are different if, in the one case, a $\text{Cr}^{2+} + \text{Cl}^{-}$ solution is allowed to react with Fe^{3+} and, in the other, both the Cr^{2+} and Fe^{3+} solutions are premixed with equivalent amounts of chloride. The reaction path k_3 is of the inner-sphere type, but the activated complex for k_4 , which also involves chloride, is less certain. In similar experiments using thiocyanate instead of chloride, Haim and Sutin (176) have shown that CrSCN^{2+} (35%) and CrNCS^{2+} (65%) are both produced (see page 165).

A quenching method has been used by Adamson *et al.* (9) to study the kinetics of the oxidation of iron(II) by cerium(IV):

$$-d[\text{Fe}^{\text{II}}]/dt = k[\text{Fe}^{\text{II}}][\text{Ce}^{\text{IV}}] \quad (141)$$

Both reactants were in the micromolar concentration range, the overall rate constant k being of the order of $10^3 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ at 0.3° . The hydrogen-ion dependence is of the approximate form

$$k = a[\text{H}^{+}] + b + c[\text{H}^{+}]^{-1} \quad (142)$$

and, since the principal Ce^{IV} species is CeOH^{3+} and not Ce^{4+} , this corresponds to reaction steps $\text{Ce}^{4+} + \text{Fe}^{2+}$, $\text{CeOH}^{3+} + \text{Fe}^{2+}$, and $\text{Ce}(\text{OH})_2^{2+} + \text{Fe}^{2+}$, respectively. The reaction is catalyzed by bisulfate and fluoride, but not by chloride.

The reaction of iron(II) with manganese(III)



has been studied by Diebler and Sutin (104) using a flow technique, and by Nicol and Rosseinsky (289) using a polarographic method. At 25° , k_{obs} is of the order of $10^4 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$, where

$$k_{obs} = k_1 + k_2[\text{H}^{+}]^{-1} \quad (144)$$

Activation parameters for k_1 are $\Delta H^\ddagger = 12.1$ kcal mole⁻¹ and $\Delta S^\ddagger = -1.3$ eu. The one-equivalent reaction of manganese(II) with cobalt(III) ($k_{obs} \sim 10^2$ l·mole⁻¹ sec⁻¹ at 25°) has been studied in less detail (104). Oxidation of manganese(II) with cerium(IV) (32) in 4.5 *M* sulfuric acid proceeds to an equilibrium

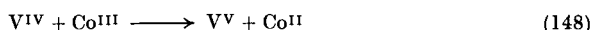
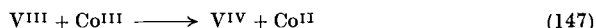


the equilibrium constant being 0.015 at $\sim 20^\circ$.

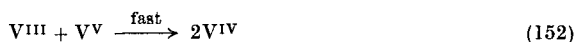
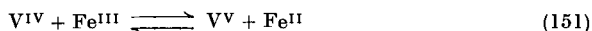
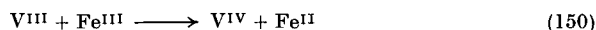
Rosseinsky and Higginson (327) have studied the reaction of vanadium(IV) with cobalt(III),



and in addition the reaction of vanadium(III) with cobalt(III). In the latter the full reaction sequence is



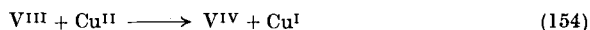
rate constants for the hydrogen ion-independent paths in Eqs. (147) and (148) being 0.192 and 0.260 l·mole⁻¹ sec⁻¹, respectively, at 0°. The reaction of vanadium(III) and iron(III) follows a similar sequence (200),



the overall reaction being represented by Eq. (150). Although the equilibrium in reaction (151) lies well to the left ($K \sim 10^{-6}$), reaction (152) is sufficiently fast to make the path provided by reactions (151) and (152) effective in the absence of large amounts of Fe^{II}. Copper(II) catalyzes the reaction, and with Cu^{II} concentrations at least equivalent to those of Fe^{III} the catalyzed reaction predominates. Under those conditions the rate is independent of Fe^{III},

$$\text{Rate} = k_{cat}[\text{V}^{\text{III}}][\text{Cu}^{\text{II}}] \quad (153)$$

which is consistent with a mechanism:



The vanadium(III)–vanadium(V) reaction has been studied by making use of the high vanadium(V) absorption in the 300–350 mμ

region, and by using low reactant concentrations (101). A feature of the reaction is the complex hydrogen-ion dependence:

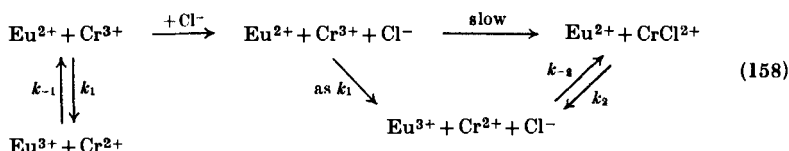
$$k_{obs} = k_1[H^+] + k_2 + k_3[H^+]^{-1} + k_4[H^+]^{-2} \quad (156)$$

The reaction of vanadium(V) with iron(II),



has been studied by two different methods (100, 288). Again there is a direct and an inverse hydrogen ion-dependent path, which suggests that the vanadium(V) ion VO_2^+ can bring either a proton or an OH^- into the activated complex.

That the reaction of europium(II) with vanadium(III) (10) is slower than the corresponding chromium(II)–vanadium(III) reaction is at least in part due to the difficulty in transferring f electrons. In the reaction of europium(II) with chromium(III) there is incomplete reaction, the equilibrium constant K being ~ 2 . The following reactions have been studied,

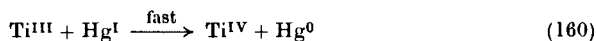


k_1 and k_{-1} being of the order of $10^{-5} \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ and k_2 around $10^{-3} \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ at 25° .

The effect which chloride ions have on a number of titanium(III) reactions is of interest. Thus with iron(III) there is a marked catalysis (97) but with plutonium(IV) (315) there is little or no effect [contrast the large effect which chloride has on the $\text{Fe}^{\text{II}}\text{--Pu}^{\text{IV}}$ reaction (286)] and, with mercury(II), chloride ions inhibit the reaction (97). Chloride ions have little or no effect on the plutonium(IV) oxidation of vanadium(III) and uranium(IV) (316), but inhibit the reaction of iron(II) with thallium(III), and the thallium(I)–thallium(III) exchange (147, 191). There is a first-order dependence on metal ion concentrations in the reaction between titanium(III) and mercury(II) (97). The first step

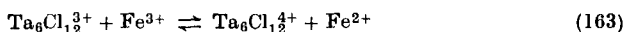
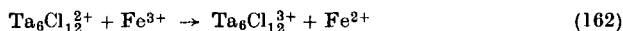


is rate-determining, and is presumably followed by



Unless mercury(II) is in excess of the titanium(III), mercury is precipitated. Similar mechanisms are observed with chromium(II) and europium(II) as the reducing ion (371). In the mercury(II) oxidation of vanadium(III) the rate equation is complex (197). The oxidation of iron(II) by mercury(II) is very slow (7).

The oxidation of tantalum clusters, $\text{Ta}_6\text{Cl}_{12}^{2+}$, with iron(III) proceeds stepwise (132):



The equilibrium constant for the second stage is less than unity, and iron(III) concentrations greater than ca. 0.01 *M* are required to effectively convert 10^{-5} *M* $\text{Ta}_6\text{Cl}_{12}^{2+}$ to $\text{Ta}_6\text{Cl}_{12}^{4+}$. With initial concentrations of iron(III) of around 10^{-4} *M*, the rate constant for reaction (162) can be determined and is found to be 620 l·mole⁻¹ sec⁻¹ at 15° and $\mu = 0.02$ *M*.

When vanadium(II) and uranium(VI) are mixed (283), the first step



is followed by



The rates observed for reactions (165), (166), and (167) are such that it is difficult to determine directly the rate of reaction (164) but, if an excess of vanadium(IV) is added, the reaction

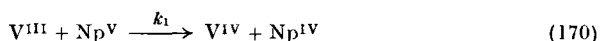


is much faster than reactions (165), (166), and (167). Under these conditions the uranium(VI) in effect catalyzes the reaction of vanadium(II) with vanadium(IV). The only term in the rate law is

$$\text{Rate} = k_1[\text{V}^{\text{II}}][\text{U}^{\text{VI}}] \quad (169)$$

and k_1 is essentially independent of the hydrogen-ion concentration. The activation parameters for k_1 are $\Delta H^\ddagger = 7.1$ kcal mole⁻¹ and $\Delta S^\ddagger = -26.1$ eu. The reaction of vanadium(III) and uranium(VI) has already been referred to (page 188).

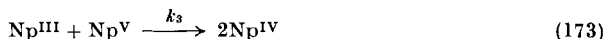
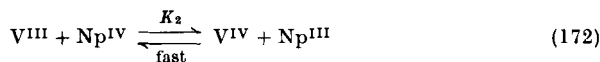
The reaction of vanadium(III) with neptunium(V) (25)



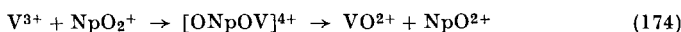
proceeds only in part by the direct route. The rate law is of the form

$$-d[\text{NpO}_2^+]/dt = [\text{NpO}_2^+][\text{V}^{3+}](k_1 + k_3 K_2[\text{Np}^{4+}][\text{VO}^{2+}]^{-1}) \quad (171)$$

which is consistent with additional steps:



The rate constant k_3 can be obtained independently, and K_2 for the equilibrium in reaction (172) can be determined directly by mixing solutions of vanadium(III) and neptunium(IV). The first stage, Eq. (170), differs from other reactions involving oxyocations in that the rate law does not have a direct hydrogen-ion dependence. This suggests that there is oxygen-atom bridging,



where the NpO_2^+ subsequently equilibrates with H^+ ions. The activation parameter corresponding to k_1 and $\Delta H^\ddagger = 14.6$ kcal mole⁻¹ and $\Delta S^\ddagger = -12.3$ eu. In the reduction of neptunium(VI) by vanadium(III) (336), there is an inverse hydrogen-ion dependence:

$$\text{Rate} = [\text{Np}^{\text{VI}}][\text{V}^{\text{III}}](k_1 + k_2[\text{H}^+]^{-1}) \quad (175)$$

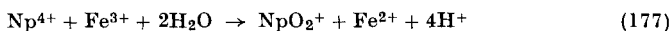
Activation parameters for k_1 are $\Delta H^\ddagger = 18.6$ kcal mole⁻¹ and $\Delta S^\ddagger = 5$ eu.

The vanadium(III) reductions of plutonium(IV) (277) and plutonium(VI) (310) have been studied, and are relatively straightforward. In both instances single-stage one-equivalent reactions are observed, and the hydrogen-ion dependence is of the form:

$$k_{\text{obs}} = k_1[\text{H}^+]^{-1} + k_2[\text{H}^+]^{-2} \quad (176)$$

With titanium(III) as the reducing ion both the plutonium(IV) (315) and plutonium(VI) (314) reactions have just one inverse hydrogen ion-dependent path.

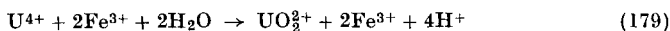
A feature of reactions in which the extent of hydrolysis of one of the reactants increases markedly in going to products is the large inverse hydrogen-ion dependence. In the oxidation of neptunium(IV) to neptunium(V), for example, the overall equation (214) being



the rate law is

$$-d[\text{Np}^{\text{IV}}]/dt = k[\text{Np}^{\text{IV}}][\text{Fe}^{\text{III}}][\text{H}^+]^{-3} \quad (178)$$

and the reaction is more favorable when the hydrolysis of Np^{4+} approaches that of the products. In the corresponding reaction of iron(III) with uranium(IV) (58), uranium(VI) is the final product,



and the first step in which uranium(V) is formed is rate-determining. Betts (58) reports a hydrogen-ion dependence:

$$-d[\text{U}^{\text{IV}}]/dt = [\text{U}^{\text{IV}}][\text{Fe}^{\text{III}}](k_1[\text{H}^+]^{-1} + k_2[\text{H}^+]^{-2}) \quad (180)$$

The reaction has also been studied in sulfuric and hydrochloric acid solutions (135). Similar kinetics are observed for the reaction with cerium(IV) (39), the rate equation being

$$-d[\text{U}^{\text{IV}}]/dt = k[\text{U}^{\text{IV}}][\text{Ce}^{\text{IV}}][\text{H}^+]^{-2} \quad (181)$$

The disproportionation of uranium(V)



is rapid (219a), the rate law showing a direct hydrogen-ion dependence,

$$\text{Rate (sec}^{-1}) = 436[\text{UO}_2^+]^2[\text{H}^+] \quad (183)$$

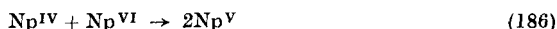
which is as expected since there is a conversion of UO_2^+ to U^{4+} . Newton and Baker (284) have shown that the disproportionation is much slower in the presence of uranium(VI) due to the formation of a binuclear complex:



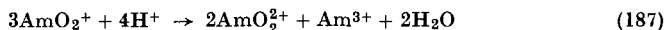
The disproportionation of plutonium(V) (309) is much slower than that of uranium(V),

$$\text{Rate (sec}^{-1}) = 3.6 \times 10^{-3}[\text{PuO}_2^+]^2[\text{H}^+] \quad (185)$$

the activation energy (19 kcal mole⁻¹) being twice that for the uranium reaction. Sullivan *et al.* (354) have obtained data for the disproportionation of neptunium(V) by studying the reverse reaction (203):



In the disproportionation of americium(V) (88), the net reaction is

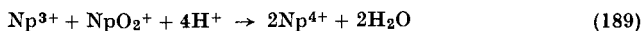


The rate equation for $\mu = 2.0 M$ perchlorate solutions is

$$-d[\text{AmO}_2^+]/dt = k_1[\text{AmO}_2^+]^2[\text{H}^+]^2 + k_2[\text{AmO}_2^+]^2[\text{H}^+]^3 \quad (188)$$

and, at 25°, $k_1 = 7.0 \times 10^{-4} \text{ l}^3 \cdot \text{mole}^{-3} \text{ sec}^{-1}$ and $k_2 = 4.6 \times 10^{-4} \text{ l}^4 \cdot \text{mole}^{-4} \text{ sec}^{-1}$. Although the acid dependence is lower than the fourth-power dependence previously reported (180, 345), it remains higher than for the other disproportionations. This difference in behavior is difficult to explain.

The reaction of neptunium(III) with neptunium(V) has been studied (202),



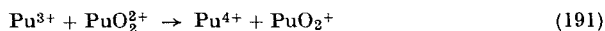
and the rate law is

$$\text{Rate (sec}^{-1}\text{)} = 43[\text{Np}^{3+}][\text{NpO}_2^+][\text{H}^+]$$

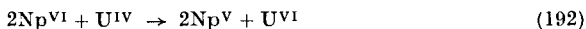
A slower rate is observed for the corresponding plutonium(III)-plutonium(V) reaction (308):

$$\text{Rate (sec}^{-1}\text{)} = 0.04[\text{Pu}^{3+}][\text{PuO}_2^+][\text{H}^+] \quad (190)$$

With plutonium(III) and plutonium(VI) (313), the reactants and products are in the same hydrolyzed state and there is no hydrogen-ion dependence:



The rate-determining step in the reaction (356)



corresponds to a change,



and the rate law (in sec^{-1}) is

$$d[\text{NpO}_2^+]/dt = 21.35[\text{U}^{4+}][\text{NpO}_2^{2+}][\text{H}^+]^{-1} \quad (194)$$

Newton has studied the reactions of uranium(IV) with plutonium(IV) (277) and plutonium(VI) (276). The reaction of neptunium(V) with uranium(IV) is complex (335).

VI. Noncomplementary and Two-Equivalent Reactions

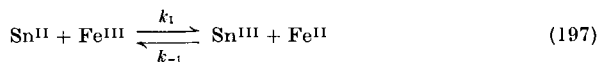
Noncomplementary reactions are those occurring between one- and two- or three-equivalent reagents. A good example is the reaction of tin(II) with iron(III):



This reaction is slow in perchloric acid solution but is strongly catalyzed by chloride ions (161), which serve to complex (and keep in solution) the tin(IV) which is formed. At high iron(III) to tin(II) ratios the rate law is of the form,

$$-d[\text{Fe}^{\text{III}}]/dt = k_{\text{obs}}[\text{Fe}^{\text{III}}][\text{Sn}^{\text{II}}] \quad (196)$$

where k_{obs} is strongly dependent on the chloride concentration. To account for data over a wide range of conditions, Weiss (397) proposed the mechanism:



Applying stationary-state kinetics for the unstable Sn^{III} state, it can be shown that

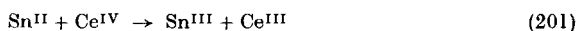
$$\frac{-d[\text{Fe}^{\text{III}}]}{dt} = \frac{2k_1 k_2 [\text{Fe}^{\text{III}}]^2 [\text{Sn}^{\text{II}}]}{k_{-1} [\text{Fe}^{\text{II}}] + k_2 [\text{Fe}^{\text{III}}]} \quad (199)$$

On adding quantities of Fe^{II} initially so that $k_{-1} [\text{Fe}^{\text{II}}] \gg k_2 [\text{Fe}^{\text{III}}]$, this reduces to an equation of the type

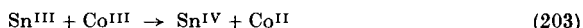
$$\frac{-d[\text{Fe}^{\text{III}}]}{dt} = \frac{a [\text{Fe}^{\text{III}}]^2 [\text{Sn}^{\text{II}}]}{[\text{Fe}^{\text{II}}]} \quad (200)$$

which is the form of the rate law found by Noyes (290). Duke and Pinkerton (112) have studied the chloride-ion dependence and found this to be complex. More recently (398), using a cobalt(III) complex as substrate, it has been possible to show that a strongly reducing intermediate is formed in 1.0 *N* hydrochloric acid solutions, and the results of a brief kinetic study are in good agreement with the mechanism outlined above. Other reaction sequences, in which there is intermediate formation of $[\text{Fe} \cdot \text{Sn}]^{\text{V}}$ or Fe^{I} , would show different kinetic behavior.

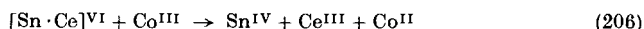
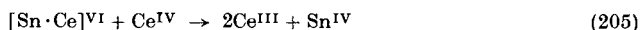
The induced reduction of cobalt(III) complexes has also been used to test for the formation of tin(III) in other reactions of tin(II) (398). In the reactions with cerium(IV), chromium(VI), and manganese(VII), it has been concluded that tin(III) or a related reducing intermediate is formed. Thus in the reaction with cerium(IV) the most likely mechanism is



with the additional step



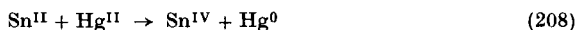
but without a full kinetic study the alternative mechanism



cannot be entirely eliminated. In the reactions with mercury(II) and thallium(III) (and hydrogen peroxide, bromine, and iodine), tin(III) does not appear to be formed as an intermediate (398). Thus the reaction with thallium(III) appears to be of the single-stage two-equivalent type,

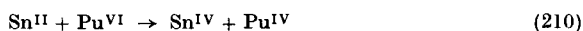


and on balance a two-equivalent first step is highly probable in the tin(II)–mercury(II) reaction:

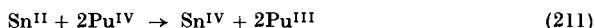


Both these reactions are rapid.

That the reduction of plutonium(VI) with tin(II) in mixed chloride-perchlorate media (317)



is much more rapid than the reduction of plutonium(V) with tin(II) has been interpreted as evidence that reaction (210) proceeds in a single step involving the transfer of two equivalents of charge. The reduction of plutonium(IV) by tin(II) becomes appreciable at chloride concentrations in the 1.5–2.0 *M* range (311),



and tin(III) is probably involved as an intermediate. That reaction (211) should be so much more susceptible to chloride catalysis than reaction (210) is reasonable since the plutonium(IV) is present as Pu^{4+} .

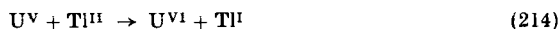
The two-equivalent reaction between uranium(IV) and thallium(III)



has been extensively studied. Harkness and Halpern (192) report a first-order dependence on both reactants, but this gives no information regarding the possible intermediate formation of U^{V} and Tl^{II} . Thus, a first step



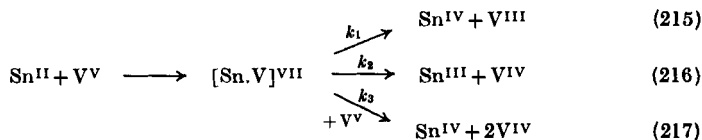
followed by the fast reaction



would give second-order kinetics, as would the mechanism involving simultaneous transfer of two electrons. Since the uranium(IV), (V), and (VI) oxidation states are predominantly U^{4+} , UO_2^+ , and UO_2^{2+} , the increase in hydrolysis occurs in the first stage, $\text{U}^{\text{IV}} \rightarrow \text{U}^{\text{V}}$, of a two-stage process, and energetically this would not necessarily provide an easier route. More recently Wear (394) has examined the effect which a 2000-fold variation in the concentrations of reactants has on the kinetics. Although his results provide general support for the work of Harkness and Halpern (192), the orders with respect to $[\text{U}^{\text{IV}}]$ and $[\text{Tl}^{\text{III}}]$ have been found to change with concentration. The variations can be accounted for by considering a second term in $[\text{U}^{\text{IV}}]^2$ in the rate equation. Such a

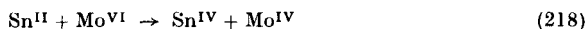
term can be explained by the polymerization of U^{IV} . Alternatively, a chain mechanism involving Tl^{II} and U^{V} can be used to provide a qualitative explanation of the data. However, since concentrations of Tl^{II} and U^{V} cannot as yet be determined, no quantitative treatment is possible. Quinn *et al.* (306) have noted small increases in rate constants in the presence of fumaric, malic, and malonic acids. It is interesting to note that with fumaric acid a maximum value in the rate constant is observed in solutions containing roughly equivalent amounts of fumaric acid and U^{IV} , and rates then decrease as more fumaric acid is added. The addition of oxalic and succinic acids results in a decrease in the rate. The reaction is complex in the presence of tartaric acid (307).

Reduction of vanadium(V) by an excess of tin(II) in dilute hydrochloric acid yields a mixture of vanadium(III) and vanadium(IV) (110). The dependence of the concentrations of these products upon reactant concentrations shows that the dominant initial step involves a two-equivalent change in oxidation states giving vanadium(III). Three distinct routes are postulated:

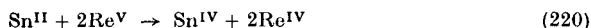


Some of the V^{III} formed in reaction (215) reacts further with V^{V} . The relative rates are $k_1 > k_2 > k_3$.

Product analysis has shown that, in concentrated hydrochloric acid, tin(II) and molybdenum(VI) react to give equimolar concentrations of molybdenum(V) and molybdenum(III) as initial products (57). This suggests that the reaction proceeds as follows,

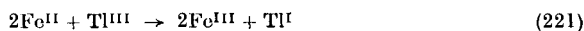


the first step being a two-equivalent change. The reaction of tin(II) with rhenium(V)



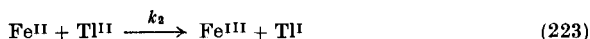
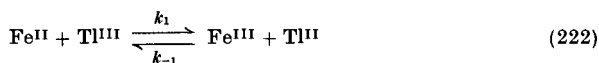
has also been studied (42).

Information regarding the mechanisms of noncomplementary reactions can often be obtained by the addition of reaction products. In the reaction,

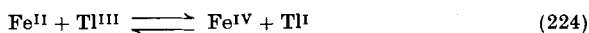


for example, curvature which second-order plots normally show after about 60% reaction becomes more pronounced with the addition of

Fe^{III} , but Tl^{I} has no similar effect (30). This is consistent with a mechanism,



but not the alternative:



Applying stationary-state kinetics for Tl^{II} in reactions (222) and (223), the rate equation

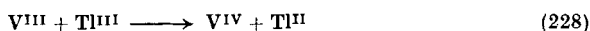
$$\frac{-d[\text{Fe}^{\text{II}}]}{dt} = \frac{2k_1 k_2 [\text{Fe}^{\text{II}}]^2 [\text{Tl}^{\text{III}}]}{k_{-1} [\text{Fe}^{\text{III}}] + k_2 [\text{Fe}^{\text{II}}]} \quad (226)$$

is obtained. Experimental data have been shown to fit the integrated form of this equation. In the presence of platinum metal, second-order plots are linear to at least 80% completion. Since the gradient is identical to that of the initial part of the plot in the absence of platinum, this suggests that there is no catalysis of reaction (222). There can therefore be no catalysis of the reverse of reaction (222), and reaction (223) is the only one which is catalyzed (195). The thallium(I)–thallium(III) exchange is also catalyzed by platinum metal (148). At an ionic strength $\mu = 3.0$ *N* the iron(II)–thallium(III) reaction is dependent on the inverse hydrogen-ion concentration, and there are terms corresponding to the inclusion of one and two OH^- ions in the activated complex (30, 221).

Reactions in which thallium(III) is reduced by vanadium(II), vanadium(III), and vanadium(IV) have been studied. The fastest of these is the reaction with vanadium(III),



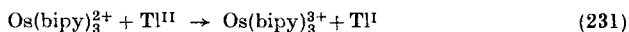
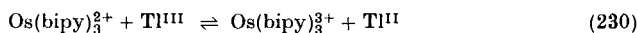
which has been studied in acid perchlorate solutions, 0.30–1.90 *M* in perchloric acid (99). The reaction is first order with respect to both vanadium(III) and thallium(III), and a mechanism involving thallium(II)



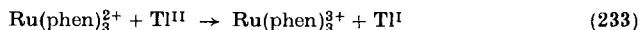
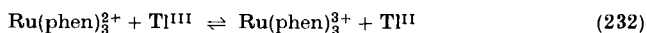
is in accordance with experiment. The data do not allow the hydrogen-ion dependence to be specified exactly, but the dependence is predomi-

nantly inverse power in $[H^+]$. At 0.5° and in $1.0 M$ perchloric acid, $k_{obs} = 353 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$. A mechanism involving a two-equivalent first step is not compatible with experimental data (99, 197). This is not unreasonable, since extensive changes in the degree of hydrolysis of the vanadium ion are required for the conversion of V^{3+} to VO_2^+ . The rate of the reaction of vanadium(II) with thallium(III) (37) is significantly less than that of vanadium(III), and the product is predominantly vanadium(IV). It is concluded (37) that there is in this instance a two-equivalent oxidation of the vanadium(II). At 0° and in $1.0 M$ perchloric acid, $k_{obs} \sim 68 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$. The reaction of vanadium(IV) with thallium(III) is slow and has to be studied at elevated temperatures (367). Thallium(II) is believed to be formed as an intermediate.

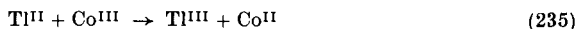
In the outer-sphere reaction between $Os(bipy)_3^{2+}$ and thallium(III) (220), the mechanism is



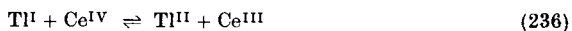
The rate increases only slightly as the hydrogen-ion concentration decreases, and Tl^{3+} and $TlOH^{2+}$ must therefore react at about the same rate. Similar results have been obtained for the thallium(I)–thallium(III) exchange (325), and the implication may be that the latter is also outer-sphere. The addition of small concentrations of chloride produces a retardation as in other thallium(III) reactions. The reactions of the tris(1,10-phenanthroline), tris(bipyridyl), and bis(terpyridyl) complexes of ruthenium(II) with thallium(III) have also been studied (268). Thallium(II) is again formed as an intermediate:



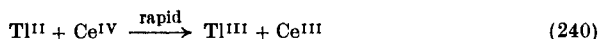
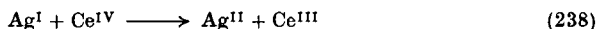
Reactions in which thallium(I) is oxidized to thallium(III) can also proceed with intermediate formation of thallium(II). Thus the mechanism of the reaction of thallium(I) with cobalt(III) (31) is



At 53.9° and in $6.2 N$ nitric acid, the reaction of thallium(I) with cerium(IV) (168) follows a similar reaction sequence,



but there are additional reactions involving hydroxyl radicals. The reaction has been studied in perchloric acid solutions at lower temperatures with silver(I) as catalyst (197), when the reaction sequence is:



Silver(I) and manganese(II) catalyze the oxidation of mercury(I) with cerium(IV) (169).

In the thallium(III) oxidation of chromium(II), thallium(II) does not appear to be formed as an intermediate (27). The reaction is first order in both the reactants, but a green binuclear chromium(III) complex is produced, and this suggests that a two-equivalent reaction

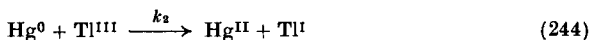
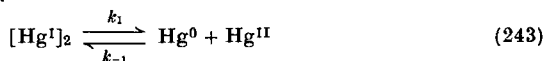


followed by



is effective. The chloride dependence of the reaction has been studied at 25° (114). The reactant TlCl_2^{2+} produces about 50% hexaquo chromium(III) and 50% monochlorochromium(III) ions, whereas TlCl_2^+ , TlCl_3 , and TlCl_4^- produce mainly monochlorochromium(III).

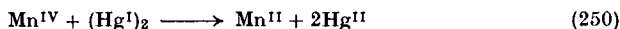
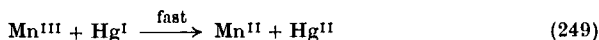
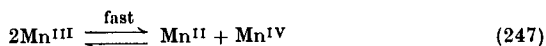
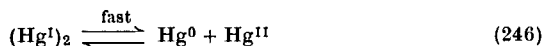
The rate of the reaction of the mercury(I) dimer with thallium(III) is inversely proportional to the concentration of mercury(II) (28, 29), suggesting the mechanism:



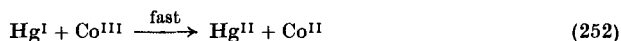
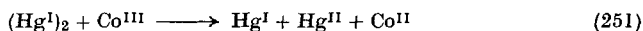
The equilibrium first step is assumed to be rapid, and the reaction between Hg^0 and Tl^{III} rate-determining. The resulting rate law is:

$$\frac{d[(\text{Hg}^{\text{I}})_2]}{dt} = \frac{k_1 k_2 [(\text{Hg}^{\text{I}})_2] [\text{Tl}^{\text{III}}]}{k_{-1} [\text{Hg}^{\text{II}}]} \quad (245)$$

Using an estimated value for k_1/k_{-1} of $\sim 10^{-9} \text{ mole}^{-1}$, k_2 is of the order of $10^4 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$. The dismutation first step is also effective in the manganese(III) oxidation of the mercury(I) dimer (326). This is followed by a more complex reaction sequence in which manganese(IV) is involved:



In the cobalt(III) oxidation of the mercury(I) dimer, a different mechanism is observed (327). The rate is first order in both reactants but there are no other concentration terms. This is consistent with the mechanism:

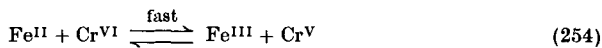


The dismutation reaction, as in reaction (243), appears to play no part in this reaction. The silver(II) oxidation of $(\text{Hg}^{\text{I}})_2$ [in the silver(I)-catalyzed oxidations of $(\text{Hg}^{\text{I}})_2$ (197)] may follow a similar mechanism, but requires further investigation.

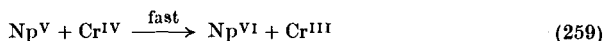
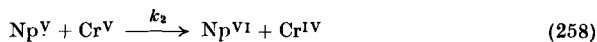
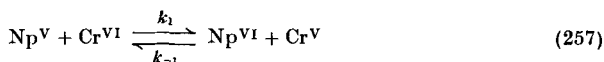
The rate law for the reaction of chromium(VI) with iron(II) (131) is

$$\frac{-d[\text{Fe}^{\text{II}}]}{dt} = [\text{H}^+]^3 \frac{[\text{Fe}^{\text{II}}]^2}{[\text{Fe}^{\text{III}}]} (k_1[\text{Cr}^{\text{VI}}] + k_2[\text{Cr}^{\text{VI}}]^2) \quad (253)$$

where the k_1 term is for the reaction of mononuclear Cr^{VI} (which is predominant), and k_2 is for the reaction of binuclear chromium(VI). The mechanism is



the second stage in which there is a reduction of Cr^{V} to Cr^{IV} being rate-determining. The latter is believed to correspond to a change in coordination number from four to six. In interpreting the data, ion pairing between Fe^{3+} and CrO_4^{2-} has to be taken into account. The analogous oxidation of tris(1,10-phenanthroline)iron(II) with chromium(VI) is not retarded by tris(1,10-phenanthroline)iron(III), and the first step is therefore not reversible (131). Fewer details of this reaction are obtained from the kinetic treatment. The kinetics of the reaction of vanadium(IV) with chromium(VI) resemble those of the iron(II) reaction (127). In the reaction of neptunium(V) with chromium(VI) (353), the series of one-equivalent steps

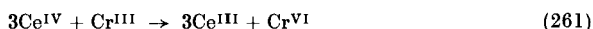


provides a reasonable mechanism for this reaction. In this case the first step is rate-determining and, assuming stationary-state kinetics for Cr^{V} , a rate law

$$\frac{-d[\text{Np}^{\text{V}}]}{dt} = 3k_1[\text{Np}^{\text{V}}][\text{Cr}^{\text{VI}}]/(1 + k_{-1}[\text{Np}^{\text{VI}}]/k_2[\text{Np}^{\text{V}}]) \quad (260)$$

is obtained, which is in agreement with experiment.

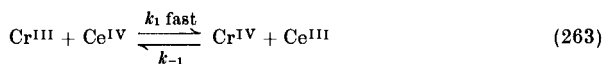
The oxidation of chromium(III) with cerium(IV) (385)



is too fast to be studied by conventional techniques in perchlorate solutions, but proceeds at a convenient rate in acid sulfate solutions. The rate law is of the form

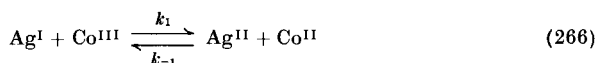
$$\frac{-d[\text{Cr}^{\text{VI}}]}{dt} = \frac{k[\text{Cr}^{\text{III}}][\text{Ce}^{\text{IV}}]^2}{[\text{Ce}^{\text{III}}]} \quad (262)$$

which is consistent with the mechanism:

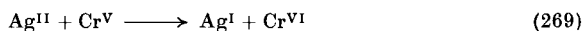
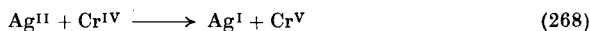
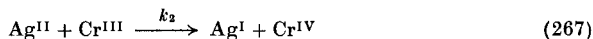


Again the slow step corresponds to the Cr^{IV} to Cr^{V} conversion.

The silver(I)-catalyzed oxidation of chromium(III) with cobalt(III) has been studied in 3 *M* perchloric acid (239). In the initial step, equilibrium concentrations of silver(II) are produced,



which can effect stepwise oxidation of the chromium(III) to chromium(VI):



The rate constants k_1 , k_{-1} , and k_2 have been evaluated. It is difficult to explain why the direct reaction between cobalt(III) and chromium(III) should be so slow.

In the reaction of silver(II) with thallium(I) in 6.18 *N* nitric acid (117), the nitrate radical is believed to be formed as an intermediate which then oxidizes the Tl^{I} to Tl^{II} .

Sutcliffe and colleagues have also studied the kinetics of the reduction of lead(IV) by cerium(III) (55) and cobalt(II) (54) in acetic acid media. Lead(III) is believed to be formed as an intermediate in both instances, and there is evidence for a dimeric form of cobalt(II).

VII. Outer-Sphere Reactions and Theoretical Considerations

The theoretical approach for outer-sphere reactions is relatively simple since no metal-ligand bonds are made or broken during the electron-transfer step, and arbitrary parameters which occur in theoretical studies of most other reactions in chemical kinetics are therefore absent. For reactions between two species differing only in oxidation states, there is no difference in the stability of products compared with reactants (i.e., $\Delta G^0 = 0$), and such reactions provide simple examples on which to base a theoretical treatment (359). A feature of outer-sphere reactions is that they are generally rapid. There are exceptions, however, and as a general rule the ligand type would seem to be important. Thus ligands such as water and ammonia appear to be much less effective in "conducting" electrons between metal ions than unsaturated ligands such as cyanide, phenanthroline, and bipyridine, the complexes of which are characterized by a high degree of π -bonding and electron delocalization. Reactions involving hexachloroiridate(IV) are also rapid, and again there is electron delocalization from the central metal atom (166).

The theoretical approach for the simplest electron-transfer reactions in solution is more complicated than that for electron-transfer reactions in the gas phase. This is because inner-coordination spheres of metal ions have to be taken into account, and other solvent or ion-pair interactions may also be important. In outer-sphere reactions, energy conservation requires that inner- and outer-coordination spheres of the reactants rearrange to some nonequilibrium configuration before electron transfer takes place. For an isotopic exchange reaction, this intermediate configuration is one in which the coordination spheres of the two reactants are identical. For reactions in which $\Delta G^0 \leq 0$, the coordination spheres of the reactants reorganize to a lesser extent and vibrational excitation energy of the products is probably liberated as part of the standard free energy change of the reaction. This means in effect that the structure of the activated complex tends to approach that of the reactants (359). A favorable free energy change serves therefore to decrease the free energy of activation, and there is a corresponding increase in rate. For outer-sphere reactions at least, electrostatic repulsion between the reactants has at the most only a small effect on the rate.

For a more detailed account of the theoretical approach, the reader is referred to articles by Marcus (253, 254), Sutin (359, 361), and Halpern (181). Of particular interest here are the correlations which have been possible using the Marcus equation,

$$k_{12} = (k_1 k_2 K_{12} f)^{1/2} \quad (270)$$

where

$$\log f = \frac{(\log K_{12})^2}{4 \log (k_1 k_2 / Z^2)} \quad (271)$$

In the above, k_{12} and K_{12} are the rate and equilibrium constants, respectively, for the redox reaction, and k_1 and k_2 are the rate constants for the corresponding exchange reactions. The collision frequency, Z , is for two uncharged molecules in solution and is assumed to have a value of $10^{11} \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$. In a number of instances when $K_{12} \rightarrow 1$, the f term may be assumed to be unity [see, for example, Dulz and Sutin (115)]. Equation (270) can also be expressed in terms of activation free energies and the standard free energy change:

$$\Delta G_{12}^\ddagger = 0.5 \Delta G_1^\ddagger + 0.50 \Delta G_2^\ddagger + 0.5 \Delta G_{12}^0 - 1.15 RT \log f \quad (272)$$

Equations (270) and (272) are applicable to outer-sphere reactions and are not in the first instance applicable to inner-sphere reactions.

For a series of reactions between Fe^{2+} and substituted 1,10-phenanthroline complexes of iron(III), Ford-Smith and Sutin (136) have shown that there is a linear relationship between the free energy of activation, ΔG_{12}^\ddagger , and the standard free energy change, ΔG_{12}^0 . The absence of specific steric effects suggests that the Fe^{2+} has to some extent penetrated between the phenanthroline ligands. The reactions of Fe^{2+} with the 2,2'-bipyridine and 2,2',2''-tripyrindine complexes of iron(III) have also been studied.

Other results of Sutin and colleagues have been discussed in terms of the Marcus approach. Thus the rates of the iron(II) reduction of $\text{Ag}(\text{phen})_2^{2+}$, $\text{Ag}(\text{bipy})_2^{2+}$, $\text{Ru}(\text{bipy})_3^{3+}$, $\text{Os}(\text{bipy})_3^{3+}$, and IrCl_6^{2-} have been studied in perchloric and sulfuric acid solutions and shown to increase with the standard free energies of the reactions (152). A number of reactions between positively charged complexes, as well as those between oppositely charged complexes, have been shown to proceed with rate constants which are larger than $10^8 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ (Table XVII). The rates for the oxidation of ferrocyanide ions by IrCl_6^{2-} , MnO_4^- , and OsCl_6^{2-} , on the other hand, are considerably slower and increase with the standard free energy change of the reaction (152).

The kinetics of the oxidation of a number of substituted tris(1,10-phenanthroline)iron(II) complexes by cerium(IV) in dilute sulfuric acid have been studied (115), and activation free energies are again related to the standard free energy change. In the oxidation of $\text{Fe}(\text{bipy})_3^{2+}$, $\text{Fe}(\text{bipy})_2(\text{CN})_2$, $\text{Fe}(\text{bipy})(\text{CN})_4^{2-}$, and the corresponding phenanthroline complexes, oxidation of the mixed ligand complexes proceeds more rapidly than the oxidation of complexes containing identical ligands

(74). The kinetics of the oxidation of Ru(phen)_3^{2+} by cerium(IV) (267), and of various substituted iron(II)-phenanthroline complexes by manganese(III) (104) and cobalt(III) (74), have also been studied. For other reactions involving a wide range of substitution-inert complexes, rate constants calculated from Eq. (270) are in good agreement with experimentally observed values (Table XVIII).

TABLE XVII

SECOND-ORDER RATE CONSTANTS FOR SOME OUTER-SPHERE REDOX REACTIONS AT 25° (152)

Reaction ^a	Medium	ΔE^0 (volts)	k ($\text{l} \cdot \text{mole}^{-1} \text{sec}^{-1}$)
$\text{Os(bipy)}_3^{2+} + \text{IrCl}_6^{2-}$	0.5 N HClO_4	0.23	$> 10^8$
$\text{Fe(CN)}_6^{4-} + \text{Fe(phen)}_3^{3+}$	0.5 N HClO_4	0.23	$> 10^8$
$\text{Fe(CN)}_6^{4-} + \text{Os(bipy)}_3^{3+}$	0.5 N HClO_4	0.11	$> 10^8$
$\text{Fe(t-phen)}_3^{2+} + \text{Ru(bipy)}_3^{3+}$	0.5 N H_2SO_4	0.46	$> 10^8$
$\text{Os(bipy)}_3^{2+} + \text{Ru(bipy)}_3^{3+}$	0.5 N HClO_4	0.44	$> 10^8$
$\text{Os(bipy)}_3^{2+} + \text{Fe(phen)}_3^{3+}$	0.5 N HClO_4	0.23	$> 10^8$
$\text{Fe(p-phen)}_2^{2+} + \text{Ru(bipy)}_3^{3+}$	0.5 N H_2SO_4	0.19	$> 10^8$
$\text{Fe(t-phen)}_3^{2+} + \text{Fe(d-bipy)}_3^{3+}$	0.5 N H_2SO_4	0.14	$> 10^8$
$\text{Fe(d-bipy)}_3^{2+} + \text{Fe(phen)}_3^{3+}$	0.5 N HClO_4	0.11	$> 10^8$
$\text{Fe(CN)}_6^{4-} + \text{IrCl}_6^{2-}$	H_2O	0.66	1.2×10^5
$\text{Fe(CN)}_6^{4-} + \text{IrCl}_6^{2-}$	0.5 N HClO_4	0.34	4.1×10^5
$\text{Fe(CN)}_6^{4-} + \text{MnO}_4^-$	0.1 N NaOH	0.10	1.34×10^4
$\text{Fe(CN)}_6^{4-} + \text{OsCl}_6^{2-}$	H_2O	0.07	1.79×10^{-1}

^a tripy = 2,2',2''-tripyridine; d-dipy = 4,4'-dimethyl-2,2'-dipyridine; t-phen = 3,4,7,8-tetramethyl-1,10-phenanthroline; p-phen = 5-phenyl-1,10-phenanthroline.

The same theoretical approach has been considered for reactions between two hexaquo ions, although it is not yet known whether these proceed by inner- or outer-sphere mechanisms (115). With one or two notable exceptions, there is good agreement between calculated and experimental rate constants. In the case of the Fe^{2+} - Co^{3+} reaction the discrepancy is $\sim 10^5$, however (115). The reactions Fe(phen)_3^{2+} - Co^{3+} (74) and $\text{Ru(NH}_3)_6^{2+}$ - $\text{Co(NH}_3)_6^{3+}$ (122) are also exceptions, and it is perhaps significant that all three involve the cobalt(II)-cobalt(III) couple. It may be that spin-multiplicity restrictions (page 168) are responsible for the anomalous behavior of these systems. There is also a serious discrepancy between observed and calculated rate constants (700 and

$1.3 \times 10^6 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$, respectively, at 0°) for the reaction of Fe^{2+} with Ce^{4+} in $0.5 N$ perchloric acid (9).

Favorable free energy changes are not always necessary for reactions to be fast, and rate constants approaching the diffusion-controlled limit of $\sim 2 \times 10^9 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ have been observed for reactions in which the equilibrium constant K is of the order of unity, and ΔG^0 for the

TABLE XVIII

A COMPARISON OF OBSERVED AND CALCULATED RATE CONSTANTS
FOR SOME OUTER-SPHERE REACTIONS (74)

Reaction	k_{12} (observed) ($\text{l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$)	k_{12} (calculated) ($\text{l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$)
$\text{W}(\text{CN})_8^{4-} + \text{Ce}^{\text{IV}}$	$> 10^8$	6.1×10^8
$\text{Fe}(\text{CN})_6^{4-} + \text{Ce}^{\text{IV}}$	1.9×10^6	6.0×10^6
$\text{Mo}(\text{CN})_8^{4-} + \text{Ce}^{\text{IV}}$	1.4×10^7	1.3×10^7
$\text{W}(\text{CN})_8^{4-} + \text{IrCl}_6^{2-}$	6.1×10^7	8.1×10^7
$\text{Fe}(\text{CN})_6^{4-} + \text{IrCl}_6^{2-}$	3.8×10^5	5.7×10^5
$\text{Mo}(\text{CN})_8^{4-} + \text{IrCl}_6^{2-}$	1.9×10^6	1.0×10^6
$\text{W}(\text{CN})_8^{4-} + \text{Mo}(\text{CN})_8^{3-}$	5.0×10^6	1.7×10^7
$\text{Fe}(\text{CN})_6^{4-} + \text{Mo}(\text{CN})_8^{3-}$	3.0×10^4	2.7×10^4
$\text{W}(\text{CN})_8^{4-} + \text{Fe}(\text{CN})_6^{3-}$	4.3×10^4	5.1×10^4

forward and back reactions ~ 0 . The temperature-jump method is particularly useful for studying such reactions. A fairly large standard enthalpy change is desirable so that the temperature jump produces a significant change. One way in which this can be achieved is by having oppositely charged reactants (Table XIX).

Sutin (360) has found that the rate constant for the inner-sphere reaction between Cr^{2+} and FeCl_6^{2+} can be calculated from Eq. (270). In this instance, the exchange rate constants k_1 and k_2 are for the reactions of Cr^{2+} with CrCl_6^{2+} and Fe^{2+} with FeCl_6^{2+} (the chloride bridging paths only). The agreement of the observed log of the rate ($7.3 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$) with the calculated rate ($8.5 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$) is encouraging, and suggests that an equation of this form may also be applicable to inner-sphere reactions.

Free energy correlations of a different type have been proposed by Bächmann and Lieser (34). For the rate constants for electron exchange between different complexes of iron(III) and Fe^{2+} , the following relationship was found to hold:

$$\log_{10} k = 1.1 + 0.5 \Delta \log_{10} K \quad (273)$$

In this equation, $\Delta \log_{10} K$ is the difference between the logarithms of the stability constants for the iron(III) and iron(II) complexes with the same ligands. As far as stability constants are known, all the rate constants would seem to conform to this relationship.

Factors which determine entropy of activation of a redox reaction have also been considered. Newton and Rabideau (287) have reviewed

TABLE XIX

RATE CONSTANTS ($l \cdot \text{mole}^{-1} \text{sec}^{-1}$) FOR FORWARD (k_f) AND BACK (k_b) REACTIONS AS DETERMINED BY THE TEMPERATURE-JUMP METHOD

Reaction ^a	Temp. (°C)	k_f	k_b	Ref.
$\text{Os}(\text{bipy})_3^{2+} + \text{Mo}(\text{CN})_6^{3-} \rightleftharpoons \text{Os}(\text{bipy})_3^{3+} + \text{Mo}(\text{CN})_6^{4-}$	10	2.0×10^9	4.0×10^9	(75)
$\text{Fe}(4,7\text{-DMP})_3^{2+} + \text{IrCl}_6^{2-} \rightleftharpoons \text{Fe}(\text{DMP})_3^{3+} + \text{IrCl}_6^{3-}$	10	1.1×10^9	1.0×10^9	(184)
$\text{Fe}(5,6\text{-DMP})_3^{2+} + \text{IrCl}_6^{2-} \rightleftharpoons \text{Fe}(5,6\text{-DMP})_3^{3+} + \text{IrCl}_6^{3-}$	10	2.2×10^8	2.8×10^9	(217)
$\text{IrBr}_6^{3-} + \text{IrCl}_6^{2-} \rightleftharpoons \text{IrBr}_6^{2-} + \text{IrCl}_6^{3-}$	20	1.2×10^7	1.8×10^6	(218)
$\text{Fe}(4,7\text{-DMP})_3^{2+} + \text{IrBr}_6^{2-} \rightleftharpoons \text{Fe}(4,7\text{-DMP})_3^{3+} + \text{IrBr}_6^{3-}$	10	1.6×10^8	1.9×10^9	(217)
$\text{Fe}(\text{DMPY})_3^{2+} + \text{IrCl}_6^{2-} \rightleftharpoons \text{Fe}(\text{DMPY})_3^{3+} + \text{IrCl}_6^{3-}$	10	9.6×10^8	2.0×10^8	(217)
$\text{Ru}(\text{phen})_3^{2+} + \text{RhCl}_6^{2-} \rightleftharpoons \text{Ru}(\text{phen})_3^{3+} + \text{RhCl}_6^{3-}$	10	2.5×10^9	2.7×10^8	(217)

^a DMP = 4,7-dimethyl-1,10-phenanthroline; DMPY = 4,4'-dimethyl-2,2'-bipyridine.

the kinetics of aqueous oxidation-reduction reactions of uranium, neptunium, and plutonium, and shown that the entropies of the various activated complexes depend primarily on their charges. For activated complexes of charge +3, +4, +5, and +6, values of S^\ddagger , the entropy of the activated complex, were found to lie in the ranges 29–40, 63–81, 72–106, and 102–128 eu, respectively. Daugherty and Newton (100) have extended this approach to a consideration of reactions which do not involve actinide ions. Higginson *et al.* (197) have drawn attention to the linear correlation between $-\Delta S^\ddagger$ and the charge of the activated complex for a number of isotopic exchange reactions. Many reactions show deviations from this correlation in the direction of the entropy of reaction. For example, a number of reactions were found to have positive entropies of activation, when negative values might have been expected. The relationship may be summarized by the equation,

$$\Delta S^\ddagger = \Delta S_0^\ddagger + \alpha \Delta S^0 \quad (274)$$

where ΔS^\ddagger and ΔS^0 refer to the redox reaction in which there is net chemical change, and ΔS_0^\ddagger is the corresponding entropy of activation (for similar charge types) from the correlation observed for isotopic exchange

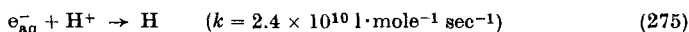
reactions. The coefficient α was found to have values ranging from 0.5 to 1.0. For reactions in which there are hydrolytic changes, for example reactions in which V^{3+} is oxidized to VO^{2+} , entropy correlations suggest that at least partial hydrolysis occurs during the lifetime of the activated complex (197).

Other outer-sphere reactions, already referred to, include the $Fe(CN)_6^{4-}-Fe(CN)_6^{3-}$ (234, 339), $Co(NH_3)_6^{2+}-Co(NH_3)_6^{3+}$ (59), and $MnO_4^{2-}-MnO_4^-$ (273) reactions. A number of V^{2+} reactions are believed to be outer-sphere (107).

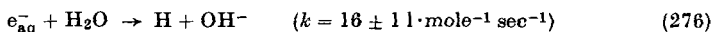
VIII. Reactions of the Solvated Electron with Metal Ions

Recent application of the technique of pulse radiolysis (108), using short bursts of high-energy electrons (or X-rays), has led to a confirmation of the existence of the solvated electrons in water (194, 231), methanol (1), ethanol (374), and dioxane (48). It has also enabled reactions of the solvated electron to be studied, and transient intermediates resulting from these reactions to be identified.

Reactions of the hydrated electron with metal ions are considered in this section. Water as a solvent is more dissociated ($K \sim 10^{-14}$ liter⁻² mole²) than ammonia ($K \sim 10^{-30}$ liter⁻² mole²), and reactions of the solvated electron with H^+ (or H_3O^+) (159)



together with the reaction



result in a much more rapid decay of e_{aq}^- . Reactions of the hydrated electron are studied by having solutes present in the sample of water which is irradiated, the decay of the e_{aq}^- absorption at 700 m μ (50) being more rapid than would otherwise be observed. A necessary requirement is that the hydrogen-ion concentration be small, and values $< 10^{-5} N$ are generally used. For some reactions an allowance has to be made for the reaction $e_{aq}^- + e_{aq}^-$ ($k = 5 \times 10^9 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$).

Alkali and alkaline-earth ions (with the possible exception of Mg^{2+}) do not affect the rate of decay of the electron absorption. The reaction with Mg^{2+} is relatively slow and a rate constant $k < 10^5 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ has been observed (18). This is as expected in view of the standard electrode potential of around -2.5 volts for the hydrated electron. Baxendale and colleagues (49) have found that neutral solutions of Cd^{2+} , Pb^{2+} , Co^{2+} , and Ni^{2+} are readily reduced by e_{aq}^- . With Zn^{2+} , Fe^{2+} , and Mn^{2+} , the rate constants are somewhat less (Table XX), the

slower rate for Mn^{2+} being reflected in the higher activation energy ($7.7 \pm 0.5 \text{ kcal mole}^{-1}$) compared to that for Co^{2+} ($5.7 \pm 0.5 \text{ kcal mole}^{-1}$). Transient absorbing species with maxima at around $300 \text{ m}\mu$ have been detected in all but the Fe^{2+} reaction, and it is concluded that these are due to the lower oxidation states Cd^+ , Pb^+ , Co^+ , Ni^+ , Zn^+ , and Mn^+ . The existence of Zn^+ and Cd^+ has been confirmed by ESR studies on

TABLE XX

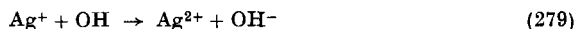
RATE CONSTANTS FOR THE REACTIONS OF e_{aq}^- WITH METAL IONS (AT ROOM TEMPERATURE AND $\text{pH} \sim 7$) (19, 49)

Reactant	k ($\text{l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$)	Reactant	k ($\text{l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$)
Cd^{2+}	5.2×10^{10}	Ag^+	3.2×10^{10}
Pb^{2+}	3.9×10^{10}	Tl^+	3.0×10^{10}
Co^{2+}	1.2×10^{10}	Cu^{2+}	2.9×10^{10}
Ni^{2+}	2.2×10^{10}	Sn^{2+} (pH 11)	3.4×10^9
Zn^{2+}	1.5×10^9	Cr^{2+}	4.2×10^{10}
Fe^{2+}	1.6×10^8	Cr^{3+}	6.0×10^{10}
Mn^{2+}	4.0×10^7	Al^{3+}	2.0×10^9

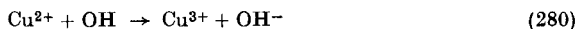
irradiated ice containing Zn^{2+} and Cd^{2+} , respectively (271). The decay of Zn^+ and Ni^+ has been followed in some detail (49). While Zn^+ appears to react by disproportionation,



the decay of Ni^+ is not as simple. The reductions of silver(I) and copper(II) ions are also rapid. With silver(I) there appear to be competing reactions,



but with $\sim 10^{-3} \text{ M}$ solutions of copper(II) the reaction with e_{aq}^- is predominant, and there is no transient absorption other than that of e_{aq}^- . At concentrations $> 5 \times 10^{-3} \text{ M}$ a transient absorption is produced which is attributed to the reaction:



Anbar and Hart (19) report additional data for the reactions with Sn^{II} , Cr^{II} , Cr^{III} , and Al^{III} . On increasing the pH from 7 to 14 there is almost invariably a decrease in the observed rate constant. With aluminum(III) the decrease is from 2.0×10^9 to $5.5 \times 10^6 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$.

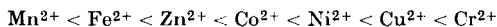
In the case of the permanganate and chromate oxyanions, fast rates are observed (49). With permanganate, manganate ions are first formed,



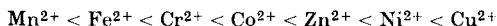
and with higher dose rates further reduction to MnO_4^{3-} can occur. Chromate differs from permanganate in that transient species are observed. Chromium(V) ions, CrO_4^{3-} or CrO_3^- , are believed to be formed by reaction with e_{aq}^- and H-atoms. They are quickly reoxidized to CrO_4^{2-} , however, probably by OH radicals.

Rate constants for reactions with a series of 3+ rare-earth ions are of the order of $10^8 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ (49, 380). Freshly made solutions appear to react more slowly than those which have been standing for some time. In the reaction of Eu^{3+} with e_{aq}^- the relatively stable Eu^{2+} product has been identified (160). A linear correlation of reactivity with the $\text{M}^{2+}/\text{M}^{3+}$ redox potentials has been reported for the reactions of Sm^{3+} , Yb^{3+} , and Eu^{3+} (380).

In other reactions, however, it can be concluded that the reactivity is not solely determined by the free energy change. Thus, the rate constants for the reactions of a number of ammine and aquo complexes having the same central metal atom have been shown to be similar (19), in spite of a quite pronounced variation in the oxidation-reduction potential. An explanation of relative rates in terms of electron affinity is also unsatisfactory, since the order of rate constants for 2+ transition metal ions (21) is



and the order of electron affinities is



Anbar has suggested that the availability of a vacant d orbital on the central metal, and the gain in exchange energy on adding an electron are the major factors which determine the reactivity of transition metal ions (15). Thus addition of an electron to the $\text{Cr}^{2+}(t_{2g}^3 e_g^1)$ ion is particularly favorable since the electron spin is parallel to the four spins already present. With $\text{Mn}^{2+}(t_{2g}^3 e_g^2)$ on the other hand, a sixth electron must have its spin anti-parallel to the electrons already present and the reaction is less favorable. In the case of Cu^{2+} the gain in energy is similar to that of Cr^{2+} , but Zn^{2+} is expected to have a low reactivity since all the $3d$ orbitals are filled.

Ligands such as cyanide may affect the reactivity of the central atom by changing the ligand field and hence the electron density distribution. For example ferrocyanide with a t_{2g}^6 configuration is relatively unreactive

($k < 10^5 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$) (16). With low-spin $\text{Mn}(\text{CN})_6^{4-}$, on the other hand, an electron is added to the last vacancy in the t_{2g} level, and the complex is much more reactive ($k = 2.5 \times 10^{10} \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$) than Mn^{2+} (16). Ligands such as the halide ions, which do not interact strongly with d orbitals, may affect the reactivity of a complex toward e_{aq}^- by channeling the electron from the solvent to the central atom (15). From a rather limited series of rate constants, Anbar and Hart (19) have suggested that the efficiency of bridging groups is

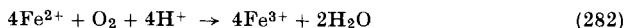


Other results obtained by Baxendale *et al.* (49) for a series of cobalt(III) complexes are not entirely consistent with this order. The fact that the hydroxo complexes $\text{Al}(\text{OH})_4^-$ and $\text{Zn}(\text{OH})_4^{2-}$ are so inert is important (19). No d orbitals are involved in these two instances and it must be concluded that OH^- is an extremely poor bridge for electrons. This is in accord with the observation that the rate of the outer-sphere reduction of, for example, $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$ with $\text{Ru}(\text{NH}_3)_6^{3+}$ is 100 times slower than with $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ (122). The effectiveness of halide ions is similar to that observed for outer-sphere reactions. Marcus (255) has outlined assumptions, equations, and several applications of a recently formulated theory for the reactions of e_{aq}^- .

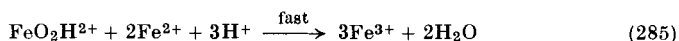
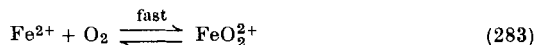
From the kinetics alone it can be concluded that the solvated electron is not an intermediate in electron-transfer reactions (366, 377).

IX. Reactions of Metal Ions with Compounds of Nonmetallic Elements

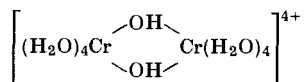
The reactions of molecular oxygen with Fe^{II} (146), V^{III} (319), Pu^{III} (278), and U^{IV} (190) in aqueous solutions (to give Fe^{III} , V^{IV} , Pu^{IV} , and U^{VI} , respectively) are believed to involve peroxide forms as intermediates. Thus, for the reaction



there is evidence for the mechanism:



With Cr^{2+} (27, 114), the dimer



is formed (228), and in ammoniacal solutions the final product is $(\text{NH}_3)_5\text{Cr}\cdot\text{O}\cdot\text{Cr}(\text{NH}_3)_5^{4+}$ (227). When oxygen is passed through ammoniacal cobalt(II) solutions, the complex $(\text{NH}_3)_5\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_5^{4+}$ can be isolated (390). That the brown vanadium(III) dimer is formed as an intermediate in the reaction of vanadium(II) with oxygen provides evidence for two-equivalent oxidation to vanadium(IV) in the first step (365). Substantial oxygen-atom transfer has been shown to occur in the ozone oxidation of manganese(II) and thallium(I) to manganese dioxide and thallium(III) oxide, respectively (133).

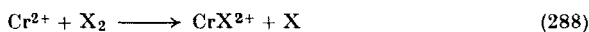
Zabin and Taube (411) have investigated the reactions of chromium(II) with the metal oxides MnO_2 , PbO_2 , Tl_2O_3 , Mn_2O_3 , Co_2O_3 , and CeO_2 , and found that $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ is the predominant form of the chromium(III) product. When the oxidizing agent has a higher oxygen content, as with Pb_3O_4 or Ca_2PbO_4 , a chromium(III) dimer (or a higher polymer) is formed. There is no oxygen transfer from PbO_2 to Cr, but some does occur in the reactions with MnO_2 , Tl_2O_3 , and Mn_2O_3 . The reactions are more rapid with those oxides containing metal ions which undergo two-electron changes (e.g., MnO_2 , PbO_2 , Tl_2O_3).

Halpern and colleagues (241, 302, 395) have shown that molecular hydrogen reacts homogeneously with a number of metal ions in aqueous solutions, reducing them to the metal or to a lower oxidation state. The reactions with Cu^{2+} , Hg^{2+} , Hg_2^{2+} , and MnO_4^- all show a first-order dependence on both reactants. Silver(I) catalyzes the reduction of $\text{Cr}_2\text{O}_7^{2-}$ (395) and there are terms in $[\text{Ag}^+]$ and $[\text{Ag}^+]^2$ which correspond to rate-determining steps:



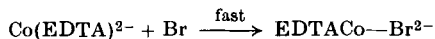
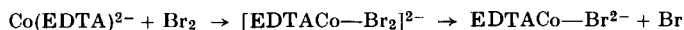
The reduction of Ag^1 to metallic silver has also been studied (396).

The oxidation of chromium(II) solutions with halogens (379) provides with bromine and iodine a convenient means of preparing the 1:1 chromic halide complexes:



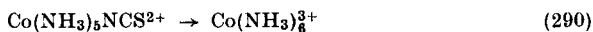
With chlorine there is incomplete retention of the chloride, which suggests that the reaction might proceed at least in part via the labile chromium(IV) state. In the reactions of tin(II) with bromine and iodine (398), tin(III) was not detected as an intermediate. A full kinetic study has been made of the reaction between titanium(III) and iodine

(222), and iron(II) and chlorine (96). In the latter it was not possible to decide whether Cl_2^- or Fe^{IV} is formed as an intermediate. Solutions containing the cobalt(II)-EDTA complex are oxidized by bromine,

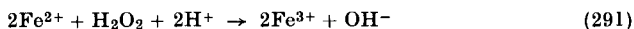


and the pentacyano cobalt(II) complex CoCN_5^{2-} is likewise oxidized by halogens to $\text{Co}^{\text{III}}(\text{CN})_5\text{X}^{3-}$, although there is only a poor yield with chlorine (3). The reactions of Fe^{II} (83) and U^{IV} (154) with bromine have also been studied.

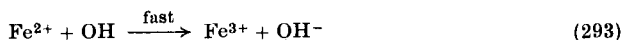
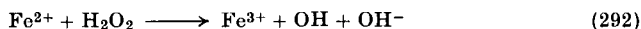
Chlorine oxidation of $\text{Co(en)}_2\text{XBr}^+$ complexes (where $\text{X}^- = \text{NH}_3, \text{Cl}^-, \text{Br}^-$) results in the formation of $\text{Co(en)}_2\text{XCl}^+$ with retention of the configuration of the complex (321). Chlorine has also been used as a reagent for oxidizing the isothiocyanate ligand in $\text{Cr}(\text{H}_2\text{O})_5\text{NCS}^{2+}$ (384) and $\text{Cr}(\text{H}_2\text{O})_5\text{SCN}^{2+}$ (176, 177). The products are $\text{Cr}(\text{H}_2\text{O})_5^{3+}$ and $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$, respectively. The cobalt-nitrogen bond is preserved in the oxidation of the isothiocyanato ligand of cobalt(III) complexes with KIO_3 and H_2O_2 (332):



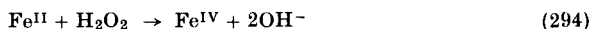
The oxidation of iron(II) (43) with hydrogen peroxide has been shown to conform reasonably well to the equation



at hydrogen-ion concentration $> 0.01 M$. The first-order dependence on both reactants under these conditions is consistent with the mechanism:



Cahill and Taube (71) have suggested an alternative first step,



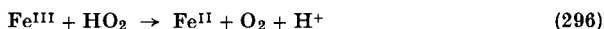
but recent experiments by Conocchioli *et al.* (93) seem to exclude this possibility. More complex behavior is observed under other conditions (43). Hydroxy radicals have been detected by ESR in the corresponding reaction with titanium(III) (106). In the reactions of hydrogen peroxide with Cr^{II} (23) and V^{II} (365) the products are the same as in the reactions with oxygen, and Cr^{IV} and V^{IV} are probably formed as intermediates. Chromium(III) is oxidized to chromium(VI) in alkaline solutions (41), there being a first-order dependence on both reactants. A μ -peroxo-dicobalt(III)

intermediate, $\text{EDTACo} \cdot \text{O}_2 \cdot \text{CoEDTA}^{4-}$, is formed during the oxidation of the cobalt(II)-EDTA complex to cobalt(III) by hydrogen peroxide (409).

The reactions in which Fe^{III} (43), $\text{Fe}(\text{CN})_6^{3-}$ (149), Ce^{IV} (98), and U^{IV} (38) are reduced with hydrogen peroxide have also been studied. In the reaction with Fe^{III} , the initial step

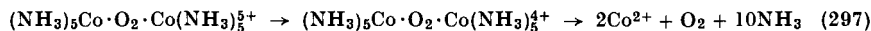


is followed by



The oxygen which is liberated has the same isotopic composition as the hydrogen peroxide (69). Again the kinetics are complex since the product also reacts with H_2O_2 , as indicated above. Ardon and Bleicher (26) report the isolation of a new intermediate formed during the reduction of chromium(VI) with hydrogen peroxide. The compound may well have the structure $(\text{H}_2\text{O})_5\text{Cr} \cdot \text{O}_2 \cdot \text{Cr}(\text{H}_2\text{O})_5^{5+}$. At 26.5° and hydrogen-ion concentration 0.2–4.0 *N*, the first-order rate constant for the decomposition of the complex is $\sim 1.4 \times 10^{-4} \text{ sec}^{-1}$. The complex is reduced by iodide and iron(II).

It now seems best to assume that the green complex $(\text{NH}_3)_5\text{Co} \cdot \text{O}_2 \cdot \text{Co}(\text{NH}_3)_5^{5+}$ is essentially two cobalt(III) ions bridged by a superoxide ion O_2^- (331), whereas the brown complex $(\text{NH}_3)_5\text{Co} \cdot \text{O}_2 \cdot \text{Co}(\text{NH}_3)_5^{4+}$ contains two cobalt(III) ions bridged by a peroxide O_2^{2-} ion (387). In acid solutions the latter is unstable. The 1:1 reductions of the green complex with Fe^{II} , V^{IV} , Sn^{II} , I^- , and $\text{S}_2\text{O}_3^{2-}$ (368) give two cobalt(II) ions and oxygen, the reaction sequence being:

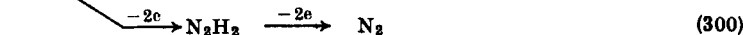


With sulfite and nitrite, on the other hand, 1:2 reactions are observed (368),

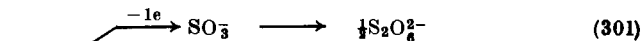


and both bridging oxygen atoms may be transferred to the sulfate.

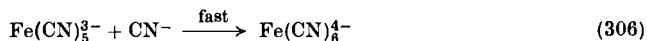
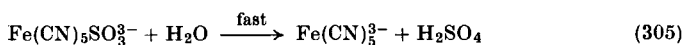
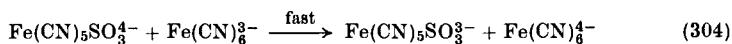
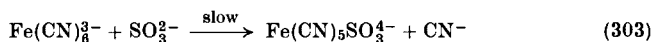
Different stoichiometries and products are observed in the oxidation of hydrazine, depending on whether one- or two-equivalent reagents are involved. The two reaction paths are (198, 199, 201, 236):



One-equivalent reagents react by paths (299) and (300), and two-equivalent reagents exclusively by path (300). A similar distinction is possible in the reactions with sulfite (196):

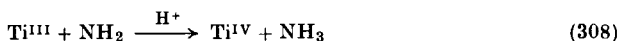


One-equivalent reagents (e.g., Ce^{III} , Co^{III} , Fe^{III} , and V^{V}) react by paths (301) and (302) to give dithionate and sulfate (stoichiometry between 1.0 and 2.0), and two-equivalent reagents (e.g., I_2 , Br_2 , Cl_2 , IO_3^- , H_2O_2 , and Tl^{III}) by path (302) to give sulfate only (stoichiometry 2.0). No dithionate is produced in the oxidation of sulfite with $\text{Fe}(\text{CN})_6^{3-}$, however (388). A mechanism,



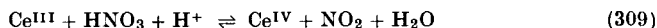
in which the sulfite becomes coordinated in the inner-sphere, has been suggested. Other inert complexes, $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{2-}$, $\text{Fe}(\text{CN})_5\text{NH}_3^{2-}$, $\text{Fe}(\text{bipy})_3^{3+}$, and $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$, show similar behavior, but with labile complexes such as Fe^{3+} and $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$, sulfate and dithionate are formed (389).

When hydroxylamine is reduced by titanium(III), NH_2 radicals and not OH radicals are produced in the first step (102):



The oxidation of hydroxylamine by cerium(IV) (393) appears to involve prior coordination of NH_2OH to the metal ion. The radical NH_2O , which is first formed, is oxidized further to N_2O except at low Ce^{IV} concentrations when N_2 is formed.

Parker and Spence (297) found that nitric oxide is a major product when molybdenum(V) is oxidized by nitrate ions. The molybdenum(V) is believed to be present predominantly as a dimer, the rate-controlling step being the reaction of mononuclear Mo^{V} with nitrate ions. The reaction of cerium(III) with nitric acid is a reversible reaction,

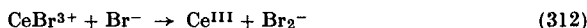


which has been studied at 90–110° in 12–16 *N* nitric acid. The nitrite ion oxidations of molybdenum(V) (344) and iron(II) (386) have also been studied.

The kinetics of the reactions of bromide ions with Ce^{IV} (232), and of iodide with neptunium(V) (334) and $(\text{NH}_3)_5\text{Co} \cdot \text{O}_2 \cdot \text{Co}(\text{NH}_3)_5^{5+}$ (369), fit the same sort of general pattern. Thus rate equations are of the type,

$$\text{Rate} = [\text{Ce}^{\text{IV}}] (k_1[\text{Br}^-] + k_2[\text{Br}^-]^2) \quad (310)$$

which is consistent with a mechanism:

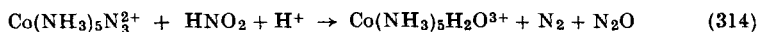


Subsequent reactions of the radicals Br and Br_2^- (with each other or the Ce^{IV}) are rapid. The rates of the reactions of Fe^{III} (372) and $\text{Fe}(\text{CN})_6^{3-}$ (4) with iodide also show first- to second-order dependence on iodide.

Perchlorate ions are reduced by V^{II} , V^{III} (235), Ti^{III} (113), $\text{Ru}(\text{NH}_3)_5^{2+}$, and $\text{Ru}(\text{NH}_3)_6^{2+}$ (123), but not by Cr^{II} or Eu^{II} (10). Gordon and Tewari (158) find that chlorite ions oxidize vanadium(II) to vanadium(III) and rule out the intermediate formation of vanadium(IV). Subsequent reactions are rapid as in the corresponding reaction with chromium(II) (381). In the latter it was found that chromium(II) reductions of chlorine dioxide, chlorite, hypochlorite, and chlorine were all at least 10^3 – 10^5 times faster than the reaction with chlorate ($k = 39.0 \text{ l} \cdot \text{mole}^{-1} \text{ sec}^{-1}$ at 20°).

Peroxodisulfate ions have been shown to oxidize Ce^{III} (89), Cr^{III} , and V^{IV} (410) in the presence of Ag^{I} as catalyst. Either Ag^{II} or Ag^{III} or both may be involved as intermediates in these reactions. The iron(III) oxidation of thiosulfate (294–296), cerium(IV) oxidation of hypophosphorus acid (82), and mercury(II) oxidation of carbon monoxide (193) have been studied.

Anbar (17) has recently reviewed the oxidation and reduction of ligands. The oxidation of an azide ligand with nitrite in complexes $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ (178), $\text{Co}(\text{CN})_5\text{N}_3^{3-}$ (175), and *cis*- and *trans*- $\text{Co}(\text{en})_2(\text{N}_3)_2^+$ (248) are of interest because five-coordination intermediates are believed to be formed:



In the presence of various anions ($\text{X}^- = \text{F}^-$, Cl^- , Br^- , NO_3^- , SCN^- , H_2PO_4^- , and SO_4^{2-}), Haim and Taube (178) have found that $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ complexes are formed as well as $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$, and conclude that $\text{Co}(\text{NH}_3)_5^{3+}$ is an intermediate. Pearson and Moore (298) have concluded that the intermediate in these oxidation-induced aquations are not the

same as those produced in the spontaneous aquation of these complexes. The oxidation of $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$ by two-equivalent oxidants ($\text{H}_2\text{O}_2/\text{Mo}^{\text{VI}}$ or Cl_2) produces $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$. With one-equivalent oxidants (Ce^{IV} , Co^{3+} , and $\text{S}_2\text{O}_8^{2-}/\text{Ag}^+$), on the other hand, Co^{2+} is formed (330). When at 50° a solution of Ag^{I} is added to an acid in solution of $\text{S}_2\text{O}_8^{2-}$ and $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$, a small fraction of the cobalt(III) complex is reduced to cobalt(II) (383).

Espenson (128) has found that oxidation of the coordinated iodide in CrI^{2+} by iodate ions proceeds according to the rate law:

$$-d[\text{CrI}^{2+}]/dt = k[\text{Cr}^{2+}][\text{I}_2] \quad (315)$$

The reaction rate is independent of the concentration of iodate, a reactant, and is directly dependent on the concentration of iodine, a product.

The oxidation of hydroxyethylenediaminetriacetic acid by vanadate(V) ions is largely suppressed when the ligand is coordinated to chromium(III) or cobalt(III). This result is consistent with a mechanism for the vanadate oxidation which requires the formation of a complex between the ligand and vanadate(V) prior to the electron-transfer step (225). Other reactions of metal ions with organic reagents (399) may proceed in a similar manner.

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MIXED VALENCE CHEMISTRY—A SURVEY AND CLASSIFICATION

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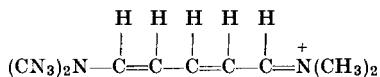
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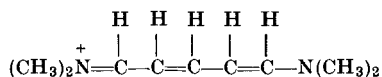
I. Introduction

This review is concerned with the neglected class of inorganic compounds which contain ions of the same element in two different formal states of oxidation. Although the number of references cited in our review shows that many individual examples of this class have been studied, yet they have very rarely been treated as a class, and there has never before, to our knowledge, been a systematic attempt to classify their properties in terms of their electronic and molecular structures. In the past, systems containing an element in two different states of oxidation have gone by various names, the terms "mixed valence," "nonintegral valence," "mixed oxidation," "oscillating valency," and "controlled valency" being used interchangeably. Actually, none of these is completely accurate or all-embracing, but in our hope to avoid the introduction of yet another definition we have somewhat arbitrarily adopted the phrase "mixed valence" for the description of these systems.

The concept of resonance among various valence bond structures is one of the cornerstones of modern organic chemistry. The most important feature of resonance among degenerate or near-degenerate structures is that the states resulting from the resonance have properties quite different from those expected of any one of the structures taken separately. Thus, for example, the pentamethinium ion requires the two degenerate structures



and



for an adequate description of its ground state, and, as a consequence of the resonance interaction between them, has a deep green color. On the other hand, either of the structures taken alone would be expected to have the color of 1,3,5-hexatriene, i.e., would be colorless. In this example, the resonance and the consequent green color spring from the fact that the nitrogen atoms can assume two valencies, 3+ and 4+, and are in equivalent positions in the ion so that on interchanging the nitrogen valencies, an equivalent structure results. There is ample reason to believe that exactly similar results would follow if a molecule could be synthesized in which the nitrogens were replaced by, say, Fe(II) and Fe(III). Thus it seems clear from the dramatic effects of resonance in organic chemistry that one can expect unusual properties in inorganic materials

possessing the same metal ion in different oxidation states, properties not to be found in the salts of either oxidation state taken separately.

Occasionally one finds examples of mixed valence among the inorganic nonmetals (the triiodide ion contains iodine atoms with formal valence zero and minus one). However, it is easily understood that by far the largest number and greatest variety of such compounds to be encountered in chemistry involve the transition and B subgroup metal elements, since many of these elements can exist in a variety of oxidation states. It is paradoxical, then, that the revitalization of transition metal chemistry brought about by the successes of the crystal field and ligand field theories has not been extended to the area of mixed valence compounds and their properties. It is the aim of this article to carry the renaissance of inorganic chemistry into this neglected area.

Mixed valence systems are, or should be, of great interest because their properties are rarely just the sum of the properties of the two metal ions taken separately; as with resonating organic molecules, there frequently is an "interaction" between the metal ions which results in the most dramatic changes in the physical properties of the system. Thus, as examples, $\text{W}^{\text{VI}}\text{O}_3$ and $\text{LiW}^{\text{V}}\text{O}_3$ ¹ are insulators whereas the mixed valence compound $\text{Li}_x\text{W}_x^{\text{V}}\text{W}_{1-x}^{\text{VI}}\text{O}_3$ is a conductor, the crystals $\text{K}_4\text{Fe}^{\text{II}}(\text{CN})_6$ and $\text{Fe}_2^{\text{III}}(\text{SO}_4)_3$ are pale yellow whereas $\text{KFe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6$ is deep blue, and paramagnetic substances may become ferromagnetic or diamagnetic, all by changing the oxidation state of a part of the metal ions in the system by one or more units. Thus, for those interested in the interrelationships between electronic structure, molecular structure, electronic spectra, electronic conduction, and molecular magnetism, the mixed valence systems offer a class of compounds unique in chemistry. As would be expected, a study of such mixed valence systems suggests a close correlation between their color, crystal structure, magnetism, and electronic conductivity, which hopefully will allow one to predict aspects of all the above properties, after determining any one of them.

The most obvious and striking feature of many mixed valence compounds is the presence of intense absorption in the visible region of the spectrum, not present in compounds containing either valence state alone. Thus, whereas the colors of almost all $\text{Fe}(\text{III})$ and $\text{Fe}(\text{II})$ compounds are colorless, pale orange, or pale green, the color of almost all mixed valence systems simultaneously containing $\text{Fe}(\text{III})$ and $\text{Fe}(\text{II})$ is deep blue to black. And there is another paradox here, for although the blue-black systems are being actively ignored today in the midst of a

¹ In this work, the Roman numeral which follows an atomic symbol refers to the formal oxidation state of the metal ion, and is not to be confused with similar numerals used differently by atomic spectroscopists for the same purpose.

flurry of quantum mechanical activity on the pale orange ones, in the dark ages of the prequantum mechanical days, when no one could guess the explanation for the color of the Fe(III) ion, there was presented a very reasonable rationale for the deep blue color of Prussian blue, $\text{KFe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6$. Because the deep colors of mixed valence systems were so unexpected, they could not be ignored for long, with the result that an explanation of the effect was presented with which we today can find little fault.

Thus, Wells (759), describing with great insight the very dark colors of various Au(I) , Au(III) , Sb(III) , Sb(V) , Fe(II) , Fe(III) , and Cu(I) , Cu(II) chromophoric groupings, wrote:

"The chromophore grouping that has been presented here is a very curious thing. In the cases of Au(I) – Au(III) and Sb(III) – Sb(V) there is a difference of two units of valency, while with Fe(II) – Fe(III) and Cu(I) – Cu(II) there is a difference of only one unit, and, furthermore, these four pairs of valencies are all different. It is particularly remarkable that the three chlorides, CsCl , SbCl_3 , and SbCl_5 , which constitute one of the examples of the chromophore grouping, are all of them colorless compounds.

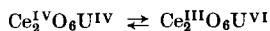
It seems possible that the action of this chromophore may be explained by exchanges of negative electrons between the atoms that differ in valency. It is supposed that in passing from one valency to another an atom gives up or takes on one or more electrons, and, if it is assumed that the atoms of a metal in two states of valency in the same molecule, instead of retaining fixed individual valencies, continually make these exchanges of electrons, it may be supposed that light, passing through such molecules, is in some way affected, so that colors or opacity are produced."

As the reader will find on reading ahead, in a good many systems so little work has been done on this phenomenon that we can add little today to what Wells wrote over 45 years ago. It is interesting to note that Wells' idea predates the pioneering work of Bury (116) on resonance in organic dyes by over 10 years.

The history of mixed valence chemistry goes far beyond the work of the twentieth century chemists, beginning with the synthesis in 1704 of one of the first coordination compounds, Prussian blue (572). The early history of the mixed valence phenomenon can be clearly seen as consisting of two phases. In the first earlier phase, we have the slow recognition of the mixed valence color phenomenon and an appreciation of the conditions which must prevail for its appearance. Thus, as early as 1847, Berzelius (63) described the blue-black ink derived from tannin-containing gall nuts as a double salt of Fe(II) and Fe(III) ions, similar to the other blue iron salts then known to contain these ions simultaneously. Werner (764) also commented on the extraordinary colors and metallic sheen of certain Pt(II) , Pt(IV) oxalate complexes he newly synthesized, comparing their colors to that of the tungsten bronzes and

hydroquinone, the common denominator in all these systems being the simultaneous presence of oxidizing and reducing species. Hofmann (365) followed shortly thereafter with convincing evidence that the blue color of Prussian blue and other iron cyanide complexes was due to the presence of iron in two different oxidation states in the molecule. The significance of the mixed valence phenomenon to the colors of certain iron-containing minerals was later elucidated by MacCarthy (470), who explained that the presence of Fe(II) and Fe(III) in minerals leads to deep colors, black if the mineral is anhydrous, blue if it is hydrated. In addition to these few examples, a long list of citations can be made of the appearance of transient dark colors in the course of oxidation and/or reduction of many transition metal compounds.

In the historical second phase, the seemingly logical inferences are drawn that in fact the different valences are not uniquely fixed, one to each ion, but oscillate rapidly in a mixed valence system, and that the result of this unique valence oscillation is a unique absorption of light, i.e., color. Thus, in 1915 Hofmann and Hörschle (366) suggested that the blue color of "cerium-uranium blue," a mixed oxide of UO_2 and CeO_2 , was the result of the valence oscillation,

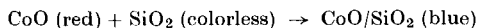


and coined the phrase "constitutive coloration" to describe this and other systems having colors which are not the sum of the colors of their components, but unexpectedly appear only on the union of these components:

"It is necessary that the distribution of oxidation states within the molecule can exchange under the influence of light so as to produce the light absorption and hence the color. This situation occurs most frequently in inorganic chemistry when the same element is present in different valence states in the same molecule."

Wells (759) shortly after, and without reference to the work of the Germans, came to the same conclusion quoted above, proposing in addition that the "spontaneous electronic activity" present in mixed valence compounds must also result in enhanced electrical conductivity. This latter conclusion of Wells made understandable the earlier work of Streintz (688), who found that white, yellow, red, and gray powders do not conduct electricity, whereas the deeply colored ones may show metallic conduction. Biltz (69) soon followed with an article outlining the origins of the colors of various inorganic materials, giving space to mixed valence colors and many examples of compounds wherein the same element occurs in two different oxidation states, and also to the situation wherein two different elements are present in different oxidation states.

This latter collection of examples is complicated by the possibility that the color change on mixing arises not from an oscillation of valence between different metal ions, but instead from a change in the ligand field about one of the components on going into the mixed crystal. Thus, the combination



is given as an example of the formation of a mixed valence, constitutive coloration. However, the red-to-blue color change given above could reasonably be interpreted as that expected for Co(II) in an octahedral site of CoO going into a tetrahedral site of SiO₂. The question raised here can obviously be settled by a study of the electronic spectrum, but until this is done there remains an ambiguity, which we take as an example of the fact that not *every* color change observed on mixing can be attributed to the mixed valence phenomenon.

Finally, the work of Stieglitz (687) must be mentioned as being of historical importance, for he expressed the thought that the deep color of many inorganic substances was intimately connected with the interatomic oxidation-reduction tendency of the compound. Thus, in mixed valence systems, he pointed out that intense colors can result from photochemical oxidation-reduction, the electrode potentials permitting, and that there is no compelling need to introduce an oscillation of the valences. As we shall see later, these two views are simply the extreme solutions of the same general problem, and many mixed valence systems can be found which support each of the two seemingly opposite positions.

Up to the present time, mixed valence phenomena have not very often been considered in the wider context of theories of spectroscopy and the solid state, but rather as peculiar occurrences occasionally met with here and there, their consequences here having no relationship to their consequences there. In fact, as we shall illustrate, mixed valence is found in a tremendous number of places, and it is hoped that a systematic study of the electronic phenomena related to its occurrence will serve to unite many seemingly unrelated facts. In Table I we list a number of the scientific areas in which mixed valence is encountered, together with examples. In a great many cases, the mixed valence introduces profoundly new effects.

Our first task is to cast the older, qualitative description of the mixed valence phenomena into a more modern, qualitative quantum mechanical one, relying heavily on ligand field theory. The accent here will be on the relationship between electronic spectra, electronic structure, and molecular structure. Following this, we will consider the experimental results at hand and attempt to apply our quantum

theoretical generalizations to them. Hopefully, by proceeding in this way, with all the data gathered in one place, we will uncover unexpected relationships and generalities, and, by pointing out where more work is needed, stimulate the completion of this work.

TABLE I
AREAS IN WHICH EXAMPLES OF MIXED VALENCE CAN BE FOUND

Area	Example
(1) Metal-metal bonding	$[\text{Ta}_6\text{Cl}_{12}]^{2+}$
(2) Nonstoichiometry	UO_{2-x}
(3) Coloration of glasses	Blue color of silicate glasses containing iron
(4) Biology	Hemocyanin
(5) Reaction intermediates	$\text{Fe}(\text{OH})_2$ (colorless) $\xrightarrow{\text{air}}$ (blue) $\xrightarrow{\text{air}}$ $\text{Fe}(\text{OH})_3$ (brown)
(6) Spot tests, qualitative analysis	$\text{Fe}^{\text{II}} + \text{Fe}^{\text{III}}(\text{CN})_6 \rightarrow$ blue solution
(7) Solid state	Self trapping, color centers, Na in NaCl (?)
(8) Electronic conduction	Controlled valency spinels
(9) Magnetic interactions	Ferromagnetic double exchange (LaMnO_3)
(10) Minerals	Biotite, Fe_3O_4
(11) Photochemistry, photography	Iron oxalate blueprint reaction, phosphotungstous acid images
(12) Metals in molten salts	Bi in BiI_3
(13) Intermetallics	$\text{In}^{\text{I}}\text{In}^{\text{III}}\text{Te}_2$
(14) Polyhalides	I_3^-
(15) Unusual oxidation states	Cs_2SbCl_6 , GaCl_2 , Pb_2O_3
(16) Statistical mechanics	Entropy-induced defect structures and shear phases
(17) Electrochemistry	AgO electrodes, Pb_2O_3
(18) Superconductivity	Tungsten bronze, Ag_2F
(19) Dyes, pigments, inks	Mo_3O_8 , W_3O_8 , Prussian blue
(20) Valence isomerization	$\text{Cu}^{\text{II}}\text{Ta}^{\text{IV}}\text{O}_3 = \text{Cu}^{\text{I}}\text{Ta}^{\text{V}}\text{O}_3$

II. Theory of Mixed Valence Effects

Our theory of mixed valence effects begins with a simple one-electron theory of the electronic structure of mixed valence systems, and then goes on to discussions of the electronic spectra, resistivity, and magnetic

interactions in such systems, followed by a few words about geometry and valence. The theory of mixed valence will use the concepts of ligand field theory as a basis, and is phrased in very broad and general terms. This is because there are very little quantitative data available on mixed valence compounds, and consequently very little need as yet for a detailed theory. The theory as outlined, however, is sufficient for drawing important preliminary qualitative conclusions about the electronic structures of these materials, and offers a foundation for a valuable classification scheme.

A. THE WAVE FUNCTIONS AND MIXED VALENCE CLASSIFICATION

Our initial concern is with the delineation of the mixed valence wave functions, the prime value of which is as a qualitative measure of the extent of delocalization of the valence shell electrons. Although these

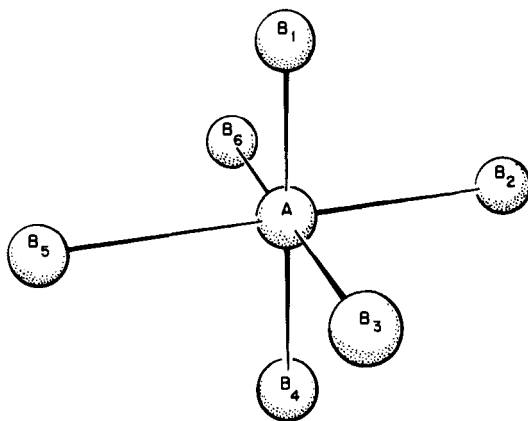


FIG. 1. A hypothetical mixed valence system consisting of the reduced metal ion at A, and six oxidized metal ions at the equivalent B sites. The ligands are not shown.

wave functions will not actually be used in a direct calculation of excitation energies, they can be of use in estimating other spectral properties, such as relative excitation energies, the number of excited states and their ordering, and spectral intensities. The extent of delocalization also correlates with the resistivity of mixed valence solids and their magnetic properties.

Consider the set of seven metal ions having the geometrical arrangement shown in Fig. 1. The metal ion in site A differs from those in the B sites not because of their relative geometrical arrangement, but because

the fields of the ligands, not shown, are supposed to be of different strengths and/or symmetries at the two sites. All the B sites are equivalent. Let us also suppose that the ion in the A site is of formal valence III [Ti(III), say] and that the ions in the B sites are all of formal valence IV [Ti(IV), say].

Neglecting explicit mention of the ligand wave functions, the ground state wave function of the system in *zeroth* order may be taken as

$$\Psi'_0 = \psi_A^{\text{III}} \psi_{B_1}^{\text{IV}} \psi_{B_2}^{\text{IV}} \cdots \psi_{B_s}^{\text{IV}} \quad (1)$$

where ψ_A^{III} is the wave function of the trivalent ion in the A site, and the $\psi_{B_i}^{\text{IV}}$ are the wave functions of the quadrivalent ions in the B sites. On transferring one electron from the A site to the B site, the A site and B site wave functions will change their oxidation state labels by +I and -I, respectively, yielding excited state wave functions, which may be written as:

$$\Psi_k = \psi_A^{\text{IV}} \sum_j C_{kj} \psi_{B_1}^{\text{IV}} \psi_{B_2}^{\text{IV}} \cdots \psi_{B_j}^{\text{III}} \cdots \psi_{B_s}^{\text{IV}} \quad (2)$$

There will be six Ψ_k 's, each with numerical coefficients C_{kj} chosen to normalize Ψ_k and chosen to guarantee that Ψ_k will transform according to one of the representations of the appropriate symmetry point group.

Suppose also that one of the Ψ_k 's, say Ψ_l , has a symmetry appropriate for mixing with Ψ'_0 , i.e., Ψ'_0 and Ψ_l belong to the same representation. The ground state, Ψ_0 , will then be taken as the linear combination

$$\begin{aligned} \Psi_0 &= \sqrt{1-\alpha^2} \Psi'_0 + \alpha \Psi_l \\ &= \sqrt{1-\alpha^2} \psi_A^{\text{III}} \psi_{B_1}^{\text{IV}} \psi_{B_2}^{\text{IV}} \cdots \psi_{B_s}^{\text{IV}} + \alpha \psi_A^{\text{IV}} \sum_j C_{lj} \psi_{B_1}^{\text{IV}} \psi_{B_2}^{\text{IV}} \cdots \psi_{B_j}^{\text{III}} \cdots \psi_{B_s}^{\text{IV}} \\ &= \sum_j \frac{\sqrt{1-\alpha^2}}{6} \psi_A^{\text{III}} \pi_{B_j} \psi_{B_j}^{\text{IV}} + C_{lj} \alpha \psi_A^{\text{IV}} \pi_{B_j} \psi_{B_j}^{\text{III}} \end{aligned} \quad (3)$$

where π_{B_3} is defined as

$$\pi_{B_3} = \psi_{B_1}^{\text{IV}} \psi_{B_2}^{\text{IV}} \psi_{B_4}^{\text{IV}} \psi_{B_5}^{\text{IV}} \psi_{B_6}^{\text{IV}}, \quad (4)$$

and similarly for the other π_{B_j} 's. Thus,

$$\Psi_0 = \frac{1}{N} \sum_j \pi_{B_j} \left\{ \frac{\sqrt{1-\alpha^2}}{6} \psi_A^{\text{III}} \psi_{B_j}^{\text{IV}} + C_{lj} \alpha \psi_A^{\text{IV}} \psi_{B_j}^{\text{III}} \right\} \quad (5)$$

where $1/N$ is a normalization factor.

At this point let us presume for simplicity that the reduced species in any site consists of one electron outside of a closed shell, so that we may take

$$\begin{aligned} \psi_A^{\text{IV}} &= \phi_A^C; & \psi_{B_j}^{\text{IV}} &= \phi_{B_j}^C \\ \psi_A^{\text{III}} &= \phi_A^C \phi_A^*; & \psi_{B_j}^{\text{III}} &= \phi_{B_j}^C \phi_{B_j}^* \end{aligned} \quad (6)$$

where ϕ^C represents the wave function for the closed-shell core, and ϕ^* is the only orbital outside the core. Using the above relations, one finds

$$\begin{aligned}\Psi_0 &= \frac{1}{N} \sum_j \pi_{B_j} \left\{ \frac{\sqrt{1-\alpha^2}}{6} \phi_A^C \phi_A^* \phi_{B_j}^C + \alpha C_{lj} \phi_A^C \phi_{B_j}^C \phi_{B_j}^* \right\} \\ &= \frac{1}{N} \sum_j \phi_A^C \phi_{B_j}^C \pi_{B_j} \left\{ \frac{\sqrt{1-\alpha^2}}{6} \phi_A^* + C_{lj} \alpha \phi_{B_j}^* \right\}\end{aligned}\quad (7)$$

The prefactor $\phi_A^C \phi_{B_j}^C \pi_{B_j}$ is simply the product of all the closed-shell core functions, κ , and can be carried along from this point onward without further comment. Thus,

$$\Psi_0 = \frac{\kappa}{N} \left[\sqrt{1-\alpha^2} \phi_A^* + \alpha \sum_j C_{lj} \phi_{B_j}^* \right] \quad (8)$$

We recognize the wave function in Eq. (8) as describing the optical electron in a *molecular orbital* written as a sum of atomic orbitals spanning both A and B positions. Notice that, since the A and B sites are distinguishably different and no symmetry operation will take a wave function centered on A into one centered on B, the two fragments ϕ_A^* and $\sum_j C_{lj} \phi_{B_j}^*$ must have the same symmetry if they are to be mixed. That is, the only Ψ_l which will be mixed in with Ψ'_0 must have its sum of $\phi_{B_j}^*$ orbitals transform like the ϕ_A^* orbital. Thus the electron will be delocalized from A onto the B sites only if the orbitals on A and B have the same point group symmetry, a result already well known in molecular orbital theory.

For normalized wave functions, the value of α^2 can be derived to be

$$\alpha^2 = N^2 \left[1 - \left\{ 1 + \frac{2E_l^2 - 2E_l \sqrt{E_l^2 + 4V^2} + 4V^2}{4V^2} \right\}^{-1} \right] \quad (9)$$

from the solution of the secular equation which expresses the mixing between Ψ'_0 and Ψ_l . In this equation, V is the mixing matrix element $\langle \Psi'_0 | V | \Psi_l \rangle$ and E_l is the energy of Ψ_l above Ψ'_0 . With an appropriate change of the zero of energy, the energies E_0 and E_l may be taken as approximately the valence state ionization potentials of the reduced ion at A and the reduced ion at B, respectively.

One sees from Eq. (9) that, as E_l approaches zero, both α and $\sqrt{1-\alpha^2}$ approach $(N\sqrt{2})/2$, whereas, for very large E_l , α tends to zero and $\sqrt{1-\alpha^2}$ to one. Thus if E_l is large, then α is small, and Eq. (8) reduces to the *zeroth order* Eq. (1) for the wave function of the system in the ground state, but Eq. (8) becomes more appropriate the smaller is E_l and the larger is α . A large value of E_l may come about either because the ions in

the two sites are of different elements, or because the sites differ in ligand field strength or ligand field symmetry. Inasmuch as this review considers only mixed valence compounds in which the oxidation states involved are those of the same element, nonzero values of E_i will be associated only with differences in ligand field strength and/or ligand field symmetry.

We now propose a mixed valence classification scheme which is based essentially upon the strength and symmetry of the ligand fields about the metal ions, and their relationship to the value of α appropriate to a particular system. By definition, in a class I system, the ions of differing valence are in sites of very different symmetry and ligand field strength, so that E_i is large and α approaches zero. In a class I system the simple product function of Eq. (1) is used to describe the ground state. An example of a class I system would be a mixed valence cobalt compound in which the Co(III) ions were in octahedral ligand fields with low-spin configurations, and the Co(II) ions were in tetrahedral ligand fields with high-spin configurations.

On the other hand, if the Co(II) and Co(III) ions are in exactly equivalent sites, so that E_i is zero and $\alpha = (N\sqrt{2})/2$, then the system is class III, and the molecular orbital description, Eq. (8), is needed for the ground state of the system. Class III mixed valence systems can be further subdivided into classes III-A and III-B, depending upon whether or not discrete polynuclear ions can be distinguished in the crystal. An intermediate classification, class II, is defined for cases in which delocalization does take place ($\alpha > 0$), but the two types of site are still distinguishable, and so the optical electron does not spend equal times on them. As an example, a class II system might have both oxidized and reduced cations in octahedral sites, but with the metal-ligand distances shorter at one site than at the other. It is not easy to draw a precise demarcation between classes I and II, but, in the vast majority of cases, class II systems have at least one ligand which bridges the two ions of differing valency, whereas in class I systems the metal ions are either removed from one another by two or more ligands which are relatively non-interacting, or have very different coordinations.

A further point arising from Eq. (9), and relevant to our selection of compounds as examples of mixed valence, is that α can become large not only when E_i is small, but also when V becomes large. It is for this reason that we have, with very few exceptions, excluded sulfides, arsenides, and all other compounds in which there is likely to be extreme metal-ligand covalency. In many single valence examples of this type, electron delocalization can occur with such a small expenditure of energy that the resulting low-frequency absorption bands and high

electronic conductivity would be difficult to distinguish from that to be ascribed to mixed valence interaction. Our approach to mixed valence systems is thus predominantly an ionic one, in which electron delocalization, if it occurs, involves primarily the metal ions whose valences are under discussion, and the ligands to a much smaller extent.

The motivation for the classification scheme outlined above sprang from our observation that each of the classes as defined exhibits certain easily recognized physical properties which are characteristic of that class. Thus, by a measurement of a single property which is characteristic of one of the four classes, many of the other physical properties of the system can be guessed, or become understandable. Because compounds with properties common to more than one class are rare, the classification scheme is of rather greater utility and has been used extensively in the discussion of the mixed valence compounds (Section III).

B. MIXED VALENCE SPECTRA

Since we are neither capable nor desirous of calculating spectra in a review of this kind, our goal is to present some generalizations which, although they are phrased in the form of a theory, in fact were arrived at by a study of the experimental results reported in the literature. Thus our effort here is to rationalize "the truth" in terms of a simple model which, by its generality, will be of use in the discussion of the spectra of a wide variety of mixed valence compounds.

Our fundamental concern in this section is with the mixed valence electronic transition,

$$\frac{\kappa}{N} \left[\sqrt{1 - \alpha^2} \phi_A^* + \alpha \sum_j C_{ij} \phi_{B_j}^* \right] \rightarrow \frac{\kappa}{N'} \left[\beta \phi_A^* - \sqrt{1 - \beta^2} \sum_j C_{mj} \phi_{B_j}^* \right] \quad (10)$$

where β plays the same role for the excited state that α does for the ground state. It is electronic transitions of this sort that comprise the mixed valence absorption spectrum in all three classes. Because the classification scheme is based essentially on geometry, and since the nuclei in the excited state will be considered as fixed in the ground state configuration, the ground and excited states of mixed valence transitions are assumed to belong to the same mixed valence class.

A study of the literature shows that in systems which are known by their crystal structures to be mixed valence class I ($\alpha = \beta = 0$), the mixed valence absorption bands fall at frequencies higher than $27,000 \text{ cm}^{-1}$, for they are almost all colorless. Those class I systems that do show absorption in the visible invariably contain a colored ion as a constituent, their

visible spectra being merely sums of the spectra of the constituent ions, and nothing more. Virtually all the colorless class I systems involve nontransition metal ions, which are quite stable in the ground state as M^n and M^{n+2} , but which are relatively unstable in the M^{n+1}, M^{n+1} configuration of the mixed valence upper state. Actually, a mixed valence absorption has never been observed in a class I system, so there is no evidence as to where in the spectrum it might be found.

In contrast, the class II mixed valence systems are characterized by an absorption band in the visible region of the spectrum ($14,000\text{--}27,000\text{ cm}^{-1}$) which is absent in the spectra of the constituent ions taken separately. In the simplest approximation, the energy of this transition is

$$h\nu = E_A + E_B + E_{mad} \quad (11)$$

where E_A and E_B are the changes in internal energy at sites A and B, respectively, on transferring an electron from A to B, and E_{mad} is the Madelung energy expended in moving the optical electron from A to B in the electrostatic field of all the other charges in the crystal. This last term can be calculated from a cycle in which adjacent ions are removed from the crystal to infinity, an electron transferred adiabatically between them, and the ions then returned to their sites in the crystal. The two internal energy terms in Eq. (11), however, correspond to the ionization potential and electron affinity of sites A and B, respectively, and as yet cannot be estimated or measured for inorganic complexes. Inasmuch as a class II mixed valence transition is a photochemical oxidation-reduction, the possibility of somehow adapting half-cell potentials to the estimation of the internal energy terms is attractive. However, it should be mentioned that the only application of such potentials to mixed valence systems resulted in the incorrect valence assignment for the ground state of Prussian blue (754).

Although the various contributions to the energy of the lowest-frequency mixed valence absorption band in class II compounds cannot yet be interpreted in detail, certain other features of the spectrum are more readily understood. It seems clear that in class II compounds, even though α and β are nonzero, the perturbation of the wave function can be sufficiently small so that constituent ion absorptions can still be recognized, albeit not at exactly their normal frequencies. Thus the $29,000\text{ cm}^{-1}$ transition characteristic of the $\text{Sb}^{\text{III}}\text{Cl}_6$ group is identified at $31,000\text{ cm}^{-1}$ in the blue class II compound $\text{Cs}_4\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Cl}_{12}$, and the $50,000\text{ cm}^{-1}$ charge transfer bands of the $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ ion are observed at this frequency in the class II compound $\text{KFe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6$. Because of this, the electronic spectrum holds promise for resolving ambiguities in the ground state valence configurations of many class II mixed valence

compounds. Similar constituent ion absorptions can be found in the infrared and Mössbauer spectra of class II compounds. For example, the ν_3 stretching frequency of the $[\text{Sb}^{\text{V}}\text{Cl}_6]^-$ ion in $\text{Cs}_4\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Cl}_{12}$ is shifted only 5 cm^{-1} from its position in $\text{RbSb}^{\text{V}}\text{Cl}_6$.

A second interesting point, which also follows from the slight perturbation of the constituent ion levels in class II systems, involves the remaining mixed valence spectrum. For illustration, consider the d -orbital pattern of a hypothetical class II $\text{Cu}(\text{I}), \text{Cu}(\text{II})$ complex in which

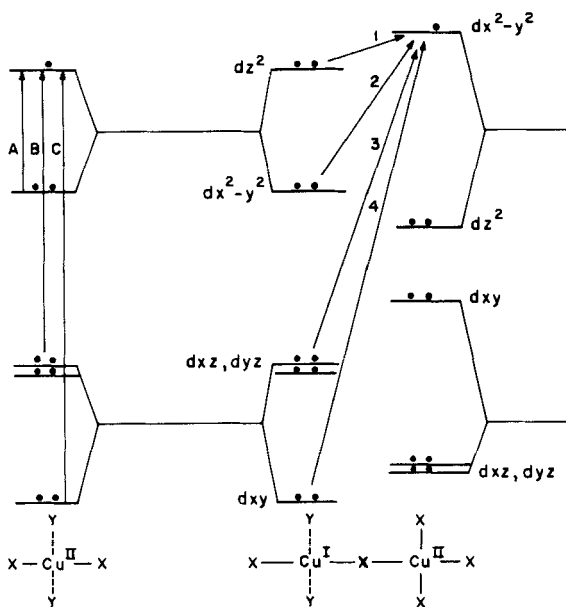


FIG. 2. The molecular orbital scheme for the hypothetical class II mixed valence system $\text{Cu}^{\text{I}}\text{Y}_2\text{X}_2\text{Cu}^{\text{II}}\text{X}_3$, showing how the energy difference between the two mixed valence transitions 2 and 1 is equal to the crystal field transition A in $\text{Cu}^{\text{II}}\text{X}_2\text{Y}_2$, etc.

the $\text{Cu}(\text{I})$ is in square coordination with two X and two Y ligands, and $\text{Cu}(\text{II})$ is in square coordination with four X ligands (Fig. 2). In such a simple system there will be four mixed valence absorption bands, labeled 1, 2, 3, and 4. The point of interest here is that the energy difference between mixed valence transitions 1 and 2 will be equal to the first crystal field excitation energy of the $\text{Cu}(\text{II})$ ion in the $\text{Cu}(\text{I})$ ion site, i.e., transition A ($dx^2 - y^2 \rightarrow dz^2$) in the oxidized ion. Similarly, mixed valence transition 3 will appear displaced from transition 1 by the $\text{Cu}(\text{II})$ crystal field excitation B ($dxz, dyz \rightarrow dz^2$). Thus in this case, the entire crystal field spectrum of the oxidized ion, $\text{Cu}(\text{II})$, in the reduced

ion site (A) appears in the mixed valence spectrum, shifted from where it ordinarily would appear by the energy of the lowest mixed valence transition. Other samples exist where the mixed valence spectrum consists of the crystal field spectrum of the reduced ion in the oxidized ion site, or of combinations of both kinds of spectrum. However, not all crystal field states will necessarily appear in the mixed valence spectrum, since many of the excited crystal field configurations require two-electron excitation when attained from the mixed valence ground state. Only one example of the shifting of the crystal field spectrum by the mixed valence excitation energy has so far been reported (591).

The intensities of electronically allowed transitions in class II systems are another interesting aspect of mixed valence spectra. In an electronically allowed transition, the orbital $\sum_j C_{mj} \phi_{Bj}^*$ of the upper state must transform differently under the operations of the symmetry point group than does $\sum_j C_{lj} \phi_{Bj}^*$, so that $\sum_j C_{mj} \phi_{Bj}^*$ cannot mix with ϕ_A^* , and thus β is zero. The intensity of such an electronically allowed mixed valence transition is proportional to the square of the transition moment integral,

$$\mu = \frac{g^{1/2}}{NN'} \int \left[\sqrt{1 - \alpha^2} \phi_A^* + \alpha \sum_j C_{lj} \phi_{Bj}^* \right] \mathbf{M} \sum_j C_{mj} \phi_{Bj}^* d\tau \quad (12)$$

where g is the orbital degeneracy of the transition, and \mathbf{M} is the electric moment operator. By neglecting overlap distributions between the A and B sites, the x component of Eq. (12) can be reduced to

$$\mu_x = \frac{\alpha g^{1/2}}{NN'} \int \sum_j C_{lj} \phi_{Bj}^* \text{ex} \sum_j C_{mj} \phi_{Bj}^* d\tau \quad (13)$$

$$= \frac{e\alpha g^{1/2}}{NN'} \sum_j C_{lj} C_{mj} x_j \quad (14)$$

in which x_j is the x coordinate of the j th site. Exactly similar equations hold for the y and z moments. The utility of Eq. (14) lies in the fact that, if the system is sufficiently regular geometrically so that the C_{lj} 's and C_{mj} 's are determined by symmetry, and the x_j 's are known from a crystal structure determination, α can be obtained from a measurement of μ ; μ is calculated from the equation

$$\mu^2 = 9.17 \times 10^{-4} \int \epsilon d \log \lambda \quad (15)$$

in which ϵ is the molar extinction coefficient of the mixed valence absorption band at wavelength λ , and μ^2 is measured in cm^2 .

There is one complication worth considering here, and that is the case where there are two types of orbital at each B site, call them

$\phi(z^2)_j^*$ and $\phi(x^2 - y^2)_j^*$, say. The possibility then arises for a transition involving the two types of orbital, leading to the transition moment:

$$\mu = \frac{\alpha g^{1/2}}{NN'} \int \sum_j C_{lj} \phi(z^2)_j^* \mathbf{M} \sum_j C_{mj} \phi(x^2 - y^2)_j^* d\tau \quad (16)$$

$$\mu = \frac{\alpha g^{1/2}}{NN'} \sum_j C_{lj} C_{mj} \int \phi(z^2)_j^* \mathbf{M} \phi(x^2 - y^2)_j^* d\tau \quad (17)$$

The transition moment integral in Eq. (17) is one between atomic orbitals on the same atom, and can be zero even though the selection rules predict an allowed transition between Ψ_0 and Ψ_m . This is possible because the selection rule allowing a transition between Ψ_0 and Ψ_m guarantees that the intensity generated in one part of the molecular system is not canceled by that in another part, but by itself does not guarantee that the intensity within this part of the molecular system is not itself zero. Inasmuch as the intensity of an electronically allowed mixed valence transition does depend upon α , it can readily be appreciated that there can be no *intense* ($\epsilon \geq 4000$) mixed valence absorption unless ϕ_A^* and some ϕ_B^* have a nonzero overlap.

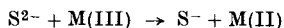
That highly hydrated mixed valence compounds have only the pale color of their constituent ions, but become more deeply colored as the water is removed, is one of the mixed valence facts of life. This is understandable, since water is not a bridging ligand and would promote the formation of a class I system when present in large proportions. However, as the water is removed, the empty sites must be filled by ligand anions which can bridge two metal ions and thereby turn the compound into a more deeply colored class II system.

Polynuclear mixed valence anions, cations, and neutral species in which the sites of all metal ions are equivalent are classified as III-A. The interpretation of the spectral properties of class III-A systems differs from that of class II systems, for in class III-A the distinction between A and B sites is lost completely, so that $E_A = -E_B$, and E_{mad} is zero. The excitation energies in class III-A are instead dependent upon ligand field splittings and molecular orbital resonance integrals, just as they are in an ordinary polynuclear complex having metal-metal bonds. Also, unlike class II, there will be no recognizable constituent ion spectra in class III-A compounds.

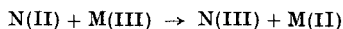
Class III-B systems are metals and as such show an absorption edge, usually in the infrared, and are opaque with a metallic reflex in the visible region.

In a broader sense, there is really nothing unique about mixed valence systems, for mixed valence properties are to be expected in any

system containing simultaneously an oxidizable and a reducible species in close contact. Thus, transition metal sulfides may have many properties in common with class II mixed valence systems, for the excitation



may be thought analogous to the excitation



in a mixed valence system. The difference between these two examples is one of degree only, for if the N and M ions are of the same element and are in identical ligand fields, then the energy difference between $N(II) + M(III)$ and $N(III) + M(II)$ will be as small as zero, whereas no such statement can be made for $S^{2-} + M(III)$ versus $S^{-} + M(II)$.

The relationship of inorganic mixed valence systems to the organic charge transfer complexes is also a close one. In fact, the charge transfer complex quinhydrone is mentioned in Biltz's early article on inorganic mixed valence systems (69). The unexpected deep black color of quinhydrone was correctly seen by Biltz to be a consequence of having formed a crystal containing an intimate mixture of the oxidized material (benzoquinone) and the corresponding reduced material (hydroquinone), in every way equivalent to the formation of a deep blue color in crystals which contain $Fe(III)$ (an oxidized material) and $Fe^{II}(CN)_6$ (a reduced material).

C. MAGNETISM AND ELECTRON TRANSPORT

The magnetic and electron transport properties of mixed valence compounds are closely related to one another, and the wide variations observed in their behavior give further weight to our proposed classification scheme. In particular, we can make operational distinctions between class I and class II compounds on the basis of these properties in a way not possible from a knowledge of the crystal structure alone.

In a class I mixed valence material, the electrons which distinguish the valence of one ion from another are so firmly trapped that virtually no magnetic coupling between partly filled shells on adjacent metal ions is possible, and these substances are paramagnetic down to very low temperatures. Thus a class I compound such as $Co^{II}Co_2^{III}O_4$ will have a molar magnetic susceptibility precisely that expected for a mixture of one mole of $Co(II)$ in tetrahedral coordination and two moles of $Co(III)$ in octahedral coordination. That electron transfer can occur only at the expense of a large amount of energy also means that class I materials are electrical insulators.

At the opposite extreme, when α in Eq. (9) has its maximum value, the odd electrons responsible for the mixed valence occupy a band spanning the entire cation sublattice (we are ignoring the possibility that they have any appreciable density on the anion sublattice, as mentioned above). In such a case, two electrons occupy each state of the energy band up to the Fermi surface so that, with completely filled inner shells and in the absence of a magnetic field, each atom has no net spin, and atomic moments exist only through induction by an applied field. By Lenz's law, such moments give a diamagnetic susceptibility, but for collective electrons there is a further possibility that an applied field might alter the populations of the electron states, producing what is known as temperature-independent Pauli paramagnetism. If each cation contributes either zero or two electrons to a band, then the band will be either completely empty or completely filled, and in either case the material will be an insulator. However, by their very nature of being mixed valence, the cations in class III-B materials will contribute, on the average, an intermediate number of electrons to the band, filling it only partially. Thus class III-B mixed valence materials will show metallic conductivity. The class III-B tungsten bronzes are good examples of these mixed valence effects, for they have temperature-independent paramagnetic susceptibilities and metallic conductivities. A second type of magnetic behavior in class III-B systems is described below.

The possibility of ferromagnetic ordering between the local magnetic moments in transition metals was first considered by Zener (812), who proposed that, in the metallic state, it was the conduction electrons which coupled the d -shell moments together. Since, according to Hund's rule, the lowest energy configuration within each d -shell has the spins of all of the unpaired electrons parallel, if the conduction electrons are to carry their spins unchanged from atom to atom, they must move in an environment of parallel spins, i.e., the moments of all the atoms must point in the same direction. Contrasting the Heusler alloys, which are conducting and ferromagnetic, with MnF_2 , which is an antiferromagnetic insulator, Zener concluded that ferromagnetism would never occur in the absence of conduction electrons (812). Shortly afterwards, the properties of a series of metallic mixed valence manganites, $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-x}^{\text{III}}\text{Mn}_x^{\text{IV}}\text{O}_3$, were investigated by Jonker and van Santen (392, 393), and these have since become the classic examples of Zener's "double exchange" phenomenon. The relationship between ferromagnetism and conductivity is brought out most clearly by a simple example. In contrast to the metals described above, between each manganese ion in the perovskite structure of $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-x}^{\text{III}}\text{Mn}_x^{\text{IV}}\text{O}_3$

there is an oxide ion, through which any electron transport must occur, although, as we have noted several times, the initial and final states of electron transfer are assumed to have very little unpaired spin density on any intervening ions. This is equivalent to saying that we could write wave functions for systems such as those described by Eqs. (1) and (2) as if their metal-ligand electronic configurations were $\text{Mn}_A^{\text{III}}\text{O}^{2-}\text{Mn}_B^{\text{IV}}$ and $\text{Mn}_A^{\text{IV}}\text{O}^{2-}\text{Mn}_B^{\text{III}}$. The magnetic exchange energy of such a system is given by

$$E_m = \int \psi_A^{\text{III}} \psi_0 \psi_B^{\text{IV}} (H - E_0) \psi_A^{\text{IV}} \psi_0 \psi_B^{\text{III}} d\tau \quad (18)$$

where H is the Hamiltonian for the entire system, and E_0 is the energy associated with the initial states, assumed degenerate. The dominant term of the exchange integral contains a product of wave functions $\psi_A(1)\psi_0(1)\psi_0(2)\psi_B(2)$, suggesting that one visualize the electron transfer from one manganese to the next as a transfer of electron (2) from the oxygen to the Mn_B^{IV} ion with a simultaneous transfer of electron (1) from Mn_A^{III} to the oxygen; a connection between ferromagnetic coupling and electronic conductivity is thus apparent. That the interaction in a mixed valence compound is ferromagnetic arises in the following way. Of the two antiparallel electron spins on the oxide ion, Hund's rule predicts that the oxide ion electron with spin parallel to those of the $3d^3$ Mn (IV) ion will be transferred the more readily, leaving behind the electron of opposite spin. Similarly, the $3d^4$ Mn(III) ion will transfer an electron to the O^- ion which has a spin opposite to that remaining on O^- . The net result is that the manganese ions are coupled via the oxide ligand only if the spins on the two metal ions are parallel, i.e., in ferromagnetic alignment.

If the magnetic exchange energy in the system discussed above is E_m , the "extra" electron, when placed on one of the manganese atoms, will oscillate between them with a frequency

$$\nu = 2E_m/\hbar \quad (19)$$

and will have a diffusion coefficient

$$D = a^2 E_m / \hbar \quad (20)$$

where a is the cation-cation separation. Using the Einstein relation between electrical conductivity, σ , diffusion coefficient, and the number of ions per unit volume, n ,

$$\sigma = ne^2 D / kT \quad (21)$$

one then finds that

$$\sigma = ne^2 a^2 E_m / \hbar kT \quad (22)$$

If we further assume, along with Zener and Heikes (814), that $E_m \simeq kT_c$, where T_c is the ferromagnetic Curie temperature, then the resistivity at this temperature for a typical cation-cation separation of 3 Å is approximately 10^{-3} ohm cm. As we shall see, the resistivities of a number of class III-B mixed valence materials at room temperature are in order of magnitude agreement with this estimate. The number of charge carriers/cc in a class III-B metal is estimated simply from the density of the material and the difference in the formal oxidation states of the cations involved in the mixed valence.

We now want to consider the magnetic and electrical properties of the intermediate, mixed valence class II materials. Mott (519) was the first to point out that there should exist some critical interatomic separation at which the types of molecular orbital (or band, in the limit of an infinitely extended lattice), which we have set up, are no longer the best approximation for treating the interactions between cations. For large interatomic separations, a Heitler-London approach, which assigns a fixed integral number of electrons to each cation and does not permit polar states as does the molecular orbital model, would have to be used. This argument was originally proposed to account for the fact that transition metal oxides like NiO, with incompletely filled d -shells and bridging anions separating the cations, are not metals but insulators. As will be discussed below, it is this model which is most appropriate to class II materials.

Zener assumed that the two configurations $\text{Mn}^{\text{III}}\text{O}^2-\text{Mn}^{\text{IV}}$ and $\text{Mn}^{\text{IV}}\text{O}^2-\text{Mn}^{\text{III}}$ were indistinguishable, which is equivalent to setting $E_t = 0$ in Eq. (9), so that the system belongs to class III-B. If this were not the case and the "extra" electron were trapped by lattice polarization ($\text{Mn}^{\text{III}}-\text{O}$ and $\text{Mn}^{\text{IV}}-\text{O}$ bond lengths different), further work must be spent in rendering the bond lengths equal so that electron migration can occur. This activation energy corresponds to ΔG , the change in Gibbs free energy of the system, and the diffusion coefficient would then be:

$$D = a^2\nu_0 e^{-\Delta G/kT} \quad (23)$$

Heikes and Johnston (351), who first derived expressions for the so-called "hopping model," identified ν_0 with the lattice vibration frequency, and values obtained from their work on lithium-doped mixed valence transition metal oxides are of the expected magnitude (about 10^{13} sec $^{-1}$).

The temperature dependence of conductivity implied by Eq. (23) is that of a semiconductor, and we thus expect this type of electronic activity in class II substances. Inasmuch as class II compounds have relatively low conductivities as compared with class III-B compounds, according to Eq. (22), they will have correspondingly weaker ferro-

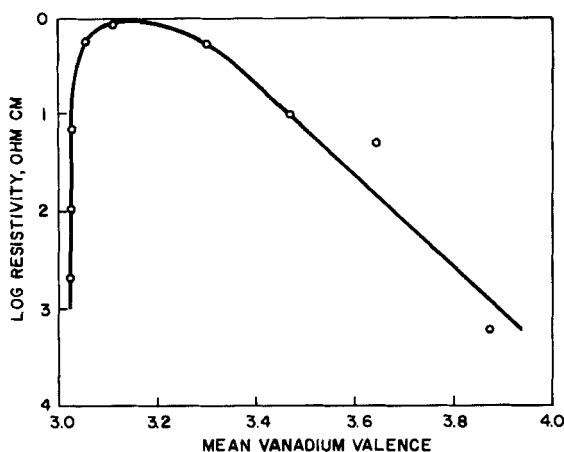


FIG. 3. The resistivity of mixed crystals of $\text{MgV}_2^{\text{III}}\text{O}_4$ and $\text{Mg}_2\text{V}^{\text{IV}}\text{O}_4$ as a function of the mean valence of the vanadium ions (581).

magnetic interactions. Thus they will remain paramagnetic down to much lower temperatures than will class III-B materials, and at low temperatures may go either ferromagnetic or antiferromagnetic, depending upon the relative strengths of the interactions between like and unlike valences.

TABLE II
CONTROLLED VALENCY SEMICONDUCTORS

Host	Dopant ^a	Valence introduced	Crystal lattice
$\text{Ni}^{\text{II}}\text{O}$	Li_2O	Ni^{III}	Rock salt
$\text{Mn}^{\text{II}}\text{S}$	Li_2O	Mn^{III}	Rock salt
$\text{CaTi}^{\text{IV}}\text{O}_3$	La_2O_3	Ti^{III}	Perovskite
$\text{BaTi}^{\text{IV}}\text{O}_3$	La_2O_3	Ti^{III}	Perovskite
$\text{CaMn}^{\text{IV}}\text{O}_3$	La_2O_3	Mn^{III}	Perovskite
$\text{LaMn}^{\text{III}}\text{O}_3$	CaO	Mn^{IV}	Perovskite
$\text{LaFe}^{\text{III}}\text{O}_3$	SrO	Fe^{IV}	Perovskite
$\text{Fe}_2^{\text{III}}\text{ZnO}_4$	TiO_2	Fe^{II}	Spinel
$\text{Fe}_2^{\text{III}}\text{O}_3$	SnO_2	Fe^{II}	Hematite
$\text{Ti}^{\text{IV}}\text{O}_2$	Ta_2O_5	Ti^{III}	Rutile
$\text{MgW}^{\text{VI}}\text{O}_4$	Cr_2O_3	W^{V}	Wolframite

^a In each of these systems, the dopant cation is thought to replace the cation listed first in the formula of the host crystal.

TABLE III
CHARACTERISTICS OF THE FOUR CLASSES OF MIXED VALENCE COMPOUNDS

Class I	Class II	Class III-A	Class III-B
(1) Metal ions in ligand fields of very different symmetry and/or strength, i.e., tetrahedral vs. octahedral	(1) Metal ions in ligand fields of nearly identical symmetry, differing from one another by distortions of only a few tenths Å	(1) Metal ions indistinguishable but grouped into polynuclear clusters	(1) All metal ions indistinguishable
(2) $\alpha = 0$; valences very firmly trapped	(2) $\alpha > 0$; valences distinguishable, but with slight delocalization	(2) α maximal locally	(2) α maximal; complete delocalization over the cation sublattice
(3) Insulator; resistivity of 10^{10} ohm cm or greater	(3) Semiconductor; resistivity in the range 10 – 10^7 ohm cm	(3) Probably insulating	(3) Metallic conductivity; resistivity in the range 10^{-2} – 10^{-6} ohm cm
(4) No mixed valence transitions in the visible region	(4) One or more mixed valence transitions in the visible region	(4) One or more mixed valence transitions in the visible region	(4) Absorption edge in the infrared, opaque with metallic reflectivity in the visible region
(5) Clearly shows spectra of constituent ions, IR, UV, Mössbauer	(5) Shows spectra of constituent ions at very nearly their normal frequencies	(5) Spectra of constituent ions not discernible	(5) Spectra of constituent ions not discernible
(6) Magnetically dilute, paramagnetic or diamagnetic to very low temperatures	(6) Magnetically dilute, with both ferromagnetic and antiferromagnetic interactions at low temperatures	(6) Magnetically dilute	(6) Either ferromagnetic with a high Curie temperature or diamagnetic, depending upon the presence or absence of local moments

Among the mixed valence manganites (392, 393), the connection between composition, Curie temperature, and resistivity is well established, and, in other systems in which the concentrations of two valence states can be varied, the conductivity also varies strongly (Fig. 3). Verwey and co-workers (730) have successfully altered these concentrations in a great many oxides, producing what are known as "controlled valency semiconductors." As illustrated in Table II, the addition of an insulating dopant to an insulating host crystal can alter the mean valency of the host's cations so as to render the system class II mixed valence and semiconducting.

The characteristics of the four classes of mixed valence compounds are compared in Table III.

D. MOLECULAR GEOMETRY

Inasmuch as the class of a mixed valence compound is intimately related to its crystal structure, the a priori prediction of the class of a mixed valence compound is equivalent to the a priori prediction of its crystal structure, a feat to which we can only aspire. The only mixed valence species upon which one can readily perform a calculation is the H_3^+ molecule-ion, which, from very complete calculations (147), would appear to be class III-A. A simple calculation on this molecule-ion reveals the two factors of importance in determining whether any mixed valence system will belong to class III or to a class of lower symmetry.

The total energy of the ground state of H_3^+ in various configurations was calculated, using as a basis nine *s*-type Gaussian orbitals on each proton, scaled to reproduce a Slater orbital with an effective nuclear charge of 1.414. In the first configuration (Fig. 4), the proton is situated 0.89 Å from each of the protons in H_2 (internuclear separation, 0.74 Å) and the two electrons are localized within the H_2 molecule. With the electrons still localized, the H_2 molecule is then stretched from 0.74 Å to 0.89 Å internuclear separation, raising the total energy by 24 kcal/mole and making all three protons equivalent. In the third configuration, the valence oscillates with the electrons moving over all three nuclei, and the total energy is then lowered by 135 kcal/mole.

This example of the H_3^+ molecule-ion illustrates the two opposing factors which must be considered in any problem of mixed valence geometry: (a) the reorganization energy which must be expended to stretch and/or compress certain bonds so as to make all the sites equivalent, and (b) the resonance energy stabilization which accrues from the oscillation of valence. If the second factor is larger than the first, then the system will belong to class III-A or III-B, whereas, if it is smaller than

the first, then the system will belong to class II or I. As explained in the previous section, if the reorganization energy is of the order of thermal energies, then the valence may oscillate via a hopping process.

Other attempts to predict which class a pair of mixed valence metal ions might prefer are frustrated by the fact that unusual coordinations can result in mixed valence compounds. Thus, for example one would ordinarily guess that Cu(I),Cu(II) systems would be class I or II, for

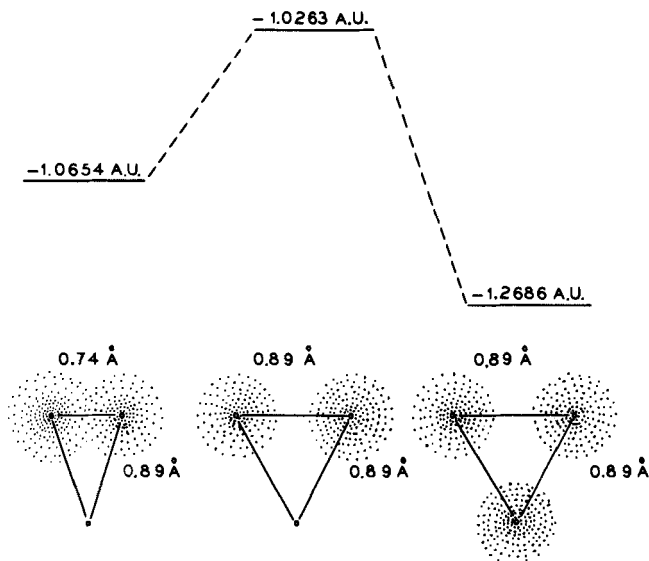


FIG. 4. The relative effects of reorganization and resonance on the total energy and geometry of the H_3^+ mixed valence molecule-ion.

these ions in general have very different coordination symmetries. However, in $KCu_3Cu^{II}S_3$, all the copper ions are in identical regular tetrahedral sites, a geometry never found for Cu(II) salts. There are other examples of unexpected geometries in class III systems.

III. Survey of the Elements

An indiscriminate study of mixed valence chemistry rapidly takes one from the simple salts and oxides into the realm of sulfides, tellurides, arsenides, and a vast array of other intermetallics. In an effort to keep this review of manageable length, we have arbitrarily ignored all but a very few compounds of this latter group, concentrating instead on the mixed valence oxides, halides, cyanides, and other simple salts, as well as coordination compounds. Many of the properties of mixed valence

compounds described in Section II can also be found in mixed metal complexes, such as $\text{KMn}^{\text{II}}\text{Fe}^{\text{III}}(\text{CN})_6$, which also have been ignored in this review. Similarly, we have neglected mention of all thermodynamic properties of mixed valence compounds, and have paid only slight attention to areas such as mixed valence kinetic and mechanism studies, fused salt chemistry, and the defect solid state.

In general, a mixed valence compound is most readily identified as such by its formula. However, there are certain difficulties in this, since in many cases the proposed formula is little more than a statement of analytical results, and a poor analysis might mistakenly turn a single valence material into a mixed valence one. A second problem, which arises most especially with oxides, is that of mixtures mistaken for pure mixed valence materials, and we mention this possibility wherever it seems advisable. Our emphasis throughout is first on structure, since this enables one to make a preliminary estimate of a compound's mixed valence class, and then on electronic properties as enumerated in Section II.

The order of presentation follows that of the Periodic Table, starting with the first-row transition elements, followed by the second- and third-row transition elements considered jointly, the groups III-A, IV-A, and V-A elements, and finally the lanthanide and actinide elements.

A. TITANIUM

The most extensively studied titanium mixed valence compounds are the oxides. That they provide a good example of the sensitivity of physical properties to stoichiometry is demonstrated by Verwey's early work on TiO_x (727), which has a resistivity of 10^{10} ohm cm when $x = 2.000$, decreasing to 10 when $x = 1.999$, and to 1.2 for $x = 1.995$. In addition to studies of the optical and electrical properties of $\text{Ti}^{\text{IV}}\text{O}_2$ containing small amounts of $\text{Ti}(\text{III})$, interest in the titanium mixed valence oxides has centered on the structures of the numerous oxides intermediate between Ti_2O_3 and TiO_2 , although it is unfortunate that rather less attention has been devoted to their physical properties.

The first X-ray phase analysis of the titanium-oxygen system, by Ehrlich (216), uncovered four phases with homogeneity ranges $\text{TiO}_{2.00}$ – $\text{TiO}_{1.90}$, $\text{TiO}_{1.80}$ – $\text{TiO}_{1.65}$, $\text{TiO}_{1.56}$ – $\text{TiO}_{1.46}$, and $\text{TiO}_{1.25}$ – $\text{TiO}_{0.6}$. After some disagreement (15, 349) as to whether the composition variation was due to random removal of some of the oxygen atoms or addition of extra titanium atoms to the parent TiO_2 rutile lattice, it is now recognized that in the $x = 1.65$ – 1.80 range there are at least seven stable

oxides, all with the general formula $\text{Ti}_n\text{O}_{2n-1}$, with $n = 4-10$ (18). Members of the series with $n = 1, 2$, and 3 are also known. The occurrence of such "homologous series" or Magneli phases (474) among mixed valence transition metal oxides is quite frequent, and further examples are described in the sections on vanadium, niobium, and molybdenum and tungsten. In each case, blocks of the parent lattice structure (here rutile) are interrupted by regions of higher cation concentration, which can be thought of as resulting from the "shearing" (738) of one block past another. In the present example, blocks of the rutile (MO_2) structure are interleaved with layers of corundum (M_2O_3) structure. In the rutile structure, TiO_6 octahedra are joined through their corners and edges, but, in an oxide such as Ti_5O_9 (18) (Fig. 5), every fifth TiO_6 in one

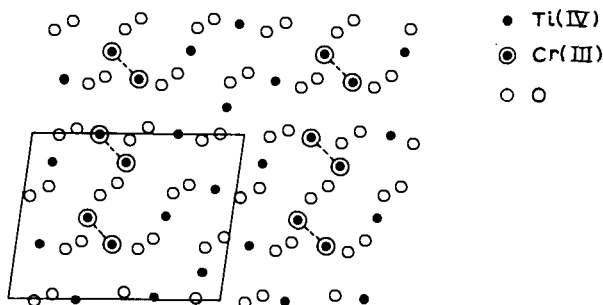


FIG. 5. The crystal structure of Ti_5O_9 and the isostructural compound $\text{Cr}_2\text{Ti}_3\text{O}_9$, viewed along $[100]$ (18).

direction is joined to one of its neighbors by sharing one of their octahedral faces. The distance between the face-sharing pairs of titanium atoms in Ti_5O_9 is 2.81 Å, compared with 2.56 Å for the closest metal-metal distance in Ti_2O_3 , which has a corundum structure in which the TiO_6 units share both faces and edges. While there is no conclusive evidence that this series of oxides could be described as class II mixed valence systems of the sort $\text{Ti}_{n-2}^{\text{IV}}\text{Ti}_2^{\text{III}}\text{O}_{2n-1}$, there are two pieces of evidence that make the suggestion plausible. First, it has proved possible to isolate several mixed oxides of Ti(IV) and Cr(III), isostructural with the above homologous series, which have the general formula $\text{Ti}_{n-2}^{\text{IV}}\text{Cr}_2^{\text{III}}\text{O}_{2n-1}$ (8). Thus each block of rutile lattice, regardless of its size, accommodates only two chromium ions, and the question is whether these are randomly distributed or, as seems more likely, located in the face-sharing pairs of octahedral sites at the ends of each rutile block (the circled atoms in Fig. 5). ESR or static susceptibility measurements would settle the question if they could show whether or not the Cr(III) ions were mag-

netically coupled in pairs. The second piece of evidence bearing on the pairing of Ti(III) ions in $\text{Ti}_n\text{O}_{2n-1}$ has to do with a set of magnetic susceptibilities determined by Ehrlich (216) on samples which, in the light of the more recent structural work, may have been phase mixtures. Measurements were made at -183°C and $+20^\circ\text{C}$ only, but the form of the plots of molar susceptibility against composition at the two temperatures suggests that, when $x = 1.95\text{--}2.00$, the Curie-Weiss law applies. When larger amounts of Ti(III) were incorporated in the TiO_2 lattice, the molar susceptibility fell rapidly, and Ehrlich calculated that, in the region of $\text{Ti}_n\text{O}_{2n-1}$ formation, the antiferromagnetic interaction between the Ti(III) ions was as marked at -183°C as in Ti_2O_3 , as might be expected if the magnetic Ti(III) ions were in face-sharing pairs. If we are right in regarding the shear structures of the $\text{Ti}_n\text{O}_{2n-1}$ compounds as sheets of corundum-like Ti_2O_3 separating blocks of rutile TiO_2 , the mixed valence interaction is between cations situated in octahedra which share edges rather than faces. Because all the metal ions, regardless of valence, are in octahedral sites, the $\text{Ti}_n\text{O}_{2n-1}$ compounds are catalogued as class II. However, more physical measurements will be needed before the picture can be made more precise. Although the $\text{Ti}_n\text{O}_{2n-1}$ oxides are all dark blue to black, the facts that Ti_2O_3 is violet because of the $d\text{--}d$ transitions of the octahedrally coordinated Ti(III) ion (16), and also that the $\text{Ti}_{n-2}^{\text{IV}}\text{Cr}_2^{\text{III}}\text{O}_{2n-1}$ compounds are "graphite gray" (16), mean that no simple conclusions about the interaction absorption in these compounds can be drawn from the qualitative reports of their colors.

Although its formula fits the $\text{Ti}_n\text{O}_{2n-1}$ sequence, Ti_3O_5 has a structure in which rutile and corundum fragments cannot be distinguished. Two forms of Ti_3O_5 exist, a high-temperature modification (anosovite), whose structure was determined by Zhdanov and Rusakov (815), and a black modification stable at room temperature, investigated by Asbrink and Magneli (26). These phases provide an interesting contrast, for anosovite appears to be a class III-B system with all the TiO_6 octahedra having somewhat similar distortions and all sharing six edges with their neighbors, whereas in the low-temperature phase there are three ways in which the octahedra, although similarly distorted, share edges with their neighbors. In anosovite there are no exceptionally close metal-metal contacts but, in low-temperature Ti_3O_5 , one pair of titanium atoms per unit cell is separated by only 2.61 Å, and other metal-metal distances are intermediate between this and 3.1 Å. Thus the system is class II, although the valence distribution cannot be unambiguously defined.

Since small deviations from stoichiometry in TiO_2 due to traces of Ti(III) darken the color of this white pigment, and are therefore extremely important to the paint industry, a number of optical studies

of reduced TiO_2 have been reported. Weyl (385) suggested that the discoloration of rutile on firing was due to reduction of some of the cations, and found that a similar result could be achieved by doping the rutile with pentavalent ions. Working with medium and strongly reduced rutile crystals, Cronmeyer (169) found a very broad absorption band near $10,000 \text{ cm}^{-1}$, whose intensity was proportional to the room temperature conductivity of the samples. An equally broad band also occurs at nearly the same frequency in samples containing only very small concentrations of Ti(III) (735). These results, as well as much of the earlier work on the optical and electrical properties of reduced TiO_2 (306), were interpreted on the assumption that the defect centers were oxygen vacancies acting as doubly charged donors. That the correct description involves interstitial Ti(III) ions is shown not only by the structural studies of the $\text{Ti}_n\text{O}_{2n-1}$ compounds, described above, but also by a good deal of ESR work (135, 136, 805). Reduced and niobium- and tantalum-doped samples of TiO_2 were studied, as well as centers produced by γ and ultraviolet irradiation, and in all cases the "extra" electrons were found trapped on titanium atoms, as shown also by the presence of weak hyperfine structure due to titanium nuclei with spins $5/2$ and $7/2$. To explain the results of his electrical conductivity, Hall effect, and thermoelectric power measurements on reduced rutile single crystals, Frederikse (260) therefore started from the assumption that, at very low temperatures, nearly all the electrons were self-trapped on cation sites by polarization of the surrounding lattice. The traps are sufficiently shallow to be thermally ionized, however, and so, at higher temperatures, conduction occurs in a narrow $3d$ band associated with the titanium ions, which is equivalent to a class III-B mixed valence system. This conclusion was broadly confirmed by recent high-temperature conductivity experiments over a wide range of oxygen pressure (76). If the energy required to discharge a trapped $3d$ electron into a conduction band is indeed within the range of thermal energies, there must be some doubt whether the system should be described as class II or III-B in our classification. Strictly speaking, therefore, the criteria of the classification ought to be applied at absolute zero.

Compounds which are more likely to belong in class III-B at all temperatures are the alkali metal (17, 739) and lanthanum (411) titanium bronzes, $\text{Na}_x\text{Ti}_4\text{O}_8$ and $\text{La}_{(2/3+x)}\text{TiO}_3$. Both series are said to form blue-black or black electrically conducting crystals with a metallic luster, but no detailed optical or conductivity experiments have been reported. A series of manganese titanates, $\text{Mn}_{(1+x)}^{\text{II}}\text{Ti}_{2(1-x)}^{\text{III}}\text{Ti}_x^{\text{IV}}\text{O}_4$, with spinel structures (459) might be class II or III-B mixed valence systems, according to the distribution of the cations. An X-ray study of the

$x = 0.48$ compound showed that the tetrahedral sites were exclusively occupied by Mn(II) (as indeed they are in MnTi_2O_4 and Mn_2TiO_4), suggesting that Ti(III) and Ti(IV) occupy the octahedral sites, but conductivity measurements have not been made on this apparently class III-B system.

In addition to the many Ti(III),Ti(IV) oxides, one oxide containing Ti(II) and Ti(III) has been reported. Both TiO and LiTiO_2 crystallize in rock salt lattices, and mixed crystals $\text{Li}_x\text{Ti}_{1-2x}^{\text{II}}\text{Ti}_x^{\text{III}}\text{O}$ can be prepared in which x lies between 0 and 0.5, and the cations are randomly distributed. The room temperature resistivity rises monotonically from 5×10^{-3} ohm cm for TiO, which is in any case a metal, up to 2 ohm cm for LiTiO_2 . Thus there appears to be no enhancement of conductivity over that of TiO due to the presence of the mixed valences.

Interaction absorption between Ti(III) and Ti(IV) has been detected in aqueous solutions as well as oxide lattices. Partial oxidation of sky blue Ti(III) solutions in 12 *M* HCl gives a deep purple coloration, which was studied by Jorgensen (395). The spectra of such solutions were said to be a superposition of the *d-d* bands of the Ti(III) ion (at 15,100 and 17,400 cm^{-1}) and an intense new absorption band at 20,200 cm^{-1} , which also had a shoulder at 16,100 cm^{-1} . Furthermore, absorption in the near-ultraviolet was very much intensified compared with single valence solutions. Arguing from the known formation constants of the Ti(III) and Ti(IV) chloro complexes, it was suggested that the interaction complex might be $[\text{Ti}^{\text{III}}\text{Cl}]^{2+}[\text{Ti}^{\text{IV}}\text{Cl}_6]^{2-}$, but there is no direct evidence that this is so. In 20 % sulfuric acid a 1 : 1 Ti(III),Ti(IV) interaction complex is also formed, with an absorption maximum at 21,200 cm^{-1} (298), but is destroyed by higher concentrations of acid.

B. VANADIUM

The vanadium mixed valence compounds whose structural and electronic properties have received the greatest attention are the oxides intermediate between V_2O_3 and V_2O_5 . Hoschek and Klemm (370), who were the first to make a systematic study of the system, identified three mixed valence phases, α ($\text{VO}_{1.80}\text{--VO}_2$), α' ($\text{VO}_2\text{--VO}_{2.2}$), and β ($\text{VO}_{1.65}\text{--VO}_{1.8}$), in addition to V_2O_3 , which has a structure similar to corundum, and V_2O_5 , whose structure is based on very distorted octahedral VO_6 units (36). It is not immediately obvious whether the intermediate phases should all be formulated as V(III),V(V) compounds or whether the mixture of valences is V(III),V(IV) for compounds in the range $\text{VO}_{1.5}\text{--VO}_2$, and V(IV),V(V) in the range $\text{VO}_2\text{--VO}_{2.5}$. This problem has

attracted the attention of a number of investigators (318, 370, 437), who have attempted to resolve the dilemma by performing magnetic susceptibility measurements. However, since many of the compounds are strongly antiferromagnetic, such measurements are not easy to interpret without a detailed knowledge of the signs and magnitudes of the magnetic interactions between ions of like and unlike valence states.

The VO_2 - V_2O_5 phase region was examined in greater detail by Aebi (3), who found evidence for only one intermediate compound, with a formula $\text{VO}_{2.17}$, i.e., V_6O_{13} , and a structure which was considered to be derived from that of V_2O_5 by the regular removal of one third of the planes consisting solely of oxygen atoms (276). It is interesting that, of all the vanadium oxides, only products with compositions between V_2O_5 and V_6O_{13} are good oxidation catalysts, a result which may be explicable in terms of the ease with which oxygen atoms can migrate through channels in the lattice of V_2O_5 (276). V_6O_{13} forms needles of the same blue-black color as VO_2 (3). It is antiferromagnetic, with a Neel temperature of 154°K (437), above which it behaves as a semiconductor having a conductivity and activation energy not very different from V_2O_5 (318). Below the Neel point, the conductivity increases approximately 10-fold, in contrast to VO_2 and V_2O_3 , which at their Neel points undergo a transition from the metallic to the semiconducting state, accompanied by a decrease in conductivity of about five orders of magnitude. Above the Neel point in V_6O_{13} , the effective magnetic moment per paramagnetic vanadium atom is either 2.13 B.M. (437) or 1.95 B.M. (318) compared with either 2.16 B.M. (437) or 3.10 B.M. (318) for VO_2 above its Neel point. The very large divergence between these results, not to mention the difficulty in interpreting effective magnetic moments for substances having very large Weiss constants, makes it unprofitable to consider their significance any further. That the phase is paramagnetic and the conductivity low seem to indicate that in the ground state the valences are trapped. Alternative valence structures, $\text{V}_4^{\text{V}}\text{V}_2^{\text{III}}\text{O}_{13}$ or $\text{V}_2^{\text{V}}\text{V}_4^{\text{IV}}\text{O}_{13}$, can be written, in both of which the two valence states are present in the stoichiometric ratio 2:1. A closer examination of Aebi's structure shows that there are indeed two types of metal ion sites present in this ratio, and Gillis' view (276) of the structural relationship with V_2O_5 leads to the conclusion that the minority sites are most likely to be occupied by the pentavalent ions. A neutron diffraction study of the magnetic ordering in this lattice would be of great value.

In the phase region labeled α by Klemm (370), a series of more accurate X-ray studies (13, 14, 18) has revealed the existence of a homologous series of Magneli shear phases, $\text{V}_n\text{O}_{2n-1}$, isostructural with the titanium-

(III,IV) series based on the rutile and corundum structures. Members of the series with $4 \leq n \leq 8$ have been identified. The two magnetic studies (318, 437) again disagree on the precise effective moments of these compounds, but agree that they lie in the range 2–3 B.M. and that all except V_6O_{11} and V_7O_{13} are antiferromagnetic, with Neel temperatures

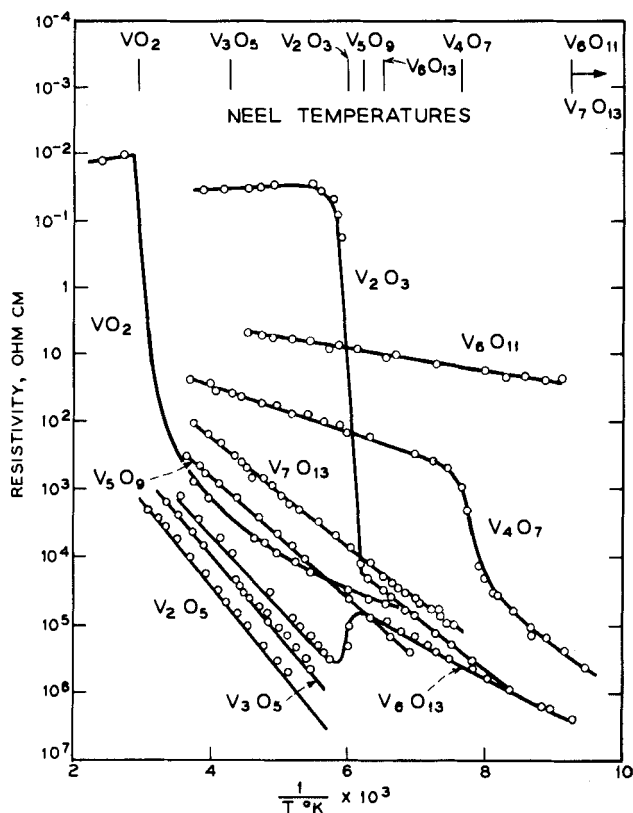
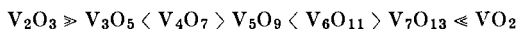


FIG. 6. The Neel temperatures and resistivity-temperature curves of various vanadium oxides (402).

somewhat lower than that of VO_2 . The two exceptions remained paramagnetic down to the lowest temperatures studied ($90^\circ K$). The compounds, which are all blue-black (13), behave as semiconductors, although with widely and apparently randomly varying resistivities and activation energies (402), as shown in Fig. 6. On feature apparent from this figure is that, among the mixed valence phases below their Neel temperatures, only V_4O_7 has a conductivity more than one order of magnitude greater than the single valence compounds V_2O_3 and VO_2 below their

Neel temperatures. Furthermore, at temperatures above their magnetic transitions, none of the mixed valence compounds conducts better than either V_2O_3 or VO_2 , although at all temperatures they all conduct better than V_2O_5 . It is therefore safe to say that, even when their spins are disordered, these remain class II systems. A further mysterious feature of the resistivity results is that, although one of the Magneli phases (V_4O_7) does undergo a discontinuous resistivity change at the Neel temperature, V_5O_9 shows no change in resistivity with magnetic ordering. Possibly this is connected with the fact that, for a given temperature above the Neel points of all the Magneli phases, there is a very marked alternation in conductivity with increasing size of the rutile-like slabs:



Clearly this interesting system deserves a very careful study.

There exist a number of V(IV), V(V) minerals, usually designated by the blanket term "vanadyl vanadates." The unit cell dimensions of several have been reported (601), but no other detailed structural or physical data are available.

The lower mixed valence oxides of vanadium have been of greater interest to metallurgists than to chemists. Oxygen dissolves interstitially in vanadium, yielding a number of different phases up to $VO_{0.57}$ (see Stringer (692) for a review). Vanadium monoxide is stable over a wide range of composition, since defects can occur at either cation or anion sites (13, 35, 641). Although stoichiometric VO has been shown to undergo a semiconductor-metal transition (35) at the Neel point, as do V_2O_3 and VO_2 , no physical properties of nonstoichiometric samples have been reported.

There exist two series of alkali metal vanadium bronzes with the general formulas $A_xV_2O_5$ and $A_xV_3O_8$, the structures of which have been determined by Wadsley (736, 737). Both contain double strings of octahedra sharing edges, and strings of octahedra distorted so much that they might almost be regarded as trigonal bipyramids. Since the formulas of the bronzes are continuously variable over wide limits, these two types of coordination can hardly correspond to the distribution of the valences in a class I or class II system, although in the compound LiV_2O_5 , where there are equal numbers of V(IV) and V(V) ions, this may well be the case. The latter compound contains two types of vanadium site (267), around one of which the oxygens approach more closely than around the other. LiV_2O_5 is also said to be blue, the characteristic color of V(IV) surrounded by oxygen atoms, so that there may be a smaller degree of mixed valence interaction in this class II compound than in the other bronzes. The first electrical measurements on the vanadium bronzes were made by

Flood (253), but more recently Ozerov (554) and Sienko (661) have studied these compounds. Ozerov found that, at room temperature, single crystals of $\text{Na}_{0.33}\text{V}_2\text{O}_5$ in the form of black needles showed very anisotropic resistivity, ρ being 0.046 ohm cm along and 20 ohm cm perpendicular to the needle axis. When measured between 400° and 600°C a compressed pellet of the same material behaved as a semiconductor, not a metal like the tungsten bronzes of comparable sodium content. Sienko also reports that $\text{Na}_{0.33}\text{V}_2\text{O}_5$ is a semiconductor, but with a room temperature resistivity and activation energy much lower than Ozerov's. The compound's magnetic susceptibility at room temperature is an order of magnitude higher than that of any sodium tungsten bronze, and actually agrees with expectation for a full spin-only contribution from the appropriate number of trapped V(IV), $3d^1$ ions. As in the tungsten bronzes, there is no detectable Knight shift in the ^7Li or ^{23}Na NMR spectra (273), so the mixed valence electrons are confined to the vanadium-oxygen framework. Since the observed g factors in the ESR spectra (1.96) are close to that reported for V(IV) in other compounds, we may confidently describe the vanadium bronzes as weakly trapped class II systems. Unfortunately, no hyperfine lines due to electron coupling with the ^{51}V nuclei could be detected in the ESR spectra.

The mixed valence vanadium oxide whose electronic structure is known in greatest detail is probably the black crystalline hydrate first prepared by Glemser (283) by reducing a suspension of V_2O_5 in concentrated ammonium chloride solution with zinc for several hours. Glemser gave the compound, which has an effective vanadium oxidation state of 4.66, the formula $\text{V}_3\text{O}_5(\text{OH})_4$, but a careful reexamination of the preparation under a variety of conditions suggested (59) that it should rather be written $\text{V}_6\text{O}_{20}\text{H}_{12}$. An X-ray powder photograph was compatible with a tetragonal unit cell. The electronic structure of this compound has recently been the subject of some magnetic studies (60, 701). First the intensity of the ESR spectrum of a powdered sample was measured as a function of temperature and shown to obey Curie's law between -150° and +300°C. Thus by comparison with a sample of diphenylpicrylhydrazyl, the concentration of paramagnetic centers could be calculated and compared with that expected from the formula if the compound contained two V(IV) ($3d^1$) and four V(V) ($3d^0$) ions per mole. The agreement was excellent ($n_{\text{obs}} = 1.4 \times 10^{18}$ spins/mg, $n_{\text{calc}} = 1.9 \times 10^{18}$ spins/mg). Assuming that the V(IV) ion lies in a field of tetragonal symmetry with $dxy(b_2)$ lowest in energy, the observed g values (1.970 and 1.920) could be fitted by excitation energies $E_e(dxzdyz) - E_{b_2}(dxy)$ and $E_{b_1}(dx^2 - y^2) - E_{b_2}(dxy)$ of 10,000 cm^{-1} and 15,000 cm^{-1} ,

respectively, if the vanadium spin-orbit coupling constant was taken as 150 cm^{-1} . Hence the relative ordering of the $3d$ orbitals of the V(IV) ions is $b_2 < e < b_1 < a_1$, suggesting a tetragonally compressed octahedral environment. The spin-spin and spin-lattice relaxation times (t_2 and t_1) of the ESR signal in Glemser's oxide were measured by two independent methods, one involving rapid modulation and the other progressive saturation of the signal. The two methods agreed that t_2 is virtually invariant with temperature, and that t_1 varies only a little, both being in the region of 10^{-7} sec. Theobald (701) assumed that exchange played the dominant part in the relaxation processes, and, from the line width of the signal, calculated that the exchange integral J was large enough (3000 MHz) to act as a thermostat so that t_1 did not vary with temperature, and was close to t_2 . As a result of these experiments we therefore have the beginnings of a very satisfying view of the class II mixed valence interaction in Glemser's hydrate, but without a complete structure determination there is little more to be said at this stage. One point of great interest in relation to the role of water in mixed valence interactions (see subsection E on iron) is Theobald's statement (701) that the exchange interaction in other anhydrous vanadium(IV,V) oxides is almost zero.

Glemser's compound is probably a hydrate of one of the reduced isopolyvanadic acids. Further examples were prepared and their formulas characterized by Ostrowetsky (549, 550) in a comprehensive survey of the mixed valence chemistry of V(IV) and V(V) in acid and alkaline solutions. Above pH 10, no mixed valence absorption could be detected but, between pH 7 and 10, spectrophotometry revealed the existence of a single polyanion which was isolated as a dark gray-green sodium salt, $\text{Na}_3[\text{V}_6\text{O}_{15}\text{H}]\cdot 6\text{H}_2\text{O}$. In weakly acid solutions, six polyanions corresponding to varying degrees of reduction of $[\text{V}_{10}^{\text{V}}\text{O}_{28}]^{6-}$ were identified, although only two, formulated by Ostrowetsky as $[\text{V}_7^{\text{V}}\text{V}_3^{\text{IV}}\text{O}_{26}\text{H}]^{4-}$ and $[\text{V}_3^{\text{V}}\text{V}_7^{\text{IV}}\text{O}_{24}\text{H}]^{4-}$, are at all stable. Since these anions almost certainly retain the $\text{V}_{10}\text{O}_{28}$ skeleton, whose structure was determined by Evans (227), they are probably better written as $[\text{V}_{10}\text{O}_{28}\text{H}_5]^{4-}$ and $[\text{V}_{10}\text{O}_{28}\text{H}_4]^{4-}$. The others, which have $\text{V(V)}/\text{V(IV)}$ ratios of 8/2, 6/4, 5/5, and 4/6, are formed only within very narrow ranges of pH, temperature, and concentration, and readily disproportionate into $[\text{V}_{10}^{\text{V}}\text{O}_{28}\text{H}_2]^{4-}$ and $[\text{V}^{\text{IV}}\text{O}]^{2+}$ or into mixtures of either of the latter and the 7/3 and 3/7 compound, according to their composition. The spectra of all these compounds, which vary in a most interesting way with degree of reduction, are collected in Fig. 7. Excepting the 5/5 and 4/6 compounds, they all have absorption maxima in the $13,000\text{--}20,000\text{ cm}^{-1}$ region. In energy and width, these bands resemble the ligand field bands of vanadium(IV),

but, because they are at least an order of magnitude more intense, should probably be assigned as mixed valence absorptions. Their significance is not likely to become apparent until more is known of the structures of

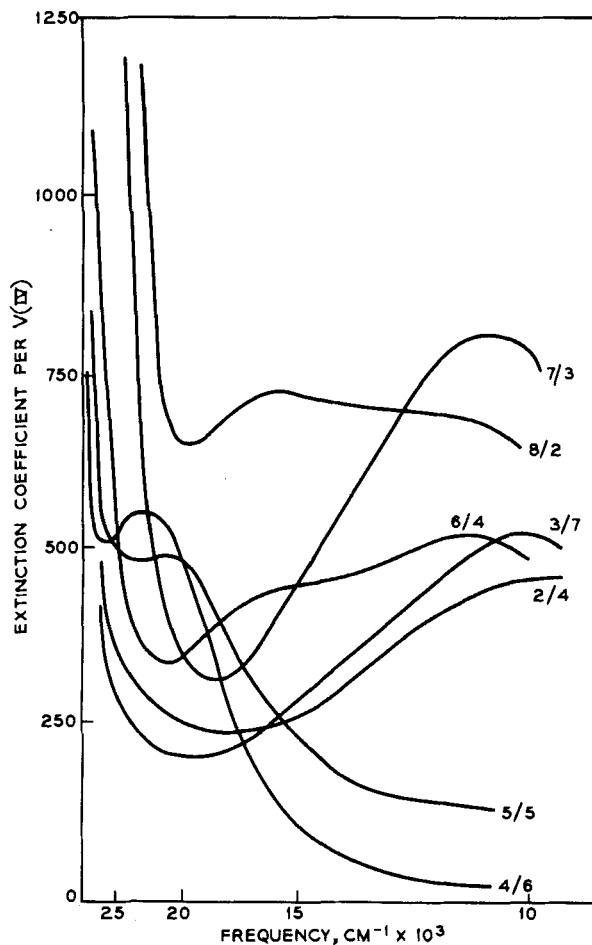


FIG. 7. Electronic spectra of the isopolyvanadate ions $[V_{10}O_{28}]^{n-}$ of various $V(V)/V(IV)$ ratios (550).

the polyanions. In particular, we have no information at this stage on whether the valences are trapped by distortion of the appropriate number of vanadium sites or, indeed, whether some are class II and others class III-A, except for the two compounds with no intense low-energy absorption, which must surely be class I. The low molar extinction coefficients of the mixed valence absorption bands in all cases indicate a

rather firm trapping of the valence. ESR measurements on glassy solutions would certainly help to decide the question. Another intriguing question is the exceptional stability of the 7/3 and 3/7 anions, for which the structure (227) of the parent ion $[V_{10}O_{28}]^{6-}$ suggests no obvious explanation.

The only other vanadium species detected in solution, which might be mixed valence, appears as an intermediate in the reaction between V(II) and V(IV) in acid perchlorate solutions (530). A dark color, which developed much more rapidly than the rate of the overall reaction to produce V(III), was shown to be due to the formation of the ion $[VOV]^{4+}$, identified by the author as a hydrolytic dimer of V(III). However, the intensity of the absorption (ϵ_{\max} calculated as 6800 at $23,200\text{ cm}^{-1}$) suggests that a V(II),V(IV) class II system is formed.

C. CHROMIUM

A discussion of the mixed valence compounds of chromium is hampered by the fact that this element can assume integral valences from 1+ to 6+. Thus, whereas Cr_3O_8 is clearly a mixed valence compound, the formula of KCr_3O_8 , for example, could be written as either $KCr^{VI}Cr^{III}O_8$, $KCr^{IV}Cr^VCr^{IV}O_8$, or $KCr_3^VO_8$, for all four oxidation states, 3+, 4+, 5+, and 6+, are known for chromium. Although there are experiments (optical absorption, magnetic susceptibility, X-ray structure analysis, etc.) which will distinguish between these alternatives, they have not always been performed as yet and hence limit our discussion to the more obvious mixed valence compounds.

In contrast to titanium and vanadium, chromium forms mixed valence halides as well as oxides, two types of mixed valence chromium halide (Cr_2X_3 and Cr_2X_5) having been reported. The halides Cr_2Br_3 and Cr_2I_3 are formed as brown-black solids in the thermal degradation of the appropriate tetraphenylchromium halides, $(C_6H_5)_4CrX$ (352). Cr_2F_5 is formed as green translucent crystals from both the oxidation of CrF_2 and the incomplete reduction of CrF_3 (693). Since CrF_3 is yellow-green and CrF_2 is blue-green, and since the refractive indices of Cr_2F_5 are intermediate between those of CrF_2 and CrF_3 , there appears to be no low-lying mixed valence transition in this material. As a class I substance, Cr_2F_5 should therefore be an insulator. The crystal structure of Cr_2F_5 (Fig. 8) shows the expected trapping of the chromium valences as Cr(II) and Cr(III), for one half of the chromium ions are found at the centers of almost regular fluoride ion octahedra with an average Cr—F distance of 1.89 Å, whereas the other half occupy tetragonally distorted octahedral sites with four Cr—F distances at 1.96–2.01 Å and the remaining two

at 2.57 Å (683). That these are to be identified with Cr(III) and Cr(II) ions, respectively, follows not only from the Cr—F distances but also from the structures of CrF₃ and CrF₂ themselves, which contain, respectively, octahedrally and tetragonally coordinated chromium ions. Steinfink and Burns (683) explain that the three 3*d* electrons in the Cr(III) ion occupy nonbonding *t*_{2g} orbitals, but Cr(II) must place its fourth 3*d* electron in an antibonding *dz*² orbital, thereby extending the octahedron in the *z*

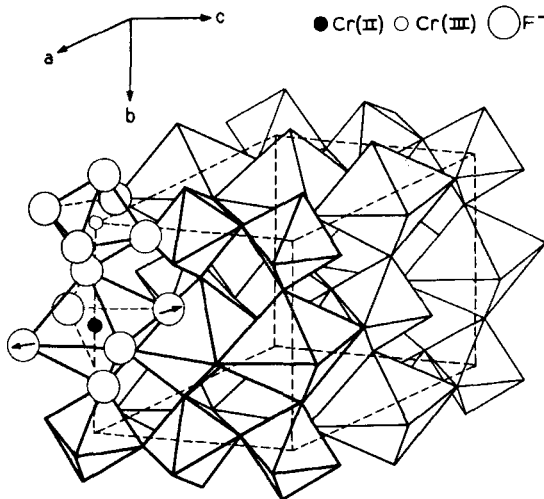


FIG. 8. The crystal structure of class I Cr₂F₅. In this substance, the Cr(III)—F distances in a Cr^{III}F₆ octahedron average 1.89 ± 0.01 Å, whereas the neighboring Cr^{II}F₆ octahedron is distorted, as shown by the arrows, four of the Cr(II)—F distances being 1.98 Å and the other two being 2.572 Å (683).

direction. Osmond (546) suggests that, according to qualitative superexchange considerations, the chains of cations in Cr₂F₅ should be ferromagnetically aligned in the (001) direction with neighboring chains coupled antiferromagnetically, resulting in an overall antiferromagnetic ground state. There are no experimental data on this point.

The oxides of chromium present a bewildering array of possible mixed valence compounds. Extrapolating from what very little is known, one can say, in general, that the ions involved in mixed valence chromium oxides are almost always Cr(VI) and Cr(III) in appropriate ratios, and that, since Cr(VI) appears always as a tetrahedrally coordinated species whereas the 3*d*³ configuration of Cr(III) prefers octahedral coordination, the oxides will be class I systems. The discussion begins with the better known oxides and then proceeds to the more speculative materials. It should be mentioned that, although little is known of the intermediate

chromium oxides, they have a great commercial value as catalysts for the polymerization of olefins.

Suchow *et al.* (695) were the first to point out that, although the chromium in KCr_3O_8 has an average valence of 5+, their preliminary crystal structure suggests that two of the chromium ions are of one type and one of the chromiums of another, suggesting in turn the formulation of the compounds as $\text{KCr}_2^{\text{VI}}\text{Cr}^{\text{III}}\text{O}_8$ with the Cr(III) ions in octahedral coordination and the Cr(VI) in tetrahedral coordination. Wilhelmi (775, 777) confirmed this view, demonstrating that the Cr(III) ions are in very nearly octahedral coordination with Cr—O distances averaging 1.97 Å,

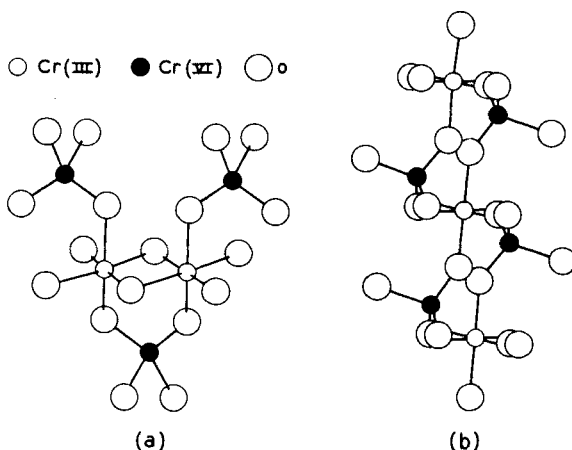


Fig. 9. The relative orientations of $\text{Cr}^{\text{VI}}\text{O}_4$ tetrahedra and $\text{Cr}^{\text{III}}\text{O}_6$ octahedra in the class I substances (a) Cr_5O_{12} , and (b) KCr_3O_8 (775, 778).

and that the Cr(VI) ions are surrounded tetrahedrally by oxide ions at an average distance of 1.60 Å, as in Fig. 9. Klemm (428) pointed out that the question of the chromium valences in KCr_3O_8 might also be answered by a measurement of the magnetic susceptibility, for magnetically dilute KCr_3O_8 would have an effective moment of 3.00 B.M., whereas $\text{KCr}_2^{\text{VI}}\text{Cr}^{\text{III}}\text{O}_8$ would have an effective moment of 3.87 B.M. His measurements yield an effective magnetic moment for KCr_3O_8 which varies from 4.09 to 4.36 B.M. over the temperature range 90°–295°K. Applying a correction for temperature-independent paramagnetism gives an upper limit of 3.97–4.23 B.M., which does not disagree with that expected for the Cr(III),Cr(VI) mixed valence formulation of KCr_3O_8 . The material is black and said to have a very high electrical resistivity (777). Wilhelmi (779) reports that the lithium and cesium salts of HCr_3O_8 similarly

contain octahedral $\text{Cr}^{\text{III}}\text{O}_6$ and tetrahedral $\text{Cr}^{\text{VI}}\text{O}_4$ groups sharing corners.

The alkaline earth chromium oxides, $\text{M}_3^{\text{II}}\text{Cr}_2\text{O}_8$, form another class of compounds in which the chromium has an average valence of 5+. Alternatively, one can write a mixed valence formula for the compound, $\text{M}_3^{\text{II}}\text{Cr}_4^{\text{IV}}\text{Cr}_2^{\text{III}}\text{O}_{24}$, which has a Cr(VI)/Cr(III) ratio of 2, as in KCr_3O_8 . Surprisingly, the evidence seems to be in favor of the single valence formulation, for not only do Ford and co-workers (256–258) and others (278) point out that $\text{Ca}_3\text{Cr}_2\text{O}_8$ has a powder pattern very much like that of $\text{Ca}_3(\text{P}^{\text{V}}\text{O}_4)_2$, but Klemm (640) finds an effective moment of 1.7 B.M. per chromium ion in $\text{Ba}_3\text{Cr}_2\text{O}_8$, where the pentavalent formula requires 1.73 B.M. and the mixed valence formula requires 2.24 B.M. Ford *et al.* and Vasenin (723) also describe the preparation of the oxides $\text{Ca}_2\text{Cr}_2\text{O}_7$, CaCr_2O_5 , $\text{Ca}_4\text{Cr}_3\text{O}_{10}$, and $\text{Ca}_6\text{Cr}_4\text{O}_{15}$, the last three of which are green, as is also $\text{Ca}_3\text{Cr}_2\text{O}_8$. Only a combination of optical, magnetic, and X-ray studies can settle the question of the chromium valence in these compounds.

Bashilova's (45) thallium chromate $\text{Tl}_2\text{Cr}_2\text{O}_8$, if taken as a salt of $\text{Tl}(\text{III})$, is analogous to the calcium salt mentioned above, for it can be written as either $\text{Tl}_2^{\text{II}}\text{Cr}_2^{\text{V}}\text{O}_8$ or $\text{Tl}_6^{\text{I}}\text{Cr}_4^{\text{VI}}\text{Cr}_2^{\text{III}}\text{O}_{24}$. Bashilova, however, maintains that it is the thallium mixed valence oxide, $\text{Tl}^{\text{I}}\text{Tl}^{\text{III}}\text{Cr}_2^{\text{VI}}\text{O}_8$. The latter formulation would be diamagnetic, whereas the other two would have effective magnetic moments of 1.73 B.M. and 2.24 B.M., depending on whether the chromium is, respectively, Cr(V) or Cr(III), Cr(VI).

Because of the difficulty of preparing pure intermediate chromium oxides, it seems probable that, of the large number of different anhydrous chromium oxides reported in the literature, a significant fraction will prove to be mixtures, or are in fact the same compound masquerading under different stoichiometries. The list of intermediate chromium oxides encompasses the following: Cr_2O_5 , Cr_3O_4 , Cr_3O_5 , Cr_3O_8 , Cr_4O_9 , Cr_5O_9 , Cr_5O_{12} , Cr_5O_{13} , Cr_5O_{19} , Cr_6O_{15} , Cr_7O_{18} , Cr_8O_{15} , Cr_8O_{21} , and $\text{Cr}_{32}\text{O}_{93}$, in addition to many "nonstoichiometric" materials of the formula CrO_x , which are not easily expressed as small whole number ratios of chromium and oxygen.

The materials described by Schwartz *et al.* (647) as Cr_3O_8 , and by Simon and Schmidt (664) as Cr_5O_{13} , are crystallographically identical, according to later work by Glemser and co-workers (281, 282), who feel that the formula Cr_5O_{13} better fits their analytical data. Cr_5O_{13} , as prepared by the thermal decomposition of CrO_3 , is a black substance and has a magnetic susceptibility consonant with the mixed valence description $\text{Cr}_3^{\text{VI}}\text{Cr}_2^{\text{IV}}\text{O}_{13}$ (8), although it has been said that its ESR

spectrum is characteristic of the Cr(III) ion (596). Rode *et al.* (596) first proposed that Cr_5O_{13} was really Cr_8O_{21} , and later work by Lorthioir and Michel (468) has confirmed Cr_8O_{21} as a product of the thermal decomposition of CrO_3 . According to their study, Cr_8O_{21} in water gives Cr(III) and Cr(VI) ions in 1:3 ratio, and has a magnetic susceptibility compatible with its formation as $\text{Cr}_2^{\text{III}}\text{Cr}_6^{\text{VI}}\text{O}_{21}$.

Cr_5O_{12} , also reported as Cr_2O_5 (281), is one of the few chromium oxides for which a crystal structure has been determined. Wilhelmi (778) found that Cr_5O_{12} contains structural units much like those found in KCr_3O_8 , i.e., octahedrally coordinated Cr(III) ions sharing ligands with tetrahedrally coordinated Cr(VI) ions. The structure is built up of Cr_5O_{18} units (Fig. 9), in which the Cr(VI)—O distances in the tetrahedral sites are 1.65 Å on the average, and the Cr(III)—O distances in the octahedral sites average 1.97 Å, as was found in KCr_3O_8 . Although this oxide is black, possibly suggesting a class II spectrum, its electrical resistivity is reported to be 1.78×10^{10} ohm cm at 360°C and 72 atm oxygen (446), as expected from the class I crystal structure. Cr_5O_{12} is ferromagnetic, with a Curie point at about 80°C (597), above which it shows an ESR signal attributable to the Cr(III) ion (596). An apparently related hydrated oxide, $\text{Cr}_5\text{O}_{12} \cdot 3\text{H}_2\text{O}$, is formed as a brown precipitate on mixing a solution of $\text{Cr}^{\text{III}}\text{Cl}_3$ with $\text{Ag}_2\text{Cr}^{\text{VI}}\text{O}_4$ (292).

Chromium dioxide, CrO_2 , presents a rather curious picture of conflicting claims, for, although CrO_2 has been said not to have a homogeneity region and to be quite stoichiometric (22, 647), materials ranging from $\text{CrO}_{1.89}$ (133) to $\text{CrO}_{2.14}$ (776) have been described in the literature as " CrO_2 ." Moreover, whereas Chapin *et al.* (776) have studied the electrical conductivities of samples in the range $\text{CrO}_{1.89}$ – $\text{CrO}_{2.02}$ and explained their quasi-metallic nature (ρ is approximately 3×10^{-3} ohm cm) on the basis of a *d*-band model involving Cr(IV) ions, Kubota (446) claims that the extraordinary conductivity results from the presence of Cr(III) and Cr(IV) ions in the rutile crystal lattice. In support of the mixed valence formulation, Rode *et al.* (596) interpret the ESR spectrum of CrO_2 above its Curie point (119°C) as showing that the oxide is a Cr(III),Cr(VI) compound. The saturation magnetization of CrO_2 at 0°K yields an effective moment of 2.07 B.M. per chromium atom (325), whereas Cr(IV) is expected to have an effective moment of 2.83 B.M. The decision as to whether CrO_2 is a mixed valence oxide or simply contains Cr(IV) clearly cannot be made without further physical measurements.

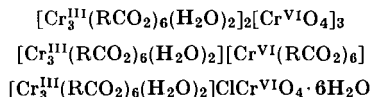
The hydrated material formed by mixing an aqueous solution containing Cr(III) with one containing $[\text{Cr}^{\text{VI}}\text{O}_4]^{2-}$ presents a situation related to that discussed above for CrO_2 . According to King and Neptune (423),

the mixing of Cr(III) and $[\text{Cr}^{\text{VI}}\text{O}_4]^{2-}$ in acidic solution leads to the formation of a 1 : 1 complex ion, $[\text{Cr}^{\text{II}}\text{Cr}^{\text{VI}}\text{O}_4]^+$, probably with sharing of oxo and/or hydroxyl ligands. Interestingly, the stoichiometry of this complex was determined, using its interaction absorption band at $14,300\text{ cm}^{-1}$, thereby showing that a class II absorption can occur in a Cr(III),Cr(VI) system. Krauss and Gnatz (440) confirmed the 1 : 1 nature of this complex by a conductivity titration, but also showed that the precipitate from the solution has the composition $\text{H}_4\text{Cr}_3\text{O}_8 \cdot x\text{H}_2\text{O}$ (x is continuously variable), which can be formulated as either $\text{H}_4\text{Cr}_3^{\text{IV}}\text{O}_8 \cdot x\text{H}_2\text{O}$ or $\text{H}_4\text{Cr}_2^{\text{III}}\text{Cr}^{\text{VI}}\text{O}_8 \cdot x\text{H}_2\text{O}$. Aten *et al.* (32) showed conclusively that the latter formulation is the proper one by mixing a solution of radioactive Cr(III) with inactive $[\text{Cr}^{\text{VI}}\text{O}_4]^{2-}$ ion, dissolving the $\text{H}_4\text{Cr}_3\text{O}_8$ so formed, and precipitating and counting the $[\text{CrO}_4]^{2-}$ as PbCrO_4 . As the PbCrO_4 showed less than 1 % of the original activity, it is clear that the two types of chromium in this substance at no time were equivalent as they would be if they were all Cr(IV). Formulations of $\text{H}_4\text{Cr}_3\text{O}_8 \cdot x\text{H}_2\text{O}$ as a compound of Cr(IV) also demands an effective magnetic moment of 2.83 B.M. per chromium, whereas the calculated effective moment of the mixed valence compound is 3.16 B.M., in excellent agreement with the experimental value of 3.15 B.M. (440). The same dark brown material forms at the cathode on electrolysis of a 25 % solution of CrO_3 in HClO_4 (450).

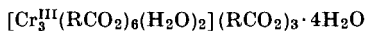
Sisler and co-workers (201, 669) have shown that liquid ammonia will partially reduce CrO_3 to a mixture containing, among other things, the brown polymeric materials $[\text{Cr}^{\text{III}}(\text{NH}_3)_3]_{2n}(\text{Cr}^{\text{VI}}\text{O}_4)_{3n}$ and $[\text{Cr}^{\text{III}}(\text{NH}_3)_3\text{NO}_2\text{Cr}^{\text{VI}}\text{O}_4]_n$, both of which are postulated to be class I systems with the Cr(III) ions in octahedral and the Cr(VI) ions in tetrahedral coordination, the two being joined by oxo bridges.

The thermal decomposition of chromyl chloride, $\text{Cr}^{\text{VI}}\text{O}_2\text{Cl}_2$, leads to the formation of a number of polychromyl chlorides having the general formula $(\text{CrO}_2)_n\text{Cl}_2$, where n is equal to 3, 4, 5, or 7 (479). Although a mixed valence formula for these substances can be written $(\text{Cr}^{\text{VI}}\text{Cr}_{n-1}^{\text{IV}}\text{O}_{2n}\text{Cl}_2)$, little is known of their physical properties, other than that they are brown-black in color and sensitive to moisture.

The formates and acetates of chromium offer further examples of class I mixed valence systems. Trivalent chromium forms a very stable trinuclear cationic species having the general formula $[\text{Cr}_3^{\text{III}}(\text{RCO}_2)_6(\text{H}_2\text{O})_2]^{3+}$, where RCO_2^- is an acetate or formate anion. Combinations of this trinuclear cation with chromium-containing anions yield salts (292), such as:



That the above are class I systems seems evident from the fact that they are all green, the color of the single valence compound:



Recoura (579) reports the preparation of the dark brown sulfates $\text{K}_{2n}\text{Cr}_2^{\text{III}}(\text{Cr}^{\text{VI}}\text{O}_4)_n(\text{SO}_4)_3$, where $n = 1, 2$, and 3 . They are also most likely class I systems.

D. MANGANESE

As with most of the other elements of the first transition series, the most important examples of mixed valence in manganese compounds involve oxide lattices. At one time it was suggested (208a) that there existed a continuous series of oxides with formulas intermediate between MnO and MnO_2 , of which no less than eleven had been reported between 1862 and 1907! Very few of these nonstoichiometric oxides have survived the passage of time and closer scrutiny, and we shall therefore concentrate attention only on those based on stoichiometric phases. Of the latter, Mn_3O_4 , the mineral haussmannite, is the best known. When heated in air to 1000°C , all manganese oxides and hydroxides are converted to Mn_3O_4 , which forms as black crystals with a metallic sheen, or as a dark red powder when finally divided. Its electrical conductivity was studied many years ago (181, 731), using compressed pellets. Although behaving as a semiconductor, the fact that it is much less conducting than Fe_3O_4 at room temperature led de Boer and Verwey (181) to suggest that it was a normal spinel, $^2\text{Mn}^{\text{IV}}\text{Mn}_2^{\text{II}}\text{O}_4$ or $\text{Mn}^{\text{II}}\text{Mn}_2^{\text{III}}\text{O}_4$, and not of the inverse type $\text{Mn}^{\text{II}}(\text{Mn}^{\text{II}}, \text{Mn}^{\text{IV}})\text{O}_4$ or $\text{Mn}^{\text{III}}(\text{Mn}^{\text{II}}, \text{Mn}^{\text{III}})\text{O}_4$. This conclusion has been confirmed, but disagreement continues as to the valence structure of the compound. A recent magnetic susceptibility study (569) showed that, between 90° and 800°C , the susceptibility followed a Neel hyperbola, but below the Curie point it was consistent with a ferromagnetic model for an $\text{Mn}(\text{II}), \text{Mn}(\text{IV})$ normal spinel. On the other hand, the observed intensities of neutrons diffracted by powdered specimens at 4.2° , 77° , and 298°K (404) agree very well with those calculated for a model based on $\text{Mn}^{\text{II}}\text{Mn}_2^{\text{III}}\text{O}_4$. The latter results are probably the more reliable.

² A spinel compound has the formula AB_2O_4 and a lattice containing octahedral and tetrahedral cation sites in the ratio 2:1. In a normal spinel the B cations occupy the octahedral sites and the A the tetrahedral, whereas in an inverted spinel the tetrahedral sites are exclusively occupied by B cations so that the octahedral sites are occupied by equal numbers of A and B cations (see Fig. 16).

In a number of other instances, different methods of estimating the valence distributions in manganese oxides also appear to yield differing results. For example, X-ray analysis showed that the structure of manganite (γ - MnOOH) was based on sheets of O^{2-} and OH^- ions enclosing trivalent manganese ions (112, 237), but measurements of magnetic anisotropy appear to suggest that half of the manganese is divalent and half quadrivalent. Also the crystal structure of the mineral bixbyite (α - Mn_2O_3) agrees with a trivalent formulation (563), but it has been stated that chemical decomposition leads to divalent and quadrivalent ions (264). The latter result is of doubtful importance, however, when one considers the ease with which Mn(III) disproportionates in aqueous solution.

Another stoichiometric manganese oxide phase, which seems to have been fully characterized, has the formula Mn_5O_8 . The X-ray diagram of the black powder indexes as monoclinic (551) with unit cell dimensions very similar to those of $\text{Cd}_2\text{Mn}_3\text{O}_8$, and approximate structure factor calculations show that the two compounds are isotypic. Thus the valence structure of Mn_5O_8 is clearly $\text{Mn}_2^{\text{II}}\text{Mn}_3^{\text{IV}}\text{O}_8$, and the compound belongs to either class I or class II.

In common with a number of other first series transition metals, mixed valence manganese oxide systems based on perovskite lattices may be prepared with formulas intermediate between $\text{M}^{\text{III}}\text{Mn}^{\text{III}}\text{O}_3$ and $\text{M}^{\text{II}}\text{Mn}^{\text{IV}}\text{O}_3$, where the trivalent metal is commonly lanthanum and the divalent metal is one of the alkaline earths. The magnetic (392) and electrical (722) properties of these compounds have been the subject of extensive study over the past 15 years. They are all ferromagnetic, but their Curie temperatures are very strongly dependent on composition, with maxima in the region 25–40% M(II) (392). Values of the saturation magnetization as a function of composition also showed that, over the same region of composition, all the $3d$ electrons contribute their full spin moments, although without appreciable orbital contribution. The form of the relationship between magnetization and composition can be understood qualitatively if one assumes that the $\text{Mn(III)}\text{--Mn(III)}$ interaction is almost zero (very low Curie temperature), and that there is a very strong $\text{Mn(III)}\text{--Mn(IV)}$ magnetic interaction with a positive exchange integral raising the Curie temperature with increasing Mn(IV) concentration. Finally, to explain the asymmetrical position of the maximum magnetization with respect to composition, it is necessary to assume a somewhat weaker negative interaction between Mn(IV) and Mn(IV) . Elegant confirmation of this picture was obtained by Wollan and Koehler (791) from neutron diffraction experiments on $(\text{La}_{1-x}\text{Ca}_x)\text{MnO}_3$. They found that the phase is purely ferromagnetic only over a small range of

composition near $x = 0.35$, and that, from 0 to 0.25 and from 0.40 to 0.50, ferromagnetic and antiferromagnetic interactions were simultaneously present. Thus LaMnO_3 is ferromagnetic along all three axes. In the mixed valence phases many different kinds of spin superlattice are built up, according to the distribution of manganese valence in the lattice. Some of the possibilities are shown in Fig. 10. To explain the occurrence of these superlattices, Goodenough (295) used a valence bond model in which the Mn(III) ions have dsp^2 (square) and the Mn(IV) ions have

LABEL	ONE OCTANT OF MAGNETIC UNIT CELL	IONS PER UNIT CELL				
		$\text{Mn}^{+3} \rightarrow 8$	6	4	2	0
		$\text{Mn}^{+4} \rightarrow 0$	2	4	6	8
A						
B						
F						

FIG. 10. Some of the possible spin superlattices in mixed valence calcium lanthanum manganese perovskites (791).

d^2sp^3 (octahedral) hybridization, and invoked a concept called "semi-covalence." This is equivalent to saying that electron transfer from a filled anion p orbital to an unfilled cation d orbital occurs with greater probability for an electron having the same spin as those already occupying the d -shell of the cation. Similarly, electron transfer from the lower-valent cation to the oxidized anion will align their spins, thus resulting in a net coupling of the spins of the two mixed valence cations, as described more fully in Section II.

Since all the manganese ions of $(\text{La}_{1-x}\text{Ca}_x)\text{MnO}_3$ are in equivalent sites in the perovskite lattice, the series of compounds is class III-B and should have metallic resistivities. This is confirmed by the work of van Santen and Jonker (722), who found a minimal resistivity of 3×10^{-2} ohm cm at 100°K for samples of $(\text{La}_{1-x}\text{Sr}_x)\text{MnO}_3$ having x between 0.2 and 0.4.

It has been suggested (667) that CuMn_2O_4 has a normal rather than an inverse spinel structure, because the valence distribution is $\text{Cu}^{\text{I}}(\text{Mn}^{\text{III}}, \text{Mn}^{\text{IV}})\text{O}$ rather than $\text{Cu}^{\text{II}}\text{Mn}_2^{\text{III}}\text{O}_4$, which requires that $\text{Cu}(\text{II})$ occupy a tetrahedral site in preference to $\text{Mn}(\text{III})$. In the absence of resistivity measurements, which would readily distinguish between the two valence distributions, it is not possible to comment further on this interesting suggestion. The structure of another $\text{Mn}(\text{III}), \text{Mn}(\text{IV})$ oxide, $\text{DyMn}^{\text{III}}\text{Mn}^{\text{IV}}\text{O}_5$, has been deduced by Abrahams and Bernstein (1a) as being class I, with $\text{Mn}(\text{III})$ in penta-coordination and $\text{Mn}(\text{IV})$ in octahedral coordination. As expected from its class I structure, $\text{DyMn}^{\text{III}}\text{Mn}^{\text{IV}}\text{O}_5$ has a resistivity of 10^{10} ohm cm at room temperature.

Unlike the $\text{Mn}(\text{III}), \text{Mn}(\text{IV})$ perovskites, the $\text{Mn}(\text{II}), \text{Mn}(\text{III})$ lattice in the compounds $\text{Li}_x\text{Mn}_{1-x}\text{O}$ does not show ferromagnetic ordering (386). As the lithium content is increased, the susceptibility curves change from a typically antiferromagnetic to a paramagnetic form, merely as a result of diluting the magnetic cations.

The naturally occurring minerals braunite, $\text{Mn}_7\text{SiO}_{12}$ (119), and pinakiolite, $\text{Mg}_3\text{Mn}^{\text{II}}\text{Mn}_2^{\text{III}}\text{B}_2\text{O}_{10}$ (698), are other $\text{Mn}(\text{II}), \text{Mn}(\text{III})$ compounds whose structures have been solved. The unit cell of braunite contains 48 octahedrally coordinated $\text{Mn}(\text{III})$ ions with average $\text{Mn}-\text{O}$ distances of 2.09 Å, and eight octa-coordinated $\text{Mn}(\text{II})$ ions with $\text{Mn}-\text{O}$ equal to 2.16 Å. Evidently the system is class I. Although all the manganese ions in pinakiolite are in octahedral sites, the distortions of the sites are sufficient to render the system class II.

While studying the reduction of transition metal cyanide complexes by sodium in liquid ammonia, Kleinberg and co-workers (142, 175) isolated the only mixed valence manganese compound not containing oxide as a ligand. The dark brown product of the reduction had an empirical formula $\text{K}_{11}\text{Mn}_2(\text{CN})_{12} \cdot 2\text{NH}_3$, and was thought to contain equimolar proportions of $\text{Mn}(0)$ and $\text{Mn}(\text{I})$. It was paramagnetic, with a room temperature magnetic moment of 1.25 B.M., but no further experiments were carried out on it.

E. IRON

The mixed valence compounds of iron form by far the largest group presently known for any element. This group of compounds is exceptional not only for its size, but also for its variety, for it contains oxides, hydroxides, halides, sulfates, cyanides, phosphates, carbonates, acetates, silicates, borates, and sulfites. There is also no small historical interest here, for the mixed valence iron cyanides were among the earliest

coordination compounds investigated, and a large number of the qualitative ideas presently used in thinking about mixed valence chemistry arose first in consideration of mixed valence iron compounds.

The study of mixed valence iron chemistry has recently received impetus from the discovery of the Mössbauer effect. Because the Mössbauer spectrum is potentially capable of indicating the valences of the iron ions in a solid, as well as their amounts and their coordination, its use can take one a long way towards understanding the structural elements of an iron compound [see, for example, Fluck *et al.* (254)].

The preparations of the mixed valence fluorides $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$, $\text{Fe}_2\text{F}_5 \cdot 3\text{H}_2\text{O}$, and the anhydrous material Fe_2F_5 have recently been reported (93). The first of these compounds, $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{F}_5 \cdot 7\text{H}_2\text{O}$, is but one member of a large class of compounds of general formula $\text{M}^{\text{II}}\text{Fe}^{\text{III}}\text{F}_5 \cdot 7\text{H}_2\text{O}$. Because the Fe(II) in this compound can be replaced readily by other M(II) ions and also because of its yellow color, it appears that $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ is a class I crystal which, consequently, does not involve sharing of ligands, there being just six ligands per metal ion. Because water inhibits the formation of a deep mixed valence color, it is not surprising that dehydrating the yellow heptahydrate to the trihydrate yields crystals which are deep red. Further dehydration to Fe_2F_5 yields a steel-blue compound, which by its color and stoichiometry is at least class II, and may even be class III and metallic.

Deussen (192) first showed that the colorless iron fluoride thought to be $\text{FeF}_3 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ in reality was the mixed valence salt $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{F}_8 \cdot 10\text{H}_2\text{O}$. The chlorides (451) and bromides (288) of the $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{X}_8 \cdot 10\text{H}_2\text{O}$ systems are also known and, as expected from the large amount of water in them, are yellow in color. There also exists a reduced chloride $\text{Fe}_2^{\text{II}}\text{Fe}^{\text{III}}\text{Cl}_7 \cdot 10\text{H}_2\text{O}$ with the expected yellow color (288). In the bromide series, dehydration of $\text{Fe}_3\text{Br}_8 \cdot 10\text{H}_2\text{O}$ to the hexahydrate changes its color from yellow to black (542), indicating a transformation from class I to class II. The mixed valence bromide Fe_3Br_8 forms a number of other interesting adducts; thus, $\text{Fe}_3\text{Br}_8 \cdot (\text{CN})_2 \cdot 3\text{BrCN}$ (brown-black), $\text{Fe}_3\text{Br}_8 \cdot 4\text{BrCN}$ (dark brown), $\text{Fe}_3\text{Br}_8 \cdot 5\text{HCN}$ (black-brown), and $\text{Fe}_3\text{Br}_8 \cdot [(\text{CN})_2]_x$ are all known (542). However, since $\text{Fe}^{\text{II}}\text{Br}_3 \cdot 4\text{BrCN}$ is itself almost black, nothing can yet be said of the colors of the mixed valence adducts.

The large number of $\text{Fe}_3\text{X}_8 \cdot \text{Y}$ compounds so far described (and others, see below) at first suggests the presence of a trinuclear Fe_3X_8 species. Such a polynuclear species would necessarily be at least class II because of the shared ligands, and should have the deep color characteristic of this class. That there are no polynuclear species involved here follows from the pale colors of several of the Fe_3X_8 hydrates, and also

from the crystal structure of $\text{Fe}_3\text{Br}_8 \cdot 16\text{H}_2\text{O}$ published by Zvonkova (820). In this substance, the bromide ions and water molecules form chains of octahedra ($2\text{Br}^-, 4\text{H}_2\text{O}$) sharing corners. Three fourths of these octahedral sites are filled statistically with iron, the average Fe—Br distance being 2.60 Å and the average Fe—O distance being 2.01 Å. Although Zvonkova extrapolates from this *average* structure to the conclusion that $\text{Fe}_3\text{Br}_8 \cdot 16\text{H}_2\text{O}$ is a mixed valence class III-B system much as Fe_3O_4 (see below), more careful work will probably show that in fact the ligand-metal distances about the Fe(II) and Fe(III) ions in this compound are quite different, and that the valences are firmly trapped.

Walden (742) reports the preparation of the triple bromides $\text{KFe}_3\text{Br}_9 \cdot 3\text{H}_2\text{O}$ and $\text{RbFe}_3\text{Br}_9 \cdot 3\text{H}_2\text{O}$. As one can guess by the high proportion of iron to water in these substances, the crystals are deeply colored. Although rather unstable, the crystals of these iron bromides are deep green and opaque.

McConnell and Davidson (497) have investigated the mixed valence absorption of HCl solutions containing the Fe(II) and Fe(III) ions. As with antimony, tin, and copper, the mixtures of $\text{Fe}^{\text{II}}\text{Cl}_2$ and $\text{Fe}^{\text{III}}\text{Cl}_3$ in concentrated HCl showed an absorbance in the region 11,000–22,000 cm^{-1} , which was much greater than that measured for the sum of the FeCl_2 and FeCl_3 solutions taken separately. This enhancement of absorption was found to decrease on lowering the HCl concentration, so that, in aqueous solutions of $\text{Fe}^{\text{II}}(\text{ClO}_4)_2$ and $\text{Fe}^{\text{III}}(\text{ClO}_4)_3$, there is no noticeable mixed valence absorption. It was concluded that the mixed valence chromophore involves a chloride-containing species having equal numbers of Fe(II) and Fe(III) ions. There is a suggestive relationship between this work and electron exchange kinetic studies, in which it was found that the thermal electron transfer between Fe(II) and Fe(III) is accelerated by the presence of Cl^- ions (129). In fact, Weiss (755) quotes several such catalyzed reactions: the Cl^- -catalyzed exchange between Eu(II) and Eu(III), and the F^- -catalyzed exchange between Ce(III) and Ce(IV). It would be interesting to see if these systems show mixed valence absorption bands in solution analogous to that shown by HCl solutions of Fe(II) and Fe(III).

Hathaway and Holah (347) have found that the oxidation of elemental iron by halogens in various solvents leads to the formation of mixed valence compounds formulated as $[\text{Fe}^{\text{II}}(\text{Sol})_6][\text{Fe}^{\text{III}}\text{X}_4]_2$, where Sol is a solvent molecule and X is a halide ion. As expected from the class I geometry and the lack of shared ligands in these materials, the spectra show only the absorptions of the component ions.

The low ratio of ligand to iron in the mixed valence alkali iron carbonates $\text{M}^{\text{I}}\text{Fe}_2^{\text{II}}\text{Fe}^{\text{III}}(\text{CO}_3)_3(\text{OH})_2 \cdot \text{H}_2\text{O}$ (47, 288) demands a rather

intimate association of the ferric and ferrous ions. In accord with this, the crystals are green and their solutions in water test negative for free Fe(III).

A mixed valence iron acetate has been reported, which may be related to the carbonate described above. The acetate,

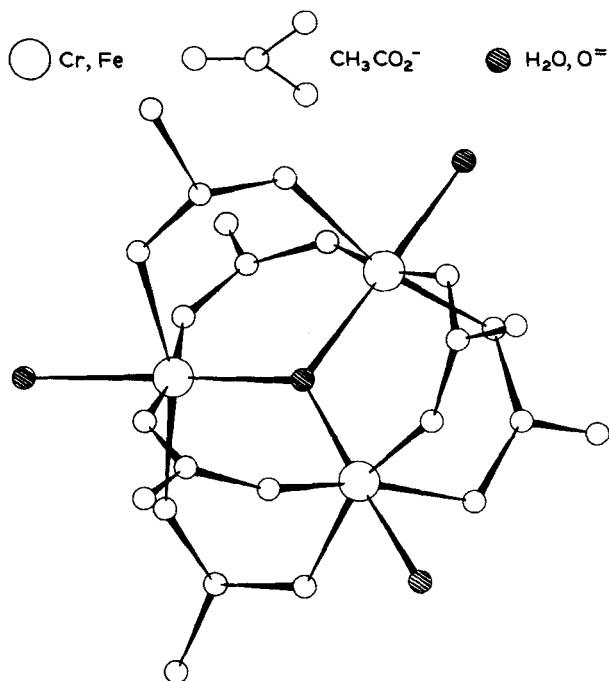
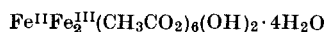
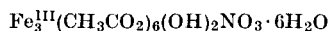


FIG. 11. The structure of the $[\text{M}_3(\text{CH}_3\text{CO}_2)_6\text{O} \cdot 3\text{H}_2\text{O}]^{n+}$ trinuclear ion.

is described as dark brown and, like the carbonate, yields a polynuclear ion in solution (141). There also exists here a possible connection with the ferric acetate with formula



which is known to involve a triangular array of Fe(III) ions in a cluster complex (Fig. 11) (251).

The mixed valence iron cyanides have been the object of constant study for over 250 years (572), a large part of their allure springing no doubt from their deep blue colors. Although it was long held that Prussian blue, made by adding Fe(III) to $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, and Turnbull's

blue, made by adding Fe(II) to $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$, were distinct compounds, an overwhelming amount of evidence has since accumulated demonstrating that they are identical materials (66–68, 209, 225, 254, 753). We shall call this material Prussian blue. There are two kinds of Prussian blue, the first of which, soluble Prussian blue, is generally taken to be $\text{M}^{\text{I}}\text{Fe}_2(\text{CN})_6$, whereas insoluble Prussian blue is $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. The earlier history of these “iron blues” has been reviewed by Holtzman (368).

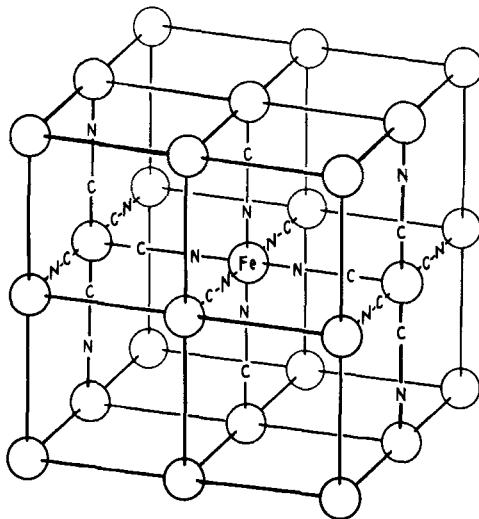


FIG. 12. The unit cell of Prussian blue-type crystals. In “soluble” Prussian blue ($\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$), four potassium ions occupy octant sites and surround the body-centered ion tetrahedrally, whereas, in “insoluble” Prussian blue ($\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$), hydrated Fe(III) ions are thought to occupy octant sites.

The crystal structures of soluble and insoluble Prussian blue are closely related to one another (409, 754), and to a large number of other heavy metal ferricyanides and ferrocyanides (588, 718) having face-centered cubic lattices with iron ions at the corners of a cube and cyanide ions bridging the irons along the cube edges. The centers of the cubes are filled with charge-compensating cations, if necessary, and/or water (Fig. 12). The iron-iron distance in Prussian blue is 5.1 Å as deduced from X-ray powder pattern data, which, however, were inadequate for determining the Fe—C, C—N, or N—Fe distances. Due to the roomy caverns at the cube centers, Prussian blue-type crystals are zeolitic and act as molecular sieves with channel diameters of ca. 3.2 Å (650). This is consistent with dehydration isotherm studies, which showed that Prussian blue is not a definite hydrate (753). Since the differentiation

between the Prussian blues as "soluble" and "insoluble" stems not from any real solubility of the "soluble" material, but instead from the ease with which it can be peptized to form a colloidal dispersion, knowledge of the crystal structure of soluble Prussian blue is essential to understanding the properties of its "solutions."

Both Thompson (703) and Korshunov and Lebedeva (436) have shown that, when Prussian blue is formed from inactive Fe(III) and radioactive $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ and then decomposed by base, the resulting $\text{Fe}^{\text{III}}(\text{OH})_3$ is completely inactive. This demonstrates first that the Prussian blue crystal is not class III-B, as suggested indirectly by Emeleus and Anderson (221), and also that the cyanide ions do not rotate in the crystal or become carbon-bonded to the Fe(III) ions on forming the crystal. Thus, as can be readily seen from Fig. 12, there are two varieties of octahedral site in the class II Prussian blue crystal: those coordinated by the carbon ends of the cyanide ligands, and those coordinated by the nitrogen ends of these same ligands. It has been a problem of great interest to demonstrate which iron ion valence resides in which site, i.e., are the valences in Prussian blue trapped as ferric ferrocyanide or ferrous ferricyanide?

The magnetic susceptibility of Prussian blue, as measured by Davidson and Welo (176) and by Cambi (128), is consistent with either high-spin, $3d^5$ Fe(III) ions in the nitrogen sites and low-spin, $3d^6$ Fe(II) ions in the carbon sites, or high-spin, $3d^6$ Fe(II) ions in the nitrogen sites and low-spin, $3d^5$ Fe(III) ions in the carbon sites. On the basis of oxidation-reduction potentials in aqueous solutions, Weiser *et al.* (754) argue for the latter, claiming that Prussian blue is the ferrous salt of ferricyanic acid. A flood of more direct evidence has recently shown that, in fact, Prussian blue is better considered as the ferric salt of ferrocyanic acid. Thus, for example, on the basis of the fact that the C—N stretching frequencies of various ferrocyanides fall at 2090 cm^{-1} and below, whereas the C—N stretches in ferricyanides are found at 2150 cm^{-1} and above, Emschwiller (222) demonstrated that Prussian blue contained ferrocyanide ions since the C—N stretch in this compound lies at 2080 cm^{-1} . Again, Robin (591) has interpreted the first two bands at $14,700\text{ cm}^{-1}$ and $25,000\text{ cm}^{-1}$ in the electronic spectrum of Prussian blue as being associated with the transfer of an electron from a low-spin, $3d^6$ ferrocyanide ion to a high-spin, $3d^5$ ferric ion. The most compelling evidence for the formulation of Prussian blue as ferric ferrocyanide rests on the results of the many Mössbauer spectral studies of this material. As shown in Fig. 13, the Mössbauer spectrum of soluble Prussian blue consists of a pair of lines, 2 and 3, which are identified as the quadrupole split components of the high-spin Fe(III) ion in octahedral coordination,

and the single line, 1, due to the $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ ion. The ratio of the intensities of lines 2 plus 3 to line 1 is 1.0 in soluble Prussian blue and almost 4/3 in insoluble Prussian blue (209, 225, 254, 410, 591).

Because the valences are firmly trapped, one can draw an orbital diagram for Prussian blue, using the orbitals of the $\text{Fe}^{\text{II}}(\text{CN})_6$ and $\text{Fe}^{\text{III}}(\text{NC})_6$ ions taken separately (591). This is shown in Fig. 14, where the mixed valence transition responsible for the blue color of Prussian blue ($14,700\text{ cm}^{-1}$, Fig. 15) is depicted by the arrow labeled 1. According to this assignment, the ground state of Prussian blue is $\text{KFe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6$,

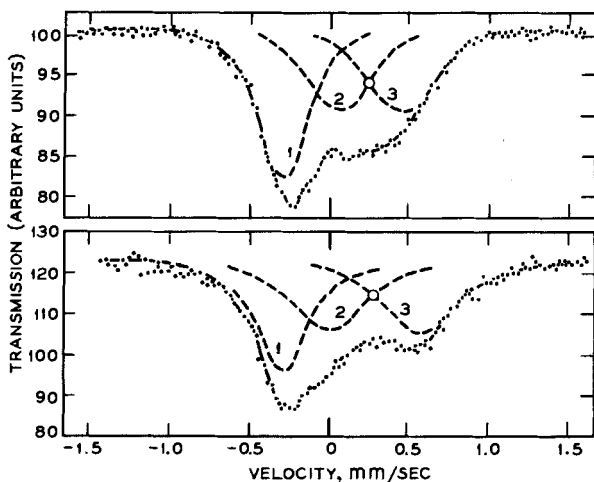


Fig. 13. The Mössbauer spectra of soluble Prussian blue ($\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$), upper, and insoluble Prussian blue ($\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$), lower, both at 143°K (254).

and the Turnbull's blue formulation, $\text{KFe}^{\text{II}}\text{Fe}^{\text{III}}(\text{CN})_6$, is more appropriate to the first excited state. Actually, because of configuration interaction, the system in the ground state is a mixture of the Prussian blue and Turnbull's blue configurations, in a proportion which can be estimated from the mixed valence absorption intensity. Application of Eq. (14) to the $14,700\text{ cm}^{-1}$ band of Prussian blue ($\epsilon = 9800$; $\mu = 1.23\text{ eÅ}$) yields a value of α^2 equal to 0.01, showing that the optical electron spends 99 % of its time in a carbon hole and 1 % in a nitrogen hole in the ground state.

Because Prussian blue is a class II crystal, with distinguishable oxidation states, its spectrum should contain not only the first mixed valence absorption (arrow 1), but a second band related to the first by a spectral interval in the high-spin $\text{Fe}(\text{II})$ ion, and also bands due to the $\text{Fe}(\text{III})$ and $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ ions. The transition labeled 2 is assigned as the

band observed at $25,000\text{ cm}^{-1}$, for it is weak and separated from transition 1 by the $t_{2g} \rightarrow e_g$ separation ($10,000\text{ cm}^{-1}$) in the high-spin Fe(II) ion, as predicted for a class II system. The low intensity of this band follows from the fact that it is a transition between t orbitals on one center and e orbitals on another, and, according to Eq. (17), this is forbidden. The strong band in the $45,000\text{--}50,000\text{ cm}^{-1}$ region of the

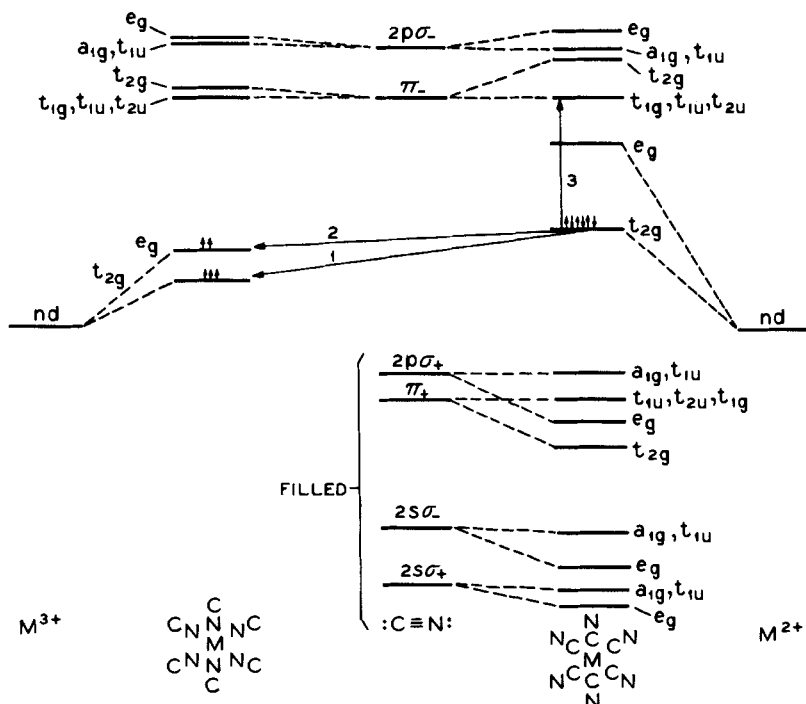


FIG. 14. A molecular orbital scheme for class II Prussian blue. The symmetry labels on any column of levels are appropriate only to the molecule listed at the foot of that column, and the transitions labeled 1, 2, and 3 correspond to the bands of Fig. 15 labeled in the same way (591).

Prussian blue spectrum is readily assignable as the intramolecular charge transfer excitation of the ferrocyanide ion (arrow 3 in Fig. 14). The bands at $35,000\text{--}40,000\text{ cm}^{-1}$ are tentatively assigned as transitions from a CN π -bonding orbital to the t_{2g} orbital of the Fe(III) ion. Braterman (85) has generalized the Prussian blue assignment scheme to include complexes in which the ions in the two holes are of different metals.

Also in accord with its class II assignment, Prussian blue has a room temperature resistivity of about 10^7 ohm cm , and is an intrinsic semi-

conductor with a negative temperature coefficient of resistance (250). Although ferromagnetic with a Curie temperature of 3.5°K (367), Prussian blue is not an example of mixed valence, Zener-type double exchange, for the Fe(II) ions in the ground state are diamagnetic.

There are numerous composition variations that can be made in the iron blues. A reduced form of Prussian blue, $\text{Fe}_2^{\text{II}}\text{Fe}^{\text{II}}(\text{CN})_6$, is colorless as one might expect, but the oxidized form, $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6$, is green instead of the expected orange-brown color of $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$. Ibers and Davidson (373) present their spectrum of $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6$ as well as those of Fe(III) and $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$, from which one sees clearly an "extraneous" absorption in $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6$ centered at 20,000 cm^{-1} . DeWet and

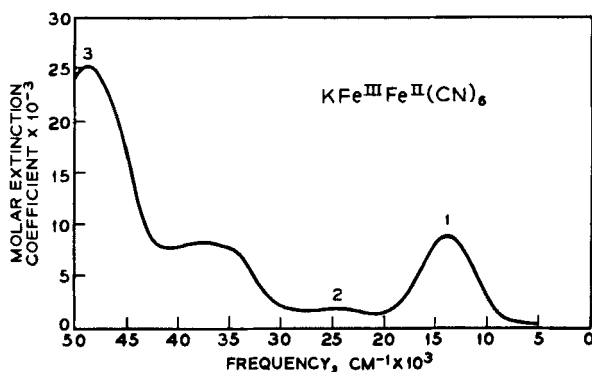


FIG. 15. The electronic spectrum of soluble Prussian blue as a colloidal dispersion in water (591).

Rolle (193), however, have demonstrated that $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6$ is very readily reduced by water to a mixed valence Prussian blue-type compound, which no doubt is the cause of the 20,000 cm^{-1} band of " $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6$." Both the oxidized and reduced compounds have the face-centered cubic lattice of Prussian blue (409).

Although Ibers and Davidson (373) were able to demonstrate a mixed valence absorption in solutions containing Fe(II) and Fe(III) ions, mixtures of the corresponding hexacyanides gave no such absorption. The lack of mixed valence absorption here is due in part to the impossibility of sharing ligands between these ions, and in part to the difficulty of forming pairs between ions of the same charge. However, they do exchange electrons rapidly in solution (703).

There are a large number of pentacyanide ions of the formula $[\text{Fe}^{\text{II}}(\text{CN})_5\text{X}]^{y-}$, where X is H_2O , NH_3 , AsO_2^- , SO_3^{2-} , NH_2NH_2 , or CO, all of which form deep blue precipitates with Fe(III) ion. On combining

the salts of $[\text{Ru}^{\text{II}}(\text{CN})_6]^{4-}$ or $[\text{Os}^{\text{II}}(\text{CN})_6]^{4-}$ with $\text{Fe}(\text{III})$ ion, blue to purple sols are formed which have electronic spectra virtually identical to that of Prussian blue (591).

As one might expect from the ubiquitous distribution of iron in nature, there are great numbers of naturally occurring minerals containing $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})$, both as major constituents and as impurities. As with the other iron compounds, the combination of X-ray crystallography and Mössbauer spectroscopy can be a great aid in determining the amounts, valencies, and coordinations of the iron ions in mixed valence minerals. From this information one can proceed to a qualitative understanding of their electronic structures. In this section, mixed valence iron minerals will be considered for which structures have been determined, together with only a few of the many other minerals which suggest themselves for future mixed valence study.

MacCarthy (470) many years ago presented the results of a study aimed at correlating the colors of a large number of iron-containing minerals with the oxidation state of the iron. Iron minerals as found in nature span the color spectrum, being colorless, yellow, red, brown, green, blue, purple, or black. MacCarthy showed that, in general, the colorless minerals contained only $\text{Fe}(\text{II})$, that the yellow, orange, and red ones were totally $\text{Fe}(\text{III})$, but that mixtures of these valence states led to blue materials if hydrated, black if anhydrous. The greens and purples were accounted for as physical mixtures of the other, more basic pigments. However, before one adjudges a naturally occurring mineral to be mixed valence on the basis of its unusual color, the possible contamination of the sample by colored impurities must be ruled out.

Both the partial reduction of colorless $\text{Fe}^{\text{III}}\text{PO}_4$ and partial oxidation of colorless $\text{Fe}_2^{\text{II}}(\text{PO}_4)_2$ lead to the formation of deeply colored $\text{Fe}(\text{II}), \text{Fe}(\text{III})$ phosphates (699). Thus, depending upon conditions, the reduction of slurried FePO_4 in H_2O with H_2 under pressure leads to green, blue, or black crystals (374). Vivianite, a naturally occurring mineral with composition $\text{Fe}_3^{\text{II}}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, presents a dramatic example of the development of a deep color on attaining mixed valence, for the mineral is colorless until cleaved and exposed to the air, whereupon it oxidizes and develops a dark blue color. Since the reduced mineral contains pairs of ferrous ions in oxygen octahedra sharing an edge (514), it is clear how a chromophoric grouping can result on partial oxidation. A similar situation holds for iron in silicate and borate glasses (767) in which, for example, ferrous iron is colorless and ferric iron is brown, but glasses of intermediate oxidation are blue. The blue-color centers in these glasses must be "dimers" in the sense that no mixed valence color can develop if the $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})$ ions are too far separated.

Iron lazulite is another basic iron phosphate mineral. It is described as being "shiny, jewel-like black in color," and contains Fe(II) and Fe(III) in face-sharing octahedral coordination (407). The close approach of the Fe(II) and Fe(III) ions to class III geometry suggests that iron lazulite will have a low electrical resistivity, a quantity which is unmeasured as yet. A similar situation holds for barbosolite (462), $\text{Fe}_2^{\text{II}}\text{Fe}_4^{\text{III}}(\text{PO}_4)_4(\text{OH})_4$, a material in which the oxygen octahedra surrounding the Fe(II) and Fe(III) ions share faces and corners.

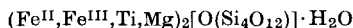
There are a great many silicate minerals containing iron in two valence states. Crocidolite is a bright blue, fibrous silicate containing Fe(II) and Fe(III) in octahedral coordination. The Mössbauer spectrum of crocidolite shows the presence of discrete Fe(II) and Fe(III) ions, as expected for a class II mixed valence system (275). That its blue color is due to a mixed valence interaction is apparent both from the fact that when the Fe(II) fraction is oxidized to Fe(III) the band responsible for the blue color at $16,000\text{ cm}^{-1}$ disappears, and from the fact that this band is polarized along the fiber axis, which is also the direction of shortest Fe(II)–Fe(III) separation (465). Crocidolite is a semiconductor along the fiber axis, but has a very high resistivity perpendicular to this axis.

Biotite is a micaceous mineral in which variable amounts of Al(III) and Mg(II) have been replaced by Fe(III) and Fe(II). As a result of this substitution into the layered mica structure, biotite appears quite black in light polarized with its electric vector within the layers but is colorless perpendicular thereto. Because of the mixed valence aspect of this material and the obvious related electronic conduction mechanism, it is clear why the best insulating micas are lowest in iron. Because the Mössbauer spectrum of biotite shows absorption due to clearly defined Fe(II) and Fe(III) ions, the system is mixed valence class II, as is also clear from its crystal structure (83).

Lievrite is a black mineral having the composition

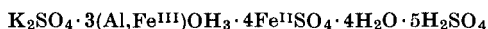


with both the Fe(II) and Fe(III) ions in distorted octahedra sharing edges (53). Taramellite, another iron-containing silicate, also contains chains of octahedral Fe(II) and Fe(III) ions sharing edges, and has the overall formula (490):



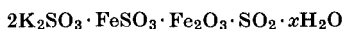
Cronstedtite is a layered mineral, $\text{Fe}_2^{\text{II}}\text{Fe}_2^{\text{III}}\text{SiO}_5(\text{OH})_4$, which has both Fe(II) and Fe(III) ions in octahedral coordination as well as Fe(III) in tetrahedral sites (354). The mineral is black in thick sections and emerald green in thinner ones.

Voltaite is an interesting mixed valence iron sulfate mineral with the composition



which is easily synthesized in the laboratory (300). Consistent with a class II mixed valence formulation, voltaite has a deep black color in massive form, but is green when viewed by transmission in thin sections. Synthesis of the corresponding material having $\text{Cd}^{\text{II}}\text{SO}_4$ replacing $\text{Fe}^{\text{II}}\text{SO}_4$ results in an almost colorless solid, as expected. In contrast to the black color of voltaite, the mixed valence iron sulfate mineral romerite ($\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}$) has only a reddish brown color (634, 635). However, dehydration of romerite to the dihydrate yields a blue-black material, just as in the case of the ferrous-ferric fluorides mentioned above. Pending a report of the structures of these minerals, one might guess that in voltaite the Fe(II) and Fe(III) ions are in rather close association with their octahedra probably sharing ligands, whereas in hydrated romerite these ions are effectively separated by "insulating" water molecules.

Gmelin (288) lists a number of synthetic mixed valence iron sulfates of rather similar composition: $\text{FeSO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{SO}_4$ (rose colored), $4\text{FeSO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ (yellow-green), $6\text{FeSO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 10\text{H}_2\text{O}$ (pale green), and $3\text{FeSO}_4 \cdot 2\text{Fe}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ (colorless). There is also an Fe(II), Fe(III) sulfite (57a),



which is a colorless material.

A cursory look through a modern book of mineralogy (172) will reveal a large number of other iron-containing substances of potential mixed valence interest. For example, the ferrous minerals augite (black, distinctly dichroic), riebeckite (dark blue, dichroic), glaucophane (blue, dichroic), hornblende (dark green to black), tourmaline (all colors, strongly dichroic), ludwigite (black, dichroic), and osumilite are all thought to contain ferrous and ferric ions.

The mineral magnetite, Fe_3O_4 , offers many illustrative examples of mixed valence effects. On the basis of its stoichiometry, Gay-Lussac first described Fe_3O_4 as involving a "special" valence state of iron. Shortly thereafter, Dalton and Berzelius proposed instead that Fe_3O_4 was a compound of $\text{Fe}^{\text{II}}\text{O}$ and $\text{Fe}_2^{\text{III}}\text{O}_3$ in 1 : 1 ratio. As we shall see, there is a certain amount of truth in both of these ideas. Fe_3O_4 is a cubic spinel, consisting of a cubic close-packed arrangement of oxide ions which define both octahedral and tetrahedral sites (Fig. 16). In a normal spinel with eight molecules per unit cell, eight of the tetrahedral holes are filled by M(II) metal ions, while sixteen of the octahedral holes are filled by

M(III) metal ions. In magnetite, however, because of the propensity of Fe(III) for tetrahedral coordination, all eight tetrahedral sites are filled by Fe(III) and the remaining sixteen edge-sharing octahedral sites are filled by eight Fe(II) ions and eight Fe(III) ions (726, 728). Thus if it were a normal spinel, magnetite clearly would be a class I mixed valence system, but the inverse spinel structure described above results in class III-B behavior within the octahedral sites and class I behavior between octahedral and tetrahedral sites.

Verwey *et al.* (729) felt that the rapid electron exchange implied by the mixed valence occupation of the octahedral sites in magnetite was

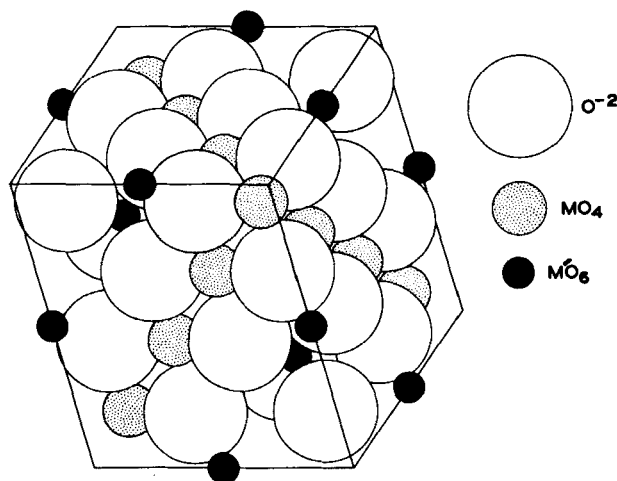


FIG. 16. The unit cell of the spinel MM'_2O_4 , in which the M cations are in tetrahedral and the M' in octahedral sites.

responsible for its unusually low resistivity (4×10^{-3} ohm cm at 300°K). Unlike many oxides which show maximal resistance when stoichiometric and a decreasing resistance as the composition departs from stoichiometry, Fe_3O_4 is just the opposite, for the addition of defects and other valences of iron only act to trap the valence locally and thereby increase the activation energy for conduction (726).

Fe_3O_4 is ferrimagnetic with a Curie point at 500°–600°C. Neutron diffraction experiments (660) show that the Fe(II) in the tetrahedral sites is antiferromagnetically coupled to the ferromagnetically coupled Fe(II), Fe(III) ions in the octahedral sites, the net ferrimagnetism resulting from the larger numbers of octahedral sites.

Verwey *et al.* (729) reported that, on cooling Fe_3O_4 below 120°K, the resistivity rose abruptly by two orders of magnitude and became

distinctly anisotropic whereas above 120°K it is isotropic. They suggested that above 120°K the Fe(II) and Fe(III) in the octahedral sites are in "dynamic disorder," but that below this temperature the crystal is orthorhombic and the Fe(II) and Fe(III) ions become ordered, occupying perpendicular rows of octahedral sites. We can paraphrase Verwey and presume that the octahedral Fe—O distances alter abruptly at 120°K so as to trap the Fe(II) and Fe(III) valences, thereby making the octahedral system more class II, i.e., insulating. If the valences are partly trapped at room temperature through the introduction of Fe₂O₃ into the crystal, then the 120°K transition is absent. Careful neutron diffraction work by Hamilton (335) fully confirmed Verwey's conjectures, for Hamilton showed not only that the low temperature form of Fe₃O₄ was orthorhombic but that, whereas the Fe—O distance in the octahedral sites at 300°K is uniformly 2.0590 ± 0.0016 Å, in the low temperature phase there are two octahedral sites, one having Fe(III)—O equal to 2.00 Å, and one having Fe(II)—O equal to 2.123 Å. These Fe(II) and Fe(III) ions are in perpendicular rows, as predicted. Calhoun's resistivity measurements show that the anisotropy increases with decreasing temperature, indicating a firmer trapping at lower temperatures (126).

The Mössbauer spectra of Fe₃O₄ at 300°K and 85°K offer striking confirmation for the views expressed above (49). At room temperature, the Mössbauer spectrum of Fe₃O₄ shows that the magnetic fields at the octahedral sites are indistinguishable, indicating an oscillation of valence more rapid than 10^8 /sec. On the other hand, at 85°K, the Fe(II) and Fe(III) ions in the octahedral holes can be distinguished as expected for a class II system.

Magnetite can be brominated to yield a dark brown material of the composition (Fe₃O₄)₃Br₂ (360). This bromide still possesses a spinel lattice like Fe₃O₄ and although ferromagnetic, is less so than Fe₃O₄.

The binary oxides of barium and iron contain, among their number, two mixed valence materials. Derbyshire *et al.* (190) and Fraker (259) have shown that the barium iron oxide thought to be BaFeO₃ really contains only 76 % of its iron as Fe(IV), the remainder being Fe(III). This leads to a probable formula Ba(Fe^{III},Fe^{IV})O_{2.9}. A second oxide, BaFe^{II}Fe^{III}₁₆O₂₇, has a spinel-type structure (95) and, like magnetite, is an electrical conductor and ferromagnet (763).

We will present here only one of many examples of the dramatic effects that low-level doping can produce through mixed valence. In yttrium iron garnet, 3Y₂O₃·5Fe₂O₃, three fifths of the Fe(III) ions are found in tetrahedral sites and two fifths in octahedral sites, the stoichiometric crystal being an insulator with a resistivity of about 10^{11} ohm cm.

On doping such crystals with approximately 0.02 atom of silicon per formula weight, an equivalent amount of Fe(III) is reduced to Fe(II) and the resistivity decreases by seven orders of magnitude (792). It is not yet known whether the Fe(II) ions reside in the tetrahedral or the octahedral sites of the garnet.

The process of iron corrosion has been shown to proceed through an intermediate "green rust" of composition $2\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, which precedes the formation of brown rust, $\gamma\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (1, 174, 803). Abe (1) showed that $2\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, when made by the combination of $\gamma\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{Fe}(\text{OH})_2$, is really a blue material, and that "green rust" is probably a mixture of this blue compound and the brown rust. Shively and Weyl (659) also report that the partial oxidation of $\text{Fe}(\text{OH})_2\text{-Al}(\text{OH})_3$ coprecipitates yields dark blue materials. In a more detailed study, Feitknecht and Keller (238) report that the air oxidation of colorless $\text{Fe}(\text{OH})_2$ leads to the formation of a deep green material, which has the crystal structure of $\text{Fe}(\text{OH})_2$ although containing up to 10% Fe(III). Air oxidation of buffered FeCl_2 solutions yields a dark green mixed valence oxychloride of ideal composition $\text{Fe}_4^{\text{II}}\text{Fe}^{\text{III}}\text{Cl}(\text{OH})_{10} \cdot x\text{H}_2\text{O}$, which, however, can have appreciable amounts of its Fe(II) replaced by Fe(III) (238). Selwood (652) mentions that ferromagnetic gels can be formed by addition of base to solutions containing mixtures of ferric and ferrous ions.

There are two biologically important iron-containing materials of potential interest to our study. The first, photosynthetic pyridine nucleotide reductase, contains two nonheme Fe(III) ions per molecule. On photoreduction, one of the two Fe(III) ions is reduced to Fe(II) and the protein *decolorizes* (263). This fact suggests strongly that the two iron ions are not closely associated in the photoreduced protein. Ferredoxin contains seven iron ions per molecule, all of which appear to be Fe(III) (74). However, it is postulated that these ions are involved in electron transport, and that some of the Fe(III) is reduced on reduction of the protein.

F. COBALT

Like manganese and iron, cobalt forms a mixed valence oxide with a spinel structure, Co_3O_4 , and, as with the other two oxides, there has been a good deal of discussion about the distribution of the valency in it. In principle, four possibilities exist: normal or inverse $\text{Co}(\text{II}), \text{Co}(\text{III})$ spinels and normal or inverse $\text{Co}(\text{II}), \text{Co}(\text{IV})$ spinels. In common with Mn_3O_4 and in contrast to Fe_3O_4 , Co_3O_4 has a high resistivity (458, 741),

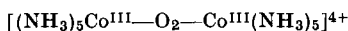
suggesting that the manganese and cobalt compounds are normal spinels (725). Cossee (158) measured the magnetic susceptibilities of tetrahedral Co(II) in $(\text{Co}^{\text{II}}, \text{Zn})\text{O}$, of Co(III) octahedrally coordinated in the spinel $\text{ZnCo}_2^{\text{III}}\text{O}_4$, and of Co_3O_4 from 77° to 1000°K and found that the effective magnetic moment per Co(II) in ZnO was 4.05 B.M., but that the moment of Co(III) in ZnCo_2O_4 was zero, as expected for a low-spin $3d^6$ configuration. The effective magnetic moment per mole of Co_3O_4 , 4.14 B.M., can then be interpreted in terms of the structure $\text{Co}^{\text{II}}\text{Co}_2^{\text{III}}\text{O}_4$ with Co(II) in tetrahedral and Co(III) in octahedral coordination. At 40°K , Co_3O_4 becomes antiferromagnetic (602), and the spin interaction between the Co(II) ions is an order of magnitude stronger than in the spinel CoAl_2O_4 , possibly as a result of indirect exchange involving the empty e_g orbitals of the Co(III) ions. The nuclear magnetic resonance chemical shift of ^{59}Co in Co_3O_4 (403, 509) contains a temperature-independent contribution due to mixing of the low-lying excited configuration $t_{2g}^5 e_g^1$ with the t_{2g}^6 ground state, and a temperature-dependent part attributed to hyperfine coupling between the nuclear spins of the diamagnetic Co(III) ions and the electron spins of the Co(II) ions at the tetrahedral sites.

Cobalt(III,IV) perovskites can be prepared with formulas intermediate between $\text{LaCo}^{\text{III}}\text{O}_3$ and $\text{SrCo}^{\text{IV}}\text{O}_3$, just as was found for the Mn(III),Mn(IV) manganites (394). In contrast to the octahedrally coordinated, low-spin Co(III) in Co_3O_4 , that in LaCoO_3 is high-spin, and all the mixed valence phases are ferromagnetic, with Curie temperatures that rise sharply with increasing Co(IV) concentration. LaCoO_3 behaves as a semiconductor, but when doped with strontium the room temperature resistivity drops sharply and the temperature coefficient of resistivity finally becomes positive. As in the case of the Mn(III),Mn(IV) manganites, the ferromagnetism of the mixed valence cobaltites is attributed to a strong positive Co(III)–Co(IV) interaction. As described in Section II, Zener (813) showed that the resonance energy between the canonical structures $\text{Co}^{3+}\text{—O}^{2-}\text{—Co}^{4+}$ and $\text{Co}^{4+}\text{—O}^{2-}\text{—Co}^{3+}$ is larger if the electron spins on the metal atoms are parallel. Since the integrals determining the interaction in Zener's model are those involving simultaneous electron transfer from O^{2-} to Co^{4+} and Co^{3+} to O^- , the spin correlation and electrical resistivity would both be accounted for by mixed valence interaction, were it not for the fact that there is no anomaly in the resistivity at the Curie temperature. This observation has not yet been satisfactorily explained.

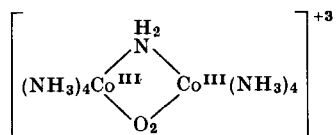
A further interesting example of a Co(II),Co(III) system with oxide ligands occurs among the class of heteropolytungstates. Powerful oxidizing agents, such as hot persulfate solution, oxidize the emerald

green anion $[\text{Co}_2^{\text{II}}\text{W}_{12}\text{O}_{42}]^{8-}$ to a mixed valence anion, the alkali metal salts of which form very dark brown to black cubic crystals. The anion was at first (37) formulated as $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{42}]^{7-}$, with an "extra" Co(II) attached to the outside of the Keggin structure (408) characteristic of polytungstates. Very recently, however, the evidence for this formula has been reexamined (38) and the anion is now considered to be $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}\text{W}_{11}\text{O}_{40}]^{9-}$, in which Co(II) replaces one of the tungsten atoms of the $\text{W}_{12}\text{O}_{40}$ framework, and is thus octahedrally coordinated by oxygen. The paramagnetic susceptibility of the potassium salt of this anion exhibits a most curious dependence on temperature, changing only 13% between -143° and 23°C , so that, although the two cobalt ions are in octahedral and tetrahedral coordinations and the system belongs to class I, there appears to be appreciable intraionic interaction. An ESR study would be rewarding.

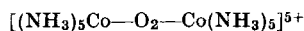
Peroxo-bridged binuclear cobalt complexes have been known for over 100 years (262) and were systematically investigated by Werner (765, 766). Diamagnetic cations such as



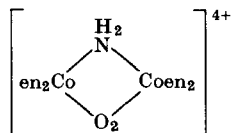
and



undergo one-electron oxidations (702), forming paramagnetic species, and the question is whether Werner's formulation with one Co(III) and one Co(IV) is correct, or whether the electron has been removed from the bridging peroxo group, i.e., is the oxidized cation a mixed valence species belonging to class II or III-A, or a single valence species containing the radical ligand O_2^- ? A number of workers established that the complexes



and



had magnetic moments corresponding to one unpaired spin (287, 480), but were unable to distinguish between the alternative formulations and, indeed, Malatesta (480) envisaged a resonance between them.

In 1938 Mathieu (488) measured the rotatory dispersion and circular

dichroism of the optically active ethylenediamine compounds of the peroxo-bridged cobalt complexes, but, in the absence of a quantum mechanical theory of rotational strengths in metal complexes, was unable to interpret them. Mathieu (488) and Ohyagi (544) reported some solution absorption spectra, but the most reliable available appears to

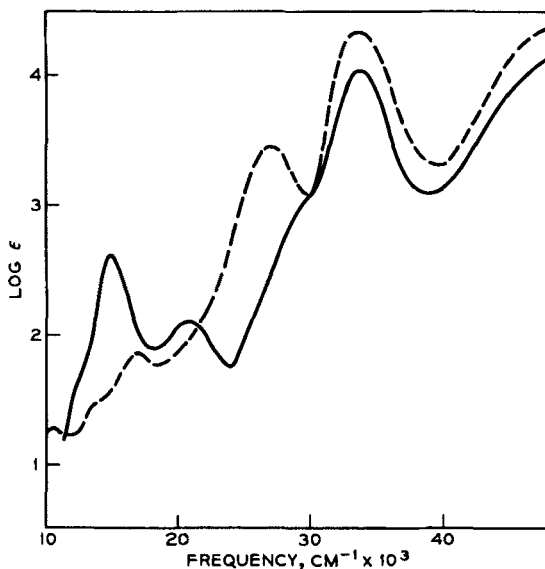
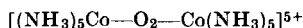
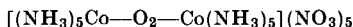


FIG. 17. The electronic absorption spectra of the $[(\text{NH}_3)_5\text{CoO}_2\text{Co}(\text{NH}_3)_5]^{5+}$ (—) and $[\text{Co}(\text{NH}_3)_5\text{I}]^{2+}$ (---) ions in aqueous solution (463, 464).

be that of Linhard and Weigel (463, 464) (Fig. 17), who also were the first to note that the spectrum of

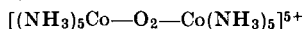


resembled the ligand field spectrum of an octahedral Co(III) complex, $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}$, in which the ligand field strength of X was very different from that of NH_3 . Yamada *et al.* (797) had previously measured the polarized crystal spectrum of

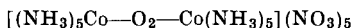


and concluded that the first absorption band was polarized parallel to what they call the $\text{Co}-\text{O}-\text{O}-\text{Co}$ direction, but, as the crystal structure of the compound had not been determined at that time, it is difficult to see how they arrived at this conclusion.

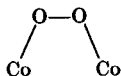
Dunitz and Orgel (210) attempted to rationalize the electronic structure of



using qualitative arguments based on π -bonding between t_{2g} orbitals on the cobalt atoms and $2p$ orbitals on the oxygens, with the assumption that the Co—O—O—Co unit was linear. Unfortunately, the first crystal structure determination (721) revealed that the O—O bond was at right angles to the metal-metal line. In either case, the two cobalt atoms would be equivalent, and the complex would be a class III-A system. That the two cobalt atoms are magnetically equivalent was clearly shown by the ESR spectrum of the cation in concentrated sulfuric acid solution (58). The fifteen observed hyperfine lines result from the interaction of the single unpaired electron with both cobalt nuclei ($I = 7/2$). The spectra of both peroxo- and peroxo-imino-bridged complexes were asymmetrical and varied with the acidity, viscosity, and temperature of the solvent in a manner which could be explained by a relaxation effect depending on protonation of the oxygen atoms (214). A further relaxation mechanism might come from rotation or torsional oscillations about the O—O bond, an effect made more likely by the fact that unpublished crystallographic work by Okaya, cited in (214), showed that in



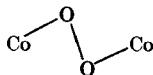
the two cobalts are cis to one another:



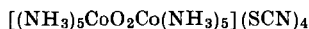
The crystal structure determination of Vannerberg and Brosset (721), in which both oxygen atoms were equidistant from the two cobalts, has been criticized recently by Schaefer and Marsh (623), who pointed out that it was based on only 234 reflections and refined to an R factor of only 19%, even after assuming that there was disorder in the lattice. Schaefer and Marsh measured 1458 reflections from



and refined their proposed structure to an R value of 7.7%. In this crystal, each oxygen is bonded to one cobalt as in Okaya's structure but in a trans



rather than a cis arrangement, which parallels that found in the diamagnetic compound (720):



The cobalt and oxygen atoms all lie in a plane, the Co—O—O angles are almost 120° , and the O—O bond length (1.31 ± 0.02 Å) is close to what one would expect for the O_2^- superoxide ion. The Schaefer and Marsh structure appears to be well substantiated, but without further details of Okaya's work it is not possible to state for certain whether there are two geometrical isomers of this cation. One can say that it is in fact not a class II or class III-A mixed valence system at all, but rather an example of the extremely small group of metal complexes which have a radical ligand. Polarographic reduction studies have been reported for the various peroxo and peroxo-imino complexes (302, 415), but the reduction reactions are complicated and difficult to interpret. The complexes have also been considered as potential semiconductors (249) on the basis of the ease of transferring electrons to or from them, but it is clear from dielectric constant measurements that they are not.

A binuclear cyanide complex $[(CN)_5CoO_2Co(CN)_5]^{5-}$ has also been prepared (333) as a deep red potassium salt. The intense absorption band at $32,000\text{ cm}^{-1}$ ($\epsilon = 6800$) probably corresponds to the band at $33,800\text{ cm}^{-1}$ ($\epsilon = 10,000$) in $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$, although, because of the higher position of cyanide in the spectrochemical series, no ligand field bands like those of the amine complex are seen.

By the action of HCN on Co(II) solution in an inert atmosphere, one obtains a rose-colored precipitate with a Co:CN ratio of 1:2.4 and an effective magnetic moment of 3.2–3.6 B.M. per cobalt atom (127, 555, 584). Numerous crystallographic studies of this (716, 717) and a related hydrate (247) have led to the conclusion that the compound is cobaltous cobalticyanide, i.e., that the valences are firmly trapped and the system is class II. $Co_3^{II}[Co^{III}(CN)_6]_2$ has a cubic lattice isomorphous with the cobalticyanides of other divalent first transition metals and closely resembles that of Prussian blue. The diffuse reflectance spectrum of the compound (85) has been interpreted as a simple superposition of the ligand field bands of $[Co^{III}(CN)_6]^{3-}$ and Co(III) octahedrally coordinated by the nitrogen ends of the cyanides. That there is no mixed valence absorption like that found in Prussian blue (591) indicates the greater difficulty of reducing a low-spin, $3d^6$ Co(III) ion than a high-spin, $3d^5$ Fe(III) ion.

G. NICKEL

Being almost the only mixed valence compound of nickel, the lithium-doped nickel oxide system has played a central role in our understanding of the electrical properties of mixed valence solids (described in Section

II). Pure, stoichiometric NiO is a green compound with a room temperature resistivity greater than 5×10^{14} ohm cm and an absorption spectrum in the visible region closely resembling that of $\text{Ni}(\text{H}_2\text{O})_6^{2+}$. When heated with lithium carbonate at 800°C , however, Li^+ ions replace a variable number of Ni(II) ions in the rock salt lattice, and a corresponding number of Ni(II) ions are oxidized to Ni(III). The solids so produced range from gray to black and are semiconductors with activation energies and room temperature resistivities which decrease sharply with increasing lithium content. Thus, the presence of 2% lithium in NiO lowers the room temperature resistivity of a pressed pellet to only 10^2 ohm cm (719). De Boer and Verwey (182) first suggested that such enhanced conductivity would arise only when ions of differing valency were present at crystallographically indistinguishable sites, and since then many others have applied this idea, both to Ni_{1-x}O (348, 351, 730) and to many other systems (see subsections D and F on manganese and cobalt, for example).

As regards the mixed valence classification of Ni_{1-x}O , the question is whether, in the ground state at absolute zero, the Ni(II) and Ni(III) ions can be distinguished, in which case the system belongs to class II, or whether it would be more appropriate to speak of holes in a conduction band consisting of $3d$ orbitals on the metal ions (class III-B). There have been several magnetic studies of lithium-doped nickel oxides (239, 378, 566), but the observed ferromagnetism of some samples (378, 566), which might have been correlated with coupling between the bound $3d$ electrons and the conduction electrons (813), most probably results from impurities. The most comprehensive study to date (296) reveals that, when less than 30% of the nickel has been replaced by lithium, the lattice is antiferromagnetic and cubic above the Curie temperature; but when the lithium content is higher, the lattice is rhombohedral and ferrimagnetic, probably because the lithium and nickel ions are partly ordered in alternate (111) planes. The moments within each plane are either ferromagnetically coupled or paramagnetic. On the assumption that all Ni—O—Ni interactions are antiferromagnetic, the variation in magnetization per molecule with composition is explained much better by assuming that the Ni(III) ions are low-spin, with the $t_{2g}^6 e_g^1$ configuration. Such a configuration, however, having only one electron in the e_g orbitals, will promote a tetragonal elongation (see the earlier example in Cr_2F_5), which will trap the valence and make the system class II. Thus, even though the presence of Ni(III) results in a vast decrease in resistivity, the indirect exchange mechanisms providing antiferromagnetic coupling between near neighbors appear to be of lower energy than Zener-type double exchange.

Although the ground state electronic structure of these oxides places them firmly in class II, there remains the question of the conduction mechanism. Verwey *et al.* (730) thought that conduction arose by the motion of a positive hole from Ni(III) to Ni(II), the activation energy being that required to ionize the hole on Ni(III) from neighboring lithium ions. That this is not the case follows from the fact (351) that, at very high lithium concentrations, the activation energy, although decreasing, does not tend to zero. Heikes and Johnston (351) later proposed that conduction should be regarded as a thermally activated diffusion process, in which the activation energy comes from the self-trapping of the hole by its polarization field (802) (described in Section II). Extensive series of conductivity and Seebeck effect measurements as a function of temperature and lithium content (719) were held to confirm Heikes and Johnston's view, but all these considerations have recently been placed in question by measurements of the Hall effect (816), which show it to be much larger than those calculated using the thermal diffusion (hopping) model. Further, and more damaging, the Hall mobility does not increase exponentially with temperature as the hopping model requires. A reconsideration of the previous Seebeck measurements, which were carried out on heavily lithium-doped samples, and new measurements on very lightly doped samples (80), have also led to the same conclusion. Whether these observations spell the demise of the hopping model altogether, or only for this system, remains very much to be seen. There is the possibility that a model similar to the one proposed by Frederikse (260) for slightly reduced rutile (see Section III,A on titanium) may prove appropriate, but a further factor that has to be kept in mind is the possibility of compound formation in the lightly doped nickel oxides. Thus semiconductivity plots have been published (433) for pellets of Ni_{1-x}O , with x as large as 0.12, giving room temperature resistivities as low as 10^2 ohm cm. However, a study (77) of the nickel-oxygen phase diagram does not reveal the existence of stoichiometric higher oxides, such as Ni_3O_4 .

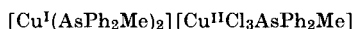
In addition to the Ni(II),Ni(III) oxides, one Ni(III),Ni(IV) system is known (453). The compounds $\text{BaNi}^{\text{IV}}\text{O}_3$ and $\text{Ba}_2\text{Ni}_2^{\text{III}}\text{O}_5$ are both black materials having low resistivities and magnetic moments, so the properties of the intermediate mixed valence phase $\text{Ba}_3\text{Ni}_2^{\text{III}}\text{Ni}^{\text{IV}}\text{O}_8$ will not be a clear guide to its classification.

H. COPPER

A wide variety of mixed valence copper compounds have been described, the majority containing halide ligands, although examples

with oxygen, nitrogen, and sulfur donors exist. Of the halides, a large number appear to fall into class I, in which the environments of the metal ions in the two oxidation states are very different and there are no bridging ligands. Thus, salts with empirical formulas $\text{Cu}_3\text{Br}_4(\text{pyr})_2$ and $\text{Cu}_3\text{Br}_4(\text{ant})_5(\text{H}_2\text{O})_6$ [pyr = dipyramidon, ant = antipyrine] were prepared some time ago by Souchay (672), who measured the conductivities of their solutions in acetone and concluded that they contained, for example, $[\text{Cu}^{\text{II}}(\text{pyr})_2]^{2+}$ and $[\text{Cu}^{\text{I}}\text{Br}_2]^-$. The colors of the solids (reported as dark green and yellow-green, respectively) are what one would expect for such a formulation. More recently, a large number of similar complexes were prepared (341–343) with simpler ligands, such as ammonia and ethylenediamine, which have the general formula $[\text{Cu}^{\text{II}}\text{A}_4][\text{Cu}^{\text{I}}\text{X}_2]_2$ or $[\text{Cu}^{\text{II}}\text{A}_4][\text{Cu}^{\text{I}}\text{X}_3]$. Compounds with similar formulas and presumably similar structures can also be prepared containing Cu(II) and Ag(I) (344–346), which, when vigorously shaken with water, decompose to AgX leaving $[\text{CuA}_4]^{2+}$ in solution. The chlorides and bromides were reported as deep blue or violet, but the iodides were all brown or black. Further compounds of the same type were prepared by Brauer and Eichner (90). Compounds in which X is CN^- have also been recognized for many years (513, 706) and other examples have been added more recently (506). Their colors suggest that they are all class I systems, with formulas analogous to those of the halides. Another class I cyanide containing one Cu(II) and two Cu(I) ions per mole has been reported by Cooper and Plane (146).

Attempts to prepare cupric complexes of methyldiphenylarsine (AsPh_2Me) always result in reduction of the copper to Cu(I), but Burrows and Sandford (115) isolated two compounds from the reaction, one blue and one brown, both of which appeared to have the empirical formula $\text{Cu}_2\text{Cl}_3 \cdot 3\text{AsPh}_2\text{Me}$. The original explanation offered for the apparent isomerism was in terms of ionic structures such as



but, reinvestigating the reaction, Nyholm (540) found that the arsine had been oxidized, and that the analyses were much better described by the empirical formula $\text{Cu}_3\text{Cl}_4(\text{OAsPh}_2\text{Me})_4$. In nitrobenzene, the blue compound was an electrolyte, and the structural formula would appear to be



i.e., similar to the compounds containing ammonia and ethylenediamine discussed above. Because the blue compound became brown on storage, and also when exposed to chlorine gas, Nyholm concluded that the anion was oxidized to $[\text{Cu}^{\text{II}}\text{Cl}_3]^-$. Although the intensity of color of the brown

compound suggests that it may result from mixed valence absorption, this may perhaps be misleading, since on prolonged exposure to chlorine a red compound analyzing as



was isolated. Since all the copper in this compound is divalent, the color of this and possibly the other mixed valence compound may be related to that of red CsCuCl_3 .

A series of chlorocuprates (I,II) in which the color is clearly due to mixed valence absorption was first prepared by Mori (516). When hexaminecobalt(III) chloride solution is added to an aqueous solution of either CuCl or CuCl_2 containing excess chloride ions, orange-yellow crystals are obtained, but if the solution contains both CuCl and CuCl_2 the resulting crystals are brown or black, depending on the mole fraction of each valence state present. By measuring diffuse reflectance spectra, Mori found the new absorption band in the mixed valence material to be near $17,000\text{ cm}^{-1}$ (518), and its intensity was shown by the same method to be proportional to the product of the mole fractions of the two valence states (171). The crystal structures of the two single valence compounds are closely related, so that both valence states may be present in a crystal in any proportion with only minor structural variations. The chlorocuprate(II) has the formula $\text{Co}(\text{NH}_3)_6\text{CuCl}_5$, with a structure based on a cubic rock salt lattice of $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Cu}^{\text{II}}\text{Cl}_5]^{3-}$ ions (517), but the cuprous salt has the much more complicated formula, $[\text{Co}(\text{NH}_3)_6]_4\text{Cu}_5\text{Cl}_{17}$. Its crystal structure, however, is also cubic with $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $\text{Cu}(\text{I})$ ions forming a rock salt lattice. Each $\text{Cu}(\text{I})$ is surrounded by four chloride ions, one of which forms a bridge to a $\text{Cu}(\text{I})$ at the body center of the cubic unit cell (522) (Fig. 18). Thus, the anion is a pentamer, $[\text{Cu}_5\text{Cl}_{16}]^{11-}$, considered as derived formally from condensation of four $[\text{CuCl}_4]^{3-}$ anions through addition of a fifth $\text{Cu}(\text{I})$. When compounds are formed containing only a small mole fraction of $\text{Cu}(\text{I})$, it may be presumed that it enters the $[\text{Cu}^{\text{II}}\text{Cl}_5]^{3-}$ lattice as $[\text{Cu}^{\text{I}}\text{Cl}_4]^{3-}$, but at higher mole fractions of $\text{Cu}(\text{I})$ there is an increased probability of finding four $[\text{CuCl}_4]^{3-}$ ions on adjacent, tetrahedrally related sites, and then $[\text{Cu}_5\text{Cl}_{16}]^{11-}$ may be formed by incorporating an extra $\text{Cu}(\text{I})$ and a chloride ion at another site (Fig. 19). The formula variation with mixed valence composition which this model suggests is substantiated by chemical analyses (179). It is worth noting that, apart from nonstoichiometric and doped oxides, these class II chlorocuprates(I, II) are among the very small number of systems in which the proportions of two valence states may be varied over the whole range of composition from 100% of one to 100% of the other.

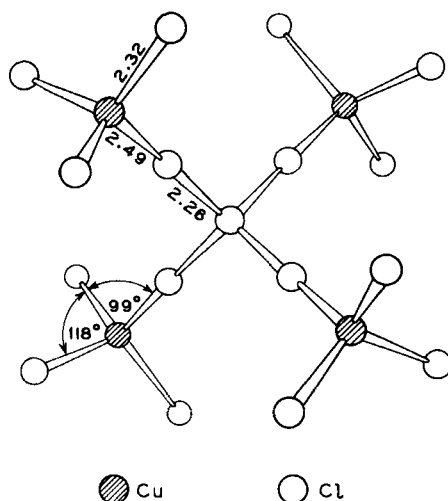


FIG. 18. Bond distances (Å) and angles in the $[\text{Cu}_5\text{Cl}_{16}]^{11-}$ ion (522).

The electrical resistivities of the chlorocuprates(I,II) have also been investigated (171). They are high resistance semiconductors, and at room temperature the specific conductivities, like the interaction absorption intensities, were proportional to the product of the mole fractions

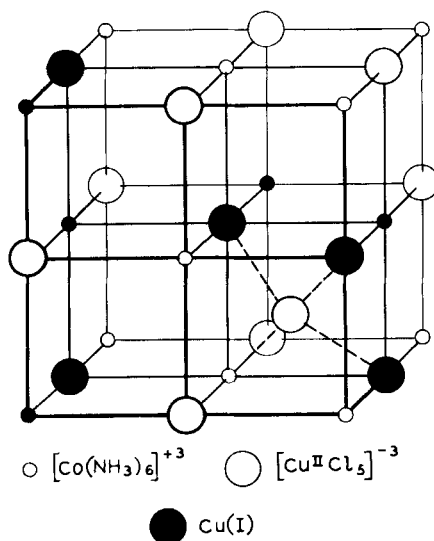


FIG. 19. The distribution of metal atoms in the mixed valence hexamminecobalt chlorocuprate(I,II) crystal.

of the two valence states. Plots of the mixed valence absorption intensity and room temperature resistivity as a function of the mole fraction of Cu(I) are shown in Fig. 20. As was also found with the interaction absorption energy, the semiconduction activation energy did not vary with mixed valence composition, although the value obtained was different from that for either of the single valence chlorocuprates. It was also reported that, unlike either single valence salt, all the mixed valence chlorocuprate salts obeyed Ohm's law quite accurately.

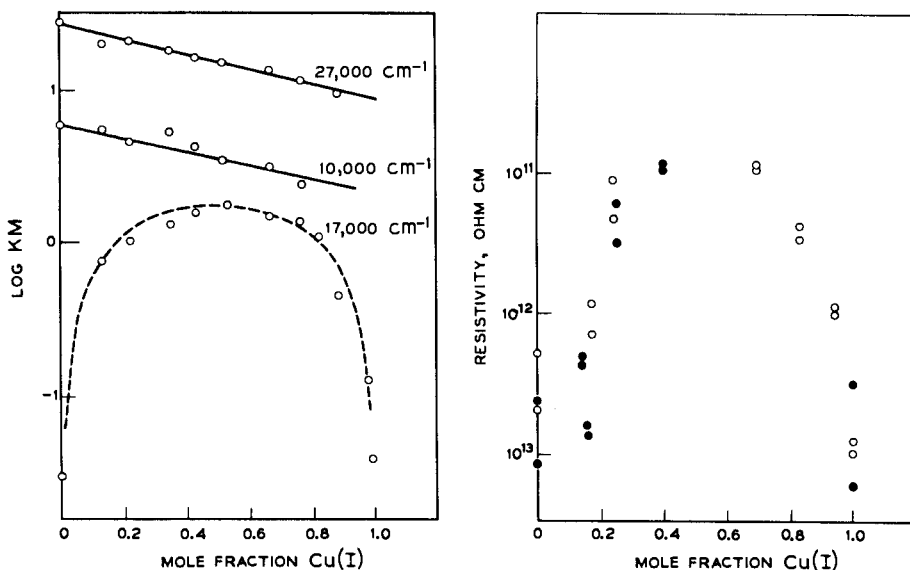
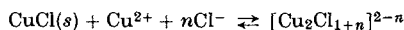


FIG. 20. The intensity of reflected light at three frequencies, and the room temperature resistivity of solid hexamminecobalt(III) chlorocuprates(I,II) as a function of the mole fraction of copper as Cu(I) in the sample (171).

Mixed valence copper chloro complexes have also been extensively studied in aqueous solution. Doehlemann and Fromherz (200) were the first to show that addition of CuCl to a solution of CuCl₂ in 10 *M* HCl caused a marked increase in absorption in the visible region (Fig. 21). It is of interest that the difference in the spectra of a mixed valence solution and two single valence solutions of equivalent concentration has a maximum at 18,000 cm⁻¹, close to that of the solid chlorocuprates(I,II) discussed above. It is clear from this figure and from Fig. 20 that the bands at 10,000 cm⁻¹ and 27,000 cm⁻¹ are Cu(II) constituent ion absorptions. Diehl *et al.* (195) demonstrated that the interaction complex contained equal amounts of Cu(I) and Cu(II). In an effort to determine the formula and association constant of the species responsible

for the mixed valence light absorption, McConnell and Davidson (496) worked at higher dilutions so that they could make use of previously determined association constants for the single valence chloro complexes. For solutions saturated with CuCl, they assumed that the equilibrium was



and found that, in solutions containing up to 0.30 *M* Cu(II) and 0.40 *M* chloride ion, *n* was very close to 2. At higher copper and chloride concentrations, *n* began to increase, and it was noticeable that the difference

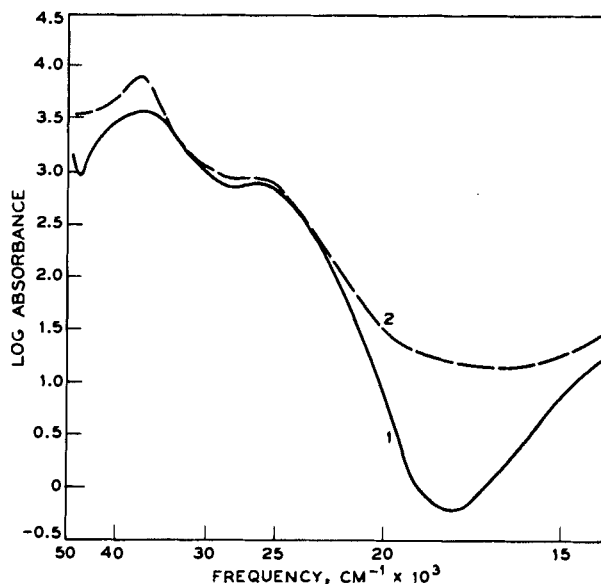


FIG. 21. The electronic spectra of 5.18 *M* solutions of CaCl_2 containing (1) 0.47 *M* Cu(II), and (2) 0.235 *M* Cu(II) and 0.273 *M* Cu(I) (200).

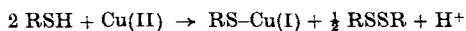
spectrum shifted to lower energy, approaching that found by Doehlemann and Fromherz. The formula of the interaction complex, Cu_2Cl_3 , alone does not permit a distinction between bridged or outer-sphere arrangements, since there is no indication of the manner in which the coordination spheres of the two metal ions are completed by water molecules. If the absorption band in the solid chlorocuprates(I, II) is due to an intermolecular (outer-sphere) charge transfer between $[\text{Cu}^{\text{II}}\text{Cl}_5]^{3-}$ and either $[\text{Cu}^{\text{I}}\text{Cl}_4]^{3-}$ or $[\text{Cu}_5^{\text{I}}\text{Cl}_{16}]^{11-}$, depending on the composition, then the fact that its energy is so similar to that of the mixed valence complex in solution suggests that the latter may also be an outer-sphere complex.

The rate of electron transfer between Cu(I) and Cu(II) in concentrated HCl solution was measured by McConnell and Weaver (498) in one of the first experiments to use NMR line broadening for this purpose. The ^{63}Cu resonance in a 1 *M* solution of CuCl in concentrated HCl was completely flattened by adding Cu(II) ions to a concentration of 10^{-2} *M*, which, using the theory worked out by McConnell and Berger (499), gave a bimolecular rate constant equal to 0.5×10^8 liter mole $^{-1}$ sec $^{-1}$, one of the highest ever measured up to that time. Unfortunately, however, it is not clear to which transition state this rate constant refers.

One of the first mixed valence copper compounds to be prepared was Chevreul's salt, $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$ (91a, 137). A recent determination of the crystal structure (418) places the compound in class I since the Cu(II) ions are surrounded by a distorted octahedron of oxygen atoms, two from water molecules at 1.92 Å and four from the sulfite ions, two at 2.03 Å and two at 2.47 Å, whereas the Cu(I) ions have a very different environment from the Cu(II) ions, being within a distorted tetrahedron consisting of three sulfite oxygen atoms (2.11–2.14 Å) and a sulfur atom (2.14 Å). The compound is reported to be red, but since the crystal structure shows it to be class I the color is most likely that of the constituent cupric sulfite. A related compound, Rogojski's salt, $\text{Cu}_2\text{SO}_3 \cdot \text{H}_2\text{O}$, was found by X-ray powder photography to be a mixture of Chevreul's salt and metallic copper (173).

A mixed valence copper thiosulfate salt, $\text{NaCu}^{\text{II}}\text{Cu}^{\text{I}}(\text{S}_2\text{O}_3)_2$, has been reported (663), but its blue-green color suggests that it belongs to class I, like the aminothiosulfate salt prepared by Ferrari *et al.* (243, 248). The structure of the latter, recently determined, contains well separated $[\text{Cu}^{\text{II}}(\text{NH}_3)_4]^{2+}$ square planar ions and $[\text{Cu}_n^{\text{I}}(\text{S}_2\text{O}_3)_{2n}]^{3n-}$ polyanions in which each Cu(I) is surrounded by four thiosulfate groups while each thiosulfate bonds two Cu(I) ions.

Because of their intense colors, a number of biological copper-containing compounds have been thought to contain the element in both valence states. Klotz *et al.* (429) investigated the reaction between thiomalic acid, $\text{HOOC}-\text{CH}_2-\text{CH}(\text{SH})-\text{COOH}$, and Cu(II) ions as a model system for hemocyanin, an oxygen-carrying protein. The intense violet color, similar to that of hemocyanin, appeared only when the Cu(II): thiomalate ratio reached 0.5, so assuming that the initial reaction was



the color could have been due to a mixed valence complex $\text{Cu}^{\text{II}}(\text{RSCu}^{\text{I}})_4$. About 20 % of the copper in the violet complex could be extracted with penten, following which the violet color was replaced by the blue color

of the Cu(II)-penten complex. The absorption spectrum of the violet complex has a single broad band at $19,200\text{ cm}^{-1}$ with an extinction coefficient of 6000 per $\text{Cu}_5(\text{SR})_4$ unit, indicating the presence of a class II species with appreciable delocalization, if indeed this band is a mixed valence absorption. From the violet solution a gray solid has been isolated (668), which is reported to have a Cu:SR ratio of 5:4, and a room temperature magnetic moment of 2.13 B.M. per Cu(II). Thio-glycolic acid and β -mercaptoethylamine both give similar violet colors, but β -mercaptopropionic acid and cysteine do not.

Ceruloplasmin, another intensely blue copper protein, contains eight copper atoms per molecule, of which approximately four could be exchanged with ionic Cu(II) and four reacted with biquinolyl, as is characteristic of Cu(I) (75). When all the copper is in the reduced state, the compound is colorless and diamagnetic, but in partially reduced samples the intensity of the visible absorption band at $16,400\text{ cm}^{-1}$ is proportional to that of the ESR absorption. The hyperfine splitting of the latter shows that the Cu(II) are magnetically dilute, but there remained the possibility that the color was due to mixed valence absorption, with the Cu(I) and Cu(II) in slightly different environments (class II) (75). However, a number of instances have since been discovered of copper proteins having optical and ESR properties similar to those of ceruloplasmin, but which contain only one copper atom per molecule (487). Thus, if ceruloplasmin is a mixed valence compound, the metal atoms of differing valence are sufficiently separated for there to be no detectable interaction between them in the ground or excited state, i.e., the system is class I.

For reasons set out at the beginning of this section, we have not generally included sulfides among the mixed valence systems reviewed here. Nevertheless, there are a number of copper sulfides whose mixed valence nature is clear enough to be worth mentioning. Of these, the most famous is probably the mineral covellite, CuS , the structure of which was investigated in some detail by Berry (61). This deep blue compound is not, as the formula implies, a simple Cu(II) salt, but contains both S^{2-} and S_2^{2-} ions as well as copper atoms in two distinctly different coordination sites, one planar triangular and the other tetrahedral. It appears from the crystal structure that the correct formulation is $\text{Cu}_4\text{Cu}_2^{\text{II}}(\text{S}_2)_2\text{S}_2$. The fact that covellite is a metal, and below 1.35°K a superconductor (111), shows either that covellite is an inverse structure (class III-B) with both Cu(I) and Cu(II) in the tetrahedral sites, or that one cannot draw firm conclusions about mixed valence class behavior from the crystal structures of highly covalent materials.

The series of dark blue mixed valence compounds $\text{Na}_2\text{Cu}_3\text{S}_3$,

$K_3Cu_8S_6$, KCu_4S_3 , and $RbCu_4S_3$ can be made by fusing copper metal, an alkali metal carbonate, and sulfur at various temperatures (605). Whereas the stoichiometries of these materials suggest that, of the m copper ions in each molecule, one is Cu(II) and $m-1$ are Cu(I), the crystal structures of isostructural KCu_4S_3 and $RbCu_4S_3$ (Fig. 22) show that all the copper atoms in these crystals are in equivalent ligand fields of sulfur atom tetrahedra, which form sheets separated by the alkali

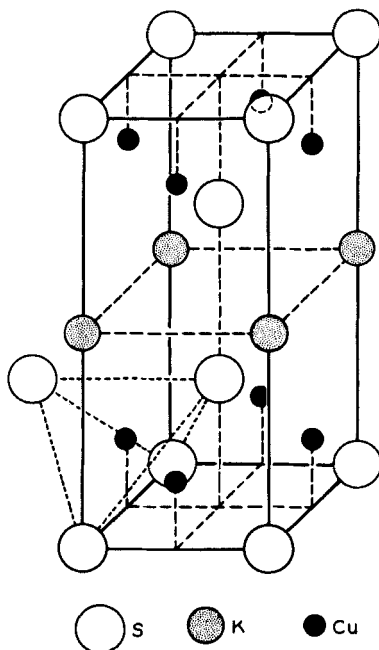


FIG. 22. The class III-B crystal structure of KCu_4S_3 , demonstrating the equivalence of the Cu(I,II) ions in the tetrahedral sites (605).

metal ions. Within the sheets, the copper-copper spacing is 2.76 Å, and not surprisingly these class III-B compounds are good conductors, with resistivities at 20°C of 2.5×10^{-2} and 1.7×10^{-2} ohm cm for KCu_4S_3 and $RbCu_4S_3$, respectively. Inasmuch as $Na_2Cu_3S_3$ and $K_3Cu_8S_6$ have resistivities comparable to those of KCu_4S_3 and $RbCu_4S_3$, these compounds may also have class III-B structures.

Gmelin's *Handbuch* lists many other supposed Cu(I),Cu(II) compounds, including sulfites and amino-cyanides, as well as more bizarre compounds such as $Cu_2Cl(VO_3)_2$, the majority of which were prepared over 50 years ago, and have not been investigated since. A random example is $Cu_4^I Cu_2^{II} Fe_3(CN)_{14} \cdot 2H_2O$ (?) (*sic*), prepared (645) as a black

shiny mass in 1856! We are unable to pass judgement on the status of these substances.

I. ZIRCONIUM AND HAFNIUM

Doubtless as a result of the extremely reducing character of the lower oxidation states of these two elements, there are no compounds of either which have ever been considered as possible mixed valence systems.

J. NIOBIUM AND TANTALUM

The mixed valence halides of niobium and tantalum, numbering over twenty with many as yet only briefly investigated, offer an interesting area for the experimental and theoretical study of mixed valence chemistry. It has become apparent during the last 5–10 years that a remarkable number of these compounds have in common a structural unit of high stability and most interesting electronic structure. It is with the properties of this structural unit that we will be almost totally occupied in dealing with the halides.

The first of the niobium and tantalum mixed valence halides synthesized have since proved to have the composition $M_6X_{14} \cdot 7H_2O$. The fact that the niobium and tantalum compounds of this composition yield only one seventh of their halide ions to aqueous silver nitrate (134, 340) was an early indication that these solutions contain the $[M_6X_{12}]^{2+}$ complex ion. In support of this conclusion, Vaughan, Sturdivant, and Pauling (724) later found that the X-ray diffraction patterns obtained from alcoholic solutions of $Nb_6Cl_{14} \cdot 7H_2O$, $Ta_6Cl_{14} \cdot 7H_2O$, and $Ta_6Br_{14} \cdot 7H_2O$ were interpretable as due to scattering by a polynuclear ion, the idealized structure of which has six metal ions at the face centers of a cube and twelve halide ions at the midpoints of the cube edges (Fig. 23). Single crystal X-ray work has since confirmed this structure of the $[M_6X_{12}]^{2+}$ ion and proved its presence in a number of other niobium and tantalum subhalides. Most recently it has been found that many of the $[M_6X_{12}]^{2+}$ ions can be oxidized to net charge 3+, 4+, and, in one case, a reported 5+, without change of the basic geometry, thereby increasing considerably the number of compounds containing the mixed valence M_6X_{12} structural unit. Many of these mixed valence niobium and tantalum subhalides are discussed in the recent metal-metal bonding review of Schäfer and Schnering (627).

According to the X-ray scattering data (724), the $[\text{Nb}_6\text{Cl}_{12}]^{2+}$ ion in solution has cis Nb—Nb distances of 2.85 Å and Nb—Cl distances of 2.41 Å, the former indicating appreciable metal-metal interaction in view of the 2.86-Å Nb—Nb distance in niobium metal. The authors admit, however, that there is little evidence that the symmetry of the complex ion is as high as they describe it. Indeed, the single crystal study of the anhydrous salt $\text{Nb}_6\text{Cl}_{14}$ (665) shows that in this material the $[\text{Nb}_6\text{Cl}_{12}]^{2+}$ octahedron is compressed along a fourfold axis so as to yield cis Nb—Nb distances from 2.89 to 2.95 Å, and Nb—Cl distances from 2.40 to 2.58 Å.

$\text{Nb}_6\text{Cl}_{14}$ has no free spins, its paramagnetism being of the temperature-independent type ($\chi_{\text{mol}} = 579 \times 10^{-6}$ cgs, corrected for diamagnetism) (665). The heptahydrate, however, has been reported to have an effective moment of 1.48 B.M. as deduced from the Curie-Weiss behavior of the susceptibility (443). Robin and Kuebler (593), however, found this material to have a temperature-independent paramagnetism ($\chi_{\text{mol}} = 850 \times 10^{-6}$ cgs, corrected for diamagnetism) in the temperature range 42°–290°K. In support of a closed-shell ground state configuration for the $[\text{Nb}_6\text{Cl}_{12}]^{2+}$ ion, Mackay and Schneider (471) also find a temperature-independent paramagnetism ($\chi_{\text{mol}} = 456 \times 10^{-6}$ cgs, corrected for diamagnetism) in the double salt $[(\text{C}_2\text{H}_5)_4\text{N}]_4\text{Nb}_6\text{Cl}_{18}$.

Chemically, $[\text{Nb}_6\text{Cl}_{12}]^{2+}$ is rather stable and can be used as a cationic species for the formation of compounds such as $\text{Nb}_6\text{Cl}_{12}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and $\text{Nb}_6\text{Cl}_{12}\text{Br}_2 \cdot 7\text{H}_2\text{O}$ (340). The $[\text{Nb}_6\text{Cl}_{12}]^{2+}$ ion has also found use as a "heavy atom" in the X-ray analysis of the structure of wet lysozyme chloride (157). It has been suggested (10) that in alkaline solution the $[\text{Nb}_6\text{Cl}_{12}(\text{OH})_4]^{2-}$ ion forms, and that hydroxyl groups may even be introduced as bridges replacing the chloride ions. The deep green aqueous solution of $\text{Nb}_6\text{Cl}_{14}$ can be oxidized with I_2 in a two-electron step (493), with only the first electron being lost, however, in alcoholic solutions (471).

The oxidized species $[\text{Nb}_6\text{Cl}_{12}]^{3+}$ has been isolated as the double salt $[(\text{C}_2\text{H}_5)_4\text{N}]_3\text{Nb}_6\text{Cl}_{18}$ (471), and has an effective magnetic moment (1.61 B.M.) corresponding closely to that expected for one unpaired electron. The ESR spectrum of the $[\text{Nb}_6\text{Cl}_{12}]^{3+}$ ion shows a symmetrical 49-line pattern, which is that expected if the unpaired electron has the same hyperfine interaction with all six niobium nuclei (spin 9/2). Further oxidation yields $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Nb}_6\text{Cl}_{18}$, a compound with an effective moment of 0.47 B.M. Because Mackay and Schneider presume that this compound is, in fact, diamagnetic but contains a large amount of paramagnetic impurity, its true susceptibility is still open to question.

In alcoholic solution, the $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ ion also has the structure shown

in Fig. 23, with the cis Ta—Ta distances amounting to 2.88 Å and the Ta—Cl distances to 2.44 Å (724). The recent crystallographic study of the heptahydrate $\text{Ta}_6\text{Cl}_{14} \cdot 7\text{H}_2\text{O}$ by Burbank (113) shows that the crystal contains one molecule per unit cell (probably $P\bar{3}1m$) with both disorder and stacking faults present. In this material, the $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ ion appears as a distorted octahedron, principally tetragonally extended, with the nonbridging chloride ions coordinated to the tantalums on the tetragonal fourfold axis. The cis Ta—Ta bond distances range from 2.63 to 3.27 Å and the bridging Cl to Ta distances range from 2.28 to 2.72 Å, thereby demonstrating not only a distortion of the $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ ion, which is much larger than that measured (665) for the $[\text{Nb}_6\text{Cl}_{12}]^{2+}$ ion, but which also

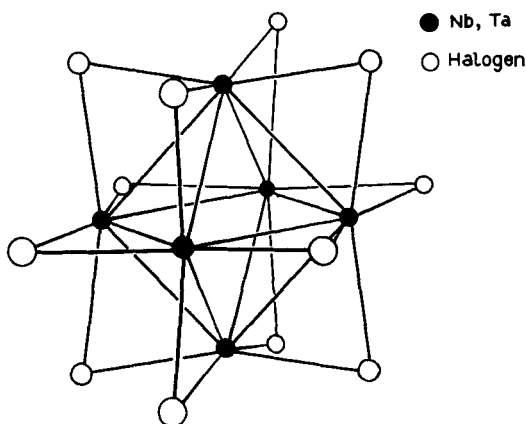


FIG. 23. The idealized geometry of the niobium and tantalum subhalide ions, $[\text{M}_6\text{X}_{12}]^{n+}$, showing the metal atom octahedron and bridging halide ions.

has a different sense to the tetragonality. Careful analytical work on the "heptahydrate" of $\text{Ta}_6\text{Cl}_{14}$ suggests that the true formula is instead $\text{Ta}_6\text{Cl}_{14} \cdot 8\text{H}_2\text{O}$ (630).

As with $\text{Nb}_6\text{Cl}_{14} \cdot 7\text{H}_2\text{O}$, the tantalum analog was first reported to have an effective moment of 1.39 B.M. (443), whereas later work (593) showed that this substance had a zero susceptibility, implying a temperature-independent paramagnetism equal to the diamagnetic correction. The close similarity in properties of the niobium and tantalum subhalides suggests that, like $\text{Nb}_6\text{Cl}_{14} \cdot 7\text{H}_2\text{O}$, $\text{Ta}_6\text{Cl}_{14} \cdot 7\text{H}_2\text{O}$ has a closed-shell ground state.

Reduction of TaCl_5 with aluminum foil in the appropriate temperature gradient yields the greenish brown material $\text{Ta}_6\text{Cl}_{15}$ (447). X-ray (626) and magnetic susceptibility (626, 665) measurements show the presence of the $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ ion having one free spin. The same species is

produced as a stable ion in solution by the oxidation of $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ by either Fe^{3+} or Cl_2 , and probably by O_2 as well (226, 493). Ferric ion can further oxidize the 3+ ion to 4+ in aqueous solution, from which the diamagnetic salt $\text{Ta}_6\text{Cl}_{16} \cdot 9\text{H}_2\text{O}$ can be recovered (226, 494).

Air oxidation of ethanolic solutions of $\text{Nb}_6\text{Cl}_{14} \cdot 8\text{H}_2\text{O}$ results in the formation of $\text{Nb}_6\text{Cl}_{16} \cdot 3\text{C}_2\text{H}_5\text{OH}$, which was demonstrated to contain the $[\text{Nb}_6\text{Cl}_{12}]^{4+}$ ion by the close similarity of its optical spectrum to that of the $[\text{Nb}_6\text{Cl}_{12}]^{2+}$ ion (681). More will be said of this similarity below. Surprisingly, the anhydrous, green niobium subhalide $\text{Nb}_6\text{Cl}_{16}$ does not contain the M_6X_{12} structural unit, but rather has a layered lattice much like that of CdI_2 with only 3/4 of the metal sites filled (733). The Nb—Nb distance within the metal atom layer is 2.78 Å (638), a distance significantly smaller than that in $\text{Nb}_6\text{Cl}_{14}$. The substance, better written as Nb_3Cl_8 , however, may not be metallic as is Ag_2F with the anti- CdI_2 structure (class III-B), for it is reported (638, 666) that the niobiums are grouped into triplets (class III-A), and that the effective magnetic moment amounts to 1.83 B.M., as expected for an isolated Nb_3Cl_8 molecule containing an odd number of d electrons. Actually, Nb_3Cl_8 is the end member of a homogeneous mixed valence system of considerable breadth, the other end member being NbCl_4 . This presents the interesting possibility that NbCl_3 is really a mixed valence compound, being composed of equal parts of Nb_3Cl_8 and NbCl_4 (638, 648).

The niobium oxychloride $\text{Nb}_3\text{O}_7\text{Cl}$ presents another possibility as a mixed valence system, for when it is prepared in an oxidizing atmosphere it is colorless, as expected for a $4d^0$ system, but when prepared in the absence of O_2 the product presumably contains lower oxides of niobium and is colored blue. Identical color changes have been observed in the preparation of the $4d^0$ systems Nb_2O_5 and NbOCl_3 (624).

The mixed valence niobium and tantalum subbromides present little that is new and interesting. $\text{Nb}_6\text{Br}_{14} \cdot 7\text{H}_2\text{O}$ possesses a temperature-independent paramagnetism, as does the corresponding tantalum compound (593). Just as was found with the chloride of this composition, $\text{Ta}_6\text{Br}_{15}$ has one free spin (628, 629) and the $[\text{Ta}_6\text{Br}_{12}]^{2+}$ ion in aqueous solution can be oxidized with Fe^{3+} or Br_2 to $[\text{Ta}_6\text{Br}_{12}]^{4+}$ (593). An extensive phase study revealed that, in addition to the $\text{Ta}_6\text{Br}_{14}$ (green) and $\text{Ta}_6\text{Br}_{15}$ (black) compounds, an even higher bromide, $\text{Ta}_6\text{Br}_{17}$, can exist (492), but there is no other information on this substance.

$\alpha\text{-Nb}_3\text{Br}_8$ is isostructural with the chloride, and our comment about “ NbCl_3 ” would apply also to “ NbBr_3 ” (56, 625). Simon and von Schnering (666) report the preparation and properties of a second form of Nb_3Br_8 , the β -form. The black crystals of this substance have a temperature-dependent effective magnetic moment (0.5 B.M. at 90°K, 1.95 B.M.

at 573°K), and a structure composed of Nb_3 triangular units having an irregular octahedron of halide ions about each niobium ion. As with $\text{Nb}_6\text{Br}_{14}$, there appears to be appreciable metal-metal bonding in the $\beta\text{-Nb}_3\text{Br}_8$ system, judging from the 2.88-Å separation between niobium atoms. The system is class III-A.

The preparation and properties of the mixed valence fluoride Nb_6F_{15} have recently been described (629). In this material, the $[\text{Nb}_6\text{F}_{12}]^{3+}$ groups have full octahedral symmetry, with all six of the niobiums of an octahedron being bridged to niobium atoms of other octahedra by fluoride ions. Within an octahedron, the cis Nb—Nb distance is 2.80 Å, and Nb—F equals 2.05 Å. The magnetic properties of Nb_6F_{15} have not yet been reported, but one expects one free spin per Nb_6 , just as has been found for $\text{Ta}_6\text{Cl}_{15}$, $\text{Ta}_6\text{Br}_{15}$, and $[(\text{C}_2\text{H}_5)_4\text{N}]_3\text{Nb}_6\text{Cl}_{18}$. The diamagnetism of the niobium and tantalum tetrahalides $\text{M}^{\text{IV}}\text{X}_4$ has recently been explained as due to a spin-pairing dimer formation, and not to the mixed valence $\text{M}(\text{III}), \text{M}(\text{V})$ configuration suggested earlier (600). However, since NbF_4 does not have the dimer structure and yet has a temperature-independent paramagnetism (299, 629), the mixed valence formulation is a possibility here. As described above for the chlorides, a niobium oxyfluoride $\text{Nb}(\text{O}, \text{F})_3$ also exists as a blue material (629).

The lower iodide of niobium, Nb_6I_{11} , presents an interesting variation of the subhalide structural unit (46, 48, 631, 665). In this material the six niobiums are approximately at the face centers of a cube, with the bridging halogen not at the centers of the cube edges, but instead at the cube corners, each iodide thereby bridging three niobium ions. This ideal structure is in fact distorted in the crystal to symmetry C_i , with an average Nb—Nb distance of 2.85 Å. This is surprisingly close to the Nb—Nb distances found in the $[\text{Nb}_6\text{X}_{12}]^{2+}$ ions. A more regular geometry prevails for the lower tantalum iodide. Ta_6I_{14} , the only lower iodide of tantalum (447, 492, 628), is structurally isotypic with $\text{Nb}_6\text{Cl}_{14}$ and shows a weak temperature-independent paramagnetism (48, 665). The black solid gives a green aqueous solution containing the $[\text{Ta}_6\text{I}_{12}]^{2+}$ ion, which, however, is not as stable as those of the other halides in this series. Whereas it was first thought that Nb_3I_8 might be composed of diamagnetic $[\text{Nb}_6\text{I}_{12}]^{4+}$ units, it is now known to have a trinuclear class III-A structure identical to that of $\beta\text{-Nb}_3\text{Br}_8$ and, like this substance, has a temperature-dependent effective magnetic moment (666).

The $[\text{M}_6\text{X}_{12}]^{2+}$ unit contains 16 metal d electrons in molecular orbitals formed from combinations of the metal atom d orbitals and the halide ligand p orbitals. If all the metal ions are in equivalent sites so as to form a class III-A system, then each metal atom has a formal valence of $2\frac{1}{3}+$. If, however, the $[\text{M}_6\text{X}_{12}]^{2+}$ ion is distorted so as to distinguish

two of the metal atoms from the other four, then these two may be assigned an integral valence of 3+ and the other four an integral valence of 2+, making the system class II. A trapping of the valence could almost be guaranteed in the mixed ion $[\text{Ta}_4\text{Nb}_2\text{X}_{12}]^{2+}$ if it could be made. Schäfer and Spreckelmeyer (632) made a start in this direction, having prepared a substance of the overall composition $\text{Ta}_{3.6}\text{Nb}_{2.4}\text{Br}_{14} \cdot 8\text{H}_2\text{O}$ with an optical spectrum different from that of a simple mixture of $\text{Nb}_6\text{Br}_{14} \cdot 8\text{H}_2\text{O}$ and $\text{Ta}_6\text{Br}_{14} \cdot 8\text{H}_2\text{O}$. To date, the determination of the mixed valence class and valence configurations of the $[\text{M}_6\text{X}_{12}]^{2+}$ polynuclear ions has been attempted using a simplified ligand-field theory analysis of optical spectra and magnetic susceptibility data together with X-ray structure analysis.

Cotton and Haas (159) first derived the molecular orbital ordering appropriate to the $[\text{M}_6\text{X}_{12}]^{2+}$ unit on the assumption that this ordering is determined, with one exception, solely by the various metal-metal interactions. From overlap considerations, they decided that the level ordering depended upon the internuclear separation and the effective nuclear charge, but that, for reasonable values of these parameters, a ground state³ with occupation

$$dxzdyz(t_{1u})^6 dz^2(a_{1g})^2 dxzdyz(t_{2g})^6 dxy(a_{2u})^2$$

was predicted, which is diamagnetic, as observed for the $[\text{M}_6\text{X}_{12}]^{2+}$ ions. The Cotton-Haas orbital diagram (Fig. 24) is derived under the assumption that the orbitals arising from $dx^2 - y^2$ are too high to be of any consequence, due to σ -bonding with the ligands. Kettle (414) concurs with Cotton and Haas as to the symmetries of the occupied levels. A second calculation on this system, which considered not only metal-metal but metal-ligand interactions as well (593), showed that the relative positions of the Cotton-Haas orbitals can depend not only upon the metal-metal interaction, but also upon the metal-ligand interaction. Thus, for example, for the MO's composed of metal atom dxy orbitals only, the level ordering is $a_{2u} < t_{2g} < e_u$, whereas, with the introduction of ligand orbitals into the calculation, an inverted ordering $e_u < t_{2g} < a_{2u}$ can be obtained. The MO's resulting from the "metal d plus ligand orbitals" calculations are shown in Fig. 25, for comparison with the original Cotton-Haas scheme. This second scheme, as proposed

³ Each molecular orbital of the ground state is composed of a linear combination of only certain of the d orbitals of the metal atoms. Thus, for example, taking z as the locally out-of-plane direction, a linear combination of dxz and dyz metal orbitals can be found which transforms like t_{1u} in the octahedral group, and, if it contains six electrons, is written as $dxzdyz(t_{1u})^6$. Similarly, in the ground state the a_{1g} combination of dz^2 orbitals has two electrons in it, etc.

originally, was constructed so as to give a reasonable explanation of the electronic spectra of the $[\text{M}_6\text{X}_{12}]^{2+}$ ions. In order to do this, it was found that an apparently low-lying $d_{z^2}(a_{1g})$ orbital had to be left unoccupied in the ground state. This undesirable feature arises from the assumption

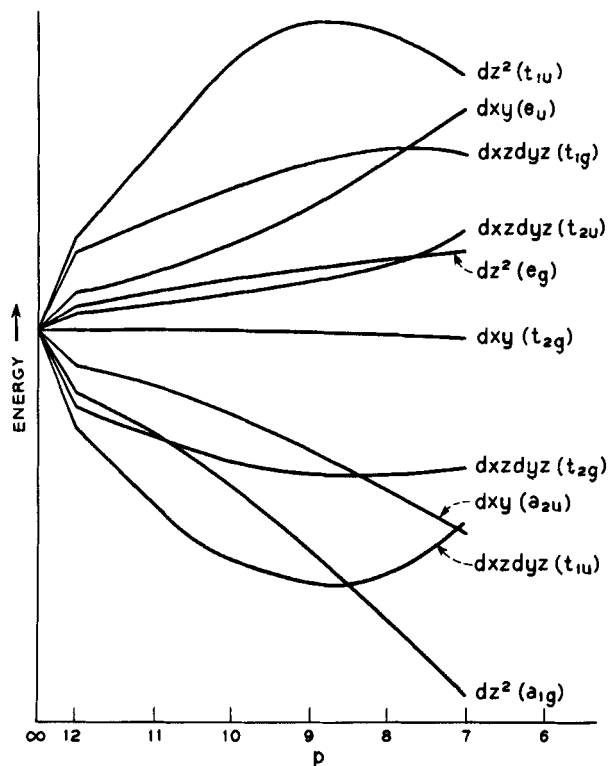


FIG. 24. The molecular orbital scheme for the $[\text{M}_6\text{X}_{12}]^{2+}$ ion as derived by Cotton and Haas (159). p is a variable equal to the product of the Slater orbital exponent of the metal d orbitals and the metal-metal distance.

that each metal atom is in the plane of the four halide ligands nearest it (local symmetry C_{4h}), when in fact the metal atoms are known to be displaced inward toward each other. As a result, the local symmetry is lowered to C_{4v} , and two of the three p orbitals on each ligand interact with the d_{z^2} manifold, raising it by an undetermined amount. Thus the closed-shell ground state configuration

$$dxzdyz(t_{1u})^6 dxzdyz(t_{2g})^6 dxy(e_u)^4$$

is attained without occupying $d_{z^2}(a_{1g})$.

On oxidation to $[M_6X_{12}]^{3+}$, both Figs. 24 and 25 predict an ion having one free spin, as observed experimentally. The real test between these two diagrams rests on the prediction for the ion $[M_6X_{12}]^{4+}$. According to

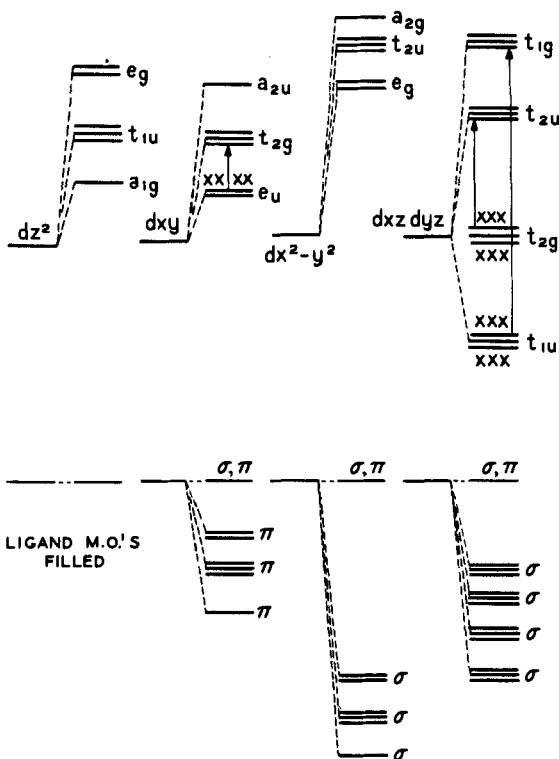


FIG. 25. The molecular orbital scheme for the $[M_6X_{12}]^{2+}$ ion according to Robin and Kuebler (593), as derived from the electronic spectrum.

Fig. 24, for p greater than 8.5, the $[M_6X_{12}]^{4+}$ ion has the closed-shell ground state configuration

$$dxzdyz(t_{1u})^6 dz^2(a_{1g})^2 dxzdyz(t_{2g})^6$$

whereas Fig. 25 predicts a triplet ground state

$$dxzdyz(t_{1u})^6 dxzdyz(t_{2g})^6 dxy(e_u)^2$$

provided that the $4+$ ion is not distorted so that the dxy (e_u) level is split and the electrons paired. Since the $[M_6X_{12}]^{4+}$ ions are claimed to be diamagnetic (471, 494), it would seem that the Cotton-Haas orbital ordering offers more hope for explaining the magnetic properties of these ions, provided that they are not badly distorted.

Electronic spectra of the niobium and tantalum subhalides have been recorded in the $10,000$ – $50,000$ cm^{-1} region by a number of invest-

igators (10, 447, 471, 593), but with only one attempt at interpretation (593). The electronic spectra of polynuclear complexes are complicated by the fact that the metal-metal transitions can be as strong as the

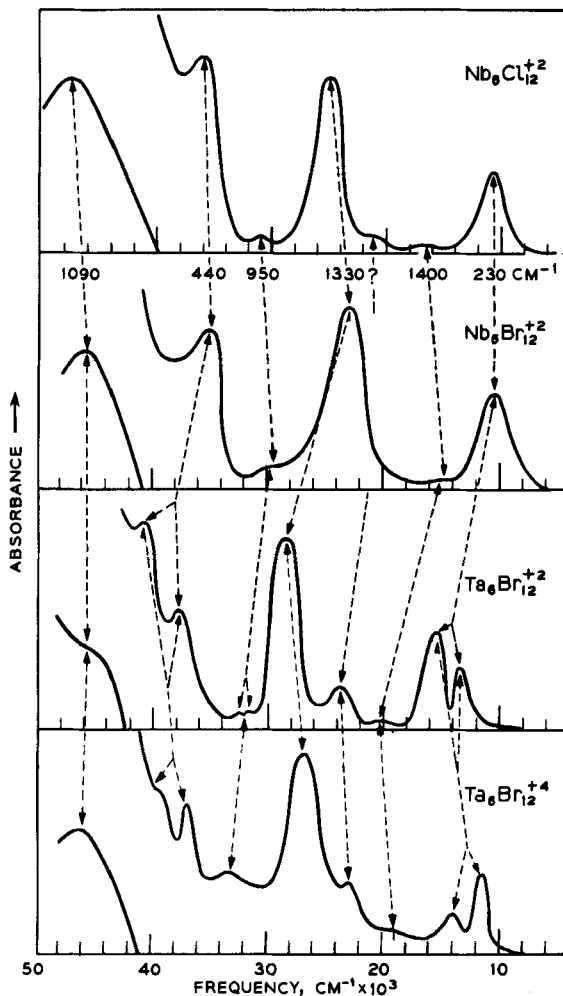


FIG. 26. Correlation of the electronic bands of oxidized and reduced $[M_6X_{12}]^{n+}$ ions in ethanol at -100°C (593).

ligand-metal charge transfer bands, so that a simple intensity argument cannot be used for their identification. In the $[M_6X_{12}]^{2+}$ series, the distinction, however, can be made by changing the ligand from, say, Cl to Br, so that the ligand-metal bands will identify themselves by a larger shift than the metal-metal bands. Figure 26 shows the spectra

of $[\text{Nb}_6\text{Cl}_{12}]^{2+}$ and $[\text{Nb}_6\text{Br}_{12}]^{2+}$ ions in alcohol at -100°C , from which it can be seen that the bands at $11,000\text{ cm}^{-1}$ and $36,000\text{ cm}^{-1}$ are allowed metal-metal transitions ($^1A_{1g} \rightarrow ^1T_{1u}$), all others being ligand \rightarrow metal charge transfer bands, on the basis of their much larger shift. The extinction coefficients of the various bands in aqueous solutions are given by Allen and Sheldon (10).

On comparing the spectra of the $[\text{Nb}_6\text{X}_{12}]^{2+}$ ions with the corresponding $[\text{Ta}_6\text{X}_{12}]^{2+}$ ions (Fig. 26), it is seen that the two metal-metal bands in the tantalum complexes have split into two components, each with intensity ratio 1:2. This splitting was interpreted as that expected of the triply degenerate $^1T_{1u}$ state for $[\text{Ta}_6\text{X}_{12}]^{2+}$ ions having an extended tetragonal distortion in solution. Spectra of the oxidized ions $[\text{Ta}_6\text{X}_{14}]^{4+}$ are very much like those of the reduced species, except that the intensity ratio of the split components is reversed, being 2:1, signaling a tetragonal distortion of the opposite sense (Fig. 26). The spectral similarities of the 2+ and 4+ ions in both the niobium and tantalum subhalides have been explained as the consequence of removing electrons from previously filled, triply degenerate levels on going from 2+ to 4+.

On the basis of this simple interpretation of the optical spectra, Robin and Kuebler concluded that, in ethanol solution, the $[\text{Nb}_6\text{X}_{12}]^{2+}$ ions are class III-A systems with all metal ions of formal charge $2\frac{1}{3}+$, whereas the $[\text{Ta}_6\text{X}_{12}]^{2+}$, $4+$ ions tend to trap integral valences through a tetragonal distortion. One might hope for some verification of these ideas through crystal structure analysis of a number of systems containing the M_6X_{12} ions. Figure 27 shows that there is no obvious regularity in the geometries of these species, except that, wherever a halogen coordinates to an M from outside the M_6X_{12} unit, the result is a displacement of that M atom outward from the symmetrical position. As concluded from the spectral study, it also appears that the distortions are larger in the tantalum complexes than in the niobium ones. The fact that the $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ and $[\text{Ta}_6\text{I}_{12}]^{2+}$ octahedra have tetragonal distortions of the opposite sense demonstrates that these distortions are in large part due to crystal forces and not to any particular preferred electronic configuration of the ions.

An amazingly large number of stable compounds have been found in the niobium-oxygen system within the range $\text{NbO}_{2.50}$ – $\text{NbO}_{2.33}$. As compiled most recently by Gruehn and Schäfer (319, 320) and by Gruehn *et al.* (321), the following mixed valence oxides of niobium have been identified:

$\text{NbO}_{2.489}$ – $\text{NbO}_{2.500}$, $\text{NbO}_{2.482}$, $\text{NbO}_{2.480}$ ($\text{Nb}_{25}\text{O}_{62}$), $\text{NbO}_{2.467}$ – $\text{NbO}_{2.480}$, $\text{NbO}_{2.467}$, $\text{NbO}_{2.474}$ ($\text{Nb}_{19}\text{O}_{47}$?), $\text{NbO}_{2.466}$ – $\text{NbO}_{2.460}$, $\text{NbO}_{2.454}$ ($\text{Nb}_{22}\text{O}_{54}$), $\text{NbO}_{2.417}$ ($\text{Nb}_{12}\text{O}_{29}$), $\text{NbO}_{2.333}$ (Nb_9O_{21})

At present, the structures of only a few of these substances have been solved, yet certain regularities are already apparent.

On the basis of a determination of the crystal structure of the high temperature modification of the single valence material Nb_2O_5 ,

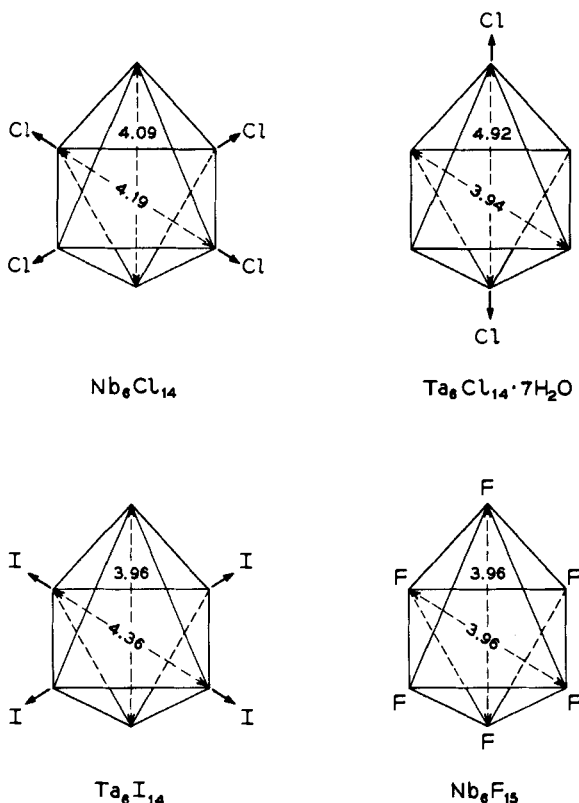


FIG. 27. Distortions of various M_6X_{12} octahedra induced apparently by the placement of halide ions on the fourfold axes of certain M ions, thereby lengthening the trans M-M distance in that direction.

Gatehouse and Wadsley (271) proposed that it is but a member of the general series $\text{Nb}_{3n+1}\text{O}_{8n-2}$, having $n = 9$. This structure consists of ReO_3 -type slabs of edge-sharing octahedra joined at the slab boundaries so as to form tetrahedral holes which are partly, but systematically, occupied by niobium atoms. Of the 28 niobium atoms in the Nb_2O_5 ($\text{Nb}_{28}\text{O}_{70}$) unit cell, 27 are in octahedral sites and one is in a tetrahedral site. It is proposed by them that the $n = 7$ mixed valence compound,

$\text{Nb}_{22}\text{O}_{54}$ ($\text{NbO}_{2.46}$), consists of smaller ReO_3 -type slabs, joined so that 21 of the niobiums are in octahedral sites and one is in a tetrahedral site, and that the $n = 5$ mixed valence compound, $\text{Nb}_{16}\text{O}_{38}$ ($\text{NbO}_{2.375}$), should it exist, would have one tetrahedrally and 15 octahedrally coordinated niobium atoms per unit cell. Although the two compounds $\text{NbO}_{2.48}$ ($\text{Nb}_{25}\text{O}_{62}$) and $\text{NbO}_{2.42}$ ($\text{Nb}_{19}\text{O}_{46}$) fit the formula for $n = 8$ and 6, respectively, Gatehouse and Wadsley point out that the members with even n will have a different crystal structure. Since the proposed $\text{Nb}_{3n+1}\text{O}_{8n-2}$ crystal structures would appear to trap valences readily, one is tempted immediately to try and assign valences to the various sites. The formula $\text{Nb}_{21}^{\text{V}}\text{Nb}^{\text{III}}\text{O}_{54}$ fits nicely for $\text{Nb}_{22}\text{O}_{54}$, for it is postulated to have two sites in 21 : 1 ratio. However, $\text{Nb}_{16}\text{O}_{38}$ by this reasoning would have to be written as $\text{Nb}_{15}^{\text{V}}\text{Nb}^{\text{I}}\text{O}_{38}$.

A straightforward accounting of electrons in $\text{Nb}_{25}\text{O}_{62}$ shows that it must be written formally as $\text{Nb}^{\text{IV}}\text{Nb}_{24}^{\text{V}}\text{O}_{62}$. Although the structure of this mixed valence oxide has not been determined in detail, it is known to be isostructural with the titanoniobate $\text{Ti}^{\text{IV}}\text{Nb}_{24}^{\text{V}}\text{O}_{62}$ (538). Moreover, although there are 24 octahedral sites to every tetrahedral one in the titanoniobate, the analysis indicates that the structure is partly inverted, in that all the sites appear to be occupied by either niobium or titanium in a random manner. If this is also true for $\text{Nb}_{25}\text{O}_{62}$, then it is a class II or class III system, rather than class I as intimated by the one-to-one correspondence of the numbers of the two types of site available and the numbers of niobium atoms of valency 5+ and 4+. Accepting a class II electronic structure for $\text{Nb}_{25}\text{O}_{62}$, it is reasonable then to postulate that its black color is in large part due to an $\text{Nb}(\text{IV})$ ($4d^1$), $\text{Nb}(\text{V})$ ($4d^0$) mixed valence class II transition, whereas $\text{TiNb}_{24}\text{O}_{62}$ is colorless due to the substitution of $\text{Nb}(\text{IV})$ ($4d^1$) by $\text{Ti}(\text{IV})$ ($3d^0$) and the consequent loss of the optical electrons.

Norin (539) has found monoclinic $\text{Nb}_{12}\text{O}_{29}$ to be an example of a Magneli phase containing corner-sharing blocks of NbO_6 octahedra, as in the ReO_3 -type structure, with edgesharing between blocks. This finding raises the possibility that $\text{Nb}_{12}\text{O}_{29}$ is but one member of a family of mixed valence niobium oxide Magneli phases. The titanoniobate $\text{Ti}_2^{\text{IV}}\text{Nb}_{10}^{\text{V}}\text{O}_{29}$ is isostructural with $\text{Nb}_{12}\text{O}_{29}$ (538), and, as with the $\text{Nb}_{25}\text{O}_{62}$, $\text{TiNb}_{24}\text{O}_{62}$ pair mentioned above, $\text{Nb}_{12}\text{O}_{29}$ is black but $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ is colorless.

Similarly, Nb_9O_{21} , recognizable as $\text{Nb}_3^{\text{IV}}\text{Nb}_6^{\text{V}}\text{O}_{21}$, is isostructural with $\text{Ti}_3^{\text{IV}}\text{Nb}_6^{\text{V}}\text{O}_{21}$ (740), a substance in which the titanium and niobium sites are both distorted octahedral. Thus, this compound is a class II system, bordering on class III. There are, however, no short metal-metal distances here so the substance may not show metallic conductivity. Although the

oxide $\text{Nb}_{22}\text{O}_{54}$ (537) can be written as $\text{Nb}_2^{\text{IV}}\text{Nb}_{20}^{\text{V}}\text{O}_{54}$, there is no evidence that its valences are trapped. Structural work has yet to be done on the other oxides mentioned above.

An electron diffraction study of oxidized thin films of niobium reveals the existence of Nb_3O_5 , a cubic compound thought to contain the niobium ions in distorted octahedral coordination (424).

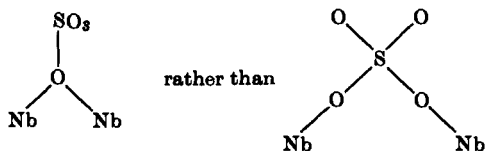
In the tantalum-oxygen system, Schönberg (642) reports a black phase (ϵ) of composition intermediate between TaO_2 and Ta_2O_5 having a complicated crystal structure. The only other compounds in this system of possible mixed valence interest are the metallic lower oxides TaO_x , having x much smaller than 1. Niebuhr has recently presented a critical evaluation of the properties of these substances (532), as well as of the oxides of niobium (533).

The importance of recognizing that such seemingly nonstoichiometric substances as the niobium oxides are, like the titanium, vanadium, molybdenum, and tungsten oxides, stoichiometric mixed valence compounds in disguise, is amply demonstrated by the studies of the electrical conductivity of "nonstoichiometric $\alpha\text{-Nb}_2\text{O}_5$ " [(377) and references cited therein]. Extensive work on materials ranging in composition from $\text{NbO}_{2.4996}$ to $\text{NbO}_{2.4284}$ shows that their resistivity is 0.1–0.01 ohm cm at 1000°C with an average carrier mobility of 0.22 $\text{cm}^2\text{V}^{-1}\text{sec}^{-1}$. These data have been interpreted in detail, using a model which presumes that the materials contain electron pairs trapped in oxygen ion vacancies, and that the electrical conductivity arises from the thermal excitation of electrons from these traps into a narrow 4d conduction band. We can see now that Nb(IV), Nb(V) compounds were in fact involved here, and that the conductivity might be more properly explained as arising from the thermal ionization of Nb(IV) ions.

Krylov *et al.* (445) report the mixed metal oxide, NbCuO_3 , in which both of the valence isomers can exist as stable phases. Thus, the sintering of Cu_2O with Nb_2O_5 yields diamagnetic $\text{Cu}^{\text{I}}\text{Nb}^{\text{V}}\text{O}_3$, whereas the sintering of CuO with NbO_2 yields paramagnetic $\text{Cu}^{\text{II}}\text{Nb}^{\text{IV}}\text{O}_3$ ($\mu_{\text{eff}} = 1.10$ B.M.). Powder patterns confirm the individuality of these valence isomers as well as those in the corresponding TaCuO_3 system.

The very large number of stable halide complexes built upon the Nb_6 octahedral framework suggests the possibility of formation of Nb_6 polynuclear complexes with other than halide ligands. The red compound $\text{K}_8\text{Nb}_6\text{O}_3(\text{SO}_4)_{12} \cdot 21\text{H}_2\text{O}$ (294, 417, 444) and the corresponding ammonium salt $(\text{NH}_4)_8\text{Nb}_6\text{O}_3(\text{SO}_4)_{12} \cdot 12\text{H}_2\text{O}$ (297, 508) would seem to be examples of just such complexes. Although no structural work has been done on these systems, it seems reasonable to predict that the niobium sulfates contain the Nb_6 octahedron with bridging sulfate

groups, and quite possibly OH^- ions situated on the fourfold axes of the niobium ions. In order to maintain the all-important Nb—Nb direct metal-metal bonding, it is necessary to postulate bridges of the form



The niobium sulfates are soluble in sulfuric acid and in this solvent the red ions migrate to the anode in an electric field, thus demonstrating their negative charge. If the colored ions are indeed M_6X_{12} species, the overall negative charge can result only if X is SO_4^{2-} , and not if X is OH^- .

Krylov and Kalugina (444) have measured the magnetic susceptibility of the crystalline salt $\text{K}_8\text{Nb}_6\text{O}_3(\text{SO}_4)_{12} \cdot 21\text{H}_2\text{O}$ and found an effective moment of 2.0 B.M. per molecule. However, this value is uncorrected for temperature-independent paramagnetism, a factor which seems to be large in the niobium polynuclear complexes (471). Application of a temperature-independent paramagnetism correction, amounting to 600×10^6 cgs, reduces Krylov and Kalugina's effective moment to 1 B.M., a value sufficiently low that it raises doubt as to whether the substance is really paramagnetic or is simply diamagnetic but impure. The latter seems possible for it is known that the substance in question can react further to produce blue substances thought to contain Nb(III) (417).

The hypothetical $[\text{Nb}_6(\text{SO}_4)_{12}]^{2-}$ unit contains eight niobium 4d electrons in metal-metal bonds. According to the scheme of Robin and Kuebler (593) (Fig. 25), the metal-metal electronic configuration for such a system would be

$$dxzdyz(t_{2g})^2 dxzdyz(t_{1u})^6$$

giving a triplet ground state. On the other hand, the Cotton and Haas (159) ground state would be

$$dz^2(a_{1g})^2 dxzdyz(t_{1u})^6$$

which is a spin singlet. Should an X-ray crystallographic study show the presence of *symmetrical* Nb_6X_{12} complexes in the niobium sulfates, an accurate determination of the magnetic susceptibility then would be of great value in deciding between the Robin-Kuebler and Cotton-Haas orbital schemes, although as it stands the Cotton-Haas scheme seems to be the better one.

K. MOLYBDENUM AND TUNGSTEN

With very few exceptions, the mixed valence compounds of molybdenum and tungsten have oxide ion as ligand. The existence of well-defined phases with formulas intermediate between MO_2 and MO_3 has been recognized for many years, but it is primarily as a result of the extensive crystallographic investigations of Hägg, Magneli, Kihlberg, and their collaborators that the structural principles governing their

TABLE IV
MIXED VALENCE MOLYBDENUM OXIDES

MoO_x	Formula	Phase	Structure	Resistivity (ohm cm, 300°K)
3.000	MoO_3	α	MoO_3	$> 10^7$ (419)
2.889	$\text{Mo}_{18}\text{O}_{52}$	ξ	MoO_3	250 (419), 932 (279)
2.889	Mo_9O_{26}	β'	ReO_3	3.7 (419), 3.95 (279)
2.875	Mo_8O_{23}	β	ReO_3	1.2 (419)
2.800	Mo_5O_{14}	θ	Mixed polygonal	< 0.05 (419)
2.765	$\text{Mo}_{17}\text{O}_{47}$	χ	Mixed polygonal	0.2 (419), 0.59 (279)
2.750	Mo_4O_{11}	η	ReO_3	0.25 (419), 1.50 (279)
2.750	Mo_4O_{11}	γ	ReO_3	
2.000	MoO_2	δ	Distorted rutile	

formation are now well established. The most important results of these labors have been several times reviewed (328, 422, 474), and we shall therefore include only a brief outline here.

The seven mixed valence compounds within the composition range $\text{MoO}_{2.75}$ – MoO_3 which have been identified from phase analyses based on X-ray powder (279, 419) and single crystal measurements (422), as well as differential thermal analysis (598), are listed in Table IV. Within this composition range, three basic structure types may be distinguished: ReO_3 , MoO_3 , and what Kihlberg (422) has called the “mixed-polygonal” type. In the “homologous” (476) series with the general formula $\text{M}_n\text{O}_{3n-1}$, based on the ReO_3 lattice, examples having $n = 8$ and 9 have been prepared which contain only molybdenum, but by incorporating increasing concentrations of tungsten it is possible to obtain further members with $n = 10, 11, 12$, and 14. The ReO_3 structure, which can be regarded as built up from MO_6 octahedra linked exclusively at the corners, extends

infinitely along only one axis in the compounds belonging to the M_nO_{3n-1} series, thus forming finite slabs whose width is determined by the value of n . In Fig. 28, the structure of Mo_8O_{23} shows how the slabs are connected through sharing of edges between the octahedra at the slab boundaries. In this way, clusters of four octahedra sharing edges occur throughout the structure, as indicated by the heavy lines. The other structures based on ReO_3 are the two forms of Mo_4O_{11} , in which the slabs of connected octahedra are joined by tetrahedra which share corners with the octahedra of two neighboring slabs. No tetrahedra or octahedra share edges in this structure.

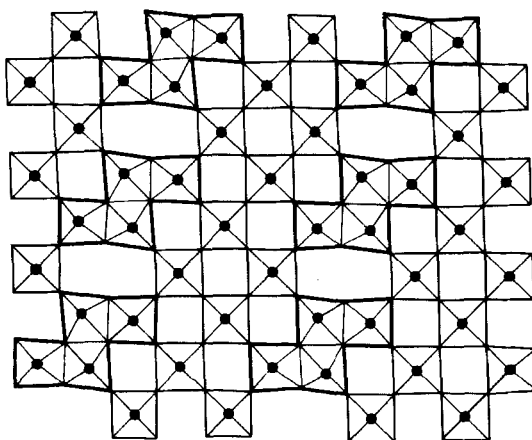


FIG. 28. The crystal structure of Mo_8O_{23} (422). The metal atom clusters are outlined in *bold lines*, while the metal atoms themselves are represented by the *filled circles*, and the oxygen atoms are found above and below the metal atoms and at the apices of the squares.

In the structures based on MoO_3 , e.g., $Mo_{18}O_{52}$, slabs of the basic lattice are once again connected by edgesharing, but, in addition, some of the metal atoms occur in tetrahedral sites. The lattices called "mixed polygonal" are distinguished by a complicated connection of coordination polyhedra in two dimensions, in which not only distorted octahedra but pentagonal bipyramids occur. This class includes mixed valence compounds such as Mo_5O_{14} and $W_{18}O_{49}$ (473), as well as single valence mixed oxides such as $MoW_{11}O_{36}$ and $MoW_{14}O_{45}$ (304). It is also interesting to note the similarity with the tunnel lattices occurring among the tetragonal and hexagonal tungsten bronzes. In the mixed polygonal oxides, the equatorial edges of the pentagonal bipyramids are shared with octahedra so that there exist pronounced metal atom clusters

(Fig. 29), which are still further condensed in $\text{Mo}_{17}\text{O}_{47}$ and $\text{W}_{18}\text{O}_{49}$ by edgesharing between pairs of octahedra attached to neighboring pentagonal clusters. Considerable variations in metal-oxygen and metal-metal distances are needed to accommodate these structural complexities, although it should be noted that they are not necessarily the result of mixed valence interactions, since MoO_2 and WO_2 are themselves distorted from rutile lattices in such a way that the metal atoms appear to form pairs (472).

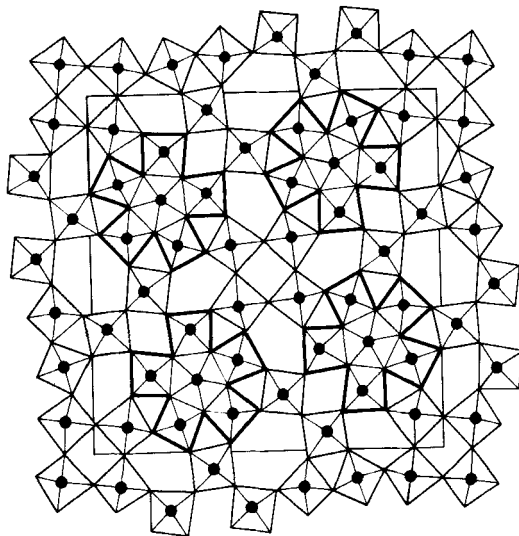


FIG. 29. The crystal structure of Mo_5O_{14} (422). The *filled circles* represent the metal atoms, and oxygen atoms are found above and below the metal atom and at the apices of the squares. The "mixed polygonal" metal clusters are indicated by the *bold lines*.

In contrast to the effort devoted to structure determinations in this series of compounds, very little has been reported which might enable one to rationalize their electronic structures with their complicated stereochemistries and stoichiometries. In closing his most recent review of the structural chemistry of the molybdenum oxides (422), Kihlberg remarks that definite conclusions about the variations in the distortion of the Mo—O coordination with valence state cannot be drawn until reliable measurements of basic physical properties, such as magnetism, have been made. Some of the distortions from regular octahedral coordination may perhaps be accounted for by "rattling" of the small cations, as originally proposed by Orgel (545). Ionic radii of Mo(IV) and Mo(VI) are in the range where this might be expected to occur.

Attempts have been made (422) to fit the observed bond lengths d_n in many of the compounds to a logarithmic relationship with bond number, n , of the kind proposed by Pauling (564)

$$d_n - d_1 = 2k \log n$$

using values for d_1 and k which fit the observed lengths in MoO_3 , and the assumption that $\Sigma n = 2$ for each oxygen atom. The sums Σn_{Mo} for the two modifications of Mo_4O_{11} were taken to suggest that there is a gradual increase in the valence state of the metal atoms from the middle of the basic ReO_3 slab toward the outside, in accord with a previous suggestion (477) that decreasing valency favors the occurrence of higher coordination numbers. However, the tenuous theoretical basis of Pauling's equation makes it difficult to use the "bond number" criterion to decide whether the valences are partly or wholly trapped. From the low resistivities of all except one of the mixed valence oxides (279, 419), one is tempted to conclude that no definite lattice sites or coordination numbers are to be allocated to specific valence states in these compounds, i.e., the compounds are very close to class III-B. Thus in Mo_4O_{11} , for example, 3/4 of the molybdenums are octahedrally coordinated and 1/4 are tetrahedrally coordinated and, furthermore, the formula is compatible with the existence of one Mo(IV) for every three Mo(VI), so at first glance the compound might appear to be a class I mixed valence system. On the other hand, the room temperature resistivity of this compound is less than 1 ohm cm (279, 419) and the bond length arguments of Kihlborg (422) suggest that the tetrahedral sites might be preferentially occupied by Mo(VI). The valence distribution would then be rather like that of an inverse as compared with a normal spinel. Nevertheless, it might prove possible to rationalize the occurrence of blocks of ReO_3 structure, together with regions of metal atom clustering in oxides such as Mo_8O_{23} or Mo_5O_{14} , by deriving bonding schemes similar to those suggested by Cotton (160) for the trinuclear single valence cluster in $\text{Zn}_2\text{Mo}_3\text{O}_8$. If we start from the assumption that the octahedra joined only through their apices contain metal ions trapped as hexavalent, and then apportion the extra electrons corresponding to the Mo(IV) or Mo(V) to the region of the clusters, we find that two d electrons are to be distributed within each cluster of four edgesharing octahedra in the $\text{M}_n\text{O}_{3n-1}$ series. Similarly, four d electrons would have to be assigned to each cluster of six molybdenums in the "mixed polygonal" series. Overlap between d orbitals on adjacent metal atoms in the former case is expected to be greatest for the dxy orbitals, which are nonbonding between metal and oxygen, but which could form σ bonds within the metal cluster. The orbital combination with the phases

shown in Fig. 30 is strongly σ -bonding and nondegenerate, and would therefore accommodate the two "extra" electrons. Unfortunately, the metal-metal distances within the clusters are not notably shorter than that expected for two normally bonded octahedra sharing edges, and there is no evidence that spin pairing of the kind postulated here actually occurs.

All the mixed valence molybdenum oxides are described as blue or blue-violet (422), but no spectra have been reported and care is needed in interpreting their colors as MoO_2 is itself reddish brown. Finally, there

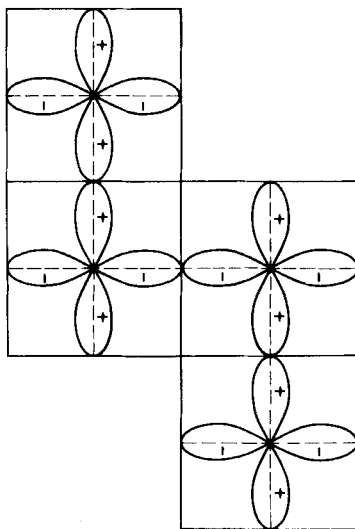


FIG. 30. A possible mode of dxy bonding within the metal atom clusters of Mo_8O_{23} .

is not even conclusive evidence that these systems involve the 4+ and 6+ rather than 5+ and 6+ oxidation states. Once again, unfortunately, our conclusion must be that a great deal more physical evidence will be needed before definite conclusions can be drawn about the electronic structures of these interesting compounds. Magnetic and spectroscopic measurements will be the most profitable lines of attack.

A much more highly reduced mixed valence oxide, Mo_3O , was reported to form when mixtures of Mo and MoO_2 were heated (643), but the preparation could not be repeated (420).

When polymolybdate(VI) and polytungstate(VI) anions are reduced in aqueous solution, the dark blue colors of the products suggest that their electronic structures may be related to those of the mixed valence

molybdenum and tungsten oxides. The photochemical reduction of polymolybdates and tungstates has been studied in connection with photographic processes (132, 789). Molybdenum blue was prepared as long ago as 1805 (110) and since then very many investigations have been reported (289), but little progress could be made in sorting out the variety of products until the structures of the parent iso- and hetero-polyanions had been determined. It was Keggin (408) who first showed that anions with the general formula $[A^{n+} X_{12}O_{40}]^{(8-n)-}$, where A may be a transition or main group element and X is Mo(VI) or W(VI), consisted of compact groups of XO_6 octahedra sharing edges and surrounding the central ion A with a tetrahedron of oxygen atoms. Further members of the series are described and illustrated by Wells (756).

Many of the attempts to characterize solid molybdenum blue compounds have been frustrated by the colloidal nature of the reduction products and the difficulty of isolating them with reproducible amounts of water. Thus Sacconi and Cini (613) claimed to have prepared a continuous series of amorphous blues with Mo(VI):Mo(V) ratios between 3.4 and 6, and Glemser and Lutz (280) showed that not only blue anhydrous oxides, but crystalline hydrates as well, could be prepared by solid phase reactions. However, only the products $Mo_4O_{10}(OH)_2$ and $Mo_8O_{15}(OH)_{16}$ were characterized by X-ray analysis. Both were insoluble in water and stable to alkali, but a range of water-soluble, amorphous products was also prepared. The final reduction product of MoO_3 with zinc in concentrated HCl is a crystalline olive-green Mo(IV) compound, $Mo_5O_5(OH)_{10}$, which when placed in vacuum loses hydrogen to give a red mixed valence compound $Mo_5O_7(OH)_8$ (284). By reducing $WO_3 \cdot H_2O$ and $WO_3 \cdot 2H_2O$ with zinc and HCl, Glemser *et al.* (285) have also succeeded in preparing a series of blue tungsten oxide hydrates which they related to the molybdenum oxides, using X-ray powder diagrams.

In contrast to the variety of solid molybdenum blues, evidence has accumulated that, in homogeneous aqueous solution, reduced species based on the isopolymolybdate structure exist in very limited numbers. When molybdic acid solutions were reduced electrolytically and extracted with butanol, the ratio Mo(VI):Mo(V) in aqueous solutions of the extract was 2.0 (23), a result in accord with the variation in the optical density at $13,300\text{ cm}^{-1}$ as a function of Mo(VI):Mo(V) ratio (675). At higher pH than is needed to form blue solutions, there is also spectrophotometric evidence for a brown hexamolybdate anion with Mo(VI):Mo(V) = 1, which has an absorption maximum at $22,200\text{ cm}^{-1}$ (547), and another having Mo(VI):Mo(V) = 0.5, in which the absorption maximum has shifted even further to the ultraviolet, to $30,800\text{ cm}^{-1}$ (548).

The reduction of 12-heteropolymolybdates and tungstates in aqueous solution has proved rather easier to study than that of the isopolyacids either in solution or in the solid state. It is now quite clear, as a result of polarographic (309–311, 571, 673, 674) and potentiometric (571, 690, 691) work, that these anions can accept limited numbers of electrons, e.g., up to four, without decomposition, and, in a number of instances, salts of the reduced anions have been isolated (331, 332). The values (571) of the reduction potentials for addition of the first electron to $[\text{PW}_{12}\text{O}_{40}]^{3-}$, $[\text{SiW}_{12}\text{O}_{40}]^{4-}$, $[\text{Fe}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$, and $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ vary with the charges in a way consistent with a model that treats the anion simply as a charged sphere. This suggests that the first electron goes into an orbital whose energy is nearly independent of the central atom. The fact that the spectra of silicomolybdates, to which two and four electrons have been added, remain very similar as to both energy and intensity (676) also suggests that the electrons are entering orbitals that are localized on particular metal atoms. There has been some disagreement about the existence of one- and three- in addition to two- and four-electron reduction products; only the latter have been isolated as solid salts (331, 332), and had been detected by Souchay (673) in his original polarographic work. However, more recently, waves due to the one-electron step have been located by two groups (571, 677). The absorption spectra of various reduced 12-silicomolybdates (676, 677) are shown in Fig. 31.

In one case at least there is clear evidence for the occurrence of Mo(V) in a reduced polymolybdate. By γ -irradiation of polycrystalline ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 6\text{H}_2\text{O}$ (562), paramagnetic centers are formed which, from their ESR spectra, can be identified with NH_3^+ and Mo(V) ions. Irradiation at room temperature gave Mo(V) spectra which were almost isotropic, the major absorption coming from isotopes with $I = 0$, with a smaller contribution from Mo^{95} and Mo^{97} with $I = 5/2$. The most interesting feature, however, is the presence of a further hyperfine interaction between the unpaired electron of the Mo(V) and the $I = 5/2$ isotope of a neighboring Mo(VI). We therefore conclude that this system at least belongs to class II of our classification, and that the first electronic transition will contain an appreciable component of charge transfer. Similar experiments on the crystalline heteropoly-blue salts or their frozen solutions would be extremely interesting. Proton nuclear magnetic resonance spectra of a number of heteropoly-blue acids have recently been measured in the solid state (484), and interpreted as resulting from fast exchange between protons bound to oxygen atoms of the anions and those attached to crystal water molecules. That a nuclear magnetic resonance spectrum can be observed at all in these substances

seems to imply that the anions are diamagnetic. Once again, magnetic measurements would be valuable.

It is not our intention to attempt a review of the very large amount of work carried out on the other class of mixed valence molybdenum and

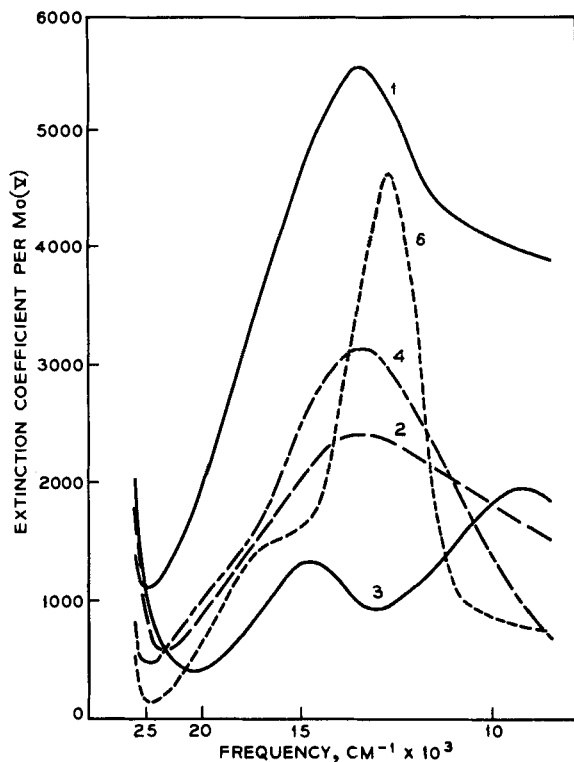


FIG. 31. The electronic spectra of 12-silicomolybdates reduced by 1-6 electrons, as indicated by the labels on the spectral curves (676).

tungsten oxides, the bronzes, since this has recently been done quite thoroughly by others (421, 694). Nevertheless it is worth emphasizing that the volume of physical measurements on these compounds far surpasses that reported for the other reduced group VI-B oxide systems considered here, and that the level of understanding of the electronic properties is correspondingly higher. We will merely record some of the more important conclusions about the crystal and electronic structures of these interesting compounds.

Hägg (326) was the first to show that the bronzes could be given a general formula $A_x\text{WO}_3$, where A was an alkali metal and x varied continuously from about 0.3 to nearly 1.0. At the latter extreme the structure approximates that of a perovskite, while for low values of x the structure goes through various lower symmetry modifications, all based on the lattice of WO_3 . At all A concentrations the tungsten atoms are equivalent and the lattice is a clear example of a class III-B mixed valence system. Ionization of the alkali metal atoms produces electrons which are evenly distributed among all the tungsten atoms. In agreement with this, the sodium bronzes in which x lies between 0.5 and 0.9 behave as metallic conductors between 4° and 800°K (217), with Hall effect coefficients which suggest that each sodium atom contributes one free electron to the conduction band (268). Further evidence that the sodium atoms lose their valence electrons completely into a conduction band that extends only across the tungsten atoms comes from nuclear magnetic resonance experiments (391), which show that the ^{23}Na resonance has an extremely small Knight shift. At high temperatures, the conductivity is nearly proportional to the sodium concentration (217), and the mobility is independent of the electron concentration. The fact that the conductances of lithium, sodium, and potassium tungsten bronzes lie on the same curve when plotted against x (421) also suggests that the alkali metal atoms do not participate directly in the conduction process.

Attempts to prepare molybdenum bronzes by reducing MoO_3 with alkali metal vapors always lead to MoO_2 , and it was only very recently that the first compounds of this type were prepared by electrolyzing fused mixtures of K_2MoO_4 and MoO_3 (789). Two samples have been definitely characterized: $\text{K}_{0.26}\text{MoO}_3$, which formed reddish plates and behaved as a typical semiconductor, and $\text{K}_{0.28}\text{MoO}_3$, a blue compound that conducted like a metal above -100°C . Despite their similarity in composition, the structures of the two compounds were different; the former contained subunits of six and the latter of ten MoO_6 octahedra sharing edges (305, 684). The subunits formed layers by sharing corners and the layers were linked together by the potassium ions. A sodium molybdenum bronze in the same composition range has also been reported (685).

The only other mixed valence molybdenum and tungsten compounds beside the oxides are a small number of halides. When yellow $[\text{W}_6^{\text{VI}}\text{Br}_8]\text{Br}_4$ is reacted with bromine at various temperatures (633, 662), compounds such as W_6Br_{14} , W_6Br_{16} , and W_6Br_{18} can be isolated. These dissolve in ethanol to give intensely red solutions, whose spectra are by no means the superposition of those of W_6Br_{12} and Br_2 . The suggestion is that

$[\text{W}_6\text{Br}_8]^{n+}$ mixed valence ions with structures like $[\text{Nb}_6\text{I}_8]^{3+}$ may be formed. The other mixed valence halide results from reactions between MoF_6 and various main group chlorides, e.g., CCl_4 , and, on the basis of conductance, infrared, and magnetic measurements, has been assigned the formula $[\text{Mo}_3^{\text{IV}}\text{Cl}_9][\text{Mo}^{\text{V}}\text{F}_6]_3$ (543, 686). The trinuclear $[\text{Mo}_3^{\text{IV}}\text{Cl}_9]^{3+}$ cation is assumed to have a similar core structure to that found in $[\text{Re}_3\text{Cl}_{12}]^{3-}$ and $\text{Re}_3\text{Cl}_{12}$. Since the anion is colorless and the cation itself is orange, the reported orange color of the salt suggests that there is no interaction absorption in the visible region and that the salt is a simple class I example.

L. TECHNETIUM AND RHENIUM

No mixed valence compounds of either of these elements appear to have been prepared, with the single exception of $(\text{NH}_4)_3\text{Tc}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ (213). The compound forms shiny black crystals which dissolve in HCl to give a turquoise blue solution having a broad absorption band at $16,300\text{ cm}^{-1}$. Cotton has published a preliminary account of an X-ray diffraction study of this compound (162), which shows the presence of $[\text{Tc}_2\text{Cl}_8]^{3-}$ groups essentially isostructural with $[\text{Re}_2\text{Cl}_8]^{2-}$ (163). Each technetium atom lies at the center of a square of chlorine atoms, and a distorted octahedral coordination is completed by one of the water molecules and the other technetium atom at a distance of 2.13 \AA , a full 0.6 \AA shorter than the $\text{Tc}-\text{Tc}$ distance in the metal. Cotton has described the electronic structure of diamagnetic $[\text{Re}_2\text{Cl}_8]^{2-}$ in terms of a σ bond, two π bonds, and a δ bond between the metal atoms (161), and a comparable description would serve for the technetium analog, which has one more d electron and whose susceptibility is consistent with one unpaired spin per $[\text{Tc}_2\text{Cl}_8]^{3-}$ ion. An ESR measurement on the technetium compound would be exceptionally interesting, as Cotton's bonding scheme for $[\text{Re}_2\text{Cl}_8]^{2-}$ (161) assumes that the relative ordering of the σ , π , and δ orbitals of the metal-metal bond is entirely due to the difference in overlap between the pairs of, respectively, dz^2 , $dxzdyz$, and dxy orbitals on each metal atom. A more detailed consideration of the bonding, taking into account π -bonding between $dxzdyz$ and the chlorine atoms, and σ -bonding between dz^2 and the water molecule, might very easily alter this relative ordering, as we noted in the case of the niobium and tantalum subhalides. It is only fair to say, however, that since the lowest empty orbital, δ^* , is not appreciably antibonding, Cotton's scheme does suggest that the $\sigma^2\pi^4\delta^2$ configuration of $[\text{Re}_2\text{Cl}_8]^{2-}$ might easily add an extra electron, forming a mixed valence system isoelectronic

with $[\text{Tc}_2\text{Cl}_8]^{3-}$. Oxidation and reduction experiments on $[\text{Re}_2\text{Cl}_8]^{2-}$ and the other rhenium halide cluster complexes might lead to other interesting class III-A mixed valence clusters.

M. RUTHENIUM AND OSMIUM

Easily the most famous ruthenium mixed valence compound is the one called "ruthenium red." It is usually prepared by allowing aqueous ruthenium trichloride to react with an excess of ammonia (388), or by exposing solutions of $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ in aqueous ammonia to air (252). Solutions of the compound have an extremely intense rose color; indeed, it has been said that a $2 \times 10^{-7} M$ solution is clearly pink. The color becomes fixed to silk, although not to wool or cotton, and has been used commercially as a dyestuff. Joly (388) formulated ruthenium red as $\text{Ru}_2\text{Cl}_4(\text{OH})_2 \cdot 7\text{NH}_3 \cdot 3\text{H}_2\text{O}$ and Morgan and Burstall (512), who prepared from it compounds which they thought were monomeric, formulated it as $[\text{Ru}(\text{OH})\text{Cl}(\text{NH}_3)_4]\text{Cl} \cdot \text{H}_2\text{O}$. Gleu and Breuel (286) showed that the latter could not be correct, as $[\text{Ru}(\text{OH})\text{Cl}(\text{NH}_3)_4]^+$ would have an effective magnetic moment of almost 2 B.M. and would be virtually colorless, whereas ruthenium red is only very weakly paramagnetic, if at all, and shows a most intense coloration.

In a very careful investigation, Fletcher *et al.* (252) found that ruthenium red contains no complexed chloride ions, and behaves as a trinuclear cation with a ruthenium: ammonia ratio of 3:14. The average oxidation number of the ruthenium, 10/3, then points to a formula



containing two oxo bridges. The molar extinction coefficient per ruthenium atom is 21,000 at the band maximum, $18,800 \text{ cm}^{-1}$, but in acid solution a reversible oxidation leads to the formation of a brown compound, whose spectrum appears to contain the same band shifted to higher energy ($21,700 \text{ cm}^{-1}$, $\epsilon = 14,100$) (Fig. 32). Ruthenium red has an effective magnetic moment of 0.77 B.M. per metal atom if no diamagnetic correction is made, whereas the moment of the brown compound is 1.13 B.M. per metal atom. The difference, $3(1.13 - 0.77) = 1.1 \text{ B.M.}$, is nearly equivalent to one electron per molecule. The spectra of both the red and brown compounds shift slightly to lower energy with increasing pH, suggesting that in basic solution they were being partly deprotonated.

Jorgensen and Orgel (399) explained the stability of the presumed linear ruthenium red framework as the result of π -bonding between the t_{2g} orbitals of the metal atoms and the $2p \pi$ orbitals of the oxygen atoms.

Aside from the σ -bonding in the linear cation, ten π molecular orbitals can be formed which group themselves as five pairs of doubly degenerate levels, with two pairs bonding, two antibonding, and one nonbonding. As there are 16 π electrons in the system, the π manifold in the ground state is filled up to and including the second highest antibonding pair, so that the net effect is a π -bonding stabilization in addition to the σ bonds. In such a linear system, the first transition is allowed, but the

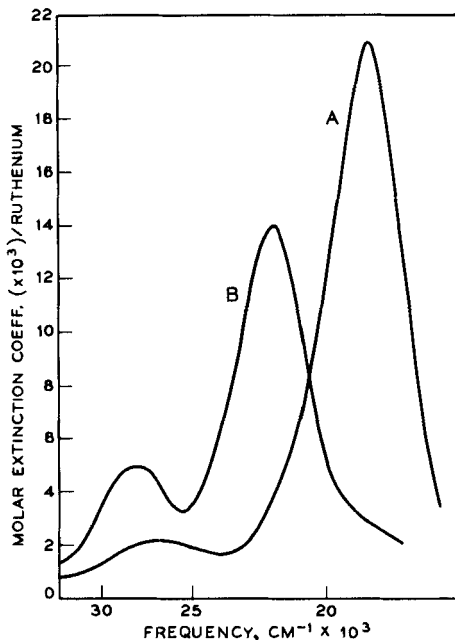
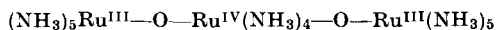


FIG. 32. The electronic spectrum of the ruthenium red cation $[\text{Ru}_3\text{O}_2(\text{NH}_3)_{14}]^{6+}$ in water (A), and the brown cation $[\text{Ru}_3\text{O}_2(\text{NH}_3)_{14}]^{7+}$ in 0.01 *N* HNO_3 (B) (252).

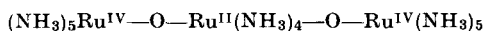
second is forbidden (as observed in Fig. 32, curve A). However, because the intensity of the first band decreases whereas that of the second band increases on bending the molecule, the spectrum of the oxidized ion (curve B) suggests that it is more bent than the reduced ruthenium red.

Regardless of whether ruthenium red is linear or bent, the ion at first appears to be class II, with the terminal ruthenium atoms in principle being clearly distinguishable from the bridging one. However, the unusually high molar extinction coefficient of 61,500 for the first band of ruthenium red in water suggests that α is very large indeed (Eq. 14), and that the delocalization of valences approaches that for

class III-A. This is confirmed by the magnetic susceptibility study, for if ruthenium red were class II with valences trapped as either



or



it would have an effective magnetic moment per ruthenium of 2.2 or 2.3 B.M., whereas 0.77 B.M. is observed, a large part of which may be temperature-independent paramagnetism. The large depression of the effective magnetic moment follows from the strong interaction between the ruthenium atoms via both π and σ bonds.

Other ruthenium mixed valence materials have been suggested as forming when RuO_4 in aqueous solution is reduced in the presence of trifluoroacetic acid (124), and it seems possible that the very dark blue-green precipitate obtained when solutions of $\text{K}_4\text{Ru}(\text{CN})_6$ are acidified after oxidation by chlorine (184, 439) may be the ruthenium analog of Prussian blue, for it analyzes as $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}(\text{CN})_5 \cdot \text{H}_2\text{O}$.

The literature appears to contain only one reference to a mixed valence compound of osmium, and doubt has been raised as to its constitution. $\text{Os}^{\text{III}}\text{Os}^{\text{IV}}\text{Cl}_7 \cdot 7\text{H}_2\text{O}$ is a red material, said to be possibly a mixture of OsCl_4 and OsOHCl_3 (290).

N. RHODIUM AND IRIDIUM

No rhodium compounds have been shown conclusively to be of mixed valence type. In ice-cold solution, ceric nitrate oxidizes a suspension of Cs_3RhCl_6 to a dark blue-green substance thought to be $\text{Cs}_2\text{Rh}^{\text{IV}}\text{Cl}_6$ (211, 212), but, since it appears that ozone oxidizes $\text{Rh}(\text{III})$ solutions to $\text{Rh}(\text{V})$ in the presence of excess chloride ions (57), the suggestion was therefore made that the Cs_2RhCl_6 salt may contain equimolar proportions of $\text{Rh}(\text{III})$ and $\text{Rh}(\text{V})$, like the isomorphous antimony compound. However, the diffuse reflectance spectrum of the blue-green compound, and its dilution in Cs_2PtCl_6 , sufficiently resemble that of Cs_2IrCl_6 to make it certain that the compound is indeed one of $\text{Rh}(\text{IV})$ (397, 398). Solutions of rhodium perchlorate of average oxidation number 4.5–5.3 (57) were said to exhibit further intense absorption bands in addition to those of $\text{Rh}(\text{III})$ and $\text{Rh}(\text{V})$, which may be taken as indicating the presence of mixed valence species in some of these solutions. The only other rhodium compound which is perhaps a mixed valence system is the dichloride (787) for which, as Kettle (413) pointed out, the original analyses agree much more closely with the formula $\text{Rh}_6\text{Cl}_{14}$. This is thus a potential example of the group of mixed valence compounds based on octahedral metal clusters, such as $[\text{Ta}_6\text{Cl}_{12}]^{2+}$.

Numerous mixed valence iridium compounds are based on a trimeric arrangement of iridium atoms bridged by sulfate groups. Lecoq de Boisbaudran (460) prepared what he thought was an Ir(III) double sulfate, $\text{Ir}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4$, which, unlike most Ir(III) salts, was not green but blue. His formulation was questioned by Delépine (187), whose analyses agreed better with the formula $\text{K}_{10}\text{Ir}_3(\text{SO}_4)_9$ and who also demonstrated that reducing agents turned the blue solution of the salt green. The original salt therefore apparently contained Ir(IV) as well as Ir(III). Delépine also prepared a green nitrido-iridium sulfate (186), which he showed, 60 years later (188), had the formula $\text{K}_4[\text{N}\{\text{Ir}(\text{H}_2\text{O})(\text{SO}_4)_2\}_3]$, i.e., it contained one Ir(III) atom and two Ir(IV) atoms per anion. Having examined the solution spectrum of the nitrido compound, Jorgensen (396) proposed that the formulas of that and Lecoq's salt were related to those of the trimeric Cr(III) acetates, $[\text{O}\{\text{Cr}(\text{H}_2\text{O})(\text{CH}_3\text{CO}_2)_2\}_3]^+$ (251), in which the oxygen atom and the three chromium atoms are found in a planar triangular arrangement, and octahedral coordination about each metal is completed by bridging acetate groups and the water molecules (Fig. 11). A rationalization of the electronic structures of these unusual compounds can be achieved by considering that, if the t_{2g} orbitals of the iridium atoms and the $2p \pi$ orbital of oxygen were fully occupied, there would be room for twenty electrons, but that one linear combination

$$\frac{1}{\sqrt{3}}[(t_{2g})_1 + (t_{2g})_2 + (t_{2g})_3]$$

forms not only a $d\pi$ - $p\pi$ bonding orbital with the $2p_z$ oxygen orbital, but a strongly antibonding orbital as well. Thus by losing two electrons and becoming mixed valence, an eighteen-electron system results which does not require occupation of the energetically unfavourable antibonding orbital. Delépine's formula (187) for Lecoq's salt becomes analogous to that of the nitrido compound, if one assumes that the three iridium atoms are in that case coordinated to an oxygen atom. If these trinuclear complexes do have the equilateral triangular geometry, then they belong to class III-A, and should be diamagnetic.

Ray and Adhikari (578) report the preparation of $\text{Ir}^{\text{II}}\text{Ir}^{\text{III}}\text{Cl}_5 \cdot 4\text{R}_2\text{S}$, where R_2S is either $\text{S}(\text{CH}_3)_2$ or $\text{S}(\text{C}_2\text{H}_5)_2$, as pale yellow crystals.

O. PALLADIUM AND PLATINUM

These two elements form mixed valence compounds with a wider range of ligands than many others, and intensive studies of their molecular structures and physical properties over many years have provided

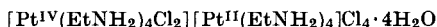
us with a clear view of their electronic structures. A few simple compounds such as oxides and halides are known, but the majority of examples contain complex ions or neutral molecules, typically with halide and amine ligands.

Hydrates of the simple oxides Pd_2O_3 and Pt_2O_3 were first prepared by Wöhler and Martin (783, 784). They are reported to be brown-black, but, since PdO_2 and PtO_2 are also black, this fact gives no information about the possibility of an M(II),M(IV) mixed valence interaction. Some controversy has surrounded the formulation and structure of another oxide, Pt_3O_4 . Galloni and Ruffo (265) described the structure as body-centered cubic, with all the platinum ions in equivalent sites (class III-B), and a Pt-Pt spacing of 3.11 Å. An oxide prepared by Waser and McClanahan (745, 746) using the same method, however, contained enough sodium to suggest the formula NaPt_3O_4 . A powder diagram of the latter revealed a simple cubic lattice in which each platinum has four oxygen neighbors and two other platinum ions at 2.85 Å. Since the structure contains infinite chains of platinum atoms, the conductivity was investigated. The volume resistivity at room temperature was about 10^4 ohm cm, but the occurrence of polarization suggested that the conductivity was ionic. The powder pattern of this preparation was quite different than Galloni and Ruffo's, whose results were said to resemble the pattern of PtO_2 . Galloni and Busch (266) reiterated that their product contained no sodium, so one must accept the compromise suggestion (747) that there exists a series of compounds with the general formula $\text{Na}_x\text{Pt}_3\text{O}_4$, based on the platinum and oxygen lattice found by Waser and McClanahan (746). It should perhaps be mentioned that, according to our classification scheme, the high resistivity reported for NaPt_3O_4 is at variance with its proposed class III-B structure.

Oxidation of PdCl_2 with BrF_3 gives black PdF_3 (608, 655), but Pt(II) salts are oxidized to PtF_4 by this reagent. The magnetic moment of PdF_3 was at first interpreted (541) in terms of a Pd(III) ion with a configuration $t_{2g}^6e_g^1$, but Bartlett and Rao (43) have recently shown that the compound is in fact $\text{Pd}^{\text{II}}[\text{Pd}^{\text{IV}}\text{F}_6]$, in which Pd(II) is assigned a high-spin configuration $t_{2g}^6e_g^2$. When Pd(II) salts react with BrF_3 in the presence of quadrivalent oxides, isostructural compounds such as PdGeF_6 and PdSnF_6 are formed. No structural studies of the other simple PtX_3 halides with $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ (784, 788) have been reported, but it seems probable that they are related to the fluoride. However, they cannot be precisely the same since the divalent metal ions in these halides are low-spin (697), and thus, no doubt, in square planar coordination. Mixed valence halides such as K_2PdCl_5 (783) and Cs_2PtCl_5 (785) may perhaps contain $[\text{M}^{\text{II}}\text{Cl}_4]^{2-}$ and $[\text{M}^{\text{III}}\text{Cl}_6]^{2-}$ ions, which, if the

compounds belong to class II, will exhibit their own characteristic absorption bands in addition to any mixed valence absorption. Unfortunately, no information on this point is available, except for the single observation that Cs_2PtCl_5 is green (785).

One of the first mixed valence platinum compounds containing halide and amine ligands to be prepared was the red salt of Wolfram (790):



Its mixed valence character was recognized first from the method of preparation, for mixing solutions of the compounds $[\text{Pt}^{\text{IV}}(\text{EtNH}_2)_4\text{Cl}_2]\text{Cl}_2$ and $[\text{Pt}^{\text{II}}(\text{EtNH}_2)_4]\text{Cl}_2$ (580) precipitates the red salt from the colorless solutions. Propylamine is the only other amine which forms similar salts. Wolfram (790) also has described similar mixed valence materials which apparently did not contain halide, for example, a nitrate, sulfate, and oxalate. The red chloride could be recovered from these salts by adding HCl solution, but no work on them has been described since 1907 (384).

Because they were able to prepare a salt with the formula $\text{Pt}(\text{EtNH}_2)_4\text{Cl}(\text{NCS})_2$, which they thought was a dimer, Drew and Tress (205) thought that Wolfram's red salt was also a dimer rather than a double salt, but a crystal structure determination (165) has confirmed the earlier conclusion. The crystal structure contains chains of platinum atoms with alternately square planar coordinated Pt(II) ions and octahedrally coordinated Pt(IV) ions. Chlorine atoms lie between the platinum atoms, 2.26 Å from the quadrivalent platinum and 3.13 Å from the divalent (as shown in Fig. 33); the compound clearly belongs to class II. The structure could not be fully refined because of the occurrence of stacking faults due to the chains slipping past one another. Craven and Hall (166) recently attempted to resolve this difficulty by determining the structure of the corresponding bromide, but these crystals also proved to be disordered.

Yamada and Tsuchida (800) studied the polarized crystal spectrum of Wolfram's red salt, and also the isomorphous bromide, which is green. Whereas neither $[\text{Pt}^{\text{IV}}(\text{EtNH}_2)_4\text{Cl}_2]\text{Cl}_2$ nor $[\text{Pt}^{\text{II}}(\text{EtNH}_2)_4]\text{Cl}_2$ showed absorption in the visible, the red salt had an absorption band near $17,000\text{ cm}^{-1}$ which was strongly polarized in the direction of the metal atom chain. The first two bands polarized normal to this direction appear to be internal transitions of the quadrivalent complex (Fig. 34), but the $17,000\text{ cm}^{-1}$ band is likely to be the class II mixed valence absorption band due to the transfer of an electron from the highest filled $5d$ orbital of $[\text{Pt}^{\text{II}}(\text{EtNH}_2)_4]^{2+}$ (probably d_{z^2} since the ligands are purely σ -bonding) to the unfilled d_{z^2} orbital of $[\text{Pt}^{\text{IV}}(\text{EtNH}_2)_4\text{Cl}_2]^{2+}$. Since the d_{z^2} orbitals on

the two centers point at one another and can overlap via the $3p\sigma$ orbital of the intervening chloride ion, the α of Eq. (15) is nonzero and the transition will be electronically allowed (although not necessarily strong), with a polarization along the Pt-Pt chain.

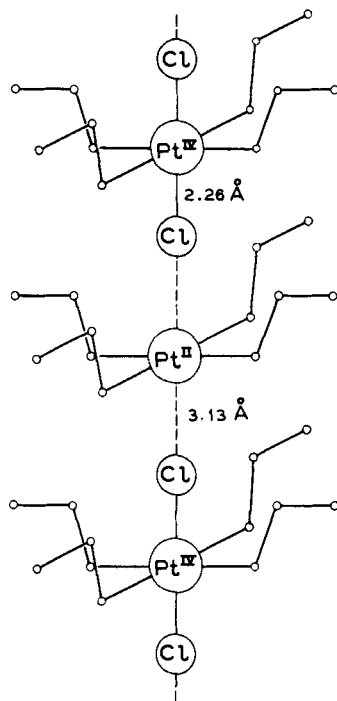
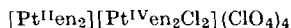


FIG. 33. The platinum atom chain in Wolfram's red salt, $[\text{Pt}^{\text{IV}}(\text{NH}_2\text{C}_2\text{H}_5)_4\text{Cl}_2]^{2+}[\text{Pt}^{\text{II}}(\text{NH}_2\text{C}_2\text{H}_5)_4]^{2-}\text{Cl}_4 \cdot 4\text{H}_2\text{O}$ (165).

A compound which appears to be related to Wolfram's red salt was recently prepared by Kida (416). Chemical analysis suggested the formula



and the compound forms dichroic needles which are red parallel to, and light yellow perpendicular to, the needle axis. A structure determination and polarized spectrum would be of interest.

The other type of mixed valence compound with halide and amine ligands has the general formula $[\text{Ma}_2\text{X}_2][\text{M}'\text{A}_2\text{X}_4]$, where M and M' may be either Pt or Pd, A is an amine, and X a halogen. The palladium salt, with an empirical formula $\text{Pd}(\text{NH}_3)_2\text{Cl}_3$, was first prepared in 1878 (614),

but many others have since been prepared containing palladium or platinum, ammonia or ethylenediamine, and either chloride, bromide, or iodide (202, 204, 205, 314, 708). The compounds are diamagnetic (376, 379, 380, 697) and, as was the case with Wolfram's salt, Drew and his coworkers (203) first thought that they contained metal-metal bonds. However, numerous crystal structure determinations (100, 334, 612, 743) have since shown that the correct formulations are as class II mixed valence compounds. Square planar MA_2X_2 and octahedral $M'A_2X_4$ molecules are stacked in chains with a halogen atom between each pair

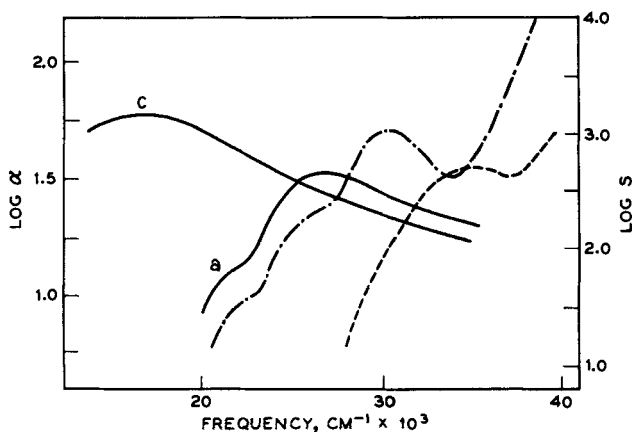


Fig. 34. The polarized absorption spectrum of crystalline $[Pt^{II}(NH_2C_2H_5)_4][Pt^{IV}(NH_2C_2H_5)_4]Cl_6 \cdot 4H_2O$ with the electric vector along the chain direction (c), and perpendicular to it (a). Spectra of the components $[Pt^{II}(NH_2C_2H_5)_4]Cl_2$ (---) and $[Pt^{IV}(NH_2C_2H_5)_4]Cl_2$ (-.-) are also shown for comparison (800).

of metal atoms within the chains (Fig. 35). The most recent determinations (612, 743) agree that the $Pt(II)-Br$ and $Pt(IV)-Br$ bonds at right angles to the chain are slightly longer than the $Pt(IV)-Br$ bond within the chain, and also that the distance between the $Pt(II)$ and the bromine atom attached to $Pt(IV)$ is somewhat smaller than expected from covalent radii. To the degree of approximation obtainable in these determinations, the $Pt(II)-Br$ and $Pt(IV)-Br$ bond lengths appeared identical. Greater precision could not be achieved because of disorder in the crystals resulting from the very weak interactions between neighboring stacks, which enables them to slip past one another. As with Wolfram's salt, the lowest mixed valence absorption in the class II $[MA_2X_2][M'A_2X_4]$ salts should be $dz^2 \rightarrow dz^2$, and allowed with a polarization along the Pt-Pt chain.

In agreement with the formulation of this class of compounds as molecular crystals, the infrared spectrum of PtBr_3 is a superposition of those of PtBr_2 and PtBr_4 (750). In the visible, however, all compounds in the series have intense absorption bands not present in either of their components. Cohen and Davidson (145) reported that $\text{Pd}(\text{NH}_3)_2\text{Cl}_3$ was highly dichroic, being lemon-yellow when the electric vector was perpendicular to the needle axis and black (even for the smallest crystals) when parallel, just as predicted above. When PtBr_3 , reportedly green, is finely ground the powder appears black (750), but

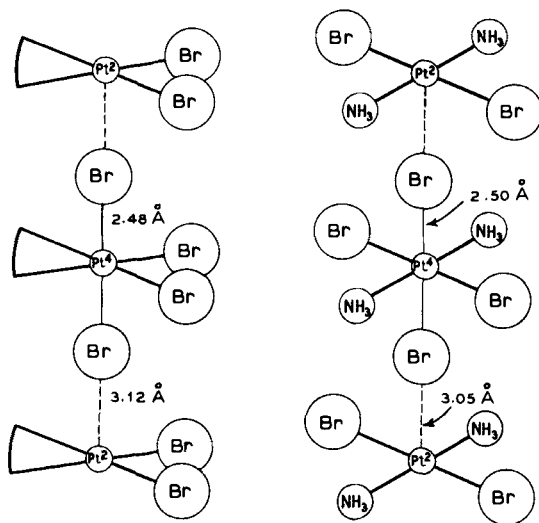
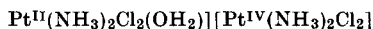


FIG. 35. The alternating $\text{Pt}^{\text{II}}, \text{Pt}^{\text{IV}}$ chains in $[\text{Pt}^{\text{II}}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2\text{Br}_2][\text{Pt}^{\text{IV}}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2\text{Br}_4]$, left, and $[\text{Pt}^{\text{II}}(\text{NH}_3)_2\text{Br}_2][\text{Pt}^{\text{IV}}(\text{NH}_3)_2\text{Br}_4]$, right (612).

when viewed in thin sections the transmitted color is purple. The green color is therefore caused by metallic reflection, indicating that the mixed valence absorption is very strong and that therefore α is very large. Attempts to measure the polarized crystal spectra of some of these compounds (798, 799) were not very successful because of the extremely intense absorption, but all the examples studied had a broad absorption band between 15,000 and 20,000 cm^{-1} , polarized in the direction of the metal-metal chains. Like the band in Wolfram's red salt, this transition is probably a mixed valence absorption band involving transfer of an electron from the divalent to the quadrivalent ion, but more refined experimental and theoretical work would be required to make the assignment more precise.

As with Wolfram's red salt, compounds of the type $[\text{MA}_2\text{X}_2][\text{MA}_2\text{X}_4]$ have also been prepared containing X groups other than halogens. For example, the salt

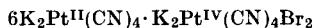


first prepared by Tschugajeff and Tschernjajeff (709) is so strongly dichroic that it has been suggested (78) for use as a polarizer. The dichroism (from black to white in the visible region) is said to extend at least from 12,000 to 29,000 cm^{-1} .

In view of the variety of solid mixed valence halides of palladium and platinum, one might expect that some mixed valence interaction would be detectable in halide-containing solutions. However, Cohen and Davidson (145) were unable to detect a change in the spectrum on mixing solutions of $[\text{Pd}^{\text{II}}\text{Cl}_4]^{2-}$ and $[\text{Pd}^{\text{IV}}\text{Cl}_6]^{2-}$, or $[\text{Pt}^{\text{II}}\text{Cl}_4]^{2-}$ and $[\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-}$. Trivalent platinum has been suggested as an intermediate in the exchange of $[\text{PtCl}_6]^{2-}$ and chloride ions, which proceeds by a chain mechanism (583) but the reaction is catalyzed by $[\text{PtCl}_4]^{2-}$, possibly via a symmetrical transition state. Similarly, electron exchange between $\text{Pt}^{\text{II}}\text{Br}_2$ and $\text{Pt}^{\text{IV}}\text{Br}_4$ is catalyzed by bromide ions, which would also allow a symmetrical transition state to be formed (491).

Mixed valence platinum oxalate complexes were first prepared 70 years ago by Werner, who reacted oxalic acid with sodium platinite, and obtained a salt whose copper color contrasted with the yellow color of the normal $\text{Pt}(\text{II})$ oxalate (764). This interesting compound has recently been reexamined by Krogmann and his co-workers (441, 442). The crystal structure of $\text{K}_2\text{Pt}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ contains isolated planar oxalato complexes (489) but, in the compound $\text{K}_{1.6}\text{Pt}(\text{C}_2\text{O}_4)_2 \cdot 2.5\text{H}_2\text{O}$, the complex anions are stacked one above the other so that the $\text{Pt}-\text{Pt}$ distance is only 2.75 Å. It is not possible to distinguish $\text{Pt}(\text{II})$ and $\text{Pt}(\text{IV})$ ions in the structure (441) and, on this basis, the compound is a class III-B system. Krogmann suggests that, whereas in $\text{K}_2\text{Pt}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ the d_{z^2} band is filled, on oxidation electrons are drawn off from that band, and an overall bonding results.

The oxidation of potassium platinocyanide with bromine or nitric acid was first investigated over 100 years ago (430), but there appears to be considerable disagreement about the nature of the products. Knop (430) assigned the formula $\text{K}_2\text{Pt}(\text{CN})_5$ to the metallic-looking coppery crystals, but, according to Levy (461), there are two products of the bromine oxidation, one a $\text{Pt}(\text{IV})$ salt $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_2$ and the other a copper-colored mixed valence salt:



Oxidation by hydrogen peroxide gave another mixed valence salt with a bronze luster, to which analysis assigned the formula $K_{1.5}Pt(CN)_4$. Hydrated lithium cyanoplatinites undergo remarkable color changes when cooled in liquid air (582), which may be related to partial oxidation and formation of a mixed valence chromophore. No work has been done on these interesting compounds since 1912.

P. SILVER

The mixed valence chemistry of silver is limited apparently to its oxides and halides, the latter being mostly mixed compounds with the Au(III) ion. Silver distinguishes itself from its congener element gold in that, whereas the most common valence states of gold are Au(I) and Au(III) and all its mixed valence compounds are formed from these, with silver the most common oxidation states are Ag(I) and Ag(II), yet the mixed valence compounds involve the valence pairs Ag(I)–Ag(0) or Ag(I)–Ag(III). Although we will treat the silver and gold compounds separately, they are closely related in that a large number of Ag(I)–Au(III) complexes have Au(I)–Au(III) counterparts.

Of the silver oxides of potential mixed valence interest, AgO is of prime importance. Reviews of the chemistry of this substance have been presented by McMillan (503) and Dirkse (198). AgO has been prepared in the past in a variety of ways, both chemical and electrochemical, and has been reported to have a variety of conflicting properties. However, AgO preparations made in six different ways by Schwab and Hartmann (646) were shown to have identical X-ray powder patterns. Apparently the purity of the sample varies with its mode of preparation.

The early suggestions that AgO is a peroxide of univalent silver of the form $Ag_2^I O_2$ has been discredited repeatedly by reports of its inability to show reactions thought to be characteristic of peroxides (39, 303). As for AgO being a divalent oxide as its formula implies, one would then expect paramagnetism due to the $4d^9$ Ag(II) ions, yet it is generally agreed that AgO is diamagnetic (425, 528, 622, 651, 696). An obvious suggestion is that AgO should be written as $Ag^I Ag^{III} O_2$, with the $4d^8$ Ag(III) ions in square coordination, thereby making them diamagnetic. Crystal structure analysis demonstrates that this indeed is the case.

It is not entirely clear whether or not AgO can be obtained as a face-centered cubic crystal as well as a monoclinic one, as some have claimed. Although several reports of face-centered cubic AgO have appeared (97, 390, 682), the possibility exists that these are higher or lower oxides

of silver, and not AgO. The monoclinic variety of AgO has been studied extensively by both X-ray and neutron diffraction techniques. Unfortunately, due to the disparity in scattering power of silver and oxygen, the X-ray experiments on powdered AgO do not permit an adequate direct determination of the oxygen positions, but silver positions can be obtained accurately and the oxygen positions then deduced from packing considerations. As determined by Scatturin *et al.* (619, 620), AgO consists of Ag(II) ions in approximately square coordination, forming infinite chains via bridging oxide ions. McMillan (502), on the other hand, finds a distinct difference in the coordination about the silver ions, half of the silver ions being four-coordinated (square) and half two-coordinated (linear). The final word would appear to be that of Scatturin *et al.* (621, 622), who turned to neutron diffraction, wherein silver and oxygen have comparable scattering power, and found that there are indeed two types of silver ion in AgO, one, presumably Ag(III), in square oxygen coordination with Ag—O equal to 2.01–2.05 Å, and the other, presumably Ag(I), in linear coordination having Ag—O equal to 2.18 Å. Monoclinic AgO by this criterion is thus a class I mixed valence system.

Owing no doubt to its importance to the battery industry, there have been a number of studies of electronic conduction in AgO, with some disagreement as to its resistivity. Le Blanc and Sachse (458) found that, whereas the resistivity of Ag₂O is 10⁸ ohm cm, a sample of *approximate* composition AgO had a resistivity of only 10 ohm cm. More recent measurements on pressed pellets of AgO at various pressures yield a resistivity of 0.012 ohm cm (390) when extrapolated to infinite pressure. This material, however, is claimed to be the face-centered cubic variety of AgO. A pellet of monoclinic AgO pressed at 12,000 kg/cm² had a resistivity of 14 ohm cm and the positive temperature coefficient expected for a semiconductor (528). The resistivity of an AgO film formed electrolytically on a metallic silver sheet is 5×10^3 ohm cm (125). These values, although disparate, all indicate a rather high electronic conductivity for AgO, much higher in fact than expected for a class I system. It must be mentioned, however, that pure AgO is a rather unstable compound and the low resistivity reported for it may be due to the presence of impurities.

There are two other compounds which must be mentioned in a discussion of the mixed valence oxides of silver. Unstable, paramagnetic Ag₄O₅, perhaps better written as Ag^IAg^{III}₃O₅, has been described as one of the materials resulting from ozonization of an acidified solution of AgClO₄ (651). It has been claimed, however, that the powder pattern attributed by the original workers to Ag₄O₅ is in fact due to a mixture of Ag₂O₃, AgO, and Ag₂CO₃ (524). A second oxide of presumed composi-

tion Ag_4O_3 has been studied by the analysis of X-ray powder patterns (732), and was said to consist of Ag_4 tetrahedra having three oxide ions bonded symmetrically to each of the silver ions. It remains to be shown if this is a genuine compound, or, as often is the case with silver oxides, simply a mixture of the better known oxides of silver (556).

Electrolysis of an acidic solution of silver nitrate leads to the formation of a black, crystalline substance at the anode having the composition $\text{Ag}_7\text{NO}_{11}$. Although this material has been the subject of a great many studies, its crystal structure only recently has been solved and its electronic structure is still in some doubt. Following the earlier crystallographic work (82, 819), more complete studies by Chou Kung-Du (140) and Naray-Szabo and co-workers (525) finally led to an acceptable structure for $\text{Ag}_7\text{NO}_{11}$. This last study, involving single crystal X-ray work and neutron diffraction on the powdered material, gave a face-centered cubic cell containing polyhedral structural units (as shown in Fig. 36). Each polyhedron (cubo-octadodecahedron) is formed from six square planar AgO_4 units (Fig. 36) and has an NO_3^- ion at its center. The polyhedra themselves are joined by a sharing of the AgO_4 faces, and the smaller cubes formed between polyhedra have Ag(I) ions at their centers. Thus there are two types of silver ion in this structure, one type having eight oxygens about it at the corners of a cube with an Ag—O distance equal to 2.52 Å, and a second type which is in square planar oxygen coordination having Ag—O distances equal to 2.05 Å. The stoichiometry of $[\text{Ag}_7\text{O}_8]^+\text{NO}_3^-$ demands that the ratio $\text{Ag(I)}/\text{Ag(III)}$ be 2/5, whereas the ratio of cubic sites to square planar sites in such a structure is 1/6. Since the cubic sites are occupied only by Ag(I) , and since all the square planar sites are equivalent, the one Ag(I) and the five Ag(III) ions in the square coordination within a polyhedral unit form a two-electron, class III mixed valence system, the metal ions of which are joined by bridging oxygen atoms. Moreover, since each polyhedral unit is joined to twelve similar units by sharing its square AgO_4 faces (Fig. 36), the class III mixed valence system encompasses the entire crystal without involving any of the cubically coordinated silver, and is therefore class III-B.

The mixed valence $[\text{Ag}_7\text{O}_8]^+\text{NO}_3^-$ system involves $4d^8$ and $4d^{10}$ ions in square coordination. Although there is considerable argument as to the ordering of the d levels in square planar systems such as these, there is universal agreement that the uppermost orbital is $dx^2 - y^2$, which thus forms the valence shell of the mixed valence system, together with the $2p\sigma$ orbitals of the bridging oxide ions through which $dx^2 - y^2$ orbitals on adjacent silver ions interact. As was discussed above, the most dramatic properties of a class III-B system are its electrical conductivity and

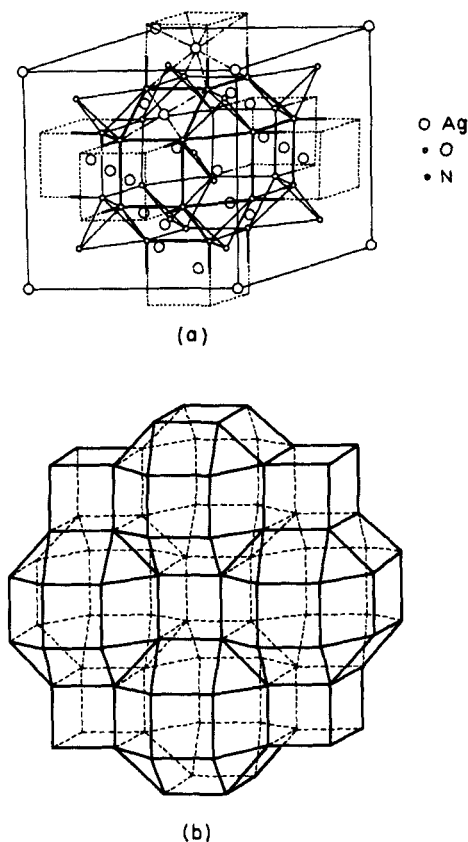


FIG. 36. The unit cell of $\text{Ag}_7\text{O}_8\text{NO}_3$ showing (a) the polyhedral cage with the NO_3^- ion at its center, and (b) the fusion of Ag_6O_8 polyhedra through sharing of the square AgO_4 faces (140, 525).

reflectivity, both of which should be metallic. McMillan (503) first reported that $\text{Ag}_7\text{O}_8\text{NO}_3$ was only semiconducting, but later work on single crystals (594) has shown that it is metallic ($\rho = 2.5 \times 10^{-3}$ ohm cm at 300°K) and is superconducting below 1.04°K . The reflectivity of $\text{Ag}_7\text{O}_8\text{NO}_3$ is also metallic, the crystals being shiny black and quite opaque. The molar susceptibility of $\text{Ag}_7\text{NO}_{11}$ has been reported by various authors as 398×10^{-6} (524), 688×10^{-6} (528), and $6379 \pm 1750 \times 10^{-6}$ (651) cgs, suggesting that the substance as ordinarily synthesized may contain a variable amount of paramagnetic impurity and that the pure substance is only feebly paramagnetic, if at all.

The NO_3^- anion of $\text{Ag}_7\text{NO}_{11}$ apparently can be replaced while keeping

the Ag_7O_8^+ framework intact, for the salts $\text{Ag}_7\text{O}_8\text{F}$ (303, 503), $\text{Ag}_7\text{O}_8\text{ClO}_4$ (503), $\text{Ag}_7\text{O}_8\text{BF}_4$ (594), and $\text{Ag}_7\text{O}_8\text{HSO}_4$ (503, 528) also have been reported, the fluoride, fluoroborate, and bisulfate having unit cell dimensions almost exactly those of the nitrate. Because crystals of the same unit cell dimensions form regardless of the radii of the anions within the polyhedral cages, the systems can be considered as clathrate salts, with mononegative ions as guests within the very rigid Ag_8O_8 cages. Careful analytical work on the fluoride and perchlorate (524) suggests that, unlike the nitrate and bisulfate, these substances may not have a fixed composition. All these substances are metals (594).

Earlier doubts as to the exact composition of Ag_2F and its existence as a stoichiometric compound were settled by the work of Wöhler (786), who showed that there is no oxygen in the substance and that, on dissolution in water, it gives equimolar amounts of AgF and metallic silver, as expected for Ag_2F . Silver subfluoride, Ag_2F , as prepared either electrolytically or by the reaction of silver metal with an AgF solution, is formed as large crystals described as being yellow to yellow-green with a bright metallic, brassy reflex (358).

Bruno and Santoro (109) have performed isotope exchange experiments on Ag_2F in an effort to determine whether or not the silver ions in this substance are equivalent. They found that, following the formation of Ag_2F from inactive AgF and radioactive ^{110}Ag metal and decomposition in H_2O , the resulting Ag metal and AgF had equal activities, indicating the equivalence of the silver atoms. However, a second experiment, in which inactive Ag_2F exchanged heterogeneously with active $^{110}\text{AgNO}_3$ in acetone solution, showed that virtually all the radioactive Ag doped into the compound could be recovered as Ag metal on H_2O decomposition.

X-ray analysis reveals the crystal structure of Ag_2F to be a simple one, having one molecule per hexagonal cell in the anti-cadmium iodide structure (552, 700) (Fig. 37). The structure may be looked upon as consisting of alternate layers of silver and fluoride ions. Within the silver layer, adjacent silver ions are separated by 2.84 Å within the unit cell and 2.989 Å between unit cells, these distances being nearly equal to the Ag-Ag separation of 2.28 Å in metallic silver. All silver atoms are in equivalent sites, and each is coordinated symmetrically by three fluoride ions at a distance of 2.44 Å, equal to the silver-fluoride distance in AgF . Since the Ag_2F stoichiometry demands that half the silver atoms be univalent and half zero-valent, the equivalence of the silver sites and the short repeat distance a lead to a class III-B mixed valence system, which should be an insulator in the c direction and metallic perpendicular thereto.

The resistivity of Ag_2F has been measured, using a four-probe technique at temperatures between 1.4° and 300°K . It increases monotonically from a value of 0.4×10^{-5} to 2.4×10^{-5} ohm cm in this temperature range (359); for comparison, the resistivity of metallic lead is 22×10^{-5} ohm cm at 300°K . Experimental (138) and theoretical (139) studies of the ^{19}F NMR spectra of AgF and Ag_2F show that the spin lattice relaxation time t_1 varies with temperature, as would be expected for relaxation by hyperfine interaction of the ^{19}F nuclei with the conduction electrons. A Knight shift calculated on this assumption is in good agreement with the shift observed between Ag_2F and AgF . The magnetic

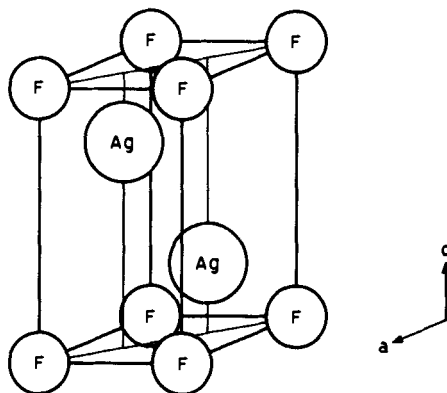


FIG. 37. The hexagonal unit cell of class III-B silver subfluoride, Ag_2F , with $a = 2.989 \text{ \AA}$, $c = 5.710 \text{ \AA}$, and $\text{Ag}-\text{Ag} = 2.84 \text{ \AA}$ (700).

susceptibility of Ag_2F has also been studied (261); the molar susceptibility of -64.3×10^{-6} cgs appears understandable only if the conduction electrons move in an anisotropic potential, in accord with the anisotropic structure of the crystal. Hall measurements (707) on Ag_2F demonstrate that there is one carrier per pair of silver atoms, as one would expect from the $\text{Ag}^0\text{Ag}^{\text{I}}\text{F}$ formulation. Ag_2F is superconducting below 0.058°K (20).

There is a second silver fluoride of interest to us. Fluorination of AgCl results in the formation of a black substance of the composition AgF_2 (609), nominally a divalent silver fluoride. In support of this, it is claimed to be strongly paramagnetic ($\chi_{\text{mol}} = 45 \times 10^{-6}$ cgs at room temperature), as a magnetically dilute divalent silver salt must be. A more detailed study of the magnetic susceptibility of samples of AgF_2 , prepared in three different ways, confirmed the above value of the molar susceptibility and in addition showed that the material is weakly ferromagnetic at 90°K (324). Through the action of fluorine on metallic

silver, a yellow form of AgF_2 is produced (383). The yellow form is poorer in fluoride than the black and has a lower magnetic susceptibility, suggesting perhaps that the black form is contaminated with paramagnetic Ag(III) salts (44). The black form has a face-centred orthorhombic, distorted CaF_2 structure with all the silver ions in equivalent sites (44). The problem as to whether AgF_2 is a salt of Ag(II) or is a mixed valence Ag(I),Ag(III) class III-B system could be clarified perhaps through a study of its resistivity. A similar question exists in regard to the "divalent" black fluoride BaAgF_4 (369).

Solution of the crystal structure of $\text{Ag}_5\text{Pb}_2\text{O}_6$ has revealed it to be a substance containing the Ag_2^+ dimer ion (123). In $\text{Ag}_5\text{Pb}_2\text{O}_6$, the quadrivalent lead ions are surrounded octahedrally by oxygen at 2.19 Å, and three of the five silver ions in the unit cell are univalent and linearly coordinated with oxygen. The two remaining silver atoms form Ag_2^+ dimers having an internuclear separation of 3.04 Å, with each silver of this pair in turn coordinated by three oxygens, much as each silver ion of Ag_2F is coordinated to three fluoride ions. However, unlike the situation in Ag_2F where short Ag-Ag distances imply a very strong interaction between silver ions of adjacent pairs, in the $\text{Ag}_5\text{Pb}_2\text{O}_6$ crystal the Ag_2^+ groups are aligned in chains with 3.39 Å separating the atoms of adjacent pairs. Thus the crystal structure suggests that the system is overall class III-A. Because the Ag_2^+ ion is an odd-electron species, a study of the magnetic susceptibility of $\text{Ag}_5\text{Pb}_2\text{O}_6$ would be of great use in determining just how strongly the Ag_2^+ ions are interacting. If the interaction were strong, then the Ag_2^+ ions form a class III-B system which would be a one-dimensional analog of the two-dimensional silver layer of Ag_2F . There are no data available on the optical, magnetic, or electrical properties of $\text{Ag}_5\text{Pb}_2\text{O}_6$, but the Ag_2^+ ion has been observed by ESR in organic glasses (658).

Q. GOLD

The best known mixed valence gold compounds are the halides of Au(I) and Au(III) and the corresponding compounds having Ag(I) in substitution for the Au(I) ion. Insofar as crystal structures have been determined, these compounds contain the trivalent gold as square coplanar AuX_4 and the univalent gold (silver) as linear bicoordinated AuX_2 (AgX_2) groups, the systems being, in general, class I or class II. The recent report of a genuine, paramagnetic Au(II) complex (749) suggests that one must use some caution in presuming that all nominally divalent gold compounds are univalent-trivalent mixed valence materials.

The AuCl-AuCl_3 system has been studied by Corbett and Druding (150), who conclude that their phase diagram and powder pattern results show no evidence for the formation of the mixed valence compound $\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_4$. However, the silver salt $\text{Ag}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_4$ (deep red) (355) and the corresponding fluoride $\text{Ag}^{\text{I}}\text{Au}^{\text{III}}\text{F}_4$ (541) have been reported. There also exists a report on the preparation of Au_2I_4 , an unstable, ether-soluble substance (106). Although the double chloride $\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_4$ has not been prepared, salts of Au(I),Au(III) and Ag(I),Au(III) with alkali metal cations abound.

One of the first mixed valence triple salts of gold and silver reported was Pollard's salt (570), originally thought to be $(\text{NH}_4)_8\text{Ag}_3\text{Au}_4\text{Cl}_{23}$, but later revised to $(\text{NH}_4)_6\text{Ag}_2^{\text{I}}\text{Au}_3^{\text{III}}\text{Cl}_{17}$ (760). A rubidium-silver-gold chloride having the same atomic ratios as Pollard's ammonium salt also has been reported (50, 761). The dark red crystals of the ammonium salt show a black-to-red pleochroism, in which the black color is most likely due to the mixed valence absorption between the $[\text{Au}^{\text{III}}\text{Cl}_4]^-$ and $[\text{Ag}^{\text{I}}\text{Cl}_2]^-$ groups. The crystal structure of this material has not been determined, but unit cell parameters are known (245).

The most famous mixed valence double salts of gold are Wells' cesium salt, $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6$, and its silver analog, $\text{Cs}_2\text{Ag}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6$ (50, 758). The structures of these two isomorphous mixed valence halides have not yet been settled, for there are two different interpretations of the experimental X-ray diffraction data. Elliott and Pauling (219, 220) propose a tetragonal structure containing $[\text{Au}^{\text{III}}\text{Cl}_4]^-$ square planar ions and $[\text{Ag}^{\text{I}}\text{Cl}_2]^-$ or $[\text{Au}^{\text{I}}\text{Cl}_2]^-$ linear ions stacked alternately within columns. One sees from Fig. 38 that each Au(III) ion is in a nominally octahedral field with a tetragonal extension, whereas each Ag(I) or Au(I) ion is nominally octahedral with a tetragonal compression. As is well known, such a tetragonal field about the $5d^8$ Au(III) ion leads to a singlet ground state, in agreement with the diamagnetism of Wells' salts (219). On the other hand, Ferrari and co-workers (240, 242) propose that the Au(III) ions in these compounds exist as octahedral $[\text{Au}^{\text{III}}\text{Cl}_6]^{3-}$ ions in a cubic unit cell. That this is inappropriate follows from the fact that the $5d^8$ Au(III) ion in an octahedral field would have a triplet ground state, in contradiction to the observed diamagnetism of these compounds. In support of the M(I),M(III) formulas of these materials, both the Ag and Au salts are described as "astonishingly" jet black in color (758), as expected for a mixed valence salt containing shared ligands. Related materials have been reported in which the two univalent cations of a double formula are replaced by a single divalent cation (242, 244, 758). Thus the triple salts $\text{Cs}_4\text{M}^{\text{II}}\text{Au}_2^{\text{III}}\text{Cl}_{12}$, wherein M is Zn(II) , Pd(II) , Cd(II) , Hg(II) , and Cu(II) , have been prepared, but

their colors are little different than the sum of the colors of the $M(II)$ and $Au(III)$ ions.

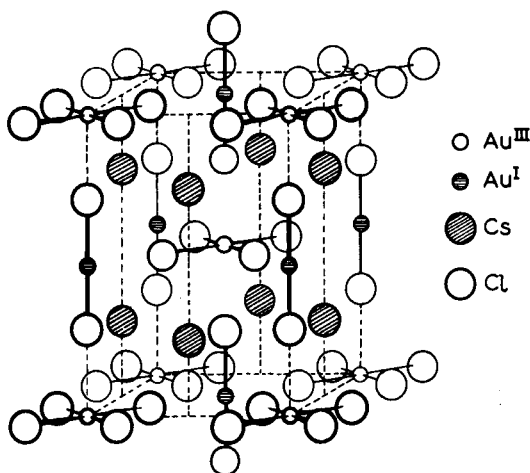
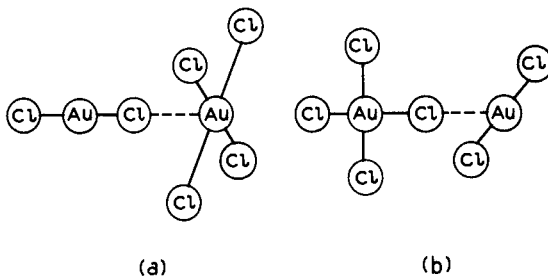


FIG. 38. The tetragonal unit cell proposed by Elliott and Pauling (220) for $Cs_2Au^IAu^{III}Cl_6$.

The black color of $Cs_2Au^IAu^{III}Cl_6$ undoubtedly arises from the class II mixed valence interaction between the $[Au^{III}Cl_4]^-$ and $[Au^ICl_2]^-$ groups. As can be seen from Fig. 38, there are two relative orientations of these groups in the crystal, redrawn below as configurations (a) and (b):



Regardless of the geometric orientations of the groups, the optical electron in the mixed valence transition can safely be regarded as originating in the axially symmetrical dz^2 orbital of the $[Au^ICl_2]^-$ ion and terminating in the $dx^2 - y^2$ orbital of the $[Au^{III}Cl_4]^-$ ion. As explained in Section II, class II mixed valence systems are characterized by a non-zero value of α , which means that the donor and acceptor orbitals must have a nonzero overlap. Inasmuch as this is the case for the chromophore

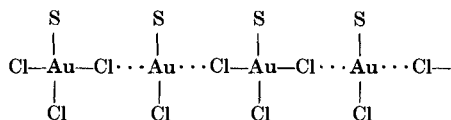
configuration (b), but not for (a), we must assume that it is configuration (b) which is responsible for the mixed valence absorption in $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6$, and that this absorption will be polarized in the ab plane.

Preliminary spectra of both $\text{Cs}_2\text{AgAuCl}_6$ and $\text{Cs}_2\text{AuAuCl}_6$ (595) show the mixed valence transition as a rather weak but distinct feature at $15,500\text{ cm}^{-1}$ followed by a stronger absorption centered at $23,500\text{ cm}^{-1}$, having the opposite polarization. The latter band is also found at $23,500\text{ cm}^{-1}$ in the salt $\text{CsAu}^{\text{III}}\text{Cl}_4$ and is due no doubt to the $[\text{Au}^{\text{III}}\text{Cl}_4]^-$ ion. Since Yamada and Tsuchida (798) report that the visible absorption of the triple salts is polarized along the c axis, perpendicular to the planes of the $[\text{Au}^{\text{III}}\text{Cl}_4]^-$ ions, the $23,500\text{ cm}^{-1}$ band must be polarized in the $[\text{Au}^{\text{III}}\text{Cl}_4]^-$ plane. The fact that the absorption spectra are polarized in Wells' salt also argues for the Elliott and Pauling tetragonal unit cell, and against the cubic cell proposed by Ferrari. However, the disagreement between the predicted ab polarization of the first mixed valence absorption band in $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6$ and the observed c polarization is still a puzzle requiring further research.

Yamada and Tsuchida (710, 799) also report the polarized crystal spectrum of an ammonium salt of composition $(\text{NH}_4)_3\text{Ag}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_7$, which has a spectrum much like that mentioned above for $\text{Cs}_2\text{Ag}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6$, i.e., two bands, centered at $18,000\text{ cm}^{-1}$ and $23,500\text{ cm}^{-1}$, with opposite polarizations. The spectral similarities suggest that the ammonium salt also contains $[\text{Ag}^{\text{I}}\text{Cl}_2]^-$ and $[\text{Au}^{\text{III}}\text{Cl}_4]^-$ groups sharing halide ions.

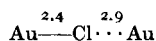
The syntheses of the bromide (241) and iodide (246) salts of the $\text{M}_2(\text{Ag}^{\text{I}}, \text{Au}^{\text{I}})\text{Au}^{\text{III}}\text{X}_6$ mixed valence system have been reported but little is known of them other than that they are black, as expected. According to Ferrari and Cecconi (241), the salt $\text{Cs}_2\text{AgAuBr}_6$ is only an end member in a series of general composition $\text{Cs}_2\text{Ag}_y\text{Au}_{(1-y)/3}\text{AuBr}_6$, as is the corresponding chloride $\text{Cs}_2\text{AgAuCl}_6$.

The properties of an interesting mixed valence compound of gold involving dibenzylsulfide as ligand have been described in detail (84). The compounds $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SAuCl}_2$ and $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SAuBr}_2$ are diamagnetic, have molecular weights in bromoform or benzene equal to those of the formulas as written above, and are nonconducting solutes in nitrobenzene. Solution of the crystal structure revealed $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SAuCl}_2$ to be composed of equal parts of the two neutral species $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SAu}^{\text{I}}\text{Cl}$ and $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SAu}^{\text{III}}\text{Cl}_3$, having the mutual orientation:

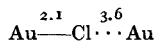


Along the chain direction in this structure, the Au—Cl distance is about 2.1 Å and Au···Cl is about 3.6 Å, but the chains are stacked in such a way in the crystal that the intrachain chloride appears crystallographically to be disordered between Au—Cl and Au···Cl. The structure of the dibromide is closely related, and a dibenzylsulfide gold diiodide has also been prepared (671) but not investigated crystallographically.

As both the component complexes, the monohalo- and the trihalo-gold dibenzylsulfide, can be prepared separately, it is not surprising that the dihalide can be prepared by mixing the components and that the dihalide dissolves to yield the component complexes. There does not appear to be much mixed valence interaction in spite of the bridging chloride ions, for the color of the dihalide is not very different from that of the trihalide, $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SAuBr}_3$ being ruby red and $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SAuBr}_2$ being brown. The reason why Wells' salt is black, whereas the dibenzylsulfides have no apparent mixed valence color, may be related to the fact that in Wells' salt the distances (in angstroms) within the chromophoric grouping are



whereas in the dibenzylsulfides they are

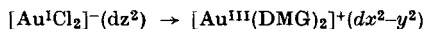


Thus, by comparison, the chlorine is not really bridging in the dibenzylsulfides, and the system is more class I than is Wells' salt.

$[\text{Au}^{\text{III}}(\text{DMG})_2][\text{Au}^{\text{I}}\text{Cl}_2]$, where DMG is the dimethylglyoxime mono-anion, is another mixed valence complex of gold containing an organic ligand. This complex, first synthesized by Rundle (611), was found by him to contain linear chains of $\text{Au}(\text{III}) \cdots \text{Au}(\text{I}) \cdots \text{Au}(\text{III})$ ions having the internal structure shown in Fig. 39. The Au(I)-Au(III) separation in the chain is 3.26 Å.

The polarized absorption spectrum of $[\text{Au}^{\text{III}}(\text{DMG})_2][\text{Au}^{\text{I}}\text{Cl}_2]$ has been recorded (798, 801), and it is interesting to compare it with similar spectra of single crystals of $\text{CsAu}^{\text{III}}\text{Cl}_4$ (799). The spectra show what appear to be only minor differences, suggesting that in both cases the spectrum can be attributed to Au(III) ions in square planar coordination, and that there is no visible mixed valence absorption in $[\text{Au}^{\text{III}}(\text{DMG})_2][\text{Au}^{\text{I}}\text{Cl}_2]$. That this is so seems reasonable, considering the very large difference in the ligand fields at the two gold sites, and also from the fact that, given the geometrical arrangement shown above, the highest-energy, filled orbital of $[\text{Au}^{\text{I}}\text{Cl}_2]^-$, d_{z^2} , is orthogonal to the lowest-energy,

unfilled orbital of $[\text{Au}(\text{DMG})_2]^+$, $dx^2 - y^2$, as in configuration (a) of $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6$, above. The symmetry of the orbitals thus makes the



optical transition forbidden, and the system belongs to class I, its amber-red color being merely that of the $[\text{Au}^{\text{III}}(\text{DMG})_2]^+$ ion.

There is only one example of a mixed valence gold oxide in the literature. Lux and Niedermaier (469) report that the dissolution of metallic gold in molten KOH in a dry O_2 atmosphere leads to the formation of a deep blue polynuclear complex containing approximately

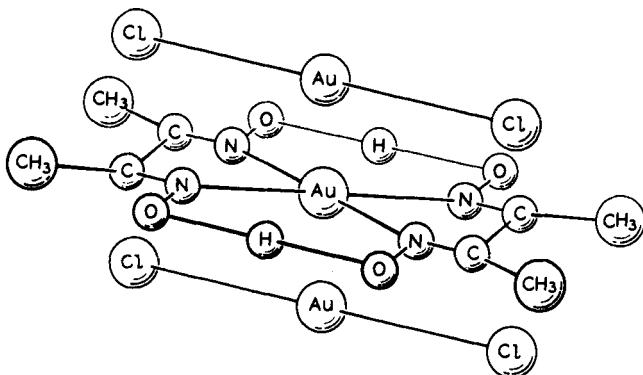


FIG. 39. The class I crystal structure of $[\text{Au}^{\text{III}}(\text{DMG})_2]^+[\text{Au}^{\text{I}}\text{Cl}_2]^-$ (611).

equal amounts of Au(I) and Au(III), as determined spectrophotometrically. Analogous complexes also were said to result in aqueous solution, but there is no evidence for their structure in either case.

R. GALLIUM

Gallium, indium, and thallium are all found in a univalent and a trivalent oxidation state. Although this simple generalization at first appears challenged by the existence of several halides of the composition MX_2 , the possibility that they are $\text{M}(\text{I}), \text{M}(\text{III})$ mixed valence compounds rather than compounds of $\text{M}(\text{II})$ is a good one. The exact constitution of these salts has been a matter of recent interest, and has been approached from a number of directions.

Klemm and Tilk (426) argued that, unlike the diamagnetic $\text{M}^{\text{I}}\text{X}$ and $\text{M}^{\text{III}}\text{X}_3$ salts, $\text{M}^{\text{II}}\text{X}_2$ compounds will be paramagnetic provided the $\text{M}(\text{II})$ ions are not dimerized. Their susceptibility measurements on GaCl_2 and InCl_2 showed that these compounds are diamagnetic and, therefore, are either dimerized like the Hg_2^{2+} ion or are $\text{M}(\text{I}), \text{M}(\text{III})$ mixed valence

compounds. GaI_2 was later shown also to be diamagnetic (148). The first unambiguous structural evidence on the nominally divalent gallium salts was presented by Woodward, Garton, and Roberts, whose Raman spectra of molten GaCl_2 clearly showed the presence of large amounts of the $[\text{Ga}^{\text{III}}\text{Cl}_4]^-$ ion, as recognized from earlier solution work on GaCl_3 in HCl solution (795). On the basis of this, the melt was held to be that of the salt $\text{Ga}^{\text{I}}[\text{Ga}^{\text{III}}\text{Cl}_4]$. This conclusion is also in accord with the high ionic conductivity of the melt (336) and the high resistivity (4.5×10^7 ohm cm) of solid GaCl_2 .

Any doubt still remaining as to the mixed valence nature of GaCl_2 was removed by the determination of the GaCl_2 crystal structure (269).

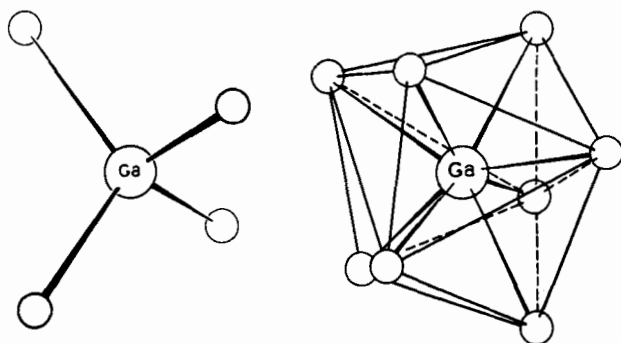


FIG. 40. The coordination about the $\text{Ga}(\text{III})$, *left*, and $\text{Ga}(\text{I})$ ions, *right*, in crystalline $\text{Ga}^{\text{I}}[\text{Ga}^{\text{III}}\text{Cl}_4]$.

In crystalline GaCl_2 , half of the gallium ions are surrounded tetrahedrally by chloride ions with $\text{Ga}-\text{Cl}$ distances equal to 2.19 Å, and are undoubtedly trivalent, whereas the other half of the gallium ions, presumably univalent, are surrounded by an irregular dodecahedron of eight chloride ions with $\text{Ga}-\text{Cl}$ distances equal to 3.2–3.3 Å (Fig. 40). The unusually large $\text{Ga}^{\text{I}}-\text{Cl}$ distance is due perhaps to the $\text{Cl}-\text{Cl}$ repulsions. GaCl_2 is thus an extreme example of class I mixed valence and, as expected, the crystal is a diamagnetic insulator having essentially the color of the constituent ions. Measurement of the vapor pressure above molten Ga_2Cl_4 suggests the presence of large quantities of genuinely divalent $\text{Ga}^{\text{II}}\text{Cl}_2$ (454), as does the optical spectrum of the vapor (751). A colorless substance of the composition Ga_4Cl_9 has been uncovered by a phase study of the $\text{Ga}-\text{GaCl}_3$ system (559); if it is a mixed valence compound it must have $\text{Ga}(\text{III})/\text{Ga}(\text{I})$ equal to 5/3.

Experiments similar to those described for Ga_2Cl_4 have been directed at elucidating the structure of GaBr_2 . Inasmuch as the Raman spectrum

of molten GaBr_2 shows the presence of large amounts of the $[\text{Ga}^{\text{III}}\text{Br}_4]^-$ ion (796), the melt has a conductance typical of a molten salt consisting of a large anion and a small cation (312), and solid GaBr_2 is colorless and diamagnetic, the compound must be formulated as $\text{Ga}^{\text{I}}[\text{Ga}^{\text{III}}\text{Br}_4]$.

Relatively little is known about the mixed valence iodides of gallium. Diamagnetic, yellow GaI_2 was reported by Corbett and McMullan (148) and later by Chadwick *et al.* (131) as being most likely $\text{Ga}^{\text{I}}[\text{Ga}^{\text{III}}\text{I}_4]$, in accord with the formulation of the corresponding chloride and bromide. The electrical conductivities and vapor pressures of the molten iodides of gallium have been studied by Riebling and Erickson (585, 586), who found that, whereas GaI_3 is a low conductance molecular melt, GaI_2 is highly ionic and probably contains the ions $(\text{Ga}^{\text{I}})^+$ and $[\text{Ga}^{\text{III}}\text{I}_4]^-$. Chadwick *et al.* (131) also described the intensely colored, diamagnetic compounds Ga_2I_3 and Ga_3I_5 as being mixed valence materials with formulas $\text{Ga}_2^{\text{I}}\text{Ga}^{\text{III}}\text{I}_6$ and $\text{Ga}_2^{\text{I}}\text{Ga}^{\text{III}}\text{I}_5$, respectively.

There appear to be no lower gallium fluorides (337). In this regard, it is pertinent to note that, unlike the tetrahedral coordination found for the $\text{Ga}(\text{III})$ ion in the Ga_2X_4 salts having $\text{X} = \text{Cl}, \text{Br}, \text{or I}$, the complex fluorides of trivalent gallium are octahedrally coordinated (574), as expected from the radius ratio.

Chemically, the salts Ga_2Cl_4 and Ga_2Br_4 are soluble in benzene from which solvent they can be recrystallized as the mixed valence complexes $\text{Ga}_2\text{X}_4 \cdot \text{C}_6\text{H}_6$ (130). Dielectric measurements on solutions of Ga_2Cl_4 in benzene are interpreted as showing the formation of the ion pair $[\text{Ga}^{\text{I}}]^+[\text{Ga}^{\text{III}}\text{Cl}_4]^-$ ($\mu = 8.9$ Debye units) at low concentrations, with aggregation at higher concentrations (504). Addition of basic ligands such as organic amines, ethers, sulfides, selenides, or arsines to the benzene solution of GaCl_2 leads to the immediate precipitation of $[\text{Ga}^{\text{I}}\text{L}_4]^+[\text{Ga}^{\text{III}}\text{Cl}_4]^-$, where L is a monodentate ligand (9, 96, 657). As expected, these mixed valence compounds are all diamagnetic and colorless, except for the 2,2'-dipyridyl complex which is red (9). As the dipyridyl ligands are relatively easily reduced, and $\text{Ga}(\text{I})$ is easily oxidized, the red color of the complex may be due to a Ga^{I} -dipyridyl charge transfer absorption. Water immediately hydrolyzes GaCl_2 to a dark brown substance analyzed to be $\text{GaClOH} \cdot \frac{1}{2}\text{H}_2\text{O}$ (97). If this substance indeed is a mixed valence material, it would appear to be one of the few reported which show a $\text{Ga}(\text{I}), \text{Ga}(\text{III})$ mixed valence absorption band in the visible region. Dehydration of this substance gives colorless GaClOH , analogous to the GaClSH formed by addition of H_2S to a GaCl_2 solution in benzene (97).

Although in the case of the nominally divalent gallium halides, GaX_2 , the possibility of spin pairing by dimer formation ($\text{X}_2\text{Ga}-\text{GaX}_2$)

is never realized, it is interesting to note, however, that, in the diamagnetic substances GaS and GaSe, dimer pairs of gallium ions are found, each gallium having three sulfide or selenide ions and one other gallium ion about it in a tetrahedral arrangement (330). Inasmuch as the gallium ions in these structures are equivalent, the systems are technically class III-A mixed valence, although in fact it is just as correct to consider them simply as divalent gallium compounds.

S. INDIUM

Unlike the situation with gallium, almost nothing has been done toward elucidating the structures of the mixed valence compounds of indium. Aside from a few isolated reports of magnetic susceptibility and qualitative reports of color, the only works of mixed valence interest are phase studies showing the existence of certain mixed valence indium halides.

The halides InF_2 (337), InCl_2 (6, 94, 144, 234), InBr_2 (94, 744), and InI_2 (567) have been described briefly. The first three have been shown to be diamagnetic, as would be expected for either $\text{In}^{\text{I}}[\text{In}^{\text{III}}\text{X}_4]$ salts or $\text{X}_2\text{In}-\text{InX}_2$ dimers, but not for $\text{In}^{\text{II}}\text{X}_2$ itself. Although the close analogy with the gallium compounds suggests that the InX_2 compounds are $\text{In}(\text{I}), \text{In}(\text{III})$ mixed valence salts, the possibility that the $\text{In}(\text{II})$ halides are really dimers is worth considering on the basis of the colors of the compounds involved (427). The trihalides InCl_3 and InBr_3 are colorless, whereas the monohalides InCl and InBr are, respectively, yellow-red and carmine red. If the InCl_2 and InBr_2 salts are class I mixed valence compounds, one would expect them to be red, the sum of the colors of their constituent ions. In fact, the dichloride and dibromide of indium are colorless, suggesting either that these compounds contain no $\text{In}(\text{I})$ and are therefore to be taken as dimers, or more probably that the $\text{In}(\text{I})$ in InX is complexed by halide ion and has either a ligand \rightarrow metal charge transfer transition or an atomic $5s^2 \rightarrow 5s^15p^1$ transition in the visible, but is complexed much more weakly in the InX_2 compounds, so that these transitions fall in the ultraviolet. It is to be remembered that, in $\text{Ga}^{\text{I}}[\text{Ga}^{\text{III}}\text{Cl}_4]$, the $\text{Ga}(\text{I})$ cation is essentially uncomplexed. The lack of color in the substance $\text{In}^{\text{I}}[\text{Al}^{\text{III}}\text{Cl}_4]$, however, does make the lack of color in In_2Cl_4 (144) rather less surprising. If InBr_2 is a mixed valence compound, it at first seems likely that the $\text{In}(\text{III})$ would be found in the crystal as $[\text{In}^{\text{III}}\text{Br}_4]^-$, just as is found in GaBr_2 . However, it is to be noted that, unlike the corresponding $\text{Ga}(\text{III})$ salt (794), InBr_3 in concentrated HBr does not form the tetrahedral tetrahalide ion $[\text{InBr}_4]^-$,

although such a species is said to form in an ether extract of the aqueous solution (793). Burns and Hume, on the other hand, have found spectrophotometrically an indium bromide species in aqueous solutions of high Br^- content having $\text{Br}/\text{In} = 4$, which they suggest is the octahedral ion $[\text{InBr}_4(\text{H}_2\text{O})_2]^-$ (114).

The phase diagram of the In-InCl_3 system has been studied rather extensively by a number of investigators, and a large number of mixed valence compounds have been uncovered. To date the list includes InCl_2 (mentioned above), In_4Cl_6 (144, 230, 231, 234, 558), In_4Cl_5 (144), In_4Cl_7 (144, 231), In_5Cl_9 (558), and several other possibilities of undetermined composition. In the In-InBr_3 system, the corresponding bromides In_4Br_6 and In_4Br_7 as well as In_5Br_7 have been found to exist (94, 511, 744). Of the compounds on this list, Clark *et al.* (144) propose that InCl_2 is not a genuine compound, but simply a mixture of In_4Cl_6 and InCl_3 , whereas Chadwick *et al.* (131) claim to have "reestablished the existence" of InCl_2 on the basis of a redetermination of the indium chloride phase diagram. On the other hand, Fedorov and Fadeev (234) can find no evidence for In_4Cl_5 , a compound claimed by Clark *et al.* Surprisingly, In_4Cl_7 exists as such in the gas phase over solid In_4Cl_7 at 450°C , according to the results of a vapor pressure study.

Clark *et al.* (144) present an interesting geometrical argument for the existence of certain but not all indium halides of a given stoichiometry. In_4Cl_6 is formulated as $\text{In}_3^{\text{I}}[\text{In}^{\text{III}}\text{Cl}_6]$, the radius ratio (565) of $\text{In}(\text{III})$ and Cl^- being such as to allow octahedral coordination as well as tetrahedral coordination. Thus, the salt $\text{In}^{\text{I}}[\text{In}^{\text{III}}\text{Cl}_4]$ also forms. In the case of the lower indium iodides, the radii are such that tetrahedral $[\text{In}^{\text{III}}\text{I}_4]^-$ can be realized but octahedral $[\text{In}^{\text{III}}\text{I}_6]^{3-}$ cannot, in agreement with Peretti's (567) finding that In_2I_4 is the only mixed valence lower iodide of indium. As Clark *et al.* point out, both tetrahedral $[\text{In}^{\text{III}}\text{Br}_4]^-$ and octahedral $[\text{In}^{\text{III}}\text{Br}_6]^{3-}$ ions can meet the radius ratio test, so that both InBr_2 and In_4Br_6 should exist, as they do (744). Applying these tests to the In_4X_7 series, it would appear that these substances contain octahedral $[\text{In}^{\text{III}}\text{X}_6]^{3-}$ ions, since they are found as the chloride and bromide, but not the iodide.

There are reports of the synthesis of mixed metal halides having compositions equivalent to several of the mixed valence halides mentioned above. Thus, corresponding to $\text{In}_3^{\text{I}}[\text{In}^{\text{III}}\text{Cl}_6]$, the salts $\text{Ag}_3^{\text{I}}[\text{In}^{\text{III}}\text{Cl}_6]$ and $\text{Tl}_3^{\text{I}}[\text{In}^{\text{III}}\text{Cl}_6]$ have been reported (235), and the salt $\text{In}^{\text{I}}[\text{Al}^{\text{III}}\text{Cl}_4]$ (144) corresponds to $\text{In}^{\text{I}}[\text{In}^{\text{III}}\text{Cl}_4]$.

Both In_2I_4 and In_2Br_4 can be ammoniated to yield the compounds $\text{In}_2\text{X}_4 \cdot 6\text{NH}_3$ and $\text{In}_2\text{X}_4 \cdot 8\text{NH}_3$ (131, 432). The fact that the iodide ammoniates are bright red and the bromides orange-red as compared

with the colorless ammonia-free In_2X_4 compounds is interesting, but perhaps not totally unexpected in view of the red color of the $\text{In}^{\text{I}}\text{X}$ compounds. However, because of the supposed instability of the $[\text{In}^{\text{I}}(\text{NH}_3)_6]^+$ cation, it has been argued that the ammoniates are $\text{In}(\text{II})$ dimers rather than mixed valence materials (431).

There is little evidence about the colors of the indium halides. If the indium dihalides are mixed valence, there is very little tendency toward class II behavior as evidenced by their lack of color. It is important to note that the dihalides of both gallium and indium can appear colored due to trace impurities of the corresponding monohalides. Thus, the report that In-InCl_3 mixtures give dark red to black, transparent crystals in the composition range 50–100 mole % InCl_3 (558) is of questionable importance to our discussion. Inasmuch as, in a class II system, the electron affinity of the oxidized species in the ground state is of consequence to the development of a mixed valence color in the visible region, the lack of color in the GaX_2 and InX_2 systems may be attributable in part to a low electron affinity of the $\text{Ga}(\text{III})$ and $\text{In}(\text{III})$ species. This suggestion is compatible with the very high energy of the ligand-to-metal charge transfer absorption in the $[\text{In}^{\text{III}}\text{Cl}_4]^-$ ($46,500\text{ cm}^{-1}$) (615) and $[\text{In}^{\text{III}}\text{Br}_4]^-$ ($42,600\text{ cm}^{-1}$) (114) ions. Spectra of InCl_2 , InBr_2 , and InI_2 in the gas phase have been reported (762), but the absorbing species are triatomic and most likely are the genuine divalent halides.

The action of H_2 and HCN on indium metal has been found to lead to the formation of $\text{In}(\text{CN})_2$, a white solid formulated as $\text{In}^+[\text{In}(\text{CN})_4]^-$ (293).

T. THALLIUM

In contrast to gallium and indium, a very large number and variety of thallium mixed valence compounds have been synthesized, although no more is known of their constitution than has been determined in the cases of gallium and indium. Crystallographically, the structures of three mixed valence thallium compounds have been solved, with surprising results. TlBr_2 (350) is isostructural with $\text{Ga}^{\text{I}}[\text{Ga}^{\text{III}}\text{Cl}_4]$ (269), discussed above. Thus, in TlBr_2 there are tetrahedral $[\text{Tl}^{\text{III}}\text{Br}_4]^-$ ions having Tl-Br distances equal to 2.51 \AA , and $\text{Tl}(\text{I})$ ions in irregular dodecahedral sites having eight bromines at a mean distance of 3.46 \AA . Surprisingly, in the isostructural diamagnetic compounds TlS and TlSe (329, 412) there are two types of thallium, one determined to be $\text{Tl}(\text{III})$ in tetrahedral coordination with, for example, the Tl-Se distance equal to 2.68 \AA , and one being $\text{Tl}(\text{I})$ having eight Se atoms as nearest neighbors,

with Tl—Se distances equal to 3.42 Å! In fact, in the gallium, indium, thallium group, only four mixed valence compounds have been studied crystallographically, and each has as its structural units the $M^{III}X_4$ tetrahedron and the M^IX_8 dodecahedron. More structures must be solved before one can see how general this combination of coordinations is in the mixed valence compounds of these elements. A preliminary investigation of Tl_2Cl_3 has shown it to have a complex structure with 32 molecules per cell (327).

The thallium halides Tl_2X_3 are probably better written as $Tl_3^I[Tl^{III}X_6]$. That Tl_4Cl_6 is not a class III mixed valence compound is indicated by the radiochemical exchange experiments of McConnell and Davidson (468, 771), which demonstrated that Tl_4Cl_6 , synthesized from radioactive $^{204}TlCl_3$ and inactive $TlCl$ in HCl solution, when decomposed and analyzed, yielded almost all its radioactivity as $Tl(III)$. This result was interpreted as showing that the $Tl(I)$ and $Tl(III)$ ions of crystalline Tl_4Cl_6 are nonequivalent. The same conclusion was reached following similar experiments with Tl_4Br_6 .

A study of the thallium NMR spectra of several thallium compounds including $TlCl_2$ and $TlBr_2$ has been reported (603). It was found that, as expected from the crystal structure of $Tl^I[Tl^{III}Br_4]$, the molten tetrachloride and tetrabromide yield ionic melts which showed two thallium resonances, the one due to $Tl(I)$ being at higher field than that due to $Tl(III)$. As the temperature of the melt was raised, the two lines fused into one, indicating exchange between the two thallium species with an average lifetime of about 10^{-5} sec at $500^\circ K$. In similar experiments, crystalline and molten $Tl(I)$ salts showed only one line at all temperatures up to $720^\circ K$.

A study of the $TlCl$ – $TlCl_3$ phase diagram by Fadeev and Fedorov (232) demonstrated the existence of only two mixed valence compounds, Tl_2Cl_4 and Tl_4Cl_6 , the first being described by earlier investigators as colorless to yellow, and the second as yellow to red, depending upon the mode of preparation. It is to be noted that $TlCl$ and $TlCl_3$ are colorless and that Tl_4Cl_6 is colorless at the temperature of liquid air. Thus the maximum of the Tl_4Cl_6 mixed valence transition must lie in the ultra-violet region. The corresponding mixed valence bromides, Tl_2Br_4 and Tl_4Br_6 , are respectively yellow and red (54, 55).

Reaction of I_2 with TlI leads to the formation of black Tl_3I_4 (55, 448, 449, 656), a mixed valence iodide having a metal/halogen ratio unlike any reported in the gallium or indium halides. Sharpe (656) proposes $[Tl_2]^+[Tl^{III}I_4]^-$ as the assignment of valences in Tl_3I_4 , but $Tl_5^ITl^{III}I_8$ seems more reasonable. A third possibility exists that it is the iodine that is mixed valence and not the thallium, i.e., Tl_6I_8 is $Tl_6^II_5I_5^-(I_3^-)$.

The deep black color of this substance is certainly consistent with a composition containing triiodide or higher polyiodide ions. This third possibility seems attractive since I^- is known to reduce Tl(III) to Tl(I) with the formation of I_3^- , thus leading one to expect that thallium iodides will not contain Tl(III), but may contain I_3^- or higher polyiodides. Such an explanation is similar to that given by Lawton and Jacobson (456) for some of the antimony halides, which were first thought to be Sb(III), Sb(V) compounds and were later shown by them to be polyhalides of Sb(V).

One finds a similar problem in the assignment of valences in the compound $Tl_3Sb_2Cl_{13}$ (223), which may be taken to be either $Tl_3^I Sb_2^V Cl_{13}$ or $Tl_2^I Tl^{III} Sb^{III} Sb^V Cl_{13}$. The deep black color of this substance argues strongly for the latter formulation, since the mixed valence absorption of Sb(III), Sb(V) halides lies at very low energy (see subsection X on antimony). In the same way, the dark violet compound $Tl_2Sb_2Cl_{10}$ (223) is more likely $Tl_2^I Sb^{III} Sb^V Cl_{10}$ than $Tl^I Tl^{III} Sb^{III} Cl_{10}$. Similar problems formally exist in the compounds $InTl_2Cl_5$ (557), $InTl_3Cl_6$ (557), and $TlGaCl_4$ (236) although their reactivity toward water should show immediately which of the ions is univalent and which is trivalent.

Evidence for the mixed valence interaction between Tl(I) and Tl(III) in perchloric acid solution was sought by McConnell and Davidson (495) in the spectral region 33,000–42,000 cm^{-1} , but no mixed valence absorption was found. However, their solution contained no halide ions which might act as bridging groups in a mixed valence complex. In this regard, it is perhaps pertinent to note that the charge exchange between Tl(I) and Tl(III) ions is considerably accelerated by the presence of bridging anions in the solution (104, 105, 339, 774).

Peroxide oxidation of an alkaline thallous salt solution precipitates TlO as an unstable, deep blue material (575, 617), which has been formulated as $Tl_2^I Tl_2^{III} O_4$. Scatturin *et al.* (618) report on various oxides TlO_x , having $x > 1.5$, which were said to contain Tl(I), Tl(III), and Tl(IV), and which had numerous reflection maxima in the 10,000–25,000 cm^{-1} region.

A fast riffle through the thallium volume of Gmelin's *Handbuch* (291) uncovers the following mixed valence compounds: $TlN_3 \cdot Tl(N_3)_3$ (yellow needles yielding Tl(I) and Tl(III) in solution), $2TlNO_3 \cdot Tl(NO_3)_3$ (colorless prisms blackening in moist air), $Tl_2SO_4 \cdot Tl_2(SO_4)_3$ (colorless crystals), $5Tl_2SO_4 \cdot Tl_2(SO_4)_3$ (pale yellow crystals) and the corresponding selenates $Tl_2SeO_4 \cdot Tl_2(SeO_4)_3$ (colorless crystals) and $5Tl_2SeO_4 \cdot Tl_2(SeO_4)_3$ (yellow crystals), $Tl_2Cl_2SO_4$ and $Tl_2Br_2SO_4$ (both yellow), $Tl_2Cl_2SeO_4$ and $Tl_2Br_2SeO_4$ (both yellow), $TlCN \cdot Tl(CN)_3$ (colorless crystals yielding Tl(I) and Tl(III) in base), $Tl_2C_2O_4 \cdot$

$\text{Ti}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$ (colorless crystals), $\text{Ti}_2\text{C}_2\text{O}_4 \cdot \text{Ti}_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{NH}_3$, and $[\text{NH}_4, \text{Ti}(\text{I})]_3\text{Ti}(\text{III})(\text{SO}_4)_3$, a mixed crystal. The compound believed to be $\text{Ti}_2\text{Cl}_4 \cdot 2\text{NOCl}$ (28) is really $\text{TiCl}_3 \cdot \text{NOCl}$ (561).

U. TIN

The interesting work of Davidson and co-workers on the interaction between the Sb(III) and Sb(V) ions in concentrated HCl solution was later extended by them to the Sn(II), Sn(IV) system. It was found that mixing Sn(II) and Sn(IV) solutions in concentrated HCl results once more in a mixed valence absorption, although much further in the ultraviolet than was found with antimony (770). As before, the intensity of the mixed valence absorption was proportional to the product of the concentrations of Sn(II) and Sn(IV), showing that in the ground state, at least, the colored species was an Sn(II), Sn(IV) dimer and not an ion containing Sn(III). In addition to the composition study, an investigation was made of the thermal isotope exchange rate (103, 771) and the effect on this of irradiation in the region of the mixed valence absorption (164). It was found that the exchange reaction, which was bimolecular, proceeded in the dark at a rate sufficiently slow to demonstrate that the mixed valence dimer was unsymmetrical in the ground state if, indeed, it had anything at all to do with the exchange process. More interestingly, it was found that irradiation of the solution in the region of the mixed valence absorption ($25,000\text{--}30,000\text{ cm}^{-1}$) at ca. 2°C substantially enhanced the exchange rate, the quantum yield of the photochemically induced exchange being estimated to be 0.2. Since a quantum yield of 0.5 is expected for such a three-level system if the excited state is symmetrical (class III-A), the significantly lower yield may be taken as evidence for an unsymmetrical upper state, as well.

The quantum yield can be interpreted within the framework of the mixed valence model in the following way. Although there is no evidence for the geometry or composition of the unsymmetrical Sn(II), Sn(IV) complex, for the sake of illustration it is represented by configuration A in Fig. 41. The starred atom is radioactive. On excitation in the mixed valence absorption band, an electron is transferred from left to right and both tin atoms become Sn(III) with a simultaneous rearrangement of ligands being quite probable, but in any case not to a symmetrical geometry (configuration B). On relaxation from the excited state B, either the system can go back to the original ground state A by transfer of an electron from right to left, or a second electron may be transferred again from left to right giving the exchanged configuration C. The

quantum yield of photoinduced exchange is thus seen to be related to the relative probabilities of transitions to the terminal states A and C from the intermediate state B. A relative probability of four to one for the $B \rightarrow A$ and $B \rightarrow C$ transitions would then explain the quantum yield of 0.2 observed for the Sn(II),Sn(IV) exchange. More precisely, the intermediate state B is really two states, one a spin singlet and one a spin triplet, and the quantum yield will depend upon the relative rates of reaching A and C from both of the B surfaces, and also on the rate of excited state singlet-triplet intersystem crossing. By whatever mechanism the relaxation from the intermediate state proceeds, it seems clear that Franck-Condon factors play an important role in determining the relative probabilities involved in the photoinduced exchange

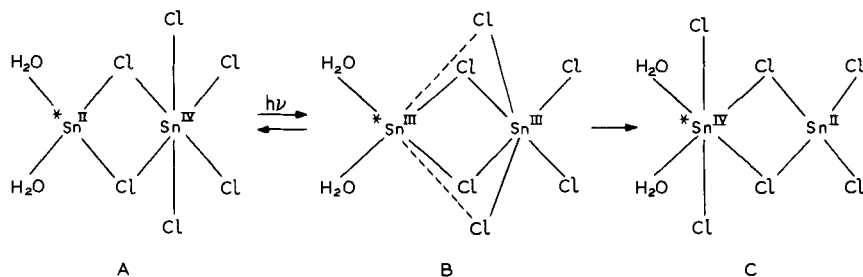


FIG. 41. Configurations involved in photochemical isotope exchange in the three-level system $\text{Sn}_2\text{Cl}_6(\text{H}_2\text{O})_2$.

phenomenon; that terminal state with the larger Franck-Condon overlap with the intermediate state will be favored.

The mixed valence tin oxide Sn_3O_4 has been identified in various thermochemical studies of SnO (678, 679). However, preliminary work on the powder pattern of Sn_3O_4 showed that it could not be indexed as tetragonal (272), this being the crystal system of the analogous lead compound Pb_3O_4 . Similar studies in the Sn-S system (7) indicate the formation of Sn_2S_3 and Sn_3S_4 , mixed valence compounds which may be related to the mixed valence lead oxides of the same stoichiometry. The preparation of the oxide $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}\text{O}_6$ by heating SnO at 475°C is described by Decroly and Ghodsi (183).

V. LEAD

The study of the mixed valence oxides of lead is confused by a number of reports on substances thought to be unique compounds, but which may well be mixtures. The mixed valence oxides of lead which

have been authenticated to date have been described most recently by White and Roy (769), who find experimental evidence for Pb_3O_4 , Pb_2O_3 , and $\text{Pb}_{12}\text{O}_{19}$. Byström (121) also discusses the structures and compositions of these compounds and others of less certain stoichiometry.

Pb_3O_4 (red lead) is obtained as transparent scarlet crystals from a solution of PbCO_3 in molten KNO_3 – NaNO_3 flux. According to the X-ray studies of Gross (317) and of Byström and Westgren (118, 122) and the neutron diffraction study of Fayek and Leciejewicz (233), Pb_3O_4 has a class I crystal structure in which lead ions in very different environments

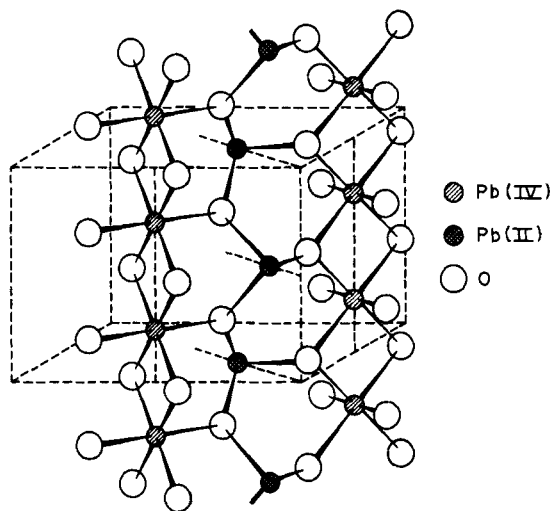


FIG. 42. The class I crystal structure of Pb_3O_4 (756).

share oxide ligands. As shown in Fig. 42, the Pb(IV) ions lie at the centers of oxygen atom octahedra which share edges to form chains and have $\text{Pb(IV)}\text{—O}$ distances equal to 2.15 Å, whereas the Pb(II) are inserted between the $\text{Pb}^{\text{IV}}\text{O}_6$ chains in such a way that each has three oxygen atoms at about 2.2–2.3 Å, the next nearest oxygen neighbor being at 3.0 Å. The O—Pb(II)—O angles are all approximately 90°. Consonant with the class I structure, polycrystalline $\text{Pb}_2^{\text{II}}\text{Pb}^{\text{IV}}\text{O}_4$ has a resistivity of 10^{12} ohm cm (769), and a color (red) which would appear to be just the sum of the colors of $\text{Pb}^{\text{II}}\text{O}$ (red) and $\text{Pb}^{\text{IV}}\text{O}_2$ (red). The bonding and hybridization in Pb_3O_4 have been discussed by Dickens (194).

An anhydrous form of lead sesquioxide, Pb_2O_3 , can be produced by hydrothermal synthesis as large crystals of a lustrous jet black color (143). The striking difference between the colors of Pb_2O_3 and Pb_3O_4 at

first suggests that the lead ion environments are not nearly as dissimilar in Pb_2O_3 as they are in Pb_3O_4 . The structure of Pb_2O_3 has been only partially solved, the all-important positions of the oxygen atoms still being in some doubt (120, 127). It appears that one type of lead atom is at the center of a distorted square with a mean Pb—O distance of 2.1 Å, whereas the second type of lead atom is at the center of a distorted octahedron with four Pb—O distances equal to 2.39 Å, and two additional oxygens at 2.81 Å. If this is so, the two types of lead ion in Pb_2O_3 would seem to form a class I system, judging from our limited experience. On the other hand, the black color of Pb_2O_3 would seem more understandable if it were a class II system. However, the black color may be due to a constituent ion absorption. Because there are two ions of lower valence for every ion of higher valence in Pb_3O_4 , and because the crystal contains twice as many metal ion sites of one type as of the other, the stoichiometry clearly suggests which oxidation states occupy which metal ion sites. Such is not the case in Pb_2O_3 . However, although the question of which oxidation state of lead occupies which type of site in Pb_2O_3 cannot be answered a priori, the bond distances suggest that the Pb(IV) ions are in the distorted square sites and the Pb(II) ions are in the distorted octahedral sites.

The resistivity of Pb_2O_3 is reported as 10^{12} ohm cm, a value which is a composite of bulk resistance, surface resistance, contact resistance, and grain-contact resistance values (769). The fact that the reported resistivities of Pb_2O_3 and class I Pb_3O_4 are of the same order of magnitude demonstrates either the difficulty of divining the significance of resistivities as measured on powders, or that Pb_2O_3 really is a class I system as intimated by its crystal structure. Only further work can decide which is the case.

An experiment widely quoted as refuting the "oscillating valence" concept was preformed by Zintl and Rauch (817) on the mixed valence hydrate $\text{Pb}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. This yellow-orange material was synthesized, using radioactive Pb(II) and inactive Pb(IV) in a way previously shown not to exchange the Pb(II) and Pb(IV) ions. The solid was irradiated for 3 hours and then decomposed, again without exchange, and the two types of lead were separated and then assayed for radioactivity. It was found that, after irradiation and decomposition, the Pb(IV) was only 1.3% as radioactive as the Pb(II). From this, the conclusion was drawn that in this compound, the valences did not oscillate on irradiation with light and, by analogy, that they did not oscillate in any other mixed valence compound. With the advantage of hindsight, one can point out that, although no structure is available for this hydrated oxide, its lack of an intense, low-energy mixed valence color suggests that the

lead ions are in very different environments in the crystal and that, although it is a three-level system (see tin, subsection U), the excited state reached in a mixed valence absorption will always relax to the no-exchange ground state. This will be especially true in crystals where nuclear rearrangements are difficult. Although the Zintl and Rauch experiment performed on $\text{Pb}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ therefore sheds no light on the problem of "oscillating valence," the experimental idea has been used with interesting results by Craig and Davidson (164) in the aqueous Sn(II),Sn(IV) system.

A brown-black mixed valence lead oxide, earlier known as $\alpha\text{-PbO}_x$ (122) and now known to have the stoichiometry $\text{Pb}_{12}\text{O}_{19}$, has been briefly described. A crystal structure, deduced both from a single crystal X-ray study (122) and from studies of the lead-oxygen phase equilibria and powder patterns (12, 769), shows that the structure of $\text{Pb}_{12}\text{O}_{19}$ is derived from that of tetragonal PbO by the insertion of a layer of oxygen atoms between the Pb-O-Pb layers. The result is a face-centered, nominally cubic cell having a small monoclinic distortion in which all lead atoms are in nearly equivalent, cubic, eightfold coordination. Because the lead atoms in $\text{Pb}_{12}\text{O}_{19}$ occupy slightly dissimilar sites (class II), its resistivity will not be metallic, but should be considerably lower than those of Pb_3O_4 and Pb_2O_3 . This expectation is fulfilled, for the resistivity of $\text{Pb}_{12}\text{O}_{19}$ is reported to be eight orders of magnitude smaller than that of Pb_3O_4 and Pb_2O_3 (769).

As expected, orthorhombic PbO is an insulator. Strangely, although $\text{Pb}_{12}\text{O}_{19}$ appears to be a relatively good conductor of electricity, it is to be noted that, according to the data of White and Roy (769), the single valence material $\text{Pb}^{\text{IV}}\text{O}_2$ has a resistivity which is three orders of magnitude smaller still than that of $\text{Pb}_{12}\text{O}_{19}$. However, it is pertinent to note that a sample of analytical reagent grade PbO_2 has been analyzed earlier to be of the composition $\text{PbO}_{1.98} \cdot 0.04\text{H}_2\text{O}$ (117), thus demonstrating that " PbO_2 " may well be nonstoichiometrically mixed valence, although nominally it is not. Byström (121) also reports a nonstoichiometric composition for commercial " PbO_2 ." There are many examples of the difficulty of getting oxide crystals of many metals free of interfering, extraneous oxidation states. Because of this, it is difficult to assess the true meaning of powder conductivities in oxides.

Infrared spectra of the mixed valence oxides are given by Roy and co-workers (768) in a paper concerned primarily with their high pressure-high temperature polymorphism.

The addition of a solution of $[\text{M}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_3$ to an HCl solution containing Pb(IV) precipitates a pale colored Pb(IV) salt, which subsequently evolves Cl_2 to form darkly colored mixed valence chloro-

plumbates(II,IV). The salts $[\text{Co}^{\text{III}}(\text{NH}_3)_6]\text{PbCl}_6$ and $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{H}_2\text{O}]\text{PbCl}_6$ have been investigated by Mori (515), who found them to be diamagnetic. This lack of paramagnetism suggests that, as in the Sb(III),Sb(V) halides, the lead in these compounds is in fact an equimolar mixture of the diamagnetic ions Pb(II) and Pb(IV) . The corresponding chromium salts $[\text{Cr}^{\text{III}}(\text{NH}_3)_6]\text{PbCl}_6$ and $[\text{Cr}^{\text{III}}(\text{NH}_3)_5\text{H}_2\text{O}]\text{PbCl}_6$ are strongly paramagnetic owing to the presence of the Cr(III) ion. This series of four salts present an interesting situation in that the two aquopentammines are pale red, as might be expected for a $\text{Pb}^{\text{II}}\text{Cl}_6$ - $\text{Pb}^{\text{IV}}\text{Cl}_6$ system, but the hexammines are reported to be violet-black. The suggestion is that the two types of salt have rather different crystal structures.

The crystal structure of the black-violet $[\text{Co}^{\text{III}}(\text{NH}_3)_6]\text{PbCl}_6$ was investigated by Atoji and Watanabe (34), who found it to be closely related to that of $[\text{Co}^{\text{III}}(\text{NH}_3)_6]\text{TlCl}_6$, a compound studied by them earlier (748). In the latter substance, the $[\text{TlCl}_6]^{3-}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$ ions form a cubic sodium chloride type lattice with four formula weights per unit cell. Each $[\text{TlCl}_6]^{3-}$ octahedron is surrounded by eight $[\text{Co}(\text{NH}_3)_6]^{3+}$ groups as nearest neighbors and eight $[\text{TlCl}_6]^{3-}$ groups as second nearest neighbors at $2^{1/2}$ times the Co—Tl distance. The powder pattern of the hexachloroplumbate compound was interpreted as showing a cubic cell much like that of the hexachlorothallate, in spite of several lines observed in the former which are not present in the latter. If the hexachloroplumbate is indeed cubic as claimed, then either all lead ions must have the intermediate valence $3+$ and be paramagnetic, or the system is metallic. The situation is completely analogous to the dilemma discussed in the case of the M_2SbX_6 salts, where a cubic structure implied a paramagnetic species, yet the compounds are observed to be diamagnetic. And just as the solution to that dilemma rested on showing that the crystals were in fact tetragonal, not cubic, it seems a good guess that a more careful study of $[\text{Co}(\text{NH}_3)_6]\text{PbCl}_6$ will show that it too is tetragonal, with valences trapped as $\text{Pb}^{\text{II}}\text{Cl}_6$ and $\text{Pb}^{\text{IV}}\text{Cl}_6$. Indeed, some of the weak lines in the powder pattern of the lead compound index as reflections not allowed in the cubic space group reported for it (180).

If the valences are really trapped, then the PbCl_6 sublattice of $[\text{Co}(\text{NH}_3)_6]\text{PbCl}_6$ is probably related quite closely to the SbBr_6 superlattice of $(\text{NH}_4)_2\text{SbBr}_6$ (Fig. 46). The analogy between the lead and antimony mixed valence halides can be carried further, since Sb(III) and Sb(V) are isoelectronic with Pb(II) and Pb(IV), except for a difference in principal quantum number, and hence should have quite similar mixed valence spectra. The powder reflection spectrum of $[\text{Co}(\text{NH}_3)_6]\text{PbCl}_6$ (shown in Fig. 43) contains intense bands at lower frequencies

than the absorptions of the component ions, which should probably be assigned as class II mixed valence transitions, although in this case some care is needed to distinguish the mixed valence absorption from absorption due to the $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion.

In this regard, it is of interest that the narrow band at $36,300\text{ cm}^{-1}$ corresponds very closely in energy to the $^1S_0 \rightarrow ^3P_1$ ($6s^2 \rightarrow 6s^16p^1$) transition of the $\text{Pb}(\text{II})$ ion in KCl (807). Again, as with the corresponding antimony halides, the frequency and intensity of the mixed valence transition in the chloroplumbates(II, IV) would appear to depend upon

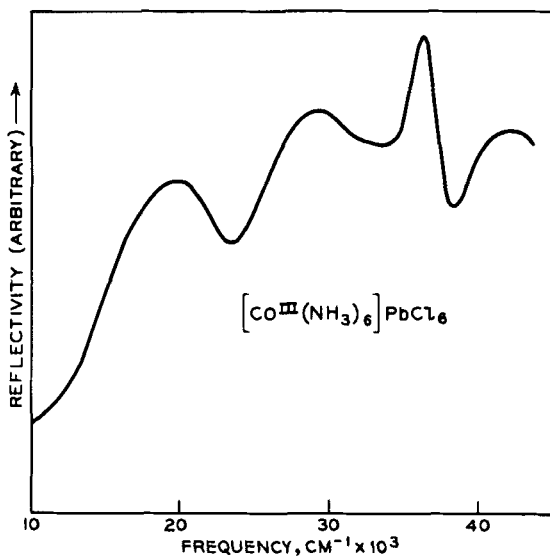


FIG. 43. The diffuse reflectance spectrum of $[\text{Co}^{\text{III}}(\text{NH}_3)_6]\text{PbCl}_6$ (180).

the overlap of halide orbitals on neighboring MX_6 groups transforming the system into class II. Not unexpectedly, the far infrared spectrum of $[\text{Co}(\text{NH}_3)_6]\text{PbCl}_6$ (42) contains a band coincident with that of $[\text{Pb}^{\text{IV}}\text{Cl}_6]^{2-}$, as well as bands at lower frequencies presumably due to $[\text{Pb}^{\text{II}}\text{Cl}_6]^{4-}$.

Arguing by analogy with the Bi_9^{5+} ion characterized by Hershaft and Corbett (356, 357), Britton (98) had proposed that the isoelectronic ion Pb_9^{4-} of Zintl and co-workers (818) also has the tripyramidal structure (Fig. 44). The suggestion of Marsh and Shoemaker (483) that the Pb_9^{4-} ion is formed of three Pb_4 tetrahedra sharing two vertices each is readily seen to be equivalent to Britton's description with allowances for distortion.

A brief note by Gasperin (270) describes the structure of a mixed

valence lead oxychloride of the composition $\text{Pb}_{3.6}\text{Cl}_{1.8}\text{O}_4$, in which 10% of the metal ion sites are empty, 50% of these sites being filled with Pb(II) and 32% with Pb(IV). In the ideal structure, all metal ion sites are equivalent, having as nearest neighbors four oxygen atoms and one chlorine atom in a square bipyramidal arrangement. As the material is reported to be yellow, it appears that the true structure involves considerable distortion from the ideal, such that the lead valences are firmly trapped as in a class I system.

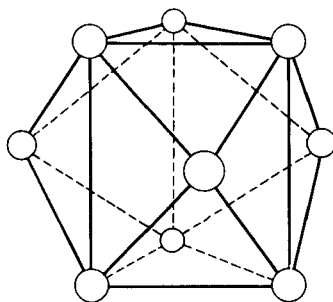


FIG. 44. The structure proposed for the Pb_9^{4-} ion and observed in the iso-electronic Bi_9^{5+} ion in crystalline $\text{Bi}_{12}\text{Cl}_{14}$.

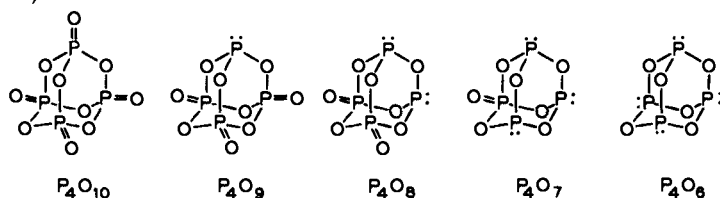
A second compound of apparently nonintegral stoichiometry, $\text{Pb}_3\text{Sb}_2\text{O}_{8.47}$, is discussed by Kuznetsov and Koz'min (452). In this substance, the ratio $\text{Sb(V)}:\text{Pb(IV)}:\text{Pb(II)}$ is equal to 4.0:1:5.0, and the two valences of lead appear trapped, the ions being in different environments. The Pb(IV) is eight-coordinated with six oxygens at 2.19 Å and two at 2.30 Å, whereas the Pb(II) is six-coordinated with oxygens at 2.43 Å. There is no description of the physical properties of $\text{Pb}_3\text{Sb}_2\text{O}_{8.47}$.

A nominally trivalent lead fluoride, PbF_3 , has been mentioned (371), but nothing appears to be known about it.

W. PHOSPHORUS AND ARSENIC

Between the two phosphorus oxides, $\text{P}_4^{\text{V}}\text{O}_{10}$ and $\text{P}_4^{\text{III}}\text{O}_6$, there exist three intermediate oxides, P_4O_9 , P_4O_8 , and P_4O_7 , each of which contains P(III) and P(V) oxidation states in the same molecule. As can be seen from the structures given below, the valences in these molecules are

firmly trapped as P(III) and P(V), and so the crystals are class I (353, 400, 401):



These mixed valence oxides are colorless and diamagnetic, as expected. Similar mixed valence oxides are reported in the arsenic oxide (466) and the phosphorus sulfide (199) systems. As might be expected from the lack of color in the solid mixed valence arsenic oxides, a concentrated HCl solution containing As(III) and As(V) failed to give a mixed valence absorption band in the 14,000–31,000 cm^{-1} region (772).

X. ANTIMONY

There are two general types of mixed valence system thought to contain Sb(III) and Sb(V) ions. The double halides of Sb(III) and Sb(V) are, with one exception, of a very dark violet, blue, or black color and all present interesting problems in electronic structure, color, magnetism, and molecular structure. The mixed valence antimony oxides, on the other hand, are colorless, and, in the light of the deeply colored halides, present yet another problem in the study of color and constitution.

Salts of antimony of the kind Cs_2SbX_6 were long ago regarded as examples of the 4+ oxidation state of antimony. Although the possibility of the presence of Sb(IV) in such halide salts now appears quite remote, there still remains considerable confusion as to the molecular and electronic structures of the component ions, in spite of recent efforts to rationalize seemingly contradictory experimental results. Setterberg (654) first synthesized the intensely blue salt Cs_2SbCl_6 from the colorless components CsCl , SbCl_3 , and SbCl_5 , and raised the question as to whether it was a salt of Sb(IV) or was to be formulated as the mixed valence compound $\text{Cs}_4\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Cl}_{12}$. For comparison, the salts $\text{Rb}_3\text{Sb}^{\text{III}}\text{Cl}_6$ and $\text{RbSb}^{\text{V}}\text{Cl}_6$ are colorless and pale yellow-green, respectively. The first indication that Cs_2SbCl_6 was a salt of Sb(IV) came from the work of Wells and Metzger (757), who showed that it was isostructural with $\text{Cs}_2\text{Pb}^{\text{IV}}\text{Cl}_6$, forming mixed crystals with it having a pale to dark green color depending upon the Sb/Pb ratio. Following this, black Rb_2SbCl_6 was found to give violet-colored mixed crystals with $\text{Rb}_2\text{Pt}^{\text{IV}}\text{Cl}_6$, as did the corresponding potassium salts, and the unstable $(\text{NH}_4)_2\text{SbCl}_6$ was

obtained readily as a deeply colored mixed crystal with either $(\text{NH}_4)_2\text{Pt}^{\text{IV}}\text{Cl}_6$ or $(\text{NH}_4)_2\text{Sn}^{\text{IV}}\text{Cl}_6$ (752). That these salts contain Sb(IV) was apparently confirmed by X-ray powder diffraction work on $(\text{NH}_4)_2\text{SbBr}_6$, Rb_2SbBr_6 , and Rb_2SbCl_6 , in which consideration of extinctions and intensities led to the conclusion that each of the salts is face-centered cubic (381), having the anti-fluorite structure of the $\text{M}_2\text{Pt}^{\text{IV}}\text{Cl}_6$ salts. Thus, in these salts all antimony ions appeared to be crystallographically equivalent, and the unusual colors were therefore ascribed to the Sb(IV) ion in octahedral coordination.

The Sb(IV) ion has the outer electronic configuration $5s^1$ and as such should show the paramagnetism characteristic of a 2S state, whereas the ions Sb(III) and Sb(V), being $5s^2$ and $5s^0$, respectively, are diamagnetic. Repeated magnetic susceptibility measurements on the M_2SbX_6 salts and on $(\text{NH}_4)_2(\text{Sb},\text{Sn})\text{Cl}_6$ have shown them in every case to be diamagnetic with $\chi_d \sim 0.3 \times 10^{-6}$ cgs (28, 29, 218, 381, 382). Although demonstrating that these substances do not contain magnetically dilute Sb(IV) ions, the observed diamagnetism may not rule out a strongly antiferromagnetic aggregation of Sb(IV). The latter possibility, however, is a remote one, for the crystal structure determination shows that neither direct Sb—Sb interactions nor bridged configurations of the type Sb—X—Sb are present, but, instead, only $\text{SbX}_6\text{—X}_6\text{Sb}$ contacts with a center-to-center distance of about 7 Å, a grouping which has never been found to give antiferromagnetic ordering at 300°K. On the other hand, the observed diamagnetism of these compounds agrees with the Sb(III),-Sb(V) formulation.

The high resistivity of the salts (29, 382) demonstrates that, if they are indeed mixed valence, the valences are firmly trapped, although it should be marked that thermally activated electron transfer remains a possibility in class II mixed valence systems. Indeed, $(\text{NH}_4)_2(\text{Sb}_x\text{Sn}_{1-x})\text{Cl}_6$ mixed crystals behave as high resistance semiconductors (33), with a room temperature resistivity which drops sharply with increasing antimony concentration. On the other hand, the thermal activation energy for conductivity is almost independent of composition, suggesting that it is dominated by the energy of mobility rather than production of charge carriers, as in mixed valence hopping semiconductors like $\text{Li}_x\text{Ni}_{1-x}\text{O}$ (Section III, G).

In an interesting application of the continuous variation technique to the problem of the valences in the solid state, Brauer and Schnell (91) attempted to refute the presence of Sb(IV) in these complexes. In this experiment, the intensity of light reflected from powdered samples was measured as the concentration of $(\text{NH}_4)_2\text{SbBr}_6$ was increased in the host crystal $(\text{NH}_4)_2\text{SnBr}_6$. Here, as in the solution work (*vide infra*), it

was found that, at low antimony concentrations, the reflectivity varied as the square root of the $(\text{NH}_4)_2\text{SbBr}_6$ concentration and not linearly as would be expected if the chromophoric grouping were $[\text{Sb}^{\text{IV}}\text{Br}_6]^{2-}$. At higher antimony concentrations, the variation of the reflected light intensity with antimony concentration was not so marked. Such solid state spectrophotometry can sometimes yield useful results when

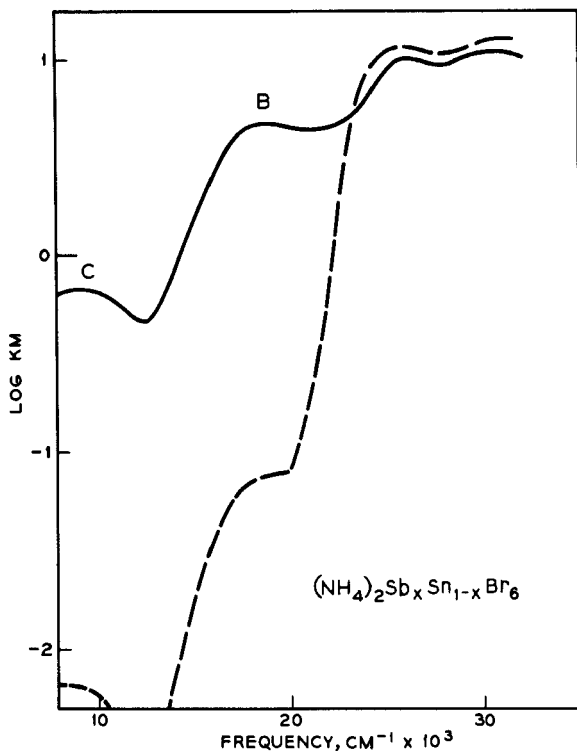


FIG. 45. The diffuse reflectance spectrum of solid solutions of $(\text{NH}_4)_2\text{SbBr}_6$ in $(\text{NH}_4)_2\text{SnBr}_6$ at high (—), and low (---) concentrations. The bands B and C are mixed valence transitions.

comparisons are made between sets of very similar samples and precautions are taken to ensure uniform particle sizes. However, it is not clear whether such precautions were taken in this case, and since the frequency at which measurements were made ($21,300\text{ cm}^{-1}$) does not correspond to the interaction absorption frequency (Fig. 45), it is difficult to draw conclusions from the experiment.

Further evidence of the mixed valence nature of the hexahaloantimonates was provided by Turco and co-workers (711-714), who have shown in a series of studies that the introduction of radioactive

Sb(III) into these salts does not yield equal amounts of radioactive Sb(III) and Sb(V) on decomposition, as would be expected if all the antimony ions in the crystal were equivalent. They also report that Rb_2SbCl_6 can be made with Sb(V)/Sb(III) ratios as large as 1.6, while still maintaining the color and external form of the 1:1 substance. Even larger deviations of the Sb(V)/Sb(III) ratio from 1.0 were reported for the mixed crystals of $(\text{NH}_4)_2\text{SbCl}_6$ in $(\text{NH}_4)_2\text{SnCl}_6$, but a recent study of this system (33) did not confirm this result.

The major objection to the Sb(III),Sb(V) mixed valence model of the M_2SbX_6 crystals was removed by Tovborg Jensen and Rasmussen (705), who found that the crystals reported as cubic by Jensen (381) are in fact tetragonal with $c/a = 1.43$, whereas this ratio is 1.414 for a cubic cell. In particular, it was found that $(\text{NH}_4)_2\text{SbBr}_6$, Rb_2SbBr_6 , and Cs_2SbBr_6 are tetragonal and that Rb_2SbCl_6 is strictly cubic but has an anomalous X-ray intensity distribution, which suggests disorder among the Sb(III) and Sb(V) ions. Recent confirmation of Tovborg Jensen and Rasmussen's powder measurements has come from single crystal X-ray work by Lawton and Jacobson (456) on $(\text{NH}_4)_2\text{SbBr}_6$. They found a small tetragonal distortion of the cubic cell resulting from ordering of the $[\text{Sb}^{\text{V}}\text{Br}_6]^-$ and $[\text{Sb}^{\text{III}}\text{Br}_6]^{3-}$ units, as shown in Fig. 46. In this structure, each $[\text{SbBr}_6]^{3-}$ is surrounded by eight $[\text{SbBr}_6]^-$ and four $[\text{SbBr}_6]^{3-}$ ions, and vice versa. The average Sb(III)—Br and Sb(V)—Br bond lengths were 2.795 Å and 2.564 Å, respectively. Thus, the sites of the two types of antimony ion are quite similar, which, when taken with the mixed valence absorption in the visible, strongly suggests that the system is class II. However, it is not immediately obvious how this can be, since there do not appear to be any shared ligands.

Experimentally, the only spectra available are those obtained by diffuse reflection by Day (178) in the systems $\text{M}_2[\text{Sb},\text{Sn}]\text{X}_6$, where $\text{M} = \text{K}, \text{NH}_4, \text{N}(\text{CH}_3)_4, \text{N}(\text{C}_2\text{H}_5)_4, \text{Rb},$ or Cs , and X is Cl or Br (Figs. 45 and 47). The latter was recorded as the difference spectrum between samples of differing dilutions and thus accentuates the visible absorption. In these spectra, the host lattice absorptions are assigned as those bands which do not lose intensity on lowering the concentration of antimony in the solid solution. In the cesium stannic chloride mixed crystal, the sharp band at $31,000\text{ cm}^{-1}$ (marked A) is most probably the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ component of the $5s^2 \rightarrow 5s^15p^1$ transition in Sb(III), which occurs at $29,000\text{ cm}^{-1}$ in $[\text{Co}(\text{NH}_3)_6][\text{Sb}^{\text{III}}\text{Cl}_6]$. The first absorption band of $[\text{Sb}^{\text{V}}\text{Cl}_6]^-$, which occurs at $37,000\text{ cm}^{-1}$ in solution (772), is hidden under the host lattice absorption. The lower frequency bands (marked B and C in Figs. 45 and 47) are clearly the interaction bands responsible for the mixed valence color in M_2SbX_6 systems.

Day (178) suggested that the two mixed valence transitions B and C are the singlet and triplet components of the lowest symmetry-allowed excitation, but it does not now seem likely that an exchange interaction

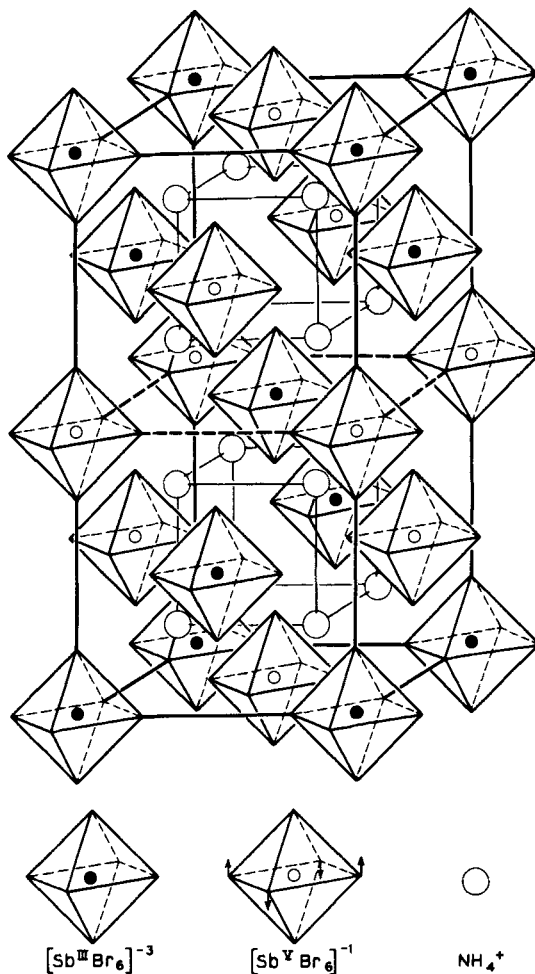


Fig. 46. The class II tetragonal unit cell of $(\text{NH}_4)_4\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Br}_{12}$, showing the relative disposition of $\text{Sb}^{\text{V}}\text{Br}_6$ and $\text{Sb}^{\text{III}}\text{Br}_6$ octahedra. The distortion of the $\text{Sb}^{\text{V}}\text{Br}_6$ octahedron is as indicated at the bottom (456).

between two $5s$ orbitals separated by about 7 \AA could produce a singlet-triplet separation of 9000 cm^{-1} . Two other explanations present themselves. As can be seen from Fig. 46, each $\text{Sb}(\text{III})$ ion in $(\text{NH}_4)_2\text{SbBr}_6$ is surrounded by four $\text{Sb}(\text{V})$ ions in a plane, and by four $\text{Sb}(\text{V})$ ions at the

vertices of a tetrahedron. If the salts that Day investigated also have this structure and are sufficiently tetragonal, then two symmetry-allowed mixed valence absorption bands would be expected, one, a doubly degenerate, in-plane-polarized transition involving the Sb(III) ion and the planar array of Sb(V) ions, and the second a nearly triply degenerate, weakly polarized transition involving the Sb(III) ion and the tetrahedral array of Sb(V) ions. Another explanation for the second band is that electron transfer occurs to higher orbitals on the Sb(V). The transition

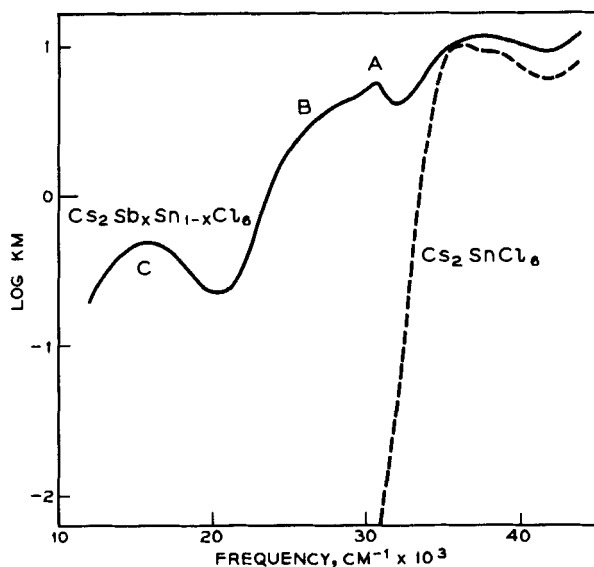


FIG. 47. The diffuse reflectance spectra of Cs_2SnCl_6 (---), and of Cs_2SbCl_6 doped into Cs_2SnCl_6 (—) (180).

$\psi_A 5s^2 \psi_B 5s^0 \rightarrow \psi_A 5s^1 \psi_B 5p^1$ is expected to lie above $\psi_A 5s^2 \psi_B 5s^0 \rightarrow \psi_A 5s^1 \psi_B 5s^1$ by an amount corresponding to the excitation $\psi_B 5s^1 \rightarrow \psi_B 5p^1$, which is about $86,000 \text{ cm}^{-1}$ in the Sb(IV) free ion (510), but could be considerably less when the Sb(IV) is imbedded in a crystal as a hexahalogen anion.

As was seen in Section II, for a mixed valence transition in the trapped valence case, the transition moment cannot be large unless there is overlap between the functions,

$$\Psi_A(5s) \text{ and } \sum C_i \Psi_{B_i}(5s)$$

The former function is that of the 5s orbital on the central antimony ion, and the sum is taken over the 5s orbitals of the surrounding antimony

ions, with the signs of the coefficients C_i taken so as to give a function which has a single nodal plane. Thus the qualitative reports, which describe the M_2SbX_6 mixed valence colors as very intense, necessitate a significant overlap between the antimony ion wave functions of neighboring $Sb^{III}X_6$ and Sb^VX_6 groups. This is rather unexpected since the Sb—Sb distance is approximately 7 Å in all cases. The required overlap between the antimony could be imagined to arise from delocalization of the $5s$ orbitals through σ -bond formation with the halide $p\sigma$ orbitals. If the halide ions on adjacent $[SbX_6]^-$ and $[SbX_6]^{3-}$ ions have a nonzero overlap, there is then formed a path over which an electron could be transferred from Sb(III) to Sb(V). That such an SbX_6-X_6Sb overlap may exist was first suggested by Jensen (382), but Lawton and Jacobson state specifically that there is nothing in the least unusual about the $SbBr_6-SbBr_6$ distances in $(NH_4)_2SbBr_6$ (456). Since it is notoriously difficult to assess absorption intensities in solids from visual depth of color, it may well be that the transition moment of the mixed valence absorption and the associated overlap are really quite small, and that it is this small ligand-ligand overlap which turns the formally class I system into a class II system with a visible mixed valence absorption. Charge transfer from halide to metal in adjacent hexahalogen anions has been proposed already by Owen to explain the antiferromagnetic interaction between the Ir(IV) ions in the lattice of K_2IrCl_6 (553).

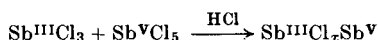
As might be expected, the substitution of the Sb(III) in $M_4Sb^{III}Sb^VCl_{12}$ by the ions Fe(III) or In(III) changes the color from black to pale yellow, since all metal ions are then fully oxidized and there is no electron readily available for low-energy transfer. Day (178) reports the intermolecular charge transfer transition of $Cs_4In^{III}Sb^VCl_{12}$ to fall at $30,800\text{ cm}^{-1}$, and that of the Tl(III) analog to fall at $29,600\text{ cm}^{-1}$. The corresponding Bi(III) compound has a deep red color with a maximum at $24,000\text{ cm}^{-1}$ in the diffuse reflectance spectrum.

Many other halide salts have been described as containing Sb(III) and Sb(V). Brauer and Schnell (89) have prepared black $Rb_3Sb_2Br_{11}$ and also mention the salt $TlSbCl_5$. Since this latter substance is reported to have only a pale color, and in view of the fact that the mixed valence thallium chloride compounds are never deeply colored, it may be more reasonable to consider it as being $Tl^ITl^{III}Sb_2^{III}Cl_{10}$ rather than $Tl_2Sb^{III}Sb^VCl_{10}$. The materials $Rb_8Sb_3Cl_{18}$, $(NH_4)_5Sb_2Cl_{12}$, $(pyH)_5Sb_3Cl_{18}$, and $(pyH)_{11}Sb_5Cl_{30}$ (752) are all brown-black crystalline solids of apparent mixed valence constitution, but a recent X-ray study of $[N(CH_3)_4]_3Sb_2Br_{11}$ (455) reveals that the compound is not an example of antimony mixed valence, for $[Sb_2^{III}Br_9]^{3-}$ groups alternate with

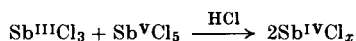
bromine molecules in the lattice. The only mixed valence antimony fluorides reported to date have the compositions $\text{Sb}_2^{\text{III}}\text{Sb}^{\text{V}}\text{F}_{11}$ and $\text{Sb}_5^{\text{III}}\text{Sb}^{\text{V}}\text{F}_{20}$ (607), and are low melting, colorless solids.

Ephraim and Weinberg (224) report a thermochromic effect in an Sb(III), Sb(V) halide system which certainly deserves more exploration, both crystallographically and spectroscopically. Addition of NH_4Cl in sufficient quantity to a molten mixture of SbCl_3 and SbCl_5 leads to the formation of a black mass which on cooling becomes colorless. Heating then restores the black color, and the white-black cycle can be repeated indefinitely. Clearly, more crystallographic and spectroscopic work will be needed before a clear picture emerges of the relationship between the color and constitution of the many mixed valence antimony halides.

The "interaction color" of concentrated HCl solutions containing both SbCl_3 and SbCl_5 , first observed by Weinland and Schmid (752), has since been studied by a very large number of workers. Hydrochloric acid solutions of SbCl_3 and SbCl_5 are colorless and pale yellow, respectively, and both obey Beer's law, showing that there are no Sb(III)-Sb(III) or Sb(V)-Sb(V) interactions in the solutions. However, the HCl solution containing both Sb(III) and Sb(V) is a deep lemon-yellow to brown color, and continuous variation studies show that the concentration of the species responsible for the mixed valence absorption, as measured by the optical density of the solutions at frequencies where the components are only weakly absorbing, is a maximum for $[\text{Sb(III)}]/[\text{Sb(V)}] = 1$. Moreover, the concentration of this colored species varies as the product $[\text{Sb(III)}][\text{Sb(V)}]$ (177, 215, 770, 772). These facts are consistent with a color-producing reaction of the sort



but inconsistent with the reaction



It is to be noted, however, that, since the two antimony atoms in a mixed valence dimer complex in solution might very well have identical ligand fields, the spectrophotometric studies do not rule out the formation of $\text{Sb}^{\text{IV}}\text{Cl}_x\text{Sb}^{\text{IV}}$ in these solutions. The susceptibilities of the Sb(III), Sb(V) solutions have not been measured.

Studies of electrochemical redox reactions (101, 102) as well as radiochemical exchange experiments (79, 434, 529) also point to the formation of an Sb(III), Sb(V) dimer in concentrated HCl solutions. Bonner and Goishi (79) made a careful study of the rate of electron exchange in HCl solutions, using ^{124}Sb as a tracer. The exchange rate increased steadily

with increasing HCl concentration, reaching a maximum at approximately 9.3 *M* HCl and decreasing again in 12 *M* HCl. Up to 8 *M* HCl, complex exchange curves were observed and explained by slow interconversion among two complexes of Sb(V) which exchange at different rates with Sb(III). To discover whether the interaction absorption complex in solution was also the reaction intermediate for exchange, they made qualitative observations on the interaction absorption in non-equilibrium solutions. Their conclusion was that the interaction absorption, which occurs only between $[\text{Sb}^{\text{III}}\text{Cl}_4]^-$ and $[\text{Sb}^{\text{V}}\text{Cl}_6]^-$ ions, does not result from a symmetrical dimer, nor does it lead to a symmetrical excited state, because there is no correlation with the rate of electron exchange. Transition states such as $[\text{Cl}_5\text{Sb}^{\text{III}}\text{ClSb}^{\text{V}}\text{Cl}_5]^{3-}$, $[\text{Cl}_4\text{Sb}^{\text{III}}\text{Cl}_2\text{Sb}^{\text{V}}\text{Cl}_4]^{2-}$, and $[\text{Cl}_4\text{Sb}^{\text{III}}\text{Cl}_2\text{Sb}^{\text{V}}\text{Cl}_3]^-$ have been suggested for the thermochemical electron exchange (434, 529), but no unequivocal choice has been made between them. However, the fact that the mixed valence dimer has a class II absorption suggests that the coordinations about the two antimony ions are very similar.

Under the influence of an electric field, the colored Sb(III),Sb(V) species in 12 *M* HCl was found to migrate to the positive electrode (215), showing that it had a negative charge. Thus, there are more than eight chloride ions in the mixed valence complex $[\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Cl}_x]^{n-}$. Although a high formal concentration of HCl is required to form the complex, a brown color is also reported to form on heating a mixture of pure SbCl_3 and SbCl_5 ⁴ (224). Usanovitch *et al.* (715) studied this system and concluded that the components reacted to form the ion pair $[\text{SbCl}_4]^-[\text{SbCl}_4]^+$.

Solution of metallic antimony in the molten halides SbX_3 might be expected to lead to the formation of reduced species in the presence of the oxidized SbX_3 , and thence to mixed valence compounds. However, Corbett and students (107, 151) have studied the product of dissolution of antimony in SbI_3 and found it to be diamagnetic Sb_2I_4 .

The oxides of antimony present a most interesting contrast, for although the mixed valence halides are black, the mixed valence oxides are colorless! The difference is even more striking when one realizes that

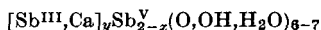
⁴ Whitney and Davidson (772) report that there is no perceptible color change on cooling the concentrated HCl solution of SbCl_3 and SbCl_5 to -80°C , and conclude that the reaction forming the colored species has a very low heat. An alternate explanation rests on the fact that, in any case, one sees only the band edge as the source of color and the intensity of absorption in the band edge will decrease rapidly with a decrease in temperature. The experimental result is then understandable as the simultaneous decrease of visible absorption intensity per absorbing molecule, and increase of the number of absorbing species as the temperature is decreased. According to such an explanation, the heat of dimer formation could be appreciable.

the oxides contain anions bridging the mixed valence antimony whereas, formally, the halides do not. As expected, the difference in color of the oxides and halides can be traced directly to differences in structure.

The primary product formed on heating hydrated Sb_2O_5 is $\text{Sb}_3\text{O}_6\text{OH}$, which contains two gram ions of Sb(V) and one gram ion of Sb(III) per formula weight, and is reported to be colorless to pale yellow, suggesting a class I crystal structure. After a few near misses (185, 527), the crystal structure of $\text{Sb}_3\text{O}_6\text{OH}$ was finally deduced by Dihlström and Westgren (196) from the powder pattern. They found a face-centered, cubic cell in which all the Sb(V) ions lie at the centers of oxide ion octahedra having an Sb(V)—O distance of 2.02 Å, whereas each of the Sb(III) ions is surrounded by six oxide ions at a distance of 2.48 Å and two OH^- ions at 2.23 Å. Since a normal Sb(III)—O distance is 2.02–2.1 Å, the Sb(III) is in effect only two-coordinated and the other six oxygens, which simultaneously surround the Sb(III) ion and form octahedra with the Sb(V) ions, have only a very weak interaction with the former. Thus it appears possible to rationalize the lack of color in this compound as the consequence of a class I crystal structure.

On further dehydration of $\text{Sb}_3\text{O}_6\text{OH}$ by prolonged heating at 900°C, the colorless, diamagnetic, insulating, mixed valence oxide $\alpha\text{-Sb}_2\text{O}_4$ is formed. Although a structure had been advanced for $\alpha\text{-Sb}_2\text{O}_4$ in which both the Sb(III) and Sb(V) ions were octahedrally coordinated (197), Wells (756) has criticized it, pointing out that the four shortest Sb(III)—O distances were 0.5 Å longer than the 2.0 Å expected. The validity of this criticism is now apparent from the work of Skapski and Rogers (599, 670), who solved the crystal structures of $\alpha\text{-Sb}_2\text{O}_4$ and of a second polymorph $\beta\text{-Sb}_2\text{O}_4$. In both the α and β forms of Sb_2O_4 the Sb(V) ions are found in layers, each Sb(V) being at the center of a slightly deformed octahedron with Sb—O distances ranging from 1.956 to 1.990 Å. On the other hand, the Sb(III) ions form columns between the layers with each Sb(III) ion having two oxide ions at 2.032 Å and two at 2.218 Å (as shown in Fig. 48). Although the color of $\beta\text{-Sb}_2\text{O}_4$ is not given, one presumes that it is colorless, like the $\alpha\text{-Sb}_2\text{O}_4$ from which it is made, and that both are class I systems. Titration of solutions of Sb_2O_4 in mineral acids is said to show that the antimony in such solutions is present as Sb(III) and Sb(V) in equal amounts (435).

There is a naturally occurring mixed valence mineral, stibiconite, which has the general formula



in which x varies from zero to almost one, and y is approximately one (486). Because this yellow mineral has been shown to be isostructural

with the pyrochlore minerals (5, 389, 810), it no doubt has a structure closely related to that of $\text{Sb}_3\text{O}_6\text{OH}$, described above, with Sb(III) and Sb(V) ions in distinctly different environments.

Thus, in the mixed valence antimony oxides, the Sb(V) ion prefers a sixfold, octahedral coordination, whereas the Sb(III) ion has only four

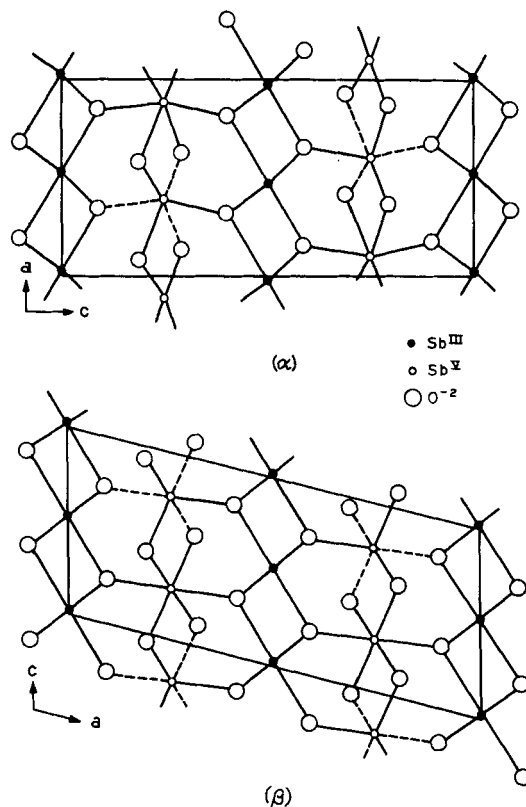


FIG. 48. The class I crystal structures of $\alpha\text{-Sb}_2\text{O}_4$, upper, and $\beta\text{-Sb}_2\text{O}_4$, lower (599, 670).

near neighbors. The fact that no mixed valence optical transition is observed in the visible region in these compounds, even though there are Sb(III)-O-Sb(V) bridges, may result not only from the difference in site symmetries, but also from the very high stability of the Sb(III) ion in fourfold coordination and its consequent resistance to thermal or photochemical oxidation. The mixed valence oxide $\beta\text{-Sb}_2\text{O}_4$ can be heated to over 1000°C in oxygen without oxidation of the Sb(III).

Y. BISMUTH

Metallic bismuth has long been known to dissolve in molten bismuth trichloride, forming lower halides of debatable composition (149). Although BiCl is a predominant species in the gas phase reaction, the condensed phase reaction has been shown by a single crystal X-ray study to yield a compound of the stoichiometry $\text{Bi}_{12}\text{Cl}_{14}$ (356, 357). The compound was shown to consist of two $[\text{BiCl}_5]^{2-}$, one-half $[\text{Bi}_2\text{Cl}_8]^{2-}$, and one mole of the mixed valence cation Bi_9^{5+} per formula weight. This latter cation is a tripyramid of nominal symmetry D_{3h} , having six bismuth atoms at the vertices of a trigonal prism and a bismuth atom placed symmetrically above each of the three rectangular faces of the prism (Fig. 44). Although the observed structure of Bi_9^{5+} is of a symmetry lower than D_{3h} , it approximates the ideal arrangement wherein all nine bismuth atoms are equidistant from a central point. As there are two types of bismuth atom in the complex (the six prism atoms and the three equatorial ones), one might at first attempt to assign integral valences in accord with the trapped valence model. However, this is not possible if the overall charge is to be $5+$. Thus the ion is a class III-A system in spite of certain inequivalences between atoms, and is best considered by using molecular orbital theory. This has been done by Corbett and Rundle (153), who found that the MO theory, using $6p$ orbitals only, predicts a diamagnetic ground state, as observed, and that the equatorial atoms are much less positive than the prism atoms.

Spectroscopically, there are no quantitative data for $\text{Bi}_{12}\text{Cl}_{14}$, but it is reported to form shiny black prisms, the color being due no doubt to the Bi_9^{5+} cation. Because the mixed valence Bi_9^{5+} units are separated by essentially insulating material, the $\text{Bi}_{12}\text{Cl}_{14}$ crystals will probably be found to be insulators, unless, however, there is an additional mixed valence interaction between the reduced Bi_9^{5+} and oxidized $[\text{Bi}^{\text{III}}\text{Cl}_5]^{2-}$ groups.

Spectra of Bi-BiCl₃ melts recorded by Boston and Smith (81) in the visible region show a large absorption tail in the 20,000–25,000 cm^{-1} region due to hot BiCl₃ (BiCl₃ in a KCl matrix shows a transition centered at 30,500 cm^{-1}) (277) and a broad band centered at 17,860 cm^{-1} with a weak shoulder claimed at 16,400 cm^{-1} , the combination of the three acting to make the melt black. The large deviation from Beer's law observed by them in the visible region was felt to be due to the presence of two species of unknown structure, each absorbing in the same spectral region. It is to be remembered, however, that, although the black substance $\text{Bi}_{12}\text{Cl}_{14}$ is a solid recovered from a solution of bismuth in BiCl₃, there is in fact no evidence for the Bi_9^{5+} ion in the melt. In a later spectral

study, Bjerrum *et al.* (71) found that solution of metallic bismuth in dilute solutions of BiCl_3 in liquid $\text{AlCl}_3\text{--NaCl}$ and $\text{ZnCl}_2\text{--KCl}$ eutectics resulted in the formation of Bi^+ ions with three bands in the 10,000–16,000 cm^{-1} region, and Bi_5^{3+} ions with major bands at 12,000 and 25,000 cm^{-1} . This latter mixed valence species may be further coordinated by halide ions.

The magnetic susceptibility of Bi--BiCl_3 solutions has been measured by Nachtrieb (523). In accord with the observed lack of electronic conduction in the dilute melts (30, 31), the Bi--BiCl_3 solutions are diamagnetic, indicating that there are neither metallic conduction electrons nor neutral ground state Bi atoms ($^4S_{3/2}$) in the melt. Thus the dissolved metallic bismuth is associated with itself and/or the BiCl_3 solvent. The susceptibilities and conductivities of solutions of bismuth metal in molten BiBr_3 (308) and BiI_3 (307, 576, 704) have also been studied recently.

There are a few bismuth oxides about which little can be said, but which may later prove to be of mixed valence interest. Zemann (811) has described the preparation and results of a crystal structure study of an orange-red "bismuth acid," thought to contain Bi(III) and Bi(IV) in a structure like that of "antimony acid," $\text{Sb}^{\text{III}}\text{Sb}_2^{\text{V}}\text{O}_6\text{OH}$. In addition to the red and brown-black forms of $\text{Bi}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ (639), anhydrous BiO has been reported (809). BiO has a slightly distorted sphalerite structure and probably contains equal numbers of Bi(I) and Bi(III) ions.

Z. LANTHANIDES

The reduction of $\text{Ce}^{\text{IV}}\text{O}_2$ by H_2 at high temperatures results in the formation of lower oxides of cerium having a deep blue-black color, which fades to pale yellow-green as the reduction proceeds to $\text{Ce}_2^{\text{III}}\text{O}_3$ (64, 65, 86, 92, 587). Similar lower mixed valence oxides can be produced by firing mixtures of $\text{Ce}^{\text{IV}}\text{O}_2$ and $\text{Ce}_2^{\text{III}}\text{O}_3$ (88, 108). Studies of the phase diagram in the region $\text{CeO}_2\text{--CeO}_{1.50}$ show the presence of three stoichiometric intermediate phases, $\text{Ce}_{11}\text{O}_{20}$, Ce_9O_{16} , and Ce_7O_{12} , and two other regions of composition $\text{CeO}_{1.70}\text{--CeO}_{1.67}$ and $\text{CeO}_{1.67}\text{--CeO}_{1.50}$ (64, 65, 88). There is no evidence for the earlier reported compound Ce_4O_7 . The stoichiometric intermediate phases have rhombohedral structures based on that of fluorite with an extension along a cube diagonal. In these structures, the cation lattice is complete, but there is presumed to be an ordering of vacancies in the anion lattice. The other two regions of lower oxide homogeneity have the type-C and type-A rare earth oxide structures, respectively (64). The lower cerium oxides are most likely

class II systems, but no other physical measurements on them have been reported as yet.

Numerous mixed valence oxides of the other lanthanide elements known to exist in oxidation states higher than 3+, i.e., praseodymium and terbium, have also been widely studied. The best known praseodymium oxide is Pr_6O_{11} , which is formed when any other praseodymium oxide or oxy-salt is strongly heated in air. There was once speculation (573) that praseodymium could be oxidized beyond 4+ in the presence of other trivalent rare earths, and, on this basis, Pr_6O_{11} was given the formula $2\text{Pr}_2^{\text{III}}\text{O}_3 \cdot \text{Pr}_2^{\text{V}}\text{O}_5$, and $\text{Pr}^{\text{IV}}\text{O}_2$ was thought to be $\text{Pr}_2^{\text{III}}\text{O}_3 \cdot \text{Pr}_2^{\text{V}}\text{O}_5$. Marsh (482), however, was able to oxidize praseodymium only to the 4+ oxidation state, a conclusion many times reconfirmed (229, 485, 500, 501). The major features of the phase diagram between $\text{PrO}_{1.5}$ and PrO_2 were mapped by Martin (485), who found two types of phase, one cubic, with essentially the fluorite lattice of PrO_2 systematically deficient in oxygen, and the other hexagonal, based on the A-type Pr_2O_3 lattice. Since 1950 many structural investigations of the PrO_x system have been made by Brauer (88) and by Eyring and his associates, whose results have recently been reviewed (229). We shall not go into details here, except to say that, for carefully annealed samples, it now seems likely that the entire range of composition between $\text{PrO}_{1.5}$ and PrO_2 will be resolved into definite compounds with narrow composition ranges separated by two-phase regions. The existence of a homologous series $\text{M}_n\text{O}_{2n-1}$ has been proposed (229), with slabs of MO_2 joined by facesharing of their coordination polyhedra, as in A-type M_2O_3 .

Similar conclusions would apply to the terbium oxides, of which Tb_4O_7 and Tb_6O_{11} were characterized by Prandtl and Rieder (573) and confirmed by Gruen *et al.* (322), and may also be relevant to the so-called solid solutions of La_2O_3 , Nd_2O_3 , and Sm_2O_3 in CeO_2 and PrO_2 . The latter were said (167, 168) to show a region of homogeneity from MO_2 to about 60% M_2O_3 , but closer examination might reveal details of ordering comparable to that found with the mixed valence transition metal oxides (compare $\text{Ti}_n\text{O}_{2n-1}$ and $\text{Cr}_2^{\text{III}}\text{Ti}_{n-2}^{\text{IV}}\text{O}_{2n-1}$, for example).

Measurements of the physical properties of the lanthanide(III,IV) oxides began with the observation of Foëx (255) that Pr_6O_{11} had a conductivity at 500°C at least 10^7 times greater than that of Pr_2O_3 , and further careful work on all the trivalent lanthanide oxides (535, 536), as well as Pr_6O_{11} and Tb_4O_7 , showed that the latter two compounds were very much more conducting than any of the others. It was also concluded that the conductivity was electronic and not ionic. In his work on the PrO_x phase diagram, Martin (485) used thermoelectric measurements to show that, while type-A Pr_2O_3 is a *p*-type semiconductor, indicating

that the Pr_2O_3 lattice can accommodate small amounts of additional oxygen, Pr_6O_{11} is *n*-type, suggesting that it is effectively PrO_2 with an oxygen deficiency, rather than Pr_2O_3 with excess oxygen. Eyring and his collaborators (228) as well as Honig [quoted in Eyring and Baenziger (228)] have begun to make electrical measurements on the praseodymium oxides as a function of temperature and oxygen pressure, but their results as reported up to the present add little to the earlier qualitative conclusions, except that the transition from *n*-type conduction in PrO_x occurs when *x* is between 1.65 and 1.83.

All the praseodymium(III,IV) oxides are reported as black (229) and those of terbium as dark brown, but, in the oxides closest in composition to Pr_2O_3 , *f-f* transitions of Pr(III) are clearly seen (734) against a background of absorption steadily increasing into the ultraviolet. There is also an extremely broad absorption in the near infrared, beginning at about $12,000\text{ cm}^{-1}$. In the terbium(III,IV) oxides, there is a very broad absorption centered near $15,000\text{ cm}^{-1}$, extending into the near infrared and as far as the ultraviolet cut-off of Tb_2O_3 . From the available structural and physical evidence it therefore appears that all these oxides are class II systems.

Mixed valence oxides of those lanthanides which form stable divalent states have been much less investigated than the quadrivalent ones. One of the best characterized compounds of this type is Eu_3O_4 (2), which, with the isomorphous compound SrEu_2O_4 (40), is related structurally to CaFe_2O_4 . A recent structure analysis (577) showed that each Eu(III) was surrounded by six oxide ions and each Eu(II) by eight, so the compound, which is dark red by transmitted light (577), belongs to class I. Nothing has been reported about its electrical properties. Another mixed valence europium oxide, LiEu_3O_4 (41), has been described as isomorphous with $\text{LiSr}_2\text{Eu}^{\text{III}}\text{O}_4$.

By melting some lanthanide metals with their respective sesquioxides, compounds LnO_x with $1.450 < x < 1.500$ were prepared for Gd, Y, Er, and Lu (507), and their dark colors were attributed to the presence of high concentrations of color centers. Whether this is the case, or whether the excess electrons are trapped on metal ions, forming Ln(II), Ln(III) mixed valence systems, remains to be seen.

Although a mixed valence cerium chloride and fluoride have been mentioned in the literature, it appears that, to the moment, the only genuine mixed valence cerium halide is an iodide. Asker and Wylie (27) mention the double fluoride $(\text{NH}_4)_2\text{Ce}^{\text{III}}\text{Ce}^{\text{IV}}\text{F}_9$, but give no details or references about it; it may well exist only as a misprint. On the basis of e.m.f. studies, Senderoff and Mellors (653) have suggested that the dissolution of Ce metal in molten CeCl_3 results in the formation of

$\text{Ce}^{\text{I}}[\text{Ce}^{\text{III}}\text{Cl}_4]$, analogous to the $\text{Ga}^{\text{I}}[\text{Ga}^{\text{III}}\text{X}_4]$ compounds. On quenching the Ce/CeCl₃ melt, an intensely black solid phase resulted which analyzed for large amounts of both metallic cerium and CeCl₃ (170). Later work (99), however, convincingly refutes the conclusions of the e.m.f. study, and so it would appear that there is no evidence for a mixed valence cerium chloride.

A phase study of the Ce–CeI₃ system by Corbett *et al.* (152) shows that, in addition to CeI₂, a lower iodide of composition CeI_{2.4} can be made. The compound is isomorphous with PrI_{2.5} and can be formulated as $\text{Ce}_2^{\text{III}}\text{Ce}_3^{\text{II}}\text{I}_{12}$. Although nothing more is known of this material, it may well be a metallic conductor, for CeI₂ itself is metallic (152) due to the fact that the Ce(II) ion prefers to put its second 4*f* electron into a conduction band of the solid, thereby becoming Ce(III). According to Sallach and Corbett (616), there are no intermediate mixed valence cerium bromides.

There are a number of lower-valent halides of the other lanthanides which may be of mixed valence interest. By dissolving lanthanide metals in the appropriate molten trihalides, the following “nonstoichiometric” phases have been detected (152, 206–208, 505, 616): NdCl_{2.37}, NdI_{1.95}, PrCl_{2.31}, PrBr_{2.38}, PrI_{2.50}, and GdCl_{1.58}. Scandium (154), yttrium, and erbium (155) do not form such compounds. Like cerium, the diiodides of praseodymium and neodymium are metals, so the corresponding mixed valence compounds may be class III-B systems with partly filled conduction bands based on 5*d* orbitals. In contrast, the other mixed valence halides have very low electrical conductivities including, surprisingly, GdCl_{1.6}, which has a magnetic moment of 7.89 ± 0.03 B.M. per gadolinium (313), very close to that expected if all the gadoliniums had effective 4*f*⁷ configurations (7.94 B.M.). What has happened to the “extra” 1.4 electrons per metal atom has by no means been determined, but the close proximity of the configurations 4*f*⁷5*d*¹ and 4*f*⁸ for Gd(II) suggests that spin pairing might have occurred through the formation of metal-metal bonds using 5*d* orbitals. The compound would then be a member of our class III-A.

AA. ACTINIDES

Stimulated in large part by their potential use as nuclear fuels, large areas of the complicated uranium oxide phase diagram have been studied, revealing many mixed valence materials. Makarov (478) attempted to bring some order to the wealth of data collected by 1961, by suggesting that the uranium oxides form a related series of compounds,

just as was found with the titanium, vanadium, molybdenum, and niobium oxides. In the case of uranium, the general formula U_nO_{2n+2} accounts for a number, but not all the reported oxides. The most studied region of the uranium oxide phase diagram (70, 72, 362, 364, 481, 589, 590) lies between UO_3 ($n = 2$) and UO_2 ($n = \infty$), wherein five members of the series with mixed valence stoichiometry have been located so far.

UO_2 , the end member of the series, is a readily oxidizable material which, at low temperature, can incorporate oxygen into its fluorite lattice up to a composition of $UO_{2.3}$ (24, 316, 568). On annealing, this oxide decomposes to a mixture of UO_2 and U_4O_9 (25, 316, 438, 481, 589). Further oxidation leads to the formation of U_7O_{16} (568), U_6O_{14} (189, 191, 364, 387, 636, 637), U_5O_{12} (636, 637), U_4O_{10} (361, 481, 610), and U_3O_8 (191, 316, 481). In addition to these compounds, the compositions $UO_{2.90}$ (51, 363, 689), U_5O_{13} (72, 637), U_3O_4 (806), $UO_{2.61}$ (589), and U_8O_{17} (481) have been reported. Many of these phases listed above have polymorphic forms and are of appreciable breadth.

In the UO_{2+x} phase, in the region $0 < x < 0.3$, the excess oxygen ions occupy interstitial sites in the host UO_2 fluorite-type lattice in a random manner (24, 781). The contraction of the UO_2 unit cell as oxygen is added to it was interpreted by Anderson *et al.* (11) to result from the partial oxidation of U(IV) to the smaller U(V) ions. Because the interstitial oxide ions form part of the uranium ions' coordination sphere, these ions effectively trap the uranium valence, turning UO_{2+x} into a class II system. Over wide variations of x , the systems all seem to have a resistivity of approximately 10^5 ohm cm at 300° K (521). The color of " UO_2 " has been reported variously as all shades between green and black, due no doubt to the ease with which UO_{2+x} is formed even at room temperature.

U_4O_9 has a structure much like that of the UO_{2+x} phase, except that the interstitial positions are filled in an orderly way (52, 782). Like UO_{2+x} , U_4O_9 is a semiconductor ($E_{act} = 0.46$ eV) (521) and is paramagnetic from 1.4° to 500° K with a maximum susceptibility at 6.4° K (301, 457). The effective magnetic moment of U_4O_9 is 2.06 B.M. per uranium, to be compared with 2.83 B.M. in pure UO_2 . Gotoo *et al.* (301) have computed the effective magnetic moment of U_4O_9 on the assumption that the valences are trapped as either $U_2^{IV}U_2^V O_9$ or $U_3^{IV}U^VI O_9$, and find 2.10 B.M. for the former and 1.42 B.M. for the latter. Although appearing to support a U(IV),U(V) configuration for U_4O_9 , it must be said that the calculation is based upon a simplified model of the structure. The compound CaU_3O_9 also has a face-centered cubic structure and very nearly the resistivity of U_4O_9 (804).

The application of X-ray (315) and neutron diffraction (467)

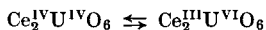
techniques to the problem of the structure of U_3O_8 was successful in showing the positions of both the uranium and oxygen atoms in the unit cell. There are two types of uranium site in U_3O_8 (467), the first having six oxygens at 2.07–2.23 Å and a seventh at 2.44 Å, and a second with six oxygens at 2.07–2.23 Å and a seventh at 2.71 Å, there being twice as many of the latter as the former. Such a structure allows one to assign the valences in U_3O_8 as either $\text{U}^{\text{VI}}\text{U}_2^{\text{V}}\text{O}_8$ or $\text{U}_2^{\text{VI}}\text{U}^{\text{IV}}\text{O}_8$. Whereas the U(VI),U(V) formulation is suggested by Loopstra (467), the U(VI),U(IV) formula is compatible with the general formula $\text{U}_2^{\text{VI}}\text{U}_{n-2}^{\text{IV}}\text{O}_{2n+2}$ for the uranium oxide series. The green color of U_3O_8 is also that expected for a material containing the U(IV) ion. A radiochemical exchange experiment on U_3O_8 , using first radioactive UO_2 and then radioactive UO_3 in the preparation of U_3O_8 , yielded equal amounts of uranium radioactivity in both oxidation states, suggesting at first that all the uranium atoms were equivalent in the structure (73). The authors admit, however, that it is more likely that an isotopic exchange occurred on formation of the U_3O_8 . Reported resistivity measurements on U_3O_8 differ by a factor of 10^6 , due no doubt to the fact that U_3O_8 and UO_3 readily form solid solutions which upset the stoichiometry. The resistivity of stoichiometric $\alpha\text{-U}_3\text{O}_8$ would seem to be 10^5 ohm cm at 300°K, with a semi-conduction activation energy of 0.6–0.7 eV (274, 521). U_3O_8 is paramagnetic with a susceptibility anomaly at 4.2°K (457), and an effective magnetic moment per mole of 1.39 B.M. (338). Assuming that the electron spin is the only source of paramagnetism, $\text{U}^{\text{VI}}\text{U}_2^{\text{V}}\text{O}_8$ has an expected moment of 1.41 B.M., and $\text{U}_2^{\text{VI}}\text{U}^{\text{IV}}\text{O}_8$ has one of 1.63 B.M., both in acceptable agreement with the experimental value.

The α - and β -forms of U_3O_7 have structures much like that of UO_2 , except that they are tetragonally deformed. As with many of the other mixed valence uranium oxides, the material is paramagnetic with a maximum susceptibility at 6.4°K (457), and, as with the others, the resistivity has been reported to be as low as 3×10^2 (780) and as high as 3×10^6 ohm cm (521) for different samples at 300°K.

There are indications that spectral studies on the uranium oxides might be of value in understanding their molecular and electronic structures, particularly as regards the distribution of valence. Thus, Narbutt and Laputina (526) have studied the X-ray fluorescence M spectra of UO_2 , U_3O_8 , and UO_3 , and find small but distinct differences between UO_2 and UO_3 , with U_3O_8 occupying an intermediate position. Gruen's study of the optical spectrum of UO_2 in ThO_2 (323) clearly shows the presence of the U(IV) ion, and his technique might be of value in determining the presence of this valence state in other class II oxides. Finally, Hoekstra and Siegel (363) report that the infrared spectra of

U_3O_8 and $\text{UO}_{2.9}$ show that neither of these substances contains the isolated $[\text{U}^{\text{VI}}\text{O}_2]^{2+}$ group.

Hofmann and Höschel (366) first reported the preparation of the deep blue materials "cerium-uranium blue," having the approximate composition $2\text{CeO}_2 \cdot \text{UO}_2$, and a dihydrate having the same Ce/U ratio. Because $\text{U}^{\text{IV}}\text{O}_2$ is brown and $\text{Ce}^{\text{IV}}\text{O}_2$ is colorless, these authors ascribed the blue color of the mixed oxides as due to an oscillation of valence:



Later investigators (87, 372, 475, 604, 606) have since shown that, because both CeO_2 and UO_2 have the fluorite lattice with only a very small difference in their lattice parameters, mixed crystals of UO_2 and CeO_2 are to be expected over a wide range of composition, and that the Ce_2UO_6 composition is but one unexceptional example of these solid solutions. In addition to the Ce/U ratio, the water content of the cerium-uranium blue "dihydrate" is also variable continuously (87). In spite of extensive X-ray work on the CeO_2 - UO_2 system, a disagreement still remains as to the upper limit of UO_2 solubility in CeO_2 , Hund *et al.* (372) claiming that a solid solution forms only in the range 0-63% UO_2 , while Magneli and Kihlberg (475) and Rüdorff and Valet (604, 606) find unlimited UO_2 solubility, with the Vegard law very nearly obeyed.

In HClO_4 - NaClO_4 solutions, the Ce(IV) ion rapidly oxidizes the U(IV) ion, according to the reaction (36a):



If such a redox reaction were to occur during the formation of cerium-uranium blue, then, depending upon whether the Ce(IV) or U(IV) ions were in excess in the crystal, there would arise the possibility of either Ce(III),Ce(IV) or U(IV),U(VI) mixed valence optical transitions. However, at the $2\text{Ce(IV)}:1\text{U(IV)}$ stoichiometry there would be no excess ions for mixed valence interaction and the blue color should fade at this composition. In fact, the intensity of the blue color is maximal at approximately the 2:1 composition (87), showing that the blue color is instead due to a Ce-U interaction. Now the U(VI) ion when in eightfold oxygen coordination, as it would be in the fluorite lattice of cerium-uranium blue, is known to always draw two of the oxygens toward itself so as to form the $[\text{UO}_2]^{2+}$ ion (756). However, were such to happen in cerium-uranium blue, the lattice would no longer be that of fluorite. Thus it appears that the blue color is due to the transfer of an electron between Ce(IV) and U(IV):



Solution of UO_2 in the not easily reduced host ThO_2 results in brownish solids, as expected (87). Pressed pellets of cerium-uranium blue of

various Ce/U ratios show a minimum resistivity of 1.6×10^2 ohm cm at about 40% CeO₂ with maximal resistivity at pure CeO₂ and UO₂ (606).

Oxidation of cerium-uranium blue leads to the formation of CeO₂-U₃O₈ mixed crystals containing up to 45 mole % U₃O₈ while still maintaining the fluorite structure. As determined from density measurements, the excess oxygen ions in CeO₂-U₃O₈ mixed crystals occupy both interstitial and cation sites. The CeO₂-U₃O₈ crystals are described as being dark green to black (606).

The mixed valence halides of uranium have been investigated but very little. There are two chlorides of possible mixed valence interest, $2\text{U}^{\text{IV}}\text{Cl}_4 \cdot \text{U}^{\text{VI}}\text{Cl}_6 \cdot 6\text{POCl}_3$, described as dark green crystals (560), and the dark brown prismatic crystals formed by the action of CCl₄ on U₃O₈, formulated as either $2\text{U}^{\text{IV}}\text{Cl}_4 \cdot \text{U}^{\text{VI}}\text{O}_2\text{Cl}_2$, or $3\text{U}^{\text{IV}}\text{Cl}_4 \cdot \text{U}^{\text{IV}}\text{OCl}_2 \cdot 2\text{U}^{\text{VI}}\text{O}_2\text{Cl}_2$ (375).

Uranium ennefluoride, U₂F₉, is a black substance formed in varying yield in many fluorination reactions (4, 531, 534). According to Zachariasen (808), U₂F₉ has a class III-B crystal structure with all uranium atoms in structurally equivalent positions. The unit cell is body-centered cubic with the uranium in ninefold coordination, the average U-F distance of 2.30 Å being intermediate between the U(IV)-F and U(V)-F distances of UF₄ and UF₅. However, the same cannot be said for the black color of U₂F₉, for UF₄ is green and UF₅ is colorless. An effective magnetic moment of 2.11 B.M. per uranium atom has been measured for U₂F₉ (595). The resistance of U₂F₉ has not been measured, but would be very interesting as it might suggest whether the system is really class III-B or class II. A second black mixed valence uranium fluoride, U₄F₁₇, has a structure described as "distorted UF₄," and a specific susceptibility of 8.8×10^{-6} cgs at 22°C (4, 531).

The physical and chemical properties of many of the uranium halides and oxides have been described in detail in reference works (406) and (649). Of the other actinide elements, there are only a few oxides whose stoichiometry suggests that they are mixed valence (649). Protactinium forms the oxide Pa₄O₉ which is cubic, as is U₄O₉, but which is white, whereas U₄O₉ is black. The lower oxides PaO_{2.25}-PaO_{2.20} (cubic), Pa₅O₁₁ (tetragonal), and PaO_{2.20}-PaO_{2.00} (cubic) are all black, however. Neptunium forms a chocolate-brown oxide Np₃O₈ isomorphous with U₃O₈ (405), and plutonium forms an oxide phase PuO_{1.50}-PuO_{1.75} isomorphous with Mn₂O₃.

BB. MISCELLANEOUS

Those elements which have as yet only a scant mixed valence chemistry are brought together in this section. The most surprising of

these is xenon, which forms a stable yellow oxide of the apparent composition $K_4Xe^{VIII}Xe_2^{VI}O_{12}$, which by its color is most likely class I (21, 680). A possible mixed valence compound of aluminum, $Al_4B[N(CH_3)_2]_3(CH_3)_6$, has been reported as a yellow solid having an average aluminum oxidation number of 1.5+ (644). Solutions of cadmium metal in molten $CdCl_2$ have been shown repeatedly to contain species formed from one cadmium atom and from one to three $Cd(II)$ ions (520), but no mixed valence compounds have yet been isolated.

Considerably more can be said about the mixed valence polyhalides; however, we shall limit our remarks to the triiodide ion, and refer the interested reader to the review by Wiebenga *et al.* (773) for information on the other polyhalides. The triiodide ion, I_3^- , is a nominally linear species with ends which are more or less equivalent, depending upon the environment in which it finds itself. Its bonding has been investigated and its electronic spectrum in water explained on the basis of a slightly bent, class III-A system (91). The blue starch-iodine complex has been described as both a class III-A (592) and class III-B (62) polymer of the triiodide ion.

IV. Conclusions

At this point, a survey study of mixed valence chemistry is rather frustrating, because the data for virtually every substance are too meager to allow the deduction and testing of firm conclusions. The reason for this lies in the fact that mixed valence compounds up to now seem to have been studied only by chance, without a real appreciation of their uniqueness and the complementary nature of their various properties. The future is bright, however, in that papers on mixed valence chemistry are presently appearing at the healthy rate of about 60 per year and could easily double, once mixed valence chemistry becomes fashionable. As it stands now, though, the dearth of information is not only in a way frustrating, but also stimulating, we think, and it is our hope that this article will prompt the work in the near future needed to build a proper understanding of this phenomenon. Moreover, the thermodynamic, kinetic, and mechanistic aspects of mixed valence are all important ones which we have not mentioned, along with mixed metal mixed valence, covalent materials, and intermetallics.

It appears that until the properties of mixed valence substances have been more completely investigated, the classification scheme presented here can be used profitably to predict the properties of a substance, given any one of them. One imagines that, in the future, as mixed valence

becomes more and more understandable, it will prove as rewarding to inorganic chemistry as the concept of resonance has been to organic chemistry.

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