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TECHNETIUM

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Introduction

HISTORY OF THE DISCOVERY OF TECHNETIUM

At the end of the first quarter of the twentieth century, elements with atomic numbers 43, 61, 85, and 87 were lacking in the periodic system of elements. The existence of these elements had been predicted by the original discoverer of the Periodic Law, D. I. Mendeleev. These elements included analogs of manganese, which he named eka-manganese and dvi-manganese (1). The element ilmenium, the discovery of which was announced in 1846 by Hermann (2), was known at that time. Because of some of its properties, including the atomic weight (about 104), ilmenium seemed entitled to occupy the place of eka-manganese. Mendeleev, however, on the basis of a thorough analysis of the properties of eka-manganese resulting from the Periodic Law, expressed doubts about the genuineness of the discovery of ilmenium. Later studies confirmed his point of view.

In 1877, Kern announced his discovery of an element resembling manganese in properties and called it davium in honor of the English chemist, Davy. Davium gave a reaction with the thiocyanate ion, that today is an analytical reaction for rhenium. Kern suggested at first that davium should occupy the place of eka-manganese, but later, after determining its atomic weight (about 154), held that davium is analogous to dvi-manganese (3). Davium as well as lucium, which was discovered by Barriere in 1896, turned out to be false elements and completed the "black list" of failures in inorganic chemistry (4).

Failure also befell Ogawa, who in 1908 announced the isolation of an element that he named "nipponium" from the minerals thorianite and molybdenite (5). This element had an atomic weight of 100 and in some of its reactions resembled manganese.

The series of errors allowed to creep into the discovery of new

elements forced researchers to evaluate the results of their experiments more critically.

Only in 1925 did the German chemists Noddack, Tacke, and Berg publish a report (6) on the discovery of new elements called masurium (eka-manganese) and rhenium (div-manganese). This discovery was the result of logical premises and conclusions and improvements in methods. Since the neighbors of element 43 are molybdenum and ruthenium, the search for this element was concentrated on minerals—columbites and tantalites—instead of manganese ores. From columbites the German scientists obtained a concentrate containing about 0.5 % masurium and about 5 % rhenium. They established the presence of these two elements on the basis of the X-ray lines K_{α_1} , K_{α_2} , and K_{β_1} (for masurium) and L_{α_1} , L_{α_2} , and L_{β_1} (for rhenium).

Repeated experiments by Noddack and others confirmed the discovery of rhenium, but not masurium (7–9). In 1927, 100 mg of rhenium had already been isolated (10).

The development of nuclear physics and radiochemistry was the precondition for the discovery of eka-manganese. Studies of the structure and properties of atomic nuclei led to the conclusion that elements not observed in nature are unstable, and can therefore be obtained only by synthesis from other elements.

In 1937 the Italian physicists Perrier and Segrè first obtained trace amounts of element 43 (about 10^{-10} g) by bombarding molybdenum with deuterons in a cyclotron via the reaction $\text{Mo}(d, n)$ (11). The new element was given the name technetium. It was the first chemical element artificially created by man. Its name was officially confirmed at a convention of chemists held on September 2–5, 1949, in Amsterdam.

A study of the physicochemical properties of technetium revealed that its stability in the heptavalent state is greater than that of manganese, and less than that of rhenium. The new element coprecipitated with rhenium as the sulfide in 6 *N* HCl, but remained in solution in 10 *N* HCl.

When moist gaseous HCl was passed through a mixture containing rhenium and technetium in 80 % H_2SO_4 , after 1.5 hours at 180°–200° all the rhenium distilled over, whereas technetium remained in the H_2SO_4 .

Despite the fact that the chemical properties of the new element were studied on unweighable amounts, Perrier and Segrè were able to establish the similarity between technetium and rhenium and, to a somewhat lesser extent, manganese. Many other nuclear reactions leading to the formation of various isotopes of this element were investigated later.

At the present time the main source of relatively large amounts of technetium is its recovery from a mixture of the fission products of uranium (12).

In a nuclear reactor, one of the longest-lived isotopes of technetium, Tc^{99} , is formed together with other fission products. The yield of this isotope from the fission of U^{235} produced by thermal neutrons is approximately 6.2%. According to the rough calculations of Hahn, the production of 10^4 g of plutonium in a uranium reactor results in the accumulation of approximately 150 g of Tc^{99} along with other fission products (13).

There are also other data according to which 100 g of plutonium and 2.5 g of technetium are obtained per day in a reactor operating at a power level of 10^5 kw. Thus, for every 10 kg of plutonium 250 g of technetium is formed under these conditions.

The total quantity of this element, formed as a result of the operation of the numerous reactors producing nuclear fuel (plutonium), is apparently measured in tens or even hundreds of kilograms.

It follows that technetium ceases to be an element unavailable to researchers. The chemistry of technetium can be studied just as well as that of other elements, and for this reason this element is finding increasingly extensive practical applications.

TECHNETIUM IN NATURE

All the isotopes of technetium are radioactive. Numerous attempts to detect technetium in the earth's crust have failed. If the half-life of a radioactive element exceeds 150 million (1.5×10^8) years, it should have been preserved until the present time in at least trace amounts.

In the 1930's the half-lives of the technetium isotopes were still unknown, and therefore the question whether these isotopes had decayed during past geological epochs remained unanswered. Detailed investigations of the properties of technetium obtained artificially, particularly a thorough study of the emission spectrum performed in 1950, provided a justification for further attempts to find this element in nature.

In 1951 Charlotte Moore published a sensational report (14) on the possible presence of technetium on the Sun. A year later the astrophysicist P. W. Merrill detected technetium in the atmosphere of certain stars (S and M classes) (15). By the time of these discoveries, the half-lives of technetium isotopes had been determined.

Since the half-life of the longest-lived technetium isotope is slightly over 2×10^6 years, it should have decayed completely on the Sun. Indeed, some scientists dispute the possibility of the presence of technetium on the Sun.

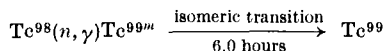
The presence of technetium on stars was also confirmed by other researchers (16); in some stars, the amount of technetium differs only slightly from the content of the neighboring elements. To account for

this fact, it is necessary to assume that technetium is being formed on the stars at the present time as well. This fact is of great significance for the development of the theory of the origin of chemical elements. It refutes numerous theories of prestellar formation of elements and shows that stars are continually operating "factories" of chemical elements. On the basis of the presence of technetium on stars, Jordan (17) called technetium the "touchstone" of cosmogonic theories.

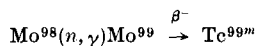
Following Moore's report on the possible existence of technetium on the Sun, the search for primary technetium on earth began again. This search is discussed in particular in the work of Herr, published in 1954 (18). For his study he selected samples of molybdenum blende from Norway and South Africa characterized by a high rhenium content. By decomposing the mineral, Herr obtained a rhenium concentrate (370 g of molybdenum blende with 0.3% rhenium content). Distillation with perchloric acid isolated the technetium-rhenium fraction from the concentrate.

In order to avoid unaccounted for losses of technetium, all the operations were carried out in the presence of a short-lived isotope of radioactive technetium, which served as a tracer for the processes of separation and isolation of this element. $\text{Ph}_4\text{AsReO}_4$ and $\text{Ph}_4\text{AsTcO}_4$ were then precipitated from the rhenium fraction. To achieve the fullest possible removal of rhenium, multiple distillations from HClO_4 were carried out, and the rhenium was precipitated with hydrogen sulfide from 9 N HCl. From the solution obtained, enriched with technetium (the quantity of technetium was practically unweighable), 1.5 mg of copper sulfide was precipitated. The copper sulfide containing occluded technetium was exposed to a neutron flux of $1.2 \times 10^{12} \text{ n}/(\text{cm}^2 \text{ sec})$ in a reactor.

The detection of an isotope with a half-life of 6 hours would make it possible to conclude that this isotope is Tc^{99m} , formed by the capture of a neutron by a Tc^{98} nucleus according to the reaction:



It was kept in mind in these experiments that Tc^{99m} could also be formed as a result of the activation of Mo^{98} and subsequent decay, as follows:



Despite the fact that a thorough chemical purification excluded the presence of molybdenum in the irradiated sample, after the irradiation an impurity was detected that decayed with a half-life of 6.6 hours.

The curve of Fig. 1 shows the change in activity of a sample obtained by a 9-hour irradiation in the reactor; the measurements were made with

an aluminum filter having a thickness of 70 mg/cm^2 . The curve is nonlinear and indicates the presence of a long-lived component with a half-life corresponding to Re^{186} . Thus, the purification method employed did not result in complete removal of the rhenium impurity. The radioactive decay of the sample, measured with a lead filter, is shown in curves 2 and 3. The decay observed occurs with a half-life that is very

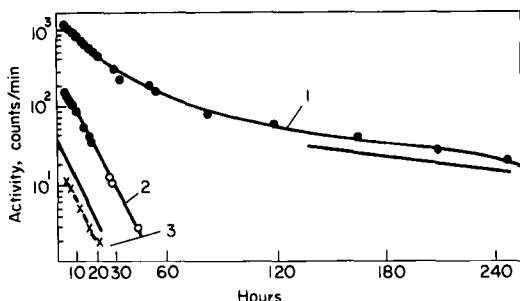


FIG. 1. Activation analysis of technetium fraction isolated from molybdenite. Change of radioactivity during measurement: (1) with aluminum filter 70 mg/cm^2 thick ($T_{1/2} = 3.6$ days, Re^{186}), (2) with lead filter 1000 mg/cm^2 thick ($T_{1/2} = 6$ hr, Tc^{99m}), (3) with lead filter 5000 mg/cm^2 thick ($T_{1/2} = 6$ hr, Tc^{99m}).

close to that of Tc^{99m} . This activity can be attributed to the radiation of unweighable quantities of Tc^{99m} , formed by the capture of a neutron by one of the technetium isotopes, Tc^{98} , present in the irradiated sample in very small amounts.

In 1955 Alperovitch and Miller reported the discovery of primary Tc^{98} in various minerals, for instance columbite (19). According to their data, a combination of coprecipitation, distillation, and ion exchange enabled them to isolate a minute quantity of technetium. After irradiation with neutrons, they observed the γ -radiation of Tc^{99m} . Similar results were obtained for many samples.

It should be noted that some isotopes interfere with the activation analysis, for Tc^{99} is formed when neutrons act upon Mo^{98} , Tc^{98} , and Ru^{99} . These results were confirmed by Anders *et al.* (20). The method of isolating technetium was analogous to that used in the preceding study.

In 1956 Boyd and Larson (21) made a thorough search for technetium in various minerals, using spectrochemical, activation, and mass-spectrometric methods. The results of this study are shown in Table I. Technetium was isolated by precipitation and ion exchange. Of the samples studied, only two gave positive results. As was shown later, one of them was contaminated with Tc^{99} , and the other with Re .

TABLE I
DETERMINATION OF TECHNETIUM CONTENT IN VARIOUS SUBSTANCES

Substance	Method of determination	Technetium content (g/kg)
MoS ₂ (Climax, Colorado)	Spectrochemical	$< 4 \times 10^{-10}$
KReO ₄ , pure	Spectrochemical	$< 8 \times 10^{-9}$
MoS ₂ (Nevada)	Spectrochemical	$< 1.5 \times 10^{-9}$
MoS ₂ (Miami, Arizona)	Spectrometric	$< 1.8 \times 10^{-7}$
MoS ₂ (Miami, Arizona)	Activation	$< 10^{-9}$
MoS ₂ (Miami, Arizona)	Spectrochemical	$< 1.7 \times 10^{-9}$
MoS ₂ (Miami, Arizona)	Activation	8.3×10^{-11}
MoS ₂ (Nevada)	Activation	1.3×10^{-10}
Osmium-iridium concentrate	Spectrochemical	$< 1.6 \times 10^{-8}$
Volatile products of molybdenum roasting	Spectrochemical	$< 1.3 \times 10^{-8}$
Yttrotantalite (western Africa)	Mass-spectrometric	$< 6 \times 10^{-11}$
Iron-nickel meteorite	Spectrochemical	$< 4.5 \times 10^{-10}$

Furthermore, it was found that the half-life of the long-lived Tc⁹⁸ is approximately 1.5×10^6 years, which completely excludes the occurrence of primary technetium in the earth's crust.

For this reason, Boyd *et al.* suggested that, if technetium does exist on earth, it is of secondary origin and results from the activation of Mo, Nb, and Ru by hard cosmic radiation and from the spontaneous fission of uranium.

This point of view is also held by Parker and Kuroda (22), who found that 10^{-14} curie of Mo⁹⁹ is at equilibrium with 1 g of U²³⁸ due to the spontaneous decay of the latter.

In subsequent studies, Kuroda *et al.* (23-27) established more precisely the relative proportions of the short-lived fission fragments of U²³⁸. The investigations showed that 1 kg of pitchblende (50% U) at equilibrium contains 2.5×10^{-10} g of Tc⁹⁹ (10.5 disintegrations/min).

The first isolation of an appreciable amount of natural technetium was achieved in 1961 by Kenna and Kuroda (28). Having processed about 5.3 kg of pitchblende mined in the Congo, they obtained three samples with a total content of 1×10^{-9} g of Tc⁹⁹, which is in good agreement with the calculated data.

I. Nuclear Properties of Technetium

A. INTRODUCTION

The unsuccessful attempts to discover element 43 prior to its artificial preparation by Perrier and Segrè were explained by the absence of this

element in appreciable quantities in nature. This is because technetium has only radioactive isotopes with relatively short half-lives. The search for natural technetium posed the question of the stability of its isotopes. This was the subject of several theoretical studies (29–32). On the basis of general principles of nuclear structure, it was shown that all the isotopes of technetium (nuclear charge $Z = 43$) should be unstable, although some of them may have very long half-lives. Indeed, for odd Z 's, a necessary although insufficient condition of nuclear stability is the presence of an even number of neutrons N .

Analysis of the curves of nuclear stability (see 30–32) shows that only isotopes with atomic weight $A = 97$ and 99 should be stable. However, according to the Shchukarev-Mattauch rule, no two stable isobars exist

TABLE II
ISOTOPES OF MOLYBDENUM, TECHNETIUM, AND RUTHENIUM^a

Element	Mass number								
	94	95	96	97	98	99	100	101	102
Mo	S	S	S	S	S	β^-	S	β^-	β^-
Tc	EC	EC	EC	EC	β^-	β^-	β^-	β^-	β^-
Ru	EC	EC	S	EC	S	S	S	S	S
	β^+	β^+							

^a S = stable; EC = electron capture.

whose nuclear charges differ only by unity. This rule is a good reflection of the general principles of the isotopic composition of various elements, although there are some exceptions (Cd^{113} and In^{113} ; In^{115} and Sn^{115} ; Te^{123} and Sb^{123}).

The nuclear charge and atomic weight of technetium (about 99) determines its position in the periodic system between molybdenum (95.94) and ruthenium (101.07). When all the known stable isotopes of these elements are tabulated (Table II), it is seen that, in the interval corresponding to the atomic weight of technetium, there is no reason to expect the existence of stable isotopes of this element.

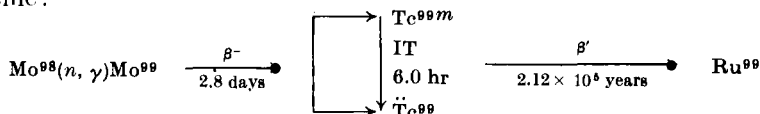
Segrè (29) also showed that the half-life of Tc^{98} should be relatively appreciable. Subsequently, the conclusions regarding the relative stability of technetium isotopes Tc^{97} , Tc^{98} , and Tc^{99} were confirmed experimentally. This is indicated by the longest half-lives of these isotopes and their position in a certain transition zone between two types of decay (positron or electron capture or β^- decay).

B. ISOTOPES OF TECHNETIUM

Sixteen isotopes of technetium with mass numbers from 92 to 107 and six isomers are known (Table III) at the present time.

A systematization of the β decay of some of them is given in the studies of Everling (53), Kienle and others (38, 54, 55). The majority of technetium isotopes are formed by the irradiation of a molybdenum target with deuterons or protons, or molybdenum or ruthenium targets with neutrons. The capture cross sections for irradiation of natural molybdenum with 10.2-MeV deuterons are given in Table IV (56).

Among the short-lived technetium isotopes, those of greatest practical importance are the isomers Tc^{95m} (60 days), Tc^{97m} (90.5 days), and Tc^{99m} (6.0 hours). The first two isomers are obtained by deuteron or proton irradiation of molybdenum, and Tc^{99m} is formed by irradiating molybdenum with neutrons in a reactor. At the same time, the Mo^{98} isotope (whose content in the natural mixture is 23.78%), is transmuted into Mo^{99} by capturing a neutron (the capture cross section of this reaction is 0.13 barn). As Mo^{99} decays further, first the short-lived isomer Tc^{99m} and then the long-lived isotope Tc^{99} are formed, in accordance with the scheme:



Usually, molybdc trioxide MoO_3 is irradiated. The radioactivity of Mo^{99}O_3 , induced by the neutron irradiation, may be calculated from the equation

$$A = 3.48 \times 10^{-12} \Phi (1 - e^{-0.248t}) \quad (1)$$

where A is the radioactivity of MoO_3 , $\mu\text{C/g}$; Φ is the neutron flux, $\text{n}/(\text{cm}^2 \text{ sec})$; and t is the irradiation time, days.

Practically, the irradiation time in a reactor usually does not exceed one to two half-life periods of Mo^{99} , i.e., 3–6 days. Commercial radioactive preparations of Mo^{99} (usually in the form of molybdc trioxide) have a specific activity of approximately $10 \mu\text{C/g}$, the activities of the daughter Tc^{99m} and Mo^{99} being approximately equal.

Owing to the absence of stable isotopes, technetium is isolated from molybdc trioxide without a carrier, and its specific activity may be very high. Tc^{99m} has also been obtained recently from the fragment product Mo^{99} (57).

The precursors of the Tc^{95m} and Tc^{97m} isomers are stable molybdenum isotopes, whereas Tc^{99m} is formed as a result of the radioactive decay of the relatively longer-lived Mo^{99} . The latter characteristic of Tc^{99m} can

TABLE III
 TECHNETIUM ISOTOPES (33–36)

Mass number	Half-life	Type of radioactive decay ^a	Particle energy (MeV)		Reaction of isotope production	Reference
			β	γ		
92	4.3 min	β^+ , EC	4.1	1.3	Mo(p, n) Mo($d, 2n$)	
93 _m	43.5 min	EC (18%) IT (82%)	—	0.39 (82%) 2.66 (18%)	Mo(d, n)	(37)
93	2.7 hr	EC ($\sim 85\%$) β^+ ($\sim 15\%$)	0.82 ($\sim 13\%$) 1.67 ($\sim 2\%$)	0.86 (2.6%) 1.35 (60%) 1.49 (30%) 2.03 (0.35%) 2.44 (0.3%)	Mo(d, n) Mo(p, γ) Mo($d, 2n$)	(37)
94 _m	52.5 min	EC (21%) IT (24%) β^+ (55%)	0.56 (1%) 2.41 (54%)	0.874 (73%) 1.85 (11%) 2.73 (1%) 3.27 ($\sim 1\%$)	Nb($\alpha, 3n$)	(37, 38) (39)
94	293 min	EC (93%) β^+ (7%)	0.9 (2%) 2.41 (5%)	0.705 (100%) 0.846 (72%) 0.874 (100%)	Mo(p, n) Mo($d, 2n$) Ru ⁹⁴ $\xrightarrow{\beta^+}$ Nb($\alpha, 3n$)	(40) (39)
95 _m	60 days	IT ($\sim 4\%$) EC $\beta^+?$	0.477 ($< 1\%$) 0.68 ($< 1\%$)	0.039 IT 0.204 (71%) 0.256 ($\sim 1\%$) 0.584 (40%) 0.617 (2%) 0.788 (13%) 0.822 (8%) 0.837 (29%) 1.042 (4%)	Mo($d, 2n$)	(41–43)
95	20 hr	EC	—	0.205 (1%) 0.680 (2%) 0.765 (82%) 0.84 (10.5%) 0.93 (1.7%) 1.06 (4%)	Mo($d, 2n$)	(37, 42)
96 _m	52 min	IT	—	0.034	Mo(p, n) Mo($d, 2n$)	

TABLE III—*cont.*

TECHNETIUM ISOTOPES (33–36)

Mass number	Half-life	Type of radioactive decay ^a	Particle energy (MeV)		Reaction of isotope production	Reference
			β	γ		
96	4.3 days	EC	—	0.310 (4%)	Nb(α, n)	
				0.770 (100%)	Mo($d, 2n$)	(44)
				0.800 (86%)	Mo(d, n)	(43, 44)
				0.840 (100%)	Mo(p, n)	
				1.115 (15%)	Ru(n, p)	
97 ^m	90.5 days	EC	—	0.090	Mo($d, 2n$)	(42)
				0.099	Mo(p, n)	
					Mo(d, n)	(42)
					Ru(EC)	
97	2.6×10^6 years	EC	—	—	Mo($d, 2n$)	
98	1.5×10^6 years	β^-	0.30	0.74	Tc ^{97m} (IT)	(45)
		γ		0.65	Ru(n, p)	(45)
					Mo(p, n)	(46)
99 ^m	6.0 hr	IT	—	0.002 (1.4%)	Mo(d, n)	
				0.140 (1.4%)	Mo ⁹⁹ $\xrightarrow{\beta^-}$	
				0.142 (98.6%)	Ru(n, p)	
					Th(ϕ)	
99	2.12×10^5 years	β^-	0.292	—	U(ϕ)Mo $\xrightarrow{\beta^-}$	
					Tc (IT)	
					U(ϕ)	
					Mo ⁹⁹ $\xrightarrow{\beta^-}$	
100	15.8 sec	β^-			U(ϕ)Mo $\xrightarrow{\beta^-}$	
		γ	2.20	0.542	Mo(n, p)	
			2.88	0.60	Tc(n, γ)	(21)
			3.38	0.71	Ru ¹⁰³ (n, α)	(47)
				0.81		
				0.89		
				1.01		
				1.14		
				1.31		
				1.49		
				1.80		
101	14.3 min	β^-	1.4	0.307	Mo(d, n)	
		γ			Ru(γ, p)	
					U(ϕ)Mo $\xrightarrow{\beta^-}$	
					Ru(n, np)	(48)
102	4.5 min	β^-	2	0.473	U(d, ϕ)	(49)
		γ		< 0.662	Ru(n, p)	
		β^-			U(d, ϕ)	(48)
103	50 sec	β^-	2.0	0.135; 0.215	Ru(n, np)	(48)
		γ	2.2	0.350	U(ϕ)	(38, 50)

TABLE III—*cont.*
 TECHNETIUM ISOTOPES (33–36)

Mass number	Half-life	Type of radioactive decay ^a	Particle energy (MeV)		Reaction of isotope production	Reference
			β	γ		
104	18 min	β^-	1.8	0.36	Mo(<i>d, xn</i>)	(38, 51)
		γ	2.4	0.89	Ru(<i>d, xn</i>)	
			3.3	2.5	Mo(<i>d, αxn</i>)	
				3.5		
				4.05	Ru(<i>n, p</i>)	
105	7.7 min (10 min)	β^-	3.4	0.110	U(ϕ)Mo $\xrightarrow{\beta^-}$	(38, 51)
					U(ϕ)	
		γ			U(ϕ)Mo $\xrightarrow{\beta^-}$	
(107)	< 1 min	—	—	—	U(ϕ) ... Ru \rightarrow	(52)

^a IT = isomeric transition.

be utilized for its preparation by the “milking” method, which is steadily gaining in importance in the case of short-lived isotopes. Essentially, the method consists in separating the short-lived daughter isotope from the relatively longer-lived mother isotope, which remains in the liquid or solid phase. The phase containing the mother isotope may serve as a kind of isotope generator for a periodic recovery of the daughter isotope. A diagram of the operation of such a generator is shown in Fig. 2. The activity of technetium in molybdenum regains its maximum in 21 hours. However, after 2, 4, and 10 hours one can already extract, respectively, 26, 46, and 79 % of the maximum. The generator retains an acceptable activity of Mo⁹⁹ and Tc^{99m} for about 2 weeks. The methods used for separating technetium from molybdenum are described in Section IV.

 TABLE IV
 CROSS SECTION OF CAPTURE OF DEUTERONS (10.2 MeV) BY Mo
 ISOTOPES

Stable Mo isotope	Capture cross section (barns)	Tc isotope formed	Stable Mo isotope	Capture cross section (barns)	Tc isotope formed
Mo ⁹⁵	1.00	Tc ^{95m}	Mo ⁹⁷	2.4	Tc ^{97m}
Mo ⁹⁵	13.3	Tc ⁹⁵	Mo ⁹⁸	12	Tc ⁹⁸
Mo ⁹⁶	3.3	Tc ^{96m}			

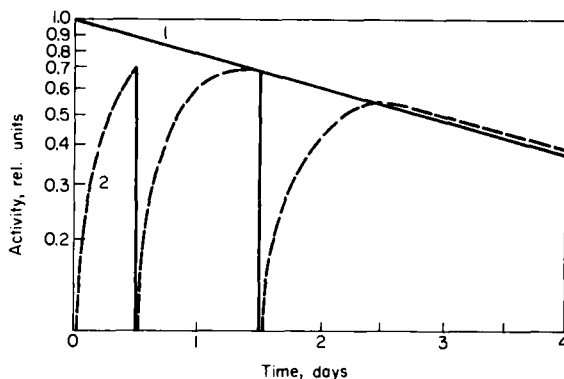


FIG. 2. Diagram of operation of Tc^{99m} generator: (1) change of activity of Mo^{99} , (2) accumulation of Tc^{99m} in Mo^{99} after 12 and 24 hours.

A large amount of technetium isotopes, mainly heavier ones, is formed by the fission of uranium, thorium, or plutonium either directly, or via the mother isotopes of molybdenum. Thus, according to the data of Katcoff (58), during the fission of U^{235} in a reactor the yield of the various technetium isotopes is approximately 1–6% (Table V).

TABLE V

YIELD OF TECHNETIUM ISOTOPES FROM FISSION OF U^{235}

Technetium isotope	Tc^{99}	Tc^{101}	Tc^{102}	Tc^{103}	Tc^{104}	Tc^{105}	Tc^{107}
Yield (%)	6.06	5.6	4.3	3.0	1.8	0.9	0.19

The main isotope, Tc^{99} , is formed in one of the highest yields during the fission of other fissionable materials as well (Table VI).

A general equation describing the accumulation of Tc^{99} in a reactor, and allowing for the fission of U^{235} and for the Pu^{239} and Pu^{241} which are formed, has been proposed by Kir'yanov *et al.* (59):

$$N_{\text{Tc}} = \frac{A}{6.02 \times 10^{23} \times 100(\sigma_c^{235} - \sigma_\gamma^{\text{Tc}})} \text{ mg/kg U} \quad (2)$$

where

$$A = 99 \times 10^3 \times \text{No}^{235} \sigma_f^{235} (1 + \beta) \delta^{\text{Tc}} [1 - e^{-(\sigma_c^{235} - \sigma_\gamma^{\text{Tc}})\Phi t}] e^{-\sigma_\gamma^{\text{Tc}}\Phi t}$$

No^{235} is the content of U^{235} nuclei in 1 kg of uranium; σ_c^{235} , σ_f^{235} are the capture and fission cross sections for U^{235} ; $\beta(A^{239, 241}/A^{235})$ is the ratio of the number of fissions of Pu^{239} and Pu^{241} to the number of fissions of

TABLE VI
YIELD OF Tc^{99} (Mo^{99}) DURING FISSION (58)

Isotope undergoing fission	Neutron energy	Yield (%)	Isotope undergoing fission	Neutron energy	Yield (%)
U^{233}	Thermal	4.8	U^{235}	Thermal	6.06
Pu^{239}	Thermal	5.9	U^{238}	Fast	6.3
Pu^{239}	Fast neutrons	5.9		neutrons	
			Th^{232}	Fast	2.7
				neutrons	
U^{235}	14 MeV	5.17	Th^{232}	8 MeV	3.1

U^{235} ; δTc is the yield of technetium during fission (assumed equal for Pu^{239} , Pu^{241} , and U^{235}); and Φt is the total neutron flux.

This formula agrees well with the results obtained from analyses of fuel elements of the First Atomic Power Station. However, all the remaining technetium isotopes obtained in the reactor are short-lived, and their rapid recovery is difficult. For this reason, in order to obtain such isotopes, small amounts of uranium are irradiated with deuterons or neutrons, and use is made of methods that permit a rapid isolation of the technetium or molybdenum isotopes (60, 61). Molybdenum and technetium isotopes obtained as a result of fission and their nuclear transformations are shown in Table VII.

The methods of recovering technetium are described in more detail in Sections IV and V. Let us mention only that these methods can be

TABLE VII
TECHNETIUM AND MOLYBDENUM ISOTOPES FORMING DURING FISSION

Ru^{100}	Ru^{101}	Ru^{102}	Ru^{103} (40 days)	Ru^{104}	Ru^{105}		
Tc^{99} (6.04 hr $2.12 \cdot 10^5$ years)	Tc^{100} (15.8 sec)	Tc^{101} (14.3 min)	Tc^{102} (4.5 min)	Tc^{103} (50 sec)	Tc^{104} (18 min)	Tc^{105} (7.7 min)	
Mo^{98}	Mo^{99} (66 hr)	Mo^{100}	Mo^{101} (14.6 min)	Mo^{102} (11 min)	Mo^{103} (1.1 min)	Mo^{104} (1.1 min)	Mo^{105} (40 sec)

considerably simplified in nuclear investigations, since frequently a quantitative yield is not required and only a relative purity of the products and their rapid isolation from the irradiated mixture are necessary. Occasionally the isolation of technetium can be dispensed with altogether, as is evident from reference (39), if the nuclear characteristics of the investigated isotope differ markedly from the nuclear characteristics of possible impurities. Usually the nature of the products formed can be predicted from the energy of the particles bombarding the target and from the target material. However, in a rigorous identification of the products of nuclear reactions, it is necessary to use other physical and chemical methods as well. Chemical identification in the case of trace amounts of elements consists in selecting appropriate carrier elements,

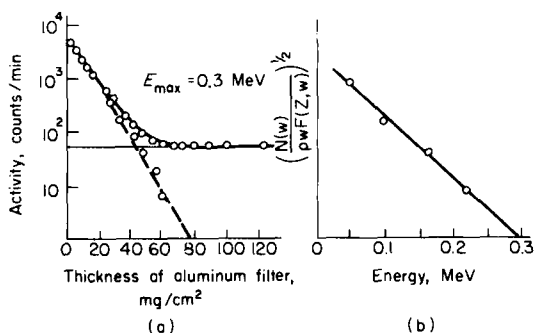


FIG. 3. Identification of Tc^{99} by its β radiation: (a) absorption of β particles in aluminum, (b) determination of maximum energy by means of β spectrometer.

and then comparing the behavior of the radioactivity of the trace component with the behavior of the carrier element during the chemical operations. Such a method was used with element 43 when the latter was prepared by irradiating a molybdenum target with deuterons (11, 62, 63). After the irradiation and dissolution of the target in a mixture of nitric and hydrochloric acids, other radioactive isotopes formed by the (d, xn) reaction could have been present in the solution obtained. These isotopes could have belonged to the closest neighbors of molybdenum (zirconium, niobium, and ruthenium) or to activated impurities of the target.

Because of the lack of stable technetium isotopes in nature, an analog of technetium, rhenium, was used as the carrier. The acid solution was evaporated to dryness, and the residue was dissolved in water made alkaline with ammonia. As carriers, salts of zirconium, tantalum, and potassium perrhenate along with the molybdate were added to various

portions of the solution. The precipitation of zirconium as ZrO_2 , tantalum as Ta_2O_5 , and molybdenum as the hydroxyquinolate showed, according to radioactivity measurements, that the presumable element 43 is occluded to a slight degree only by molybdenum hydroxyquinolate, and is completely removed from the latter by reprecipitation. Consequently, the target did not contain radioactive isotopes of zirconium, tantalum, and molybdenum in detectable amounts. The separation of the presumable ruthenium and element 43 together with the carrier rhenium was achieved by precipitating rhenium sulfide from the filtrate after the precipitation of molybdenum.

Rhenium sulfide was dissolved in an alkaline solution of hydrogen peroxide and, after addition of ruthenium to the solution obtained, nitron perrhenate was precipitated. The radioactivity was quantitatively eliminated from the solution and passed into the precipitate; hence, it could be ascribed to the isotope of an element similar in chemical properties to rhenium, i.e., technetium. The chemical methods of identification were soon supplemented by Seaborg and Segrè, who used the method of characteristic filters for technetium (64).

The physical characteristics of technetium have now been adequately studied, and are therefore widely employed by researchers today for the identification of technetium isotopes. Such identification can be performed on the basis of spectroscopic, mass-spectroscopic, and spectrophotometric data, the character and energy of the radiation, and the half-life. An example of a study that has made ample use of these techniques is the work of Spitsyn and Kuzina (65), who identified Tc^{99} by means of radiometric and spectral methods.

Figure 3 shows the absorption curve of Tc^{99} β -radiation in aluminum (66) for identifying Tc^{99} from the maximum energy of β -radiation (0.292 ± 0.003) (67), and the determination of the maximum energy of Tc^{99} β -radiation with a β -ray spectrometer (59).

II. Physical Properties of Technetium

Elemental technetium is a silver-gray metal, which, like rhenium, ruthenium, and osmium, crystallizes in a hexagonal system with close packing. The unit cell contains two atoms with a radius of 1.358 \AA (68). A study of the change in electrical resistance of technetium at pressures up to $30,000 \text{ kg/cm}^2$ and shear measurements at pressures up to $60,000 \text{ kg/cm}^2$ show that no appreciable changes occur in its crystal structure (69). The compressibility coefficient of technetium has also been calculated and found to be 0.27 mbar^{-1} (70). The atomic weight, determined chemically (from the composition of the oxide Tc_2O_7), is 98.8 ± 0.1 (71),

which is in good agreement with the value 98.913 obtained by direct mass-spectrometric determination (72), and with the value 98.911 determined from the mass of the Ru^{99} isotope and energy of the β decay of Te^{99} (73). The melting point of technetium was predicted theoretically (2257°C) by Szabo and Lakatos (74) and determined experimentally by Anderson *et al.* (75). Its value, $2200 \pm 50^\circ\text{C}$, distinguishes technetium from rhenium to a certain extent and brings it closer to manganese, since technetium melts at a temperature below the melting points of the succeeding elements. The boiling point of technetium lies around 4700°C (36). The temperature dependence of the vapor pressure of technetium is shown in Table VIII. According to X-ray structural analysis data and assuming that its atomic weight is 99, the density of technetium is 11.487 g/cm^3 (67).

TABLE VIII
VAPOR PRESSURE OF TECHNETIUM AT VARIOUS TEMPERATURES

Temperature: 1567 (°C)	1797	1930	2090	2270	2800	3100	3500	4100	4700	
Vapor pressure of technetium, (mm Hg)	10 ⁻⁸	10 ⁻⁶	10 ⁻⁵	10 ⁻⁴	10 ⁻³	10 ⁻¹	1	10 ¹	10 ²	760

At low temperatures, technetium possesses the property of superconductivity. The critical temperature (11.2°K) (76) is the highest for the elements. Another value (8.22°K) is given in a later work by Picklesimer and Secula (77) for the massive metal of 99.995% purity. A still higher critical temperature is displayed by alloys of technetium with molybdenum (78). Technetium is weakly paramagnetic, but much more so than rhenium. Its paramagnetic sensitivity per gram is $270 \cdot 10^{-6}$ c.g.s. at 298°K and $290 \cdot 10^{-6}$ c.g.s. at 780°K (79). The neutron capture cross section of the Te^{99} isotope is small (21) and decreases with increasing neutron energy (80).

Over 2000 lines of the optical spectrum of technetium in the wavelength range 2200–9000 Å have now been determined. Many of them are used for spectral determinations and identification of technetium (81). They include lines of sufficient intensity for identification of technetium with a sensitivity of 10^{-7} g (21). Characteristic spectra of X-radiation also have been obtained that are in good agreement with the position of technetium in the periodic system on the basis of Moseley's law (82).

TABLE IX
PHYSICAL PROPERTIES OF MANGANESE, TECHNETIUM, AND RHENIUM (36)

Physical property	Mn	Tc	Re
Atomic number	25	43	75
Atomic weight	54.938	98.913	186.31
Atomic radius, Å	1.306	1.358	1.373
Crystal lattice parameters, Å	$a = 8.896$ (α -Mn)	$a = 2.735$ $c = 4.391$	$a = 2.755$ $c = 4.449$
Density, g/cm ³	7.30	11.487	21.02
Melting point, °C	1244	2200 \pm 50 (75) 2140 \pm 20 (87)	3170
Boiling point, °C	2120	(4700)	5870
Critical point, °K	—	11.2; 8.8	2.42
Electronic work function, eV	3.95	(4.4)	4.8
Ionization potential, V	$U_1 = 7.432$	7.23	7.87
	$U_2 = 15.64$	14.87	16.6
	$U_3 = 33.69$	31.9	(26)
Magnetic susceptibility at 25°C, $\times 10^{-6}$ c.g.s.	527	270	69
Frequency of nuclear magnetic resonance for field of 10^{-4} gauss, Mc	10.553	9.583	9.586 (Re ¹⁸⁵)
			9.684 (Re ¹⁸⁷)
Relative sensitivity	0.178	0.376	0.133 (Re ¹⁸⁵)
			0.137 (Re ¹⁸⁷)
At constant frequency	2.89	7.43	2.63 (Re ¹⁸⁵)
			2.65 (Re ¹⁸⁷)
Magnetic moment, nuclear magnetons	3.4610	5.6572	3.1437 (Re ¹⁸⁵)
			3.1760 (Re ¹⁸⁷)
Electronic quadrupole moment, $e \times 10^{-4}$ cm ²	0.5	0.3	2.8 (Re ¹⁸⁵)
Main lines of optical spectrum and their relative intensities, Å	4034.49 (250)	4297.06 (500)	5270.96 (200)
	4033.07 (400)	4262.26 (400)	4889.14 (100)
	4030.75 (500)	4238.19 (300)	3725.76 (100)
	2605.69 (100)	4031.63 (300)	3464.73 (350)
	2593.73 (200)	3636.10 (400)	3460.46 (500)
	2576.10 (300)	3466.29 (250)	3451.88 (200)
Main lines of X-ray Spectrum, Å	$K_{\alpha_1} = 209.75$	$K_{\alpha_1} = 673.57$	$L_{\alpha_1} = 1429.97$
	$K_{\alpha_2} = 210.15$	$K_{\alpha_2} = 677.90$	$L_{\alpha_2} = 440.96$
	$K_{\beta_1} = 190.62$	$K_{\beta_{1,3}} = 600.20$	$L_{\beta_1} = 1236.03$
		$K_{\beta_{2,4}} = 588.99$	$L_{\beta_2} = 1204.15$
Half-life	Stable	2.12 $\times 10^5$	6.2 $\times 10^{10}$
		years	years (Re ¹⁸⁷)
Neutron capture cross section, barns:			
	(n, γ) reaction	10.7	20 \pm 5
	(n, n') reaction	—	0.009

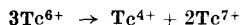
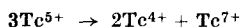
The literature contains no data on liquid and gaseous elemental technetium, with the exception of data on the vapor pressure. Only the value of the entropy (43.3 cal/mole at 25°C) (83) is known for gaseous technetium, and it has been established that the $\text{Tc}_{(\text{gas})}^+$ ion is formed in the mass spectrometer during thermal ionization or electron bombardment (84). The electronic work function, calculated from the dependence of the atomic number Z , is equal to 4.4 eV (85), and the ionization potential is equal to 7.23 V (86). The basic physical properties of technetium are listed in Table IX, where they are compared with the analogous properties of rhenium and manganese. The data pertain to the principal technetium isotope Tc^{99} .

III. Chemical Properties of Technetium

A. ELEMENTAL TECHNETIUM

Technetium is located in Group VII of the Periodic Table and is an analog of manganese and rhenium. From the similarity of the properties of technetium and rhenium, whose chemistry has been sufficiently studied, technetium could have been expected to have several valences from +7 to -1. All of these have now been established experimentally.

The most stable and characteristic oxidation state of technetium is the heptavalent one. It arises from direct oxidation of technetium by oxygen and other oxidants. Another stable oxidized form of technetium is the tetravalent state. The remaining valence states are found only in the form of various complex compounds. Compounds with valences less than 4 oxidize readily, and technetium changes to the tetra- and heptavalent state, whereas compounds of penta- and hexavalent technetium have a tendency to disproportionate, as follows:



The compounds of technetium known at the present time and its properties in the elemental state are examined below. In its chemical and physical properties, technetium is closer to rhenium than to manganese. This results from a phenomenon similar to the lanthanide contraction, which can be observed in the analog pairs Zr-Hf, Nb-Ta, and Mo-W. In the ground (unexcited) state, the atoms of technetium have the following electron configuration: $4s^2 4p^6 4d^5 5s$ ($S_{9/2}$) (88, 89). However, in some surveys (90, 91) an electronic structure of the type $4s^2 4p^6 4d^5 4s^2$ ($S_{5/2}$), similar to the electronic structures of manganese and rhenium, is given for technetium. Although the chemical properties of metallic

technetium repeat those of elemental rhenium in many respects, they differ markedly from them in many cases.

Metallic technetium slowly tarnishes in moist air (92), but does not change in dry air (93). It dissolves in acids that are oxidants: nitric acid, aqua regia, and concentrated sulfuric acid. Metallic technetium dissolves in bromine water and also in neutral and alkaline solutions of hydrogen peroxide (94), which contradicts the data of earlier reports (92, 95). The solution rate of technetium in hydrogen peroxide is apparently affected greatly by the condition of the metal surface and the presence of impurities. Under analogous conditions, metallic rhenium also dissolves readily.

Technetium burns in oxygen, forming the higher oxide Tc_2O_7 (96). At high temperatures, technetium reacts with chlorine and fluorine, and at 700° – 1100° with carbon to form the carbide TcC (97). Technetium carbide is a compound with a face-centered lattice ($a = 3.982 \text{ \AA}$) and a density of 11.5 g/cm^3 .

B. TECHNETIUM OXIDES

The existence of two technetium oxides, the volatile Tc_2O_7 and the relatively involatile TcO_2 , has now been firmly established. The combustion of technetium in excess of oxygen at 500° yields Tc_2O_7 as the only product (96, 98). The compound obtained can be readily purified by repeated sublimations. At room temperature, Tc_2O_7 is a light-yellow crystalline substance soluble in water and dioxane. In air, the crystals avidly absorb water, dissolving into a red liquid. The melting point of Tc_2O_7 is 119.5° , and the boiling point is 310.5° .

Thus, Tc_2O_7 exists as a liquid over a relatively large temperature interval as compared with Re_2O_7 , whose melting and boiling points are, respectively, 300° and 360° .

The vapor pressure of Tc_2O_7 at various temperatures is shown in Table X and obeys the following equations:

$$\begin{aligned} \text{For solid } \text{Tc}_2\text{O}_7, \log p &= 18.279 - \frac{7205}{T} \pm 8\% \\ \text{For liquid } \text{Tc}_2\text{O}_7, \log p &= 8.999 - \frac{3571}{T} \pm 1\% \end{aligned} \quad (99)$$

It is interesting to note that solid Tc_2O_7 conducts electric current, whereas liquid Tc_2O_7 does not. This behavior of Tc_2O_7 does not correspond to that of Re_2O_7 (91). X-ray diffraction has shown that crystalline Tc_2O_7 has a symmetry of a lower order than Re_2O_7 and is not isomorphous with it (91). Technetium heptoxide possesses a weak diamagnetism (39),

is a stronger oxidant than Re_2O_7 , and is readily reduced by vapors of organic substances (including vacuum stopcock grease).

When Tc_2O_7 dissolves in water, a colorless solution is formed which, when slowly evaporated over concentrated sulfuric acid, turns yellow at first, then dark yellow, dark red, and finally dark red hygroscopic crystals separate. The chemical composition of these crystals has shown that they are a hydrate of the composition $\text{Tc}_2\text{O}_7 \cdot \text{H}_2\text{O}$, i.e., anhydrous pertechnetetic acid HTcO_4 (96). Many attempts have been made to

TABLE X
TEMPERATURE DEPENDENCE OF SATURATED Tc_2O_7 VAPOR

Pressure (mm Hg):	0.1	1	10	100	760
Temperature ($^{\circ}\text{C}$):	100.5	123.6	173.2	237.0	310.5

obtain oxides of hexavalent technetium TcO_3 . Thus, Fried and Hall reported that they obtained a volatile dark red oxide by reacting oxygen with metallic technetium at 400° – 1000° . Chemical analysis of two samples of this compound led to the formula $\text{TcO}_{3.05}$. However, subsequent studies did not confirm this (99), and the question of the existence of TcO_3 has remained unanswered.

Another stable oxygen compound of Tc is the dioxide TcO_2 . It does not form by a direct reaction between metallic technetium and oxygen, but can be readily obtained by indirect means. The first sample of TcO_2 was obtained by Rogers (101) in the form of a greenish black precipitate by electrolyzing a solution of pertechnetate in 2 *N* NH_4OH . Technetium dioxide can also be obtained by reduction of aqueous solutions of pertechnetates with zinc and hydrochloric acid, by pyrolysis of ammonium pertechnetate (99), and by hydrolysis of K_2TcCl_6 (79). According to chemical analysis data, the hydrated dioxide has the composition $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$. This compound is weakly paramagnetic. On heating to 300° in a vacuum, $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ dehydrates completely, and, at 900° – 1100° , sublimation of TcO_2 takes place (79). Like ReO_2 , anhydrous black TcO_2 crystallizes in the manner of MoO_2 and has a density of $6.9 \text{ g}^3\text{cm}^3$ (102). Technetium dioxide is stable in air at room temperature but is readily oxidized by oxygen to Tc_2O_7 . At 300° , TcO_2 reacts with chlorine to form products that hydrolyze readily and can be separated by distillation.

When the hydrate $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ dissolves in a concentrated solution of sodium or potassium hydroxide, the ion $\text{Tc}(\text{OH})_6^{2-}$ is formed. The orange solution containing hydroxotechnetate(IV) ions absorbs light

with a maximum at $410\text{ m}\mu$ and is readily oxidized by hydrogen peroxide, bromine water, or ions of tetravalent cerium to form the pertechnetate (103).

C. TECHNETIC ACID AND ITS SALTS

As was mentioned, when technetium heptoxide dissolves in water, technetic acid HTcO_4 is formed, which on slow evaporation of the solution over concentrated H_2SO_4 separates in the form of dark red hygroscopic crystals. The composition of these crystals corresponds to the formula HTcO_4 . The character of the curves obtained by potentiometric titration indicates that technetic acid is a relatively strong monobasic acid and can be titrated with indicators used in acidimetry (79, 96).

The vapor pressure of technetic acid and its aqueous solutions can be calculated from the following equations:

$$\text{For solid HTcO}_4, \log p = 8.207 - \frac{2395}{T} \pm 1\%$$

$$\text{For a saturated solution, } \log p = 8.201 - \frac{2375}{T} \pm 2\% \quad (99)$$

Some salts of technetic acid, the pertechnetates, have been isolated in the pure form. Thus, NH_4TcO_4 , KTcO_4 , NaTcO_4 , RbTcO_4 , CsTcO_4 , LiTcO_4 , AgTcO_4 , TlTcO_4 , $(\text{C}_6\text{H}_5)_4\text{AsTcO}_4$, and nitron pertechnetate have been obtained thus far. The latter two salts are practically insoluble and can be used as weighing forms in quantitative analysis.

Pure ammonium pertechnetate is a crystalline, nonhygroscopic substance showing no sign of decomposition after being heated for several hours at 100° . In a vacuum at 550° , NH_4TcO_4 decomposes to form TcO_2 . However, very pure NH_4TcO_4 sublimes without appreciable decomposition.

The density of NH_4TcO_4 is 2.73 g/cm^3 . Potassium pertechnetate KTcO_4 melts at 540° and sublimes without decomposing at about 1000° .

Fragments of NH_4TcO_4 produced by electron bombardment at 80° – 160° have been studied by mass spectrometry (104). The following ions arranged in order of decreasing quantities were thus detected: Tc_2O_7^+ , TcO_4^+ , TcO_3^+ , TcO_2^+ , TcO^+ , Tc_2O_5^+ , Tc_2O_6^+ , and Tc_2O_4^+ .

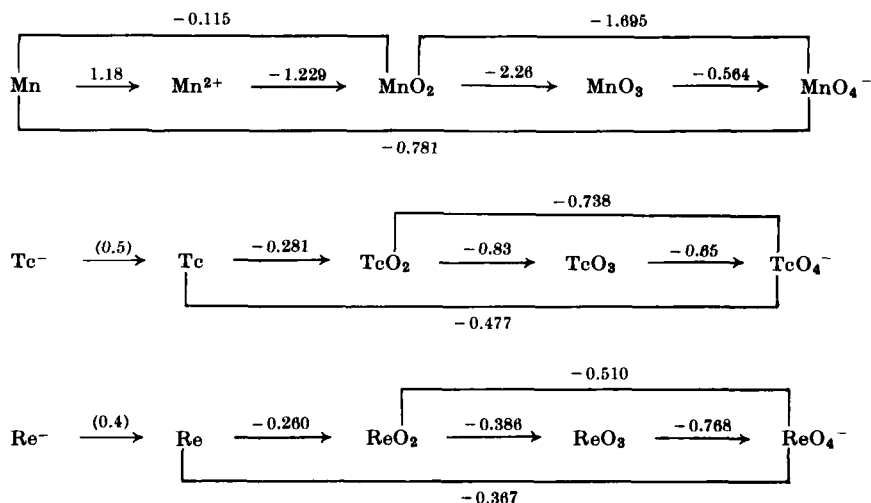
Table XI shows the lattice parameters of salts of technetic acid obtained by X-ray diffraction, and their solubility in water. All the salts of technetic acid are isomorphous with the corresponding salts of rhenic acid. The solubility of salts of technetic acid is somewhat higher than that of the corresponding perrhenates. Thus, the solubility of KTcO_4 is

21.3 g/1000 g of water, and that of KReO_4 is 14.7 g/1000 g of water (105). In aqueous solutions, the TcO_4^- ion is the most stable one. The ionic radii of Tc^{7+} is 0.56 Å (111). This value is close to the ionic radius of Re^{7+} (0.56 Å), but greater than that of Mn^{7+} (0.46 Å).

The calculated ionization potential of Tc^{7+} is 95 eV; this value is intermediate between those of Mn^{7+} (122 eV) and Re^{7+} (79 eV). The length of the Tc—O bond in the tetrahedral ion TcO_4^- is 1.75 Å, and

TABLE XI
CRYSTAL LATTICE PARAMETERS AND SOLUBILITY OF SALTS OF
TECHNETIC ACID

Compound	Lattice type	Lattice parameters (Å)			Density (g/cm ³)	Solubility in water at 20°C (g/100 g)	Reference
		a_0	b_0	c_0			
NH_4TcO_4	CaWO_4	5.790	—	13.310	2.73	—	(106, 107)
NaTcO_4	CaWO_4	5.339	—	11.869	3.4	—	(108, 109)
KTcO_4	CaWO_4	5.654	—	13.030	—	2.13	(106, 107)
RbTcO_4	CaWO_4	5.758	—	13.54	—	1.167	(107, 110)
AgTcO_4	CaWO_4	5.319	—	11.875	5.1	0.563	(107, 110)
CsTcO_4	Ortho-rhombic	5.718	5.918	14.304	—	0.412	(106, 110)
TlTcO_4	Ortho-rhombic	5.501	5.747	13.45	—	0.072	(110)



the length of the Re—O bond in ReO_4^- is 1.97 Å (112). It is not surprising therefore that the pertechnetate ion has a stability intermediate between those of the ReO_4^- and MnO_4^- ions. This is also confirmed by the oxidation-reduction diagram on page 23 (91).

It is apparent that the oxidation potential of the $\text{TcO}_2/\text{TcO}_4^-$ couple in an acid aqueous solution occupies an intermediate position between the

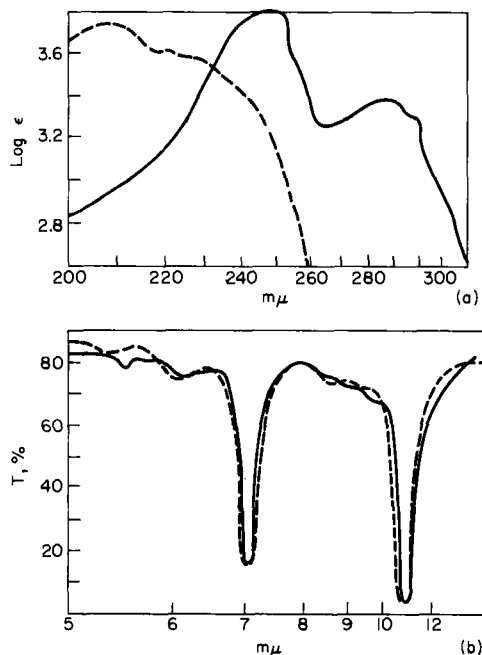


FIG. 4. Absorption spectra of KTcO_4 and KReO_4 : (a) in the ultraviolet, (b) in the infrared; —, KTcO_4 ; - - -, KReO_4 .

corresponding potentials for Mn and Re. The pertechnetate ion (TcO_4^-) is therefore a weaker oxidant than MnO_4^- , but a stronger one than ReO_4^- .

Aqueous solutions of pertechnetates display strong light absorption in the ultraviolet and infrared; this can be utilized for the quantitative determination of technetium. Figure 4 illustrates the infrared and ultraviolet regions of the absorption spectrum of KTcO_4 and KReO_4 .

Certain physicochemical properties of NaTcO_4 and KTcO_4 and dissociation constants of KTcO_4 and CsTcO_4 at 18° were determined

by continuous electrophoresis on a porous filler (113). These data are shown in Table XII.

The radius of the solvated ion, calculated from the Stokes equation, was found to be 5×10^{-8} cm, which is in good agreement with the literature data. The decrease in transference numbers and degree of dissociation for KTcO_4 with changing concentration indicates the incompleteness of its dissociation. From the equation

$$K_d = \frac{[C] \cdot U_0}{U_{\text{an}} - U_0} f_c \cdot f_{\text{an}}$$

were calculated the dissociation constants of KTcO_4 and CsTcO_4 , which at 18° are, respectively, 0.122 and 0.231. In this equation, K_d is the dissociation constant; $[C]$ is the cation concentration; U_0 is the mobility of the TcO_4^- anion, determined experimentally; U_{an} is the mobility of the TcO_4^- anion at full dissociation; and f_c and f_{an} are the activity

TABLE XII

PHYSICOCHEMICAL PROPERTIES OF NaTcO_4 AND KTcO_4 AT 18°C

Compound	Electrolyte concentration, g-eq/l	Mobility U , $\times 10^5$ cm ² /sec V	Ionic equivalent conductance, ohm ⁻¹ cm ²	Equivalent conductance, ohm ⁻¹ cm ²	Transference number of anion	Radius of solvated anion, Å	Degree of dissociation, α
NaTcO_4	0.0	53.0 ^a	51.1	94.6	0.540	4.6	1.00
	0.0005	52.1	50.3	93.1	0.540	—	1.00
	0.005	48.5	46.8	88.1	0.531	—	0.98
	0.01	49.0	47.3	87.8	0.538	—	1.00
	0.02	47.3	45.6	85.1	0.536	—	1.00
					av. 0.537		
KTcO_4	0.0	53.0 ^a	51.1	115.7	0.442	4.6	1.00
	0.0005	51.3	49.5	113.2	0.437	—	0.98
	0.02	42.2	40.7	100.2	0.406	—	0.94

^a The limiting solubility of TcO_4^- anions at 18° was obtained by extrapolation to zero concentration.

coefficients of the cation and anion for a monovalent-monovalent compound. We should note the good agreement between the dissociation constant of KTcO_4 , equal to 0.122 and obtained by the electromigration method, and the value calculated from the thermodynamic data, $K_d = 0.129$ at 25° (99).

D. TECHNETIUM SULFIDES

Technetium forms two sulfides, Tc_2S_7 and TcS_2 . When hydrogen sulfide is passed through acid solutions of pertechnetates, an insoluble sulfide of heptavalent technetium Tc_2S_7 is obtained. A detailed study of the dependence of the precipitation of technetium on time and the hydrochloric acid concentration showed that in 6 *N* HCl solution a reduction starts of the pertechnetate ions to lower oxidation states that are not precipitated by hydrogen sulfide. In 9 *N* HCl solution, this reduction goes to completion. The TcO_4^- ion differs appreciably in this respect from the ReO_4^- ion, which does not change its valence state up to 11 *N* HCl solution (Fig. 5) (62, 114, 115).

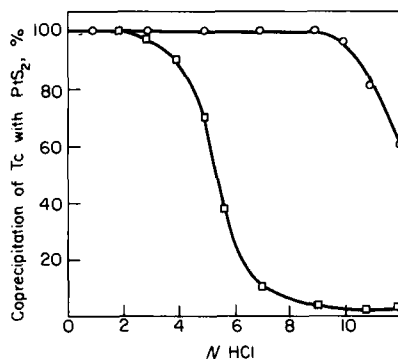


FIG. 5. Coprecipitation of Tc_2S_7 and Re_2S_7 with platinum sulfide at various HCl concentrations: \square , Tc_2S_7 ; \circ , Re_2S_7 .

The dark brown Tc_2S_7 is best precipitated from 2–4 *N* HCl or H_2SO_4 solutions at the temperature of a boiling water bath by passing gaseous H_2S through the solution (116). In a sulfuric acid medium, Tc_2S_7 can also be precipitated with thiosulfate or thioacetamide (60, 117).

The technetium heptasulfide precipitate is usually contaminated with elemental sulfur, which can be removed by thoroughly washing the precipitate with carbon disulfide. Technetium sulfide is insoluble in ammonium polysulfide, but dissolves readily in a mixture of ammonia and

hydrogen peroxide. It is analogous in this respect to Re_2S_7 . Technetium heptasulfide is fairly volatile and sublimes at 100° in a stream of chlorine (118). At higher temperature, it decomposes to form the amorphous disulfide TcS_2 (91).

Crystalline TcS_2 can be obtained by heating Tc_2S_7 with elemental sulfur in an autoclave for 24 hours at 1000° . The formation of TcS_2 from the elements is also probable (91). Technetium disulfide is isomorphous with rhenium disulfide and has an MoS_2 -type structure. When heated to 1000° in a hydrogen or hydrogen sulfide atmosphere, TcS_2 is reduced to the metal.

It should be noted that technetium heptasulfide is widely employed in various processes for isolation and purification of technetium. The concentration process is usually concluded by separating Tc_2S_7 .

E. HALOGEN COMPOUNDS OF TECHNETIUM

The known halogen and oxyhalogen compounds of technetium are shown in Table XIII.

TABLE XIII
KNOWN HALOGEN AND OXYHALOGEN COMPOUNDS OF TECHNETIUM

Degree of oxidation	Fluorine	Chlorine	Bromine
Tc^{7+}	TcO_3F	TcO_3Cl	—
Tc^{6+}	TcF_6	TcCl_6	—
	TcOF_4		
Tc^{5+}	TcF_5	TcOCl_3	TcOBr_3
Tc^{4+}	—	TcCl_4	—

When technetium metal was reacted with excess of fluorine in a closed nickel vessel for 2 hours at 400° , a volatile yellow product was formed (119). It was purified by sublimation. According to the results of chemical analysis, this compound can be expressed by the simplest formula TcF_6 . Technetium hexafluoride is a golden yellow substance, stable during storage in a closed nickel or dry Pyrex vessel. It melts into a yellow liquid at 33.4° , and boils at 55.3° . It is colorless and monomeric in the vapor phase. Table XIV shows the results of measurement of the vapor pressure of TcF_6 at various temperatures.

X-ray diffraction showed that at -5.3° TcF_6 changes its cubic structure to an orthorhombic one, which is isomorphous with the

corresponding crystal structures of the known transition metal hexafluorides. The infrared spectrum in the region $600\text{--}2000\text{ cm}^{-1}$ is similar in character to the spectra of other hexafluorides. The absorption maximum is at 745 cm^{-1} . At 300°K the magnetic moment $\mu = 0.45$ Bohr magneton. When dissolved in alkaline solutions, technetium hexafluoride hydrolyzes to form a black precipitate of technetium dioxide and pertechnetates. This behavior of TcF_6 is analogous to that of ReF_6 , which also disproportionates to the insoluble ReO_2 and soluble ReO_4^- .

TABLE XIV
VAPOR PRESSURE OF TcF_6

Pressure (mm Hg):	59	78	100	115	140	760
Temperature ($^\circ\text{C}$):	0	4.9	9.3	12.0	15.7	55.3

When technetium metal is fluorinated directly, the yellow technetium pentafluoride TcF_5 is formed as a by-product (120). It crystallizes in an orthorhombic system with unit cell parameters $a_0 = 7.6\text{ \AA}$, $b_0 = 5.8\text{ \AA}$, $c = 16.6\text{ \AA}$, and is isostructural with CrF_5 . Its melting point is 50° . TcF_5 is more stable than ReF_5 , but in glass begins to decompose at 60° . In 1962 Colton (121) reported obtaining the chloride of hexavalent technetium. When gaseous chlorine is passed over technetium metal at 200° a reaction begins, which at 400° takes place rapidly with the formation of two volatile products. One is a dark-green solid substance that melts readily to form a green liquid. Chemical analysis showed that the ratio of chlorine to technetium is approximately 6, i.e., this compound has the empirical formula TcCl_6 . When TcCl_6 dissolves in an alkaline solution, hydrolysis takes place with the formation of technetium dioxide and pertechnetate ions in the ratio 1:2, which also confirms the hexavalent state of technetium in this compound. The green technetium hexachloride is very unstable; it decomposes even at room temperature to TcCl_4 .

The chloride of tetravalent technetium is obtained together with TcCl_6 when gaseous chlorine reacts with metallic technetium at 400° (121). In addition, it can be obtained by reacting technetium heptoxide with carbon tetrachloride in an autoclave at 400° (122). Technetium tetrachloride consists of fine blood-red crystals, which sublime in a stream of chlorine. Measurement of the magnetic susceptibility over a wide temperature range showed TcCl_4 to be paramagnetic ($\mu = 3.14$ Bohr magnetons at 25° and $\theta = -57^\circ$) (123).

Technetium tetrachloride reacting with oxygen forms the oxychloride of heptavalent technetium. On dissolving in concentrated HCl, it yields the complex ion TcCl_6^{2-} (94).

In a mass-spectrometric study of the products resulting from the reaction between Tc_2O_7 and UF_4 , the existence of the oxyfluoride of heptavalent technetium was suggested (104). This compound was recently isolated and its properties were studied (124).

Technetium oxyfluoride is formed by passing fluorine over technetium dioxide at 150° ; it condenses in a trap cooled with Dry Ice. Pure TcO_3F consists of yellow crystals, which melt at 18.3° to form a liquid of the same color. The vapor pressure of the solid and liquid oxyfluoride may be obtained from the equations:

$$\text{For solid } \text{TcO}_3\text{F } [t = (-8.78) - (+18.28^\circ)], \log p = 12.448 - \frac{3239.4}{T}$$

$$\text{For liquid } \text{TcO}_3\text{F } [t = (+18.28) - (+51.82^\circ)], \log p = 8.417 - \frac{2064.6}{T}$$

According to the determinations of Selig and Malm (124), the boiling point of TcO_3F is approximately 100° , the heat of sublimation 14.832 kcal/mole, the heat of melting 5.377 kcal/mole, and the heat of vaporization 9.453 kcal/mole. Technetium oxyfluoride is stable at room temperature in nickel or monel vessels. It hydrolyzes in water to form HTcO_4 and HF. In its properties, TcO_3F occupies an intermediate position between MnO_3F and ReO_3F (Table XV).

TABLE XV

PROPERTIES OF MANGANESE, TECHNETIUM, AND RHENIUM OXYFLUORIDES

Compound	Melting point ($^\circ\text{C}$)	Boiling point ($^\circ\text{C}$)	Color
MnO_3F	-38	~ 60	Green
TcO_3F	+18.3	~ 100	Yellow
ReO_3F	+147	~ 164	Yellow

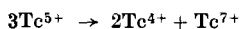
When reacting with excess of fluorine at 400° and 4 atm, TcO_3F is quantitatively converted to TcF_6 .

The oxychloride of heptavalent technetium was obtained by reacting KTcO_4 dissolved in 18 *M* H_2SO_4 with 12 *N* HCl. This compound is extracted with chloroform, carbon tetrachloride, and hexane (107). It is also suggested that technetium oxychloride is formed by the reaction of technetium chloride with oxygen (94). However, technetium oxychloride

has not been isolated in pure form and data on its properties are therefore lacking.

The oxyfluoride of hexavalent technetium is formed as a by-product of the direct fluorination of metallic technetium (120). Technetium oxyfluoride is a blue crystalline substance melting at 134°C. In its properties it resembles the corresponding rhenium analog. The magnetic susceptibility $\mu_{\text{eff}} = 1.76$ Bohr magnetons at 25° and $\theta = 9^\circ$.

When bromine vapors act on technetium dioxide at 350°, a brown product is formed that apparently is the oxybromide of pentavalent technetium TcOBr_3 (94). This compound sublimes in a stream of bromine at 400°. In aqueous solutions, it hydrolyzes according to the general equation



characteristic of compounds of pentavalent technetium and rhenium.

When gaseous chlorine reacts with technetium dioxide, a light brown product is obtained that sublimes at 900° and is paramagnetic (79, 94). However, no chemical analysis of this compound has been made, since it decomposes rapidly in aqueous solutions, via the reaction characteristic of pentavalent technetium. All this permits the assumption that the compound obtained has the composition TcOCl_3 .

F. COMPLEX HALOGEN COMPOUNDS OF TECHNETIUM

In the pentavalent and tetravalent states, technetium displays a tendency to form complex compounds of the type MeTcX_6 and Me_2TcX_6 .

When alkali metal chlorides react with a solution of technetium hexafluoride in iodine pentafluoride, complex halogen salts of pentavalent technetium are formed. In this manner, NaTcF_6 and KTcF_6 were obtained and isolated in pure form (120). They are yellow crystalline compounds, isomorphous with the corresponding salts of ruthenium but differing from the rhenium salts (Table XVI).

For NaTcF_6 , the magnetic susceptibility $\mu_{\text{eff}} = 2.25$ Bohr magnetons at 25°C and $\theta = 130^\circ$.

A common method for preparing complexes of this type, with the exception of TcF_6^{2-} , is the reduction of pertechnetates by the corresponding concentrated hydrohalic acids or the dissolution of hydrated technetium dioxide in these acids. All the halogen complexes of technetium are isomorphous with the corresponding rhenium compounds.

Potassium hexachlorotechnetate can be obtained by reducing potassium pertechnetate with concentrated HCl (117). However, in HCl the reduction is relatively slow and can be accelerated by reductants, for example H_3PO_2 or I^- (79, 91). In the latter case, the intermediate

TABLE XVI
CRYSTAL STRUCTURE OF Tc, Re, AND Ru COMPLEX FLUORIDE SALTS

Compound	Crystal structure	Crystal lattice parameters
NaReF ₆	Cubic system	$a_0 = 8.18 \text{ \AA}$,
NaTcF ₆	Rhombic system	$a_0 = 5.77 \text{ \AA}$, $\alpha = 55.8^\circ$
NaRuF ₆	Rhombic system	$a_0 = 5.80 \text{ \AA}$, $\alpha = 54.5^\circ$
KReF ₆	Tetragonal system	$a_0 = 10.01 \text{ \AA}$, $c_0 = 5.13 \text{ \AA}$
KTcF ₆	Rhombic system	$a_0 = 4.97 \text{ \AA}$, $\alpha = 97.0^\circ$
KRuF ₆	Rhombic system	$a_0 = 4.96 \text{ \AA}$, $\alpha = 97.5^\circ$

compound formed is a red binuclear complex of the composition $K_4(Tc_2OCl_{10})$ (91), which by reacting further with HCl forms K_2TcCl_6 .

The golden-yellow octahedral crystals of potassium hexachlorotechnetate have a strong paramagnetism, which obeys the Curie-Weiss equation, and are isomorphous with the corresponding rhenates and platinates. Its unit cell dimension $a_0 = 9.82 \text{ \AA}$. The effective magnetic moment is equal to 4.05 Bohr magnetons, which is in good agreement with the theoretical calculations (3.88 Bohr magnetons) for three unpaired electrons.

K_2TcCl_6 is extracted from acid solutions by various solvents, for example alcohols and a solution of trioctylamine hydrochloride in cyclohexane.

The $(TcCl_6)^{2-}$ ion, in contrast to the $(ReCl_6)^{2-}$ ion, hydrolyzes readily to form the hydrated dioxide $TcO_2 \cdot xH_2O$, and is therefore stable only in concentrated HCl solutions. By analogy with rhenium, we can expect the formation of several mixed chlorohydroxo complexes of tetravalent technetium. Indeed, Boyd (91) observed a gradual change in the absorption spectrum, which has peaks at 240 and 338 $m\mu$, even in 3 N HCl. In neutral solutions, the hydrolysis of $(TcCl_6)^{2-}$ to the dioxide takes place rapidly and completely. Hexachlorotechnetates are oxidized to pertechnetates by hydrogen peroxide, nitric acid, chlorine, and the Ce^{4+} and MnO_4^- ions (60, 117, 122), but are more resistant to the action of atmospheric oxygen than the oxygen compounds of tetravalent technetium.

On heating in a vacuum to 1100° , K_2TcCl_6 decomposes to technetium metal and chlorine, as confirmed by X-ray powder photography (79).

Potassium hexabromotechnetate K_2TcBr_6 is obtained from the hexachlorotechnetate by successive evaporation with hydrobromic acid (125). This compound forms dark red or even black crystals that crystallize in a face-centered cubic structure ($a_0 = 10.37 \text{ \AA}$). Its magnetic moment was measured only in solution and is 3.94 Bohr magnetons.

Potassium hexaiodotechnetate K_2TcI_6 can be obtained from the corresponding chloro- or bromotechnetate by evaporation with hydriodic acid (125). It consists of black crystals whose structure has not been finally determined.

The rose-colored potassium hexafluotechnetate K_2TcF_6 can be obtained by the reaction between K_2TcCl_6 or K_2TcBr_6 and molten KHF_2 (94, 126). Its structure is analogous to the structure of K_2ReF_6 (K_2GeF_6 type). Potassium hexafluotechnetate is stable in aqueous solutions and is decomposed only by hot concentrated alkali, in contrast to the other halogen complexes, which readily hydrolyze even in acid solutions. Like the other hexafluotechnetates, the free acid H_2TcF_6 can be obtained from the potassium salt by means of ion exchangers. The sodium and ammonium salts are soluble in water. The barium salt becomes less soluble on aging. The solubility of K_2TcF_6 at room temperature is 1.5 g/100 g of water.

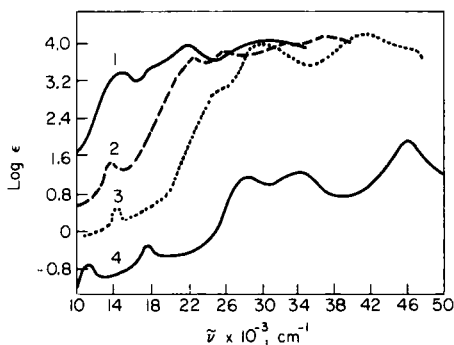


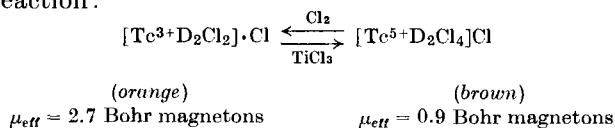
FIG. 6. Absorption spectra of halide complexes of Tc^{4+} ; (1) K_2TcI_6 , (2) K_2TcBr_6 , (3) K_2TcCl_6 , (4) K_2TcF_6 .

The ion $(TcF_6)^{2-}$ absorbs light with a maximum at 574 cm^{-1} . The absorption spectra of the various halogen complexes of technetium (Tc^{4+}) are illustrated in Fig. 6.

G. COMPLEX COMPOUNDS OF TECHNETIUM

In the lower oxidation states, technetium has a strong tendency to form complexes with various ligands. The oxidation state of technetium becomes considerably stabilized in this manner. Thus, the first compound of pentavalent technetium to be isolated and adequately described was the brown complex with diarsine (D) (*o*-phenylenebisdimethylarsine) of the composition $[Tc^{5+}D_2Cl_4]^+ Cl$ (127). It is obtained by oxidizing the

orange complex $[\text{Tc}^{3+}\text{D}_2\text{Cl}_2]\cdot\text{Cl}$ with gaseous chlorine in accordance with the reaction:



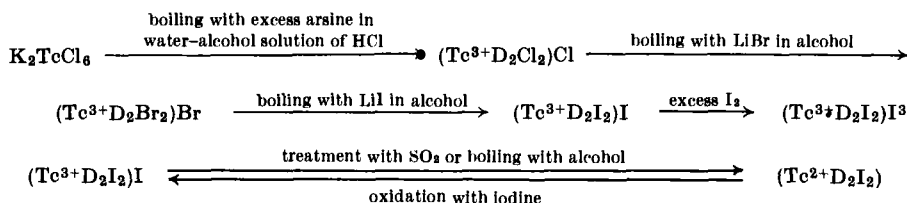
The conductivity of the complex of pentavalent technetium with diarsine in nitrobenzene and the magnetic moment agree with the formula for this compound cited earlier. Oxidation from the trivalent to the pentavalent state for technetium is somewhat more difficult than for rhenium. Thus, the Ce^{4+} ion oxidizes rhenium, but not technetium. The oxidation state of 5 for technetium has been confirmed by potentiometric titration with a standard TiCl_3 solution. The complex of pentavalent technetium is reduced to a complex of trivalent technetium, two equivalents of TiCl_3 being consumed. The corresponding compounds of technetium and rhenium are very similar in properties and are apparently isomorphous.

Complexes of technetium have also been obtained with thiocyanate (128), α -picolinic and sulfosalicylic acids (129), α -furyldioxime (130), *p*-thiocresol (131), thioglycolic acid (132), thiourea, dimethylglyoxime, potassium xanthate (133), etc. They are colored for the most part, are of interest in colorimetric determinations, and will therefore be examined in detail in Section V on analytical chemistry.

When potassium pertechnetate is reduced polarographically in 0.1 *N* potassium cyanide solution, only one wave corresponding to a 3-electron reduction is obtained, indicating the possible formation of a stable complex cyanide of tetravalent technetium (103). Indeed, by dissolving hydrated technetium dioxide or K_2TcCl_6 in an alkaline solution of potassium cyanide, one can obtain a yellow complex ion, which has been separated in the form of a dark-brown thallium salt of the composition $\text{Tl}_3[\text{TcO}(\text{OH})(\text{CN})_4]$ or $\text{Tl}_3[\text{Tc}(\text{OH})_3(\text{CN})_4]$. Under similar conditions, rhenium forms the complex ion $[\text{ReO}_2(\text{CN})_4]^{3-}$, in which rhenium is pentavalent. The ion $[\text{Tc}(\text{OH})_3(\text{CN})_4]^{3-}$ strongly absorbs light at 380 $\text{m}\mu$ with a molar extinction coefficient of 4.44×10^4 (mole cm^{-1})⁻¹. On the basis of deviations from the Lambert-Beer law, the instability constant of the complex was determined to be $K = (1.3 \pm 0.6)10^8$ mole^{-1} . The complex is readily decomposed by acids and in the presence of oxidants oxidizes to TcO_4^- (134).

In 1959 Fergusson and Nyholm (135) first isolated and characterized complex compounds of trivalent and divalent technetium of the composition $(\text{Tc}^{3+}\text{D}_2\text{X}_2)\cdot\text{X}$ and $(\text{Tc}^{2+}\text{D}_2\text{X}_2)$, where $\text{X} = \text{Cl}, \text{Br}, \text{I}$, and $\text{D} = o$ -phenylenebisdimethylarsine.

The overall scheme for the preparation of these compounds from K_2TcCl_6 is as follows:



Complex compounds of divalent technetium are obtained from the corresponding compounds of trivalent technetium when treated with SO_2 or when boiled with alcohol. The properties of these compounds are shown in Table XVII.

When $KTcO_4$ is reduced with potassium amalgam in the presence of excess KCN or $K_3[Tc(OH)_3(CN)_4]$, an olive-green solution containing complex ions of univalent technetium $[Tc(CN)_6]^{5-}$ is formed. The complex $K_5Tc(CN)_6$ has an absorption maximum at 810 cm^{-1} with a molar

TABLE XVII
PROPERTIES OF COMPLEX COMPOUNDS OF DI- AND
TRIVALENT TECHNETIUM

Oxidation state	Compound	Color	$\mu_{\text{eff}} (20^\circ)$ (Bohr magnetons)	Absorption spectrum		Molar con- ductance in nitromethane at 25° (ohm $^{-1}$) ($c = 1 \times 10^{-3}$ M^a)
				λ_{max} (m μ)	$E \times 10^{-3}$	
Tc^{3+}	$(TcD_2Cl_2)Cl$	Orange	2.7	441	3.92	75
	$(TcD_2Br_2)Br$	Red	3.2	472	5.56	77
				302	3.08	
				574	4.00	
	$(TcD_2I_2)I_3$	Dark red to black	3.4	359 294	6.69 11.23	86
Tc^{2+}	(TcD_2I_2)	Yellow	3.0	514 474	2.79 1.00	Slightly soluble, does not conduct current

^a For a monovalent-monovalent electrolyte in nitromethane at a concentration of $10^{-3} M$, 70–90 ohm $^{-1}$.

extinction coefficient of 1.2×10^2 . The salt is isomorphous with analogous rhenium and magnesium compounds and has a cubic unit cell with $a_0 = 12.106 \text{ \AA}$. $\text{K}_5\text{Tc}(\text{CN})_6$ does not contain water of crystallization, and its density is 1.8 g/cm^3 . Thallium (Tl^+) precipitates a brick-red precipitate of the composition $\text{Tl}_5[\text{Tc}(\text{CN})_6]$, soluble in ammoniacal hydrogen peroxide and dilute acids. All the compounds of Tc^+ are stable in the solid state in dry air, but are very sensitive to oxidation in solution. The oxidation product is the ion $[\text{Tc}(\text{OH})_3(\text{CN})_4]^{3-}$ (134, 136).

Carbonyl compounds of univalent and neutral technetium also have been obtained and isolated. At a pressure of 400 atm and temperature of $220^\circ\text{--}275^\circ$, carbon monoxide reacts with Tc_2O_7 or TcO_2 to form technetium carbonyl (137, 138). Measurement of the molecular weight has shown that this compound is dimeric, i.e., has the formula $\text{Tc}_2(\text{CO})_{10}$ (138).

Technetium carbonyl is a colorless diamagnetic compound, which sublimes at a moderate temperature in a vacuum and decomposes slowly in air. Its unit cell has the dimensions $a_0 = 14.73 \text{ \AA}$, $b_0 = 7.22 \text{ \AA}$, $c = 14.90 \text{ \AA}$, $\beta = 104.6^\circ$, and contains four molecules (139). In carbon tetrachloride, technetium carbonyl slowly reacts with halogens to form penta- and tetracarbonyls in accordance with the general reaction:

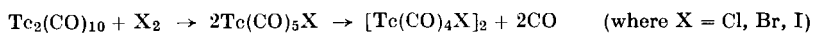


Table XVIII shows the relative rates of formation of carbonyl chlorides of technetium, manganese, and rhenium.

TABLE XVIII
RATE OF FORMATION OF Tc, Mn, AND Re CARBONYL CHLORIDES

Element	Time necessary for formation		
	$\text{Me}(\text{CO})_5\text{Cl}$	$[\text{Me}(\text{CO})_4\text{Cl}]$	Insoluble precipitate
Mn	5 min	2 days	1 week
Tc	6 days	2 weeks	2 months
Re	3 months	4 months	4 months

The chemical properties of technetium carbonyl halides are intermediate between those of the analogous compounds of manganese and rhenium. When the pentacarbonyl halide compounds are heated in air at 100° , they are converted to dimeric tetracarbonyl halides. The reverse reaction takes place in an autoclave in the course of 40 hours at

100° and a carbon monoxide pressure of 1000 atm. The iodine derivatives are the most soluble. Nitric acid oxidizes the technetium carbonyl halides to the TcO_4^- ion. Infrared spectra of the carbonyl halide compounds of technetium and their possible structures are discussed in references (140, 141). Technetium carbonyl hydride has also been obtained in unweighable quantities (140).

H. ORGANOMETALLIC COMPOUNDS OF TECHNETIUM

Organometallic technetium compounds have recently been isolated. Thus, Baumgartner *et al.* (142) report on the preparation, as a result of the β decay of $\text{Mo}^{99}(\text{C}_6\text{H}_6)_2$, of the complex technetium dibenzene cation $[(\text{C}_6\text{H}_6)_2\text{Tc}]^+$, which coprecipitates in the form of hexafluorophosphate with $\text{Re}(\text{C}_6\text{H}_6)_2\text{PF}_6$.

The reaction of TcCl_4 with a solution of sodium cyclopentadienyl in tetrahydrofuran forms bisdicyclopentadienyltechnetium $[(\text{C}_5\text{H}_5)_2\text{Tc}]_2$. It consists of golden yellow crystals unstable in air and melting at 155° (143). Bisdicyclopentadienyltechnetium is diamagnetic, is not decomposed by water at room temperature, and dissolves in 10 % aqueous tetrahydrofuran. It is interesting to note that under similar conditions rhenium forms a compound of the composition $(\text{C}_5\text{H}_5)_2\text{ReH}$ (144, 145). Determination of the molecular weight and infrared spectra indicates the absence of the $\text{Tc}-\text{H}$ bond in bisdicyclopentadienyltechnetium. However, the nature of the bond between the ring and the metal is similar to that in $(\text{C}_5\text{H}_5)_2\text{ReH}$ and differs from this bond in the paramagnetic $(\text{C}_5\text{H}_5)_2\text{Mn}$ (146). It is possible that, as in the case of technetium carbonyl, a $\text{Me}-\text{Me}$ bond exists in $[(\text{C}_5\text{H}_5)_2\text{Tc}]_2$.

During the β decay of Mo^{99} in molybdenum biscyclopentadienyltricarboxyl, $[\text{C}_5\text{H}_5\text{Mo}^{99}(\text{CO})_3]_2$, cyclopentadienyltricarboxyltechnetium, $\text{C}_5\text{H}_5\text{Tc}(\text{CO})_3$, is formed. This compound is a diamagnetic colorless substance with a melting point of 87.5°. Its absorption spectrum has a maximum at $36.5 \times 10^3 \text{ cm}^{-1}$ ($\log \epsilon_{\text{max}} = 3.69$) (147-149).

In 1963 Gobbild and Ihrman patented a method for preparing trichloromethylcyclopentadienyltechnetium, isopropylbenzene and other cyclopentadiene derivatives (150).

I. TECHNETIUM HYDRIDE

The reduction of potassium perrhenate, labeled with the Tc^{99} isotope, by a solution of potassium in ethylenediamine forms a complex rhenium hydride assigned the composition $\text{KReH}_4 \cdot 2\text{H}_2\text{O}$ (151). The rhenium hydride precipitate contained 90 % of the radioactivity of Tc^{99} introduced into the initial potassium perrhenate. When the product was

further purified by removing the unreacted KReO_4 and KOH by extraction with ethanol and ether, the radioactivity of Tc^{99} was preserved in the hydride. The authors of reference (151) concluded that TcO_4^- is also reduced to the hydride $\text{KTcH}_4 \cdot 2\text{H}_2\text{O}$, isomorphous with $\text{KReH}_4 \cdot 2\text{H}_2\text{O}$. However, later X-ray structural studies by Knox and Ginsberg (152) showed that rhenium hydride has the formula K_2ReH_8 , and the lattice parameters are $a_0 = 9.61 \text{ \AA}$ and $c_0 = 5.51 \text{ \AA}$. The X-ray powder pattern of technetium hydride was found to be similar to that of rhenium hydride, showing the analogous structure of these two compounds. Since no other studies of technetium hydride were made in this work, it is now difficult to evaluate reliably its composition and properties.

J. METHODS OF PREPARING ELEMENTAL TECHNETIUM

The methods for preparation of elemental technetium are in most cases similar to those used in the preparation of metallic rhenium. They differ only in the details of the microquantitative operations. These methods are based on the reduction of various technetium compounds with electric current or hydrogen. Such compounds can be technetium sulfide or ammonium pertechnetate. Obviously, the preparation of elemental technetium should be preceded by operations for its isolation, purification, and preparation of the corresponding compounds.

In initial studies with visible technetium samples, the chief method for isolation and purification of technetium was the precipitation of its heptasulfide. Technetium sulfide was therefore used to obtain weighable quantities of technetium metal (153). Technetium sulfide was placed in a quartz capillary connected to a system that made it possible alternately to pump out the volatile reduction products of technetium sulfide and to create a hydrogen atmosphere in the system. Such consecutive operations made it possible to obtain $100 \mu\text{g}$ of technetium metal by reduction with hydrogen at 1100°C .

Mooney (68, 154) established the elemental state of technetium by X-ray structural analysis at about the same time. The purity of technetium obtained by this method is not high, since the samples contain sulfur whose quantity depends on the temperature and time of the reduction.

When Tc_2S_7 is dissolved in a mixture of ammonia and hydrogen peroxide, ammonium pertechnetate, which is more convenient for the preparation of technetium metal, is formed in a mixture with ammonium sulfate. This mixture can be readily reduced at relatively low temperature first to the lower technetium oxides, and then to technetium metal (92).

Ammonium pertechnetate sublimates readily, and for this reason a loss of technetium can occur if the reaction mixture is heated rapidly. Therefore the reduction is carried out in two stages. In the first stage, heptavalent technetium is reduced with hydrogen to the relatively involatile TcO_2 by slowly raising the temperature to $200^\circ\text{--}225^\circ\text{C}$ for about 1 hour. In the second stage the temperature is raised to $600^\circ\text{--}800^\circ\text{C}$, and TcO_2 is reduced to the metal in the course of 1 hour. Simultaneously, ammonium sulfate is removed by sublimation. Thus, 0.6 g of spectroscopically pure technetium was obtained (92). Similarly, 10 g of technetium metal with a negligible amount (less than $10^{-5}\%$) of Na, Mo, Mg, and Si impurities was obtained from pure ammonium pertechnetate (over 99%) (93). The largest amount of technetium metal obtained by chemists to date has been about 100 g, according to published data.

Another good but still insufficiently proven method is the preparation of technetium by pyrolytic decomposition of $(\text{NH}_4)_2\text{TcCl}_6$ (94). In a nitrogen atmosphere at the temperature of red heat, this salt decomposes without melting, forming a fine silver-gray powder of technetium metal. The electrolysis of a technetium solution was used for the preliminary separation of technetium and for the purpose of obtaining it in the elemental state.

Electrolytic methods of obtaining technetium metal have not yet been sufficiently developed and do not give results as satisfactory as the method of reduction with hydrogen. Attempts to obtain technetium metal by electrolytic reduction at a platinum cathode were made by its discoverers in a study of the chemical properties of technetium (11, 118). However, instead of elemental technetium, products of its incomplete reduction were apparently obtained.

Studies of the electrodeposition of technetium have been made in recent years by Flagg and Bledner (155) and Boyd, Larson, and Motta (115). The latter showed that, in a 2 *N* solution of H_2SO_4 at 3–6 V, technetium deposits on a platinum cathode, and still better on a polished copper or nickel cathode. To exclude hydrogen overvoltage, fluoride ions were added to the solution. In this study, technetium formed an invisible microfilm on the surface of the electrodes. The yield did not exceed 60–70%. It is necessary to keep the pH constant during the electrolysis, since in the absence of a buffer a brownish black precipitate or a colloid suspension of TcO_2 is formed.

Contamination with the dioxide appears to be a drawback in the electrolytic preparation of technetium that is difficult to eliminate. For this reason, after depositing technetium, Bainbridge *et al.* (156) reduced it further with hydrogen at 1000°C . Eakins and Humphries (157) deposited metallic technetium from its solution in 2 *N* H_2SO_4 on a copper

and platinum cathode during the electrolysis of a 0.2% solution of ammonium pertechnetate. The current density was 25–30 mA/cm². Only 25% technetium was thus deposited as a film 5 mg/cm² thick. The remainder of the technetium was reduced to TcO₂ and remained in the electrolyte. A complete separation of technetium can be achieved by continually adding peroxide to the electrolyte in order to oxidize the technetium.

The authors found that the presence of fluoride ions does not improve the electrolysis.

Technetium is also quantitatively deposited on a mercury cathode, forming the corresponding amalgam. As was stated, metallic technetium can be obtained by reduction with metallic amalgamated zinc (115), but Schwochau and Herr (134) showed that a mixture of technetium metal and dioxide is apparently formed in the deposit at the same time. When the pertechnetate is reduced in an acid medium with a coarse-grained zinc powder, the content of the metal amounts to only 20%. The oxygen content in technetium metal usually is not controlled, and therefore many samples of technetium obtained by reduction with hydrogen and particularly by electrolysis contain a certain amount of dioxide or oxygen dissolved in the metal. This is confirmed by the fact that, when technetium powders are fused in an inert gas atmosphere, 10–20% of the original weight is lost (158). This loss is apparently accompanied by the sublimation of technetium dioxide. The presence of oxygen in technetium can appreciably distort its chemical and physical properties, as was shown, for example, by studies of the superconductivity of technetium (77). When technetium is used as a standard source of β -radiation, it is usually electrodeposited on metallic substrates. The presence of the dioxide may lead to a loss of technetium as a result of the oxidation of TcO₂ to Tc₂O₇ by atmospheric oxygen. Technetium deposited by electrolysis should therefore be reduced further with hydrogen.

K. TECHNETIUM ALLOYS

A considerable number of binary and ternary systems of technetium with various elements of the periodic system have now been investigated. Even before the experimental preparation and identification of the structure of technetium alloys, Ageev *et al.* (159) established the nature of the alloys formed by elements of the manganese subgroup with transition metals. Their hypothesis that the behavior of technetium in such alloys is similar to that of rhenium was partially confirmed by Compton (160), who identified the α -Mn phase in Zr–Tc and Nb–Tc alloys, similar to the α -Mn phase in the Zr–Re and Nb–Re systems. Compounds of the composition ZrTc₆ and NbTc₃ were identified at the same time.

TABLE XIX
 BINARY TECHNETIUM ALLOYS

System	Phase	Composition of alloy (at. % Tc)	Compounds of technetium with second component	Lattice parameters (Å)
Sc-Tc	α -Mn	88.5	—	$a_0 = 9.509$
Ti-Tc	MnZn ₂	66.7	—	$a_0 = 5.223$; $c_0 = 8.571$
Ti-Tc	α -Mn	87.5	—	$a_0 = 9.579$
	α -Mn	85.7	—	—
	CsCl	66.7	—	—
	CsCl	50	—	$a_0 = 3.110$
Zr-Tc	α -Mn	85.7	ZrTc ₆	$a_0 = 9.637$
	MgZn ₂	66.7	—	$a_0 = 5.219$; $c_0 = 8.655$
Hf-Tc	α -Mn	87.5	—	$a_0 = 9.603$
	α -Mn	85.7	—	—
	MgZn ₂	66.7	—	—
	CsCl	50.0	—	$a_0 = 3.270$
V-Tc	<i>bbc</i>	10	—	—
	<i>bbc</i>	25	TcV ₃	$a_0 = 3.026$
	<i>bbc</i>	30	—	—
	<i>bbc</i>	40	—	$a_0 = 3.024$
	CsCl	50	TcV	$a_0 = 3.023$
	<i>bbc</i>	60	—	$a_0 = 3.034$
	<i>bbc + hcp</i>	75	—	—
	<i>hcp</i>	95	—	—
Nb-Tc	<i>bcc</i>	5	—	—
	<i>bcc</i>	10	—	$a_0 = 3.276$
	<i>bcc</i>	20	—	$a_0 = 3.244$
	<i>bcc</i>	30	—	$a_0 = 3.217$
	<i>bcc</i>	40	—	$a_0 = 3.192$
	<i>bcc</i>	50	—	$a_0 = 3.170$
	<i>bcc + \alpha</i> - Mn	60	—	—
	α -Mn	75	NbTc ₃	$a_0 = 9.547$
	α -Mn	85	—	—
	<i>hcp</i>	97	—	—
	<i>hcp</i>	(100)	—	$a_0 = 2.743$; $c_0 = 4.400$
Ta-Tc	α -Mn	83.4	—	$a_0 = 9.565$
	α -Mn	80.0	—	—
	CsCl	50.0	—	$a_0 = 3.172$
Cr-Tc	σ	75	—	$a_0 = 9.290$; $c_0 = 4.846$
	σ	60	—	$a_0 = 9.217$; $c_0 = 4.803$
Mo-Tc	σ - β Tc	75	—	—
	σ	70	—	$a_0 = 9.509$; $c_0 = 4.945$
	Cr ₃ O	60	—	$a_0 = 4.934$

TABLE XIX—*cont.*

BINARY TECHNETIUM ALLOYS

System	Phase	Composition of alloy (at. % Tc)	Compounds of technetium with second component	Lattice parameters (Å)
	Cr ₃ O	56	—	$a_0 = 4.931$
	Cr ₃ O	53	—	$a_0 = 4.942$
W-Tc	σ	75	—	$a_0 = 9.479$; $b_0 = 5.166$
Mn-Tc	σ	60	—	$a_0 = 9.15$; $c_0 = 4.80$
Fe-Tc	σ	60	—	$a_0 = 9.130$; $c_0 = 4.788$
	σ	50	—	$a_0 = 9.077$; $c_0 = 4.756$
	σ	40	—	$a_0 = 9.010$; $c_0 = 4.713$
Al-Tc	Ni ₂ Al ₃	—	Tc ₂ Al ₃	$a_0 = 4.16$; $c_0 = 5.13$
	Mono- clinic	—	TcAl ₄	$a_0 = 5.1$; $b_0 = 17.0$
	MnAl ₆	—	TcAl ₆	$a_0 = 5.58$; $b_0 = 7.63$; $c_0 = 9.00$
	WAl ₁₂	—	TcAl ₁₂	$a_0 = 7.527$
Zn-Tc	—	—	Zn ₂ Tc ₁₁	—
P.3-Tc	MgZn ₂	—	GdTc ₂	$a_0 = 5.397$; $c_0 = 8.883$
	MgZn ₂	—	TbTc ₂	$a_0 = 5.375$; $c_0 = 8.843$
	MgZn ₂	—	DyTc ₂	$a_0 = 5.365$; $c_0 = 8.830$
	MgZn ₂	—	HoTc ₂	$a_0 = 5.353$; $c_0 = 8.813$
	MgZn ₂	—	ErTc ₂	$a_0 = 5.340$; $c_0 = 8.792$
	MgZn ₂	—	TuTc ₂	$a_0 = 5.334$; $c_0 = 8.775$
	MgZn ₂	—	LuTc ₂	$a_0 = 5.309$; $c_0 = 8.847$
	MgZn ₂	—	YTc ₂	$a_0 = 5.373$; $c_0 = 8.847$

Compounds of this type together with technetium-molybdenum alloys (78, 161) are superconductive at relatively high critical temperatures (9.7°K for ZrTc₆ and 10.5°K for NbTc₃). These critical temperatures of technetium alloys are considerably higher than those of analogous rhenium alloys. Particularly high is the critical temperature of a technetium-molybdenum alloy (40 % Tc), which is 15°K according to Compton (160) and $13.4 \pm 0.3^\circ\text{K}$ according to Darby and Zegler (78). Van Ostenberg *et al.* (162) and Morin and Maita (163) measured the nuclear magnetic resonance, magnetic susceptibility, and specific heat of the transition to the superconductive state of alloys of technetium with molybdenum and niobium. In the alloys with niobium, they found phases corresponding to crystal structures of *bcc* and α -Mn type. A similar study of several binary systems including technetium and transition metals was made by Darby *et al.* (158). Technetium and other components of high purity were

used to prepare the alloys. The small amounts of technetium at the disposal of the researchers did not permit an accurate determination of the limits of existence of the intermediate phases, but they were able to evaluate the structural types, lattice parameters, and approximate regions of existence of the phases (Table XIX). This study established that the Tc-Re, Tc-Ru, and Tc-Os alloys are characterized by a continuous series of solid solutions. In alloys with Sc, Ti, Zr, Hf, Nb, and Ta, an α phase isostructural with the α -Mn phase was found. In these alloys, this phase is stabilized by the second component only if the atomic radius of the latter is greater than the radius of the technetium atom, and the concentration of the stabilizing element depends on its position in the periodic system relative to technetium.

In contrast to the data of Mattias (161), who proposed the formation of solid solutions in the Mo-Tc system, the formation of intermediate phases is more probable (see Table XIX). The presence of the Cr_3O phase at a molybdenum content of about 46 at.% is the only exception of its kind to the stoichiometry of A_3B type usual in such cases. The presence of a CsCl-type phase in certain alloys distinguishes technetium from rhenium, where such structures are unknown for binary systems. The behavior of technetium during the formation of the σ phase also distinguishes it from rhenium and manganese.

Manganese and rhenium form σ phases in alloys with elements of the vanadium and chromium group, while technetium forms them only with elements of the chromium group. In this respect, technetium resembles ruthenium. On the contrary, when the average concentrations of technetium and rhenium in the σ phases are compared, similarities in behavior are observed. The Tc-Fe system was studied by Buckley and Hume-Rothery (164) up to a 15 at.% technetium content of the alloy. According to the data of radioautographic studies, technetium is evenly distributed, i.e., a true fusion takes place. The addition of technetium to iron causes a very slight rise of the melting point of the alloy and a lowering of the transition temperature. The slight slopes of the δ -liquidus curves in the Tc-Fe system characterize technetium as a very weak stabilizer. In the technetium-aluminum system (165, 166) a large number of phases are observed, whose composition and lattice parameters are given in Table XIX.

Van Ostenberg *et al.* (167) studied the magnetic susceptibility of alloys of technetium with vanadium. In another study (168), they determined the nuclear magnetic resonance of technetium-vanadium alloys and measured the Knight shift. The TcV and TcV_3 phases were observed in Tc-V alloys, and their crystal structure was thoroughly studied. In the Tc-V system, stable solid solutions of *bbc* type exist in the range of

technetium concentrations up to 60 at.%, and approximately 10 at.% vanadium dissolves in technetium. In the concentration interval between 60 and 90 at.% technetium, two solid solutions exist. The CsCl structure is observed at equivalent quantities of the two elements.

The solubility of technetium in zinc at 750°C was studied (169), and the $\text{Zn}_2\text{Tc}_{11}$ phase was found in technetium-zinc alloys (170). Alloys of technetium with rare earth elements having an MgZn_2 structure were obtained (171). The solubility of technetium in nickel (156) and mercury with the formation of the corresponding amalgams (157) is well known. By analogy with rhenium, alloys of technetium with Co, Pd, Pt, W, and other elements should also be expected. In addition to binary systems, certain ternary systems containing technetium are known. For example, the thermodynamic properties of the U-C-Tc system (172) were determined, and the Knight shift was measured for the V-Al-Tc system (167) in the *bcc* region. To explain the effect of technetium on the structure of alloys of uranium and fission products, alloys containing 10 wt.% of elements entering into the composition of the fission products (Zr, Nb, Mo, Tc, Ru, Rh, Pd) were studied (173). Technetium has a pronounced effect on the stabilization of the γ region. However, a comparison of the curves representing the change in hardness with the time and temperature of annealing showed that the effect of technetium on the properties of the alloy can be neglected. Some technetium alloys may be of major importance in nuclear power engineering, catalytic processes, high-temperature electrophysical investigations, and as anticorrosion coatings.

L. THERMODYNAMIC CONSTANTS OF TECHNETIUM AND ITS COMPOUNDS

The thermodynamic properties of technetium and its compounds have been studied very inadequately. The main reason for this is the difficulty of obtaining them in pure form and the instability of many of them in aqueous solutions.

Tables XX-XXII list the data that we have collected on the heat of formation, entropy, and heat of transition of certain technetium compounds.

A brief survey of the chemical properties of technetium shows that its chemistry has been insufficiently studied. For example, only two technetium oxides, Tc_2O_7 and TcO_2 , are known. The existence of the remaining ones is indicated only by indirect data obtained from mass-spectrometric study of fragments arising from the electron bombardment of NH_4TcO_4 . Incomplete and sometimes contradictory data are also encountered in connection with the description of halogen, oxy-

TABLE XX

HEAT OF FORMATION OF TECHNETIUM AND
SOME OF ITS COMPOUNDS AT 298.16°K (91)

Compound	State	Heat of formation H° (kcal/mole)
Tc	Crystalline	0.0
TcO ₂	Crystalline	103.7 \pm 2.0
TcO ₃	Crystalline	129.0 \pm 5.0
Tc ₂ O ₇	Crystalline	266.1 \pm 2.6
HTcO ₄	Crystalline	167.4 \pm 1.3
TcO ₄ ⁻ —aq	In solution	173.0 \pm 1.3
KTcO ₄	Crystalline	242.5 \pm 1.5

TABLE XXI

ENTROPY AT 298.16°K (91)

Compound	State	Entropy S° (cal/deg mole)
Tc	Crystalline	7.4 \pm 0.2
	Gaseous	43.26 \pm 0.01
TcO ₂	Crystalline	14.9 \pm 0.5
TcO ₃	Crystalline	17.3 \pm 0.6
Tc ₂ O ₇	Crystalline	45.8 \pm 2.0
HTcO ₄	Crystalline	33.3 \pm 2.0
TcO ₄ ⁻ —aq	In solution	46.0 \pm 0.1
KTcO ₄	Crystalline	39.7 \pm 0.1
K ₂ TcCl ₆	Crystalline	79.5 \pm 1.0

TABLE XXII

HEATS OF TRANSITION (98, 99, 124)

Compound	Nature of transition	Heat of transition (kcal/mole)
Tc ₂ O ₇	Solution	11.6 \pm 0.08
	Fusion	16.6 \pm 0.5
	Vaporization	16.3 \pm 0.2
	Sublimation	32.95
TcO ₃ F	Fusion	5.377
	Vaporization	9.453
	Sublimation	14.832

halogen, complex, organometallic, and other compounds of technetium. This situation has apparently developed not only because the study of technetium in the lower oxidation states is difficult owing to their instability, but also because many investigators worked with trace quantities of technetium.

It may be assumed that the development of nuclear technology will make available weighable quantities of technetium to many researchers, resulting in a more complete study of the chemical properties of this interesting element. Table XXIII lists the best known compounds of technetium.

TABLE XXIII
COMPOUNDS OF TECHNETIUM

Oxidation state	Compounds
Tc ⁷⁺	Tc ₂ O ₇ , HTcO ₄ , Tc ₂ S ₇ , TcO ₃ F, TcO ₃ Cl, MeTcO ₄ , where Me = K ⁺ , NH ₄ ⁺ , Cs ⁺ , Na ⁺ , Rb ⁺ , Li ⁺ , Ag ⁺ , Tl ⁺ , (C ₆ H ₅) ₄ As ⁺ , etc.
Tc ⁶⁺	TcF ₆ , TcCl ₆ , TcOF ₄
Tc ⁵⁺	TcF ₅ , TcOCl ₃ , TcOBr ₃ , NaTcF ₆ , KTcF ₆ , [Tc(diarsine) ₂ Cl ₄]Cl
Tc ⁴⁺	TcO ₂ , TcS ₂ , TcCl ₄ , Me ₂ TcX ₆ (Me = Na ⁺ , K ⁺ , and X = Cl ⁻ , Br ⁻ , I ⁻ , F ⁻), [Tc(OH) ₃ (CN) ₄]Tl ₃
Tc ³⁺	[Tc(diarsine) ₂ X ₂]X, where X = Cl ⁻ , Br ⁻ , I ⁻
Tc ²⁺	[Tc(diarsine) ₂ X ₂], where X = Cl ⁻ , Br ⁻ , I ⁻
Tc ⁺	K ₅ Tc(CN) ₆ , Tc(CO) ₅ X, [Tc(CO) ₄ X] ₂ , where X = Cl ⁻ , Br ⁻ , I ⁻
Tc	Tc ₂ (CO) ₁₀

IV. Methods of Isolating Technetium

A. DISSOLUTION OF SAMPLES CONTAINING TECHNETIUM

Technetium is obtained at the present time, either from nuclear fuel-processing waste or from molybdenum targets irradiated with neutrons in a reactor and with deuterons or protons in a cyclotron. Depending upon the composition of the raw material containing technetium, various methods for its processing are used. To concentrate technetium and separate it from the accompanying elements, use is made of distillation, precipitation, extraction, chromatography, etc.

In dissolving samples containing technetium, two precautions should be taken. First, acid solutions can be heated only with a reflux condenser to prevent the loss of technetium in the form of volatile compounds. Second, the dissolution should take place only in a strongly oxidizing

medium in order to convert all the technetium compounds of lower valences to the TcO_4^- ion.

The molybdenum targets used for preparing technetium by reactions of the type (n, γ) , (d, n) , (p, γ) can be dissolved in nitric acid or aqua regia, but in both cases the excess acid hinders the subsequent operations. For this reason, the dissolution is best carried out in concentrated sulfuric acid followed by neutralization of technetium with hydrogen peroxide and oxidation. Samples of natural minerals (molybdenite, yttrotantalite, etc.) are dissolved by first fusing them with a mixture of sodium hydroxide and sodium peroxide.

B. DISTILLATION

Because of the high vapor pressure of Tc_2O_7 , technetium can be distilled with acids. This process has been discussed in great detail by Boyd *et al.* (115). Figure 7 shows the results of their investigation. All

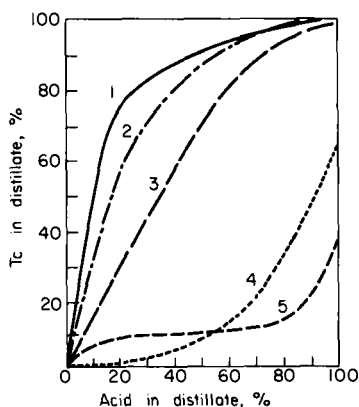


FIG. 7. Distillation of technetium with various acids: (1) HClO_4 , (2) $\text{H}_2\text{SO}_4 + \text{K}_2\text{Cr}_2\text{O}_7$, (3) $\text{H}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_8$, (4) H_2SO_4 , (5) HNO_3 .

the acids can be subdivided into three groups: acids with which technetium does not distill (HCl , HBr , HI), acids with which the distillation of technetium is incomplete and becomes appreciable only after over half the acid has been distilled off (HNO_3 , aqua regia, H_2SO_4), and acid with which technetium distills off completely, 75 % thereof being distilled off with the first 20 % of the distillate (HClO_4). Perchloric acid makes it possible not only to distill technetium in a good yield, but also to separate it partially from rhenium (114, 174, 175). In the presence of ruthenium, HClO_4 also oxidizes the latter to the volatile RuO_4 , so that a further

separation of technetium from ruthenium is required. Molybdenum is likewise partially distilled if it is not bound in a complex with phosphoric acid (156, 176).

Distillation from sulfuric acid can produce a good separation of technetium from ruthenium (degree of purification about 10^5), but the distillation of technetium is incomplete, probably because it is partly reduced by its impurities (115). The addition of oxidants (Ce^{4+} , $\text{Cr}_2\text{O}_7^{2-}$, $\text{Na}_2\text{S}_2\text{O}_8$, KIO_4 , KBrO_3) increases the amount of distillable technetium, but under these conditions the distillation of RuO_4 also takes place.

The sublimation methods of isolating technetium are also based on the volatility of Tc_2O_7 . Thus, technetium can be isolated from irradiated MoO_3 by fractional sublimation at 300°C (11). Quite recently a brief report was published concerning a new, very promising method of isolating technetium from spent nuclear fuel (177). In the course of its regeneration by the fluorination method, technetium hexafluoride TcF_6 is apparently formed (m.p. 33.4° , b.p. 55.3°) and is trapped by a magnesium fluoride packing.

C. PRECIPITATION

The most common method is the isolation of technetium in the form of the insoluble sulfide Tc_2S_7 . This method can be used to precipitate technetium with hydrogen sulfide from 4 *M* H_2SO_4 or HCl when it is present in concentrations of no less than 3 mg/liter (116, 178). At a lower concentration, it is necessary to use carriers; Pt, Re, Cu, Mn, and certain other elements can be employed. A detailed study of the process of coprecipitation has been made by several authors (11, 62, 117, 178, 179). Instead of hydrogen sulfide, thioacetamide (100) or sodium thiosulfate (117) can be successfully used to precipitate technetium. Many elements of the periodic system are precipitated under the same conditions, so that this method is more suitable for concentrating technetium than for purifying it. Technetium in the lower valence states is not precipitated by H_2S in the presence of concentrated hydrochloric acid; this can be utilized to separate Tc from Re.

In addition to the sulfide, technetium can be precipitated in the form of the pertechnetate ion, which forms poorly soluble salts with the cations Tl^+ , Ag^+ , Cs^+ , $(\text{C}_6\text{H}_5)_4\text{As}^+$, and nitron. Anions of the type YX_4^- , (ReO_4^- , ClO_4^- , IO_4^- , BF_4^-) can be used as carriers (117, 174, 180).

The coprecipitation with $[(\text{C}_6\text{H}_5)_4\text{As}]\text{ReO}_4$ is probably the fastest method of isolating technetium, for example, in extracting Tc^{102} (half-life 5 seconds) from Mo^{102} (half-life 11.5 minutes). Flegenhimer (61) precipitated and filtered a sample in 5–6 seconds. From the organic precipitate, technetium can be isolated by wet combustion, electrolysis

in concentrated sulfuric acid, or passage of an alcohol solution through an ion-exchange resin in the chloride form. The TcO_4^- ion is adsorbed by the resin and can be eluted off with an HClO_4 solution (91, 92).

D. CHROMATOGRAPHY

The pertechnetate ion is very strongly adsorbed by most anion-exchange resins (178–182) and can be eluted off only by ions having a high affinity for the resin, such as the perchlorate or salicylate ion. The perrhenate ion is firmly held by the resins, almost to the same degree as the pertechnetate ion. The ratio of the distribution coefficients of TcO_4^- and ReO_4^- ranges from 1.6 to 2, i.e., is almost the same as that of rare earth elements. Hence, their separation requires long columns and much time.

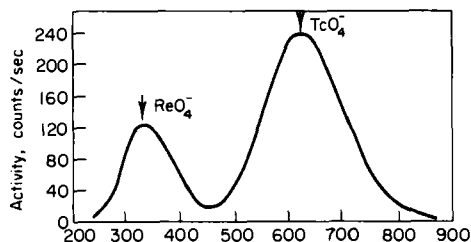


FIG. 8. Chromatographic separation of TcO_4^- and ReO_4^- on Dowex-2 anion exchanger. Volume of eluting solution (cm^3) plotted along abscissa.

Atterby and Boyd (183) separated technetium from rhenium on a Dowex-2 resin in the sulfate form by using a solution of ammonium sulfate and thiocyanate at pH 8.3–8.5 as the eluent. The separation was not sufficiently distinct, since the peaks of TcO_4^- and ReO_4^- partially overlapped. There is evidence that better results are obtained by using the perchlorate ion as the eluent (19, 21, 28, 184). Owing to certain characteristics of industrial resins, the separation factor that can be obtained practically is not more than 10^4 – 10^5 . Figure 8 shows the result of a chromatographic separation of TcO_4^- from ReO_4^- on a Dowex-2 resin. A 0.1 M NH_4ClO_4 solution was used as the eluent.

MoO_4^{2-} ions are also adsorbed by ion-exchange resins, but can be washed off with a solution of sodium hydroxide (21, 185), oxalate (186), or hydrochloric acid (187). In the latter two cases, there is danger of reducing the heptavalent technetium.

A 4 N HNO_3 solution can also be used for the elution (182, 188, 189). However, the drawback of this method is that the subsequent isolation of technetium is hindered, since the evaporation can cause its loss.

Nelson *et al.* (190) studied the adsorption of technetium and rhenium from concentrated 9 *M* solutions of HCl and HClO₄ on a Dowex-50-X4 resin. The adsorption of technetium is very slight under these conditions if an oxidant is present in the solution. In a 9 *M* HClO₄ solution, in the absence of an oxidant, technetium was apparently adsorbed in the form of its reduced species (190).

Nikitin (191) studied the possibility of a group separation of elements in solutions of hydrofluoric acid on an AB-17 anion exchanger. After the adsorption of the elements from a 1 *M* HF solution, followed by washing the column with hydrofluoric acid of increasing concentration, technetium was washed out with 20 *M* HF in the fraction containing Ti, Zr, Pd, Sn, Hf, W, Ir, and Re.

An original method of chromatographic separation of molybdenum from technetium was worked out by Ryabchikov and Borisova (192). On a column with an EDE-10 anion exchanger (100–150 mesh) in the phosphate form was placed 0.1–0.2 cm³ of a sodium molybdate solution containing daughter Tc^{99m}. Five to ten minutes after the Tc^{99m} was charged, elution was carried out with a 2 *M* solution of phosphoric acid. According to the authors' report, all the technetium was washed out with the first portions of the eluent (30 cm³). The column was then washed with water to a neutral reaction. Molybdenum was removed from the column with a 10% sodium hydroxide solution. The adsorption of technetium from a phosphoric acid solution on the resin was 4% (probably because of a partial reduction of heptavalent technetium), and that of molybdenum was 73%. This is explained by the fact that phosphoric acid displaces the TcO₄⁻ ions from the resin, and with MoO₄²⁻ ions forms the heteropoly acid H₇[P(Mo₂O₇)₆], which is firmly held by the anion exchanger. When an alkali is passed through this acid is decomposed, and molybdenum is quantitatively washed out. To remove cation impurities from the technetium concentrate, use was made of the KU-2 resin (65, 193).

Trace amounts of technetium can be removed from molybdenum and ruthenium by paper chromatography (194–196) and by paper electrophoresis (197–199). The separation of TcO₄⁻ and ReO₄⁻ ions was not observed in all the systems of solvents investigated, with the exception of some cases of selective reduction of heptavalent technetium to the lower oxidation states by hydrochloric acid (196), hydrazine, hydrobromic and hydriodic acids (197), or thiourea (200).

E. ELECTROCHEMICAL METHODS

Technetium can be recovered from solution electrochemically. According to Rogers (101), at a cathodic potential of -1.1 V relative to

the saturated calomel electrode in 2 *N* NaOH, black technetium dioxide separates. If the technetium concentration in the solution is less than 10^{-4} mole/liter, it deposits as a thin film on the cathode. Under these conditions of electrolysis, molybdenum and rhenium are partially removed from the technetium.

Flagg and Bledner (155) deposited technetium from a dilute solution of sulfuric acid (pH 2.36) on a platinum cathode at a potential of 0.8 V (relative to the saturated calomel electrode). During the electrolysis, they obtained a 99.5 % yield of deposited technetium in 65 minutes.

Boyd *et al.* (115) studied the process of electrochemical deposition of technetium in more detail. They found that the optimum results are obtained at pH 5.5 in the presence of about 10^{-3} mole of F^- ions and by replacing platinum cathodes with copper ones. At a current density of 100 mA/cm² during the first two hours, 84.5 ± 1.5 % technetium was deposited. In 2 *N* H₂SO₄, technetium deposits as the metal (91, 157), and, at lower concentrations of the acid, as the dioxide.

To deposit Tc^{99m} from irradiated molybdenum, methods have been proposed that are based on electrochemical deposition in nonaqueous solutions, particularly from ether solutions of MoCl₂ or molybdenum hydroxyquinolate (201, 202).

F. EXTRACTIVE METHODS OF ISOLATING TECHNETIUM

In view of the general advantages of extraction over other methods of isolating technetium, this method is particularly widely used for this purpose. This is also due to the fact that certain solvents (acetone, methylethyl ketone, pyridine) are practically selective toward technetium. The extractive behavior of technetium has been treated in many studies, the most important of which are those of Gerlit (117) and Boyd and Larson (203).

Technetium is extracted with an organic solvent in the form of pertechnetates or in lower oxidation states in the form of complex compounds. The TcO₄⁻ ion can be bound to various large organic cations or bases, for example tetraphenylarsonium (C₆H₅)₄As⁺, triphenylguanidine, methylcapryl chloride, quinoline (204), trilaurylamine, nitron, and apparently cupferron (205–209), although the composition of technetium cupferronate has not been established. The pertechnetate of the corresponding cation formed has a high affinity for organic solvents and is readily extracted by them from aqueous solutions.

The isolation of technetium in the form of tetraphenylarsonium pertechnetate has met with the most widespread acceptance. The equilibrium constant of the reaction



The analogous constant for the Cl^- ion is approximately 200. Tetraphenylarsonium pertechnetate is extracted with benzene, chloroform, or nitrobenzene. The latter produces a somewhat greater extraction (39). During the extraction, no separation from perrhenates and perchlorates occurs, but the removal of molybdenum, tungsten, and ruthenium in alkaline media is fairly extensive.

During the extraction, technetium is also associated with iodine and trivalent gold, which should be separated first. Reextraction of technetium into an aqueous phase is accomplished with a 0.2 N HClO_4 solution or a 12 N H_2SO_4 solution (60), or by reducing technetium to the lower oxidation states with an HCl solution of divalent chromium (39).

In addition to salts with organic cations, heptavalent technetium can be extracted in the form of technetic acid or its salts with inorganic cations. In this case, the extraction is based on the affinity of the TcO_4^- ion for the organic solvent, although the nature of the cation also plays an important part.

The general conclusions reached by Boyd, who studied the extraction of technetium with 75 solvents from acid, alkaline, and neutral media are as follows:

(a) The extraction of TcO_4^- ion by aliphatic, aromatic, and chlorohydrocarbon compounds is insignificant. Indeed, the slight extraction of technetium with chloroform (0.6–1.9%) observed (209) can be explained by the presence of water in the latter. An appreciable extraction requires the presence of a donor atom (oxygen, nitrogen).

(b) An increase in the dielectric constant favors the extraction.

(c) In homologous series, the extraction decreases with increasing hydrocarbon chains of molecules of the extracting agent.

(d) The extraction depends on the structure of the extracting agent. For instance, the distribution ratio of technetium increases from primary to tertiary alcohols, ketones, and amines. Quaternary amines and their salts have the highest distribution coefficient not only in acid but also in neutral and alkaline media. The presence of a ring in the alcohol or ketone molecule also increases the extraction.

Boyd suggests that strongly basic solvents such as amines extract technetium in the form of "onium" salts, whereas less basic solvents extract free HTcO_4 or pertechnetates. In acid media, the best extracting agents were found to be alcohols, ketones, and tributyl phosphate; in alkaline solutions, ketones and cyclic amines. An appreciable extraction of technetium from HNO_3 , HBr , HCl , and H_2SO_4 solutions can also be achieved with ether (79, 209, 210). The distribution ratio of technetium in 1 M HNO_3 is 1.267. However, the best results are obtained by

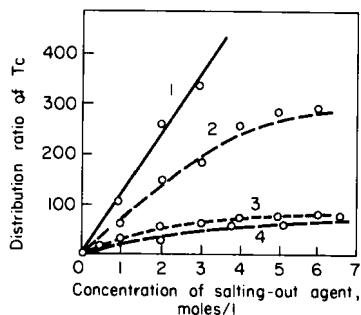


FIG. 9. Extraction of Tc^{99m} with methyl ethyl ketone with various salting-out agents: (1) Li_2SO_4 , (2) K_2CO_3 , (3) KOH , (4) $(NH_4)_2CO_3$.

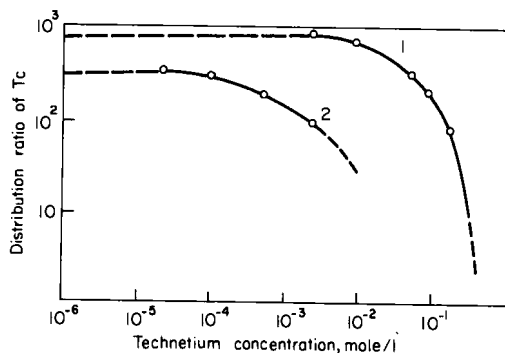


FIG. 10. Effect of technetium concentration on its extraction with acetone and pyridine from a 2 M solution of Na_2CO_3 : (1) extraction with pyridine, (2) extraction with acetone.

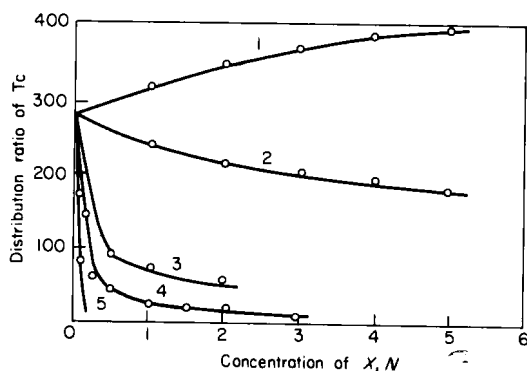


FIG. 11. Effect of extraneous anions on the extraction of Tc^{99m} with methyl ethyl ketone: (1) 2 M $K_2CO_3 + x K_2MoO_4$, (2) 2 M $K_2CO_3 + x KOH$, (3) 2 M $K_2CO_3 + x KCl$, (4) 2 M $K_2CO_3 + x NaNO_3$, (5) 2 M $K_2CO_3 + x KReO_4$.

extracting from alkaline media with acetone (211), methyl ethyl ketone (66, 117), and pyridine (93, 212) (Figs. 9-10).

As salting-out agents that raise the distribution ratio of technetium and prevent the phases from mixing, one can use strong solutions of alkalis or carbonates, and, for methyl ethyl ketone, the neutral salts Li_2SO_4 , Na_2SO_4 , Na_2MoO_4 , etc. The distribution ratio increases in the series of cations $\text{Li}^+ > \text{K}^+ > \text{Na}^+ > \text{NH}_4^+$, linked to the hydroxyl group or the CO_3^{2-} or SO_4^{2-} group. An appreciable effect on the extraction of technetium is exerted by its concentration (see Fig. 10), which becomes important beginning at approximately $10^{-3} M$.

Whereas the series of anions CO_3^{2-} , MoO_4^{2-} , SO_4^{2-} favors the extraction of technetium, the ions Cl^- , NO_3^- , CNS^- , CH_3COO^- , ReO_4^- (Fig. 11) sharply reduce the distribution coefficient of technetium, and do so at a relatively low content (for example, for ReO_4^- , about $10^{-3} M$). The negative effect of nitrates is of great importance in the extractive recovery of technetium from fuel-processing wastes, where the content of nitrates is high. This effect can be avoided to some extent by replacing pyridine with its methyl derivatives (93, 213). Apparently the compounds KNO_3 , KCl , KOH , and NH_4OH , which have a slight solubility in these extracting agents that is comparable to the solubility of the pertechnetates, decrease their distribution ratio, whereas salts that are practically insoluble therein (K_2SO_4 , K_2CO_3 , K_2MoO_4) increase this ratio. The extraction from alkaline media is extremely selective, since most ions (OH^- , CO_3^{2-} , MoO_4^{2-} , SeO_3^{2-} , AsO_4^{2-} , WO_4^{2-} , Sb^{5+} , VO_3^- , etc.) have a distribution coefficient of less than 0.001. An exception is rhenium, whose extraction coefficient is very high. In extraction with acetone, methyl ethyl ketone, and pyridine, an effective removal of ruthenium also takes place (66, 93, 117, 214).

A considerable number of studies have been devoted to the extractive recovery of technetium. Morgan and Sizeland (179) studied the extraction of TcO_4^- in hexane, butex, and other solvents; Tribalat used methyl isobutyl ketone and isoamyl alcohol (213, 215); Kan used triisooctylamine and bis-2-ethylhexylorthophosphoric acid (216). Extraction with tributyl phosphate was studied in particular detail (217, 218). Spitsyn *et al.* (208) established the formation of the compound $\text{HTcO}_4 \cdot 3\text{TBP}$. The extraction with tributyl phosphate together with the extraction with pyridine (219), methyl ethyl ketone (66, 220), acetone (211), and trilaurylamine (204) is recommended for the technological recovery of technetium from fuel-processing wastes and irradiated molybdenum.

Reextraction of technetium into the aqueous phase was achieved by driving off the excess solvent, changing the pH or the oxidation state of technetium by displacement with other ions (nitrate, perchlorate), and

diluting the extracting agent with a nonpolar solvent (117). In extracting heptavalent technetium, it is necessary to consider the possible reduction of technetium by the organic solvent or the impurities, and also the influence of extraneous radioactive radiation (221). Münze (222) explained the discrepancy in the data of various authors on the determination of the distribution coefficients of Tc^{99m} by the existence of lower valences that result from the β decay of the parent molybdenum.

In addition to technetic acid and its salts, use is made for analytical purposes of extraction of various complex compounds of technetium where the latter is selectively reduced to lower oxidation states (Table XXIV).

TABLE XXIV
EXTRACTABILITY OF COMPLEX COMPOUNDS OF TECHNETIUM

Complex-forming agent	Extracting agent	Reference
Thiocyanate	Alcohols, ethers, ketones; solution of trioctylphosphine oxide and trioctylamine chloride in cyclohexane with dichloroethane	(91, 117, 128)
<i>p</i> -Thiocresol	CHCl_3 , CCl_4 , ether, benzene, toluene	(131)
1,5-Diphenylcarbohydrazide	CCl_4	(223)
Potassium xanthate	CHCl_3 , CCl_4	(133)
K_2TcCl_6	Solution of tetraphenylarsonium salt in chloroform, trioctylamine chloride in cyclohexane	(60)
α -Picolinic acid	Extracts partially with chloroform	(129)
Cupferron	Ether, CHCl_3	(209)
3-Toluene, 4-dithiol	CCl_4	(224)
Sulfosalicylic acid	Isoamyl alcohol, toluene, ether	(129)

G. SEPARATION OF TECHNETIUM FROM RHENIUM

Rhenium has been used as a nonisotopic carrier of its chemical analog technetium in the isolation and identification of the latter, and also in geochemical investigations. In the latter case, attempts to detect technetium in nature were undertaken in the case of minerals where the rhenium content was sufficiently high. The necessity of separating technetium from rhenium can also arise in the preparation of technetium from irradiated molybdenum (225). Despite the similarity in chemical properties of the two elements, several fairly effective methods for their separation have been elaborated. In most cases, these methods involve

the separation of microquantities of technetium from macroquantities of rhenium.

1. Distillation

In the distillation from perchloric acid, a partial separation from rhenium takes place, and the first fractions of the distillate are rich in technetium (114, 174, 175). Owing to the great difference in vapor pressures of the higher oxides of technetium and rhenium, as in the first case, a certain separation of these elements can be achieved by a second alternate distillation with HNO_3 and HCl (226). However, neither method gives quantitative results, and almost no use is made of either in practice. When HCl is passed through concentrated sulfuric acid in which technetium and rhenium are dissolved, rhenium distills off as the chloride at $180^\circ\text{--}200^\circ\text{C}$, while technetium is reduced and remains in the original solution (118). The separation factor reaches 50 (179). The distillation of technetium and rhenium in the form of chlorides in a stream of chlorine yields their mixture in the distillate. From the distillate, rhenium is driven off under vacuum at 300°C . Under these conditions, technetium chloride is reduced to the metal and is not distilled (227).

2. Precipitation

In contrast to rhenium, technetium is not precipitated by hydrogen sulfide at hydrochloric acid concentrations above 9 *N*. Multiple reprecipitation of rhenium sulfide that has occluded some technetium makes it possible to separate technetium from rhenium almost quantitatively (225). The difference in oxidizing capacity of technetium and rhenium is utilized for coprecipitating with ferric hydroxide technetium forms reduced with concentrated hydrochloric acid, while the rhenium remains in solution. The lower solubility of potassium perrhenate as compared to that of pertechnetate can be used for separating large amounts of the elements by fractional crystallization ($D = 0.1$) (225).

3. Electrochemical Methods of Separation

At a platinum cathode in a 2 *M* NaOH solution at a potential of -1.1 V, technetium is reduced to TcO_2 and separated from rhenium. The concentration of technetium should be no less than 10^{-4} *N* and much below the rhenium concentration (101). We have proposed (228) a method of separating technetium from rhenium by continuous electrophoresis on a porous filler. When a solution of TcO_4^- and ReO_4^- is treated with thiourea, a selective reduction of Tc^{7+} to Tc^{5+} takes place with the formation of a cationic complex of technetium with excess

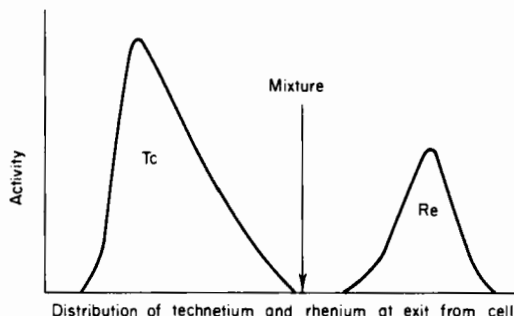


Fig. 12. Separation of technetium from rhenium by continuous electrophoresis.

reagent, while the rhenium remains in the form of the ReO_4^- anion. When the electric field is applied, a well-defined separation of technetium from rhenium occurs (Fig. 12).

4. Separations Based on the Instability of Certain Compounds of Technetium and Rhenium

Such methods include a separation based on the different stabilities of phthalocyanine complexes of technetium and rhenium (18), and a method based on the difference in hydrolyzing capacity of compounds of the type K_2TcCl_6 and K_2ReCl_6 (91).

5. Extraction

Although rhenium and technetium behave almost analogously during extraction, they are separated to some extent during extraction in the form of cupferronates (209). It is also possible to utilize the ability of technetium to form extractable complexes upon reduction with weak reductants.

6. Chromatography

These methods are the most efficient and ensure a separation factor of 10^4 – 10^5 . Technetium and rhenium are precipitated in the form of pertechnetate and perrhenate on the anion exchanger Dowex-1 (184) or Dowex-2 (183); the elements are then successively eluted with ammonium sulfate in a mixture with thiocyanate (183) or perchlorate (184) ions.

H. SEPARATION OF TECHNETIUM FROM RUTHENIUM

When technetium is obtained from the fission fragments of uranium, in which the rhenium isotopes are practically absent, the separation of

technetium from ruthenium involves major difficulties. This problem faced the researchers in the first studies of technetium, since some of its isotopes were obtained through the decay or irradiation of ruthenium.

In order to separate technetium and ruthenium, they were distilled from perchloric acid, ruthenium was reduced to the insoluble RuO_2 with alcohol (174), and this was followed by distillation from sulfuric acid. However, despite the relative complexity of the method, complete removal of ruthenium could not be achieved. Contamination of the technetium fraction with ruthenium ranged from 0.003 % in the method of Hoffman and Lundell (229) to 3 % in the method of Glendenin (174).

Subsequently, precipitation and extraction became the principal methods for separating technetium from ruthenium. The precipitants of technetium (with a rhenium carrier) used were nitron (11, 117) and tetraphenylarsonium chloride (204). The latter proved to be particularly effective, since it precipitated technetium but occluded practically no ruthenium. Analogous results are obtained in the extraction of tetraphenylarsonium pertechnetate with chloroform. In present-day schemes of isolating technetium from fission fragments, its separation from ruthenium is accomplished by a series of successive precipitations of rhenium on ferric hydroxide (230, 231) and also by the extraction of technetium with pyridine, which does not extract ruthenium (93, 214). The complexity of the extractive separation of technetium from ruthenium is due to the presence of a large number of valence and ionic forms of ruthenium, many of which are capable of being extracted with technetium. However, in alkaline media, ruthenium is reduced by the organic solvent to lower valences and is not extracted.

The extraction of ruthenium can be accomplished only in the presence of an oxidant in the solution, for example, a hypochlorite (61, 214). The extraction of technetium with methyl ethyl ketone (66, 117), acetone (211), pyridine (93, 214), and triphenylguanidine (205) makes it possible to obtain a ruthenium decontamination factor of 10^5 or higher. A poor separation was obtained by extraction with tributyl phosphate from fuel-processing wastes. Here the separation factor does not exceed a few hundred, and only in combination with ion exchange can it be raised to approximately 10^4 (218).

I. ISOLATION OF SHORT-LIVED TECHNETIUM ISOTOPES

Until recently, studies of the chemical properties of technetium involved the use of primarily its short-lived isotopes: Tc^{99m} ($T_{1/2} = 6.0$ hours), Tc^{95m} ($T_{1/2} = 60$ days), and Tc^{97m} ($T_{1/2} = 90$ days). Of these, Tc^{99m} is the most accessible and the most frequently employed. A large number of methods, which are partially listed in Anders' survey (60),

have been developed for its isolation. Some that have found uses in the isolation of Tc^{99m} from Mo^{99} by the isotope generator technique are described below.

Successful operation of such a generator requires that the method of separation of technetium and molybdenum have a high separation factor, provide a high yield of technetium, and permit the repeated use of molybdenum with a minimum loss of the latter. Furthermore, the operations should be simple and rapid, the final solutions should be obtained in a form suitable for further use, and the processing of high-activity preparations should permit the automation of the processes and be safe. Extraction and chromatography are used for this purpose. Alkaline molybdate solutions are usually employed in the extraction, and the extracting agents can be acetone (211), methyl ethyl ketone (66, 117), and pyridine (93, 212).

Although of all these extracting agents pyridine yields the highest distribution ratio, acetone and methyl ethyl ketone are the most convenient in laboratory practice. This is due to the higher boiling point of pyridine and its unpleasant odor, whereas acetone and methyl ethyl ketone evaporate readily on moderate heating.

Irradiated molybdenum trioxide is dissolved in a calculated amount of alkali with a few drops of hydrogen peroxide. The excess alkali lowers the distribution ratio, but promotes a better layer separation. The salting-out agents, which sharply increase the distribution ratio of technetium during the extraction, are the molybdate itself and concentrated solutions of Na_2CO_3 , K_2CO_3 , and $(\text{NH}_4)_2\text{CO}_3$. The distribution ratio of technetium during extraction with methyl ethyl ketone from a 3 *M* solution of K_2CO_3 is about 300, whereas for molybdenum and practically all other radioactive impurities it is $2-5 \times 10^{-4}$. Sulfates, particularly lithium sulfate, are equally effective salting-out agents. The salting-out agent is added to the molybdate solution in a quantity such that its concentration in the final solution is of the order of 2-3 moles/liter. The volume of the solution is chosen in accordance with the apparatus employed.

The extraction is carried out in separatory funnels, and, in the case of high activities, in automatic laboratory-type extractors. A certain amount of mechanically occluded molybdenum and other impurities may be present in the organic phase. They are removed by washing the organic phase with small portions of K_2CO_3 or $(\text{NH}_3)_2\text{CO}_3$. Ammonium carbonate decreases the amount of mineral salts in the technetium solution, since it decomposes on subsequent distillation of methyl ethyl ketone. After the distillation of methyl ethyl ketone, a final solution of potassium or ammonium pertechnetate "without carrier" is obtained. The purity of Tc^{99m} is controlled by means of the half-life and reaches

over 99.99 %. The yield is about 99.9 %. Practically no molybdenum is lost during the extraction, and its solution can be used many times. Only the water partially carried away with the organic solvent must be replaced. Similar results are obtained by extracting technetium with acetone, for which the distribution ratio reaches a relatively high value. However, its drawback is the extraction of a certain quantity of alkali and mixing with the solutions of neutral salting-out agents.

In addition to extraction, chromatographic methods have also been commonly adopted for the separation of technetium from molybdenum. As an example, let us discuss the isolation of Tc^{99m} by Tucker, Greene, and Murrenhoff (232). Uranium metal or uranium oxide containing the fission products is dissolved in nitric acid. The solution, diluted to a nitric acid concentration of 2–3 M , is passed through a chromatographic column containing alumina. Iodine, tellurium, and molybdenum are adsorbed from acid solutions, but the remaining fission products are not retained by the column. The column is washed with nitric acid, water, and a weak solution of ammonia to remove I^{131} . Molybdenum is isolated by passing a 1 M solution of ammonia through the column. The solution of ammonium pertechnetate obtained is acidified with nitric acid to pH 1–2, and Mo^{99} is readsorbed on alumina pretreated with nitric acid.

The column with Al_2O_3 is washed with a 0.1 M HNO_3 solution as Tc^{99m} accumulates, and the latter is washed out with small portions of 0.1 M HNO_3 . The yield of technetium is about 80 %, and its radiochemical purity is approximately 99.99 %. This relatively simple and efficient method of obtaining technetium is applicable not only to fragment Mo^{99} , but also to irradiated samples of natural molybdenum. Instead of a simple glass column used with activities of the order of a few curies, use is made of a more complex apparatus with remote control and pneumatic supply to the solutions. A drawback of all chromatographic methods as compared to extractive ones is the considerable content, in the final solutions, of mineral substances that hinder the further use of Tc^{99m} . For medical purposes therefore, where a neutral solution of technetium with a minimum content of extraneous salts is required, Scheer and Maier-Borst (233) have slightly modified the technique of Tucker and Greene. From irradiated molybdenum adsorbed on alumina, they washed out Tc^{99m} with 0.2 N H_2SO_4 solution. Subsequently, the precipitation of the SO_4^{2-} ion and neutralization of the solution were carried out with barium hydroxide.

Still better results are obtained by washing out the technetium with acetone or pyridine. Potassium molybdate precipitated on activated alumina does not dissolve in acetone and remains on the column, whereas the soluble pertechnetate is quantitatively washed out with acetone.

After the acetone has been driven off, a neutral solution from which extraneous salts have been removed and containing Tc^{99m} is obtained. Obviously, alumina is not the only adsorbent for Mo^{99} . Thus, Nelson and Kraus (234) used zirconium hydroxide for this purpose and washed Tc^{99m} out with 2 *M* HNO_3 . Ryabchikov and Borisova (192) used EDS-10P resin in the phosphate form. Technetium was washed out of the resin with 2 *M* H_3PO_4 solution. An original method of isolating Tc^{99m} was developed by Nefedov and Toropova (235). It is based on the fact that the β decay of Mo^{99} leads to the formation of daughter Tc^{99m} , which as a result of the rupture of chemical bonds is in a form substantially different from the parent substance. As a result, from a chloroform solution of irradiated molybdenum hexacarbonyl $\text{Mo}^{99}(\text{CO})_6$, extraction with water can quantitatively separate radiochemically pure Tc^{99m} .

Molybdenum hexacarbonyl (54) and molybdenum dicyclopentadienyltricarbonyl $[\text{C}_5\text{H}_5\text{Mo}^{99}(\text{CO})_3]_2$ can also be used to isolate Tc^{99m} by distillation (147). A drawback of these methods is the complexity of preparation and the relatively low radiation stability of the carbonyl compounds of molybdenum. The other short-lived technetium isotopes used in practice, Tc^{95m} and Tc^{97m} , can be separated from irradiated molybdenum only once, since they are formed directly by nuclear reactions with molybdenum and have no radioactive precursors. The methods described above are completely suited for their isolation.

J. ISOLATION OF Tc^{99} FROM IRRADIATED MOLYBDENUM

There are two ways of isolating the main long-lived isotope, Tc^{99} : extraction from fission fragments of uranium or plutonium present in the waste waters of plants processing nuclear fuel, and irradiation of natural molybdenum with neutrons in a nuclear reactor. Since the cross section of the reaction $\text{Mo}^{98}(n, \gamma)\text{Mo}^{99}$ is small, the formation of appreciable amounts of technetium requires long periods of time and the irradiation of kilogram quantities of molybdenum.

The method of isolating technetium from irradiated molybdenum cannot compete with its separation from fission fragments, since the cost of the technetium thus obtained is considerably higher (by a factor of several thousand). However, at the time when the methods of isolating technetium from fission fragments had not been sufficiently developed, both methods were used to the same extent. Owing to the extremely simple technological processing of irradiated molybdenum, primarily molybdic trioxide, this method has not yet been completely abandoned (236). If the decay and burn-up of the technetium formed are neglected, its accumulation resulting from the irradiation of molybdenum by neutrons is described by the equation

$$N = 3.5 \times 10^{-18} P\Phi t \text{ mg Tc}^{99} \text{ for metallic Mo} \quad (3)$$

$$N = 1.85 \times 10^{-18} P\Phi t \text{ mg Tc}^{99} \text{ for MoO}_3 \quad (4)$$

where N is the amount of Tc^{99} at the end of the irradiation (mg), P is the weight of the irradiated molybdenum or MoO_3 (g), and Φt is the integrated neutron flux.

Thus, the irradiation of 1 kg of molybdic trioxide in a flux of 10^{13} n/(cm² sec) for 1 year forms about 7 mg of technetium. Usually, molybdic trioxide is irradiated; despite its lower content of molybdenum atoms (lower by a factor of 5) per unit volume it considerably simplifies the subsequent processing. Since the separation of technetium and rhenium is a relatively difficult problem, prior to the irradiation it is necessary to select a raw material free from rhenium or take special steps to purify it.

Irradiated molybdic trioxide or metallic molybdenum is left standing for 1 month to allow the transmutation of all Mo^{99} into technetium and the decay of short-lived impurities. Even pure molybdic trioxide is fairly radioactive as a result of activation of the impurities, and for this reason its processing requires special protective measures. The radioactive impurities may include Co^{60} , Fe^{60} , Zn^{65} , W^{187} , Sb^{124} , Zr^{95} , etc. (237). Subsequent treatment of irradiated molybdenum is carried out by various methods.

Boyd *et al.* (225) irradiated 5.7 kg of metallic molybdenum in a reactor in the course of 1 year. The irradiated molybdenum was dissolved in sulfuric acid with simultaneous distillation of technetium. The sulfuric acid solution of technetium obtained was diluted to 4 *M* H_2SO_4 and treated with bromine water. A platinum salt was added to the solution as the carrier, and platinum sulfide, which occludes technetium, was precipitated with hydrogen sulfide. The sulfide precipitate was dissolved in ammoniacal hydrogen peroxide. The solution obtained was evaporated off, and technetium was separated from the platinum and ammonium sulfate by distillation from HClO_4 or H_2SO_4 . Since the initial molybdenum contained a certain amount (3×10^{-5} mole) of rhenium, which was concentrated together with technetium, the two metals were separated by distillation and chromatography. The total yield was 30–60 % of the initial technetium.

The processing of molybdic trioxide begins with its dissolution in alkali with the addition of a small amount of hydrogen peroxide. The dissolution is sometimes preceded by treatment of the MoO_3 with nitric acid to oxidize the technetium, but the presence of nitrates may subsequently decrease the extraction, which together with precipitation is used for the isolation of technetium.

Spitsyn and Kuzina (65, 238) coprecipitated technetium on magnesium hydrogen phosphate or magnesium ammonium phosphate. To this end, a solution of molybdate at pH 7.5–8 was mixed with magnesium hydrogen phosphate for 3 hours. After three to four adsorption operations, most of the technetium was successfully removed with the precipitate from the solution. The precipitates obtained were dissolved in 6–12 *M* HCl, and hydrogen sulfide was passed through the solution to reduce the technetium. Since the hydrogen phosphate precipitate occludes only Te^{7+} , during the subsequent precipitation of magnesium ammonium phosphate with ammonia the bulk of the technetium remained in solution. The solution containing technetium was filtered off, evaporated, and the residue dissolved in nitric acid. The nitric acid solution at pH 2 was passed through a KU-2 cation-exchange resin to separate the impurities. The filtrate was evaporated off and heated to decompose ammonium nitrate. The residue was treated with a mixture of hydrogen peroxide and ammonia and dried. The ammonium pertechnetate obtained was acidified with hydrochloric acid, and technetium sulfide was precipitated from the solution. Use of this method produced about 0.5 mg of technetium from 200 g of MoO_3 .

The best methods of isolating technetium from irradiated molybdenum are the extractive ones. Faddeeva *et al.* (66) quantitatively isolated about 1 mg of technetium by using methyl ethyl ketone.

The extraction of technetium with acetone from alkaline media, proposed by Kuzina *et al.* (211), has proven to be the most efficient method of separating technetium from irradiated molybdenum. In the presence of Na_2MoO_4 and NaOH as the salting-out agents, acetone extracts technetium almost quantitatively. Using this method, the authors processed several kilograms of molybdic trioxide and isolated several tens of milligrams of technetium (236).

Molybdic trioxide was dissolved in alkali, and alkalis or alkali metal carbonates were added as the salting-out agents to the solution so that their concentration was 2–3 *M*. Practically all the stable and radioactive impurities remained in the aqueous phase. Even a single extraction permitted the separation of 60–90 % technetium with a decontamination factor of about 10^6 relative to molybdenum and radioactive impurities. In the final purification, the extracting agent was washed with small portions of alkaline solutions. Acetone or methyl ethyl ketone was distilled off, and technetium remained as a weakly alkaline solution of the salt of the corresponding cation.

K. ISOLATION OF Tc^{99} FROM FISSION FRAGMENTS

Technetium has one of the highest yields among fragments formed

during the fission of nuclear fuel. In addition to Eq. (2) to determine the accumulation of technetium in the fission products one can use a simplified formula, relating the power of the reactor to the quantity of the technetium formed,

$$N_{\text{Tc}} = 28Pt \text{ mg} \quad (5)$$

where P is the reactor power (Mw), and t is the time of operation of the reactor (days). According to this formula, in a reactor with a power of 285,000 kw, about 8 g of technetium is formed daily, or approximately 3 kg per year.

The power of modern nuclear plants at the present time is approximately 6×10^6 kw, and therefore the total amount of technetium formed in them is appreciable and attains tens of kilograms per year. With the development of atomic power engineering in the near future, the yearly production of technetium in nuclear reactors will increase steadily. Tentative data on the increase in the production of technetium as a fission fragment, summarized by taking the planned development of nuclear power engineering in most countries of the world during 1963–1980, are shown in Table XXV.

TABLE XXV

Year:	1963	1965	1970	1980
Amount of Tc formed in nuclear power plants (kg):	60	200	500	4000

The total amount of technetium accumulated in the world by 1980 will apparently exceed 10,000 kg. However, the step of isolating technetium usually does not enter into most schemes of processing nuclear fuel. Technetium is mainly obtained only at pilot plants processing waste solutions that remain after the separation of uranium and plutonium. In such plants, only a small part of the total amount of waste solution is used for the preparation of various radioactive isotopes. Their technetium capacity amounts to several kilograms per year. The technetium content in solutions to be processed is low and amounts to 5–100 mg/liter.

Table XXVI gives some examples of compositions of waste solutions to be processed after the refining of nuclear fuel in redox processes (extraction processes involving the use of hexone as the solvent and aluminum nitrate as the salting-out agent) and in the purex processes (extracting agent—tributyl phosphate, salting-out agent—nitric acid).

In order to obtain fragment technetium, in addition to fuel-processing wastes, earlier studies (174, 205) made use of uranium preparations specially irradiated with neutrons. A typical method of this type is that proposed by Tribalat (205).

Irradiated uranium oxide was dissolved in sulfuric acid, iodide ion being added as carrier of radioactive I^{131} . Iodine was then oxidized with ammonium persulfate and extracted with toluene. Traces of elemental

TABLE XXVI

COMPOSITION OF WASTE SOLUTIONS CONTAINING TECHNETIUM (91)

Solution components	Concentration in the process	
	Redox	Purex
$Al(NO_3)_3$	1.4 M	—
NH_4NO_3	1.9 M	—
$Hg(NO_3)_2$	0.0125 M	—
HNO_3	—	3.9 M
Cs^{137}	8.87 curies/liter	4.4 curies/liter
Sr^{90}	0.94 curies/liter	4.6 curies/liter
Ru^{106}	0.10 curies/liter	9.0 curies/liter
Ce^{144}	0.87 curies/liter	88.7 curies/liter
Pm^{147}	1.06 curies/liter	17.0 curies/liter
Tc^{99}	6.5 mg/liter	41 mg/liter
Corrosion products		
Fe, Ni, Co	1–2 g/liter	—

iodine were eliminated by boiling, and the solution was neutralized with Na_2CO_3 and again boiled with $(NH_4)_2S_2O_8$ to oxidize technetium. Iodine had to be eliminated, since it is subsequently extracted together with technetium. Tetraphenylarsonium chloride, $[(C_6H_5)_4As]Cl$, was added to the solution, and technetium was extracted with chloroform as tetraphenylarsonium pertechnetate. Technetium was separated from the organic phase by evaporation or reextraction in $HClO_4$ or H_2SO_4 , followed by precipitation or distillation.

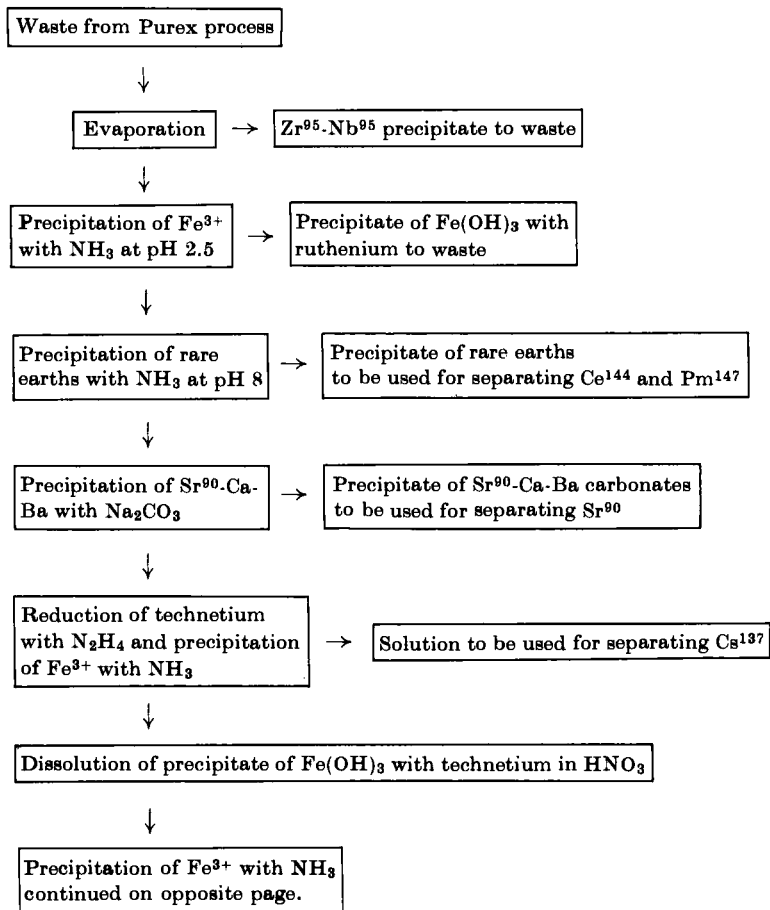
Technetium was first separated from fuel-processing wastes by Parker and Martin (71, 108). In their method, perchloric acid was added to the solution containing technetium fragments, and tetraphenylarsonium chloride was used to precipitate the isomorphous mixture $[(C_6H_5)_4As]ClO_4 \cdot [(C_6H_5)_4As]TcO_4$ on heating. The cooled solution was filtered, the filtrate containing almost all the radioactive impurities was discarded, and the residue was decomposed by electrolysis in concen-

trated sulfuric acid. The crude technetium deposited on platinum electrodes was purified by distillation from HClO_4 and deposition as the sulfide. Later, use was made of methods based primarily on the precipitation of reduced forms of technetium on ferric hydroxide.

The report of Rapp at the First International Conference on Peaceful Uses of Atomic Energy (230) cites one of the first industrial processes of this type. Waste solutions containing fission products are evaporated, and the precipitation of ferric hydroxide by means of carbamide hydrolysis or with ammonia is carried out at pH 2.5 in the presence of hydrazine. The ferric hydroxide precipitate thus occludes over 90 % ruthenium and technetium. The filtered deposit is dissolved in nitric acid, which re-oxidizes technetium to TcO_4^- ion, and tetraphenylarsonium pertechnetate is precipitated from the solution obtained. Technetium is subsequently purified by being reprecipitated as the pertechnetate and then the sulfide. Technetium sulfide is dissolved in a mixture of hydrogen peroxide and ammonia, and the ammonium pertechnetate obtained is crystallized out of the solution.

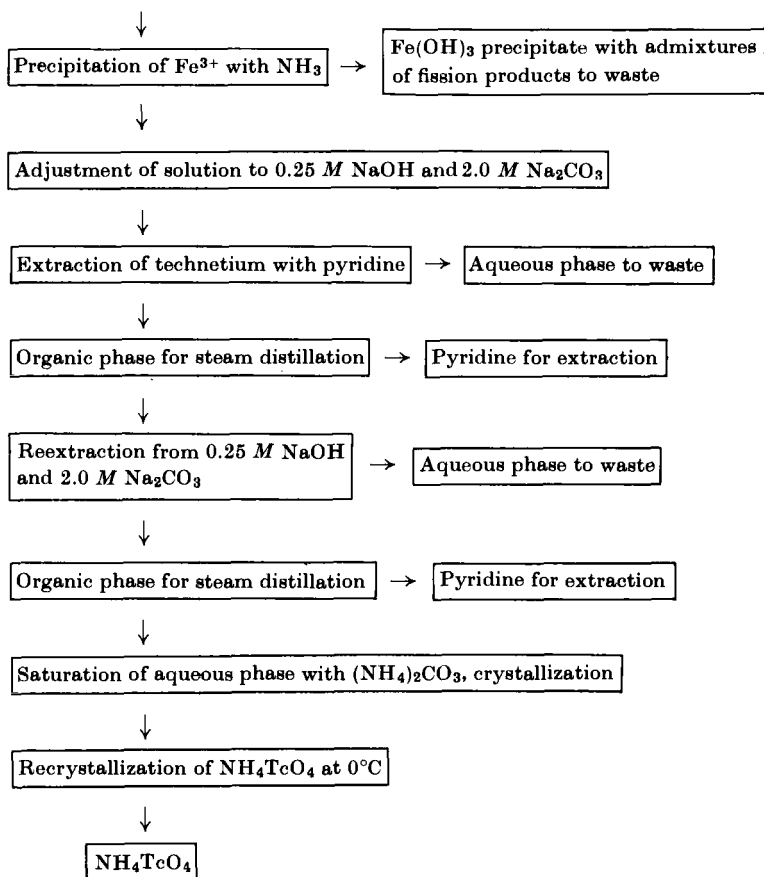
A disadvantage of all methods using the tetraphenylarsonium ion is the high cost of the reagent and the necessity of consuming large amounts of organic material. Of major interest in this respect is Boyd's suggestion concerning utilization of the tetraphenylarsonium ion. The tetraphenylarsonium pertechnetate precipitate is dissolved in alcohol and passed through an anion-exchange resin in the chloride form. The TcO_4^- ion is thus adsorbed and later eluted off with 2 *M* HClO_4 . The tetraphenylarsonium chloride that has passed through the column is reused. Subsequently, the precipitation of technetium with tetraphenylarsonium ion was successfully eliminated. Such an improved scheme of processing waste solutions into isotopes was proposed by Lamb *et al.* (231) for the purex and redox processes. In this scheme, in order to remove ruthenium from technetium, the removal of ruthenium being particularly difficult, the latter was precipitated on ferric hydroxide under conditions where technetium remained in the solution, and technetium was precipitated as the sulfide.

After Rimshaw and Malling (93) determined that pertechnetates could be extracted with pyridine and its methyl derivatives from media containing nitrates, this scheme was modified in the part involving the final purification of technetium, ruthenium and other impurities being still satisfactorily removed. Instead of precipitating technetium as the sulfide, it was subjected to a double extractive purification. The part of the scheme of processing waste solutions, involving the recovery of technetium from the wastes resulting from the extraction with tributyl phosphate (purex process), is approximately as shown in the diagram



on this page. This scheme was carried out at an experimental plant of the Oak Ridge National Laboratory.

After the solution is evaporated and the cake precipitated from the filtrate at pH 2.5 is removed, ferric hydroxide, which occludes almost all the ruthenium, is precipitated with ammonia. Rare earths and alkaline earth elements (see scheme) are then separated. After technetium is reduced with 0.1 *M* hydrazine hydrate solution, Fe³⁺ ions are added to the solution. Ferric hydroxide, which is then precipitated with ammonia at pH 3, occludes the reduced technetium and the remaining ruthenium. The precipitate is dissolved in nitric acid, and a second precipitation of ferric hydroxide is performed. Technetium is oxidized with nitric acid, and, once in the heptavalent state, is not occluded by Fe(OH)₃. Only ruthenium reaches the precipitate. The technetium solution is neutral-



ized, and its concentration is made 0.25 M in NaOH and 2 M in Na_2CO_3 . A certain excess alkalinity promotes the phase separation.

When technetium is extracted with pyridine from such a solution, the distribution coefficient of technetium is 740, whereas most impurities are practically not extracted with pyridine. The presence of nitrate ions decreases the distribution coefficient of technetium somewhat, but it nevertheless remains sufficiently high. After the extraction, pyridine is steam-distilled, a 0.25 M NaOH and $2\text{ M Na}_2\text{CO}_3$ concentration is reestablished in the aqueous solution, and a second extraction of technetium is performed. Pyridine is distilled off, and the aqueous solution containing technetium is saturated with $(\text{NH}_4)_2\text{CO}_3$ or NH_4NO_3 , and cooled to 0° in order to crystallize NH_4TcO_4 . After three crystallizations, the pertechnetate has a radiochemical purity of over

99.998 % and a chemical purity of over 99.99 %. This scheme apparently may be regarded as the most successful at the present time, although several other methods of isolating technetium from fuel-processing wastes have been proposed as well. Thus, a patent has been granted for a process of isolating technetium from waste solutions by precipitation on the anion-exchange resin "D-Acidite FF" in OH form followed by elution of technetium with 10 *M* HNO₃ and extraction with methyl ethyl ketone (220).

Coleman *et al.* (204) developed a method for isolating technetium from residues of fluorination of spent fuel by extraction with triaurylamine. Campbell (218) studied the separation of technetium by extraction with tributyl phosphate from a mixture of fission products "cooled" for 200 days. However, these methods apparently have not yet found practical application.

Brief communications (177) have recently appeared concerning a new method of obtaining technetium in the course of the processing of spent nuclear fuel in gaseous diffusion plants. Technetium hexafluoride is formed along with UF₆ during fluorination of uranium and usually escapes together with this compound. By adsorbing technetium on magnesium fluoride, one can concentrate technetium and separate it from uranium. Extraction of the concentrate with 2,4-dimethylpyridine removes fission product impurities, fluorine, sodium, etc., from the technetium, and the latter crystallizes out in the form of high-purity NH₄TeO₄. The use of this method has sharply reduced the cost of technetium and increased its production. However, further improvement in methods of isolating technetium from fission products and an increased scale of production are necessary in order to make technetium more accessible for scientific and practical purposes.

L. ISOLATION OF TECHNETIUM FROM ORES

The problem of isolating technetium from natural materials faced researchers when they attempted to find it in the earth's crust. In addition to the primary origin, a certain amount of technetium could have also formed as a result of the interaction of molybdenum and ruthenium with cosmic radiation and as a result of the spontaneous fission of uranium. The difficulty of isolating technetium from natural materials consisted in the need for an extensive concentration of microquantities of technetium and separation from macroquantities of a large number of impurities. Since the geochemical behavior of technetium should be analogous to that of rhenium because of the similarity in their chemical and physical properties, the prospecting for technetium was carried out

in minerals containing rhenium, i.e., mainly molybdenum minerals. Physicochemical analytical methods made it possible to detect 10^{-8} – 10^{-10} g of technetium, but in most cases their application involved the elimination of certain interfering elements, mainly molybdenum and rhenium. The separation of technetium from rhenium was the most difficult problem, since, because of the similarity in properties, the permissible content of rhenium in the samples analyzed should be extremely low.

An example of the method of isolating technetium from molybdenum-containing minerals is the study of Boyd and Larson (21). Molybdenite MoS_2 was fused with sodium peroxide. The radioactive tracer added to the melt was the Tc^{95m} isotope, the radioactivity of which indicated the chemical yield of technetium at all stages of the process. The melt was leached out with water and boiled in order to decompose the peroxide. The separated precipitate of ferric hydroxide was filtered off, and the filtrate was passed through a column with strongly basic resin (Dowex-2, Amberlite IRA-410), which adsorbed a certain amount of molybdates and ruthenates. The latter were eluted off the column with a 1 *M* solution of NaNO_3 or a 2 *M* solution of NaOH . The TcO_4^- and ReO_4^- ions were then eluted off with a 2 *N* solution of HClO_4 or NaClO_4 . The mixture of technetium and rhenium sulfides was then precipitated with hydrogen sulfide from the solution after an additional oxidation of technetium with bromine water. Sulfides were dissolved in a mixture of hydrogen peroxide and ammonia, and the solution obtained was evaporated almost to dryness. The residue was dissolved in 10 *N* HCl , the solution for reducing technetium was heated for 1 hour, and Re_2S_7 was precipitated with hydrogen sulfide. Technetium did not precipitate and remained in the solution. The HCl solution, diluted to 1 *N*, was treated with bromine water, and Tc_2S_7 was precipitated with hydrogen sulfide.

To lower the rhenium content, one or several similar cycles were carried out. The final separation of technetium from rhenium was performed on the Dowex-2 anion exchanger. To this end, technetium and rhenium sulfides were dissolved in a mixture of H_2O_2 and NH_4OH , and the pertechnetate and perrhenate ions formed were deposited on the column. When a solution of perchlorate was passed through the latter at a rate of 0.5 ml/min, only rhenium was at first eluted, followed by technetium. The solution containing technetium was diluted, oxidized with bromine water, and, after addition of 1 mg of Cu^{2+} as the carrier, sulfides were precipitated. Copper sulfide together with the coprecipitated technetium constituted the technetium concentrate. From the latter, after dissolving the sulfide in a mixture of hydrogen peroxide and ammonia, technetium can be isolated by electrolysis for subsequent

spectrographic determinations, or, after removal of copper, for spectrophotometric, polarographic, and mass-spectral analyses. The concentrate can also be used directly for activation analysis. This method was used to show that the technetium content in molybdenite does not exceed 10^{-9} – 10^{-10} g/kg.

To confirm the calculated content of technetium formed by the spontaneous fission of uranium, Kenna and Kuroda (28) isolated technetium from the uranium ore, pitchblende, containing 47 % uranium. The pitchblende was dissolved in nitric acid, and lead was precipitated from the solution as a sulfate. After separation of lead, the filtrate was neutralized with ammonia, and hydrogen sulfide was bubbled through for several hours. The sulfide precipitate was filtered off and dissolved in a mixture of H_2O_2 and NH_4OH . Excess of peroxide was removed by boiling and, in order to prevent loss of technetium, the solution was kept alkaline by means of ammonia. To separate the cations, the solution was then passed through a column with a Dowex resin in the H form. The bulk of the molybdenum was removed from the solution that had passed through the column by precipitation with α -benzoin oxime. The precipitate was filtered off, the filtrate was brought up to 2 *N* in acid, and several milligrams of Cu^{2+} were added. Hydrogen sulfide was used to precipitate copper sulfide, with which technetium heptasulfide coprecipitated. The sulfide precipitate was dissolved in a mixture of H_2O_2 and NH_4OH , and several milligrams of rhenium were added as the carrier to the solution formed. The uranium solution was made alkaline to 5 *N* NaOH, and technetium and rhenium were extracted with methyl ethyl ketone. Traces of molybdenum and ruthenium were thus removed from technetium. The latter was reextracted into the aqueous phase, to which 2 mg of Cu^{2+} was added, and the sulfides were precipitated. The sulfides were dissolved as described, the solution was evaporated down to 5 ml, the pH was brought to about 7, and technetium and rhenium were adsorbed on a Dowex anion exchanger in the nitrate form. To separate technetium from rhenium, they were successively eluted with 0.25 *M* NaClO_4 . To the technetium fraction obtained was added 4 mg of Cu^{2+} , the solution was acidified with hydrochloric acid, and technetium and copper sulfides were precipitated.

The sulfide precipitate was filtered off, washed, and dried. The technetium content was determined from measurements of the activity of the samples. The chemical yield of technetium in all the above isolation operations was 50 ± 10 %. The isolated amount of technetium (about 1×10^{-9} g) showed good agreement with the experimental data (approximately 4×10^{-10} g Tc/kg) and calculated data (5×10^{-10} g Tc/kg) on the technetium content of uranium ores.

V. Analytical Chemistry of Technetium

A. DETERMINATION OF TECHNETIUM FROM RADIOACTIVITY

Many publications devoted to the analytical chemistry of this element have appeared in recent years. All the existing methods for analysis of technetium consist of the following steps: dissolution of weighed amounts of the material being studied, isolation and concentration of technetium, separation of technetium from associated impurities, and determination of technetium.

Because of the extremely small amounts of technetium usually present in the initial raw material, it is difficult to draw a line between the analytical and technological methods for its isolation and purification. This problem has been discussed at some length in Section IV, and therefore we shall consider here only the methods for determination of technetium.

The first methods for determination of technetium were based on its radioactivity (11). The specific activity of the most widely distributed isotope Tc^{99} is $16.8 \mu\text{C}/\text{mg}$, which corresponds to $37,800$ disintegrations/min/ μg . However, difficulties due to the low energy of its β particles ($E_{\text{max}} = 0.29 \text{ MeV}$) arise during measurement of the radioactivity of Tc^{99} . To allow for the errors caused by self-absorption, reflection from the substrate, counting geometry, etc., the sample should be thoroughly prepared for counting. In practice, an ordinary end-window counter with a mica window can determine about 10^{-7} g of technetium (91). Use of special low-background apparatus enables one to raise the sensitivity by another two to three orders of magnitude.

For the short-lived isotopes Tc^{99m} , Tc^{95m} , and Tc^{97m} , which have found practical application, the sensitivity of the radiometric method reaches approximately 10^{-16} g .

B. GRAVIMETRIC METHODS OF DETERMINING TECHNETIUM

Among the gravimetric methods, the most popular is the weighing of the precipitate in the form of tetraphenylarsonium pertechnetate (204, 239). Its precipitation is carried out from neutral solutions with an excess of tetraphenylarsonium chloride $(\text{C}_6\text{H}_5)_4\text{AsCl}$ (174). The use of a special microtechnique has permitted the precipitation and weighing of $1.95 \mu\text{g}$ of technetium with a relative error of $\pm 4\%$ (240). Perrhenates, fluorides, iodides, bromides, oxidants, thiocyanates, mercury, bismuth, lead, silver, tin, and vanadyl ion as well as high nitrate ion concentrations (above 0.5 M) interfere with the determination.

Technetium can also be precipitated and weighed in the form of nitron pertechnetate ($\text{C}_{20}\text{H}_{17}\text{N}_4\text{TcO}_4$) (118). Nitron pertechnetate is precipitated from weak sulfuric acid or acetic acid solution with excess 5% nitron solution in 3% acetic acid at 80°C. ReO_4^- , NO_3^- , ClO_4^- , MeO_4^{2-} , and oxidants interfere with the determination.

In certain cases, a precipitate of technetium heptasulfide is used for determining technetium (116). The precipitation is carried out from 2–4 *N* hydrochloric or sulfuric acid solutions by passing through hydrogen sulfide. To achieve a better coagulation of the precipitate, the solution is heated to the temperature of a boiling water bath. The heptasulfide precipitate is usually contaminated with elemental sulfur, which should be removed before weighing by multiple washings of the precipitate with carbon disulfide. Many elements that form sulfides insoluble in acids interfere with the determination. The lower limit of the concentration of technetium at which it can be precipitated without introducing carriers is 3 mg/liter. This method is seldom used for the gravimetric determination of technetium, but is widely employed in the preparation of samples for radiometric measurement and neutron activation analysis (21).

C. COLORIMETRIC AND SPECTROPHOTOMETRIC METHODS OF DETERMINING TECHNETIUM

As has been indicated, pertechnetate ions strongly absorb ultraviolet light (see Fig. 4). Therefore the simplest spectrophotometric method of determining technetium is measurement of the optical density of TcO_4^- solutions at the absorption maxima (289 and 247 $\text{m}\mu$). The molar extinction coefficients are, respectively, 2340 and 6200. Beer's law is preserved up to a concentration of about 10^{-3} mole/liter (96). This method permits the simultaneous determination of the concentrations of technetium and rhenium, and in the determination of technetium the sensitivity is approximately 10^{-6} g (21).

In its lower oxidation states, technetium forms with various reagents colored complexes that are used for its quantitative determination. Most frequent use is made of the thiocyanate method, in which the red compound of technetium with the thiocyanate ion is subjected to photometric analysis (128) (Fig. 13). The final composition of this compound has not yet been elucidated, but it is assumed to contain pentavalent technetium. In 4 *N* H_2SO_4 , the thiocyanate ion reduces pertechnetate ions to pentavalent technetium, which forms a colored complex with an excess of the reagent. The reaction occurs slowly, and the full color develops only after 3 hours. The absorption maximum is at 510 $\text{m}\mu$, and the molar extinction coefficient is approximately 47,500, which permits

the detection of technetium at a concentration of 10^{-7} g/cm³. According to the data of Crouthamel (128), the accuracy of the determination is $\pm 2\%$.

This technique has subsequently been improved by Howard and Weber (241). Their improvement consists essentially in reducing heptavalent technetium to the pentavalent state with ascorbic acid in the presence of Fe^{3+} ions, which protect the pentavalent technetium from further reduction. The thiocyanate ions interact with pentavalent

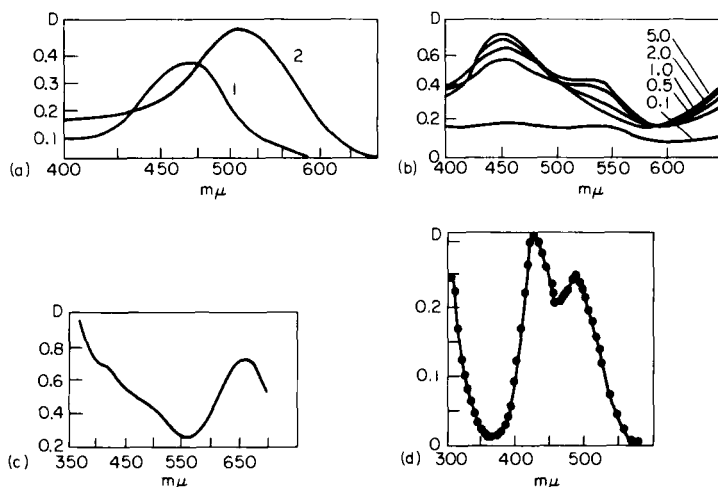


FIG. 13. Absorption spectra of complex thio compounds of technetium: (a) with thiocyanate, (1) Tc^{5+} , (2) Mo^{5+} ; (b) with toluene-3,4-dithiol ($\lambda_{\text{max}} = 450$ mμ, $\epsilon = 15,000$), (c) with thioglycolic acid ($\lambda_{\text{max}} = 655$ mμ, $\epsilon = 1800$), (d) with thiourea.

technetium to form a red complex, which is extracted with butyl acetate and subjected to colorimetric analysis. The thiocyanate complex of molybdenum absorbs light appreciably at a wavelength of 510 mμ, which corresponds to the absorption maximum of the technetium complex (the molar extinction coefficient is 50,000). Therefore the measurements are performed at 585 mμ, at which the molar extinction coefficient of the technetium thiocyanate complex is fairly high (16,500) whereas the absorption of the molybdenum complex is insignificant (100 μg of molybdenum is determined as 0.4 μg of technetium). The solution obeys the Lambert-Beer law in the range 0.1–30 μg/cm³. The relative error is $\pm 2\%$, and duration of the determination is 45 minutes. Chromium, copper, iron, manganese, nickel, ruthenium, vanadium, and tungsten do not interfere with the determination if the content of each does not exceed 1000 μg. Nitric acid present in amounts above 6% lowers the results, since it partially oxidizes technetium to the heptavalent state.

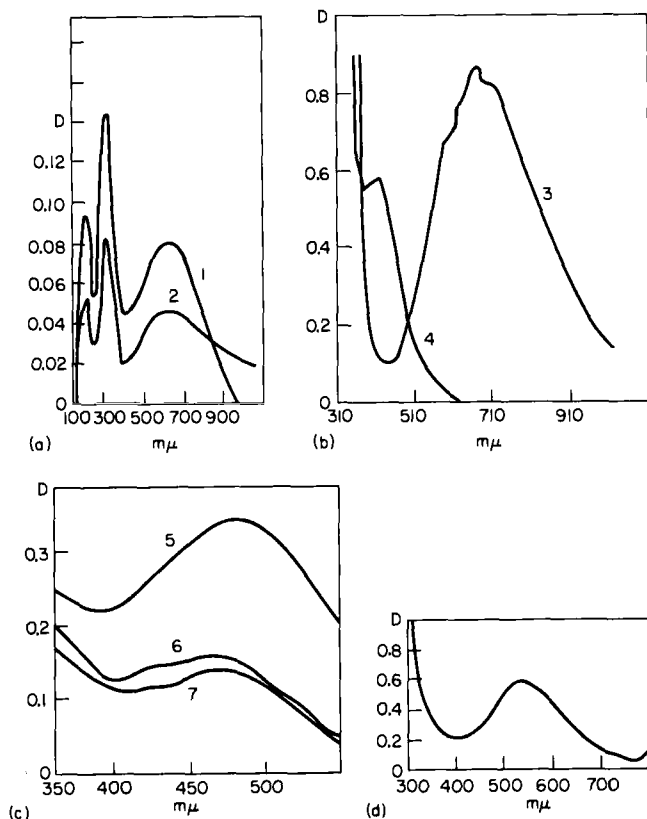


FIG. 14. Absorption spectra of technetium complexes: (a) with α -furyldioxime ($\lambda_{\max} = 520 \text{ m}\mu$, $\epsilon = 13,180$); (b) with potassium ferricyanide ($\lambda_{\max} = 680 \text{ m}\mu$, $\epsilon = 10,800$); (c) with α -picolinic acid ($\lambda_{\max} = 4800 \text{ m}\mu$, $\epsilon = 4400$); (d) with 1,5-diphenylcarbohydrazide: (1) 1 N HCl, (2) 3 N HCl, (3) $\text{Tc}[\text{Fe}(\text{CH})_6]$, (4) $\text{Re}[\text{Fe}(\text{CN})_6]$, (5) after 20 minutes, 4.3 γ Tc, (6) after 20 hours, 2.4 γ Tc, (7) after 20 hours, 5.7 γ Tc.

Thio compounds are also characteristic reagents for Tc. Thus, Tc can be determined by using toluene-3,4-dithiol (224), thioglycolic acid (132), and thiourea (133). The method for colorimetric determination of technetium with *p*-thiocresol in concentrated acetic acid has been thoroughly studied (133). The yellowish brown complex formed is extracted with one of the following extracting agents: chloroform, carbon tetrachloride, ether, benzene, toluene.

In the chloroform solution, the absorption curve has two maxima: at 320–325 and at 410 $\text{m}\mu$; at this wavelength, the molar extinction coefficient of technetium is 7350. The solution obeys the Lambert-Beer law up to a concentration of 5 $\mu\text{g}/\text{cm}^3$ (the region being studied). Ions of

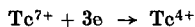
Sn, Cd, Bi, Cu, Ag, Pb, Hg, Mo, W, and Re do not interfere with the determination.

Of interest are the recently proposed methods using α -furyldioxime (130), potassium ferricyanide, sulfosalicylic acid, and α -picolinic acid (129) (Fig. 14).

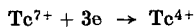
The method of determining Tc in the form of a complex with 1,5-diphenylcarbohydrazide is very sensitive (223). This compound is extracted with CCl_4 . The absorption maximum is at $520 \text{ m}\mu$ and has a molar extinction coefficient of 48,600. The solutions obey the Lambert-Beer law up to $1.5 \text{ }\mu\text{g/ml}$. The accuracy of the method is $\pm 2 \text{ rel. \%}$. Fe^{3+} , CrO_4^{2-} , and Ce^{4+} ions have an adverse effect on the determination.

D. POLAROGRAPHIC METHOD OF DETERMINING TECHNETIUM

The existence of various oxidation states of technetium indicates the possibility of using the polarographic method for its quantitative determination. Thus Magee, Scott, and Wilson (242) showed that use can be made of waves at $E_{1/2} = -0.65 \text{ V}$ in a medium of 2 N KCl or 2 N KOH with potassium tartrate, and also at $E_{1/2} = -0.85 \text{ V}$ in a medium of 2 N KOH . In all cases, technetium is reduced to the tetravalent state:



Colton *et al.* (103) confirmed the basic results of the preceding authors, but hold that in an alkaline medium the wave at $E_{1/2} = -0.85 \text{ V}$ does not correspond to a three-electron reduction, but only to a two-electron reduction of Tc^{7+} to Tc^{5+} . In addition, they showed that technetium can also be determined by using the wave at $E_{1/2} = -0.81 \text{ V}$ in a medium of 0.1 M KCN , which corresponds to the three-electron reduction:



Love and Greendale (243) worked out a rapid polarographic method for determining Tc^{99} in a mixture of fission fragments. Their method consists in a selective reduction of technetium at a dropping mercury electrode at $E_{1/2} = -1.55 \text{ V}$ (relative to the saturated calomel electrode) in a medium of 1 M sodium citrate and 0.1 M NaOH . Under these conditions, technetium is reduced to oxidation states that are soluble in mercury; the amalgam formed is removed from the solution of fission fragments by settling in CCl_4 . The amount of Tc^{99} is determined from the β activity of the amalgam. The decontamination factor for other fission fragments is about 10^6 . A single determination requires only 3 minutes, and the accuracy is $\pm 1 \text{ \%}$.

Kuzina, Zhdanov, and Spitsyn (244) used a polarographic method to determine technetium in a neutral solution with 1 M NaClO_4 as the background electrolyte. In this solution, a well-defined diffusion wave

of TcO_4^- with a half-wave potential $E_{1/2} = -0.8$ V is observed, which corresponds to a three-electron reduction (Fig. 15). The magnitude of the limiting current is directly proportional to the technetium concentration, at least in the interval studied, between 0.5×10^{-5} and 8×10^{-5} mole/liter.

As reported by Boyd (91), when the highly sensitive ORNL polarograph is employed, 5×10^{-8} g of technetium can be determined.

References (90, 244-247) also discuss the possibility of a polarographic determination of technetium in neutral and alkaline media.

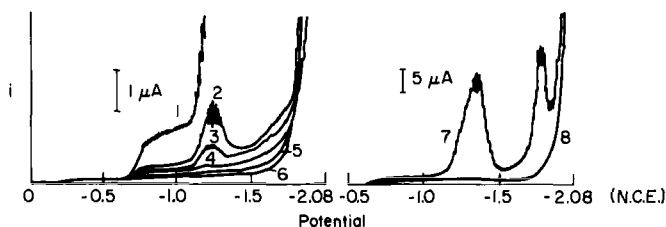


FIG. 15. Polarogram of TcO_4^- in neutral solutions and their composition. Concentration of NH_4TcO_4 : (1) 8×10^{-5} M, (2) 2.2×10^{-5} M, (3) 1.64×10^{-5} M, (4) 1.11×10^{-5} M, (5) 0.52×10^{-5} M, (6) 1 N NaClO_4 (background), (7) 1 N $\text{NaClO}_4 + 8.05 \times 10^{-5}$ NH_4TcO_4 , (8) 1 N NaClO_4 (background).

E. SPECTRAL METHODS OF DETERMINING TECHNETIUM

The method of optical spectroscopy has a comparatively high sensitivity, which permits the determination of microgram quantities of technetium. Its spectrum is very rich in lines; the detection is possible by using an arc and a spark source (81). The following lines of technetium are used for its quantitative determination: 4297.06, 4262.26, 4238.19, and 4031.63 Å. This method can be used to detect about 1×10^{-7} g of technetium.

In 1962 (248) an infrared spectroscopic method of determining technetium was developed that permits the detection of technetium in amounts of the order of 5×10^{-6} g. MoO_4^{2-} , WO_4^{2-} , Br^- , NO_3^- , CNS^- , SO_4^{2-} , PO_4^{3-} , IO_3^- , UO_2^{2+} ions and organic acids do not interfere with the determination. MnO_4^- and ReO_4^- ions absorb infrared light in a neighboring region and should therefore be removed prior to the determination.

F. OTHER METHODS OF DETERMINING TECHNETIUM

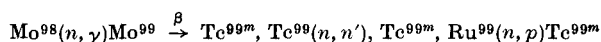
Boyd *et al.* (84) developed a mass-spectrometric method of determining technetium. Chromatographically pure technetium was deposited electrolytically on an iridium wire and roasted at 400° in a stream of

hydrogen. This wire served as the source of technetium ions in the mass-spectrometric analysis. In a technetium sample separated from a molybdenum target irradiated with 22-MeV protons, the isotopes Tc^{95} (0.5%), Tc^{97} (56.0%), Tc^{98} (17.3%), and Tc^{99} (26.7%) were found. Approximately 5×10^{-9} g of technetium can be detected by this method. Similar results were obtained by Kukavadze *et al.* (249).

TABLE XXVII
SENSITIVITY OF QUANTITATIVE METHODS FOR DETERMINING
TECHNETIUM

Method	Sensitivity (g)	Isotopes being determined
Gravimetric	2×10^{-6}	All isotopes
Spectrophotometric	1×10^{-7}	All isotopes
Spectrochemical	1×10^{-7}	All isotopes
Polarographic	5×10^{-8}	All isotopes
Mass-spectrometric	5×10^{-9}	Tc^{99} , Tc^{97} , and Tc^{98}
Neutron activation	3×10^{-10}	Tc^{98}
Radiometric	10^{-7} – 10^{-10} $\sim 10^{-16}$	Tc^{99} Tc^{99m}

Neutron activation is the most sensitive method for detecting technetium (19). For the reaction $\text{Tc}^{98}(n, \gamma)\text{Tc}^{99m}$, the thermal neutron capture cross section is 2.6 ± 1.3 barns (37), which permits the determination of 3×10^{-10} g of Tc^{98} . However, nuclear reactions forming Tc^{99m} can also take place on impurities contaminating the original technetium, namely:



For this reason, prior to the analysis it is necessary to purify the sample to be analyzed, and the degree of purification should be about 4×10^{10} for Mo, about 10^{10} for Re, and about 10^6 for Ru. For the reaction $\text{Tc}^{99}(n, \gamma)\text{Tc}^{100}$, the neutron capture cross section is 20 barns (21), which permits the determination of 2×10^{-11} g of Tc^{99} .

It is apparent from this brief survey of the analytical chemistry of technetium that methods have now been developed, which make it possible to identify and quantitatively determine technetium when its content is very low. However, it should be noted that in most methods rhenium interferes with the determination. It is therefore necessary to develop new ways of isolating and purifying technetium and specifically determining it. In conclusion, the sensitivities of the various methods are given in Table XXVII.

VI. Uses of Technetium

A. INTRODUCTION

Despite its youth and the relatively small quantities available to researchers, technetium is beginning to find practical application. Obviously, it is hardly to be expected that the scale of its production and consumption will reach a magnitude commensurate with the consumption of any other natural element, since the complexity of nuclear fuel processing makes the cost of technetium exceedingly high. However, with the development of technetium chemistry and improvement in methods for its recovery, its cost is showing a constantly decreasing trend. Whereas the first samples of technetium were sold at a price approximately 30,000 times that of gold (250), at the present time it costs only \$90 per gram (251). Nevertheless, its high price and the small quantities obtained make it impossible for a large group of researchers to work with weighable quantities of this element. This hinders detailed investigation of its physical and chemical properties. Nevertheless, even minute, sometimes imponderable, quantities of technetium have made it possible to determine some of its interesting properties that have found practical application.

B. USE OF TECHNETIUM AS A CORROSION INHIBITOR

The high corrosion resistance of technetium to various corrosive media and the comparatively small neutron cross section make technetium coatings fairly promising in nuclear power engineering (252). In his numerous studies, Cartledge (253–259) established that ammonium pertechnetate is a good corrosion inhibitor. Even in negligibly small concentrations (about $5 \times 10^{-5} M$), technetium prevents the corrosion of steel in aerated water at temperatures up to 250°C for very long periods of time. This is highly important for applications in water-cooled or water-moderated reactors.

The exact mechanism of inhibition has not yet been elucidated, but obviously differs from the mechanism proposed to account for the inhibiting properties of the ions of weak acids, CrO_4^{2-} , WO_4^{2-} , and PO_4^{3-} . It was shown that this inhibiting effect is not due to the radioactivity of technetium, since radioactive perhenates are not inhibitors. The quantity of technetium adsorbed on the surface of iron is also much smaller than would be required to form even a monolayer.

Since the inhibiting properties of technetium disappear upon addition of any electrolytes, it may be assumed that the inhibition mechanism is due to the adsorption of the TcO_4^- ion on various defects of the surface

and to the oxidation-reduction properties of the system $\text{TcO}_4^- - \text{TcO}_2$. However, Spitsyn and Kuzina (236) note a complete lack of corrosion of armco iron for 10 days at a technetium concentration of 6 mg KTcO_4 per liter and in solutions containing SO_4^{2-} and Cl^- ions. The inhibiting properties of technetium have already been utilized in preventing corrosion in a boiling nuclear reactor (177).

C. TECHNETIUM AS A SUPERCONDUCTOR

Study of the superconducting properties of technetium has shown that its critical temperature (the highest temperature at which the electrical resistance of a substance becomes zero) is 11.2°K according to the data of Daunt and Cobble (76), and 8.8°K according to the data of Darby and Zegler (78). The value of 11.2°K is the highest of all the elements. However, the studies of Darby and Zegler with massive technetium of high purity did not confirm this value. They attributed the difference in results to the presence of oxygen in the technetium. The superconductivity of technetium, particularly of its alloys with molybdenum, makes them promising materials for superconducting magnets. In this respect, technetium has advantages over an alloy of rhenium and molybdenum. An alloy consisting of 50 at.% molybdenum and 50 at.% technetium at a critical temperature of 12.6°K has an H_0 value (critical field at 0°K) of 75,000 gauss, whereas an analogous alloy of rhenium and molybdenum under the same conditions has an H_0 value of only 27,000 gauss (160). Mattias (161) cites a critical temperature of 15°K for an alloy of molybdenum with 60 at.% technetium, and 16°K for a 75% alloy. Darby and Zegler (78) determined the critical temperature for an alloy of molybdenum containing 60 at.% technetium to be $13.4 \pm 0.3^\circ\text{K}$. There is reason to believe that this value can be raised to 18°K by sufficiently purifying the materials.

D. SOURCES OF β -RADIATION BASED ON Tc^{99}

The technetium isotope Tc^{99} makes it possible to prepare standard sources of β -radiation with an energy of 0.292 MeV (156, 260). The lack of γ -radiation makes such sources safe and convenient to handle, and because of the long half-life of technetium (2.12×10^5 years) their activity remains practically constant with time.

An isotope whose properties may be close to Tc^{99} is Pm^{147} , which is also a pure β -emitter (0.227 MeV), but has a relatively short half-life (2.6 years), which makes sources based upon it unstable with time, and the separation of Pm^{147} from other rare earths presents a fairly complex problem. The specific activity of technetium, despite its long half-life, is

sufficiently high and amounts to 3.78×10^7 counts/min/mg, which is sufficient for the preparation of relatively strong sources.

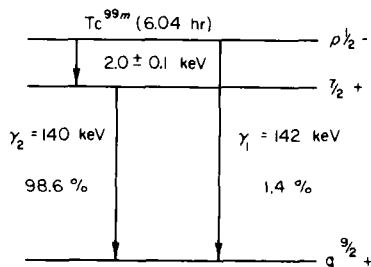
Technetium can be obtained with a very high degree of chemical and radiochemical purity (over 99.99 %). This, combined with the capacity for electrolytic deposition of technetium on metal substrates and its high corrosion resistance, makes sources of β -radiation based on technetium reliable in performance and simple to prepare. Usually, technetium is electrodeposited on a metal substrate or a part thereof and is additionally reduced with hydrogen. The active spot is extremely strong mechanically and stable to the action of the atmosphere, so that there is no need of special protective coatings, which would substantially decrease the activity by absorbing the β -radiation.

In addition, the solubility of pertechnetates in organic solvents, particularly acetone, can be utilized in the preparation of film sources containing technetium. To an acetone solution of pertechnetate of a given concentration is added a film-forming substance, which after drying or polymerization forms a film with a uniform distribution of technetium throughout its volume.

E. USE OF TECHNETIUM IN PHYSICAL INVESTIGATIONS

In the form of the Tc^{99m} isomer, technetium has proven very convenient for studying the effect of the chemical and physical state of the isotope on the radioactive decay constant. Such changes in the half-life had been determined earlier for the electron capture of the Be^7 isotope as a function of its chemical state.

It is known that the half-life of an isotope remains constant and is independent of such external factors as pressure, temperature, and chemical composition of the compound in which the element is contained. However, during radioactive transformations, such as the capture of an orbital electron and isomeric transition, the half-life depends to some extent on the configuration of the electron shells. The latter in turn is related to the chemical state in which the element exists and to certain other factors, for example, pressure. This applies primarily to the outer electron shells, which undergo the greatest changes under the influence of chemical or physical effects. Changes in electronic structure of the atom bring about a change in the coefficient of internal conversion of γ -rays as well as a change in the half-life of the isomer. The decay scheme of the Tc^{99m} isomer (261) (Fig. 16) is characterized, in the overwhelming majority of cases (98.6 %), by the presence of a two-step transition to the ground state. The γ quanta with an energy of 2.0 ± 0.1 keV that are then emitted are converted to a considerable extent.

FIG. 16. Decay scheme of Tc^{99m}

The insignificant energy of the isomeric transition leads to the assumption that the conversion may take place only on weakly bound electrons of the outermost shells, i.e., changes in physical or chemical state should affect the decay constant.

Bainbridge *et al.* (156, 262), using a differential chamber, compared the decay constants of Tc^{99m} in metallic technetium and its compounds—sulfide and potassium pertechnetate. The changes of the decay constant in these compounds had the following values:

$$\lambda_{\text{KTcO}_4} - \lambda_{\text{Tc}_2\text{S}_7} = 27 \pm 1 \cdot 10^{-4} \lambda_{\text{Tc}_2\text{S}_7}, \text{ sec}^{-1}$$

$$\lambda_{\text{Tc}} - \lambda_{\text{Tc}_2\text{S}_7} = 3.1 \pm 1.2 \cdot 10^{-4} \lambda_{\text{Tc}_2\text{S}_7}, \text{ sec}^{-1}$$

Thus, it was established that the half-life of Tc^{99m} (6.04 ± 0.03 hours) in KTcO_4 decreases by 1 second, and in Tc_2S_7 increases by 8.6 seconds as compared to elemental technetium; this is in good agreement with the theoretically predicted values (263).

Similar changes should also take place when the pressure increases. Indeed, at a pressure of 100,000 atm, the decay of Tc^{99m} is accelerated by 0.025% as compared to the metal under standard pressure (264). The value ($\Delta\lambda = 2.3 \pm 0.5 \times 10^{-4} \text{ sec}^{-1}$) agrees well with the calculated one ($\Delta\lambda = 2-4 \times 10^{-4}$), determined by Porter and McMillan (265). Changes in the radioactive decay constants of the Tc^{99m} isomer in the metal form at low temperatures were studied by Byers and Stamp (266). They established that the main factor affecting the decay rate is not the temperature (or the volume contraction that it causes), but the transition of technetium at low temperatures to the superconducting state and the associated redistribution of electrons. This is confirmed by the fact that at 77°K no appreciable changes in half-life were observed, whereas at 4.2°K (the critical temperature of metallic technetium is 8.8°K) these changes were noticeable. They decreased sharply if the superconducting state of technetium was removed by a strong magnetic field:

$$\lambda_{4.2^\circ\text{K supercond}} - \lambda_{293^\circ\text{K}} = 6.4 \pm 0.4 \times 10^{-4} \lambda_{293^\circ\text{K}} \text{ sec}^{-1}$$

$$\lambda_{4.2^\circ\text{K norm}} - \lambda_{293^\circ\text{K}} = 1.3 \pm 0.04 \times 10^{-4} \lambda_{293^\circ\text{K}} \text{ sec}^{-1}$$

Data on the influence of the chemical state and physical factors on the decay of the Tc^{99m} isomer have subsequently been frequently examined and discussed theoretically, as in references (263, 265, 267, 268).

F. USE OF TECHNETIUM IN MEDICINE

Among other isotopes of technetium, the one that has found most extensive application is its short-lived isomer Tc^{99m} . The low cost and ease of isolation of the Tc^{99m} isomer from molybdenum irradiated in a reactor permit its use in solving certain applied problems. In addition to its use in

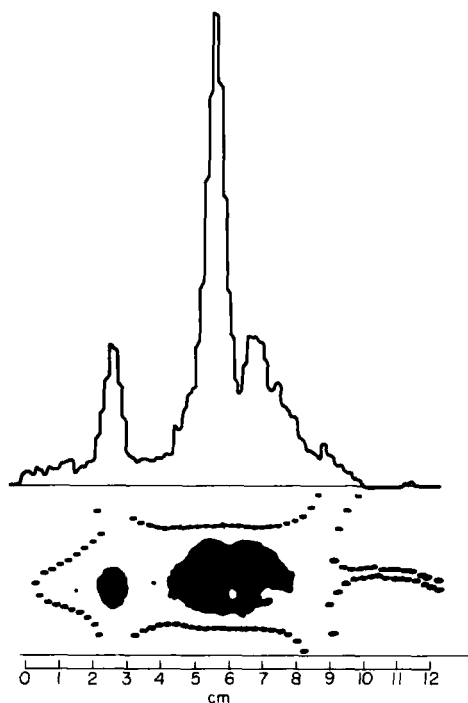


FIG. 17. Distribution of Tc^{99m} in the body of a mouse.

studies of the chemistry of technetium and investigations in nuclear physics, this technetium isomer has found particularly broad application in medicine.

As shown in the studies of Scheer and Maier-Borst (233) and Harper *et al.* (269), Tc^{99m} has advantages over other isotopes for radiation diagnostics. In addition to the already mentioned availability of Tc^{99m} , the energy of its γ -radiation (140 keV) is satisfactorily collimated by diagnostic apparatus, which makes it possible to localize exactly damaged areas in the body (Fig. 17).

Technetium diffuses extremely fast through the intracellular space and is selectively retained by the thyroid gland, salivary glands, and stomach. It does not affect the blood, even when present in relatively large quantities, and can therefore be used for rapid diagnosis of diseases of the thyroid gland in amounts up to 10 mC and more. The short half-life of Tc^{99m} ($T_{1/2} = 6$ hours) markedly lowers the irradiation dose to the organs even when technetium is retained in the body. For instance, in the diagnosis of diseases of the thyroid gland, the irradiation dose from Tc^{99m} is 1000 times smaller than when I^{131} is used. Technetium as the sulfide can be coprecipitated with sulfur, forming stable colloids capable of depositing in the liver. Introduced as the thiocyanate into fat emulsions, Tc^{99m} accumulates in the liver parenchyma and can thus be used for diagnosing primary hepatoma, giving quite clear-cut results.

Pentavalent technetium Tc^{99m} in the form of various organic complexes can also be used for various types of diagnosis. For instance, the glycine complex of Tc^{99m} can be used for diagnosing urological diseases.

G. OTHER METHODS OF UTILIZING Tc^{99} AND OTHER TECHNETIUM ISOTOPES

In addition to the problems enumerated above of a scientific and applied nature that have been or can be solved by using technetium, there are many others in which its various isotopes can be of substantial use. These include, for example, prospecting for technetium in nature for the purpose of elucidating such cosmological problems as the origin and age of the earth, and the activity of the Sun and other stars (17, 270). By analogy with rhenium, technetium can be regarded as a promising catalyst for certain chemical processes (90). It has been proposed that technetium be used for controlling the fuel burn-up in nuclear reactors (271). As in the case of rhenium, high-temperature thermocouples or resistance thermometers could apparently be prepared from technetium. In addition to Tc^{99} , short-lived technetium isotopes are also employed: Tc^{97m} (90 days), Tc^{95m} (60 days), and Tc^{99m} (6 hours). They are used as radioactive labels for the long-lived Tc^{99} in studies where the specific activity of Tc^{99} is insufficient or where its β -radiation is absorbed by the preparations. The Tc^{99m} isomer has been used to study most of the chemical and physical properties of technetium in ultralow concentrations. A brief survey of the methods of using technetium shows that during the 28 years since the date of its discovery, technetium has not only filled a vacant place in the Periodic Table, but has also become important in practical applications.

H. PHYSIOLOGICAL EFFECT OF TECHNETIUM AND SAFETY MEASURES INVOLVED IN ITS HANDLING

The physiological effect of technetium has been studied very little. Certain aspects are touched upon in the studies of Scheer and Maier-Borst (233), Bauman *et al.* (272), and Hamilton (273). According to Bauman's data, when injected, technetium penetrates into almost all the tissues of the body. Somewhat higher amounts of technetium, as compared to other organs, are found in the gastrointestinal tract, in the blood, and particularly in the thyroid gland (13–24% of the activity introduced). Although technetium can be eliminated relatively fast from the remaining organs (273), its concentration in the thyroid gland can lead to damage from the β -radiation.

Technetium has an appreciable specific activity (17 mC/g), but on the surface of dry technetium preparations the irradiation dose amounts to 0.1 r/hr/mg (71). The β -radiation of technetium ($E_{\max} = 0.292$ MeV) is absorbed by thin protective screens, layers of air, and apparatus walls. However, when technetium penetrates into the body, it may constitute a serious radiation hazard. In this connection, the volatility of many of its compounds, particularly technetium heptoxide, pertechnetate acid, chlorides, etc., should be remembered. Therefore all handling operations should be carried out in hermetically sealed apparatus where the gaseous by-products must be absorbed by alkaline solutions of oxidants. This is necessary to avoid not only the danger of radiation injury, but also losses of the costly technetium. No data are yet available on the chemical toxicity of technetium compounds.

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TRANSITION METAL COMPLEXES WITH GROUP IVB ELEMENTS

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I. Introduction¹

Metal-metal bonding in transition metal compounds has become widely recognized in the past decade. Hitherto interest has centered mainly around interactions between two or more transition metal atoms (66, 152, 154), but more recently there has been a renewed interest in bonding between transition and nontransition metals. Compounds with bismuth (181), zinc (120), cadmium (120), mercury (109, 113, 120, 156, 187, 188), Group IIIB metals (201, 204), and Group IVB metals bonded directly to transition metal ions have been prepared, and this variety has been a factor in stimulating further interest in metal-metal bonding in coordination chemistry. It has become apparent that the ability of non-transition metal elements to behave as ligands is widespread throughout the Periodic Table, and this constitutes an important link between the bonding of classical nonmetallic ligands and interactions between transition metal atoms.

Rather than to attempt to cover the whole of the emerging field of metal-metal bonding, this review has been confined to a survey of the complexes of Group IVB elements with transition metals. Nevertheless this restricted approach well illustrates the variety of complexes now known to contain metal-metal bonds, and allows them to be treated within the context of the periodic behavior of this group.

II. The General Chemistry of Group IVB

A survey of transition metal compounds can be made in terms of the general chemistry of the group as a whole. This approach proves a useful way of correlating the large number of compounds known and predicting further developments in the field. Group IVB well illustrates (68, 174) several general trends found in other periodic groups: the change from electronegative to electropositive character going down the group, the presence of the "inert pair" and an increasingly stable lower oxidation state as one goes down the group, and the discontinuity between first- and second-row elements. Carbon must be considered separately, since the

¹ Abbreviations used: X=Cl, Br (sometimes other anions); M=transition metal; E=Group IVB element; R=alkyl or aryl; Me=methyl; Et=ethyl; Pr=propyl; Bu=butyl; Ph=phenyl; Bz=benzyl; Cp= π -bonded cyclopentadienyl; NBD=norbornadiene; COD=cyclo-octa-1,5-diene; and diphosphine=bis(diphenylphosphino)ethane. L=neutral ligand, but, where ML_n is used to denote a coordinated metal atom, L may represent more than one type of ligand. The compound types R_3E-ML_n , $R_2E[ML_n]_2$, $RE[ML_n]_3$, and $E[ML_n]_4$ are referred to as mono-, di-, tri-, and tetrasubstituted complexes.

formation of carbon-metal bonds is largely determined by the unique factors of organic chemistry. For this reason organometallic compounds are not considered here except when useful comparisons can be made.

A. THE TETRAVALENT STATE

All the remaining four elements form the covalent tetravalent oxidation state to be expected from their electronic configuration. Typical EX_4 compounds have four equivalent covalent bonds described in valence bond terms by sp^3 hybridization. There is evidence (58, 69, 90) for some ($p \rightarrow d$) π -bonding in $\text{Si}-\text{X}$ bonds when X has a lone pair of electrons, such as N, O, Cl, or has π -electrons, such as in the phenyl group. This tendency to use d orbitals for π -bonding appears to decrease rapidly down the group. d Orbitals are involved in σ -bonding in EX_6^{2-} compounds (where X is a highly electronegative group), and this is more common for tin and lead, but the formation of octahedral complexes depends on steric factors as well as energetic considerations. The ability of Group IVB elements to increase their coordination number (to both five- and six-coordination) makes EX_4 compounds, and their derivatives, good Lewis bases (69), particularly toward nitrogen and oxygen donors. Covalent bonds may be formed between like and unlike elements of the group, but this tendency to catenation, although greatly extended in recent years, never approaches that of carbon. Compounds of the type $(\text{R}_3\text{E})_3\text{ER}$ and $(\text{R}_3\text{E})_4\text{E}$ are now known, but $\text{E}-\text{E}$ bonds are considerably weaker than carbon-carbon bonds and multiple bonding is unknown.

Transition metal complexes of the type $\text{R}_3\text{E}-\text{ML}_n$ and $\text{R}_2\text{E}[\text{ML}_n]_2$ are known for all Group IVB elements (with the exception of $\text{R}_2\text{Si}[\text{ML}_n]_2$), and may be regarded as normal tetravalent compounds. The tetrahedral environment of E has been confirmed by X-ray structure determinations (see Section VI,A). The extra d electrons on M can be involved in ($d \rightarrow d$) π -bonding between E and M, and there is chemical and physical evidence that this type of back-donation of electrons is occurring.

The $\text{M}-\text{E}$ bond is more stable in the monosubstituted complexes than in the disubstituted, and is generally less reactive than the $\text{M}-\text{C}$ bond in the corresponding alkyls. It is tempting to ascribe this to multiple bond character of the metal-metal bond. An order of stability, in so far as it can be assessed, is $\text{Sn} \sim \text{Ge} > \text{Si} > \text{Pb}$ and may reflect the degree of π -orbital overlap, although other factors must be important. Silicon complexes show more instability toward air and water than do those of germanium and tin, and this is in keeping with the general behavior of silicon. $\text{H}_3\text{Si}-\text{ML}_n$ complexes also react with nitrogen donors to form weak adducts through cleavage of the $\text{Si}-\text{M}$ bond. π -Bonding should

TABLE I
MONOSUBSTITUTED TETRAVALENT COMPLEXES OF GROUP IVB ELEMENTS (MIXED ORGANOHALOGEN
DERIVATIVES NOT INCLUDED)

Group VIA	Group VIIA	Group VIII
$R_3E-Cr(CO)_3Cp$ (R = Me, Ph; E = Ge, Sn, Pb) (183, 200)	$R_3E-Mn(CO)_5$ (R = H, Me, Et, Ph; E = Si, Ge, Sn, Pb) (6, 59, 61, 105, 130, 179, 222)	$R_3E-Fe(CO)_2Cp$ (R = Me, Ph; E = Si, Sn, Pb) (82, 105, 137, 199, 209, 222)
$R_3E-Mo(CO)_3Cp$ (R = Me, Ph; E = Ge, Sn, Pb) (183, 199, 200)	$X_3E-Mn(CO)_5$ (X = Cl, Br; E = Si, Ge, Sn) (5, 105, 130, 178a, 179, 181)	$X_3E-Fe(CO)_2Cp$ (X = Cl, Br, I; E = Ge, Sn) (28a, 30, 91, 105, 165, 180)
$X_3E-Mo(CO)_3Cp$ (X = Cl; E = Sn) (28a, 30)	$R_3E-Mn(CO)_4(Ph_3P)$ (R = H, Ph; E = Si, Ge, Sn) (5, 105, 179, 184)	$(R_3E)_2Fe(CO)_4$ (R = Me, Ph, cyclohexyl; E = Sn, Pb) (71, 110, 112, 115)
$R_3E-W(CO)_3Cp$ (R = Me, Ph; E = Ge, Sn, Pb) (28a, 44, 183, 200)	$R_3E-Re(CO)_5$ (R = Me, Ph; E = Si, Ge, Sn, Pb) (130, 181, 184)	
	$X_3E-Re(CO)_5$ (X = Cl, Br; E = Ge, Sn) (105, 130, 181, 184)	
	$R_3E-Re(CO)_4(Ph_3P)$ (R = Ph; E = Ge, Sn) (184)	

Group VIII	Group VIII	Group IB
$R_3E-Co(CO)_4$ (R = H, Me, Et, Bu, cyclohexyl, Ph; E = Si, Ge, Sn, Pb) (4, 33, 47, 48, 107, 115, 118, 207) $X_3E-Co(CO)_4$ (X = F, Cl, Br, I; E = Si, Ge, Sn) (47, 107, 207) $R_3E-Co(CO)_3(R^1_3P)$ (R = Me, Bu, Cl, Br; E = Sn) (28a, 118)	$(R_3E)_2Pd(R^1_3P)_2$ (R = Ph; E = Ge) (35)	$R_3E-Cu(Ph_3P)_n$ ($n = 1, 3$; R = Ph; E = Ge) (102) $X_3E-Cu(Ph_3P)$ (X = Cl; E = Sn) (86)
$R_3E-Rh(CO)_2(Ph_3P)_2$ (R = Me; E = Sn) (64)	$(R_3E)_2Pd(CN)_2^{2-}$ (R = Ph; E = Ge) (35)	$R_3E-Ag(Ph_3P)_n$ ($n = 1, 3$; R = Ph; E = Ge) (102) $X_3E-Ag(Ph_3P)$ (X = Cl; E = Sn) (86)
$R_3E-Ir(CO)_3(Ph_3P)$ (R = Me, Ph; E = Sn) (64) $R_3E-IrHCl(CO)(Ph_3P)_2$ (R = Et, Ph; E = Si) (46) $X_3E-IrHCl(CO)(Ph_3P)_2$ (X = Cl; E = Si, Sn) (46, 234)	$(R_3E)_2Pt(R^1_3P)_2$ (R = Me, Ph; E = Si, Ge) (51, 75) $(R_3E)-PtY(R^1_3P)_2$ (R = Me, Ph; E = Si, Ge, Sn, Pb) (18, 44, 51, 75, 76, 104, 150, 198) $(X_3E)PtY(R^1_3P)_2$ (X = Cl; E = Sn) (15, 72, 158, 254)	$R_3E-Au(Ph_3P)_n$ ($n = 1, 3$; R = Me, Ph; E = Si, Ge) (18, 102) $X_3E-Au(Ph_3P)$ (X = Cl; E = Sn) (86)

TABLE II
DISUBSTITUTED TETRAVALENT COMPLEXES OF GROUP IVB ELEMENTS (MIXED ORGANOHALOGEN
DERIVATIVES NOT INCLUDED)

Group VIA	Group VIIA	Group VIII
	$R_2E[Mn(CO)_5]_2$ (R = H, Me, Et, Ph; E = Ge, Sn, Pb) (105, 168, 179)	$R_2E[Fe(CO)_2Cp]_2$ (R = H, Me, Et, Ph; E = Ge, Sn) (94, 180) $X_2E[Fe(CO)_2Cp]_2$ (X = Cl, Br, I, CNS, NO ₃ , OH, etc; E = Ge, Sn) (28, 28a, 91, 94, 180, 182, 203, 228) $[R_2E-Fe(CO)_4]_2$ (R = Me, Et, Pr, Bu, Am, Ph; E = Ge, Sn, Pb) (70, 71, 110, 112, 113, 115, 118, 124, 132, 133, 145) $[R_2E-Fe(CO)_3(Ph_3P)]_2$ (R = Bu; E = Sn) (112, 113)
$R_2E[Mo(CO)_3Cp]_2$ (R = Me, Ph; E = Sn) (183, 200) $X_2E[Mo(CO)_3Cp]_2$ (X = Cl; E = Sn) (28a, 183)		
$R_2E[W(CO)_3Cp]_2$ (R = Me, Ph; E = Sn) (183) $X_2E[W(CO)_3Cp]_2$ (X = Cl; E = Sn) (183)	$R_2E[Re(CO)_5]_2$ (R = Ph; E = Ge, Sn) (181, 184)	

Group VIII	Group VIII	Mixed Metal Complexes
$R_2E[Co(CO)_4]_2$ (R = Me, Bu, Ph; E = Ge, Sn, Pb) (28, 115, 118, 207)	$X_2E[Ni(CO)Cp]_2$ (X = Cl; E = Sn) (203)	$R_2E[Mn(CO)_5][Mo(CO)_3Cp]$ (R = Me, Ph, Cl; E = Sn) (183a, 199)
$X_2E[Co(CO)_4]_2$ (X = Cl, Br, I; E = Ge, Sn) (28, 203, 207)		$R_2E[Mn(CO)_5][W(CO)_3Cp]$ (R = Me, Ph, Cl; E = Sn) (183a, 199)
$R_2E[Co(CO)_3(R^1_3P)]_2$ (R = Me, Et, Bu; E = Sn) (28, 118)		$R_2E[Mn(CO)_5][Re(CO)_5]$ (R = Ph, Cl; E = Sn) (183a)
$X_2E[Co(CO)_3(R^1_3P)]_2$ (X = Cl, Br, I; E = Sn) (28, 28a, 203)		$R_2E[Mn(CO)_5][Co(CO)_4]$ (R = Ph, Cl; E = Sn) (183a)
$\{X_2E[Co(CN)_5]_2\}^{6-}$ (X = Cl; E = Sn) (241)		$R_2E[Mo(CO)_3Cp][Fe(CO)_2Cp]$ (R = Cl; E = Sn) (28a)
<hr/> $R_2E[Ir(CO)_3(Ph_3P)]_2$ (R = Me; E = Sn) (64)		

generally affect the Lewis base character of E in its transition metal complexes.

The E—C bond in R_3E-ML_n complexes is generally easily broken, when E is germanium or tin, by the action of halogen or hydrogen halides, although the E—M bond may be preferentially attacked. In the disubstituted complexes, one E—M bond is always broken in these reactions. Pb—M bonds are invariably broken, even in monosubstituted complexes, in spite of the reactivity of Pb—C bonds. It is unlikely that normally unreactive Si—C bonds will be easily broken in R_3Si-ML_n complexes, although their behavior in this respect has not been reported.

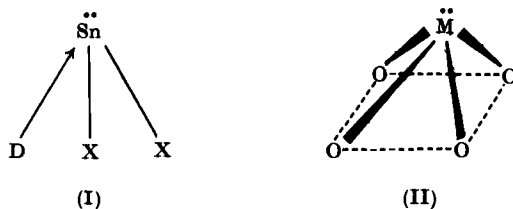
The higher substituted complexes $RE[ML_n]_3$ and $E[ML_n]_4$ are well known only for tin, although some have recently been reported for germanium and lead.

B. THE DIVALENT STATE

The formation of an "inert pair" of valency electrons, leading to the emergence of a lower valency state as the group is descended, is well illustrated in Group IVB. It first appears with germanium and becomes the dominant state with lead. It would be expected from modern ideas on stereochemistry (100) that the nonbonding pair in EX_2 compounds will influence their stereochemistries by occupying a spatially directed orbital. Tin and lead dihalides in the vapor state (160) have an angular structure, which can be described (100) by sp^2 hybridization. These compounds should then act as acceptor species toward certain electron donors by virtue of the vacant p orbital on the E atom to form compounds of the type EX_2 (adduct). Addition compounds are known for divalent halides of germanium (92, 143, 177), tin, and lead (87). The solubility of divalent tin compounds in oxy-organic solvents is attributed to their acceptor properties and the formation of solvent adducts. The divalent elements seem to act primarily as monofunctional acceptors; although a few compounds of the type $EX_2 \cdot 2$ (adduct) are known, it is not certain if both donors are bonded directly to E: in $SnCl_2 \cdot 2H_2O$ only one water molecule is coordinated directly to the tin atom (134).

The crystal structures of tin(II) compounds, of which a large number are now known (87, 219), clearly show the influence of the nonbonding electrons on stereochemistry and the acceptor character of the tin atom. The basic unit of all tin(II) compounds in the solid state is the pyramidal structure (see structure I) with the lone pair at the apex and a donor species that may be halogen, oxygen, sulfur, or selenium. It can be regarded as a distorted tetrahedral configuration with the nonbonding pair of electrons occupying a directed sp^3 hybrid orbital.

Although fewer germanium compounds have had their structures determined, it is known (87, 244) that GeS and GeSe are isomorphous with the tin compounds while CsGeF_3 (177) and CsGeCl_3 (57) show distortions from the true perovskite structure, which probably reflects the stereochemical significance of the "inert pair." GeF_2 is a fluorine-bridged chain polymer (236) with the structural unit a trigonal pyramid, but the chains are cross-linked by weak fluorine bridges so that each germanium atom can be considered to bond to four fluorines and hence d orbitals must be used in the bonding. d Orbitals are probably also involved in the SnO and PbO structures (see structure II) (176), which are based on the



square pyramid with the lone pair at the apex. Lead compounds are generally more ionic in character, but the distortion of the perovskite structure in CsPbX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) (173) can be taken as indicative of a sterically active lone pair. The structure of $\text{NH}_4\text{Pb}_2\text{Br}_5$ (214) seems more likely to be based on the Pb_2Br_5^- ion rather than on the PbBr_2 group and thus to have a pyramidal structure similar to Sn_2F_5^- (163).

Salts of the halide complexes EX_3^- are known for all halogens, and these ions are the predominant species in solutions for the systems that have been studied (87), provided an excess of halide ion is maintained. The Raman spectra of the ions GeCl_3^- (78), SnF_3^- (148), SnCl_3^- (78, 251), and SnBr_3^- (251) have confirmed that the pyramidal configuration of the solid state remains in solution. The existence of higher complexes of the type EX_4^{2-} seems to be limited at best to extremely low concentrations, although PbX_4^{2-} and higher complexes are said to exist (87, 186). $\text{K}_2\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ has been shown (135) to be the double salt $\text{KSnCl}_3 \cdot \text{KCl} \cdot 2\text{H}_2\text{O}$ with a pyramidal SnCl_3^- ion.

Other MEX_3 complexes are known (87) for tin and lead, where X can be acetate, formate, thiocyanate, or hydroxide, and EX_3^- again appears to be the predominant species in most solutions containing an excess of these ions.

The predictions made from theory are therefore confirmed by experimental results, and it seems well established that divalent EX_3^- ions and $\text{EX}_2 \cdot (\text{adduct})$ compounds have pyramidal structures with a directed

lone pair analogous to the trivalent Group VB compounds. Therefore Group IVB compounds may be expected also to exhibit donor properties through the nonbonding pair, and should behave as coordinating ligands with transition metals. Furthermore, vacant d orbitals are likely to be energetically and sterically favorable (at least in the case of Ge and Sn) for overlap with transition metal d orbitals to occur. Thus there could be significant d_{π} - d_{π} back-bonding, as is the case with trialkyl- and triaryl-phosphine, -arsine, and -stibine ligands.

In accord with theoretical predictions, the trichlorostannite ion (72, 254) and tribromostannite ion (1) behave as conventional donor ligands toward transition metals. There is chemical and physical evidence for a considerable π -contribution to the bonding, although the recent isolation of $\text{Ph}_4\text{AsSnCl}_3 \cdot \text{BX}_3$ ($\text{X} = \text{F}, \text{Cl}$) (131) shows that nonbonding electrons are capable of forming a pure σ -coordinate link. The occurrence of $\text{Ph}_4\text{AsGeCl}_3 \cdot \text{BX}_3$ (131) is evidence of similar donor properties for divalent germanium, and, although no complexes between GeX_3^- and transition metals have yet been reported, they are undoubtedly capable of existence.

However, no coordination is observed (247) between divalent lead and transition metal compounds under similar conditions. Lead(II) compounds are more ionic in character than tin(II) compounds, and the nonbonding electrons are thus more likely to approximate to a pure s orbital and to show less donor ability. Moreover, the d orbitals in lead are likely to be less favorable for ($d \rightarrow d$) π -bonding. The situation in Group VB, where bismuth is the only member of the group not to show significant coordinating power, is thus paralleled here.

III. Tetravalent Compounds

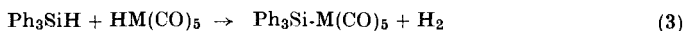
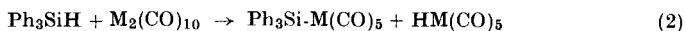
A. SILICON

The first recorded example of a silicon transition metal complex is $\text{Me}_3\text{Si-Fe}(\text{CO})_2\text{Cp}$, prepared by Piper and associates (209) in 1956. The reaction employed,



is now a standard procedure for preparing tetravalent complexes of all Group IVB elements. The complex is sensitive to oxidation and hydrolysis in contrast to the phenyl analog (137). Although $\text{Ph}_3\text{Si-Mn}(\text{CO})_5$ was originally reported (105) to be unstable toward oxygen, it has been shown (130) to have been incorrectly formulated, and authentic $\text{Ph}_3\text{Si-Mn}(\text{CO})_5$ and its rhenium counterpart are actually air-stable solids prepared by the

reaction of triphenylsilane on the metal carbonyl at elevated temperatures. A likely reaction scheme is ($M = Mn, Re$):



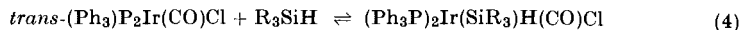
However, silane does not react stoichiometrically (168) with manganese carbonyl hydride.

Silicon complexes of manganese and rhenium generally show greater stability than their alkyl counterparts. Carbon monoxide will not insert (6) into the Si—M bond, but the action of tertiary amines on $H_3Si-Mn(CO)_5$ leads (6) to weak five-coordinate adducts $[H_3Si \cdot 2B]^+[Mn(CO)_5]^-$ ($B =$ amine base). Other silanes are known to react in this way (7, 42, 43), although the structure of the five-coordinate ions has not been elucidated. Hydrogen chloride can replace the hydrogen atoms of the H_3Si- group without affecting the Si—Mn bond (5). Similarly, triphenylphosphine will replace one carbonyl group (5) and leave the metal-metal bond intact.

Cobalt complexes of the type $R_3Si-Co(CO)_4$ (47, 48) are also remarkably stable to air and moisture in comparison with alkyl cobalt carbonyls (34, 121). Nevertheless the Si—Co bond is still comparatively reactive, being readily broken by protic reagents, halogens, and alkali (4, 107, 162). $H_3Si-Co(CO)_4$ forms the adducts $[H_3Si \cdot 2B]^+[Co(CO)_4]^-$ (6) with tertiary amines, which are stronger than those with manganese, but again carbon monoxide insertion is not observed.

The cobalt complexes are prepared (47, 48, 107) by reacting dicobalt octacarbonyl with the parent silane, but the hydride complex (4) was formed from the reaction of iodosilane with the tetracarbonylcobaltate(−1) ion.

A series of complexes with iridium-silicon bonds is formed (46) by the reversible addition of silanes to the square planar d^8 complex, *trans*-(Ph_3P)₂Ir(CO)Cl:

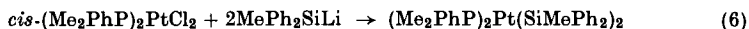


This is yet another example of what is now a very common addition reaction (63, 240). Electronegative substituents attached to silicon are necessary to promote the reaction, since trialkyl- and triarylsilanes do not react.

Although platinum(II) phosphine complexes behave as homogeneous catalysts for the hydrosilation of olefins (47), stable silicon complexes of platinum have not been isolated. However, treatment (104) of *cis*-(Et_3P)₂PtCl₂ with bis(trimethylsilyl)mercury quantitatively replaces one chlorine atom, but not both, with the trimethylsilyl moiety:

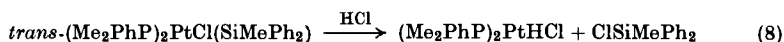


The complex is sensitive to air and moisture, but Chatt and his co-workers (51) found that aromatic silylplatinum derivatives are quite stable. The bis-silyl complex was the only product when *cis*-(PhMe₂P)₂PtCl₂ was treated with methyldiphenylsilyllithium:



However, the reaction between (Et₃P)₂PtCl₂ and Ph₃SiLi gave (18) an unstable hydride, (Et₃P)₂PtH(SiPh₃).

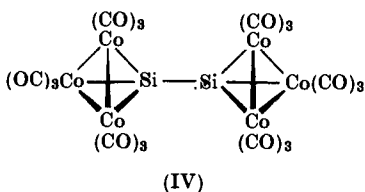
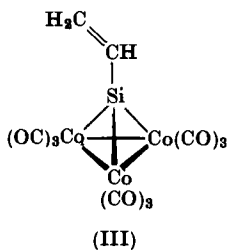
The metal-metal bonds in the bis-silyl complex are destroyed stepwise by two molecules of hydrogen chloride, with the second molecule cleaving in the opposite sense:



Infrared data on monosilyl complexes indicate that the silyl group has a high inductive *trans* effect, and this accounts for the different stepwise attack by hydrogen chloride. It might also explain why with —SiMe₃ the bis-silyl complex is not formed and the monosilyl is unstable, since the —SiMe₃ group would be expected to have an even greater *trans* effect than —SiMePh₂ (51). Trialkylsilyllithium has also been used (18) to prepare a silicon-gold complex:



This is to date the only silicon complex of this type, but the germanium compounds have been studied (102) in some detail and will be discussed (Section III,B,5).



Two unusual silicon cobalt compounds, C₂H₃Si-Co₃(CO)₉ and [SiCo₃(CO)₉]₂, have been prepared (138, 139) by reacting R₄Si (R = vinyl, Ph) with dicobalt octacarbonyl. C₂H₃Si-Co₃(CO)₉ is considered to have a tetrahedral array of metal atoms (structure III), as is found (79, 149, 231) for RC-Co₃(CO)₉. The bonding in these complexes has been discussed (139), and the interaction of silicon *d* orbitals with the cobalt cluster is possible.

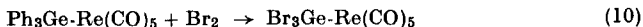
A comparison (138) of the carbonyl stretching frequencies between $\text{CH}_2\cdot\text{CH}\cdot\text{Si}\cdot\text{Co}_3(\text{CO})_9$ and $\text{RC}\cdot\text{Co}_3(\text{CO})_9$ suggests that the silicon d orbitals are involved. $[\text{SiCo}_3(\text{CO})_9]_2$ (structure IV) is analogous to $[\text{C}\cdot\text{Co}_3(\text{CO})_9]_2$ reported by Bor *et al.* (32), with the two metal tetrahedra most probably joined by an E—E bond. The silicon bond can have multiple bond character (139).

B. GERMANIUM

1. Monosubstituted Complexes

Compounds of the type $\text{R}_3\text{Ge}\cdot\text{ML}_n$ are now well known (see Table I) and have been prepared by reacting the appropriate germane with the sodium salt of the transition metal anion ML_n^- (Eq. 1). The phenyl derivatives are all stable compounds, resistant to air and to moisture; the methyl derivatives are less stable.

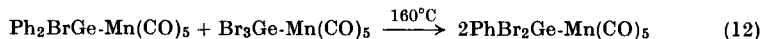
The phenyl groups in $\text{Ph}_3\text{Ge}\cdot\text{Re}(\text{CO})_5$ can be substituted by bromine without breaking the metal-metal bond only by avoiding excess of bromine or long reaction times (184):



Under similar conditions the Ge—Mn bond in the manganese compound is always broken (179),

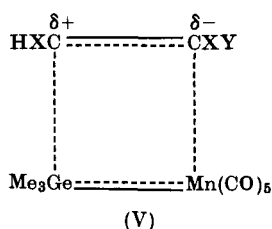


but it can be quantitatively brominated with dibromoethane. $\text{Ph}_2\text{BrGe}\cdot\text{Mn}(\text{CO})_5$ can be prepared from the disubstituted complex (Eq. 16), and the other mixed bromophenyl derivative can be prepared by a redistribution reaction (179):



Redistributions with organogermanium halides do not generally proceed readily without the aid of catalysts (215, 216). Although free bromine breaks the metal-metal bond in $\text{Ph}_3\text{Ge}\cdot\text{Mn}(\text{CO})_5$, chlorine substitutes completely to $\text{Cl}_3\text{Ge}\cdot\text{Mn}(\text{CO})_5$; however, hydrogen chloride does not react at temperatures up to 76°C . $\text{Cl}_3\text{Ge}\cdot\text{Mn}(\text{CO})_5$ has been prepared directly (178a) from $\text{ClMn}(\text{CO})_5$ and trichlorogermane, and more recently (180) $\text{Cl}_3\text{Ge}\cdot\text{Fe}(\text{CO})_2\text{Cp}$ was prepared this way. The halogen derivatives are more stable to air and light than the phenyl compounds. They sublime under high vacuum.

In both the manganese and rhenium complexes, one carbonyl group may be replaced by triphenylphosphine, -arsine, or -stibine (179, 184) without breaking the metal-metal bond. An interesting reaction of $\text{Me}_3\text{Ge-Mn(CO)}_5$ is the insertion (59) of tetrafluoroethylene into the Ge-Mn bond to give $\text{Me}_3\text{Ge}\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{Mn(CO)}_5$. Other reaction products identified indicate that there is also complete cleavage of the metal-metal bond. Reactions with other halogenated olefins gave only products resulting from total bond cleavage, and no stable insertion products were

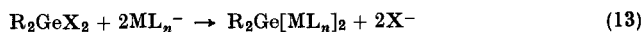


isolated. In these cases olefin insertion may well be the initiating step, although a four-center intermediate (structure V) may be the closest approach to a separate insertion reaction.

The preparation of several germanium complexes of cobalt-tetra-carbonyl has recently been reported (207). The general method of preparation is the reaction of the cobalt carbonyl anion with an appropriate substituted germane, but different stoichiometries can lead to different products. Thus phenyltrichlorogermane can give either $\text{Ph}_2\text{ClGe-Co(CO)}_4$ or $\text{PhClGe[Co(CO)}_4\text{]}_2$, and GeCl_4 (which reacts similarly with dicobalt carbonyl) gives either $\text{Cl}_3\text{Ge-Co(CO)}_4$ or $\text{Cl}_2\text{Ge[Co(CO)}_4\text{]}_2$.

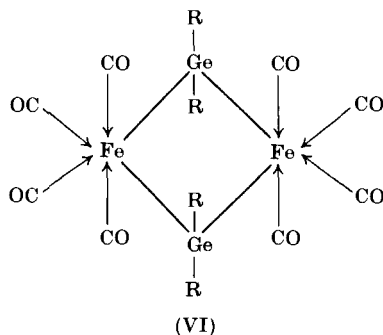
2. Disubstituted Complexes

Disubstituted germanium complexes of the type $\text{R}_2\text{Ge[ML}_n\text{]}_2$ can be prepared by the same route used for the monosubstituted complexes:

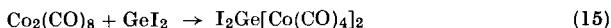
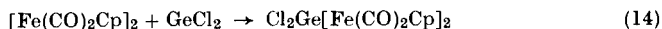


During the preparation of $\text{Ph}_2\text{Ge[Mn(CO)}_5\text{]}_2$ by this method (184), a second compound is formed in about equal amount at 15°C , but in only very low yield at -2°C . The structure of this second compound, formulated as $[\text{Ph}_2\text{GeMn(CO)}_5]_2$, is not known; but its stoichiometry would seem to rule out the dimeric structure (VI) proposed (133) for $[\text{R}_2\text{GeFe(CO)}_4]_2$, as this would suppose seven-coordination for manga-

nese. A possible explanation is the linear structure $(\text{OC})_5\text{Mn}-\text{GeR}_2-\text{GeR}_2-\text{Mn}(\text{CO})_5$, but this remains only a speculation until the compound has been investigated in greater detail.

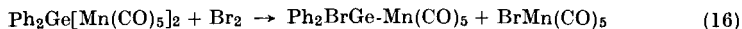


The cleavage of metal-metal bonds by germanium(II) halides (94, 180, 205) is a useful method for preparing disubstituted complexes of germanium, e.g.:

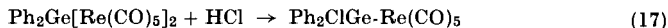


The halogen atoms in $\text{X}_2\text{Ge}[\text{Fe}(\text{CO})_2\text{Cp}]_2$ ($\text{X} = \text{Cl}, \text{I}$) may be replaced (94) by the methyl group, using methyllithium, or by the hydride ion on treatment with sodium borohydride. The behavior of $\text{I}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$ toward these reagents has not been reported, and it is not known whether the monosubstituted complexes show the same reactivity.

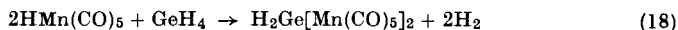
$\text{Ph}_2\text{Ge}[\text{Mn}(\text{CO})_5]_2$ will react with bromine (179), breaking one Ge—Mn bond and forming a monosubstituted complex:



A similar reaction takes place between $\text{Ph}_3\text{Ge}-\text{Re}(\text{CO})_5$ and hydrogen chloride at low temperatures:



$\text{H}_2\text{Ge}[\text{Mn}(\text{CO})_5]_2$ has been prepared (168) by reacting dimanganese decacarbonyl with germane, but is obtained in better yield from manganese carbonyl hydride:



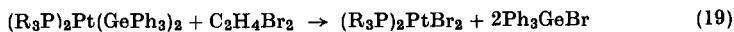
This reaction may involve intermediate reduction to GeH_2 , as mono- or trisubstituted complexes are not formed and there is no reaction with manganese pentacarbonyl halides. Silane reacts differently, although the air-sensitive reaction products have not been characterized.

It was not possible to prepare $\text{RGe}[\text{Re}(\text{CO})_5]_3$ (184), although the tin complex is known; $\text{Ge}[\text{Fe}(\text{CO})_4]_4$ has been reported (71).

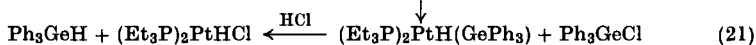
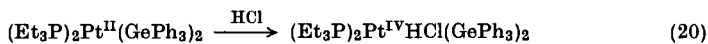
3. Platinum Complexes

Bis(triphenylgermanyl) complexes of platinum $(\text{R}_3\text{P})_2\text{Pt}(\text{GePh}_3)_2$ (Table III) have been prepared (75) by the method used for the corresponding silicon complexes (Eq. 6), although the germanium complexes were the first to be characterized. The triethyl- and tri-*n*-propylphosphine complexes have been isolated and both show *cis-trans* isomerism as expected for square planar platinum(II) complexes. $(\text{Me}_2\text{PhP})_2\text{Pt}(\text{GeMePh}_2)_2$ has also been prepared (51).

These complexes are very stable, being unaffected by air, water, or alkali, but show some very interesting chemistry. In spite of good thermal stability the Pt—Ge bond is readily cleaved on treatment with 1,2-dibromoethane, in contrast to $\text{Ph}_3\text{Ge-Mn}(\text{CO})_5$ (Section III,B,1):



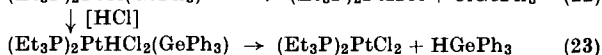
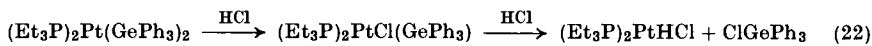
This behavior is similar to the Ge—Ge bond in hexaphenyldigermene, which although of high thermal stability is easily cleaved in like manner (103). Other halogen derivatives (e.g., carbon tetrachloride and iodine) react similarly, but with hydrogen chloride $(\text{R}_3\text{P})_2\text{PtHCl}$ and triphenylgermane are also formed. It is postulated that, in addition to direct cleavage of the Pt—Ge bond, hydrogen chloride may form an octohedral platinum(IV) complex, which will break down as follows:



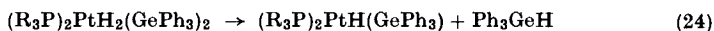
Methyl iodide may react in a similar way since both Ph_3GeI and Ph_3GeMe are isolated; the addition of both methyl iodide and hydrogen chloride to platinum(II) complexes is well known (54, 55).

However, Eqs. (20) and (21) conflict with the results of Chatt and his associates (51), who found that $(\text{Et}_3\text{P})_2\text{Pt}(\text{SiMePh}_2)_2$ reacts stepwise with hydrogen chloride (Eqs. 7 and 8) to give only $(\text{Et}_3\text{P})_2\text{PtHCl}$. This behavior is attributed to the high *trans* effect of the silyl group, and the germanyl group has a comparable *trans* effect (see Section VI,B,2). The

two observations can be rationalized if $(\text{Et}_3\text{P})_2\text{PtCl}_2$ is formed from an octahedral intermediate:

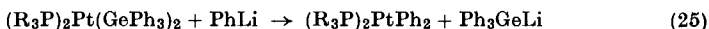


A most interesting reaction (75) is the cleavage of one Pt—Ge bond in the digermanyl complex by molecular hydrogen at room temperature and pressure. The resulting hydrides $(\text{R}_3\text{P})_2\text{PtH}(\text{GePh}_3)$ are also very stable compounds. The reaction is first order with respect to digermanyl complex, and has a low activation energy of 9 kcal/mole. An octahedral species may again be the intermediate, decomposing as follows:



The detection of small amounts of hexaphenyldigermane in the reaction mixture suggests that some decomposition of the intermediate takes place the other way, although $(\text{R}_3\text{P})_2\text{PtH}_2$ was not detected under the experimental conditions.

The reaction of $(\text{Et}_3\text{P})_2\text{PtI}_2$ with triphenylgermanyllithium appears to involve halogen-metal exchange and the formation of novel lithio-platinum intermediates (76, 102). Different products, among them $(\text{Et}_3\text{P})_2\text{PtHI}$, $(\text{Et}_3\text{P})_2\text{PtH}(\text{GePh}_3)$, and a novel ethoxy complex $(\text{Et}_3\text{P})_2\text{Pt}(\text{OEt})(\text{GePh}_3)$, can be isolated according to the initial ratio of the reactants, and lithio derivatives $(\text{Et}_3\text{P})_2\text{PtILi}$ and $(\text{Et}_3\text{P})_2\text{PtLi}(\text{GePh}_3)$ have been postulated as intermediates. However, the reaction with phenyllithium gave no evidence for lithio derivatives:



The reactions between $(\text{R}_3\text{P})_2\text{Pt}(\text{GePh}_3)_2$ and MgI_2 give a similar range of products, and the formation of platinum "Grignards" is proposed. $(\text{Et}_3\text{P})_2\text{PtI}(\text{GePh}_3)$ is also a likely intermediate in these reactions but was not isolated. The chloro complex $(\text{Et}_3\text{P})_2\text{PtCl}(\text{GeMe}_3)$ has since been prepared by reacting bis(trimethylgermanyl)mercury on $(\text{Et}_3\text{P})_2\text{PtCl}$ (see Eq. 5).

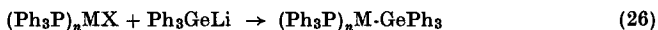
4. Palladium Complexes

Bis(triphenylgermanyl) complexes of palladium are known (35) (Table III). $(\text{Et}_3\text{P})_2\text{Pd}(\text{GePh}_3)_2$ has been isolated pure below -20°C , but decomposes above this temperature. Triethylphosphine has been replaced by the cyanide ion to give the stable ionic complex $[\text{Pd}(\text{CN})_2(\text{GePh}_3)_2]^{2-}$, but ligand replacement is complicated by the thermal instability of the phosphine complex. Complexes with triphenylphosphine, diphosphine, and dipyrityl probably also exist.

As in the case of platinum compounds, the Pd—Ge bonds are cleaved by ethylene dibromide, while molecular hydrogen gives $(\text{Et}_3\text{P})_2\text{PdH}(\text{GePh}_3)$. With hydrogen chloride only triphenylgermane and $(\text{Et}_3\text{P})_2\text{PdCl}_2$ are obtained, so octahedral palladium(IV) may also be formed. Trimethylgermane and $(\text{Et}_3\text{P})_2\text{PdCl}_2$ at 40°C give the hydride $(\text{Et}_3\text{P})_2\text{PdHCl}$, and similar exchange is observed (47) between some corresponding platinum phosphine halides and silanes, although apparently not with germanes (75).

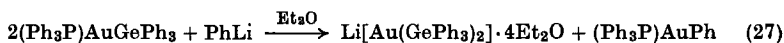
5. Complexes of Copper, Silver, and Gold

Triphenylgermanyllithium has also been used to prepare complexes of Group IB (102):

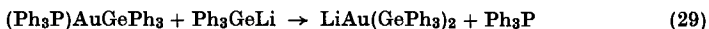
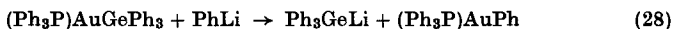


where $\text{M} = \text{Cu}, \text{Ag}, \text{Au}$, $n = 1, 3$. The stability of these compounds varies in the order $\text{Au} > \text{Ag} > \text{Cu}$, but depends very much on the number and nature of the phosphine groups. $(\text{Ph}_3\text{P})\text{AuGePh}_3$ is the only mono-phosphine complex stable to air and moisture, but the tris-phosphine complexes are generally more stable. Like the palladium and platinum complexes, the metal-metal bond is rapidly cleaved with 1,2-dibromoethane.

Gold provides the first example of a germanium transition metal complex without familiar π -bonding ligands being present:



The solvated lithium salt precipitates from solution, and is rapidly hydrolyzed to gold, lithium hydroxide, and hexaphenyldigermane. The tetraethylammonium salt is unsolvated and more stable. The reaction depends on the initial formation of triphenylgermanyllithium, which subsequently replaces the phosphine molecule in the initial complex:



C. TIN

Tin can be considered as the representative metal of group IV since it forms a wider range of compounds with transition metals than does any other member of the group, except carbon. Complexes containing both tetravalent and divalent tin are now well characterized; the latter are discussed separately. Tetravalent tin is the only Group IV element to form stable compounds ranging from $\text{R}_3\text{E-ML}_n$ to $\text{E}[\text{ML}_n]_4$. In addition,

nearly every type of complex formed by the other elements also exists for tin. This unique behavior of tin makes it a useful element for extending the chemistry in this field.

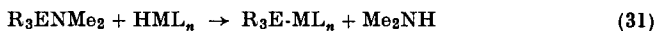
1. Monosubstituted Complexes

Tin forms a very wide range of compounds of the type R_3Sn-ML_n (Table I). The most general method of preparation is that used for silicon and germanium derivatives involving transition metal anions and organotin halides (Eq. 1). Using this approach, Collman and co-workers (64) have prepared new anionic carbonyls of rhodium and iridium as intermediates in the formation of the five-coordinate transition metal species $Me_3Sn-Rh(CO)_2(Ph_3P)_2$ and $R_3Sn-Ir(CO)_3(Ph_3P)$. The reverse reaction,

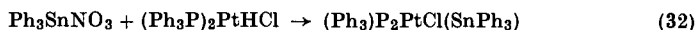


where Ph_3Sn^- is added as triphenylstannyllithium (18) or generated *in situ* by the electrolytic reduction of hexaphenyldistannane (82).

A novel reaction, likely to become a very useful synthetic procedure, is the elimination of an amine in the reaction between a Group IVB amido derivative and a transition metal hydride (44):



$Me_3Sn-W(CO)_2Cp$ and $(Ph_3P)_2PtCl(SnPh_3)$ have been prepared by this method. A related method involving the use of triphenyltin nitrate has also been used (18):



Alternatively, this latter complex can be prepared (150) from the reaction of tetrakis(triphenylphosphine) platinum with triphenyltin chloride:



Halogen derivatives X_3Sn-ML_n may be prepared by substituting the organo groups in R_3Sn-ML_n , or more directly by addition of tin(II) halides to the halogen derivative of the appropriate transition metal group. $Cl_3Sn-Fe(CO)_2Co$ (30) and $Cl_3Sn-M(PPh_3)$ ($M = Cu, Ag, Au$) (86) have been prepared by this method, and also mixed halogen complexes (165), but the reaction of $SnCl_2$ with $ClNi(Ph_3P)Cp$ does not form a nickel-tin bond (161). Pentacarbonylmanganese chloride is unreactive (30), although the diphosphine derivatives $XMn(CO)_3(\text{diphosphine})$ and $XMn(CO)(\text{diphosphine})_2$ react readily (29). Clearly the nature of the ligands around the transition metal atom exert considerable influence on its reactivity. However, steric factors may be the main cause of the inertness of $IMo(CO)_3Cp$ toward stannous chloride (165) if an eight-coordinate intermediate is required for the reaction to proceed. Herein

may lie the clue to why the cyclopentadienyltricarbonylmolybdenum dimer forms $\text{Cl}_3\text{Sn-Mo(CO)}_3\text{Cp}$ with stannous chloride (30), and not the disubstituted compound that is the usual product in this type of reaction (see Eq. 39).

A related reaction involves displacement of mercury from its organo-metallic halide (28a):



Compounds of $-\text{Fe(CO)}_2\text{Cp}$, $-\text{M(CO)}_3\text{Cp}$ ($\text{M} = \text{Mo}, \text{W}$), and $-\text{Co(CO)}_3(\text{Bu}_3\text{P})$ have been prepared by this reaction.

Cyclopentadienyldicarbonyliron dimer reacts with tin(IV) halides (91) to give monosubstituted derivatives:

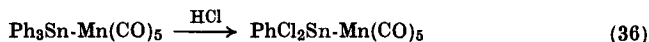


Decacarbonyldimanganese is unreactive (28) toward both tin(II) and tin(IV) chlorides, but the paramagnetic substituted monomers $\text{Mn(CO)}_3(\text{diphosphine})$ and $\text{Mn(CO)(diphosphine)}_2$ react with tin(II) chloride or bromide to give monosubstituted derivatives only.

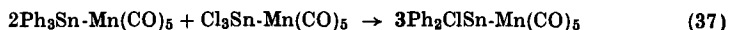
Iron pentacarbonyl reacts (71) with R_2SnCl_2 ($\text{R} = \text{Et}, \text{Pr}, \text{Bu}$) to form unstable $(\text{R}_2\text{ClSn})_2\text{Fe(CO)}_4$, which is readily converted to other tin-iron clusters (discussed in Section III,C,3). Reaction with R_3SnCl leads directly to other products with the above compound isolated in only trace amounts. However, Me_3SnH gives a high yield of $(\text{Me}_3\text{Sn})_2\text{Fe(CO)}_4$ from iron pentacarbonyl, while Me_2SnH_2 gives the dimeric species $[\text{Me}_2\text{SnFe(CO)}_4]_2$.

The tin-metal bonds are resistant to halogen attack and this fact, together with the general stability of the complexes, suggests that there may be considerable double bond character in the metal-metal bond. However, $(\text{Ph}_3\text{P})_2\text{PtCl(SnPh}_3)$ is cleaved by hydrogen chloride (18) to give triphenylstannane and $(\text{Ph}_3\text{P})_2\text{PtCl}_2$, and this behavior is similar to that of the germanium complexes.

In contrast, chlorine or bromine will replace all phenyl groups in $\text{Ph}_3\text{Sn-M(CO)}_5$ ($\text{M} = \text{Mn}, \text{Re}$) (105, 181) without breaking the metal-metal bond. Hydrogen chloride will also substitute all these phenyl groups in the rhenium compound (181) but only two (105) in the manganese one:



$\text{Ph}_2\text{ClSn-Mn(CO)}_5$ has been formed via a redistribution reaction (105) rather than by direct substitution:

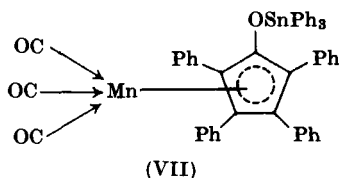


This type of reaction is a general feature of organotin chemistry (125) but occurs here under milder conditions than are usually required. Mixed bromophenyl derivatives of rhenium can be prepared by heating $\text{Ph}_3\text{Sn-Re(CO)}_5$ with the appropriate amount of bromine (184).

Hydrogen chloride will also replace only two phenyl groups (181) in $\text{Ph}_3\text{Sn-M(CO)}_3\text{Cp}$ ($\text{M} = \text{Mo}, \text{W}$). $\text{Ph}_3\text{Sn-Fe(CO)}_2\text{Cp}$ gives the trichloro-derivatives (105) under similar conditions, but the Sn-Fe bond is sufficiently weak to be cleaved by chlorine.

The carbonyl derivatives $\text{R}_3\text{Sn-M(CO)}_n$ ($\text{M} = \text{Mn}, \text{Re}, n = 5$; $\text{M} = \text{Co}, n = 4$) can take part in ligand substitution reactions without affecting the metal-metal bond. Triphenylphosphine replaces one carbonyl group (105, 118, 184) at elevated temperatures or under ultraviolet light. At room temperatures no substitution occurs, and CO exchange is slow (33) in contrast to the lability of the carbonyl groups in $\text{Hg[Co(CO)}_4\text{]}_2$ and $\text{CH}_3\text{CO}\cdot\text{Co(CO)}_4$. The substituted compounds are stable, high-melting solids sensitive to hydrolysis. Ethylene will substitute in like manner (61) in $\text{Me}_3\text{Sn-Mn(CO)}_5$ but, in sharp contrast, tetrafluoroethylene inserts (60, 61) into the Sn-Mn bond to give principally $\text{Me}_3\text{Sn-CF}_2\cdot\text{CF}_2\text{-Mn(CO)}_5$ together with some trimethylfluorostannane and fluorocarbon derivatives of manganese pentacarbonyl. Only the latter products are formed with other halogenated olefins, and no insertion adducts were isolated although they are possible intermediates (see Section III, B, 1).

The use of diphosphine (29) allows two and even four carbonyl groups to be replaced, as in $\text{X}_3\text{Sn-Mn(CO)}_3(\text{diphosphine})$ and $\text{X}_3\text{Sn-Mn(CO)}(\text{diphosphine})_2$. However, substitution with tetraphenylcyclopentadienone does not give a simple substituted complex as was first thought (105), since it breaks the Sn-Mn bond to form (106) the cyclopentadienyl derivative (VII). This may also be regarded as an insertion reaction.



2. Disubstituted Complexes

Preparation of the complexes $\text{R}_2\text{Sn[ML}_n\text{]}_2$ is generally by the method (Eqs. 1, 13) used for the monosubstituted derivatives. The procedure has been used (183a, 199) to prepare the mixed metal compounds $\text{R}_2\text{Sn[Mn(CO)}_5\text{][ML}_n\text{]}$, where ML_n is a different transition metal group such as $-\text{Mo(CO)}_3\text{Cp}$, $-\text{W(CO)}_3\text{Cp}$, $-\text{Re(CO)}_5$, or $-\text{Co(CO)}_4$.

TABLE III
GERMANIUM COMPLEXES OF PLATINUM AND PALLADIUM

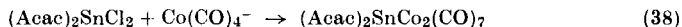
Compound	Color ^a	M.P. (°C)	IR spectra (cm ⁻¹)	Remarks	Ref.		
(PhMe ₂ P) ₂ Pt(GeMePh ₂) ₂	—	—	—	—	(51)		
(Et ₃ P) ₂ Pt(GePh ₃) ₂	p-y	d160	—	—	}		
(Pr ₃ P) ₂ Pt(GePh ₃) ₂	p-y	d120	—	<i>trans-</i>		}	
(Et ₃ P) ₂ PtH(GePh ₃)	w	d150	$\nu(\text{Pt—H})$ 2051	<i>cis-?</i>			}
(Pr ₃ P) ₂ PtH(GePh ₃)	—	—	$\nu(\text{Pt—H})$ 2051	(not pure)			
(Et ₃ P) ₂ Pt(OH)(GePh ₃)	—	d153–156	$\nu(\text{O—H})$ 3630	From ethoxy	(75)		
(Et ₃ P) ₂ Pt(OMe)(GePh ₃)	—	d172–180	Methoxy bands	complex			
(Et ₃ P) ₂ Pt(OEt)(GePh ₃)	c	d160–170	Ethoxy bands				
(Et ₃ P) ₂ Pt(O ⁱ Pr)(GePh ₃)	—	d162–172	<i>i</i> -Propoxy bands				
(Et ₃ P) ₂ PtCl(GeMe ₃)	—	—	—	—	(104)		
(Et ₃ P) ₂ Pd(GePh ₃) ₂	p-y	d97–107	—	Unstable in solution	(35)		
(Et ₃ P) ₂ PdH(GePh ₃)	g	—	$\nu(\text{Pd—H})$ 1890				
K ₂ [(CN) ₂ Pd(GePh ₃) ₂]	w	d112–120	$\nu(\text{C}\equiv\text{N})$ 2084	—			
(Me ₄ N) ₂ [(CN) ₂ Pd(GePh ₃) ₂]	c	—	$\nu(\text{C}\equiv\text{N})$ 2088	—			

^a p-y = pale yellow, w = white, c = colorless, g = gray.

TABLE IV
METAL CLUSTER COMPOUNDS: TRI- AND TETRASUBSTITUTED
COMPLEXES WITH GROUP IVB ELEMENTS

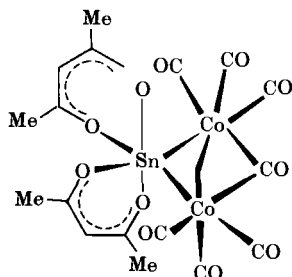
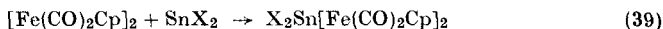
Compound	E	R or X	References
RE[Re(CO) ₅] ₃	Sn	Ph, Br	} (181)
{E[Re(CO) ₅] ₃ } ₂	Sn	—	
XE[Mn(CO) ₅][Fe(CO) ₂ Cp] ₂	Sn	Cl	} (182)
XE[Re(CO) ₅][Fe(CO) ₂ Cp] ₂	Sn	Cl	
RE[Fe(CO) ₂ Cp] ₃	Sn	Ph	
E[Fe(CO) ₂ Cp] ₂ [Mo(CO) ₃ Cp] ₂	Sn	—	(85)
E[Fe(CO) ₂ Cp] ₄	Sn	—	(182)
E[Fe(CO) ₃ NO] ₄	Sn	—	(117)
E[Fe(CO) ₄] ₄	Ge, Sn, Pb	—	(70, 71)
R ₄ E ₃ [Fe(CO) ₄] ₄	Ge, Sn, Pb	Me, Bu	(70, 71, 232)
RE[Co(CO) ₃] ₃	Si	Vinyl	(138)
{E[Co(CO) ₃] ₃ } ₂	Si	—	(139)
RE[Co(CO) ₄] ₃	Sn	Me, Bu, vinyl, Ph	} (202, 205)
XE[Co(CO) ₄] ₃	Sn	Cl, Br, I	

The reaction between bis(acetylacetonate)tin dichloride and the tetracarbonylcobalt anion gives a novel compound (206):



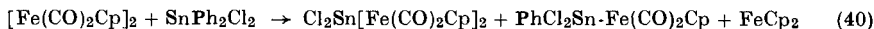
The infrared spectrum shows the complex to have a bridging carbonyl group, and structure (VIII) is postulated with a cobalt-cobalt bond to explain the observed diamagnetism. The complex may well be formed from $(\text{Acac})_2\text{Sn}[\text{Co}(\text{CO})_4]_2$, which could spontaneously lose one carbonyl group because of the smaller Co-Sn-Co angle required by the octahedral configuration of the tin atom.

Halogen derivatives are most conveniently prepared (30, 203) by the insertion of a tin(II) halide into the metal-metal bond of the appropriate dimer, e.g.:



(VIII)

The complexes $\{\text{Cl}_2\text{Sn}[\text{Co}(\text{CN})_5]_2\}^{6-}$ (241) and $\text{Cl}_2\text{Sn}[\text{Ni}(\text{CO})\text{Cp}]_2$ (203), which are prepared this way, are the only compounds known with these particular transition metal groups. Cyclopentadienyldicarbonyliron dimer gives the disubstituted complex with stannous chloride (Eq. 39) and the monosubstituted complex with stannic chloride (Eq. 35). However, both the mono- and disubstituted complexes are obtained (91) when using SnPh_2Cl_2 :

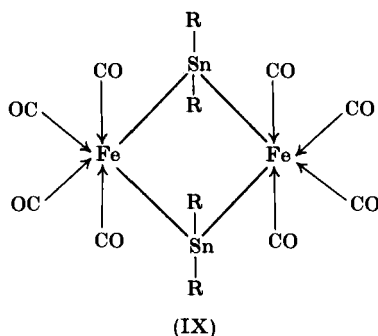


SnX_2 will also insert into transition metal-mercury bonds (28a) to form disubstituted complexes according to the equation:



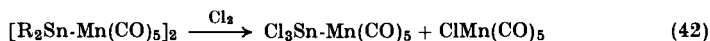
In some cases the monosubstituted derivatives are also formed, while the reaction between $\text{Hg}[\text{Co}(\text{CO})_3(\text{Bu}_3\text{P})]_2$ and SnBr_2 gives $\text{Br}_3\text{Sn}-\text{Co}(\text{CO})_3\text{Bu}_3\text{P}$ as the sole product, although the disubstituted derivative is known.

The interaction of dialkyltin dichlorides with $\text{Fe}(\text{CO})_4^{2-}$ gives $[\text{R}_2\text{Sn}-\text{Fe}(\text{CO})_4]_2$ (132, 133), and on the basis of infrared spectra and dipole moments, structure (IX) is proposed. The reaction with iron pentacarbonyl at elevated temperatures (70, 71) also gives (IX) from the breakdown of intermediate $(\text{R}_2\text{ClSn})_2\text{Fe}(\text{CO})_4$. R_3SnCl reacts similarly with both iron pentacarbonyl and dodecacarbonyltri-iron.

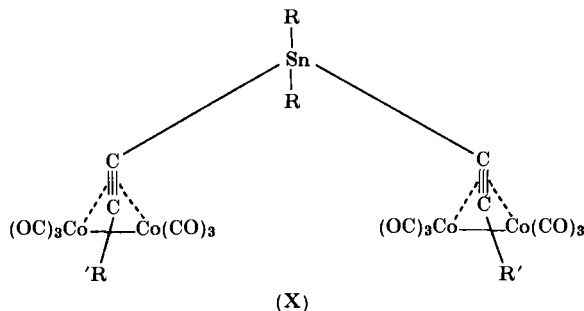


Tetraorganotins gave only traces of (IX) with iron pentacarbonyl (145), unless two of the organo groups were either vinyl or phenyl. Dialkyldialkynyltins give (IX) with dodecacarbonyltri-iron (124) by loss of the alkynyl groups. Dicobalt octacarbonyl under milder conditions reacts without loss of acetylenes to give compound (X) bridging through the carbon triple bonds. Iron compounds of this type may be intermediates in the former reaction.

Complete substitution of the organo groups in $\text{R}_2\text{Sn}[\text{ML}_n]_2$ without breaking the metal-metal bonds is achieved by the use of hydrogen chloride (105, 182, 183) and bromine (181). The use of chlorine (105) breaks one metal-metal bond:

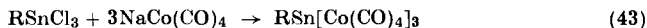


Also, alkylation of the halogen derivatives by Grignard reagents (28, 30) or alkyl lithiums (94) is possible. Mixed organohalogen derivatives have not been prepared, with the exception of $\text{PhXS}[\text{Co}(\text{CO})_3(\text{Bu}_3\text{P})]_2$ (28) and complete substitution of either alkyl or halogen derivatives takes place. Steric hindrance by the tributylphosphine group is considered to be preventing substitution of both halogens in $\text{X}_2\text{Sn}[\text{Co}(\text{CO})_3(\text{Bu}_3\text{P})]_2$ by phenyl groups. Metathetical reactions of $\text{Cl}_2\text{Sn}[\text{Fe}(\text{CO})_2\text{Cp}]_2$ replace (182) the chloride ion with thiocyanate, acetate, hydroxyl, nitrate, ethylmercapto, and sulfide ions.



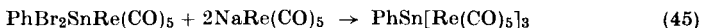
3. Tri- and Tetrasubstituted Derivatives

A logical extension of the general method (Eq. 1) has been used (182, 205) to prepare these highly substituted compounds (see Table IV):

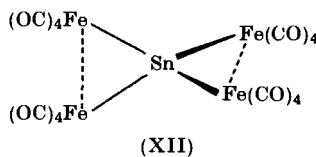
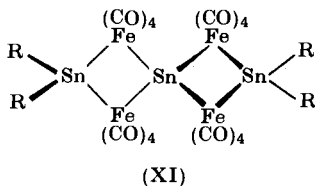


The reaction of $\text{NaFe(CO)}_3\text{NO}$ with $(\text{NH}_4)_2\text{SnCl}_6$ (117) gives both $\text{ClSn[Fe(CO)}_3\text{NO]}_3$ and $\text{Sn[Fe(CO)}_3\text{NO]}_4$. The former is also prepared from stannous chloride and $\text{NaFe(CO)}_3\text{NO}$, and disproportionates in solution to $\text{Sn[Fe(CO)}_3\text{NO]}_4$ and the lower substituted complexes.

Many workers have found it convenient to start with mono- or di-substituted complexes, e.g. (181):



The mixed metal derivatives $\text{Sn[Fe(CO)}_2\text{Cp]}_2[\text{Mo(CO)}_3\text{Cp}]_2$ (85) and $\text{ClSn[Fe(CO)}_2\text{Cp]}_2[\text{M(CO)}_5]$ ($\text{M} = \text{Mn, Re}$) (182) have been prepared from $\text{Cl}_2\text{Sn[Fe(CO)}_2\text{Cp]}_2$. $\text{Sn[Fe(CO)}_2\text{Cp]}_2[\text{M(CO)}_5]_2$ has not been reported. Attempts to prepare $\text{Sn[Re(CO)}_4\text{]}_4$ (181) gave instead $\text{Sn}_2[\text{Re(CO)}_4]_6$ with bonding between the tin atoms.



The reaction of MeSnCl_3 with tetracarbonyliron anion gives (232) the complex $\text{Me}_4\text{Sn}_3[\text{Fe(CO)}_4]_4$ (XI), which contains both di- and tetra-substituted tin (the carbonyl groups complete octahedral coordination of the iron atoms). The same complex (with methyl and other alkyl

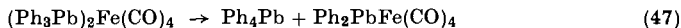
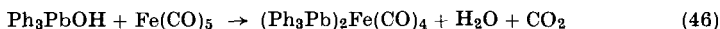
groups) is formed (70, 71) along with $\text{Sn}[\text{Fe}(\text{CO})_4]_4$ (XII) when $\text{R}_x\text{SnCl}_{4-x}$ ($x = 2, 3$) reacts with iron pentacarbonyl or dodecacarbonyltri-iron. The complexes $(\text{R}_2\text{ClSn})_2\text{Fe}(\text{CO})_4$ and $[\text{R}_2\text{SnFe}(\text{CO})_4]_2$, discussed previously, may be intermediates in their formation. $\text{Sn}[\text{Fe}(\text{CO})_4]_4$ is the only product in the reaction between hexabutylditin and iron pentacarbonyl, and is also formed by reacting stannic chloride with the tetracarbonyliron anion. The compound contains iron-iron bonds to achieve a stable rare gas configuration, but such bonds are not required in $\text{Sn}[\text{Fe}(\text{CO})_3\text{NO}]_4$ since the nitrosyl group donates an extra electron.

A novel compound $\text{Sn}[\text{Co}(\text{CO})_4]_2$ (120) is formed from cobalt(II) bromide and metallic tin under high pressures of carbon monoxide. The structure of this compound is unknown as yet, but it probably contains divalent tin since the experimental conditions are reducing. Under similar conditions, lead(IV) is reduced to lead(II) without complexing and germanium failed to react. The series $\text{M}[\text{Co}(\text{CO})_4]_n$ ($n = 1$, $\text{M} = \text{Tl}^{\text{I}}$; $n = 2$, $\text{M} = \text{Zn}$, Cd , Hg ; $n = 3$, $\text{M} = \text{In}^{\text{III}}$, Tl^{III}) is well known (120, 221).

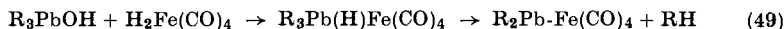
Hieber and his co-workers (119) have also prepared the compound $\text{Sn}_2\text{Fe}_5(\text{CO})_{20}$ of unknown structure. The iron is undoubtedly present as $\text{Fe}(\text{CO})_4$ groups, and its preparation from $\text{Fe}(\text{CO})_5^{2-}$ and $(\text{NH}_4)_2\text{SnCl}_6$ in alkaline solution allows the possibility of hydroxyl groups in the molecule.

D. LEAD

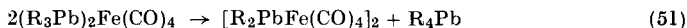
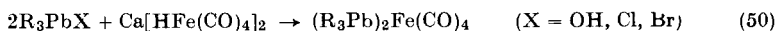
Although lead forms a more limited and less stable range of compounds than tin, some of the first complexes to be isolated were from reactions between R_3PbX compounds and iron pentacarbonyl, studied by Hein and his co-workers (110, 111, 113, 114). The reaction between Ph_3PbOH and iron pentacarbonyl gave (113) tetraphenyllead, benzophenone, and an unknown iron-lead compound. The reaction scheme proposed assumed the existence of two complexes between iron and lead:



$\text{R}_2\text{Pb-Fe}(\text{CO})_4$ with $\text{R} = \text{Et}$ was first characterized (113) in the reaction between $\text{H}_2\text{Fe}(\text{CO})_4$ and triethyllead hydroxide. Although the methyl analog was not isolated by this reaction (111), the formation of methane is consistent with an intermediate hydridocarbonyl species:

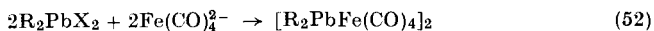


When the calcium hydrogen salt of the tetracarbonyliron anion was used (110, 111), both $R_2Pb-Fe(CO)_4$, now shown to be dimeric, and $(R_3Pb)_2Fe(CO)_4$ were isolated. In this case there was no evidence for a hydridocarbonyl intermediate:



When R is an acyclic alkyl group, $(R_3Pb)_2Fe(CO)_4$ breaks down spontaneously to the dimer and tetraalkyllead. This rearrangement does not occur so readily when R is phenyl or cyclohexyl, although $[Ph_2PbFe(CO)_4]_2$ has since been isolated (112). More recently Stone and his co-workers (71) also isolated the cluster compounds $Me_4Pb_3[Fe(CO)_4]_4$ and $Pb[Fe(CO)_4]_4$ from the reactions of iron pentacarbonyl with methyl-lead halides.

The dimer has also been obtained by direct interaction (132) between dialkyllead dihalides and the iron tetracarbonyl anion:



This type of reaction (see also Eq. 1) has been used to prepare most of the other lead compounds known. The insertion reactions of germanium(II) and tin(II) halides do not proceed with divalent lead (30). The only complex of lead reported that does not have carbonyl groups attached to the transition metal is $(Ph_3P)_2PtCl(PbPh_3)$, prepared from the reaction of $(Ph_3P)_2PtHCl$ with triphenyllead nitrate (18).

The overall instability of lead compounds compared to their tin analogs reflects a weaker metal-metal bond. Thus the $Pb-Mn$ bond in $Ph_3Pb-Mn(CO)_5$ is readily broken by hydrogen chloride and chlorine (105) under conditions where the $Sn-Mn$ bond is not. This behavior may be due to a lower π -contribution in the metal-metal bond due to less favorable overlap, although changes in polarity, hybridization, etc., must also be important.

IV. Complexes of Divalent Tin

A. ANIONIC COMPLEXES

1. Historical

Platinum metal salts have long been known to react with tin(II) chloride in hydrochloric acid to give intensely colored solutions (128, 250),

which have been used for the detection (136, 212, 235, 249) of the platinum metals. Similar color reactions occur with tin(II) bromide and iodide (24, 26, 27, 196). The colored solutions can generally be extracted into organic solvents (9-11, 99) capable of coordinating to tin(II). Detailed spectrophotometric studies of these color reactions have been made with platinum (8, 9, 25, 169, 172), rhodium (12, 170), palladium (11), and iridium (27), and they form the basis of quantitative determinations of the metals.

However, the nature of the chemical species in solution remained uncertain until quite recently. A cationic species $(\text{PtSn}_4\text{Cl}_4)^{4+}$ was reported by Ayres and Meyer (10), but it was later established (151, 189, 223) that the colored species are ionic in hydrochloric acid solutions for most of the platinum metals.

2. General Chemistry

The interesting properties of these compounds of divalent tin are best discussed by considering mainly the behavior of the transition metal, in contrast to most of this review. For this reason the complexes are written as conventional coordination complexes. The chloro complexes were formulated in this way (77, 254): $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$, $[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]^{4-}$, $[\text{RuCl}_2(\text{SnCl}_3)_2]^{2-}$, $[\text{Ir}_2\text{Cl}_6(\text{SnCl}_3)_4]^{4-}$, and $[\text{OsCl}_2(\text{SnCl}_3)_4]^{4-}$ (247).

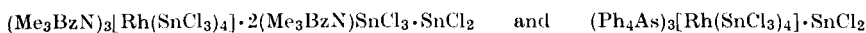
The trichlorostannite ion is considered to be acting as a donor ligand, using its lone pair of electrons. By this approach the platinum metals maintain well-known oxidation states and stereochemistries, and this is supported by magnetic and conductometric data. Furthermore, tin may be displaced, as tin(II) chloride, from these complexes (254) by strong π -bonding ligands such as carbon monoxide and triphenylphosphine. Conversely, stannous chloride can replace more weakly bound ligands such as amines from their complexes, and some replacements with strong ligands (e.g., olefins and carbon monoxide) are reversible.

All the complexes, however, are most conveniently prepared by replacing chloride ion in the chloro complexes by tin(II) chloride in hydrochloric acid (necessary to prevent the hydrolysis of the tin salt) at room temperature (Pt, Rh) or under mild heating (Ir, Ru, Os). Excess of the reagent acts as the reducing agent when the transition metal is converted to a lower oxidation state. The bromo complex of rhodium $[\text{Rh}_2\text{Br}_2(\text{SnBr}_3)_4]^{4-}$ (1) has been prepared similarly, and that of iridium detected (27) in solution.

3. Rhodium and Iridium

Spectrophotometric studies of the rhodium^{III}-tin^{II}-chloride system shows two species whose proportions depend principally on the

$\text{SnCl}_3^-:\text{Cl}^-$ ratio (99). From solutions with a low concentration of the trichlorostannite ion the binuclear anion $[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]^{4-}$ is precipitated (77, 254), and the electronic spectra of its salts and the original solutions (maxima at 419 $\text{m}\mu$ and 310 $\text{m}\mu$) are the same. In the presence of a large excess of stannous chloride (12, 99, 170, 254) the spectrum shifts to higher wavelengths (maxima 470 $\text{m}\mu$ and 330 $\text{m}\mu$), and the intensity of the visible absorption peak increases. The first spectrum can be restored by dilution with hydrochloric acid, since the change is controlled by the $\text{Cl}^-:\text{SnCl}_3^-$ ratio rather than the $\text{Rh}:\text{Sn}$ ratio. The tin-rich solutions can be extracted into isoamyl alcohol, and the ion $[\text{Rh}(\text{SnCl}_3)_4]^{3-}$ has been precipitated (99) with large cations as impure salts:



Similar spectral changes are found when the $\text{Cl}^-:\text{SnCl}_3^-$ ratio is varied in the iridium^{III}-tin^{II}-chloride system at room temperature (98), but only one spectrum results on heating (27, 98, 254). Whereas Young *et al.* (254) isolated the binuclear species $[\text{Ir}_2\text{Cl}_6(\text{SnCl}_3)_4]^{4-}$ from heated solutions, Furlani and co-workers (98) report the isolation of $[\text{IrCl}_2(\text{SnCl}_3)_4]^{3-}$ as double salts with SnCl_2 from both aqueous solution and isoamyl alcohol extracts.

4. Palladium

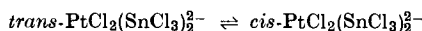
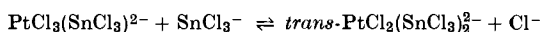
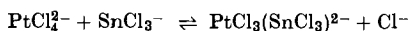
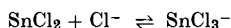
In contrast to the behavior of other platinum metals, the palladium^{II}-tin^{II}-chloride system is unstable (247), and eventually metallic palladium is deposited from ethanolic solutions. A series of color changes is observed (11, 247) as tin(II) chloride is added to palladium(II) chloride in hydrochloric acid. The addition of mercury salts (11, 224) gives a further color change. A complex between palladium and tin(II) chloride has been isolated (140) and formulated as a palladium(I) species $[\text{PdCl}(\text{SnCl}_3)_2]_2^{4-}$ on the basis of analytical data only. Its chemical properties are not reported, but in view of the complexity of the system it could be impure and may well be either a complex of palladium(II) or (0).

5. Platinum

Cis and *trans* isomers of $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$ have been isolated (254) as the tetramethylammonium salts. In solution the interconversion between the two isomers can be followed spectrophotometrically since their electronic spectra are distinct. At $\text{Pt}:\text{Sn}$ ratios of 1:2 a red isomer is first formed in solution, which rapidly changes completely to a yellow form on standing. By selective precipitation both isomers can be obtained

separately from the one solution in quantitative yield. The interconversion of the two forms is dependent on the relative concentration of stannous chloride (the Pt:Sn ratio), temperature, and nature of the cation. Both have distinct X-ray powder patterns.

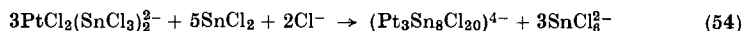
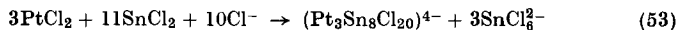
The red and yellow forms are considered to be the *trans* and *cis* isomers, respectively. Several interdependent equilibria probably exist simultaneously in solution:



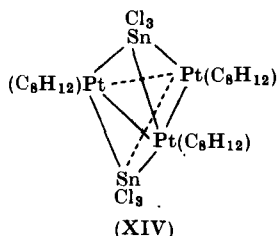
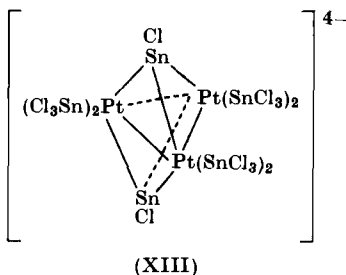
In a two-step substitution of tetrachloroplatinate by SnCl_3^- the strong *trans* effect of the latter (see below) favors the initial formation of the *trans* isomer. The conversion to the *cis* form probably occurs via a dissociative mechanism that is suppressed by the addition of excess stannous chloride.

Further coordination by stannous chloride in solutions where the Pt:Sn ratio is >5 forms (72) an unusual five-coordinate species $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$. But complex equilibria must exist in these solutions since under similar conditions Young *et al.* (254) isolated only impure solids, which are probably mixtures of $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$ and $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$ and possibly other tin species. Complexes of rhodium and iridium could not be isolated from tin-rich solutions (98, 99) without extra tin(II) chloride being precipitated also. However, a preliminary X-ray structure determination (74) of $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$ shows that the five tin atoms are disposed in a trigonal bipyramid about the central platinum atom.

Salts of other five-coordinate species $[\text{HPt}(\text{SnCl}_3)_4]^{3-}$ and $[\text{HPt}(\text{SnCl}_3)_2(\text{PEt}_3)_2]^-$ have also been prepared (74). Another unusual ionic complex, $[\text{Pt}_3\text{Sn}_8\text{Cl}_{20}]^{2-}$, has been prepared (159) by treating platinum(II) chloride or $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$ with stannous chloride according to the equations:



The complex is formulated as a platinum-tin cluster (XIII) with platinum formally zerovalent. The terminal trichlorostannite groups can be replaced by cyclo-octa-1,5-diene to give the neutral complex (XIV). Hydrolysis of solutions of (XIII) gives a brown precipitate of empirical formula $\text{PtSn}_3\text{Cl}_3 \cdot 6\text{H}_2\text{O}$, which probably also has a trimeric structure related to (XIII) with the SnCl_3 groups partially hydrolyzed.



B. CARBONYL AND HYDRIDE COMPLEXES

1. Anionic Carbonyls

Compounds of platinum and rhodium react normally with tin(II) chloride in organic solvents (254) to give solutions considered to contain the neutral species, $\text{PtCl}_2(\text{SnCl}_2 \cdot \text{solvent})_2$ and $\text{Rh}_2\text{Cl}_2(\text{SnCl}_2 \cdot \text{solvent})_4$, from which the salts can be precipitated on the addition of bulky cations. However, the reaction between sodium chloroiridate(IV) and tin(II) chloride in alcohols involves the solvent. Refluxing in ethanol or 2-methoxyethanol gives the neutral, binuclear species initially, which subsequently reacts with carbon monoxide, formed from reduction of the solvent, to give the carbonyl complex $[\text{Ir}(\text{CO})\text{Cl}_3(\text{SnCl}_3)_2]^{2-}$ (234, 252). This reaction parallels the formation of carbonyl species from the reaction between iridium salts and triphenylphosphine in alcohols (239). Analogous solvent interactions are known for ruthenium (238) and, when ruthenium trichloride is refluxed with excess stannous chloride in ethanol or 2-methoxyethanol, carbonyl species are formed (252) but have not been identified.

However, ruthenium trichloride reacts directly with carbon monoxide in hot ethanol (56), and the subsequent addition (147, 227) of tin(II) halides forms the anion $[\text{Ru}(\text{CO})_2\text{X}_2(\text{SnX}_3)_2]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$). The chloro complex is formed (252) when the chlorine bridges in polymeric $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ are cleaved by stannous chloride. The chlorine bridges in $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ are also broken (254), but one carbonyl group per rhodium atom is also displaced to form $[\text{RhCl}(\text{CO})(\text{SnCl}_3)_2]^{2-}$. Alternatively, this complex can be formed by cleaving the chlorine bridges in $(\text{Me}_4\text{N})_4[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]$ with carbon monoxide. Air-sensitive $\text{Ir}(\text{CO})_3\text{Cl}$ (53) also reacts with stannous chloride (252) to give air-stable solutions containing mixed carbonyl species, which have not been identified. In contrast, stannous chloride completely eliminates carbon monoxide from its platinum complexes (254) to give $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$

2. Ruthenium Carbonyls

When ruthenium trichloride is refluxed in ethanol under carbon monoxide, deep red solutions are obtained (56). Their composition is unknown but they contain (227) a mixture of species. By adding donor ligands, different products can be obtained depending on the conditions and the nature of the ligands. Principal products are $\text{Ru}(\text{CO})_2\text{Cl}_2\text{L}_2$ ($\text{L} = \text{amines}, \text{R}_3\text{P}, \text{SnCl}_3^-, \text{R}_2\text{S}$) (146, 147, 227) and $\text{Ru}(\text{CO})\text{Cl}_2(\text{R}_3\text{P})_3$ (227). The addition of excess of stannous chloride to the red solution gives a yellow solution from which $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{SnCl}_3)_2]^{2-}$ can be isolated. Subsequent addition of pyridine (146) gave $\text{Ru}(\text{CO})_2(\text{SnCl}_3)_2(\text{pyridine})_2$, but diethyl sulfide gave $[\text{Ru}(\text{CO})_2(\text{Et}_2\text{S})_3(\text{SnCl}_3)]\text{Cl}$. Addition of triphenylphosphine (227) gives the unusual complex $\text{Ru}_2\text{Cl}_3(\text{SnCl}_3)(\text{CO})-(\text{Ph}_3\text{P})_3(\text{acetone})_2$ as the initial product. The compound contains free and coordinated acetone and is a 1:1 electrolyte, although the SnCl_3 group is not ionized. On warming in benzene it changes to $\text{Ru}_2\text{Cl}_3(\text{SnCl}_3)(\text{CO})-(\text{Ph}_3\text{P})_4$, and on repeated recrystallization gives $\text{Ru}(\text{CO})_2\text{Cl}_2(\text{Ph}_3\text{P})_2$. Addition of triphenylstibine to the yellow solution gives $\text{Ru}(\text{CO})_2\text{Cl}_2(\text{Ph}_3\text{Sb})_2$, which cannot be obtained directly from the original red solution.

3. Iridium Carbonyls and Hydrides

Iridium salts are known to react with alcohols and related solvents in the presence of triphenylphosphine to form hydrides (237), carbonyls (239), and carbonyl hydrides (239). In the presence of stannous chloride alone, iridium salts form the carbonyl complex discussed in Section IV,B,1, and their reactions with both triphenylphosphine and stannous chloride in alcoholic solvents have been investigated (234). In ethanol, $(\text{Ph}_3\text{P})_3\text{IrHCl}(\text{SnCl}_3)$ is formed under milder conditions than were used by Vaska (237) to prepare $(\text{Ph}_3\text{P})_3\text{IrHCl}_2$. Successive recrystallizations result in complete loss of stannous chloride to give the latter complex. In 2-methoxyethanol, a dihydride complex $(\text{Ph}_3\text{P})_3\text{IrH}_2(\text{SnCl}_3)$ is the main product, and can also be formed by treating $(\text{Ph}_3\text{P})_3\text{IrH}_2\text{Cl}$ with stannous chloride.

Another versatile reaction in iridium chemistry is the formation of iridium(III) complexes by addition reactions (63, 239) of the square planar d^8 complex $(\text{Ph}_3\text{P})_2\text{Ir}(\text{CO})\text{Cl}$ (Eq. 4). Treatment with stannous chloride in acetone (234) involves the unusual addition of HSnCl_3 to form the solvated complex $(\text{Ph}_3\text{P})_2\text{Ir}(\text{CO})\text{HCl}(\text{SnCl}_3)\text{acetone}$. This compound may also be obtained directly from $(\text{Ph}_3\text{P})_2\text{Ir}(\text{CO})\text{HCl}_2$. The solvent molecule is not coordinated and is lost on recrystallization, but repeated

recrystallization leads to a breakdown of the complex to both $(\text{Ph}_3\text{P})_2\text{Ir}(\text{CO})\text{HCl}_2$ and $(\text{Ph}_3\text{P})_2\text{Ir}(\text{CO})\text{Cl}$.

Ethyl methyl ketone and ethyl acetate also promote the addition of HSnCl_3 , but alcohols, aldehydes, and aliphatic acids do not. If D_2O is added to the active solvents the deuterated complexes are formed. Thus the origin of the hydride ion is from trace amounts of water, and the selectivity suggests that keto-enol equilibria may be responsible for this novel hydrogen transfer reaction.

Stannous chloride also reacts with $(\text{Ph}_3\text{P})_2\text{Ir}(\text{CO})\text{H}_2\text{Cl}$ to give $(\text{Ph}_3\text{P})_2\text{Ir}(\text{CO})\text{H}_2(\text{SnCl}_3)$, but $(\text{Ph}_3\text{P})_2\text{Ir}(\text{CO})\text{Cl}_3$ remained inert in accordance with other observations (52).

4. Rhodium Hydrides

A reversible reaction occurs between *trans*- $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl}$ and stannous chloride (247) but a hydride species was not formed, and it is considered that the orange product is most probably $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{-(SnCl}_3)$ although analytical data were unsatisfactory. However, stannous chloride can catalyze the formation of rhodium hydrides. The reaction between rhodium trichloride and stannous chloride in acidified ethanol in the presence of phenyldimethylarsine gave $(\text{PhMe}_2\text{As})_3\text{RhHCl}_2$ (252). The complex is a different isomer from the product of the hypophosphorous acid reduction of $(\text{PhMe}_2\text{As})_3\text{RhCl}_3$ (155).

5. Platinum Hydrides

$(\text{Me}_4\text{N})_3[\text{Pt}(\text{SnCl}_3)_5]$ absorbs hydrogen at 30°C and 50 atm (74) to give $(\text{Me}_4\text{N})_3[\text{PtH}(\text{SnCl}_3)_4]$, and the reaction may be followed spectroscopically at lower pressures. A solution of $(\text{Et}_3\text{P})_2\text{PtCl}_2$ containing two molecules of stannous chloride rapidly absorbs hydrogen at 1 atm, and $[(\text{Et}_3\text{P})_2\text{PtH}(\text{SnCl}_3)_2]^-$ can be isolated as the tetraethylammonium salt. This complex is also formed by the reaction of $[(\text{Et}_3\text{P})_2\text{PtH}(\text{SnCl}_3)]$ (158) with $(\text{Et}_4\text{N})\text{SnCl}_3$. Two distinct isomers of $(\text{Ph}_3\text{P})_2\text{PtH}(\text{SnCl}_3)$ (15, 18) have been prepared from *trans*- $(\text{Ph}_3\text{P})_2\text{PtHCl}$ and stannous chloride. A trace of SnCl_2 will catalyze *cis-trans* isomerization in the hydrido complexes.

C. COMPLEXES WITH GROUP V LIGANDS

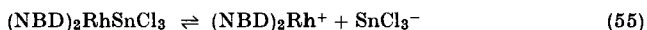
Addition of triphenylphosphine to ethanolic $\text{PtCl}_2(\text{SnCl}_2 \cdot \text{solv.})_2$ precipitates $(\text{Ph}_3\text{P})_2\text{PtCl}(\text{SnCl}_3)$ (254). The complex disproportionates

readily in acetone to form $(\text{Ph}_3\text{P})_2\text{PtCl}_2$, which will react (18, 72, 254) with excess stannous chloride to give the tin complex again. Two isomers of the complex have been isolated (18), and $(\text{Ph}_3\text{P})_2\text{Pt}(\text{SnCl}_3)_2$ has been reported (72) when a large excess of stannous chloride is used. $(\text{Ph}_3\text{As})_2\text{PtCl}(\text{SnCl}_3)$ is less easily dissociated (254) and requires excess of chloride ion to completely displace SnCl_3^- . Stannous chloride also adds readily to other phosphine complexes to give $(\text{R}_3\text{P})\text{PtX}(\text{SnCl}_3)$, where X = fluorophenyl, phenyl (158, 198), hydroxide (15), and hydride (15, 18). $(\text{Ph}_3\text{P})_2\text{PtHCl}$ also reacts (18) with stannic chloride to give the platinum(IV) complex $(\text{Ph}_3\text{P})_2\text{PtCl}_2(\text{SnCl}_3)_2$, which readily reverts to the divalent species on recrystallization.

Treatment of $\text{Rh}_2\text{Cl}_2(\text{SnCl}_2 \cdot \text{solv.})_4$ with triphenylphosphine gives $(\text{Ph}_3\text{P})_3\text{RhSnCl}_3$ (254) on refluxing. A phosphine group and SnCl_2 both readily dissociate from the complex in solution. The lability of the phosphine molecule must be related to the behavior of $(\text{Ph}_3\text{P})_3\text{RhCl}$ (20, 193), since the tin(II) complex can be prepared directly from the chloride (247). $(\text{PhMe}_2\text{As})_3\text{RhCl}_2(\text{SnCl}_3)$ is formed (252) when rhodium trichloride and the arsine are refluxed in ethanol with excess of stannous chloride. The compound is unusual in that rhodium has not been reduced to the +1 state, but $(\text{PhMe}_2\text{As})_3\text{RhCl}$ may be an intermediate since, when hydrochloric acid is present, $(\text{PhMe}_2\text{As})_3\text{RhHCl}_2$ is formed. This system was first investigated by Dwyer and Nyholm (88), who described several compounds containing both tin and rhodium; it now seems likely that these compounds contained the trichlorostannato ligand.

D. OLEFIN COMPLEXES

The addition of diolefins to ethanolic $\text{Rh}_2\text{Cl}_2(\text{SnCl}_2 \cdot \text{solv.})_4$ generally gives (254) the well-known dimeric species $(\text{diolefin})_2\text{Rh}_2\text{Cl}_2$ by direct displacement of the tin groups. But when norbornadiene (NBD) (2.2.1-bicyclohepta-1,5-diene) is used, a new tin complex $(\text{NBD})_2\text{RhSnCl}_3$ is formed (254). The complex is monomeric and nonconducting in nitromethane, but shows appreciable conductance in dimethylformamide (252). From hot aqueous solutions a tetraphenylborate salt can be precipitated (254), leaving tin(II) chloride in solution:



One diolefin molecule can be replaced by another bidentate or two monodentate ligands (see Table V). The complex also adds chlorine (247) to form an insoluble rhodium(III) complex, $(\text{NBD})_2\text{RhCl}_2(\text{SnCl}_3)$. The compound is probably six-coordinate, since the infrared spectrum shows the characteristic absorption of an uncoordinated double bond; in solu-

tion it readily reverts back to its rhodium(I) precursor. The dipyridyl derivative also adds chlorine (247) to form (NBD)(dipyridyl)RhCl₂-(SnCl₃) but, since no free double bond was detected in this compound, the dipyridyl molecule may be acting as a monodentate ligand.

TABLE V

OLEFIN COMPLEXES OF RHODIUM AND IRIIDIUM WITH SnCl₃

Compound	Color	M.P. (°C)	Δm mhos (10 ⁻³ M)		Reference
			MeNO ₂	DMF*	
(NBD) ₂ RhSnCl ₃	Yellow	d170-177	3.3	75	(254)
(NBD) ₂ RhBPh ₄	White	—	—	25	
(NBD)(Ph ₃ P) ₂ RhSnCl ₃	Orange	134-135	8.7	9.1	
(NBD)(Ph ₃ As) ₂ RhSnCl ₃	Orange	d177-179	5.1	7.7	
(NBD)(Ph ₃ Sb) ₂ RhSnCl ₃	Orange	d200	5.0	—	
(NBD)(diphosphine)RhSnCl ₃	Yellow	—	—	—	(247)
(NBD)(dipyridyl)RhSnCl ₃	Purple	135-136	—	—	
(NBD) ₂ RhCl ₂ (SnCl ₃)	Orange-pink	—	(dissociates)	—	
(NBD)(dipyridyl)RhCl ₂ (SnCl ₃)	Orange-pink	—	—	—	
(NBD) ₂ IrSnCl ₃	Pale yellow	d230-240	(insol.)	65	(254)
(COD) ₂ IrSnCl ₃	Yellow	d178-180	9.7	68	(213, 254)
(COD) ₂ IrBPh ₄	White	d225-230	—	—	(254)
(COD)(Ph ₃ P)IrSnCl ₃	Yellow	d127-130	21	30	
(COD)(Ph ₃ As) ₂ IrSnCl ₃	Yellow	171-174	11	16	
(QAS)IrSnCl ₃	Orange	330	—	—	(213)
[(QAS)IrCl(SnCl ₃)]Cl	Pale yellow	330	—	—	

* DMF = dimethylformamide.

Iridium also forms diolefin complexes of the type (diolefin)₂IrSnCl₃ (213, 254) with norbornadiene and cyclo-octa-1,5-diene. Cyclo-octa-1,3-diene is isomerized on reaction to form the 1,5 complex, a well-known rearrangement in transition metal chemistry (97, 185, 217), but the less common isomerizations of 4-vinylcyclohex-1-ene to cyclo-octa-1,5-diene (COD) and cycloheptatriene to norbornadiene are also observed (254).

(NBD)₂IrSnCl₃ is rather inert; it does not ionize appreciably, does not undergo substitution, and has high thermal stability. However, (COD)₂IrSnCl₃ ionizes in aqueous dimethylformamide solutions and both diolefin molecules are displaced (213) by the quadridentate arsine, tris(diphenylarsinophenyl)arsine (QAS) to give (QAS)IrSnCl₃. The latter can be oxidized by chlorine to give [(QAS)IrCl(SnCl₃)]Cl, although addition of chlorine to (R₃P)₂(COD)IrSnCl₃ was not observed (247). A crystal

structure determination (213) of $(\text{COD})_2\text{IrSnCl}_3$ shows it to have a distorted trigonal bipyramidal configuration with the SnCl_3^- group occupying an equatorial position.

V. Catalytic Behavior of Group IVB Complexes

There has been renewed interest in recent years in the role of transition metal complexes in the catalytic reactions of unsaturated organic molecules. Group IVB complexes have been found to have useful catalytic properties toward some reactions of olefins.

A. HYDROGENATION OF OLEFINS

Methanolic solutions of tin(II) chloride and chloroplatinic acid will quantitatively reduce (72) ethylene and acetylene with hydrogen at ambient temperature and pressure. It is one of the few catalysts that will reduce simple olefins and acetylenes under these conditions without the presence of activating groups. The reaction is first order with respect to platinum and is a maximum at Sn:Pt ratios $>5:1$. A hydride species $[\text{PtH}(\text{SnCl}_3)_4]^{3-}$ has been detected (74) under the conditions of catalysis, while the action of ethylene alone forms Zeiss's salt $\text{K}[\text{PtCl}_3 \cdot \text{C}_2\text{H}_4] \cdot \text{H}_2\text{O}$ (72) and rapid exchange between free and coordinated ethylene is observed in solution. Thus the ability of the platinum-tin(II) chloride species in solution, probably $\text{Pt}(\text{SnCl}_2 \cdot \text{solv.})_5$, to cleave the hydrogen molecule, and to coordinate both a hydrogen atom and the organic molecule, allows reaction between the two to take place at the metal probably via an alkyl intermediate. These factors, which are relevant to current ideas on catalytic hydrogenation, have been discussed at length elsewhere (193). The failure of this system to hydrogenate higher olefins appears to be due to their inability to complex with platinum as a result of steric and electronic factors.

The same system has also been used successfully (15, 17, 96) to hydrogenate polyunsaturated fatty esters, such as occur in soybean oil, at moderate temperatures and pressures (90°C, 500 psi). The products are predominantly mono-olefinic esters with only small amounts of the saturated esters being formed. Complexes with Group V donors, $(\text{R}_3\text{M})_2\text{PtCl}_2$ ($\text{M} = \text{P, As, Sb}$), which are soluble in organic solvents, give only limited hydrogenation. This is increased by the addition of Group IV halides (17). For $(\text{Ph}_3\text{P})_2\text{PtCl}_2$, catalytic activity decreases in the order $\text{SnCl}_4 > \text{SnCl}_2 > \text{GeCl}_4 > \text{GeCl}_2 > \text{PbCl}_2 > \text{SiCl}_4 > \text{SiHCl}_3$. Reactions between tin chlorides and $(\text{Ph}_3\text{P})_2\text{PtCl}_2$ are known (18, 72, 254) to give

trichlorostannato complexes, so it is likely that a direct reaction between the other Group IV halides and platinum also takes place. Both $(\text{Ph}_3\text{P})_2\text{Pt}(\text{GePh}_3)_2$ and $(\text{Ph}_3\text{P})_2\text{PtCl}(\text{SnCl}_3)$ can activate hydrogen (74, 102) under catalytic conditions to give hydride complexes.

The catalytic activity of $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ is also enhanced (126) by the addition of stannous chloride and to a lesser extent by germanous chloride, and it is more effective than the platinum complex. The cyanide complex $(\text{Ph}_3\text{P})_2\text{Pd}(\text{CN})_2$ is a good catalyst on its own and does not react with stannous chloride, but the platinum compound is inactive. By contrast, the catalytic action of bis(triphenylphosphine)nickel halides is inhibited (127) by the addition of stannous chloride.

With these catalysts, hydrogenation essentially stops at the mono-enes and considerable isomerization of the double bonds is also observed. It is considered (17, 96) that the double bond migration precedes hydrogenation and continues until a conjugated system is formed. The conjugated olefin can coordinate strongly enough for hydrogenation, but the ensuing mono-ene does not remain at the platinum atom for further reduction. This is in keeping with the failure of $\text{Pt}(\text{SnCl}_2 \cdot \text{solv.})_5$ to reduce olefins higher than ethylene (72), so that isomerization (31, 73) becomes the dominant reaction.

The formation of platinum hydrides under the conditions of catalysis is observed (15, 17) but, since hydrogenation can occur in methanol in the absence of hydrogen (17), hydride abstraction from the solvent must occur. Hydride ion transfer from alcohols to a transition metal ion is now a common synthetic procedure (101), and the dehydrogenation of isopropanol to acetone is catalyzed (49) by $\text{Rh}_2\text{Cl}_2(\text{SnCl}_2 \cdot \text{solv.})_4$.

The coordinating power of the solvent also affects the rate of hydrogenation, and the nature of the ligands is important too. Thus the catalytic activity depends on the π -bonding abilities of the Group VB ligands (17) and the nature of the halide ion (127), but the efficiency of such catalysts probably depends not only on the lability and stability of the intermediate hydride complexes, as determined by electronic factors, but also on the ability of the metal to increase its coordination number (17, 193).

$(\text{Ph}_3\text{P})_2\text{PtH}(\text{SnCl}_3)$ has been used (129) to reduce the chelating non-conjugated diolefin norbornadiene to norbornane. $(\text{Ph}_3\text{P})_3\text{IrH}_2(\text{SnCl}_3)$ forms a complex with norbornadiene and hence does not reduce it, but sodium hexachloroiridate(IV) with stannous chloride will catalyze this reaction. The rate is a maximum at $\text{Sn} : \text{Ir} = 3.5$, which suggests that $\text{Ir}_2\text{Cl}_6(\text{SnCl}_2 \cdot \text{solv.})_4$ is the active species. $\text{Rh}_2\text{Cl}_2(\text{SnCl}_2 \cdot \text{solv.})_4$ has been used (194) to hydrogenate hex-1-ene to hexane, whereas under similar conditions but-1-ene was only isomerized (126).

B. HYDROSILATION OF OLEFINS

The addition of silicon halides to carbon double bonds, as catalyzed by chloroplatinic acid, has been studied in detail by Speier and his co-workers (220, 226). It has recently been shown (46, 220), contrary to earlier assumptions (19), that the catalysis is homogeneous. Olefin complexes of platinum(II) and rhodium(I) (46) and dicobalt octacarbonyl (48, 108) are also good hydrosilation catalysts, although extensive isomerization occurs in all cases.

The major requirements for good hydrosilation catalysts (46) are similar to those for hydrogenation (193), namely: (i) the ability to activate the silane (Si—H bond breaking), (ii) the ability to activate the olefin, and (iii) the resistance to destructive reduction. The failure of palladium compounds as catalysts is due to factor (iii), while platinum(II)- and iridium(I)-phosphine complexes are probably ineffective as the result of (ii). However, the formation of stable silicon complexes with the latter may be the real problem, since it has been shown (48) that the catalytic power of dicobalt octacarbonyl is decreased by the formation of silicon complexes. This will inhibit olefin coordination by the effective blocking of a coordination site.

C. HYDROGERMANATION OF OLEFINS

Recently evidence has been obtained (93) that the addition of alkylgermanes to olefins is also catalyzed homogeneously by chloroplatinic acid. The 1,4 addition of trimethylgermane to cyclopentadiene and butadiene is an example of "coordination control" by the catalyst. Similarly, 1,4- and 1,5-cyclo-octadiene are converted to the 1,3 isomer in the presence of both chloroplatinic acid and trimethylgermane, at a much faster rate than hydrogermanation. In the absence of either chloroplatinic acid or trimethylgermane, there is no isomerization (and no hydrogermanation).

D. ISOMERIZATION OF OLEFINS

Mention has been made of the concurrent migration of double bonds in olefins during reduction reactions by transition metal catalysts. The features of catalytic isomerization (73) are similar to those of reduction reactions, namely, the formation of a metal hydride, generally from a co-catalyst such as hydrogen, alcohol, or acid, and the simultaneous coordination of an olefin molecule that can rearrange via an alkyl complex. The isomerization of butenes by $\text{Pt}(\text{SnCl}_2 \cdot \text{solv.})_5$ and $\text{Rh}_2\text{Cl}_2(\text{SnCl}_2 \cdot \text{solv.})_4$ has been studied in detail (126). The rearrange-

ment of diolefins during the preparation of $(\text{diene})_2\text{IrSnCl}_3$ was mentioned earlier.

E. REDOX REACTIONS

It is possible that the reduction of metal ions to a lower oxidation state by tin(II) chloride can in many cases involve an intermediate complex between the two. Thus the reduction of chloroplatinic acid to $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$ may involve an initial complex between platinum(IV) and tin(II) chloride, which decomposes to the platinum(II) complex [see, for example, Baird (18)]. The chloro complexes of platinum(II), rhodium(I), and ruthenium(II) (see p. 118) have very intense bands in their visible spectra, which indicate considerable charge transfer between the two metal atoms. A redox reaction will be initiated by a complete charge transfer from the metal to the tin atom in the higher valency complexes, and this process can continue right to the metal, as with palladium, or to a stable zerovalent complex (159). During the reduction of uranium(VI) to uranium(IV) a 1:1 complex between U(IV) and Sn(II) (175) was detected spectrophotometrically. The kinetic first order dependence of both reagents suggests that the formation of this complex may be the rate-determining step. A 1:1 complex between U(IV) and Sn(II) was also observed, but no further reduction takes place. It has been suggested (89) that complex formation may also be involved in the reduction of vanadium(V). However, it is considered (225) that an electron transfer process can take place between divalent tin and a transition metal ion across a bridging chelate ligand, such as tartrate or citrate.

VI. Bonding in Group IVB Complexes

A. STRUCTURAL STUDIES

The bonding between a coordinated transition metal and Group IVB moiety creates nothing new in the stereochemistry observed for either the transition metal or the Group IVB atom. Therefore it is only necessary to consider effects causing distortions of coordination and the lengths of the metal-metal bonds. Table VI lists data from reported crystal structure determinations, which are relevant to the following discussions.

1. Bond Angles

Monosubstituted complexes, whose structures are known, all show slight but significant deviations from regular tetrahedral coordination

TABLE VI
 STRUCTURAL DATA FOR GROUP IVB COMPLEXES

Compound	Bond lengths (Å)		Con- traction ^a	Bond angles (°) ^b		Ref.
	M—E	e.s.d.		C-E-C or Cl-E-Cl	M-E-M or M-E-C	
Cl ₃ Si-Co(CO) ₄	2.254	0.003	0.015	105	113 ^c	(218)
Ph ₃ Ge-Mn(CO) ₅	2.54	0.02	0.05	—	—	(141)
	2.60	—	0.01	—	—	(229)
Cl ₂ Ge[Fe(CO) ₂ Cp] ₂	2.36	0.01	0.10	96	128	(41)
Me ₃ Sn-Mn(CO) ₅	2.674	0.003	0.10	107	112 ^c	(40)
Ph ₃ Sn-Mn(CO) ₅	2.674	0.004	0.10	106	113 ^c	(242)
Ph ₃ Sn-Mn(CO) ₄ (Ph ₃ P)	2.627	0.01	0.14	105	115 ^c	(38)
Ph ₂ Sn[Mn(CO) ₅] ₂	2.70	0.01	0.07	100	117	(142)
Ph ₃ Sn-Fe(CO) ₂ Cp	2.536	0.003	0.10	105	113 ^c	(39)
Cl ₂ Sn[Fe(CO) ₂ Cp] ₂	2.49	—	0.15	94	128	(65)
Me ₄ Sn ₃ [Fe(CO) ₄] ₄	2.747	0.008	-0.11 ^d	—	99, 115	} (232)
(internal)						
2.265	0.008	0.01	108	105		
(terminal)						
Sn[Fe(CO) ₄] ₄	2.54	0.01	0.10	—	69, 133	(70, 71, 157)
Cl ₃ Sn-Ir(COD) ₂	2.642	0.002	0.12	—	113, 124 ^c	(213)

^a Comparison with the sum of metallic covalent radii (see text).^b Average values.^c Values for M—E—C angles.^d Bond lengthening.

about E. The more marked distortion from regular tetrahedral bond angles at the tin atom that occurs in Ph₂Sn[Mn(CO)₅]₂ (142), compared with Ph₃Sn—Mn(CO)₅ (242), probably arises from mutual repulsion of the two bulky manganese pentacarbonyl groups. It has been suggested (232) that the molecular geometry of Me₄Sn₃[Fe(CO)₄]₄ (structure XI), which has similarly distorted bond angles, is the result of distortion from normal octahedral and tetrahedral valency angles and bond lengths to relieve steric interactions. The bond angles in Cl₂E[Fe(CO)₂Cp]₂ [E = Ge (41), Sn (65)] are even more distorted and approach those in Sn[Fe(CO)₄]₄ (71, 157), where three-center Fe—Sn—Fe bonds involving *d* orbitals on the tin atom have been postulated. Thus it is likely that the localized E—Fe bonds have some multiple bond character arising from *d*_π–*d*_π overlap.

2. Bond Lengths

Reported metal-metal distances provide evidence for multiple bonding. Nearly all observed metal-metal bonds show appreciable shortening

from the theoretical bond lengths calculated from metallic covalent radii (230). [Examination of reported bond lengths (22, 152, 190, 230) shows that the metallic radii are reasonable values for effective covalent radii in organometallic complexes.] It is realized that bond lengths will be sensitive to other electronic and steric factors. In crystallographic studies, only differences greater than 3 times the estimated standard deviation (e.s.d.) are considered significant. The reported bond lengths for a number of other Group IVB complexes (195, 229) have not been considered, since calculations were made from two-dimensional determinations and e.s.d.'s are not reported. Values of e.s.d.'s are quoted in Table VI.

In $R_3Sn-Mn(CO)_5$ (40, 242) the observed Sn—Mn bond length is independent of R and about 0.1 Å less than the sum of the covalent metal radii. Substitution of the carbonyl group *trans* to R_3Sn by a phosphine molecule of lower π -acceptor properties shortens the Sn—Mn bond still further (38). This is consistent with an increase in multiple bond character in the metal-metal bond as a result of less competition by the phosphine group for the electrons in *d* orbital on the manganese atom, which are used in Sn—Mn π -bonding. Bond shortening in $Ph_3Sn-Fe(CO)_2Cp$ (39) is similar to that in $Ph_3Sn-Mn(CO)_5$, which suggests that, in the first transition period at least, the important factor is the π -bonding abilities of the remaining ligands. An order of π -bonding ability appears to be $Cl_3Sn > Ph_3Sn > Ph_3Ge$; the presence of the highly electronegative chlorine atom attached to E is expected to increase the π -acceptor properties of a group.

In $Ph_2Sn[Mn(CO)_5]_2$ (142) the Sn—Mn bond is longer than in $Ph_3Sn-Mn(CO)_5$ (242), and competition for the *d* orbitals of the tin atom might be expected to reduce the π -contribution in each Sn—Mn bond. In $Me_4Sn_3[Fe(CO)_4]_4$ (structure XI), the four iron atoms attached directly to the central tin atom actually have bonds longer than the sum of the atomic radii, and this fact, together with the observed bond angle distortions, may be deemed solely the result of steric interactions (232). Thus there is a progressive lengthening in the metal-metal bonds when more transition metal groups bond to tin. The molecule $Sn[Fe(CO)_3]_4$ (71, 157) has Sn—Fe bonds shorter than expected and severely distorted bonding angles, and in this case there are iron-iron interactions involving the tin *d* orbitals. Therefore even shorter Sn—Fe bonds in $Cl_2Sn[Fe(CO)_2Cp]_2$ (65) give good evidence for considerable π -bonding in the separate metal-metal bonds. There are no Fe-Fe interactions, but there are only two irons attached to tin and two electronegative chlorines. Furthermore, the Sn—Cl and Ge—Cl bonds are close to the covalent radii sum and longer than those in the ECl_4 compounds (230), and it seems plausible that a significant (*d* \rightarrow *d*) π -bonding between the metals

is preferred to any ($p \rightarrow d$) π -bonding in the E—Cl bond. From bond length data an order of π -bonding ability for disubstituted compounds would be $\text{Cl}_2\text{Sn} > \text{Cl}_2\text{Ge} > \text{Ph}_2\text{Sn}$.

Effects on σ -bonding can effectively be ignored. Electronegative substituents on E will be expected to lengthen the metal-metal σ -bond, by increasing the positive charge on E, and shorten E—X bonds. Distortions in coordination affect bond lengths and this may be considered by using the concept of hybridization. There is NMR evidence that the s character in the metal-metal σ -bond is increased to about 30 %, and distortions from tetrahedral symmetry at E are generally observed in the crystalline state. Bent (23) finds that changes in bond length are less than 0.05 Å for first-row elements when changing from sp^3 to sp^2 hybridization. E—E bond lengths in $\text{X}_3\text{E}-\text{EX}_3$ compounds where there is no π -bonding vary only slightly with the nature of X.

B. INFRARED SPECTRA

1. Carbonyl Stretching Frequencies

$\text{R}_3\text{E}-\text{Mn}(\text{CO})_5$ complexes have a ($2A + E$) band pattern in the carbonyl region (130) consistent with C_{4v} symmetry for the $\text{Mn}(\text{CO})_5$ group (67, 192), and this is confirmed by structural determinations in the solid state. A further band is observed in some cases and can be assigned to the Raman-active B_1 mode. Accidental degeneracy can also occur. The appearance of this normally infrared inactive mode is due to the non-spherical top symmetry of the R_3E group, and is most marked when the group is asymmetric as for $\text{Me}_2\text{ClSn}-$ (130). Infrared data and band assignments for the $\text{R}_3\text{E}-\text{Mn}(\text{CO})_5$ complexes and some related compounds are given in Table VII. Qualitatively, the lowering of the carbonyl frequencies is of the order expected for changes in electronegativity: $\text{Cl} > \text{Br} > \text{Me} > \text{Ph}_3\text{E}$, but it can be seen that by this criterion the higher apparent electronegativity of X_3Sn compared with X shows that inductive effects are not the only factor to be considered.

Force field calculations (130) by the method of Cotton and Kraihanzel (67) give force constants that separate the inductive and mesomeric effects. In Table VII, the k_1 and k_2 listed refer to stretching force constants for the carbonyl groups *trans* (axial) and *cis* (equatorial), respectively, to the substituent group; k_1 will be affected more by changes in the d -orbital interactions between E, M and *trans*-CO, while k_2 is influenced mainly by inductive electronic effects. Increasing values of k_1 reflect increasing π -acceptor properties of the substituent group, and increasing values of k_2 reflect increasing electron-withdrawing power, although inductive effects will probably contribute to some extent to the values of

TABLE VII
INFRARED SPECTRA OF MANGANESE PENTACARBONYL COMPLEXES

Compound	Carbonyl stretching frequencies (cm ⁻¹)							Ref.
	<i>A</i> ₁ ⁽¹⁾	<i>E</i>	<i>B</i> ₂ ^a	<i>A</i> ₁ ⁽²⁾	<i>k</i> ₂ ^b	<i>k</i> ₁ ^b	10 ² (<i>k</i> ₂ - <i>k</i> ₁) ^b	
ClMn(CO) ₅	2138	2054	2022	1999	17.48	16.22	126	(122)
HCF ₂ -CF ₂ Mn(CO) ₅	2134	2044,	2073	2015	17.33	16.51	82	(246)
		2041						
MeMn(CO) ₅	2116	2011	—	1990	16.82	16.11	71	(130)
Ph ₃ Si-Mn(CO) ₅	2098	2003	2030	2003	16.67	16.36	31	
Ph ₃ Ge-Mn(CO) ₅	2097	2006	2032	2002	16.70	16.33	37	
Ph ₃ Pb-Mn(CO) ₅	2091	2003	2029	2003	16.64	16.35	29	
Ph ₃ Sn-Mn(CO) ₅	2093	2002	2027	2002	16.64	16.34	30	
Me ₃ Sn-Mn(CO) ₅	2089	1991	2021 ^c	1998	16.49	16.29	20	
Me ₂ ClSn-Mn(CO) ₅	2101	2006	2039	2015	16.72	16.57	15	
Br ₃ Sn-Mn(CO) ₅	2126	2046	2060	2039	17.26	16.88	38	(130)
Cl ₃ Sn-Mn(CO) ₅	2122	2043	2070 ^c	2037	17.31	16.91	40	

^a Normally infrared inactive mode.

^b Values in mdynes/Å from Jetz *et al.* (130).

^c *B*₂ mode not observed, calculated value given.

*k*₁. Such criteria indicate that R₃E groups have better π -accepting properties than the chloride ion, and the replacement of the organo groups on E by halogens greatly enhances this. The order of π -acceptor abilities based on force constant data is Cl₃Sn ~ Br₃Sn > Me₂ClSn > Ph₃E > Me₃Sn > Cl > Me, whereas that of inductive effects is Cl > X₃Sn > Me > Me₂ClSn > Ph₃E > Me₃Sn. Similar results are obtained (130) from a consideration of the corresponding rhenium derivatives. However, such calculations are approximate, and it would be unwise to predict the order of π -accepting properties in the Ph₃E series from the small differences observed in their *k*₁ values. The difference (*k*₂ - *k*₁) might give a better measure of the π -bonding of a substituent, provided the inductive effects are the same for both force constants. It is found that the R₃E groups cause much smaller (*k*₂ - *k*₁) differences (*k*₂ > *k*₁) than occur when strong σ -bonding substituents are present. This can be attributed to their greater effect on *k*₁ through π -bonding, although the values for Ph₃Ge and Cl₃Sn seem anomalously high.

Hagen and MacDiarmid (107) have recently analyzed the spectra of silicon cobalt tetracarbonyls. The carbonyl stretching frequencies are consistent with C_{3v} symmetry both in the gas phase and in solution (47) and have been assigned to (2*A* + *E*) modes (Table VIII). (Splitting of the *E* mode is observed in solution and when the silicon group is asymmetric.)

This finding is in agreement with the structure determination of $\text{Cl}_3\text{Si-Co}(\text{CO})_4$ (218). From these assignments, force constants k_e (for the equatorial carbonyl) and k_a (for the axial carbonyl, *trans* to the substituent) have been calculated by Cotton and Kraihanzel's method (67). By arguments similar to those used for the manganese pentacarbonyl complexes,

TABLE VIII
INFRARED SPECTRA OF COBALT TETRACARBONYL COMPLEXES

Compound ^a	A_1 (equatorial)	A_1 (axial)	E (equatorial)	k_e^b	k_a^b	$10(k_e - k_a)$	Ref.
$\text{HCF}_2\text{-CF}_2\text{Co}(\text{CO})_4$	2126m	2060s	2052vs, 2048vs	17.62	17.15	47	(245)
$\text{CF}_3\text{Co}(\text{CO})_4^c$	2103m	2066vs, sh	2051s	17.67	17.25	42	(116)
$\text{MeCo}(\text{CO})_4^c$	2111w	2046m	2031s	17.34	16.91	43	(167)
$(\text{MeO})_3\text{Si-Co}(\text{CO})_4$	2105s	2040vs	2025vs, 2010vs, sh	17.17	16.81	36	(47)
$\text{F}_3\text{Si-Co}(\text{CO})_4^c$	2128w	2073m	2049s	17.63	17.36	27	} (107)
$\text{Cl}_3\text{Si-Co}(\text{CO})_4^c$	2125w	2071m	2049s	17.60	17.33	27	
$\text{Ph}_3\text{Si-Co}(\text{CO})_4$	2100s	2040s	2015vs, 2010s, sh	17.08	16.81	27	
$\text{Me}_3\text{Si-Co}(\text{CO})_4^c$	2100m	2041ms	2009s	17.07	16.83	24	} (107)
$\text{Cl}_3\text{Ge-Co}(\text{CO})_4$	2122ms	2069ms	2050vs	17.59	17.30	29	
$\text{Br}_3\text{Ge-Co}(\text{CO})_4$	2118ms	2066ms	2048vs	17.52	17.25	27	
$\text{I}_3\text{Ge-Co}(\text{CO})_4$	2113s	2062ms	2042vs	17.44	17.18	26	
$\text{PhCl}_2\text{Ge-Co}(\text{CO})_4$	2112s	2056s	2038vs, 2027vs	17.36	17.09	27	
$\text{Ph}_2\text{ClGe-Co}(\text{CO})_4$	2101s	2043s	2026vs, 2010vs	17.14	16.86	28	} (207)
$\text{Ph}_3\text{Ge-Co}(\text{CO})_4$	2091s	2030s	2006vs	16.96	16.65	31	
$\text{Cl}_3\text{Sn-Co}(\text{CO})_4$	2120s	2068ms	2048vs	17.54	17.28	26	
$\text{I}_3\text{Sn-Co}(\text{CO})_4$	2109s	2058m	2037vs	17.37	17.11	26	
$\text{Ph}_3\text{Sn-Co}(\text{CO})_4$	2087ms	2027m	1999vs	16.88	16.57	31	
$\text{Me}_3\text{Sn-Co}(\text{CO})_4$	2082s	2020ms	1988vs	16.74	16.49	25	
$\text{Ph}_3\text{Pb-Co}(\text{CO})_4$	2081s	2022m	1997vs	16.80	16.52	28	

^a Spectra measured in hydrocarbon solvent.

^b Values in mdynes/Å.

^c Gas phase.

k_a is affected predominantly by changes in π -bonding, and k_e by inductive changes. Comparisons have been made by considering their difference ($k_e - k_a$), which is insensitive to the phase in which the spectra are measured. π -Bonding by the substituent will increase k_a more than k_e and hence decrease the difference between them. The fact that ($k_e - k_a$) for the silicon complexes is about half that for methyl and fluorocarbon complexes strongly suggests that there is π -bonding in the Si—Co bond.

Related germanium, tin, and lead complexes (207) have similar infrared spectra, and the same assignments have been made in the carbonyl region. Calculations of the force constants for these compounds have been made (253) using Hagen and MacDiarmid's equations (107) and, although there is evidence (207) of appreciable coupling between the $A_{1(a)}$ and $A_{1(e)}$ modes, which has been ignored, similar results are obtained. The $(k_e - k_a)$ values lie between 0.24 and 0.30 for all R_3E derivatives ($R =$ halogen, phenyl, methyl), which suggests that π -bonding occurs in all cases. If these differences fairly represent π -bonding capacity, then the general order is $Me_3E > X_3E > Ph_3E > (MeO)_3E$, which is different from the order generally accepted (3, 191) when E is replaced by P , As , or Sb . The high value of $(k_e - k_a)$ for $(MeO)_3Si$ may well be the result of ($p \rightarrow d$) π -bonding between silicon and oxygen (58, 90) competing with the overlap of π orbitals in the metal-metal bond. The values for the halide and phenyl derivatives are probably also affected in the same way, although the relative extent of this effect is not known. Values for germanium and tin suggest that π -bonding with halogens falls off from chlorine to iodine with germanium and is absent with tin, but that in both cases π -bonding with phenyl is appreciable. Thus the observed order of π -accepting ability for Group IVB ligands is not a simple picture.

Values of k_a give the expected order $X_3E > Ph_3E > Me_3E$, but there is no universal order of π -bonding for metals E . Different orders are obtained depending on the nature of their attached atoms and whether $(k_e - k_a)$ or k_a values are considered. There are too many assumptions inherent in the calculations to allow this point to be resolved satisfactorily. Similar conclusions are found for the manganese pentacarbonyl complexes: $(k_2 - k_1)$ values are spread more widely but give the order $Me_3Sn > Ph_3Sn > X_3Sn$, while k_1 values give $X_3Sn > Ph_3Sn > Me_3Sn$.

The spectra of $R_3E-M(CO)_3Cp$ ($M = Cr, Mo, W$) derivatives show three strong terminal carbonyl stretching frequencies, as do the halogen compounds (211), and most probably have the same molecular symmetry as $EtMo(CO)_3Cp$ (21) and $[Mo(CO)_3Cp]_2$ (248) although the alkyl derivatives (211) have only two carbonyl bands. Qualitative considerations of the frequencies give an order of "effective electronegativity" based on mean carbonyl frequencies as $Cl_3Sn > X > alkyl > Me_2ClSn > Ph_3E$. The position of Cl_3Sn suggests that there is appreciable π -bonding in these complexes too, although without the separation of inductive and mesomeric effects no further conclusions can be drawn.

Similarly, $X_3Sn-Fe(CO)_2Cp$ complexes (191) have the same spectra as the alkyl (211) and halogen (208, 210) compounds. The order of "effective electronegativity," $CN > X \sim X_3Sn > PhCl_2Sn > Ph > Me > Me_3Sn$, indicates that the probable π -bonding order is $CN > Cl_3Sn > Cl$, which

is in agreement with a more quantitative assessment (158). The *cis* configuration of $(R_3E)_2Fe(CO)_4$ has been proved from infrared data. D_{4h} symmetry of the *trans* isomer would give only one infrared-active mode (E_g), whereas four are expected (A_1 , A_2 , B_1 , B_2) for the *cis* isomer (C_{2v} symmetry), as observed (132). This was confirmed by dipole moment measurements.

Disubstituted compounds are more difficult to analyze. Compounds of the type $R_2Sn[Co(CO)_3L]_2$ (28) often show more carbonyl bands than are required for local symmetry of the cobalt atoms but less than are required for total symmetry. Spectra measured in chlorinated solvents indicate that L is *trans* to the R_3Sn group, but in nonpolar solvents a greater number of bands is observed. A partial assignment of bands has been made (207) for the germanium complexes. An assignment can be made (133) for $[R_2E-Fe(CO)_4]_2$ on the basis of D_{2h} symmetry. Carbonyl frequencies increase in the order $Pn < Sn < Ge$.

An interpretation of the spectra for $R_2E[Fe(CO)_2Cp]_2$ considered (94) three distinct structures of C_{3v} , C_s , and C_1 symmetries, which all predict the observed number of carbonyl frequencies. From analysis of relative intensities, the alkyl derivatives were assigned C_s symmetry and the halogen compounds C_1 . However, a recent structure determination (41) of $Cl_2GeFe(CO)_2Cp_2$ shows it to have C_2 symmetry in the crystal; but this case was not considered in the infrared analysis, although it will give rise to the same number of carbonyl bands that are observed.

2. Metal-Halogen Stretching Frequencies

Platinum-chlorine stretching frequencies have been used by Adams *et al.* (2) as a measure of the *trans* effect of Y in the series *trans*- L_2PtYCl , since $\nu(Pt-Cl)$ is insensitive to the nature of L. If Y is a ligand with a strong inductive *trans* effect, then a large decrease in $\nu(Pt-Cl)$ overshadows any effects from changes in the electronegativity of Y. Table IX shows that silicon and germanium ligands have very strong inductive *trans* effects, considerably greater than alkyls or aryls, while Ph_3Sn and Ph_3Pb are comparable to the hydride ion. $\nu(Pt-Cl)$ for the trichlorostannato ion seems abnormally high in view of the high *trans* effect found from n.m.r. data (158). But the mesomeric origin of this effect can actually lead to a strengthening of the $Pt-Cl$ bond, as appears to be the case for $(COD)PtCl_2$, and also allows a greater electronegativity effect (2). It has been found (18) that *cis*- and *trans*-(Ph_3P) $_2PtCl(SnCl_3)$ have the same infrared spectra, with the $\nu(Pt-Cl)$ appearing as a shoulder at 315 cm^{-1} on the tin-chlorine stretching frequencies. This suggests that Ph_3P and Cl_3Sn have similar *trans* effects, and that the *trans* ligand may have little effect on $\nu(Sn-Cl)$.

In trichlorostannato complexes, the tin-chlorine stretching frequencies (Table X) show a considerable increase in frequency upon coordination. Frequencies in the boron halide adducts (131), where there is only σ -bonding, are similar to those of free SnCl_3^- . In transition metal complexes, where π -bonding is possible, the tin-chlorine stretching frequencies have values intermediate between those for divalent and tetravalent tin chlorides. The changes in frequency have been related (222a)

TABLE IX
PLATINUM-CHLORINE STRETCHING FREQUENCIES IN THE
COMPLEXES *trans*- L_2PtClY

L	Y	$\nu(\text{Pt}-\text{Cl})$ (cm^{-1})	Reference
Et_3P	Cl	340	(2, 75)
Ph_3P	Cl	345	
Ph_3P	SnCl_3	315	
Ph_3P	SnPh_3	298	
Ph_3P	PbPh_3	286	
Ph_3P	H	287	(18)
PhMe_2P	H	282	
Et_3P	H	269	
Et_3P	Me	274	(2)
Et_3P	Ph	270	
PhMe_2P	GeMePh_2	248	(51)
PhMe_2P	SiMePh_2	242	

to the electron affinities of the transition metal atoms by consideration of electronic changes at the tin atom. However, the π -acceptor properties of the SnCl_3 group were ignored, and there is a rough correlation between $\nu(\text{Sn}-\text{Cl})$ values and the number of other π -bonding ligands attached to the central metal atom. It has been argued (1) that the far-infrared spectrum for $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$ supports the trigonal bipyramidal structure (74) by the absence of platinum-chlorine stretching frequencies. However, Table IX shows that $\nu(\text{Pt}-\text{Cl})$ would be expected at similar frequencies to $\nu(\text{Sn}-\text{Cl})$ in *trans*- $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$, if SnCl_3 has a similar *trans* effect to triphenylphosphine. In view of the poor resolution reported (1), the datum does not distinguish unequivocally between the two compounds. The spectra of authentic *cis*- and *trans*- $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$ have not been reported, but, because good resolution of bands is not achieved (222a) in other compounds containing metal chlorine bands, the problem may not be easily resolved.

TABLE X
TIN-CHLORINE STRETCHING FREQUENCIES OF SnCl_3 IN
TRANSITION METAL COMPLEXES

Complex	$\nu(\text{Sn—Cl})$ (cm^{-1})		Ref.
	Asymmetric	Symmetric	
SnCl_3^-	297	256	(251)
$(\text{Ph}_4\text{As})\text{SnCl}_3$	289	252	} (131)
$(\text{Ph}_4\text{As})\text{SnCl}_3 \cdot \text{BCl}_3$	284	255	
$(\text{Ph}_4\text{As})\text{SnCl}_3 \cdot \text{BF}_3$	294	267	
$(\text{NBD})_2\text{RhSnCl}_3$	307	284	(222a)
$(\text{Ph}_3\text{P})_3\text{CuSnCl}_3$	309	286	} (86)
$(\text{Ph}_3\text{P})_3\text{AgSnCl}_3$	313	288	
$(\text{Ph}_3\text{P})_3\text{AuSnCl}_3$	315	288	
$(\text{COD})_2\text{IrSnCl}_3^a$	317	300, 290	} (222a)
$(\text{Ph}_3\text{P})_3\text{RhSnCl}_3$	327	302	
$(\text{Ph}_3\text{P})_2\text{PtH}(\text{SnCl}_3)$	331	309	} (18)
$(\text{Ph}_3\text{P})_2\text{PtCl}(\text{SnCl}_3)$	341	325	
$(\text{Ph}_3\text{P})_2\text{PtPh}(\text{SnCl}_3)$	341	318	(198)
$(\text{Me}_4\text{N})_4[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]^b$	339	323	(222a)
	362	335	} (1)
$(\text{Et}_4\text{N})_3[\text{Pt}(\text{SnCl}_3)_5]$	ca. 337		
$(\text{Me}_4\text{N})_2[\text{RuCl}_2(\text{SnCl}_3)_2]$		329	} (222a)
$(\text{Ph}_3\text{P})_2(\text{CO})\text{IrHCl}(\text{SnCl}_3)$	339	320	
$(\text{Me}_4\text{N})_4[\text{Ir}_2\text{Cl}_6(\text{SnCl}_3)_4]$	ca. 340		
MeSnCl_3	384	366	(233)

^a Assignment not unequivocal.

^b Different assignments made by different workers.

3. Metal-Metal Stretching Frequencies

A large number of metal-metal frequencies have been measured (1, 45) but little can be said at present about their significance.

4. Metal-Hydrogen Stretching Frequencies

The metal-hydrogen stretching frequencies in the series *trans*-(Et_3P)₂PtHY (Table XI) have been correlated with the *trans* effect of ligand Y (55), as have the chemical shifts of the hydrogen atoms in n.m.r. spectra. The *trans*-effect series on this basis, $\text{X} < \text{SCN} < \text{SnCl}_3 < \text{SiPh}_3 < \text{CN} < \text{GePh}_3 < \text{H}$, is in only fair agreement with that obtained from $\nu(\text{Pt—Cl})$ values. The overall trends are similar, however, and confirm the high mesomeric effect of SnCl_3 and the strong inductive effects of Ph_3E .

TABLE XI
Trans EFFECT SEQUENCE FOR LIGANDS IN THE SERIES
trans-(Et₃P)₂PtHY

Y	NO ₃	Cl	Br	I	NCS	SnCl ₃	SiPh ₃	CN	GePh ₃	H
$\nu(\text{Pt—H})$ cm^{-1a}	2242	2183 ^b	2178	2156 ^c	2112	2105 ^d	2056 ^e	2041	1957 ^f	1731 ^g
$\delta(\text{Pt—H}) \tau^h$	33.1	26.9	25.6	22.7	23.2	19.2 ^d	—	17.8	—	—

^a Chatt *et al.* (50), hexane solution.

^b Cf. (Pr₃P)₂PtHCl, 2183 cm⁻¹; (Ph₂EtP)₂PtHCl, 2206 cm⁻¹; (Ph₃P)₂PtHCl, 2220 cm⁻¹ (50).

^c Cf. (Ph₃P)₂PtHI, 2186 cm⁻¹ (50).

^d Lindsey *et al.* (158). Cf. (Ph₃P)₂PtHSnCl₃, 2056 cm⁻¹ (18).

^e Baird (18).

^f Value for (Pr₃P)₂PtH(GePh₃) (75).

^g Value assigned to (Pr₃P)₂PtH₂ (75). Cf. (Ph₃P)₂PtH₂, 1620 cm⁻¹ (164).

^h Chatt and Shaw (55), benzene solution.

C. N.M.R. SPECTRA

The n.m.r. spectra of methyltin derivatives have been studied (130, 203) and some results are given in Table XII. It has been shown (36) that the methyl resonances shift to lower fields as the methyl groups in tetramethyltin are replaced by chlorine atoms. It has been suggested that this may not be due solely to the inductive withdrawal of shielding electron density, since chemical shifts are less (36, 243) when (*p* → *d*) π -bonding between metal and chlorine is favorable. A similar trend is observed (130, 200) when the methyl groups are replaced by transition metal groups and the observed chemical shifts are smaller than those in the methyltin chlorides, which may be the result of π -bonding between the two metals.

The tin-proton coupling constants $J(^{119}\text{Sn—Me})$ for the methyl groups also decrease with successive replacements of the methyl groups by transition metals (64, 130, 199, 200, 206). The coupling has been related (95, 123) to the *s* character of the tin-methyl bonds, and the values for the transition metal derivatives, which are lower than that for tetramethyltin, imply a higher degree of *s* character (about 30 % in the metal-metal bonds) than is expected for pure *sp*³ hybridization. These findings are corroborated by structure determinations, which show deviations from regular tetrahedral bond angles that are larger in the disubstituted complexes. Correlations have been made (37) between $J(^{119}\text{Sn—Me})$ values and Sn—C stretching frequencies, and it is interesting to note that there is a close similarity (61, 130) between the coupling constants and

$\nu(\text{Sn—C})$ in Me_6Sn_2 and $\text{Me}_3\text{Sn—Mn}(\text{CO})_5$. Similar trends exist in the methyllead compounds (95) and their related transition metal complexes (130, 200).

Parshall (197, 198) has used intramolecular ^{19}F shielding to estimate the relative σ and π contributions in a metal ligand bond in square planar complexes of platinum. The chemical shift of the fluorine atom in *trans*-(Et_3P) $_2\text{PtX}(m\text{-fluorophenyl})$ is affected only by inductive effects in the

TABLE XII

N.M.R. SPECTRA OF METHYLTIN CHLORIDES AND SOME
TRANSITION METAL COMPLEXES

Compound	τ_{Me}	$J(^{119}\text{Sn—Me})$ (cps)	Reference
Me_6Sn_2	9.78	48.4	(36, 37)
Me_4Sn	9.93	54.0	(36, 37, 199)
Me_3SnCl	9.37	59.7	} (36, 123)
Me_2SnCl_2	8.84	71.0	
Me_3SnCl	8.35	100.0	
$\text{Me}_3\text{Sn—Mo}(\text{CO})_3\text{Cp}$	9.52	49.0	(200)
$\text{Me}_3\text{Sn—Mn}(\text{CO})_5$	9.54	48.3	(61, 130)
$\text{Me}_3\text{Sn—W}(\text{CO})_3\text{Cp}$	9.40	48.7	(200)
$\text{Me}_3\text{Sn—Re}(\text{CO})_5$	9.58	46.7	(130)
$\text{Me}_3\text{Sn—Fe}(\text{CO})_2\text{Cp}$	9.55	49.0	(199)
$\text{Me}_3\text{Sn—Ir}(\text{CO})_3(\text{Ph}_3\text{P})$	—	49.0	(64)
$\text{Me}_2\text{ClSn—Mo}(\text{CO})_3\text{Cp}$	9.02	47.7	(200)
$\text{Me}_2\text{ClSn—Mn}(\text{CO})_5$	9.00	45.3	(130)
$\text{Me}_2\text{Sn}[\text{Mo}(\text{CO})_3\text{Cp}]_2$	9.15	37.4	(200)
$\text{Me}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$	9.17	36.7	(130)
$\text{Me}_2\text{Sn}[\text{Mo}(\text{CO})_3\text{Cp}][\text{Mn}(\text{CO})_5]$	9.20	36.9	(199)
$\text{Me}_3\text{Sn—Co}(\text{CO})_4$	9.37	52.6	} (202)
$\text{Me}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$	8.88	49.7	
$\text{MeSn}[\text{Co}(\text{CO})_4]_3$	8.98	33	

Pt—X bond, while the chemical shift in the *p*-fluorophenyl analog is a measure of both the σ and π contributions. Thus the two effects can be separated and have been measured (158, 197, 198) for a variety of ligands. Results show that the trichlorostannato ion is a weak σ -donor but a strong π -acceptor ligand comparable to the cyanide ion and should thus have a high *trans* effect. This prediction is confirmed by infrared data.

VII. Conclusions

A. THE NATURE OF THE METAL-METAL BOND

1. Multiple Bonding

Chemical and physical evidence points toward considerable π -bonding in the E—M bonds resulting from overlap of d orbitals. All R_3E complexes are very much more stable than their methyl analogs, although they are still sensitive to oxidation. In general, stability is in the order $X_3E > Ph_3E > Me_3E$ and is enhanced by the introduction of a phosphine molecule into the coordination sphere. Disubstituted complexes are less stable than their monosubstituted analogs.

The metal-metal bonds show widely different reactivities depending on the nature of R_3E and the transition metal atoms. Thus for the phenyl derivatives, Sn—Mn and Ge—Re bonds are remarkably stable toward halogens; Sn—Re and Ge—Mn bonds are less so, and Sn—Fe, Pb—Mn, and Si—Co bonds are readily broken. Disubstituted derivatives are more reactive and at least one metal-metal bond is broken by the action of halogens. However, insufficient detail is at present known about the chemical behavior of Group IVB complexes in general.

Metal-metal bond distances and infrared and n.m.r. data support ($d \rightarrow d$) π -bonding, but again there is a lack of comprehensive data. Many competing factors must be considered such as inductive effects, π -bonding between E and its other substituents, and hybridization changes. Therefore it is not instructive to make specific predictions about the relative π -acceptor abilities of the Group IVB metals, since they are sensitive to the nature of the transition metal ion and their substituent atoms. Further work is clearly needed to clarify the role of π -bonding in these complexes.

2. Divalent and Tetravalent Compounds

The divalent halides EX_2 react readily with transition metal compounds to form two classes of compounds. With the platinum metals, tin(II) chloride forms $SnCl_3$ complexes whose chemical behavior suggests that tin remains formally divalent. With other transition metals, particularly those of the first row and earlier periodic groups, the mono- and disubstituted complexes behave as tin(IV) compounds. In both cases the $SnCl_3$ group behaves as a strong π -acceptor so that the difference in behavior must lie in the σ -component of the bonding. If the overlap of d orbitals between tin and the platinum metals is favorable, it is possible that the coordinate link is predominantly a π -bond, with the electron

pair from the tin atom that is responsible for initiating the bonding remaining close to its parent atom. With first-row transition metals where overlap is less favorable, or where there are less *d* electrons, a stronger, less polar σ -link may be required to draw the atoms close together for strong π -bonding. Reactions of the metal-metal bond would then favor the tin atom retaining its electron pair in the former case, but tend to split the bond homolytically in the latter.

These distinctions do not seem to exist in the alkyl or aryl derivatives, which can be prepared from R_3ELi , although there is evidence (18) that $(Ph_3P)_2PtCl(EPh_3)$ ($E = Sn, Pb$) decomposes to give diphenyltin and diphenyllead. This is to be expected from the lower stability of divalent organo compounds. Reactions of iron(II) (13, 171) and molybdenum(V) or (VI) (14) with tin(II) chloride in the presence of dimethylglyoxime may be exceptions to the above generalization, although the structure of these complexes is not known. It is possible that the two metals can be linked by a dimethylglyoxime molecule without a direct metal-metal bond.

B. COMPOUND TYPES

All the Group IVB elements readily form monosubstituted complexes with a variety of transition metals. At present the range is greatest with tin and germanium, which is a reflection of their general stability; the lack of silicon and lead complexes is probably a result of less experimental effort, and in the next few years many more compounds will probably be synthesized.

To date only germanium and tin have been found to form disubstituted complexes and, when this review was begun, tri- and tetrasubstituted complexes were almost entirely confined to tin. However, more recently (70, 71, 132, 133) the metal cluster compounds between tin and $Fe(CO)_4$ have been extended to germanium and lead. Otherwise, tetrasubstituted complexes have been confined almost entirely to iron compounds with $Fe-Fe$ bonds present only when it is necessary to maintain a rare gas configuration. Apart from $Sn[Fe(CO)_2Cp]_2[Mo(CO)_3Cp]_2$ (85), no tetrasubstituted compounds with other transition metals are known. Attempts to prepare $Sn[Re(CO)_5]_4$ gave only $Sn_2[Re(CO)_5]_6$ (181) and $X_{4-n}Sn[Co(CO)_4]_n$ with all but $n = 4$ being known.

The silicon complex $RSiCo_3(CO)_9$ probably contains three $Co(CO)_3$ groups held together by $Co-Co$ bonds as in the carbon complexes (231). It has been suggested (144) that the compound forms by spontaneous loss of carbon monoxide from intermediate $RSi[Co(CO)_4]_3$. The tin compounds $RSn[Co(CO)_4]_3$ show no tendency to lose carbon monoxide,

although the mass spectra (205) of these compounds do not give the $\text{RSnCo}_3(\text{CO})_{12}^+$ ion but a moderately high abundance of $\text{RSnCo}_3(\text{CO})_{11}^+$. However, the intensity of the $\text{RSnCo}_3(\text{CO})_9^+$ is low so that the condensed system of this sort is probably not very stable. It may be noted that $\text{Ph}_3\text{Sn-Mn}(\text{CO})_5$ does not show this stepwise loss of carbonyl groups in its mass spectrum (153). It is possible that multiple bond character in the Sn—Co bonds is sufficient to outweigh any gain in bonding energy that might result from forming the tetrameric structure. The behavior of germanium and lead in this respect has not been reported.

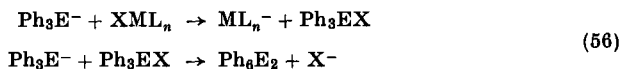
A metal-metal bond is postulated in $(\text{Acac})_2\text{SnCo}_2(\text{CO})_7$, and a crystal structure determination of this compound would be of considerable interest. The compound is considered to arise from the spontaneous loss of a carbonyl group (207) from $(\text{Acac})_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ because of constraint in the Co—Sn—Co bond angle arising from octahedral coordination of the tin atom. But electronic factors may also be important, since the mass spectrum of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ (205) indicates that there is preferential loss of one carbonyl group in this complex also.

C. SYNTHETIC METHODS

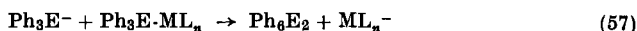
The most common preparative method for all classes of compounds is the reaction of organohalides with the transition metal anions in nucleophilic substitution reactions. Thus one can use R_3EX , R_2EX_2 , REX_3 , and EX_4 to give mono-, di-, tri-, or tetrasubstituted derivatives, respectively, although behavior is not always systematic. Thus SnCl_4 gives $\text{Sn}[\text{ML}_n]_4$, while GeCl_4 gives $\text{Cl}_3\text{Ge-ML}_n$; R_2EX_2 and REX_3 frequently give $\text{R}_2\text{XE—}$ and $\text{RX}_2\text{E—}$ derivatives, respectively. Often higher substituted compounds can be formed by further nucleophilic substitution on mixed organohalogen derivatives. This method is particularly useful for preparing mixed metal complexes.

The reverse substitution on transition metal halides by R_3E^- or X_3E^- has been commonly used, particularly with the platinum metals. In a series of papers (80–84), Dessey and his co-workers have reported important polarographic studies on the formation of metal-metal bonds. They show that reactions between two metal species are dependent on the nucleophilicity of the relevant metal ion and the path of the reaction. $\text{Ph}_3\text{E-Fe}(\text{CO})_2\text{Cp}$ ($\text{E} = \text{Sn, Pb}$) can be formed by reaction of either Ph_3E^- or $\text{Fe}(\text{CO})_2\text{Cp}^-$ with the chloride of the other metal group and these reactions are said to commute (82). The systems $\text{Ph}_3\text{Sn/Mo}(\text{CO})_3\text{Cp}$ and $\text{Ph}_3\text{Pb/Mn}(\text{CO})_5$ do not commute. Direct nucleophilic substitution is observed in the reactions of Ph_3SnCl with $\text{Mo}(\text{CO})_3\text{Cp}^-$ and Ph_3Pb (acetate) with $\text{Mn}(\text{CO})_5^-$; but their commutative reactions give

products suggesting that either metal-halogen interchange is taking place,



or the intermediate $\text{Ph}_3\text{E}\cdot\text{ML}_n$ complex is broken down through the elimination of ML_n^- (83) by the stronger nucleophile Ph_3E^- (81),



On the other hand, reactions in the noncommutative set $\text{Ph}_3\text{Sn}/\text{Mn}(\text{CO})_5$ seem to involve a one-electron transfer to give radicals that can take part in random or selective coupling.

These results are of considerable importance to the synthetic chemist since they enable predictions to be made on the success of reaction routes. For instance, Ph_3Pb^- can be used to prepare $\text{Ph}_3\text{Pb}\cdot\text{Fe}(\text{CO})_2\text{Cp}$ but not the $\text{Mn}(\text{CO})_5$ or $\text{Mo}(\text{CO})_3\text{Cp}$ complexes. Also $\text{Sn}[\text{Fe}(\text{CO})_2\text{Cp}]_2\cdot[\text{Mo}(\text{CO})_3\text{Cp}]_2$ is the predicted product in the reaction between $\text{Cl}_2\text{Sn}[\text{Fe}(\text{CO})_2\text{Cp}]_2$ and $\text{Mo}(\text{CO})_3\text{Cp}^-$, as has been found (85), but the commutative reaction should give $\text{Sn}[\text{Fe}(\text{CO})_2\text{Cp}]_4$ since $\text{Mo}(\text{CO})_3\text{Cp}^-$ is the weaker nucleophile.

Other related synthetic procedures involve the elimination of a neutral molecule, as in the reaction of R_3EX with HML_n ($\text{X} = \text{NR}_2$, NO_3 , H) or R_3EH with ClML_n .

An important reaction is the addition of divalent halides to metal-halogen bonds in X^1ML_n to give $\text{X}_2\text{X}^1\text{E}\cdot\text{ML}_n$, or to metal-metal bonds to give $\text{X}_2\text{E}[\text{ML}_n]_2$. The mechanism of this reaction remains uncertain. It is possible that it involves nucleophilic attack through the donor properties of the lone pair of electrons on EX_2 . Support for this idea is found in the ready reaction of compounds that can accept a donor molecule (e.g., $\text{IFe}(\text{CO})_2\text{Cp}$), whereas $\text{IMo}(\text{CO})_3\text{Cp}$, which has a higher coordination number and must increase this further, does not react. Alternatively, EX_2 might behave as a carbenoid entity (28, 28a, 178). The increase in reactivity of $[\text{Co}(\text{CO})_3\text{PR}_3]_2$ with SnCl_2 (28) as the π -accepting ability of the phosphines decreases is in line with electrophilic attack of this type. It is interesting that the reverse reaction, involving attack by the carbenoid entity $(\text{Ph}_3\text{P})_2\text{Pt}$ on R_3SnX , has been used (150) to prepare platinum-tin complexes.

D. CONCLUDING REMARKS

A large number of recent papers have increased severalfold our knowledge in this field. There is little doubt that, by the time this review is published, much more information will be available, but it has been the

present aim to provide a comprehensive survey of the topic as it stood in mid-1967. It is clear that more work remains to be done in the synthetic structural, spectral, and chemical reactivity aspects, and it must be left to the reader to judge how far this has been achieved in the intervening time. The study of these complexes is providing useful information on metal-metal bonding, and emphasizes the link between transition and nontransition metals as equal partners in inorganic chemistry.

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METAL CARBIDES

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I. Introduction

Over eighty of the elements in the Periodic Table are metals, most of these chemically combining with carbon to form carbides. Elements

definitely not metals, and therefore excluded from this article, are the six noble gases: helium, neon, argon, krypton, xenon, and radon, and the halogens: fluorine, chlorine, bromine, iodine, and astatine. The elements oxygen, nitrogen, and hydrogen form important compounds with carbon, but these elements are not metals and the compounds they form are not carbides. Phosphorus and sulfur are excluded for the same reasons. On the other hand, the metalloid silicon forms silicon carbide, SiC , a carbide with important industrial and practical uses, both as an abrasive and as a refractory.

The major applications of metallic carbides are as cutting materials (abrasives) or for resistance to high temperatures (refractories); however, a number of metals form compounds with carbon having simple formulas such as CaC_2 and are metallic carbides. Because they yield acetylene, C_2H_2 , on contact with water, such substances are usually termed acetylides. The acetylides are included in this review. Although ternary and more complex carbides are known, most of the available and reliable information is on binary carbides, chemical combinations between one metal and carbon. Many of the carbides in steels and ferrous alloys contain three or more elements, and these carbides have been extracted and studied in detail.

HISTORY

1. *Prior to Moissan*

The existence of metal carbides was mentioned by Berthollet and others as early as 1786, in connection with the changes produced in iron by small amounts of carbon (34). Ten years later A. F. de Fourcroy, one of the authors in de Morveau's *Encyclopedia* (233), proposed the term "carbide" in analogy to the similar terms sulfide and phosphide. In 1820 Berzelius (35) thought he had produced a definite series of carbides by heating the cyanides of some of the metals with ferrocyanides. Later work showed that what was actually obtained was a mixture of carbides of iron and the other metal. Berthelot (33) in 1866 described sodium and potassium carbides and showed how these two substances were related to acetylene, which is produced by these two carbides on treatment with water. The explosive carbides of copper, silver, and gold were also prepared, and descriptions of some of their properties appeared in the literature soon afterward. Other isolated investigations of carbides were published between 1820 and 1890, but systematic investigation of metallic carbides was due mainly to the work of H. Moissan, beginning about 1890 and covering a period of some 15 years after this date.

2. Work of Moissan

a. Preparation Methods. Moissan used most of the methods of carbide preparation known at the present time. He made extensive use of arc and tube electric furnaces, publishing one of the first books about them in 1897 (209). Three common methods for producing carbides are electric arc fusion of the metal or its oxide, passing carbonaceous gases over the heated metallic or oxide powder, and vapor phase deposition upon a hot filament. These will be discussed in more detail later.

Moissan was a pioneer in the use of all types of electric furnace then known for chemical applications, particularly in the preparation of carbides. Apparently he did not use the induction furnace, which was a somewhat later development. For example, in 1892, prior to the granting of a United States patent on a similar process the next year, he published a comprehensive account of the production of calcium carbide, CaC_2 (214). This was accomplished by using the electric arc to fuse calcium oxide with carbon. In his account, Moissan observed that, if the lime was impure and contained magnesia, fusion of the charge was delayed due to the higher melting point of MgO . Working with A. Etard (226), Moissan produced one of the rare earth carbides, yttrium carbide, YC_2 , by heating the proper proportions of the metallic oxide and sugar charcoal in a carbon tube electric furnace. Reaction occurred upon fusion of the oxide. In his book on the electrical furnace, Moissan described the production of one of the two beryllium carbides by heating, in an ordinary electrically heated tube furnace, beryllium oxide and carbon mixed with a small quantity of oil. Reaction took place after 10–15 minutes at a high temperature.

As an example of the carburization method, Moissan (215) produced an impure magnesium carbide by passing acetylene over heated magnesium powder. The product so obtained had considerable quantities of free carbon as a contaminant. The vapor phase method, now widely used, involves deposition of the carbide or other product on a hot filament, the metallic portion of the compound formed being obtained by the decomposition of the metallic halide vapor. This process was developed by Van Arkel and others some 20 years after Moissan completed his work on carbides. However, one of the methods used by Moissan in the production of SiC involved vapor phase deposition (217).

Although the very high vacuum equipment now in use was not available 60 years ago, he did make use of reduced pressures. After preparing an acetylide of sodium, Moissan prepared sodium carbide by warming the acetylide under vacuum. Although he did not originate the common methods of producing acetylides, Moissan used and developed them.

These preparation methods include passing gaseous acetylene into aqueous metallic solutions made ammoniacal, passing acetylene into liquid ammonia solutions containing the dissolved metal, and heating the metal or oxide with carbon. The last of these three processes was used by Moissan in the production of diberyllium carbide (Be_2C), as was mentioned above (215). Techniques involving the use of gaseous acetylene to produce the acetylide followed by decomposition of the acetylide to form a carbide, as in the decomposition of $\text{K}_2\text{C}_2 \cdot \text{C}_2\text{H}_2$ to give K_2C_2 , were used by Moissan to produce acetylides and carbides of the metals Li, K, Na, Rb, and Cs (229).

b. Carbides Produced by Moissan. At the time of his death in 1907, the Periodic Table ended with uranium, atomic number 92. If we exclude the noble gases including radon, the halogens including astatine, carbon itself, hydrogen, nitrogen, oxygen, phosphorus, and sulfur as nonmetals, we have a total of seventeen such elements. This leaves us with seventy-five metals including the metalloid, silicon, a very important carbide former. Six metallic elements, technetium, promethium, hafnium, rhenium, francium, and protactinium, were not discovered and isolated until long after the death of Moissan. Moissan prepared and published carbide preparations of thirty-one of the remaining sixty-nine metallic elements. Only the more important references will be given, as these elements are listed below in this section. Other references to the work of Moissan on these carbides will be cited as the elements are discussed individually.

At first glance, production of carbides for less than half the metals does not seem to be an imposing achievement but actually the reverse is true, as this section and the one immediately following will show. The work of Moissan on binary carbides was complete with analyses, reactions, and descriptive chemistry when published, and has remained largely, although not entirely, unchanged to the present day.

Moissan prepared both acetylides and carbides of the alkali metals lithium, sodium, potassium, rubidium, and cesium (229). In the family of alkaline earths, he made carbides of magnesium, calcium, strontium, and barium. He also made boron carbide and one of the beryllium carbides (Be_2C) (215, 218). In addition to producing silicon carbide or carborundum by more than one method, Moissan was one of the first to produce aluminum carbide, Al_4C_3 (223). Other elements between calcium, atomic number 20, and lanthanum, atomic number 57, from which Moissan made carbides and which have not been listed up to this point include titanium, vanadium, chromium, manganese, iron, yttrium, zirconium, niobium, molybdenum, and lanthanum itself (210). For the lanthanide series with atomic numbers between lanthanum and lutetium, atomic

number 71, working either by himself or with others, he produced carbides of cerium, praseodymium, neodymium, and samarium (210). The last four elements for which Moissan produced binary carbides were tantalum, for which a carbide had been previously produced by Joly in 1876, tungsten, thorium, and uranium (163, 210).

c. Elements without Carbides Studied by Moissan. Two of these elements were cobalt and nickel. For both of these metals, Moissan reported small solubility of carbon in the molten metal and separation of carbon as graphite with no carbide formation upon solidification (204). However, the carbides of nickel and cobalt were prepared at a much later time (147, 206). In two separate investigations, one in 1896 and another in 1906, Moissan reported that ruthenium, rhodium, palladium, iridium, and platinum also dissolved measurable amounts of carbon when molten, with all of this carbon precipitating as graphite without any chemical combination after freezing of the melt took place (225). These same five binary metal-carbon systems were studied again as recently as 1960 by Nadler and Kempter (236). Their findings were essentially the same as those of Moissan. The other four metals which Moissan reported as forming no carbides were tin, lead, bismuth, and thallium (219, 227).

The eleven metals for which Moissan reported no carbide formation, together with the thirty-one chemical elements for which he made binary carbides, give a total of forty-two. What about the other twenty-seven metallic elements known at the time of the death of Moissan in 1907? Four of these—copper, silver, gold, and mercury—had known and published carbides or acetylides when Moissan began his carbide studies about 1892 (33, 264). Due perhaps in part to experimental difficulties connected with their radioactivity, no carbides of polonium, radium, or actinium have been made. There are also no known binary carbides of osmium, indium, antimony, or tellurium. Among the six metals discovered after the death of Moissan, no carbides have been reported for promethium, rhenium, and francium.

A carbide of lutetium has now been thoroughly investigated and established, but preparation of carbides of the lanthanide metals, gadolinium, terbium, dysprosium, europium, erbium, and thulium, as well as of scandium (which is not a lanthanide), was not completed until after the close of World War II. The remaining six metallic elements, zinc, gallium, germanium, arsenic, selenium, and cadmium, have been reported as forming carbides usually by only one or two investigators, and therefore the existence of such carbides is doubtful. For example, in 1923 Durand (82) reported the formation of a lead carbide, PbC_2 , by adding calcium carbide to neutral lead acetate, but this has not been subsequently confirmed. This result is, of course, in contradiction to the findings of Moissan

on the lack of formation of any lead carbide upon the freezing of a mixture of carbon and molten lead.

II. General Methods of Carbide Preparation

A. BINARY CARBIDES

1. *Arc Fusion*

This was probably the first method of carbide preparation which differed considerably from previously used chemical methods. It is often called the "Moissan fusion method," as the high temperature of the electric arc causes chemical combination and carbide formation directly between the metal and carbon. This was the first method of preparation of carbides of tungsten, molybdenum, titanium, and zirconium. Commercial tungsten carbide, W_2C , is still prepared on a large scale by this method, particularly when cast shapes which can be poured from the carbide melt are desired (299). Due to inability to control the arc temperature closely, and to unwanted decomposition of many carbides under the arc, other electrical heating methods have been used, such as direct resistance heating of the oxide and carbon mixture or use of carbon tube or other type of electrical furnace used solely as a source of heat and a high temperature. Moissan used other electrical methods such as those just mentioned, and they are still in use.

2. *Carburization*

In order to have lower temperatures which can be more accurately measured and more closely controlled than those obtained in the arc method, the metallic powder or the powder of its oxide is reacted with carbon. The source of carbon may be finely divided sugar carbon or carbon black, which is mixed with the oxide and heated either in air or in a suitable protective atmosphere. Sometimes carbon is supplied in both solid and gaseous forms and, in other cases, the metal or metal oxide powder is carburized entirely by a gaseous mixture, usually of hydrocarbons.

Since most metals or their oxides react with carbon at temperatures far below their melting points, a temperature range of 1200°–2000°C is sufficient for forming many carbides. As the reactants are solids, they can be intimately mixed by milling. This often results in the formation of oxide films, and this, together with loss of carbon to some types of protective atmosphere, makes it necessary in some preparations to use an excess of 5–10 % of solid carbon over stoichiometric proportions. Due to closer temperature control and lower temperatures involved, this method is widely used. It is used for the commercial production of carbides of molybdenum, tungsten, and tantalum (292).

Gaseous phase carburization, the carbon source being vaporized hydrocarbons, methane, carbon monoxide, or mixtures of these, has been used mainly on wires of metals such as tungsten (314) and tantalum (30). It is not a commercial method. However, the carburization of tungsten powder, using carbon monoxide and methane separately, has been reported (144), and seems to have large-scale carbide production possibilities.

3. *Vapor Phase Deposition*

The principal difference between this method and the gaseous phase carburization just described is in the use of metallic halide vapors. This method, by which metallic halide vapors and gaseous hydrocarbons react and deposit their carbide product on a heated filament, was first used by Van Arkel (10) in 1923. Using this procedure, he prepared carbides of tantalum and zirconium of high purity. The method produces not only carbides, but metals such as titanium and zirconium essentially free of metallic contamination, except for the slight amount that might come from the filament on which the element or compound is deposited. As a result of this wide and continued use, the variables involved in the method have been extensively studied.

4. *Other Carbide Preparation Methods*

The extraction of carbides by strictly chemical means such as acids, or by the use of electrolysis of steels and ferrous alloys, was used at least as long ago as 1887. In that year, Shimer (312) prepared TiC by treating a titanium-bearing cast iron with hydrochloric acid. Many of the known mixed carbides have been extracted from alloy steels by this method. It does have large-scale applications for the production of tantalum carbide (197). A carbide which is a solid solution of tungsten and titanium for the metallic portion has been made in this way, and a patent granted (196). The variation from a conventional electrolytic extraction consists of introducing the carbides into superheated molten nickel for formation of the solid solution. After cooling, the nickel is extracted by acid, leaving the solid solution carbide. Some advantages are claimed for such carbides as cutting tools over single carbides produced by carburizing. The methods outlined so far are used especially in the production of the carbides of vanadium, chromium, titanium, tantalum, tungsten, and molybdenum, the carbides used for machine tools. There are other carbide production methods, some of which can be used for making carbides of several elements, while others are isolated instances in the literature in which a single carbide has been reported without subsequent confirmation. No claim is made that this section covers all methods for the production of binary carbides.

One of the methods in rather wide use is the double decomposition method of Moissan. The metallic oxide and calcium carbide are heated to a temperature high enough to cause reaction. The products are the carbide of the metal and calcium oxide. The carbides of aluminum, chromium, molybdenum, and tungsten were prepared thus by Moissan (227). All four of these elements had been previously made by him by the arc fusion method. Another method that has been studied considerably is fused salt electrolysis of carbonates under such conditions that free carbon and metal are formed, which then unite and form a carbide (8). Tungsten and molybdenum carbides have been made by this method, but not on a commercial scale. Some of the difficulties encountered in the fused salt electrolysis method include high temperatures with accompanying instability of the carbonates and amounts of carbon set free by the various reactions involved, which are too small and too variable for carbide formation.

The mass spectrometer method has been widely used for preparation and identification of minute amounts of many substances, as well as in the separation of complex mixtures. A single report of the production of gallium carbide, GaC_2 , by use of the mass spectrometer, was found (66). Within the evacuated spectrometer system, a graphite crucible and lid fitted with an effusion window were placed. The gallium contained in the crucible was melted by electron bombardment from a tungsten filament. The temperature was then raised by this means until enough gallium carbide vapors were produced to allow escape through the effusion window to the other portions of the mass spectrometer, where the carbide was identified. A report of a binary germanium carbide was also found. This element forms ternary carbides, which have been prepared repeatedly, but no confirmation of GeC has been found to date. In a French patent to Hamlet, granted in 1959 (130), a three-layer electroluminescent cell was described. One of the layers was stated to be GeC , with a thickness of 5–10 microns. It could not be determined from the patent abstract whether this carbide had been formed in the cell or otherwise prepared.

B. ACETYLIDES

1. *Preparation from Metallic Ammonia Solutions and Gaseous Acetylene*

The preparation of acetylides goes back at least a century to the work of Berthelot (32) and others. The first acetylides were prepared by passing gaseous acetylene C_2H_2 into aqueous solutions of the metallic ions, which had been made ammoniacal. The explosive acetylides of copper, silver, and gold were among the first to be made by this procedure. Somewhat later, the metal for which an acetylide was desired was dissolved in liquid

ammonia and acetylene gas was passed into the solution. Among the acetylides thus produced, those of sodium and potassium will be discussed briefly. The acetylide of sodium, NaHC_2 , is used in some organic syntheses, and its formation and decomposition to Na_2C_2 have been studied over the temperature range $100^\circ\text{--}183^\circ\text{C}$, and an equation for the dissociation pressure of the "hydroacetylide" NaHC_2 has been obtained (118). The behavior of potassium is, as usual, similar, forming KHC_2 in liquid ammonia, which then decomposes to the "normal" carbide K_2C_2 upon careful heating. Other typical acetylides prepared by the liquid ammonia method include those of rubidium and cesium (229).

2. Preparation from the Oxide Heated with Carbon

Typical of this method are the electric furnace formation of calcium carbide from calcium oxide and carbon, and the similar formation of diberyllium carbide, Be_2C , by heating the oxide beryl and carbon to 1300°C . Both of these substances have previously been discussed.

Different authors are not consistent in their use of the term "acetylide." The term originated in part from the fact that the three alkaline earths form CaC_2 , BaC_2 , and SrC_2 , which yield pure acetylene on contact with water (213). However, Mellor (203) refers to "carbide or acetylide." The preparation of substances, definite in composition by weight and in crystal structure, by use of the gaseous C_2H_2 seems to be logical justification for the term "acetylide"; so does the use of the term "hydroacetylide" for compounds such as NaHC_2 . Not all carbides yield pure or nearly pure acetylene when placed in contact with water. Aluminum carbide, Al_4C_3 , yields practically pure methane under such conditions. Moissan (216) found that the carbides CeC_2 , LaC_2 , ThC_2 , and YC_2 give mixtures of methane and acetylene.

The behavior of the uranium carbide to which Moissan assigned the formula U_2C_3 is still more complex. Upon contact with water, this carbide produced a gaseous mixture consisting chiefly of methane, but also containing ethylene and hydrogen. In addition to gases, solid and liquid hydrocarbons are obtained when this carbide decomposes in cold water.

C. TERNARY OR HIGHER CARBIDES

1. Ferrous Alloy Carbides

For research purposes, these carbides are usually prepared by preparing a steel melt and adding the proper alloys to make the desired carbides (183). Vacuum induction melting is usually followed where highest purity is desired. If the carbides are to be extracted from larger melts of steel, where results representative of commercial materials are

desired, more conventional methods are used, such as induction or arc melting (37). The carbides of high-speed steels have been studied by metallographic and X-ray means for many years (12, 360). So have the carbides of other alloy steels. In addition to these two very common techniques, electron microscopy and lineal analysis—counting of particles of carbides along a number of lines of known length—have been used to a lesser extent and more recently (153, 195).

In some investigations, X-ray diffraction patterns have been made on suitably ground and prepared steel specimens, and the carbides found on the patterns were then identified by comparison with knowns or by other standard diffraction methods (68). However, in most investigations the carbides have been extracted from the steel matrix and the extract studied. One of the reagents that has been used for carbide extraction is a dilute solution of HCl (5–10 % by volume). Dissolution of the steel by this reagent and analysis of the resulting carbide powder are at least as old as the work of Arnold (11) in 1914. The same reagent is still used, although at present electrolytic, rather than purely chemical, solution of the iron phase of the sample is usually employed (37). One of the advantages of the electrolytic technique over the use of only the acid is that the more rapid solution occurring, when the specimen is an electrolytic anode, reduces the danger of reaction of the reagent used to dissolve the iron with carbide phases present. Other difficulties that arise are formation of finely divided carbon as a soot, and flaking or peeling of the specimen, so that carbides are mechanically lost. A number of devices and a variety of apparatus and reagents have been used to overcome and reduce some of these difficulties. These include the construction of somewhat elaborate two-compartment electrolytic cells, use of a magnet to remove large flakes of the specimen from the carbide powder, and use of vacuum desiccators for drying, with admission of a limited and controlled amount of air to give slight surface oxidation for better storage. Two other reagents that have been used quite widely for electrolytic extraction of carbides from alloy steels are based, respectively, on citrate solutions and cadmium iodide. Investigations into the factors controlling electrolytic carbide extraction have been made by Blickwede and Cohen (36), and more recently by Gurry and others (126). Gurry and his co-workers made a quantitative study of practically all the reagents previously suggested for this purpose. They also used absolute methyl alcohol to prevent hydroxide formation, and a two-compartment cell. Cadmium iodide solution was found to be the most suitable electrolyte, and a hammer actuated by a cam, with the cam driven by a motor, was used to give constant removal of carbide from the specimen. This prevented reaction between the carbides and the reagent, as well as accumulation of a carbide layer on the specimen anode,

thus allowing faster solution of the specimen. With more widespread use of the electron microscope, particularly since commercial high-resolution instruments have become available, papers describing special techniques for extraction of the small amounts of carbides needed for electron microscope study have been published (80, 357). Objections to previously used methods include lengthy and uncertain procedures, and the use of a carbon support film 100 Å thick, which caused scatter and reduced resolution in electron microscopes, having a resolving power of 10 Å or less. Another fault of older electron microscopy replica methods was failure to remove very small carbide particles from the specimen.

2. Carbides of Indium, Germanium, and Tin

Ternary carbides of indium and germanium with the transition group metals nickel, cobalt, iron, and manganese have been prepared (231). A ternary carbide, having tin as the second element and manganese as the transition group metal, has been prepared and studied. The method used by Morgan to prepare these ternary carbides was to use an arc furnace under an inert atmosphere. The transition group metal and carbon were first melted and the third metal (indium, germanium, or tin) was then added. The argon atmosphere prevented volatilization first of the transition group metal, especially in the case of manganese, and then of the third metal of lower melting point which was also added last to prevent loss. Hutter and Stadelmaier made ternary carbides of indium and germanium with the same transition group elements that Morgan used, but using a high-frequency induction furnace and a graphite container for their charges (157).

III. Simple Carbides with Important Applications

A. ABRASIVE OR REFRACTORY CARBIDES

1. Boron

The first preparation of a boron carbide in an amount large enough for extensive study was by Moissan (218) in 1893. This was by an arc method. Between 1894 and 1905, several electric furnace methods for preparing boron carbide were devised. These are described by Hebert (137). In many instances the charge was contained in a carbon crucible. If extra carbon was needed, sugar carbon was usually used. The source of boron was either boric acid or amorphous boron prepared by use of magnesium (220). The arc method is still used for large-scale production. Scott (305), in a patent granted in 1964, describes a presently used electric furnace. The outer walls are formed by a steel cylinder cooled by a water spray.

The charge consists of B_2O_3 and coke, together with partially converted material from a previous run. Two electrodes are placed in the charge and a U-shaped current path is arranged so that, as the electrodes are raised, the boron carbide forms as two ingots, one beneath each electrode. The design is such that more material can be charged during the run. Initial current is 4000 amp at 120 V, increasing to about 6700 amp during most of the operation.

A higher purity boron carbide is produced by vapor phase deposition. Mierzejewska and Niemyski (207) produced pure crystalline boron carbide by thermal decomposition of BCl_3 and CCl_4 vapors on the surface of a heated graphite rod. A hydrogen carrier was used to regulate flow rate, and to help formation of boron carbide by removal of HCl from the reaction zone. Crystals 3–4 mm long were obtained under optimum growth conditions, which were stated to depend on flow rate and amount of hydrogen present with a temperature range of 1550°–1650°C. A British patent (143) describes production of boron carbide by treating BCl_3 vapor with methane at 1700°–2000°C and a pressure of about 5 mm Hg. Another report describes the production of boron carbide whiskers up to 1 cm in length by evaporation of boron carbide into vapor, which is carried by an appropriate gas flow over a heated substrate. The whiskers thus formed on the substrate were stated to support stresses up to 965,000 psi in tension, with an indicated modulus value of approximately 65×10^6 psi. These boron carbide whiskers were produced in connection with a study of the deposition of boron carbide as a strengthening material for an epoxy-based structural composite (106).

As a refractory, boron carbide has low thermal shock resistance and only fair resistance to oxidation at high temperatures. In a study of the use of boron carbides in cermets, it was found by Hamjian and Lidman (129) that, by milling commercial boron carbide powder of good purity with steel balls and allowing an intentional iron pickup, thermal shock resistance and oxidation behavior were both considerably improved. The iron-containing boron carbide powder after sintering withstood up to 25 cycles of thermal shock at 1800°F, compared to 3 and 9 cycles for two similar specimens without an iron addition. Oxidation behavior measured by unit weight loss at 1600°F was about two-thirds that of iron-free boron carbide.

A recent British patent (109) has been granted on the use of a mixture of boron carbide and boron nitride or diamonds as an abrasive. In this connection it is interesting to note that, in his discussion of boron carbide as known in 1905, Hebert (137) mentions that Moissan, during his researches on diamonds, found that boron carbide was hard enough to very slowly cut facets on diamonds.

The boron carbide produced in large quantity is usually given the formula B_4C . However, in a publication appearing in 1966, Lipp (189) states that the unit cell of boron carbide contains three B_4C molecules and therefore should be assigned the formula $B_{12}C_3$. Study of the bond lengths showed that boron carbide is predominantly covalent, and that one of the three carbon atoms can be replaced by another metallic element such as silicon or aluminum. This led to the discovery of a new class of compounds, $B_{12}C_{3-n}M_n$, in which M represents a substituted metal atom. In collaboration with Roder (190), Lipp published two subsequent papers on these compounds. The first describes the compound obtained when the substituted atom is aluminum, the second the result of making the M atom silicon. In a mass spectrographic study of the boron-carbon system, Verhaegen and his co-workers (353) identified as gaseous species the molecules BC_2 and B_2C . In addition to identifying these other two boron carbides in a gaseous state, they also measured their respective atomization energies.

2. Silicon

Space limitations do not permit a detailed review of the very large number of papers on silicon carbide, SiC , also commonly called carborundum. The original process, which Acheson (3) first patented in 1893, is still used for large-scale production. A coke core is placed between two graphite electrodes to give a conducting layer, which is then covered with sand to a height of about 8 feet in the center of the pile. At the start of the run, a current of about 1700 amp at 165 V is used. After some 90 minutes, the current is increased to 6700 amp. Both amorphous and crystalline silicon carbides are obtained as products.

The fact that the vapor phase method was used by Moissan in addition to the arc method for making SiC was mentioned previously. Commenting on the Acheson process in his book, Moissan (211) states that, in the Acheson method, there are a large number of small arcs of varying intensity along the length of the charge when the current is first established, rather than a single arc as is usual in other types of electric arc furnace. He further states that the current does not attain a steady value until some 5 hours after the beginning of the run. The Acheson process for producing SiC was in commercial operation at the time that Moissan began his study of the electric furnace and compounds such as carbides and nitrides in 1892.

A typical method for preparation of high-purity SiC is that of Merz and Adamsky (205). By the thermal decomposition of CH_3SiCl_3 in hydrogen at $1500^\circ \pm 50^\circ C$, a high-purity silicon carbide of wurtzite

structure was obtained. The present status of silicon carbide as an abrasive and refractory has been reviewed by Parche (251).

The number of different structural forms, or polytypes, of SiC is so large that two different notations, one due to Ramsdell (265) and one due to Zhdanov (374, 375), are in use to designate them. According to Verma (354), over forty different polytypes have been described, and no one theory is able to provide a completely satisfactory explanation for the growth of all the structural types. Certain features of some of these structurally different forms fit a screw dislocation growth theory, but many other growth features do not (313, 355).

3. *Titanium*

The binary carbides of the Group IV metals—titanium, zirconium, and hafnium, the Group V metals—vanadium, niobium (columbium), and tantalum, and those of Group VI—chromium, molybdenum, and tungsten—have been critically reviewed with respect to their high-temperature use by Storms (323). His survey covers the literature on the carbides of these nine transition metals as well as the carbides of uranium, thorium, and plutonium. Much of the earlier work on the high-melting transition metal carbides, especially where property measurements are concerned, is stated by Storms to have little value due to varying oxygen content in the carbides made by these earlier investigators.

Titanium, zirconium, and hafnium all form only one carbide having a simple NaCl-type structure. This structure is maintained over a wide composition range which, according to Storms (325), extends to $\text{TiC}_{1.0}$ and $\text{HfC}_{1.0}$, respectively, but ZrC apparently is not found as a single phase at $\text{ZrC}_{1.0}$. The separation of a titanium carbide from cast iron by Shimer in 1887 (312) was mentioned earlier. Commercially, most TiC is still prepared by arc reduction of TiO_2 with carbon, the method described and published by Moissan (224) in 1895. This method yields a titanium carbide satisfactory for hard metal use, but the product thus obtained has a variable amount of oxygen, and drastic modification of the arc method or use of different methods is necessary for preparing a pure oxygen-free TiC.

Three methods that produce titanium carbide of high purity are the vapor deposition method, use of calcium carbide, and special arc melting methods. Vapor deposition from TiCl_4 , hydrogen, and hydrocarbon vapor, with the formation of the titanium carbide on a tungsten wire, was developed by Campbell and others (61) in 1949. If calcium carbide free of hydroxide and oxide is used, the reaction between CaC_2 , TiCl_4 , and H_2 at 800°C yields a pure TiC, calcium chloride, and gaseous HCl as

products. The carbide can be washed free of calcium chloride and calcium carbide with water. This method was published by Imai and others (158) in 1957. In principle it follows the old double decomposition method of Moissan, but varies from the original method in the use of gaseous reactants. Cadoff and Nielsen (60) prepared a pure TiC by the arc method. They used iodide titanium and spectroscopic grade carbon as the starting materials. Oxygen and nitrogen contamination were prevented by first evacuation to a low pressure, argon flushing, and melting under a partial pressure of specially purified argon. The leak rate of the furnace was also held to a low and controlled value.

The sodium chloride structure extends from $\text{TiC}_{1.0}$ or very nearly integral stoichiometry down to $\text{TiC}_{0.49}$. As an example of the drastic changes of properties when enough carbon is removed to leave the TiC single-phase field (below $\text{TiC}_{0.49}$), Storms (324) states that the hardness is halved, although the contraction in lattice parameter is only 0.01 Å. In spite of this, titanium carbide of high purity is certainly one of the three hardest carbides formed by any of these nine metals, and may have the highest penetration hardness. The oxygen present in commercial material does not cause appreciable hardness loss for refractory or cutting tool applications, but causes so much variation in quantitative values that measurements without an accompanying statement of the oxygen content of the TiC tested are of no significance. The other pure monocarbide that may equal or exceed TiC in hardness is VC.

4. Zirconium

A zirconium carbide mixed with graphite made by use of the electric arc was prepared by Troost (346) a century ago in 1865. Until the separation of hafnium from zirconium in 1923, all zirconium carbides contained hafnium as an impurity. In addition, for the same reasons discussed for the preparation of titanium carbide, oxygen and nitrogen may be present even when zirconia or zirconium metal free of hafnium is used as a starting material. The reduction of ZrO_2 with carbon takes place in three steps with formation of Zr_2O_3 , then ZrO , and finally ZrC . Long heating under a partial vacuum reduces the oxygen content of zirconium carbide thus prepared to a low value, but Storms (326) states that there is no reliable analytical method for oxygen under these particular conditions.

In order to obtain a carbide with low oxygen content, carbon is reacted with zirconium metal or zirconium hydride. Another similarity between preparation of zirconium and titanium carbides is that diffusion and reaction between carbon and the metal are slow even when the temperature is high enough so that liquid is present. Vapor phase deposition from a mixture of ZrCl_4 , hydrogen, and gaseous hydrocarbons produces a

pure crystalline ZrC. The reaction temperature range is 1730°–2430°C. Both ZrC and TiC prepared in this way were reported in the same 1949 publication by Campbell and his associates. In the investigation of the zirconium-carbon system published by Sara in 1965, the starting materials were zirconium hydride and spectrographic grade graphite powders. Impurities in the graphite were stated to be under 0.5 ppm; the zirconium hydride contained hafnium 94 ppm, nitrogen 80 ppm, and hydrogen 2.12%. The powders were mixed, presintered under vacuum at 800°C, and then heated to desired temperature-reaction ranges in vacuum resistance furnaces up to a temperature level of 2850°C. Above this temperature, a special flux concentrator was employed in which either vacuum or gaseous atmosphere could be used.

Sara (286) used metallographic techniques, differential thermal analysis, and X-ray diffraction methods in addition to melting point determinations and chemical analysis in his investigation. He reported the maximum on the liquidus for single-phase ZrC of NaCl-type structure at 3420°C and approximately 46 atomic % carbon. At 1800–3200°C Sara reported the lower composition limit of the ZrC phase field as 38.5 atomic % carbon. In agreement with the work of Farr as quoted by Storms (99), Sara found the carbon-rich side of the ZrC field at 49.4 atomic % carbon at 2400°C, and at 49.1 atomic % at a eutectic temperature of 2850°C. On the basis of his own work, Sara reported a limit for the ZrC field at 3200°C at 48.9 atomic % carbon. Hence, as was mentioned above, zirconium monocarbide ZrC apparently does not extend to integral stoichiometry. Both Storms and Sara also found that the lattice parameter of ZrC has a maximum. Sara reports this maximum at 48.5 atomic % carbon. Compositions richer in carbon but still in the single-phase field show lower lattice parameters. This behavior is unusual.

The chief technical use of zirconium carbide is as a component of cemented hard metal cutting tools. Cobalt is often used as a metallic binder. Due to a comparatively low price for zirconium oxide of high purity as a starting material, as well as the ability of ZrC to form solid solutions with other carbides, attractive practical possibilities exist (300). Applications of zirconium carbide for limited use and of small practical importance include using the substance as an electrode material, for refractory crucibles, or as incandescent filaments. Due to the low neutron capture cross section of zirconium, there are nuclear applications of both the metal and the carbide. Zirconium carbide has been used as a coating 1–2 mm thick to delay release of fission products from uranium carbide fuel elements (28). Measurements of properties of fuel elements in the form of rods of $U_{0.5}Zr_{0.5}C$ have been reported (122). Thermal emission and electrical conductivity were among the properties studied.

5. Hafnium

The same preparation methods discussed for the carbides of titanium and zirconium are used in making HfC. At temperatures of 1800°–2000°C, reduction of HfO₂ with carbon yields hafnium carbide. Long heating under vacuum is necessary to remove small amounts of oxygen so that HfC_{1.0} is closely approached. Vapor deposition of HfC on a tungsten filament from a mixture of HfCl₄, hydrogen, and methane produces high-purity material. This type of preparation of HfC was also reported in the work of Campbell and others in 1949 (61). The vapor phase technique was apparently first applied to the production of hafnium carbide by Moers (208) in 1931. In 1959 Nowotny and his associates produced oxygen-free hafnium carbide by the reaction of hafnium hydride (HfH) and carbon (245).

The hafnium-carbon system shows a single carbide of NaCl-type structure existing over a wide composition range, which apparently extends to HfC_{1.0}. Choice of the best value of lattice parameter is complicated by the presence of zirconium, oxygen, and nitrogen, as well as by carbon deficiency and the fact that, as HfC_{1.0} is approached, the lattice parameter becomes almost independent of composition. Based in part on his own work, Storms (327) quotes a value of 4.639 Å for oxygen-free HfC_{1.0} containing no zirconium. He also states that, in view of the maximum in lattice parameter with variation in carbon content known to exist in the zirconium-carbon system, the possibility of a similar occurrence for HfC cannot be excluded. The lower limit of the single-phase HfC at 1550°C was placed, by Benesovsky and Rudy in 1960, at 37 atomic % carbon (31). Apparently the only fairly recent phase diagram for the system hafnium-carbon also appeared in this same 1960 paper. It was reprinted with very little change by Kieffer and Benesovsky in their review of transition metal carbides, which appeared in 1964 (174).

In 1930 Agte and Alterthum (6) published melting point values for a number of the carbides of these same nine transition group metals. Among their melting point values were: HfC 4160° ± 150°K (3887°C), and TaC 4150° ± 150°K (3877°C). The value for hafnium carbide has been quoted widely in the literature since then, accompanied in many cases by statements that HfC was the highest melting or one of the highest melting carbides. These melting points were determined by use of a calibrated optical pyrometer by the method of Pirani and Alterthum (260), in which a rod-shaped specimen is heated by passing a strong direct current through it. A small hole is drilled obliquely to the axis of the rod to provide a black body for temperature determination. For metals, liquid will flow out of the hole when fusion occurs; with carbides, the melting point is taken as the temperature at which liquid appears at the bottom of the

black body hole. It is interesting to note that, in their original determinations, Agte and Alterthum gave the melting points of tantalum carbide and hafnium carbide as being only 10 degrees apart. Later publications tended to show hafnium carbide melting at least 100 degrees above tantalum carbide. In 1962 Russian workers (20) published a melting point for $\text{HfC}_{0.91}$ of only 3520°C. This material was contaminated with oxygen. However, in 1963 Adams and Beall (4), working with hafnium carbide that contained 2 % by weight zirconium, oxygen, and nitrogen averaging 260–420 ppm and 70–110 ppm, respectively, found substantially the same melting point for hafnium carbide as that of Agte and Alterthum. Stoichiometric HfC contains 6.3 % by weight carbon; the zirconium content of the material used by Beall and Adams raised theoretical total carbon content to 6.42 %. Using a specially built melting point apparatus after the design of Agte and Alterthum, and a calibrated optical pyrometer, they found the following melting points: carbon 5.29 %, 3880°C; carbon 5.81 %, 3795°C; carbon 6.22 %, 3895°C; carbon 6.59 %, 3870°C. The melting point uncertainty is stated as $\pm 150^\circ\text{C}$. Rudy and Benesovsky also used a value of 3900°C for the melting point of stoichiometric HfC in the phase diagram of the Hf-C system published in 1960. Beall and Adams found their maximum melting point lying at a composition to the left of $\text{HfC}_{1.0}$. On the other hand, Storms (330) gives the melting point of TaC as 4000°C at a composition of $\text{TaC}_{0.8}$ in his phase diagram of the Ta-C system published in 1964.

Due in part to scarcity and higher cost, hafnium carbide has found limited use in hard metal cutting tools. Recent lowering in the price of hafnium-containing starting materials may change this. The high melting point of hafnium carbide makes it useful for applications such as nuclear rocket nozzles and other such rocket parts (69). A French patent has recently been granted on the plasma flame spraying of hafnium, titanium, and zirconium carbides (76).

6. Vanadium

Methods of preparation of vanadium carbides closely follow those previously discussed for hafnium, titanium, and zirconium carbides. Moissan's preparation of a carbide having a formula close to $\text{VC}_{1.0}$ was mentioned previously. Starting with coal ashes having a vanadium content, he prepared V_2O_5 . Mixing this with sugar carbon, he heated the mixture electrically in a carbon tube to obtain the carbide in a crystalline form. Commercial production of vanadium carbide is from graphite mixed by ball milling with ammonium vanadate, vanadium pentoxide, or vanadium sesquioxide as the source of vanadium. In a few cases vanadium metal powder is used (293). After pressing into compacts the mat-

erial is carburized under hydrogen at 1800°C. The product of this first carburization ranges from 15.8 to 16.9 % by weight combined carbon. The theoretical carbon content for vanadium monocarbide $VC_{1.0}$ is 19.08 % by weight. A second carburization of commercially produced crude carbide under vacuum at 1600°–1700°C raises the combined carbon content to as much as 18.5 % by weight. Free graphite is found in almost all commercial products. Some of the difficulty in attaining a carbide that is truly $VC_{1.0}$ is due to the formation of isomorphous vanadium nitride and vanadium monoxide. Another method of obtaining vanadium carbides is from vanadium-containing alloy steels by dissolving away the iron matrix in suitable solvents.

Vapor phase deposition of vanadium monocarbide on a tungsten wire was reported by Moers (208) in 1931, and by Campbell and others (61) in 1949. The gaseous materials used were VCl_4 , hydrogen, and a hydrocarbon. The temperature range of carbide formation is 1500°–2000°C. Difficulty due to formation of vanadium metal, which then alloys with the tungsten deposition wire so that separation is not possible at high filament temperatures, is encountered. To overcome this, the temperature is first held at about 1430°C until a layer of vanadium carbide of sufficient thickness is formed to cover the filament and enable a clean separation of the deposited material. The temperature can then be raised to 1500°–2000°C for more rapid carbide formation and deposition. According to Storms (328), another objection to the vapor deposition method is that a product of varying composition is obtained. However, single crystals of vanadium carbide can be produced by the vapor deposition method.

Freedom from nitrogen, carbon monoxide, and especially oxygen is also necessary to produce a vanadium carbide of uniform composition and high combined carbon content. With pure starting materials, a carbide free of impurities can be produced by careful arc melting. Upon powdering the arc melted button, or by slow reaction upon exposure to air, recontamination will take place. Storms recommends using powdered vanadium metal or vanadium hydride with carbon as starting materials, and melting in a good vacuum (under 10^{-5} torr). By using a graphite crucible and holding somewhat below the melting point, volatile metallic impurities will also be removed. In contrast to TiC and HfC, vanadium monocarbide does not reach $VC_{1.0}$. The phase diagram of Storms and McNeal (337) published in 1962 shows the single-phase VC field extending to $VC_{0.88}$ at 1000°C, and having a slightly lower carbon content at the temperature of peritectic decomposition near 2650°C. The lower limit of the monocarbide field is from $VC_{0.60}$ at 2165°C to $VC_{0.72}$ at the base temperature of the diagram, 1000°C.

The vanadium-carbon equilibrium diagram also illustrates another

feature common to the carbide systems of the three metals of this group—vanadium, niobium, and tantalum. This is the confirmed existence of a second carbide usually represented as V_2C , Nb_2C , or Ta_2C . All three of these compounds show structures belonging to the hexagonal system. Another feature common to all three of these metal-carbon systems is the existence of one or more rather unstable carbides of unknown crystal structure, which are often approximated as M_3C_2 ($M = V, Nb, \text{ or } Ta$). The V_2C phase forms peritectically at $2165^\circ C$ having a composition at this temperature of $VC_{0.56}$; the composition at the eutectic temperature ($1630^\circ C$) is $VC_{0.33}$. At the base temperature of $1000^\circ C$, the V_2C field extends from $VC_{0.47}$ to $VC_{0.50}$. The eutectic horizontal extends from $VC_{0.09}$ to $VC_{0.33}$. The solubility of carbon in solid vanadium is reported as less than $VC_{0.01}$ at $1000^\circ C$ (125). Therefore hexagonal V_2C extends practically to pure vanadium at temperatures lower than about $1100^\circ C$. As would be expected from periodic relationships, the systems niobium-carbon and tantalum-carbon also show a eutectic as carbon is added to the liquid metal, with formation of an M_2C carbide by a peritectic reaction at higher carbon content and at a higher temperature.

The principal use of the carbides of vanadium is in alloy steels. They have been used to a limited extent in solid solution with other carbides for hard metal cutting tools. Although vanadium carbide is easily produced and relatively inexpensive for a hard metal carbide, it has found little use thus far because commercial vanadium carbide is thought to be of insufficient cutting hardness. According to Storms (329) and Gurevich and Ormont (125), this is not true of a vanadium carbide uniform in composition and high in carbon content, such as $VC_{0.88}$. Material of this kind and composition will show a penetration hardness reading exceeded only by TiC .

7. Niobium

This chemical element is often referred to in the United States as columbium. In this review, it will be designated as niobium. The monocarbide can be formed by the Van Arkel vapor deposition method, as is true for the other Group IV and V metals reviewed. The first niobium carbide was produced by the reduction of $K_2O \cdot 3Nb_2O_5$ with carbon at a temperature of about $1500^\circ C$ by Joly (164) in 1877. Large-scale production of niobium carbide uses Nb_2O_3 , Nb_2O_5 , or niobium metal powder. This is heated with carbon black to $1300\text{--}1400^\circ C$ in a carbon tube furnace. Freedom from oxygen for technical purposes is stated to present no special difficulties (294). A niobium carbide of higher purity can be prepared by careful reduction of Nb_2O_5 or by heating elemental niobium and carbon powders properly mixed, provided a sufficiently high temperature

is reached. Storms and Krikorian (336) found that heating in vacuum for 30 minutes at 1900°C eliminated 0.28 % by weight oxygen and 0.66 % nitrogen in a commercial NbC sample. However, to react all the carbon in this type of material required much longer times. At 1800°C elimination of free carbon required about 38 hours. Use of a hydrogen atmosphere or a higher temperature shortens the carbon elimination time considerably.

Among the differences between the phase diagrams for the vanadium-carbon and niobium-carbon systems are the higher temperature ranges for Nb-C. Storms shows a maximum melting point for the NbC phase field of near 3500°C at a composition $\text{NbC}_{0.86}$. At the base temperature of 1500°C the NbC field extends very nearly to $\text{NbC}_{1.0}$. The composition and temperature of maximum melting were given by Engelke and others (95) in 1960 as 3420°C for a composition $\text{NbC}_{0.92}$, estimated from the lattice parameter. In 1958, using the same arc melting method, Brownlee (55) obtained 3485°C for $\text{NbC}_{0.95}$. In his diagram of the Nb-C system published in 1964, Storms shows a horizontal line extending to the right from the high-carbon boundary of the NbC field at a temperature of about 3300°C. There is evidence that this is a eutectic horizontal. Storms states that this illustrates the fallacy of expecting the maximum melting point to appear at the stoichiometric ratio, as $\text{NbC}_{1.0}$ melts some 200°C below the maximum melting point attained at a composition containing slightly less carbon. Formation of hexagonal Nb_2C is by a peritectic reaction analogous to the peritectic formation of hexagonal V_2C . Storms shows this peritectic temperature as 3090°C, while the peritectic temperature in the V-C system is only 2165°C. The extent of the Nb_2C field at the base temperature of the diagram is very narrow and not fully confirmed. It apparently extends to $\text{NbC}_{0.5}$ and is shown by Storms as bounded at this value. The corresponding region of the V_2C phase field is appreciably wider. Another difference between the two systems is the existence of small but measurable solid solubility of carbon in niobium metal. The body-centered cubic terminal solid solution (designated "alpha" by Storms) extends from a maximum of $\text{NbC}_{0.08}$ at the eutectic temperature (2335°C) to only 100 ppm at 1500°C.

Niobium carbide used alone has not found cutting tool applications. As is also the case for the vanadium carbides, solid solution carbides containing fairly large amounts of NbC have found limited use. For special applications, where a material free of tungsten carbide is desirable and where high wear resistance is not required, NbC-cobalt, VC-NbC, and NbC-TaC mixtures have been used (302). Niobium carbide has also been used to improve the stability of uranium monocarbide (UC) fuel elements (368). Using powder metallurgy methods, UC-NbC and UC-ZrC solid

solution carbide pellets were formed for possible use in high-temperature gas-cooled reactors. Some of the advantages found included increased resistance to water corrosion, prevention of undesirable lattice transformations in UC with accompanying dimensional changes, increased compatibility with graphite to 2000°C, and increased resistance to atmospheric oxidation. The extension of compatibility with graphite to 2000°C required that the NbC content be above 63 mole %.

8. *Tantalum*

Tantalum carbide was made by Joly (163) in 1876, a year before his production of niobium carbide. The method used was heating Ta_2O_5 or tantalites with sodium carbonate and carbon at about 1500°C. Other preparation methods are very similar to those used for obtaining niobium or vanadium carbides. Tantalum carbide can be made by the vapor deposition method with suitable modifications in technique to prevent deposition of tantalum metal on the tungsten wire. The menstruum method with aluminum as menstruum has also been used. Arc melting may be employed; however, it tends to produce a carbon-deficient TaC. Commercial TaC can be made by carburizing an intimate mixture of Ta_2O_5 and carbon black at either 1700°C under purified hydrogen or at 1600°C in vacuum (295). This carbide can also be made cheaply by melting a ferrotantalum alloy high in tantalum (60–70 %) in an induction furnace and adding enough carbon to make the melt viscous. After cooling, the brittle melt is crushed and the tantalum carbide extracted by treatment with HCl. The carbon-deficient material thus obtained is mixed with carbon and carburized under hydrogen at 1600°–1700°C.

Preparation of high-purity tantalum carbide usually begins with carefully outgassed elemental powders. The procedure adopted by Lesser and Brauer (188) was to heat the powdered mixture in a graphite crucible under vacuum at 1000°C until reaction began with gas and heat evolution. After cessation of gas evolution, the temperature was raised to about 2000°C and held 15 minutes. After cooling, the product was powdered to aid diffusion of carbon. The powder thus obtained was then reheated, and this heating and powdering cycle was continued until a pure product was obtained. High temperature and a hydrogen atmosphere aid in the formation of pure tantalum carbide in a shorter time. In general, oxygen and nitrogen are more difficult to remove from tantalum carbide than from niobium carbides containing the same amounts of these two gaseous impurities.

The phase diagram for the tantalum-carbon system is similar, in most respects, to that of niobium-carbon. Terminal solid solubility exists at the tantalum end; there is a eutectic between the terminal solid solution

and hexagonal Ta_2C , which in turn is formed by a peritectic reaction from TaC and liquid at a higher temperature. TaC has a wide range of temperature and composition existence. In composition, the monocarbide phase field extends to or attains the stoichiometric ratio $\text{TaC}_{1.0}$. Eberle and others (83), in a 1966 publication, state that at a temperature of 2000°C the monocarbide extends from $\text{TaC}_{0.8}$ to $\text{TaC}_{1.0}$. The diagram of Sara and Lowell (285) in 1964 places the carbon-rich TaC boundary at 49.5 atomic % carbon at 2250°C , with the low-carbon boundary for this same temperature at 41.7 atomic % carbon. TaC, in a manner similar to NbC, also melts at a very high maximum temperature and an accompanying carbon content less than stoichiometric.

The other principal feature of the Ta-C system is the proven existence of a TaC-C eutectic. All of the above features appeared on the first complete diagram of the tantalum-carbon system, published by Ellinger in 1943 (85). This carbon-rich TaC-C eutectic is placed, by Sara and Lowell, at 61.2 atomic % carbon at a temperature of 3375°C . They also place the temperature of peritectic formation of Ta_2C at 3240°C , with no change from stoichiometric Ta_2C below this temperature. The low-carbon boundary at the eutectic temperature of 2825°C is at 26.5 atomic % carbon. Above the eutectic temperature, the $\text{Ta}_2\text{C}/\text{Ta}_2\text{C} + \text{liquid}$ boundary was found at 29 atomic % carbon. Below the eutectic Ta_2C again becomes richer in carbon by a slight amount. The peritectic formation and the limits of the Ta_2C phase field are not completely confirmed.

The chief point of interest for the Ta-C system is the maximum melting temperature and accompanying composition of the monocarbide TaC. The melting points of TaC at 3877°C and of HfC at 3887°C , made by Agte and Alterthum in 1930, were mentioned in connection with the Hafnium-carbon system. A melting point for $\text{TaC}_{0.8}$ of 4000°C , given by Storms in his 1964 phase diagram for Ta-C, is based on drawing the solidus in this region to match the general shape of the similar Nb-C diagram (330). On the basis of extensive experiments by different methods, Sara and Lowell (285) place the maximum melting point of TaC at 3825°C ($+100^\circ$, -0°) and at a composition of about 48.5 atomic % carbon. Sara (287), in a paper published late in 1965, using the same techniques employed for determining the melting point of TaC, gives a maximum melting value for HfC of 3830°C at a composition containing 47.5 atomic % carbon. This value was based on melting values obtained from some fifty hafnium carbide samples. The composition range of this maximum melting region was found to be only about 2 atomic % carbon wide, dropping almost vertically to 3150°C on the high-carbon side. On the hafnium-rich side, the decrease in temperature of the solidus was more gradual, but the formation of liquid in large amounts prevented unimpaired recovery of

the samples for chemical analysis. Thus, after some 35 years, the melting points of these two refractory carbides seem to remain within the uncertainty range originally given by Agte and Alterthum.

Primary interest in tantalum carbide has been in its use as a refractory during the last decade. Although TaC does not have the extreme hardness of TiC or VC, it is important in carbide cutting tools because of its tendency to reduce the welding tendencies of the steel chips removed by the cutting tool. In solid solution mixtures with other carbides, TaC has been used to obtain tungsten-free cutting tools for use during time of war when countries, such as Germany during World War II, were cut off from supplies of tungsten (301).

9. Chromium

The phase diagram for the chromium-carbon system, published by Bloom and Grant (38) in 1950 and republished by Schwarzkopf and Kieffer, unchanged, in 1964, shows three chromium carbides. Cr_3C_2 decomposes peritectically slightly above 1900°C ; Cr_7C_3 , also peritectically, at 1782°C . The third carbide of chromium to which Bloom and Grant assigned the formula Cr_4C , but which is now most often referred to as Cr_{23}C_6 , forms by a third peritectic reaction at 1518°C . The respective crystal structures are: Cr_3C_2 , orthorhombic with 20 atoms per unit cell; Cr_7C_3 , hexagonal with 80 atoms per unit cell; and Cr_{23}C_6 complex face-centered cubic with 116 atoms per unit cell. Other carbides have been reported, particularly CrC, which Bloom and Grant made repeated unsuccessful attempts to produce. Hansen and Anderko (132), in their review of this binary carbide system and accompanying diagram published in 1958, also found insufficient evidence for the inclusion of CrC. In his critical review of refractories published in 1964, Storms (331), states that the work done on the chromium-carbon system does not furnish sufficient information to warrant the construction of a valid phase diagram. The only one of three chromium carbides with a melting point high enough to be of refractory or cutting tool interest is Cr_3C_2 . The melting point of this compound at about 1900°C is almost the same as that of the metal chromium at 1875°C . In explanation of the fact that the metals of Group VI (Cr, Mo, and W) have higher melting points, although their carbides have lower melting points, Storms suggests that the strong metal-to-metal bonds, which are broken by dissolved carbon, are not replaced by stronger metal-carbon bonds in the carbide. This formation of stronger metal-carbon bonds, especially in the formation of hafnium and tantalum carbides, is borne out by the heats of formation. In Group VI, the carbide heats of formation are much lower and the carbides are much less stable than those of Group IV (Ti, Zr, Hf) and Group V (V, Nb, Ta).

Historically, the first production of a chromium carbide was by Moissan (212) in 1893. Using an inclined carbon tube electrically heated, he produced 20 kg chromium metal by reducing Cr_2O_3 with carbon. By the use of a large excess of carbon, masses of crystals of Cr_3C_2 were obtained. The carbide to which Moissan assigned the formula Cr_4C was found in the form of short reddish brown needles on the chromium ingots he prepared. Technical preparation of Cr_4C_2 is still by reduction of Cr_2O_3 (296). Powder compacts containing 3 parts Cr_2O_3 and 1 part carbon black, intimately mixed and pressed, are heated to 1600°C in a carbon tube furnace under hydrogen. For best results, this temperature must be maintained fairly closely, as the lower carbides form under the same conditions at lower temperatures. Below 1300°C , the major product is Cr_7C_3 . Due to the importance of chromium in alloy steels, many of the studies on chromium carbides have been made on material isolated from these steels. Iron is also a major impurity in chromium metal. For these reasons, much of the published work is on Fe-Cr-C rather than the binary chromium-carbon system. Thermal decomposition of chromium carbonyl (250) produces a layered mixture of Cr and Cr_3C_2 . Chromium carbides can also be produced by arc heating of the elemental powders but, due to the high vapor pressure of chromium at its melting point, metal losses by vaporization are considerable.

Cr_3C_2 has been used with limited success in carbide cutting tools low in tungsten or tungsten-free. In this case, it is used in small amounts in conjunction with other carbides. Large amounts (60–85 % Cr_3C_2) of this chromium carbide, used with a nickel or copper-nickel binder free of cobalt, form a material that is acid-resistant and wear-resistant of special use for valve parts in the chemical industry (174). A cermet containing about 35 % Cr_3C_2 , together with TiC , and nickel as an infiltrating agent, has been prepared and used with some success by Kaizo and Suto (168). In such applications, the chromium content gives a marked increase in resistance to atmospheric oxidation.

10. Molybdenum

There is general agreement that slight but measurable terminal solid solubility of carbon in molybdenum exists, and that the eutectic between the molybdenum-rich alpha solid solution and the Mo_2C phase is at about 2200°C (83). Mo_2C is the only carbide of molybdenum stable thermodynamically below 1000°C . The width of this phase field is placed, by Storms (332), at $\text{MoC}_{0.44}$ to $\text{MoC}_{0.50}$ from a base temperature of 1000°C to the eutectic temperature at 2200°C . The formation of Mo_2C takes place by a peritectic reaction at a temperature of about 2400°C . This is the only molybdenum carbide having any practical use. The crystal structure of

Mo_2C was formerly believed to be hexagonal but, since the neutron diffraction determination of Parthe and Sadagopan (252) in 1963, an orthorhombic Mo_2C seems to be quite firmly established.

The diagram published in 1966 by Eberle and others (83), as well as the Mo-C diagram of Kieffer and Benesovsky (174) 2 years earlier, shows MoC as melting congruently with the maximum on the liquidus at slightly above 2500°C . The 1964 diagram also shows the MoC (or gamma) phase participating in a eutectic with carbon at 2470°C . Eberle states that at 2000°C the homogeneity ranges in the entire Mo-C system are not worth mentioning. There has been considerable disagreement in the literature over the formulas and crystal structures of reported molybdenum carbides, richer in carbon than Mo_2C . Elliott (87) lists ten "MoC" phases with hexagonal close-packed, hexagonal, face-centered cubic, and WC-type structures. In the earlier literature, this carbide was often termed Mo_3C_2 . The summary given by Rudy and others (275) in 1963 is consistent and in accord with most of the recent experimental results. At about 2700°C a carbide, Mo_3C_2 , crystallizes from the melt. The stacking sequence of the layers of metal atoms is face-centered cubic (ABCABCA...). Between 2000 and 2200°C , the face-centered cubic structure changes with great velocity into a hexagonal type (eta "MoC"), in which the metal atoms are characterized by the vertical layer sequence ABCACBABCA. Below 1800°C the hexagonal structure decomposes, but at a much slower rate, into Mo_2C and carbon. By the use of high pressures (67) or by very rapid quenching of the melt (274), it is possible to obtain the cubic form at room temperature. Most of these observations made by Rudy in 1963 were confirmed in 1965 by the work of Heetderks and others (138). Using differential thermal analysis methods, the temperature of decomposition of the hexagonal (eta) MoC_{1-x} into Mo_2C and carbon was found to be 1665°C ; the decomposition temperature of cubic (alpha) MoC_{1-x} into the hexagonal eta phase is listed as 1960°C .

Priority in the preparation of molybdenum carbides belongs to Moissan. He first prepared Mo_2C in 1893 by reducing molybdenum oxide with carbon in the electric arc (222). Working with Hoffmann (230) in 1904, a carbide approximating MoC was obtained by fusing molybdenum and aluminum in the presence of coke, and treating the solidified mass with NaOH or sodium carbonate to isolate the carbide. The carbide Mo_2C can be prepared by a number of methods. These include reduction of MoO_3 with carbon, carburizing molybdenum metal powder with graphite in a carbon tube vacuum furnace, reaction of molybdenum metal with CO or CH_4 , decomposition of molybdenum carbonyl vapor on an electrically heated carbon rod above 1300°C under vacuum, and fused salt electrolysis of MoO_3 with sodium borate, sodium carbonate, and

lithium fluoride. Technical production of molybdenum carbides begins with reduction of pure MoO_3 to the metal with hydrogen at about 900°C . The molybdenum powder is then intimately mixed with carbon black and carburized under hydrogen in a carbon tube furnace at 1400° – 1500°C (297).

Technical Mo_2C is too soft to be used alone in cutting tools. It is used in solid solution with other carbides, particularly where tungsten-free mixtures are desired. Some Mo_2C crucibles and coatings have been employed in the preparation of aluminum from aluminum oxide by processes involving aluminum carbide or aluminum nitride as an intermediate step. Cermets for reactor fuel elements have been made by coating Al_2O_3 granules with a mixture of molybdenum and molybdenum carbide, obtained by the thermal decomposition of molybdenum carbonyl vapor (364).

11. Tungsten

Historically, the first production of tungsten carbide was by Moissan (222, 227), using the carbon arc furnace for fusion, as was previously mentioned. Moissan produced W_2C either by recombining molten tungsten metal with carbon or by reduction of WO_3 with either carbon or calcium carbide in the carbon arc. Technically, the fusion process permits practical production of W_2C and W_2C -WC eutectic mixtures, which can be cast into desired shapes or used in the manufacture of tungsten carbide base hard facing materials.

The monocarbide (WC) is technically produced for large-scale use in cemented hard metals by carburizing tungsten metal powder with carbon black in carbon tube or, sometimes, in open high-frequency furnaces under hydrogen. Other methods of producing tungsten carbides include isolation from tungsten-bearing steels and iron, carburization of metallic tungsten or WO_3 , carburization of tungsten wires using carbon monoxide or naphthalene vapors, and fused salt electrolysis in a manner similar to that used in the preparation of molybdenum carbides. Due to the importance of both tungsten metal and tungsten carbides, many different production methods that can be used for making tungsten carbides are known. Some of these, such as production of ammonium paratungstate from tungsten carbide scrap, are of practical importance in special cases. A number of others are mainly of academic interest. Schwarzkopf and Kieffer have given a lengthy review of carbide production methods for tungsten in 1953 (298) and again in 1960 (303).

In his extensive study of the tungsten-carbon system, published in 1965, Sara (286) used tungsten powder, Acheson graphite powder, and tungsten monocarbide (WC). The monocarbide analyzed 6.15% carbon,

0.11 % oxygen, and 93.72 % by weight tungsten. The tungsten analyzed 99.14 % W, 0.05 % C, and 0.90 % by weight oxygen. The graphite showed 99.99 % by weight carbon. After blending, the samples were prepared by hot- and cold-pressing. The hot-pressing was carried out in carbon molds at 1800°C under an argon atmosphere. Use of inert atmosphere enabled composition changes during processing to be held to within ± 0.5 %. The cold-pressed samples were sintered in vacuum at 1100°C before being used at higher temperatures.

The two principal methods of study were differential thermal analysis and quenching studies. Phase analysis was by chemical, metallographic, and X-ray diffraction techniques. Temperatures were measured by means of a calibrated optical pyrometer. Metallographic and X-ray methods correlated directly in all cases. Due to precipitation taking place in most samples, lattice parameter measurements could not be used to establish solid solution ranges. This fact casts doubt on previously reported work for this system in which solid solubility was established by the lattice parameter method. Due to the extremely high temperatures involved and the problem of containing the melts, no attempt was made to establish liquidus relations for any region of the system.

The equilibrium relations of the system based in large part on one hundred and twenty-five quenching samples are shown as data points on the published diagram. Beginning at the tungsten side, the diagram shows a eutectic between W and W_2C occurring at a temperature of 2710°C. The eutectic liquid contains 25 atomic % carbon. No investigation has been made of the solubility of tungsten in carbon. The solubility of carbon in tungsten was reported by Goldschmidt and Brand (116) to be 0.3 atomic % carbon at the eutectic temperature, decreasing to about 0.05 atomic % near 2000°C and to trace amounts at lower temperatures. Goldschmidt and Brand used lattice parameter measurements and metallographic examination. No attempt was made by Sara to determine the solid solubility of carbon in tungsten. The extent of the W_2C solid solution field (simple hexagonal) was found, by Sara, to be much wider than was previously believed. At a temperature of 2795°C and a composition of 30 atomic % carbon ($W_{2.35}C$), Sara found a maximum on the solidus. This is in good accord with the classic work of Sykes (340), who gave the temperature of the W_2C maximum as between 2650 and 2750°C. No evidence was found by Sara with any of the methods he used—metallographic examination, differential thermal analysis, or X-ray diffractometry—of the existence of a high-temperature modification of W_2C , previously reported by several investigators including Goldschmidt and Brand in 1963. On the low-carbon side, the phase relations of W_2C are fairly simple. At the eutectic temperature (2710°C), the composition

is about 26 atomic % tungsten ($W_{2.84}C$). With decreasing temperature, there is a slight increase in solid solubility of carbon to 28 atomic % at the lowest measured temperature (2460°C) for $W_{2.57}C$. The corresponding high-carbon limit at 2460°C for the W_2C solid solution field is $W_{2.00}C$. However, relations for the high-carbon side of this single-phase solid solution field are more complex. At a temperature of 2525°C, Sara found decomposition of a high-temperature form of WC (cubic beta WC) by a eutectoid reaction into alpha WC (simple hexagonal) of stoichiometric composition and into W_2C . Metallographic examination showed that at the eutectoid temperature W_2C could take carbon into solution. No attempt was made by Sara to find the maximum carbon solubility in W_2C at this temperature. The eutectoid composition is given as approximately 37.5 atomic % carbon. With increasing temperature, W_2C returns to the stoichiometric $W_{2.00}C$ at 2670°C and remains at this value to 2760°C, where it participates in another eutectic for which the eutectic liquid contains 36 atomic % carbon. The other solid freezing from this second eutectic is the high-temperature form of WC.

All samples containing over 38 atomic % carbon melted at temperatures above 2785°C. Differential thermal analysis showed that melting temperatures were virtually isothermal at approximately 2770°C, between W_2C and carbon. On the basis of metallographic examination of quenched samples containing 38, 40, and 45 atomic % carbon, it was concluded that the high-temperature cubic (beta) WC formed by a peritectic reaction at 2785°C from elemental carbon and a liquid containing about 40 atomic % carbon. Based upon metallography and differential thermal analysis, beta WC was found to decompose by a peritectoid reaction at 2755°C with carbon into alpha WC (hexagonal), which remained at nearly stoichiometric composition to the lowest temperature measured (2460°C).

The eutectoid decomposition of beta WC has been described. This reaction was first detected by a heat effect, observed on cooling for all compositions richer in carbon than W_2C , by differential thermal analysis methods. It was fully confirmed by metallographic examination, which showed typical eutectoid microstructures. Further metallographic studies on quenched samples, with compositions between 37.5 % and 50 atomic % carbon, showed that the solvus for the beta WC field extended over to alpha WC. Subsolidus quenching experiments, conducted on the tungsten-rich side of the field W_2C and beta WC at temperatures from 2550°C up to the solidus, showed coexistence of beta WC and W_2C up to the beginning of melting. On the basis of these findings, Sara concludes that the cubic high-temperature phase is the monocarbide and not W_2C as previously postulated by others. X-ray studies by microfocus methods

on retained beta WC showed a face-centered cubic pattern with a lattice parameter of 4.215 Å. This was for a composition $WC_{0.82}$. No attempt was made to obtain a range of compositions and a correlation between cell constant and carbon content. Sara states that, from the metallographic evidence, beta WC may be thought of as having approximate limits of $0 \leq x \leq 0.41$ in WC_{1-x} at the solidus line. These limits change with decreasing temperature until the eutectoid temperature is reached at 2525°C and $x = 0.40$. No mention of the work of Orton (249) was made by Sara. According to Elliott (88), Orton found by thermodynamic calculations and reaction studies that W_2C decomposed by a eutectoid reaction at 1215°C into W and WC. Orton also found a peritectoid decomposition of WC into W_2C and carbon at 1315°C. These temperatures and reactions are very much different from those found by Sara. The experimental difficulties in detecting such heat effects by differential thermal analysis methods in this temperature range, well over 1000 degrees below the corresponding reactions studied by Sara, should have been very much less and therefore more easily detectable.

Cutting tools based on tungsten carbides were the first of this type of material to be introduced during World War I. Compositions based upon tungsten carbides continue to dominate the cutting tool field to the present time. The two most widely used types are WC plus $WC-Mo_2C-TiC$ solid solutions and $WC-TiC-TaC$ alloys. Although WC apparently does not have as great penetration hardness as TiC, the wear resistance and cutting action of WC-cobalt mixtures on short chip materials, such as cast iron, glass, and porcelain, lead to almost exclusive use of WC-Co in such applications. Due to the high density of tungsten and its carbides, they are generally used as an insert or refractory facing in applications where saving weight is of primary importance. As an example of such carbide coatings for tools and dies, Fellom (102) has described a spark discharge method by which a very thin WC coating is placed on the base metal, good shock resistance being obtained. A German patent granted to Frehn (103) describes the use of a small boron addition to tungsten carbide cobalt alloys that are to be used for plasma flame spraying. The boron aids by giving better and faster bonding to the base metal, and also suppresses undesirable decomposition of WC into carbon and W_2C .

B. ACETYLIDES

1. Calcium

Both $Ca(HC_2)_2$ and CaC_2 will be discussed in this section. The first of these substances was prepared by Moissan (229) in 1898 by the action of

acetylene on calcium dissolved in liquid ammonia. More recent studies, particularly of stability of $\text{Ca}(\text{HC}_2)_2$, were made by Vaughn (352) in 1937 and by Corbellini and Turner (70) in 1960. The same method of preparation was used in these subsequent studies of the compound.

The second compound, CaC_2 , has wide and important industrial and practical applications. The preparation, use, and chemical future of calcium carbide, as well as a full account of initial production of the substance, have been thoroughly covered by Seobie (304). In this article, the four long-recognized polymorphs of CaC_2 are listed as follows: CaC_2 "IV," cubic, stable above 447°C ; CaC_2 "III" is known only as a metastable phase; below 25°C the form CaC_2 "II" is found; and tetragonal CaC_2 "I"—stable between 447 and 25°C —is the one most common in commercial calcium carbide. These polymorphic relations are in agreement with those published by Bredig (48) in 1942. In 1959 Borchert and Roder (43) published work based on Weissenberg and rotation X-ray diffractometry, indicating that the polymorphs II and III of the above scheme belonged to the tetragonal system, having very large unit cells ($a_0 = 23.40 \text{ \AA}$). The high-temperature polymorph IV, in agreement with previous work, was reported to be cubic. These two workers also expressed the view that the polymorph stable below about 435°C was III, and that I and II were metastable phases produced by "application of pressure." In his comments on the work of Borchert and Roder published in 1961, Bredig (51) states that the structure of the polymorphs II and III cannot be considered to be established, and that the tetragonal symmetry found by Borchert and Roder was in disagreement with earlier work indicating lower symmetry, perhaps triclinic for II. He strongly disagrees with the pressure relations of Borchert and Roder, and sets forth his views that the common tetragonal form I is stable from room temperature to around 450°C , and that the polymorph stable below room temperature, designated by Bredig as II, is one of lower symmetry.

2. Sodium

Both the carbides of sodium (NaHC_2 , the hydroacetylide, and Na_2C_2 , the dicarbide) were prepared and described by Berthelot (33) in 1866. The dicarbide, Na_2C_2 , is a brown substance, usually prepared by carefully heating NaHC_2 . The dicarbide has very little, if any, practical use. The hydroacetylide, NaHC_2 , finds considerable use in organic syntheses such as the preparation of acetylenic carbinols and glycols. Preparation of NaHC_2 is usually by passing gaseous acetylene into liquid ammonia in which metallic sodium has been dissolved. Recently Ashby and Foster (13) used sodium hydroacetylide in the preparation of boranes.

C. REACTOR USE

1. Uranium

Uranium has three binary carbides, UC, U_2C_3 , and UC_2 . Obtaining the carbides of uranium, especially the monocarbide UC, in a condition in which there is freedom from dissolved oxygen or nitrogen is a difficult and not completely solved problem. The literature concerning the preparation and properties of the purest known uranium carbides has been critically reviewed through 1963 by Storms (333). Although a large amount of work has been done on the system uranium-carbon, the diagram is not yet completely established, particularly in composition ranges richer in carbon than the sesquicarbide, U_2C_3 .

On the basis of extensive experience at Los Alamos, Storms states that UC and UC_2 can be prepared with a high degree of purity by arc melting uranium and carbon in an inert atmosphere, preferably one of helium. Carbon is used in the form of spectroscopic graphite, uranium as freshly cleaned metal. The ingredients are placed in a shallow depression on the copper furnace hearth. Air is evacuated, after which the system is filled with either argon or helium. For greater purity, the arc is struck with a carbon electrode rather than with tungsten; use of helium shortens the melting time and reduces carbon pickup. A zirconium button is usually melted first to further purify the inert gas. After this, the arc is transferred to the uranium carbon mixture. The button is usually turned on edge and remelted several times to ensure homogeneity. Mixtures of UC and UC_2 can be produced by reacting uranium with methane or propane. Using methane, the product below 650°C is mainly UC; above 900°C mostly UC_2 is obtained. Kalish and Litton (169) prepared a uranium carbide UC (4.4% by weight carbon) by carburizing uranium hydride with methane or propane. This product was suitable for use as a reactor fuel element. Preparation of uranium carbides from carbon and oxides of uranium is attractive from a cost standpoint, but the product thus obtained is impure and must be purified by arc melting or lengthy high-vacuum purification. Mallett (201) and others prepared master alloys containing up to 12% by weight carbon by heating UO_2 with monatomic carbon (Norblack) at temperatures of 1700 – 1900°C , using induction heating and a graphite container for the charge. These master alloys were mixed with uranium chips and then subjected to repeated arc melting for homogeneity and purity.

The monocarbide UC is face-centered cubic; UC_2 is cubic at high temperatures and tetragonal at low temperatures; the sesquicarbide U_2C_3 , which seems to be a nearly stoichiometric compound, is body-centered cubic. Identification of the structure type by X-ray diffraction has been carried out by many investigators. In addition, the carbon

positions in all three of the uranium carbides have been determined by neutron diffraction by both Austin (19) and Atoji and Medrud (14); the results are in good agreement and substantiate the X-ray diffraction results.

Preparation of U_2C_3 in a nearly pure form has presented difficulties. The compound is not usually found in material quenched from above 1800°C. By heating UC and UC_2 mixtures in the temperature range 1250–1800°C, and mechanically stressing the solid mixture, Mallett (200) showed that larger and larger amounts of U_2C_3 were produced as the theoretical composition (7.03% by weight carbon) was approached. The fact that mechanical stressing was essential in the production of U_2C_3 was also noted by later workers, but other factors are involved in its formation and retention. Henney *et al.* (139) suggested that ease of formation of U_2C_3 was a function of the nitrogen and oxygen content. The sesquicarbide apparently forms sluggishly after an incubation period by a process of nucleation and growth. This was the conclusion of Norreys (243), who followed the formation of U_2C_3 by the electrical resistivity method. Witteman and Bowman (366) also found that U_2C_3 formation was by nucleation and growth. The method used by Witteman and Bowman to follow the formation of U_2C_3 was a refined thermal analysis method, in which the negative of the slope of the first derivative of the cooling curve was simultaneously displayed on the oscilloscope screen with the cooling curve itself. This greatly increased the ability to detect solid state changes. On the other hand, Gillam (110) suggested that U_2C_3 may form from UC_2 by a slight shift in the position of the uranium atoms and that, although the transformation is sluggish, it is of a diffusionless shear or martensitic type.

Many of the features of the uranium carbon phase diagram are still in dispute, but the tentative diagrams of Storms (334) and Bowman (46) are recent, and seem to be accepted. The following list of the principal features of the U-C system is based upon the discussion of Storms:

(a) Uranium metal melts at 1132°C. The solidified metal has three crystal forms, the transition from alpha (orthorhombic) to beta (tetragonal) taking place at 667°C. The second transition from beta to gamma (body-centered cubic) is at 775°C. Addition of carbon lowers the transitions to eutectoids at 665.9 and 771.8°C, respectively. The solubility of carbon in uranium is very slight, not over 185 ppm at the eutectic temperature 1117°C. The values quoted are based on the careful and accurate work of Blumenthal (40) and his associates.

(b) From the eutectic point, which is placed by Blumenthal at 500 ppm by weight carbon (0.98 atomic % carbon), the liquidus rises sharply to a maximum at about 2550°C near stoichiometric UC. This portion of

the liquidus was redetermined by Blum (39) in 1965. Based on experimental points to 2400°C, Blum extrapolates to a maximum for stoichiometric UC at about 2550°C. Storms shows a maximum at 2560°C for UC_{1.0}.

(c) There is retrograde solubility along the portion of the solidus between the UC maximum and the eutectic at 1116.6°C. Blum places the minimum at 4.36 % by weight carbon (UC_{0.94}) and at a temperature of about 2150°C. Below 1500°C, the solidus rejoins the composition vertical for UC (stoichiometric) down to the eutectic temperature. This last statement varies slightly from the diagram of Storms, who shows a dashed and therefore uncertain region of "cubic solid solution" that does not rejoin the UC_{1.0} vertical until the eutectoid at 665.9°C is reached upon cooling.

(d) There are three compounds, UC, U₂C₃, and UC₂, in the uranium carbon system. UC is face-centered cubic and stable (although it may contain oxygen and nitrogen and be either hypostoichiometric or hyperstoichiometric as well) from room temperature to its melting point, the value of this maximum melting having been discussed under (b). The sesquicarbide U₂C₃ is body-centered cubic and decomposes without melting at about 1800°C. The dicarbide UC₂ is stable from about 1500°C to its melting range, which is placed by Storms above 2450°C. There is also a crystal structure change in UC₂ from tetragonal (below) to cubic (above) near 1785°C. The portion of the diagram in which this takes place is uncertain and therefore left blank by Storms and Bowman. Elliott (89), from the literature published through 1961, gives the transition temperature of UC₂ as 1820°C and shows a eutectoid at 61.6 atomic % carbon occurring at 1800°C. The "cubic solid solution" of Storms [mentioned under (b)] decomposes at this eutectoid point to UC and tetragonal UC₂ according to the diagram proposed by Elliott. Elliott's diagram also agrees very closely with the U-C phase diagram of Chubb and Dickerson (64), published in 1963.

(e) Between the stoichiometric compositions of UC and UC₂, there is a minimum melting solid solution. The temperature of the minimum is placed by Storms at near 2450°C with a composition approximately UC_{1.5}. Elliott places this minimum at 57.5 atomic % carbon and at a temperature of 2350°C.

(f) The sesquicarbide U₂C₃ apparently decomposes by a peritectoid reaction at a temperature slightly below 1800°C. Storms shows the vertical as a solid line, indicating that the peritectoid decomposition is fairly certain, but does not indicate the temperature of the peritectoid horizontal. This value is given by Elliott as 1775°C; Elliott shows the U₂C₃ vertical dashed and therefore uncertain above 1400°C.

(g) Above 1800°C, there is a "hat-shaped" solid region containing UC and beta (cubic) UC₂. This miscibility gap rises to a maximum. The temperature of the maximum and the composition limits of this two-phase solid region constitute one of the greater uncertainties of the U-C system. Storms places the maximum at 2050°C and at UC_{1.35 ± 0.05} with the lower boundary at 1800°C extending from UC_{1.06} to about UC_{1.6}. Later work by Sears (306) and others places the maximum above 2090°C, the decomposition horizontal at 1820°C, and the miscibility gap limits between UC_{1.1} and UC_{1.2} on the uranium-rich side, and at about UC_{1.65} on the carbon-rich side.

The retrogression of the solidus along the carbon-rich boundary of the liquid plus UC phase field may be influenced by the presence of dissolved oxygen, particularly if any free uranium is present that could increase the ease with which oxygen will dissolve. The resulting U(C, O) solution, if heated in a vacuum in the absence of any free UO₂, could form free uranium with evolution of CO. This retrograde behavior was first suggested by Buckley (56) in 1961, from examination of quenched alloys in the UC composition range that contained various impurities, as well as free uranium. Buckley also found that rapidly quenched UC was a defect structure. From the behavior of the lattice parameter, he suspected a retrograde behavior of this portion of the solidus. The retrogression was found, experimentally, by Magnier and Accary (198) in 1963. They ascribed this behavior to formation of an unidentified compound by a peritectic reaction. No experimental support for such behavior has been found, according to Storms.

Two other points in connection with the presence of oxygen in the U-C system will be briefly mentioned. The first is the maximum in the lattice parameter of UC. This was first reported by Accary (2) in 1963. He found that the lattice parameter rose from 4.9598 Å for his purest sample to 4.9613 Å for UC containing 1800 ppm by weight of oxygen. This behavior has been found by several other investigators, including Anselin and his co-workers (9). After the maximum is passed, the lattice parameter rapidly decreases to a saturation value, reported by Stoops and Hamme (322) in 1964 to be 4.9519 Å.

The second point is the presence of dissolved "UO" in compositions near UC_{1.0}. Uranium monoxide of stoichiometric composition is not known as an isolated stable phase. In what is properly the ternary system U-C-O, the limits found for a single U(C, O) phase in equilibrium with UO₂ and U below 1400°C range from compositions as low as UC_{0.75}O_{0.25}, as reported by Stoops and Hamme, to as high as UC_{0.2}O_{0.8}, reported by Sano (284) in 1963. On the other hand, Anselin states that UC in equilibrium with U₂C₃ and UO₂ can dissolve no more than about 5 atomic %

oxygen, while UC_2 and U_2C_3 dissolve essentially no oxygen. Other factors discussed by Storms, which affect solubility and ease of solution of oxygen, include stoichiometry of the UC, annealing temperature, and CO pressure. The difficulty of excluding all oxygen affects both the high- and low-carbon UC phase boundaries as well as the lattice parameter.

Nitrogen is essentially insoluble in UC_2 and U_2C_3 . The effect of nitrogen on the lattice parameter of UC above 1200°C is one of contraction, the opposite of the effect of oxygen. In fact, all or any part of the carbon atoms in UC can be replaced by nitrogen. It was found by Rough and Chubb (273) that nitrogen reacts with the molten carbide to displace carbon from the monocarbide and produce some UC_2 . If such behavior of nitrogen is not known and taken into account, a low and incorrect value would thus be obtained in attempting to locate the high-carbon UC phase boundary.

In conclusion, two recent applications and nonresearch aspects of uranium carbides will be reviewed. The first of these is pilot production of slightly hypostoichiometric UC by a fluidized bed technique (257). Finely divided uranium metal particles were reacted in a stainless steel vessel, using hydrogen propane atmospheres and pressures of 1, 10, and 20 atmospheres. Temperatures used were 600, 700, and 750°C with times ranging from 3 to 20 hours. Stoichiometric UC could be obtained and was produced. The advantage for reactor fuel elements of a uranium monocarbide slightly less than $\text{UC}_{1.0}$ is that there is greater compatibility with the stainless steel cladding, as well as less carbon present that might diffuse to the cladding wall and cause detrimental grain boundary corrosion of the stainless steel. The low-melting uranium metal resulting from such monocarbide decomposition would also tend to cause premature failure of the reactor fuel elements.

Uranium carbide in combination with zirconium carbide (UC-ZrC) has also been studied with regard to fabrication, cladding, diffusion, and fission product release both as a fuel and in connection with thermionic emission for space power applications (369). Many of the problems encountered in using uranium carbides and those of other metals in reactors are discussed in the two-volume work edited by Russell (281).

D. FIRST TRANSITION GROUP METALS

1. Manganese

The carbides of manganese in isolated form have practically no use. They are important in steels and other ferrous alloys, either as compounds of manganese and carbon, or in more complex metallic alloys in which manganese is one of the metallic elements of the carbide. In analogy to

cementite (Fe_3C), the manganese carbide known and studied for the longest period of time has often been assigned the formula Mn_3C . However, there is not general agreement on the number of carbides in the system Mn-C, their formulas, and crystal structures. The early studies of manganese carbides were upon material obtained by acid or electrolytic isolation from steels and cast irons. Most of the work published during the past 15 years has been on carbides prepared from distilled manganese and graphite or sugar charcoal. The volatility of manganese, attack upon the refractories, and affinity of manganese for oxygen and nitrogen have complicated the problem of obtaining the manganese carbides as pure substances of definite composition.

The diagram of the manganese-carbon system shown by Hansen (133) is based on the work of Isobe (159) and Kuo and Persson (184). Older diagrams did not show the four polymorphic forms of manganese. Considerable efforts have been made, with varying degrees of success, to show that carbides of manganese are isomorphous with carbides, nitrides, and other compounds of other elements, particularly those of iron and chromium, which are the horizontal nearest neighbors of manganese in the periodic table.

The table of Kuo and Persson, published in 1954 and reproduced by Hansen, shows five manganese carbides. In order of increasing carbon content, these are: Mn_{23}C_6 of cubic structure, presumably isomorphous with Cr_{23}C_6 ; a carbide of unknown crystal structure, stable at 850–1000°C, to which Kuo assigned the formula Mn_7C_2 (22.22 atomic % carbon); Mn_3C orthorhombic and isomorphous with Fe_3C ; Mn_5C_2 monoclinic and stable up to 1050°C; and, finally, Mn_7C_3 trigonal and isomorphous with Cr_7C_3 .

In 1957 Picon and Flahaut (259) published the results of a study of the carbides of manganese in which analytical and X-ray diffraction methods were used. They were unable to index the carbide that was richest in manganese as cubic with formula Mn_{23}C_6 , finding that their diffraction patterns were consistent with a tetragonal structure to which they assigned the formula Mn_4C . Two carbides having the formula Mn_6C_2 were obtained. One of these was orthorhombic, having lattice parameters in good agreement with those published by Kuo. Picon and Flahaut indexed the other carbide of formula Mn_6C_2 as belonging to the hexagonal system. Three other carbides of formula Mn_8C_3 , with structures in order of increasing carbon content triclinic, hexagonal, and cubic, respectively, were also found by these two investigators, making a total of six different carbides in the system Mn-C. In commenting on this work, Elliott (90) stated that it was not definitive enough to warrant changes in the equilibrium diagram proposed by Hansen.

The agreement in the case of Mn_3C shown between the results of Picon and Flahaut and of Kuo does not seem to be disputed by later researchers. Investigations by Senateur and others (309) in 1962, as well as by Jack (160) and Duggin and Hofer (78) in 1966, confirm the existence of monoclinic Mn_5C_2 as suggested by Kuo. The carbide of unknown structure to which Kuo and Persson tentatively assigned the formula Mn_7C_2 was prepared and studied by Bouchard and Fruchart (44) in 1964. From the results of Seeman-Bohlin powder patterns (iron K alpha radiation) and from chemical analysis and density determinations, a formula Mn_{15}C_4 with a hexagonal unit cell ($a_0 = 7.492 \text{ \AA}$, $c_0 = 12.070 \text{ \AA}$) was found to fit their results.

Bouchard and Fruchart (45) also re-examined the region of the Mn-C system in which Picon and Flahaut found three manganese carbides having the formula Mn_8C_3 . The results of these two studies were not in agreement, for the portion of the system where manganese was present associated with quantities of carbon greater than or equal to the concentration of Mn_7C_3 . From temperatures averaging 850°C , Bouchard and Fruchart found a trigonal carbide Mn_7C_3 in agreement with the work of Kuo and Persson. If the same manganese carbon mixtures were heated above 900°C and cooled slowly, only one phase was again obtained and not a mixture of three phases. However, this last carbide gave a Seeman-Bohlin powder pattern in which intensities did not vary with the manganese:carbon ratio, but the pattern was more complex than that of the 850°C product. This slowly cooled phase was determined by Bouchard and Fruchart to have an orthorhombic pseudo-hexagonal structure. They also pointed out that the structure thus assigned to Mn_7C_3 was very similar to the structures assigned to Ru_7B_3 and Cr_7C_3 . The work of Fruchart and his collaborators also agrees with that of Kuo in the existence of Mn_{23}C_6 isomorphous with Cr_{23}C_6 .

In summary, the bulk of the evidence at the present time seems to indicate the existence of five carbides of manganese: Mn_{23}C_6 cubic, Mn_3C orthorhombic, Mn_5C_2 monoclinic, Mn_7C_3 orthorhombic pseudo-hexagonal, and Mn_{15}C_4 of hexagonal symmetry corresponding to the Mn_7C_2 of unknown crystal structure reported by Kuo and Persson.

2. Iron

The enormous literature on the carbides of iron contains numerous fragmentary references to carbides with various suggested formulas not subsequently confirmed. The review on the nature of iron carbides published by Hofer (149) in 1966 after 20 years of work in the field obviates the necessity of discussing various unconfirmed iron carbides. The only carbide of iron that forms from ordinary atmospheric cooling of liquid

iron-carbon melts is cementite, Fe_3C , now called theta iron carbide. The "iron-carbon" diagram is usually terminated for this reason at the carbon content corresponding to Fe_3C (6.7 % by weight carbon). There is also no point in discussing here the iron-carbon diagram. The reviews given by Hansen (134) and Elliott (91) selectively summarize the many noteworthy papers concerning the metastable iron-iron carbide and the stable iron-graphite systems. The crystal structure of cementite is orthorhombic and the analysis of its structure published by Lipson and Petch in 1940 (191) is still accepted.

Hofer discusses five iron carbides, cementite (theta), hexagonal close-packed iron carbide (epsilon), Hagg carbide (chi), Eckstrom and Adecock carbide (FeC), and Pomey carbide (hexagonal). Except for cementite, these carbides mainly find uses as catalysts in syntheses, such as the Fischer-Tropsch, which produce higher hydrocarbons and waxes from hydrogen and carbon monoxide. In fact, the Eckstrom and Adecock carbide has been found only in the catalysts of synthetic liquid fuel installations and had not been separately synthesized in the laboratory by 1965. Epsilon iron carbide is also formed during the tempering of hardened martensitic steels, and a large number of papers concerning the relations of epsilon iron carbide in the tempering processes have appeared during the last 20 years. Greek letter distinction of the iron carbides has been suggested to reduce some of the confusion in the literature, and to designate the three most common carbides. As was previously mentioned, both Pomey carbide and epsilon carbide are characterized as belonging to the hexagonal system.

Epsilon iron carbide is quantitatively formed by the reaction of the carbon in carbon monoxide with finely divided alpha iron at temperatures near 170°C . The composition of the product thus formed is within 2 atomic % carbon of Fe_2C . The structure is quite simple and analysis of the powder X-ray diffraction pattern gives an unambiguous determination of a close-packed hexagonal structure. The carbide formed during the tempering of steels seems to be lower in carbon content, one suggested formula being $\text{Fe}_{2.4}\text{C}$. The variation in carbon content can be explained by analogy with the iron-nitrogen system, if epsilon carbide is assumed to be a nonstoichiometric compound in which there is variation, from nearly three iron atoms per carbon atom to two iron atoms per carbon atom at the other end of the range. Since decomposition occurs near the Curie temperature of epsilon carbide, this cannot be precisely determined, but is not more than 20 degrees above 380°C .

Chi iron carbide can be obtained in a condition free of detectable traces of epsilon iron carbide by allowing carbon monoxide to react with finely divided alpha iron at a temperature near 230°C . This carbide can

also be produced by isothermal vacuum decomposition of epsilon carbide at temperatures above 230°C. Above about 420°C, the chi iron carbide formed by such a process decomposes, in turn, to theta iron carbide. The powder diffraction pattern of chi iron carbide (formula assigned Fe_2C without insistence upon stoichiometry) has been indexed as belonging to the orthorhombic system, but the lattice parameters thus obtained are rather large. According to Hofer, the indexing, crystal class, and lattice parameters of chi iron carbide are questionable. However, the Curie temperature is known accurately as 247°C, which compares with 210°C for cementite and near 380°C for epsilon carbide. However, a number of techniques, such as X-ray diffraction, gravimetric carbiding studies, thermomagnetic measurements, studies on oxides and nitrides, and information obtained from the tempering of steels, must also be taken into account in distinguishing and characterizing the carbides of iron.

The Pomey (262) carbide has been known only since 1954, and was found in connection with the study of bainitic transformations in steels. Extensive studies of this carbide (which is also assigned the formula Fe_2C) have not been made. Determinations of the Curie point as 380°C and of a hexagonal structure from a powder X-ray diffraction pattern are based upon material electrolytically extracted from heat-treated steel (263).

The Eckstrom and Adcock (84) carbide seems to have a composition near FeC and a Curie point of about 250°C. According to Hofer, attempts to synthesize this carbide in an isolated form in the laboratory have so far been unsuccessful.

3. Cobalt

Probably the most important use of cobalt carbides is as part of mixed carbides such as $\text{Co}_3\text{W}_3\text{C}$ in tool steels and high-speed steels. The isolated carbides of cobalt have been studied mainly in connection with the Fischer-Tropsch process. Catalysts based upon cobalt were standard for this synthesis in Germany from about 1938 to 1944, but have been superseded since that time both in Germany and elsewhere by catalysts based upon iron, which are cheaper in first cost and more flexible. The carbon-cobalt phase diagram has been reviewed by Hansen (135) and supplemented through 1961 by Elliott (92). There is evidence of terminal solid solubility of carbon in cobalt and of a eutectic of cobalt with graphite. Hansen places this eutectic at 1309°C and at a composition of 10.8 atomic % carbon in his partial carbon-cobalt diagram.

The preparation of a cobalt carbide Co_2C was reported by Bahr and Jessen (25) in 1930. By allowing carbon monoxide to react with finely divided cobalt below 225°C, a product containing 9.25 % by weight

carbon (which is the amount for the formula Co_2C) was obtained after some 400 hours. No further gain in weight was experienced in this temperature range for times nearly double 400 hours. The work of Bahr and Jessen was repeated by Hofer and Peebles (145) in 1947. From X-ray diffraction patterns of their Co_2C , Hofer and Peebles concluded that the structure was orthorhombic with a narrow composition range. This carbide preparation was repeated by several other sets of research workers between 1947 and 1952. Considering the catalytic nature of the carbide formation, good agreement was obtained for the orthorhombic lattice parameters. In addition, Drain and Michel (77) determined that the structure of Co_2C was isotypic with Co_2N , whose structure had been established by Juza and Sachse (166) in 1945.

In 1937 Meyer (206) reported a carbide Co_3C prepared by carburizing cobalt with illuminating gas at temperatures of $450^\circ\text{--}600^\circ\text{C}$. The identification of the carbide as Co_3C was based on an X-ray diffraction pattern nearly identical with cementite Fe_3C . In commenting on the work of Meyer, Hofer states (147) that, in performing similar experiments, he and his associates never found such a cementite-like carbide. In 1961 Nagakura (238) carburized thin evaporated films of cobalt with illuminating gas for several hours at temperatures below 550°C . He found two orthorhombic carbides, identified by electron diffraction, having formulas of Co_2C and Co_3C . Nagakura's values for Co_3C showed reasonably good agreement with those of Meyer, and for Co_2C with those tabulated by Hofer.

4. Nickel

There is agreement on the existence of a single carbide of nickel having a hexagonal structure and the formula Ni_3C . Hofer (148) mentions other reported but unconfirmed carbides such as Ni_6C . Attempts to establish the structure of Ni_3C as orthorhombic rather than hexagonal, partially by analogy with cementite (Fe_3C), have failed. Some question has also been raised as to the stability of nickel carbide. This is answered, to some extent, by the results of Nagakura (237). In 1957 he published results of formation of Ni_3C by carburizing thin nickel films below 450°C . He found that the lattice parameters of the Ni_3C prepared in this way were those of a hexagonal structure, and that they remained unchanged after 1 year.

One of the first reported preparations of nickel carbide was by Bahr and Bahr (24) in 1928. The preparation was similar to that of cobalt carbide. Finely divided nickel was treated with carbon monoxide at 250 or 270°C . The curve of % carbon absorbed against time became horizontal at the composition Ni_3C . A limited use of nickel as a catalyst in early

developments of the Fischer-Tropsch process led to other studies involving nickel carbide. After 1945, the development of the cheaper and more flexible iron catalysts made the study of nickel catalysts and nickel carbide of only academic interest. The reaction between nickel and carbon monoxide has recently been studied by Escoubes (97) and his associates. Temperatures below 330°C and pure finely divided nickel were found essential to formation of Ni_3C .

In an initial report on high-pressure synthesis of diamond, Strong (338) mentions the formation of nickel carbide in some instances. There is also evidence that nickel-carbon melts, especially under high pressure, act in a manner similar to iron and carbon, forming two eutectics, one with graphite and another with nickel carbide.

IV. Binary Carbides of the Other Metals

A. ELEMENTS WITH ESTABLISHED CARBIDES WITHOUT USE

1. *The Alkali Metals*

Except for the use of NaHC_2 in organic syntheses, the carbides of the other alkali metals—lithium, potassium, rubidium, and cesium—seem to be without application. It seems pertinent to mention the “interstitials” or “insertion compounds” of these metals. These substances are excluded from this review as being chemically different from the carbides of alkali and other metals, which show nearly stoichiometric compositions involving small numbers of metal and carbon atoms. The “interstitial” compounds, also sometimes called “graphites,” are assigned formulas such as KC_8 , CsC_{16} , and RbC_{16} . They have been reviewed at length by Hennig (142). Other insertion products of lithium, sodium, and potassium with graphite have recently been found by Stein (321).

a. Lithium. The acetylide of lithium was prepared by Moissan (229) by passing acetylene into liquid ammonia containing dissolved lithium. The product was obtained in the form of transparent crystals, which Moissan analyzed. He also prepared the carbide Li_2C_2 by heating lithium carbonate and carbon in an electric furnace, using a carbon tube closed at one end as a container. The results of two recent preparations and structure determinations of Li_2C_2 are in disagreement. In 1962 Secrist (307) prepared single crystals of the carbide by heating lithium and graphite in an argon atmosphere at 700°C, using an iron capsule as a container. From Weissenberg photographs the structure of Li_2C_2 was found to be monoclinic. However, in 1965 Juza and Volker (167) made a structure determination of Li_2C_2 , which they reported as of 98.8–99.2% purity.

They obtained good agreement between measured and calculated densities for an orthorhombic structure. The lattice parameters obtained showed large differences from the parameters of Li_2C_2 published by Secrist.

b. Potassium. The acetylide of potassium KHC_2 is prepared by reaction of acetylene with potassium dissolved in liquid ammonia. The dicarbide K_2C_2 is obtained by careful heating of potassium acetylide. The acetylide has been determined to be face-centered tetragonal; one of the first determinations of this structure was by von Stackelberg (318) in 1930.

c, d. Rubidium and Cesium. Moissan (229) prepared RbHC_2 , Rb_2C_2 , CsHC_2 , and CsC_2 by the same methods as for potassium acetylide and carbide. In 1960 these four substances were prepared by Corbellini and Turner (70), using the Moissan techniques. A study of the stability of the hydroacetylides (MHC_2) of the alkali metals at 20°C showed KHC_2 to be the most stable, NaHC_2 the least stable, with the rubidium and cesium acetylides occupying intermediate positions.

2. Alkaline Earths; Beryllium and Aluminum

a. Beryllium. Most of the published work is for diberyllium carbide, Be_2C . The reduction of BeO with carbon yielding Be_2C was thermodynamically studied by Motzfeldt (234) in 1964 over the temperature range $1500^\circ\text{--}2050^\circ\text{C}$. The melting point of this carbide was reported by Hansen (136) to be near 2400°C . Reduction of beryllia with carbon was used by Lebeau (187) in 1895 and by Moissan (215) to produce a beryllium carbide to which they assigned the formula Be_4C_3 . Moissan used two electrical furnace methods, heating the mineral beryl in a carbon tube and mixing beryl and calcium carbide, then heating the mixture electrically. Recently a patent was granted to Schwartz (290) covering the use of Be_2C as part of a reactor core material used with a ceramic coating to prevent oxidation. Preparation of beryllium dicarbide (BeC_2) by passing acetylene over beryllium powder heated to $450^\circ\text{--}600^\circ\text{C}$ was reported by Durand (81) in 1924.

b. Magnesium. An impure magnesium carbide prepared by passing acetylene gas over magnesium powder was reported by Berthelot (33) in 1866. Moissan (228) also prepared magnesium carbide by this method in 1898. Two magnesium carbides, MgC_2 and Mg_2C_3 , were established by the work of Novak (244) in 1910. Both of these carbides were also prepared and studied by Bredig (49) in 1943 and Schneider and Cordes (288) in 1955. The tetragonal MgC_2 can be prepared by heating a ternary mixture of MgCl_2 , calcium carbide, and NaCl above the ternary eutectic at 425°C , or by passing pentane vapors over molten magnesium at a

temperature of 700°C, In 1964 Jonich and Reu (165) reported preparation of Mg_2C_3 by dipping graphite yarn in a magnesium solution and then exploding the "wire" of graphite by charged capacitors. Bredig prepared Mg_2C_3 by passing acetylene over magnesium shavings held at 500°C.

c. Strontium. Preparation of $\text{Sr}(\text{HC}_2)_2$, by passing acetylene into a liquid ammonia solution containing strontium and subsequent decomposition of the acetylide into SrC_2 , was also investigated by Corbellini and Turner in 1960. The acetylides of the alkaline earths were found to be less stable than those of the alkali metals. At 20°C, a reduced pressure (0.5 mm Hg) was found to be favorable for decomposition of strontium acetylide. About 20 hours were necessary for complete formation of SrC_2 . At present there seems to be little interest in the carbides of strontium, which have been known since the time of Moissan.

Bredig (48) included a tabulation of the different crystalline forms of strontium and barium carbides in his study of the polymorphs of calcium carbide. For strontium these were: SrC_2 face-centered cubic, stable above 370°C and unstable below this temperature; $\text{SrC}_2(\text{I})$, face-centered tetragonal, metastable below -30°C, stable from -30 to 370°C, and unstable above 370°C; $\text{SrC}_2(\text{II})$ of unknown crystal structure, stable below -30°C, metastable from -30°C to an unknown upper limit, completely unstable above 370°C. Small amounts of impurities cause marked changes in stability ranges.

d. Barium. As would be expected, there are marked similarities between strontium and barium carbides. The same methods of preparation produce barium acetylide $\text{Ba}(\text{HC}_2)_2$ and the carbide BaC_2 . The stability of barium acetylide is very small. Vaughn (352) found that $\text{Ba}(\text{HC}_2)_2$ decomposed at ambient temperature under an atmosphere of ammonia in a few minutes. By comparison, the corresponding sodium acetylide NaHC_2 remained white and undecomposed for 10 hours in dry air at room temperature. Bredig reported two polymorphs of BaC_2 , a face centered cubic form stable above 150°C ($\pm 50^\circ\text{C}$), unstable below this range on slow cooling, and metastable on quenching in the same temperature interval. The other form, $\text{BaC}_2(\text{I})$, was found to be face-centered tetragonal, unstable above 150°C ($\pm 50^\circ\text{C}$) and stable below this range. In 1964 Nelson and others (240) used BaC_2 containing radioactive carbon-14 in a study of the permeation of polymer films. Hydrolysis of the barium carbide yielded acetylene containing tagged carbon atoms and barium hydroxide.

e. Aluminum. In 1924 Durand (81) reported preparation of an aluminum acetylide $\text{Al}_2(\text{C}_2)_3$ by passing acetylene over finely divided aluminum at a temperature of 450°-500°C. Most of the work on aluminum carbide has been done on Al_4C_3 , which was prepared by Moissan (223) in 1894 by heating aluminum and carbon in the electric furnace. Many later

workers have also used this method. A different and somewhat novel method for making hexagonal Al_4C_3 was reported by Horiguchi (152) in 1966. The carbide was prepared by causing reaction between aluminum powder and acetylene black by means of an explosive charge. The hexagonal crystal structure of Al_4C_3 was determined by von Stackelberg (319) in 1934 and has been confirmed by the results of many subsequent investigations, including that of Cox and Pidgeon (71) in 1963.

3. *Lanthanides; Scandium and Yttrium*

Scandium and yttrium, together with lanthanum, which are vertically above each other in the Periodic Table, are included here with the fourteen rare earth elements from cerium through lutetium. The only element for which a monocarbide is generally agreed upon is ScC for scandium. No mention of any carbides of promethium was found in the literature, so this element is excluded from this section of the review. A dicarbide of europium EuC_2 has recently been prepared and similar dicarbides, such as YC_2 , LaC_2 , and GdC_2 , are known for all of these elements except scandium and promethium. Most of these dicarbides are tetragonal in crystal structure, having a structure type similar to calcium chloride. Cubic sesquicarbides, such as Pr_2C_3 (isotypic with Pu_2C_3), have been shown to exist for lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, terbium, and dysprosium. Holmium carbide was found by Spedding and others (316) to be dimorphic, showing both a cubic structure of plutonium sesquicarbide type and a structure similar to Y_2C_3 . The structure of Y_2C_3 is also shown by the sesquicarbides of erbium, thulium, and lutetium. The symmetry of these sesquicarbides is lower than tetragonal or hexagonal, and has not been determined. Tri-rare earth carbides such as Sm_3C were prepared by Spedding and others (316) for all of the elements from samarium, atomic number 62, through lutetium, atomic number 71, with the exception of europium. The structure of these tri-rare earth carbides was of an iron nitride (Fe_4N) type belonging to the cubic system. Many of these metal-rich carbides show a considerable range of carbon solubility with M_3C (M = metal) usually being found near the center of the range of composition.

In 1964 Dean and others (74) published the results of X-ray studies of the carbides of gadolinium, dysprosium, holmium, erbium, and yttrium, showing the existence of rhombohedral Gd_2C , Dy_2C , Ho_2C , Er_2C , and Y_2C . In addition to information from X-ray diffraction studies, some of the dicarbides (e.g., CeC_2) and sesquicarbides (e.g., Tb_2C_3) have been studied by neutron diffraction methods. This will be noted below for the carbides for which such neutron diffraction studies have been published.

Most of the dicarbides, sesquicarbides, and tri-rare earth carbides

(Y_3C) were prepared by compressing filings of the purified metal with carbon and arc melting the resulting compact. The precautions taken with these reactive rare earth metals and other details of carbide preparation are given by Spedding and his associates (316). Arc melting was done under a helium or argon atmosphere, and glove boxes with positive pressure and an inert atmosphere were also necessary. In order to avoid repetition, carbides that can be prepared by arc melting of the metal (or, in some cases, the oxide) with carbon will not be described for each element. Special preparation methods (such as the tantalum bomb method for carbides of samarium, thulium, europium, and ytterbium) will be outlined.

a. Scandium. The carbide of formula Sc_4C_3 reported in 1925 by Friederich and Sittig (104) was not subsequently confirmed. Preparation of ScC by heating Sc_2O_3 and carbon above $1500^\circ C$ was accomplished by Vickery and his co-workers (356) in 1959. A similar preparation was made by Nowotny and Auer-Welsbach (18) in 1961. In this last investigation, a carbide that reached stoichiometric ScC was not obtained, and it was suggested that a formula such as $Sc(C, O)$ or ScC_{1-x} might be in better accord with the experimental results. Vickery reported ScC as hexagonal, Nowotny cubic scandium monocarbide. Another preparation of ScC made by Samsonov and others (283) was reported to produce a cubic product. All of these structures were based upon powder X-ray diffraction patterns and, as Vickery pointed out, an unambiguous determination of crystal structure would require single crystals of scandium monocarbide. Such a determination apparently has not been made and published.

b. Yttrium. The dicarbide of yttrium YC_2 has been known since its preparation by Moissan and Etard in 1896 (226). The determination of the crystal structure as body-centered tetragonal, of calcium chloride type, is based upon X-ray diffraction work by several investigators including Gschneidner (316) and confirmed by the neutron diffraction determination made by Atoji (15). The existence of yttrium sesquicarbide Y_2C_3 is not questioned. As reported by Gschneidner (124), the symmetry is lower than tetragonal or hexagonal, similar to the sesquicarbides of erbium, thulium, and lutetium and not fully worked out or determined.

Samsonov and others (179, 283) have published two reports of the preparations of a monocarbide YC . In the first, published in 1962, YC was prepared by heating Y_2O_3 with carbon *in vacuo*. The formation temperature of YC thus prepared was reported as 1800° – $1900^\circ C$. The melting point of yttrium monocarbide was stated to be $1900^\circ \pm 50^\circ C$. In the second report published in 1964, Y_2O_3 was reduced with CO *in vacuo*. At a temperature of approximately $1700^\circ C$ an oxycarbide, to which the formula Y_2C_2O was assigned, apparently formed, which de-

composed at approximately 1900°C to YC and CO. Support for the existence of such an oxycarbide came from room temperature oxidation studies. When YC was oxidized there was an initial increase in weight, indicating oxycarbide formation; on the other hand, when YC₂ was similarly oxidized there was a continuous loss of weight.

As a result of microscope studies of some low yttrium-carbon alloys, a face-centered cubic carbide covering a range from YC_{0.25} to YC_{0.40} (Y₄C to Y₅C₂) was found by Spedding and others (316). Since the composition Y₃C is approximately midway between these solubility limits, this carbide was termed "triyttrium carbide." No evidence of any ordered structure was found in the powder X-ray diffraction patterns of this carbide of yttrium or for the similar tri-rare earth carbides of samarium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. Spedding and his associates suggested that the atoms of lanthanum, cerium, praseodymium, and neodymium were too large to permit formation of tri-rare earth carbides.

In the 1964 study of the yttrium carbon system by Dean and his co-workers (74), the interval YC_{0.30} to YC_{0.65} was re-examined. The published work also covered a similar composition range for the systems of gadolinium, dysprosium, holmium, and erbium with carbon. It was found that, as carbon was increased from metal-C_{0.3}, the face-centered cubic structure in which the carbon atoms were randomly arranged changed, particularly in the vicinity of metal-C_{0.5} (e.g., Y₂C), to a distorted rhombohedral structure. This change was explained as being due to an ordering of the carbon atoms. Samples prepared at low temperatures (800°–1300°C) were found to be M₂C to the exclusion of MC. The rhombohedral phase was found to disappear at about metal-C_{0.6}. High temperatures and compositions far from MC_{0.5} tended to prevent the formation of the rhombohedral phase. However, for some compositions in the vicinity of MC_{0.5}, the rhombohedral structure was found to persist even after arc melting and subsequent solidification. The rhombohedral determination was based upon the appearance of single, double, and triple diffraction lines, which indexed much better for a rhombohedral than for a face-centered cubic unit cell.

c. *Lanthanum*. Lanthanum has two carbides, the dicarbide LaC₂, body-centered tetragonal of calcium chloride type, and a sesquicarbide La₂C₃, cubic and of Pu₂C₃ structural type. Neutron diffraction studies by Atoji (17) confirm the structures determined by X-ray diffraction. A phase diagram for the lanthanum-carbon system has been published by Spedding and others (317), covering the lanthanum-rich part of the diagram which includes both carbides. At a temperature of 0°C, both La₂C₃ and LaC₂ exist over composition ranges of 1–2 weight % carbon.

La_2C_3 decomposes peritectically at 1415°C into liquid and LaC_2 , which at that temperature contains 12.8% carbon. Up to a temperature of about 1200°C , LaC_2 shows a constant composition, 14.4% by weight carbon. At 1800°C , tetragonal alpha LaC_2 changes to cubic beta LaC_2 , remaining cubic to a congruent melting point at about 2355°C . This polymorphic change in lanthanum dicarbide is in agreement with the work of Bredig (50).

d. Cerium. Tetragonal CeC_2 , the dicarbide, and cubic Ce_2C_3 , the sesquicarbide, of cerium are both prepared by conventional arc melting techniques. Neutron diffraction investigations confirming X-ray diffraction results as to crystal structure and carbon atom positions have been made by Atoji (17), for both of the cerium carbides. The existence of a cubic or hexagonal monocarbide CeC , as suggested by Brewer and Krikorian (52) and Vickery (356), was not confirmed by the later work of Spedding and others (316) or by Warf and Palenik (358). Spedding suggested that the CeC reported by Brewer and Krikorian was probably a solid solution of carbon in cerium. A tricarbonide CeC_3 , suggested by Vickery, was not found by either Spedding or Warf and Palenik. At the composition for CeC_3 given by Vickery, Spedding and his associates found, from the results of microscopic examination, chemical analysis, and X-ray diffraction, only mixtures of free carbon and CeC_2 . The same results were obtained whether such alloys were quenched or slow-cooled from the liquid state.

e. Praseodymium. There is agreement that this element has two carbides, the dicarbide PrC_2 , tetragonal and isotypic with calcium chloride, and a cubic sesquicarbide Pr_2C_3 . A neutron diffraction determination of structure and carbon atom positions has been carried out by Atoji and Williams (16) for the sesquicarbide.

f. Neodymium. Neodymium likewise has two carbides, Nd_2C_3 body-centered cubic, showing a structure like that of U_2C_3 , and NdC_2 tetragonal with calcium chloride structure type.

g. Samarium. Since the boiling point of samarium is below 2000°C , arc melting could not be used for preparation of samarium carbides. Weighed amounts of the metal and carbon were therefore heated in a tantalum bomb for periods of 2–24 hours at appropriate temperatures in the range $1200^\circ\text{--}2000^\circ\text{C}$ (316). Samarium is one of the metals for which a cubic carbide of iron nitride (Fe_4N) type, having the formula Sm_3C with some range of carbon solubility, was prepared by Spedding, Gschneidner, and others (316). As is true of the other rare earths except promethium, which apparently has no known carbides, there is a tetragonal dicarbide of samarium SmC_2 , and the usual cubic sesquicarbide Sm_2C_3 .

h. Gadolinium. In addition to cubic Gd_2C_3 and tetragonal GdC_2 as

listed by Gschneidner (124), Dean and his associates (74) in 1964 found a rhombohedral Gd_2C similar to Y_2C , which has already been discussed. It is also of interest to note that, due to the large neutron capture cross section of gadolinium, it is one of the metals mentioned in a patent for preparing carbide spheres as reactor fuels or poisons, which was granted to Goeddel (113) in 1965. The other cubic carbide is Gd_3C .

i. Terbium. No carbide Tb_2C was reported by Dean and others. The three carbides TbC_2 , Tb_2C_3 , and Tb_3C have the same crystal structures as the corresponding gadolinium carbides. Atoji (17) made neutron diffraction studies of both TbC_2 and Tb_2C_3 .

j. Dysprosium. A rhombohedral Dy_2C was reported by Dean and his co-workers (74). Apparently no neutron diffraction determinations have been made of the other three carbides—cubic Dy_3C , tetragonal DyC_2 , and cubic Dy_2C_3 .

k. Holmium. Preparation of a holmium carbide was reported by Petterson in 1895 (258). The method of Moissan was followed, reduction of oxide mixed with carbon by means of an electric arc. The rhombohedral carbide Ho_2C , found by Dean and his associates in 1964, was subjected to neutron diffraction analysis by Bacchella and others (22), confirming the rhombohedral structure and establishing numerical values for C-Ho and Ho-Ho interatomic distances. Holmium sesquicarbide was found by Gschneidner (124) to have two crystal forms, one of lower symmetry, similar to Y_2C_3 , the other form being body-centered cubic of Pu_2C_3 structure type. The tri-rare earth carbide Ho_3C is cubic (Fe_4N type); the dicarbide HoC_2 is tetragonal, as are the other rare earth dicarbides.

l. Erbium. Dean, Lallement, and others (74) also reported rhombohedral Er_2C . The other three erbium carbides, Er_3C , ErC_2 , and Er_2C_3 , are the same in structure as the corresponding dysprosium carbides.

m. Thulium. Carbides of thulium, as is also true for those of samarium, are prepared in a tantalum bomb rather than by arc melting. As is also true of the other rare earth elements from samarium to lutetium, a tri-rare earth carbide Tm_3C is formed. Thulium sesquicarbide Tm_2C_3 is of Y_2C_3 type of lower symmetry and unknown crystal structure. The other carbide TmC_2 fits into the series of the other rare earth dicarbides belonging to the tetragonal system.

n. Ytterbium. The three carbides YbC_2 , Yb_2C_3 , and Yb_3C are prepared by the tantalum bomb method. The tetragonal dicarbide YbC_2 has been studied by Atoji (15) by neutron diffraction methods. Knowledge of the structure of the sesquicarbide is incomplete but, according to Spedding, Gschneidner, and others (316), Yb_2C_3 does not seem to belong to either the Pu_2C_3 or Y_2C_3 structure types. The other carbide is cubic Yb_3C .

o. Lutetium. The three carbides of lutetium can be prepared by arc melting. Following the usual rules, LuC_2 is tetragonal, Lu_3C is cubic, and the sesquicarbide Lu_2C_3 is of symmetry lower than tetragonal or hexagonal and seems to be of Y_2C_3 type.

p. Europium. Preparation of europium dicarbide, EuC_2 , was reported by Gebelt and Eick (107) in 1964. Two methods of preparation were used. Europium sesquioxide (Eu_2O_3) was mixed with spectroscopic graphite, and heated by induction in a graphite crucible with a lid of graphite having an orifice allowing effusion under a vacuum better than 10^{-5} mm Hg at 1450°C . The dicarbide was also prepared by heating europium metal mixed with graphite in a stainless steel bomb under a helium atmosphere for 12 hours at 1050°C . Gebelt and Eick suggested that previous failures to prepare EuC_2 by the induction heating method were probably due to vaporization of EuC_2 from the crucible, or disproportionation and loss of europium as the metallic vapor. X-ray diffraction powder photographs showed agreement between the structure of EuC_2 and the other rare earth dicarbides. The unit cell was body-centered tetragonal. A French patent granted in 1966 to Holtzberg and others (151) described preparation of EuC_2 , Eu_2C_3 , and a tri-rare earth type carbide Eu_3C . Preparation was by heating stoichiometric amounts of europium metal and graphite under vacuum. The charge was contained in a refractory metal crucible, and heating was by induction to 1500°C with rapid cooling. In agreement with the work of Gebelt and Eick, EuC_2 was body-centered tetragonal of calcium chloride type. The Curie temperature of the dicarbide was found to be 40°K . The sesquicarbide Eu_2C_3 was reported to be body-centered cubic of Pu_2C_3 structure type. In agreement with the similar rare earth carbides from samarium through lutetium, Eu_3C had a body-centered cubic defect lattice of Fe_4N type. The vaporization of EuC_2 has also been studied by Gebelt and Eick (108), the temperature dependence of the vapor pressure of europium in equilibrium with solid EuC_2 being measured over the temperature range $1130^\circ\text{--}1600^\circ\text{K}$.

4. The Actinides

a. Thorium. Two carbides of thorium approximating, if not including, the stoichiometric compositions ThC and ThC_2 have been studied extensively. The two preparation methods most widely used are arc melting of thorium metal and carbon, and heating compressed powder mixtures of the metal and carbon below the melting point. Questions of purity arise in the discussions of lattice parameter and other properties of thorium carbides, because of the reactivity of the metal with nitrogen and especially with oxygen. Generally speaking, higher purities are obtained by arc melting.

The monocarbide ThC is face-centered cubic, of NaCl type with defect structure. Recent work by Takeuchi, Honma, and others (343) places the maximum carbon content for ThC at 49 atomic % carbon from 1350°C to room temperature with no composition change. The melting point of the monocarbide is near 2600°C. The value published by Wilhelm and Chiotti (363) in 1950 is in agreement with the results of Henney and Jones (140) published in 1966. The recent investigations by Henney and Jones, covering the composition range from ThC to ThC₂, and by Takeuchi and his associates, from thorium metal to ThC, supplement each other without overlap. However, considering the many changes found in the Th-C system since Wilhelm and Chiotti published a Th-C phase diagram in 1950, these two recent publications cannot be considered to completely and finally establish the phase relations for this system.

The chief features of the thorium-rich portion of the phase diagram are (1) a eutectic at about 1650°C, the horizontal extending from beta thorium (0.5 at. % C) to alpha thorium (6.5 at. % C) with the eutectic composition 4.5 atomic % carbon, and (2) a peritectic reaction at about 1875°C. The peritectic horizontal extends from about 5 atomic % carbon at the liquid end to ThC with a composition at this temperature of 33 atomic % carbon. The peritectic point is at 16 atomic % carbon, and the peritectic product is alpha thorium. According to the diagram of Takeuchi and others, the alpha field widens rapidly below the peritectic temperature, extending from thorium to about 8 atomic % carbon at the base temperature (about 1000°C). Although they did not determine the melting point of ThC, it is stated that the boundary, between the two-phase field liquid plus ThC and the single-phase field for solid ThC, shifts toward the high-carbon side and reaches the melting point of thorium monocarbide.

Thorium dicarbide is monoclinic at temperatures below 1400°C, at least on the thorium-rich side. This structure has been accepted since publication of single crystal determinations, including neutron diffraction results, by Hunt and Rundle (156) in 1951. In 1962 Kempter and Krikorian (172) indexed the low-temperature form of thorium dicarbide as pseudo-orthorhombic. In 1965 Gantzel, Langer, and others (105), using standard thermal analysis, differential thermal analysis, and high-temperature X-ray diffraction, found thorium dicarbide remaining monoclinic to 1427°C, then changing to tetragonal. The tetragonal structure persisted to 1481°C, changing to cubic above this temperature and remaining cubic to a high melting temperature near 2600°C. Similar results were obtained by Henney and Jones in their work on the portion of the Th-C system from ThC to ThC₂, as was previously noted. Henney and Jones also made metallographic studies of thorium carbon alloys in

addition to using the techniques employed by Gantzel, Langer, and their co-workers. Henney and Jones placed the monoclinic-tetragonal change of ThC_2 at 1410°C , and the tetragonal-cubic transformation at about 1500°C . For the region between ThC and ThC_2 , these transformations occurred at about 1290°C and 1490°C , respectively. They also found that, above about 2100°C , a solid solution between cubic ThC_2 and ThC existed. The high-temperature forms (cubic and tetragonal) of the dicarbide could not be retained to room or other low temperature by rapid cooling or quenching. These high-temperature forms were identified by high-temperature X-ray diffraction supplemented by differential thermal analysis.

In order to try to resolve the question as to whether ThC and ThC_2 can be prepared with stoichiometric compositions, an investigation was carried out by Bradley and Kegley (47) in 1964. Chemical analyses were supplemented by X-ray diffraction and metallographic examination. It was found that thorium monocarbide existed over a composition range from $\text{ThC}_{0.94}$ (4.6 wt. % C) to at least $\text{ThC}_{0.81}$ (4.0 wt. % C) and probably lower. The high-carbon limit for the single-phase dicarbide field was found to be $\text{ThC}_{1.95}$ (9.2 wt. % C), not attaining the theoretical composition $\text{ThC}_{2.0}$. Specimens having thorium-carbon ratios $\text{ThC}_{0.99}$ to $\text{ThC}_{1.88}$ (4.9–8.9 wt. % C) were found to be two-phase mixtures of mono- and dicarbides. This range of composition for the ThC - ThC_2 phase field is in agreement with the phase diagram for the portion of the Th-C system from 4 to 11 weight % carbon, published in 1966 by Henney and Jones.

By analogy with the uranium-carbon system, a sesquicarbide Th_2C_3 might be expected. Electrical resistivity measurements for the Th-C system, made in 1964 by Korbitz (178), gave some indication of the existence of a thorium sesquicarbide. However, Henney and Jones found no indication of such a sesquicarbide either in their high-temperature X-ray diffraction investigations of the binary Th-C system in the region where Th_2C_3 should be found, or in their subsequent investigation (141) of the thorium-uranium-carbon system. No mention of Th_2C_3 was made by Gantzel and others in their work on the Th-C system by the methods (except metallographic examination) used by Henney and Jones.

It is not completely accurate to say that thorium carbides are without practical use, as both thorium carbides and thorium-uranium carbides are used in nuclear reactors. Typical of such applications is the patent granted in 1963 to Goeddel and Simnad (112). The patent describes production of reactor fuel bodies by mixing finely divided graphite and silicides of thorium and uranium in the desired proportions, and adding a small amount (3–4 wt. %) of a diffusion bonding agent, such as finely divided zirconium, molybdenum, titanium, or other suitable elemental

powder; the mixture is then heated to 1500°–1800°F under mechanical pressure (above 3000 psi) and slowly cooled.

b. Protactinium. Two references to carbides of this element were found. In 1954 Sellers and his co-workers (308) reported preparation of PaC by reduction of PaF₄ with barium in a carbon crucible at 1400°C. Due to health hazards and small amounts of available material, only minute amounts (50–100 micrograms) were prepared. The report of the compound as PaC was based on an X-ray diffraction pattern, but the data thus obtained would not differentiate protactinium monocarbide from the monoxide of the element. No lattice constant was reported. In 1962 Lonsdale and Graves (192) used the Knudsen effusion technique to measure the vapor pressure of PaC₂ over a dilute solid solution of PaC₂ in ThC₂. The temperature range covered was 2000°–2900°K.

c. Neptunium. Three carbides of neptunium have been prepared. The crystal systems and structure types for each carbide have been established by X-ray diffraction methods. As in the case of protactinium, small amounts (microscale) were made. The preparation of NpC, Np₂C₃, and NpC₂ was published by Sheft and Fried (311) in 1953. The X-ray diffraction analyses and structure determinations were carried out by Zachariasen and Flettinger (373). In the preparation of all three carbides, the carbon source was a graphite crucible containing the neptunium compound. The crucible was placed within a vacuum system in which a small partial pressure of hydrogen was maintained. The dicarbide NpC₂ was prepared from neptunium oxide at a temperature, obtained by induction heating, of 2660°–2800°C. For preparation of the other two carbides, neptunium trifluoride (NpF₃) was reduced with lithium vapor at about 1200°C in a tantalum wound resistance furnace. Analyses of the reduction products by X-ray diffraction showed about 5 parts Np₂C₃ to 1 part NpC. The sesquicarbide Np₂C₃ was found to be cubic, isotypic with Pu₂C₃. The monocarbide NpC was found to belong to the cubic system. The dicarbide NpC₂ was very similar to ThC₂, monoclinic, but also indexing very well with a pseudotetragonal unit cell. The thermionic emission of Np₂C₃ was determined by Cranston and Barger (72), as part of an investigation of the thermionic emission constants of actinide carbides and oxides.

d. Plutonium. Due to uses of plutonium carbides in reactors, a considerable and increasing amount of literature exists pertaining to these carbides. This is true in spite of the high health hazards encountered in laboratory or large-scale work on plutonium and its compounds. Phase relationships in the system plutonium-carbon are complicated by the fact that the metal plutonium has six polymorphic forms. Four carbides are known and generally agreed upon. PuC, cubic with a carbon-deficient

NaCl-type structure, is formed peritectically at about 1650°C. This carbide is the most important in applications of plutonium carbides. The single-phase composition range at about 590°C is placed by Storms (335) between $\text{PuC}_{0.77}$ and $\text{PuC}_{0.9}$, narrowing at lower temperatures. Pu_3C_2 , of unknown crystal structure, is apparently a line compound rather than an intermediate phase having a composition range. Each of the six polymorphic forms of the metal plutonium transforms in contact with Pu_3C_2 which, in turn decomposes into epsilon Pu and the monocarbide PuC at 575°C. The sesquicarbide Pu_2C_3 is cubic, having a structure type similar to that of many other carbides, particularly the rare earth sesquicarbides. It was identified and characterized by Zachariasen (372) in 1952. It forms peritectically at about 2050°C with nearly stoichiometric composition. The remaining carbide PuC_2 , of unknown crystal structure, forms above 1750°C and is shown on the Pu-C phase diagram, given by Mulford and his associates (235), as the product of another high-temperature peritectic reaction at about 2250°C. There are a number of uncertainties in the phase diagram of the plutonium-carbon system, particularly in the high-carbon region from 60 atomic % carbon (Pu_2C_3) to 100 atomic % carbon. However, most of the features of the Pu-C system diagram published by Mulford and others in 1960 have subsequently been confirmed in the diagrams of Burnham and others (59) and by Storms.

Plutonium carbides of high purity are prepared by arc melting either the metal or PuO_2 with carbon, or by powder metallurgy methods. According to Storms, if the starting materials are pure and the arc melted button is remelted at least 6 times, homogeneous products are obtained. Arc methods fail for Pu_2C_3 and compositions in this range, due to extreme sensitivity of this carbide to thermal shock, making it necessary to use compressed powder techniques. When this is done, the powders used as starting materials are generally the element plutonium, PuO_2 , or $\text{PuH}_{2.8}$ mixed with carbon.

Technical methods for producing plutonium and plutonium-uranium carbides include carbothermic reduction of the oxide or oxides, reaction of the metal with elemental carbon, or reactions with gaseous hydrocarbons. Riley (271) outlines a representative preparation of plutonium carbide on a scale larger than that intended solely for laboratory use such as X-ray diffraction samples. Batches (400 gm) of PuO_2 or PuO_2 and UO_2 were mixed with the desired amount of carbon by ball milling (under CCl_4) for 12 hours. A portion of the mixture was then wrapped in tungsten foil and hot-pressed at temperatures of 1000°–2000°C under pressures up to 3 tons psi. By use of two hot-pressing stages, densities greater than 90 % of theoretical were achieved.

5. Unstable Carbides and Acetylides

The compounds of the metals gold, silver, copper, and mercury formed by the action of acetylene have been known for many years. In the case of copper, acetylides have been known since the work of Quet (264) in 1858. All of the acetylides are unstable and some are violently explosive. Recent interest in these compounds has centered around their use, particularly silver acetylide nitrates ($\text{Ag}_2\text{C}_2 \cdot \text{AgNO}_3$), as detonators and for explosive forming at low temperatures.

a. Copper. If acetylene is passed into an ammoniacal solution of cuprous chloride, a precipitate of Cu_2C_2 is formed. If cupric chloride is used, a red precipitate of CuC_2 is obtained, which is very unstable and cannot be dried without decomposition. In fact both copper acetylides explode upon drying, which has been known since the work of Quet in 1858 and Berthelot (32) in 1860. Powder X-ray diffraction patterns of copper acetylides, silver acetylides, and $\text{AgC}_2 \cdot \text{AgNO}_3$ have been published by Tanaka and Mizushima (344).

b. Silver. Moissan (221) found no evidence of the formation of any carbide upon solidification of molten silver containing carbon. The silver acetylides were prepared by Quet in 1858 and Berthelot in 1860 by passing acetylene into ammoniacal silver nitrate. Thermal and photodecomposition of silver acetylide (Ag_2C_2) has been studied by McCowan (194). The decomposition produced hexagonal silver and carbon as an amorphous residue. Use of silver acetylides in slurry form as an explosive-forming technique was reported by Baker and Hoesel (26) in 1965.

c. Gold. One method of preparing Au_2C_2 is by passing acetylene into aqueous aurous thiosulfate, $\text{Au}_2\text{S}_2\text{O}_3$. Gold acetylides were prepared by Berthelot (33) in 1866. Other gold acetylides obtained by mixing AuI in liquid ammonia with $\text{KC}\equiv\text{CH}$ yielded first Au_2C_2 , then $\text{K}_2(\text{HC}\equiv\text{CAuC}\equiv\text{CH})$ as well as $\text{Au}_2\text{C}_2 \cdot \text{NH}_3$, according to Nast and Kirner (239). The colorless complexes are strong electrolytes, nonexplosive but sensitive to light and moisture. The brown $\text{Au}_2\text{C}_2 \cdot \text{NH}_3$ was found to be highly explosive.

d. Mercury. The mercurous compound $\text{Hg}_2\text{C}_2 \cdot \text{H}_2\text{O}$ can be formed by passing acetylene, for a period of 30 hours, into an aqueous suspension of mercurous acetate kept in the dark. The mercurous acetylide is obtained as a white precipitate. Attempts to eliminate the water in $\text{Hg}_2\text{C}_2 \cdot \text{H}_2\text{O}$ by drying at 100°C result in decomposition. Early work on preparation of mercurous acetylides was by Plimpton (261) and by Burkard and Travers (58) in 1902. Mercuric acetylide HgC_2 was obtained by Keiser (170) in 1893 from the action of purified gaseous acetylene on a solution of mercuric and potassium iodides containing a little potassium hydroxide. This compound darkens upon slow and gradual heating to 100°C . Rapid

heating causes violent explosive decomposition to carbon and finely divided mercury. In 1952 Babko and Grebel'skaya (21) reported the preparation of HgC_2 by passing acetylene into 0.1 *N* $\text{K}_2\text{Hg}(\text{CN})_4$ solution that contained 0.1 *N* KOH. Solubility products for $\text{Hg}(\text{C}_2\text{H}_2)_2$ have recently been calculated by Tur'yan (349).

B. METALS WITHOUT REPORTED BINARY CARBIDES

1. *The Transuranium Elements (atomic numbers 95 through 103)*

This group includes the elements americium, curium, berkelium, californium, einsteinium, fermium, mendelevium, nobelium, and lawrencium. Beyond einsteinium, it is doubtful if isotopes are known having long enough half-lives for carbides to be prepared. All of these elements except americium are available in only very small quantities. Since americium is similar in chemical behavior to europium, it seems to be a reasonable although admittedly speculative assumption that, in addition to experimental difficulties resulting from the radioactivity of americium, there are other difficulties similar to those only recently overcome in the preparation of a carbide of europium. No mention of carbides was found for any element beyond plutonium, atomic number 94.

2. *Members of the Second and Third Transition Groups*

a. Ruthenium. A hexagonal carbide RuC similar to WC was reported by Kempter and Nadler (171) in 1960. The carbide was found as a minor phase in compressed ruthenium carbon pellets inductively heated to high temperatures in a helium atmosphere. The largest amount of the minor RuC phase was obtained by heating pellets compressed from a mixture of 1 part metal to 10 parts graphite for 4 hours at 2600°C. X-ray powder diffraction data were obtained in an 114.59-mm diameter Debye camera, using iron radiation filtered with cobalt. This was supplemented by back-reflection examination. Hexagonal lattice constants were reported as $a = 2.90775$ and $c = 2.82176 \pm 0.00001$ Å for RuC . An attempt to duplicate the work of Kempter and Hadler was made by Jeantet and Knapton (161) without success. In addition to using ruthenium-graphite mixtures, they added tantalum in an effort to stabilize RuC . In their X-ray diffraction work they used a 90-mm diameter Debye camera and filtered copper radiation. They remarked that the agreement between hexagonal WC and the hexagonal RuC found by Kempter and Nadler was very good.

Kempter discussed the work of Knapton in a later paper published in 1964 (173). The previous work of Kempter and Nadler was repeated and RuC was again found to be present. An extensive spectroscopic examina-

tion of samples having RuC lines showed the absence of W or Ta, as well as other elements that might have formed or stabilized carbides.

b. Rhodium. In 1960 Nadler and Kempter (236) reported a eutectic temperature in the rhodium-carbon system of $1694 \pm 17^\circ\text{C}$. No attempt was made to determine the eutectic composition. Preparation of rhodium carbide by heating rhodium metal with graphite in a high-temperature spectrographic furnace was reported by Lagerqvist and Scullman (186) in 1966. The band spectra were examined and determined, using a high-pressure xenon lamp as light source. An optical pyrometer was not available that would measure the temperatures reached, which were stated to be sufficient to melt metallic tungsten. No investigation was made of the low temperature stability of RhC.

c. Palladium. No report of simple palladium carbides was found in the literature. Nadler and Kempter (236) in 1960 found a eutectic temperature in the palladium-carbon system of $1504 \pm 16^\circ\text{C}$ for palladium with maximum impurities of 7 ppm by weight. The graphite used was of spectrographic grade. Complex organic acetylenides of palladium were prepared by Greaves and Maitlis (117) in 1966.

d. Rhenium. Modern work on the rhenium-carbon system begins with that of Hughes (154) in 1959. He reviewed the previous contradictory literature and conducted extensive investigations, which were negative as to the formation of a rhenium carbide. Hughes found a eutectic temperature on the rhenium-rich side of the system at 2480°C and 16.9 atomic % carbon. This was in good agreement with the 1960 determination of this eutectic by Nadler and Kempter (236), who reported a value of $2486 \pm 18^\circ\text{C}$. For alloys above the eutectic composition, carbon separated as flake graphite. The results published in 1963 by Evstyukhin and others (98) confirm the work of Hughes as to the Re-C eutectic temperature and composition. From X-ray diffraction patterns of quenched Re-C alloys, the existence of a dicarbide or monocarbide of rhenium is suggested. As many as five additional diffraction lines above those for graphite and rhenium metal were found in some diffraction patterns.

e. Osmium. In the same papers mentioned above for the ruthenium-carbon system, the osmium-carbon system was also examined. The same preparation techniques and methods of identification were used. Kempter and Nadler (171) in 1960 and again in 1964 (173) reported preparation of OsC having a hexagonal WC-type structure. Lattice constants were reported as $a = 2.90572 \pm 0.00007$ and $c = 2.82166 \pm 0.00019$ Å. Jeantet and Knapton (161) also failed in attempts to produce OsC as well as RuC.

f. Iridium. No report of a simple binary approximately stoichiometric carbide of iridium was found in the literature. The eutectic temperature for the iridium-rich side of the iridium-carbon system was found

by Nadler and Kempter (236) to be 2296°C for spectroscopic grade graphite and iridium having total impurities of 430 ppm by weight.

g. Platinum. Using the high-temperature spectrographic methods discussed above for rhodium, Neuhaus and others (242) recently reported band spectra for Pt-C. Nadler and Kempter (236) found a Pt-C eutectic at $1736^{\circ} \pm 13^{\circ}\text{C}$ from work on platinum wires in contact with spectrographic graphite.

3. Lanthanides

a. Promethium. This element is now the only rare earth metal for which no published report of a carbide was found. This may be due partly to the fact that promethium has been isolated for only some 20 years and that only small quantities are available. Preparation of a number of promethium compounds including the oxide, oxalate, phosphate, fluoride, and chloride was recently reported by Weigel (359).

4. The Radium Metals

a. Francium. Due to the short life of the isotopes of francium and to the minute quantities available, the chemistry of francium can be studied only on the tracer level. This makes the preparation of a carbide very difficult and unlikely. From a direct search for francium carbides, no published report of such compounds was found.

b. Radium. Again, no published report of the preparation of radium carbide was found. This may be due to experimental difficulties connected with the radioactivity of the element and to lack of interest. From its position in the Periodic Table just below barium, an acetylide and a carbide probably having the formula RaC_2 would be expected.

c. Actinium. Lack of published information on a carbide of actinium is apparently for the reasons just given for radium. Since one of the isotopes of actinium has a half-life of 22 years and there are reports of commercial production of the metal, it is available in amounts large enough for laboratory carbide production. Carbides of other elements in the actinide series—thorium, protactinium, uranium, neptunium, and plutonium—are known, and have been discussed.

5. Other Metals without Binary Carbides

Some of the elements in this and the next section, for which no binary carbides are reported or for which the evidence of such compounds is somewhat scanty, have ternary carbides to be mentioned later.

a. Indium. No published information on binary carbides was found. Ternary carbides containing indium are known.

b. Tin. The work of Moissan, repeated by Ruff and Bergdahl (279) in 1919, showed that only traces of carbon dissolved in molten tin, precipitating as graphite on freezing. Ternary metallic carbides containing tin are known.

c. Antimony. Ruff and Bergdahl (279) found that boiling antimony dissolves a maximum of 0.094 % by weight carbon, which precipitates as graphite on freezing. No published information on either binary or ternary carbides of antimony was found.

d. Tellurium. No binary carbides are reported in the literature.

e. Germanium. A French patent granted to Hamlet (130) in 1959 reported preparation of a layer of germanium carbide (GeC) 5–10 microns thick as one of the three layers of an electroluminescent cell. In 1966 Sharanina and others (310) reported preparation of $\text{Cl}_3\text{GeC}:\text{C}(\text{CH}_3)$ from germanium tetrachloride and trialkylstannylacetylene.

f. Bismuth. Ruff and Bergdahl (279) found the solubility of carbon in boiling bismuth to be 0.023 % by weight carbon, which completely separated as graphite on freezing. The solubility of carbon in liquid bismuth at lower temperatures (750°–300°C) was investigated by Griffith and Mallett (121) in 1953. Again, all carbon separated as graphite on completion of freezing, and no evidence of formation of any carbide of bismuth was reported. The solubility of carbon in liquid bismuth was very slight, varying from 0.0003 % by weight carbon at 750°C to 0.00016 % by weight carbon at 300°C.

g. Polonium. According to Bagnall (23), reaction between milligram amounts of polonium and carbon monoxide does not occur. Polonium has high volatility. It is suggested that, if polonium metal is deposited on silver, a polonium carbonyl may be formed, the silver acting as a catalyst when the deposit is exposed to carbon monoxide. Direct search of the literature gave no evidence of polonium carbide.

C. BINARY CARBIDES REPORTED BUT NOT CONFIRMED

1. Gallium

The gaseous species Ga_2C_2 was identified in 1958 by Chupka and his associates (66), using mass spectrometric methods. The compound was prepared by placing gallium metal in a graphite crucible with a graphite lid. The lid contained an effusion window allowing escape of the Ga_2C_2 vapor. The crucible was heated by electron bombardment from a tungsten filament surrounding the graphite effusion cell. Ternary metallic carbides containing gallium are known.

2. Technetium

In 1962 Trzebiatowski and Rudzinski (348) reported preparation of a technetium carbide, which X-ray diffraction studies indicated to be a face-centered cubic phase TcC. The diffraction lines of TcC were found for technetium-carbon compositions between 1.5 and 11.5 weight % carbon. The carbide was prepared by carburizing technetium metal with hydrogen-benzene mixtures or by heating the metal with a large excess of graphite at temperatures of 700°–1100°C. Giorgi and Szklarz (111) in 1966 reported preparation of technetium carbide of unspecified composition by vacuum inductive heating of technetium metal contained by a graphite crucible to its melting point. The technetium metal was specially purified, spectrographic analysis showing 10 ppm of iron as the only detectable impurity. Magnetic susceptibility studies showed that the technetium carbide thus prepared became superconducting at 3.85°K.

3. Selenium

In 1955 a patent was granted to Morningstar (232) for carbon diselenide prepared from carbon tetrachloride and hydrogen selenide. The compound was stated to be insoluble in water, with a boiling point of 124°C and a melting point of –45°C. In 1939 Barrow (27) reported the emission spectrum of CSe in the vapor of selenium heated with carbon, but this has not been confirmed by isolation of the solid compound.

4. Zinc

Durand (81) in 1924 reported preparation of zinc carbide (ZnC_2) by two methods. The first method was passing acetylene over pure zinc dust, temperature reported as 450°C; the second was passing acetylene through a solution of zinc-ethyl, $\text{Zn}(\text{C}_2\text{H}_5)_2$, in ligroin (b.p. 129°–130°C). Reiffenstein and others (269) in 1965 reported preparation of ternary carbides (of eta type) containing zinc. In these ternary carbides, niobium or tantalum was about 44 atomic %, carbon about 14 atomic %, and the remaining 42 atomic % was mainly aluminum with intentional replacement of part of the aluminum by zinc in some of the carbides prepared.

5. Arsenic

The preparation of arsenic tricarbidide (AsC_3 or As_2C_6) from AsCl_3 and $\text{Mg}_2\text{C}_2\text{I}_2$ was reported by de Mahler (199) in 1921. In 1966 Kuz'min and Pavlova (185) published preparations for acetylene derivatives of arsenic, in which the atomic refraction of arsenic was significantly different from that in ordinary arsines. The simplest of these compounds was $\text{Pr}_2\text{AsC}:\text{CAsPr}_2$ ($\text{Pr} = \text{CH}_3\text{CH}_2\text{CH}_2$). By passing acetylene into ethylmagnesium bromide dissolved in diethyl ether, a bifunctional Grignard

reagent was formed as a dark oil; Pr_2AsI was added and, after refluxing an hour and allowing the mixture to stand overnight, the arsine formed upon treatment with acidified NH_4Cl .

6. *Thallium*

Schwarz (291) reported a superconducting thallium carbide in 1932. The carbide was said to be superconducting up to 9.2°K . No method of preparation or formula was given; also no subsequent confirmation was found in the literature. Ternary carbides of perovskite type such as Dy_3TlC were prepared by Haaschke and others (127) in 1966.

7. *Lead*

In 1923 Durand (82) reported the preparation of a lead carbide of formula PbC_2 by adding calcium carbide to an aqueous solution of neutral lead acetate. Durand stated that this was the first compound known in which bivalent lead was combined directly with carbon. No published report of successful repetition of this work was found. Masson and Cadot (202) in 1965 reported preparation of acetylene derivatives of lead. The method used was similar to that used in preparing simple acetylides of other metals. One of the simplest of these lead derivatives of acetylene was $(\text{Et})_3\text{PbC}:\text{CCH}_3$. Suitable sodium alkynides were dissolved in liquid ammonia or hydrocarbons, and triethyl- or triphenyllead halides were added to the dissolved sodium alkynides. In addition to determining melting points and boiling points, infrared and ultraviolet spectra were measured and for some substances nuclear magnetic resonance.

8. *Cadmium*

Durand (81) also reported preparation of cadmium carbide, CdC_2 , by passing acetylene over fine cadmium shavings at an elevated temperature. As is also true of the carbides of lead and zinc that Durand reported, subsequent published confirmation was not found.

V. Carbides Containing Three or More Elements

A. COMPLEX CARBIDES IN FERROUS ALLOYS

As was previously stated, this article is mainly a review of binary carbides. No extensive or complete coverage of ternary and more complex carbides will be attempted. A number of elements having no known or well-established binary carbides have fairly well-confirmed ternary

carbides. Many ternary carbides are members of the same class or group such as the perovskite-type carbides, while other complex carbides do not fit known structure types. Only recent and representative carbides and publications will be discussed.

Two of the carbides found widely in alloy steels may be quite simply represented by type formulas M_6C and $M_{23}C_6$ (in which M = metal atoms, and C = carbon). Substitution of two or more metals causes formation of ternary or more complex carbides. Formulas vary quite widely from author to author; generally such substitutions of metal atoms do not change the crystal structure class of the resulting carbide, so Greek letter designations are used. This letter notation is fairly uniform although some exceptions are found. Some of these classes, such as those of the eta (η) carbide type, are also found in other ternary or complex carbides not based upon iron.

Historically, the first investigation of ternary carbides using X-ray diffraction methods, in addition to the techniques of metallography, heat treatment, and older metallurgical methods, was published by Westgren and Phragmen (360) in 1928. From Laue and rotation photographs of ferro-tungsten crystals and from synthetic melts, these workers assigned the most probable formula Fe_4W_2C to a face-centered cubic structure having a unit cell containing a large number of atoms. A similar ternary carbide Fe_4Mo_2C was also found. The possibility that Fe_3W_3C might be more correct was mentioned. It can be seen that these formulas all conform to M_6C . The 1928 publication was stated to be a preliminary report. This carbide type is generally referred to as an eta (η) carbide, and there are also variations to be mentioned later in this section. For carbides of this type, as found in high-speed steels, which were first extensively investigated as to their ternary carbides, the range of solid solubility is from Fe_3W_3C to Fe_4Mo_2C in tungsten-based steels, and from Fe_3Mo_3C to Fe_4Mo_2C in molybdenum-based alloys. The unit cell contains 112 atoms (96 metal and 16 carbon atoms) and the lattice parameter is $a = 11.06 \text{ \AA}$. These results were obtained for such carbides by Westgren (361) in 1933 on what he termed "the double carbide of high-speed steel," which is now by general agreement called the eta carbide type. In this paper, Westgren gave the space group and atomic positions, assigning Fe_3W_3C as the most probable formula. In the same year he also published a structure determination of $Cr_{23}C_6$, which with substitution gives rise to another widely found type of complex carbides (362). For $Cr_{23}C_6$, his published structure determination showed that the carbide was face-centered cubic with 116 atoms per unit cell (92 chromium and 24 carbon); the space group is O_h^5 , and the positions and coordinates of all the carbon and chromium atoms are given. Westgren also pointed out that this $M_{23}C_6$ type of carbide was

widely distributed in stainless steels and in low-alloy steels containing tungsten and molybdenum. The heavier metal atoms were found to preferentially occupy one set of atomic positions, not being randomly or statistically distributed. Two such substituted carbides mentioned in this paper are $\text{Fe}_{21}\text{W}_2\text{C}_6$ and $\text{Fe}_{21}\text{Mo}_2\text{C}_6$.

In 1954 Carroll, Darken, and others (63) found a similar iron borocarbide of formula $\text{Fe}_{23}(\text{C}, \text{B})_6$, in which part of the carbon atoms had been replaced by boron. This compound was found in steels having intentional boron additions. The numerical and structural results were very close to those of Westgren obtained 20 years earlier. This Cr_{23}C_6 "type" of structure also occurs widely in ternary carbides, not exclusively in ferrous alloys. Goldschmidt (114) termed these carbides, which he represented by $(\text{Cr}, \text{Fe}, \text{Mo}, \text{W})_{23}\text{C}_6$, kappa (κ) carbides, and others have followed this notation.

The paper in which Goldschmidt proposed this kappa notation was published in 1948, and was the first part of an investigation of the structure of carbides in alloy steels. It was an extensive review of binary and ternary carbides in ferrous alloys, and is still a valuable source. In Part Two of this investigation, published by Goldschmidt (115) in 1952, the experimental results of an investigation of the quaternary iron-chromium-tungsten-carbon system and of work on various commercial-type high-speed steel alloys were set forth. Compositions and carbides in the high-speed steel portion of the quaternary were the chief object of the investigation. The original composition of high-speed steel found by Taylor and White was (by weight) 18W-4Cr-1V, carbon 0.70%, sulfur and phosphorus each below 0.05, manganese 0.25, silicon 0.25, and the balance iron. The major change since the adoption of this "original" high-speed steel in the decade 1900-1910 has been partial replacement of tungsten by molybdenum. As can be seen from Westgren's results for eta carbides, such a partial molybdenum replacement is of little importance as far as the carbides of high-speed and other alloy steels are concerned. In addition to eta and kappa carbides, Goldschmidt found two other carbides in variously heat-treated high-speed steels. One of these two carbides was V_4C_3 of rock salt structure. This was found only in compositions with excess vanadium; lesser amounts of vanadium occurred as a substituent in eta and kappa carbides. Finally, Goldschmidt also found that with certain heat treatments a new cubic carbide, which he designated as η^* (eta star), was formed with simultaneous liberation of tungsten. The cube edge of this new eta carbide was much shorter (10.96 kx) than that of normal eta carbide (11.07 kx). With respect to the carbides of high-speed steels, the work of Goldschmidt seems to be still substantially correct.

A third important type of ternary carbide found in ferrous alloys is formed by substitution of part of the iron atoms in orthorhombic cementite, Fe_3C , by other elements without change in the crystal structure. Such elements are manganese or chromium and, in smaller amounts, tungsten, molybdenum, or vanadium. Such substitution produces carbides that are written as $(\text{Fe}, \text{Mn})_3\text{C}$ or $(\text{Fe}, \text{W})_3\text{C}$ and similarly for other elements that partially replace the iron atoms in cementite. A recent study of such a carbide, synthesized from the elements iron, manganese, and carbon and to which the formula $(\text{Fe}_{1.8}\text{Mn}_{1.2})\text{C}$ was assigned, has been carried out by Duggin and others (79). The experimental techniques used included chemical analysis, electron microprobe analysis, X-ray diffraction, and neutron diffraction. The results obtained showed that the iron and manganese atoms were randomly distributed, the deviation from a statistically random distribution being about 5%. Comparison of results for $(\text{Fe}_{1.8}\text{Mn}_{1.2})\text{C}$ was made with those obtained by Fasiska and Jeffrey (101) in 1965 for $(\text{Fe}_{2.7}\text{Mn}_{0.3})\text{C}$. The atomic coordinates of the carbon atoms in both of these carbides were found to agree very closely. The importance of the investigation by Fasiska and Jeffrey was that it was perhaps the first single crystal investigation of the cementite structure. In order to obtain single crystals, it was necessary to introduce manganese, hence the formula $(\text{Fe}_{2.7}\text{Mn}_{0.3})\text{C}$. The refinements (including use of computer programs) that Fasiska and Jeffrey were able to make enabled determination of the position of iron atoms to a standard deviation of 0.001 Å, and of carbon atoms to a standard deviation of 0.01 Å. However, these final positions were within 0.12 Å for carbon atoms and within 0.03 Å for iron atoms of those obtained for Fe_3C by Lipson and Petch (191) in 1940, which have since been generally accepted.

B. OTHER COMPLEX CARBIDES

Mention has been made of the eta and kappa types of ternary or more complex carbides, and of differences in the use of Greek letter designations. The difference in the use of "kappa" illustrates this. As proposed by Goldschmidt, kappa carbides were those of Cr_{23}C_6 type with substitutions, face-centered cubic with 116 atoms per unit cell. On the other hand, Rautala and Norton (268) used the term "kappa" for a carbide in the hexagonal system found in the ternary Co-W-C having a proposed formula $\text{Co}_3\text{W}_{10}\text{C}_4$ with a range of homogeneity of less than 1%. The next year (1953) Kuo (182), in a discussion of the work of Rautala and Norton, agreed with this designation of a hexagonal kappa carbide, listing two

other similar such carbides he had found in the systems Ni-W-C and Mn-W-C. Kuo proposed no specific formulas for his two kappa carbides. For all three of these hexagonal kappa carbides, the a and c parameters had identical values. This use of "kappa" to designate a hexagonal structure in carbide and other phases has been followed by Nowotny and his associates. In a paper on "New Kappa Phases" by Reiffenstein, Nowotny, and others (270) published in 1966, fifteen such phases are tabulated. All the c/a axial ratios are close to unity, ranging from 1.048 for $\text{Mn}_3\text{Al}_{10}$ to 0.986 for a kappa phase in the quaternary system W-Mn-Al-C. Formulas were allocated to only a few of these kappa phases, such as $\text{Mo}_{12}\text{Cu}_3\text{Al}_{11}\text{C}_6$. Other quaternary systems, such as W-Fe-Al-C and Mo-Co-Al-C, showed hexagonal kappa phases. Thus, the Greek letter designation is not always consistent for kappa phases.

More consistency is found for the eta or M_6C carbides, which apparently are always cubic with the unit cell containing 112 atoms as first described by Westgren (361). The division into two types— η_1 (eta sub-one), for which $\text{V}_3\text{Cr}_3\text{C}$ is a typical formula, and η_2 (eta sub-two), which includes the "double carbide" $\text{Co}_2\text{Mo}_4\text{C}$ and $\text{Ni}_2(\text{Ta}, \text{Ti})_4\text{C}$ —was proposed by Kuo (181) in 1953. The cube edge for the η_2 carbides was longer than for η_1 . A publication by Reiffenstein and others in 1965 (269) follows the proposals of Kuo and Westgren, and describes a number of new eta carbides. The alloys investigated contained: Nb or Ta about 44 atomic %, carbon about 14 atomic %, and the remaining 42 atomic % was Al + (V, Cr, Mn, Fe, Co, Ni, Cu, or Zn). The usual atomic % values for Al were 6, 14, 20, or 30 atomic %, various quaternary combinations being obtained to make up the balance of the desired quaternary alloy from one of the metals within the parentheses. The eta carbides thus prepared were identified by powder X-ray diffraction patterns. A wide range of homogeneity was found in several of these quaternary systems, and it was tentatively concluded that aluminum was important for the formation of these eta carbides. A comparison of calculated and observed intensities for $\text{Ta}_3\text{CrAl}_2\text{C}$ showed good agreement for a structure of eta carbide type.

It was previously mentioned that a number of metals, without binary carbides or with doubtful binary carbides, have ternary or more complex carbides that are fairly well confirmed. A single such ternary carbide for these metals, when known, will now be listed, although gallium, indium and germanium, which seem to be without binary carbides, are found in many ternary carbides of different structure types. Many of the known ternary carbides can be placed in a few structure types, although information on the ternary system as a whole may be incomplete and sketchy.

Probably the structure type with the largest number of known examples is that of the perovskite carbides. These carbides have

face-centered cubic structures with atoms of a lower melting metal at the cube corners, atoms of a transition metal at the six face centers forming an octahedron around a carbon atom at the interior (or body) center of the cube. All of the following carbides have this perovskite structure, and are taken from the tables of Nowotny and others (247) published in 1964: palladium— Pd_3InC , platinum— Pt_3InC , indium— Fe_3InC , tin— Mn_3SnC , germanium— Co_3GeC , gallium— Mn_3GaC , zinc— Ni_3ZnC , thallium— Ti_3TlC , and lead— Pd_3PbC .

Cadmium (247) and arsenic (42) have ternary hexagonal carbides, which have been termed "H" phases by Nowotny and his associates. Part of the carbon atoms are at the center of an octahedron formed by six transition metal atoms. The vertical stacking sequence for this hexagonal type of structure is: A (low melting metal, arsenic or cadmium in this particular instance); B (transition metal); A (transition metal); B (low melting metal). Carbon atoms are at the centers of the octahedra formed by two successive transition metal layers. For cadmium, such an H phase has the assigned formula Ti_2CdC ; for arsenic, the H phase V_2AsC is found in the V-As-C ternary system.

In 1967 Holleck and Thummler (150) found, in the system Zr-Os-C, a cubic carbide with lattice parameter 12.4 Å, of partially filled Ti_2Ni structure to which the formula $\text{Zr}_4\text{Os}_2\text{C}$ was assigned. Carbides of rhenium and iridium were not reported in this paper, but an eta nitride phase $\text{Zr}_4\text{Ir}_2\text{N}$, cubic with edge length 12.35 Å, was found; a complex oxide of rhenium (also having the same partially filled Ti_2Ni structure), $\text{Zr}_4\text{Re}_2\text{O}$ ($a = 12.35$ Å), was also prepared.

The other carbide structure types (for ternary and more complex carbides, nitrides, oxides, and intermetallic compounds) included in the 1964 classification by Nowotny and others (247) are:

(a) $\text{T}_3\text{M}_2\text{X}$ phases with a filled beta-manganese type cubic structure such as $\text{Mo}_3\text{Al}_2\text{C}$ and $\text{Nb}_3\text{Al}_2\text{N}$. In this notation, T denotes a transition group metal, M is a metatmetal or lower melting point metal from Groups IIB through VB of the Periodic Table excluding silicon and germanium, and X is a metalloid, usually carbon or nitrogen, but occasionally boron or oxygen.

(b) Phases with partially filled Mn_5Si_3 structure. This structure type is hexagonal, space group $D8_8$. The type formula is $\text{T}_5\text{M}_3\text{X}_{(1-x)}$, the metalloid varying in composition as the subscript $(1-x)$ indicates. A phase of this type has been found in the ternary system Zr-Si-C (no specific formula assigned); other examples include $\text{Mo}_5\text{Ge}_3(\text{C})$, $\text{Nb}_5\text{Si}_3(\text{X})$, and binary compounds such as Mg_5Hg_3 , Y_5Si_3 , and Mo_5Si_3 .

These structure types—eta, kappa, H phases, perovskite, $\text{T}_3\text{M}_2\text{X}$, and $\text{T}_5\text{M}_3\text{X}_{(1-x)}$ —classify over two hundred substances, chiefly ternary

carbides and nitrides. Over eighty of the listed phases are ternary carbides. However, new structure types are also found as more research on ternary and complex carbides is completed and published. An example of such a new carbide structure type is contained in a 1967 paper by Jeitschko and Nowotny (162) on the crystal structure of Ti_3SiC_2 . From a single crystal X-ray investigation, this carbide was found to belong to the hexagonal crystal system, $a = 3.068$, $c = 17.669$ Å; $c/a = 5.759$, with space group $D_{6h}^4 - P6_3/mmc$.

No consideration of the methods of producing these complex carbides has been made up to this point. One of the first preparations of one of these ternary carbides was by Morgan (231) in 1954. One of his formulas was $\text{Mn}_{65}\text{In}_{15}\text{C}_{10}$. An arc furnace was used with an argon atmosphere instead of vacuum to avoid volatilization of manganese. Many of the perovskite carbides have been prepared by Stadelmaier and his co-workers. In 1959 Hutter and Stadelmaier (157) described an induction furnace method by which they prepared perovskite-type carbides. The transition metal was manganese, iron, cobalt, or nickel, and the second metal was indium or germanium. In order to obtain alloys of high carbon content, the transition metal was melted with carbon and the charge in many cases was placed in a graphite container. After melting the transition metal, the lower melting point metal such as indium or germanium was then added to minimize loss.

The other principal method of producing these complex carbides is by the techniques of powder metallurgy. Among other advantages, some of the problems associated with the high vapor pressures of metals, such as zinc and cadmium, at the temperatures of molten transition metals, such as iron and nickel, are avoided. In commenting on the production of these carbides, Nowotny, Jeitschko, and others (247) state that many of them can be produced by hot-pressing. Times up to 1500 hours at temperatures of $700^\circ\text{--}900^\circ\text{C}$ may be necessary. The transition metal employed is usually of very fine particle size (10 microns or smaller); the lower melting metal is used as larger particles (up to 0.5-mm diameter) in order to avoid loss, and the pressing is carried out under pressures of several atmospheres. In some cases, better results were obtained if the two metal powders were cold-pressed with graphite so that they were embedded in a graphite matrix, before hot-pressing. For carbides containing zinc, cadmium, or gallium, the hot-pressing method could not be used. Closed quartz tubes were used to contain the powders, and extremely long sintering times were necessary to obtain reaction and carbide formation. A week at 900°C for Mo-Ga-C gave no sign of reaction. Other papers mention heating times as long as 1500–2000 hours to obtain measurable carbide formation in some systems.

VI. Properties of Carbides

A. CRYSTALLOGRAPHIC PROPERTIES

Extensive numerical property tables for carbides seem unnecessary. Large collections and tables including the crystallographic information about most carbides are already available. For X-ray crystallographic information, the largest single source is probably the ASTM Powder Data

TABLE I
CRYSTALLOGRAPHIC DATA FOR SELECTED CARBIDES

Nominal formula	Crystal system	Ref.	Lattice constants (in Å)		
			<i>a</i>	<i>b</i>	<i>c</i>
EuC ₂	Tetragonal	(107)	4.045		6.645
V ₂ C	Orthorhombic	(370)	4.577	5.742	5.037
V ₂ C	Hexagonal	(370)	2.885		4.560
Nb ₂ C	Hexagonal	(371)	5.407		4.960
Nb ₂ C	Orthorhombic	(371)	10.920	4.974	3.090
Ti ₃ SiC ₂	Hexagonal	(162)	3.068		17.669
Zr ₃ Fe ₃ C	Cubic	(150)	11.80		
Zr ₄ Os ₂ C	Cubic	(150)	12.41		
Nb ₄ Co ₂ C	Cubic	(150)	11.63		
Nb ₄ Ni ₂ C	Cubic	(150)	11.64		
Ta ₄ Co ₂ C	Cubic	(150)	11.59		
Ta ₄ Ni ₂ C	Cubic	(150)	11.61		

File (367). Another large collection of similar information is Pearson's (254) book *Handbook of Lattice Spacings and Structures of Metals and Alloys*. The extensive (15 volumes to date) *Structure Reports*, published by the International Union of Crystallography (255), contain many carbide structure determinations. A similar set of such tables, containing 60 pages of carbide, boride, hydride, nitride, and oxide structures, is the volume by Taylor and Kagle (345) published in 1963.

Another considerable problem is the variation of lattice parameter with purity and composition, including a large number of carbides that apparently are never stoichiometric, but have defect or excess structures. For the carbides of the important refractory metals, such as titanium, zirconium, hafnium, tantalum, niobium, chromium, molybdenum, vanadium, and tungsten, the values available have been critically reviewed (up to 1964) and discussed at length by Storms (323). A similar review of

crystallographic and other properties of the carbides of iron was published by Hofer (149) in 1966. Much of the recent work (especially for 1962–1967) on ternary and complex carbides by Nowotny, Benesovsky, and their associates and students has been published in the journal *Monatshefte für Chemie*. For these reasons, the short Table I is limited to values for a few carbides such as europium dicarbide which is comparatively new, to carbides such as V_2C and Nb_2C where recent redeterminations have been made, and to a small number of ternary carbides. Some (but not all) of these results have previously been given in the text of this review.

B. DENSITIES, MELTING POINTS, AND TEMPERATURE-STABILITY RANGES

Again, repetition of a large amount of data from other sources seems needless. Densities are almost always listed with X-ray diffraction data; the temperature-stability ranges of carbide polymorphs are dependent upon purity, as is also true for lattice parameters. The work of Bredig (48) on the polymorphic carbides of calcium, strontium, and barium has been discussed. The formation and rapid decomposition of molybdenum monocarbide MoC have been mentioned, showing the effect of small amounts of other elements in stabilizing a carbide. Nowotny (246) states that small additions of other elements, such as $(Mo_{0.95}Hf_{0.05})C_{1-x}$ or non-metals such as $MoC_{1-x}B_{0.03}$, will stabilize the MoC phase. Stability of the important refractory carbides (of Groups IVA, VA, and VIA of the Periodic Table) with respect to chemical and temperature stability has been discussed by Storms (323).

The melting temperatures of tantalum and hafnium carbides were discussed previously. A very recent publication by Rudy and Progulski (278) presents in detail the results of 2 years of investigation into the melting points of carbides, refractory metals, high-temperature eutectic and peritectic isotherms in carbide and boride systems, and boride melting points. A modified and refined Pirani-type furnace was employed. In the Pirani method, the specimen is of bar type, having a black body hole drilled in it for temperature determination, the specimen being supported by two water-cooled electrodes and heated by electrical means. An optical pyrometer sighted on the black body hole allows reading of the temperature as liquid appears. The paper contains a long discussion of methods for reducing and compensating for temperature errors in the use of the optical pyrometer and in calibrating the instrument to a high limit of about $4000^{\circ}C$. The question of maintaining specimen purity is also discussed. The chief improvement over previous Pirani-type furnaces was the use of a fast-response power-feedback circuit to eliminate runaway

problems, as well as incorporation of suitable preheating techniques to overcome poor electrical conductance of some materials at low temperature. (The original paper should be referred to for experimental details.)

The values published by Rudy and Progulski were stated to be based upon material of high purity, analytically defined. Each numerical value was the average of a large number of measurements, since the melting points obtained were part of a 2-year investigation into the phase diagrams of refractory metal systems for carbides and borides. As a matter of interest, the melting points of six of the highest melting monocarbides, as stated by Rudy and Progulski, are compared in Table II with those given previously in this review. According to this latest work, TaC is the highest congruent melting carbide with a melting point exceeding that of HfC by about 60°C. Rudy and Progulski mention in their paper that the data of Agte and Alterthum (6) obtained by the Pirani method must still be considered of high precision, although their results were published over 30 years ago.

TABLE II
CONGRUENT MELTING POINTS OF CUBIC (NaCl) CARBIDES

Carbide	M.P.	Reference	T_f^a	Rudy and Progulski	
				Composition (at. % C)	Average reproducibility
TiC	(none)		3067° ± 25°	44 ± 1	±15°
ZrC	3420°	Sara (286)	3440° ± 25°	45 ± 1	±10°
HfC	3895°	Beall (4)	3928° ± 40°	48.5 ± 0.3	±20°
VC	(none)		2648° ± 12°	43 ± 0.5	±8°
NbC	3485°	Brownlee (55)	3613° ± 26°	44 ± 1	±8°
TaC	3825°	Sara (285)	3983° ± 40°	47 ± 0.5	±15°

^a Mean value and estimated overall temperature uncertainty. All temperatures in centigrade degrees.

VII. Available Phase Diagrams

A. BINARY CARBIDES

If a single reliable source had to be chosen for phase diagrams for binary metal carbides, the volume *Constitution of Binary Alloys* by Hansen and Anderko (131), in conjunction with the supplement by Elliott (86), would serve the purpose. The literature is reviewed through 1961 in

these two volumes. The binary metal-carbide systems of industrial and refractory importance (titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, and tungsten) are shown in later phase diagrams (1964 in both cases) in the review by Storms (323) and in the article by Kieffer and Benesovsky (174) in the Kirk-Othmer *Encyclopedia of Chemical Technology* (177). A later article covering most of these transition-metal carbide systems is that by Eberle and others (83) in 1966. Hansen's work covers all known binary metal-carbon systems. Where more detail is necessary, the literature must be consulted.

B. TERNARY AND HIGHER CARBIDES

1. *Ferrous Alloys*

Although the binary metal-carbon systems are reliably evaluated by Hansen, no comparable collection seems to be available for any of the ternary or quaternary systems whether ferrous or nonferrous. To say that any ternary metal-carbon diagram is completely known would probably be a misleading and inaccurate statement. The great number of possible combinations in comparison to binary diagrams, and the need in ternary diagrams for a considerable number of vertical and horizontal sections, increase the work required to put a ternary diagram into final form beyond the present state of knowledge. The available information ranges from studies made over 40–50 years for such ferrous alloy systems as Fe-Cr-C in stainless steels and Fe-W-C in high-speed and other alloy steels to fragmentary reports of a single carbide, such as $\text{Zr}_4\text{Os}_2\text{C}$ recently reported by Holleck and Thummler (150) in the system Zr-Os-C. Three areas in which considerable work has been done on ternary and more complex carbide systems are ferrous alloy systems, refractory transition metal-carbon systems, and those based mainly upon uranium, of interest primarily in nuclear reactors. Sufficient interest due to financial and other reasons exists to maintain continuing investigations in these fields. For other ternary or more complex metal-carbon systems, investigations are sporadic and uneven in nature and content.

In order to give an idea of work on important ferrous ternary alloy carbide systems, Fe-Cr-C and Fe-W-C will be used. The system Fe-Cr-C occurs in stainless, high-speed, and many other alloy steels. The system Fe-W-C contains the carbides that allow a cutting edge to be maintained at a dull red heat, which is the origin of the designation 'high-speed steel.'

A ternary diagram for a portion of the system Fe-Cr-C, based partly upon their own work on austenitic stainless steels, was published by

Aborn and Bain (1) in 1930. In the same year and in the same journal, Krivobok and Grossmann (180) published another ternary diagram for this system. The literature to 1940 was collected and reviewed by Kinzel and Crafts (176, 176a). The iron-carbon-chromium phase diagram up to 4% by weight carbon and to 38% chromium was reinvestigated by Bungardt *et al.* (57) in 1958. Metallographic, dilatometric, and X-ray diffraction methods were used. A still later investigation of alloys near 70% chromium was published by Pepperhoff and others (256) in 1962. Strauss (339) began his investigations into nonrusting steels as early as 1909, and in 1924 published a structural diagram for the iron-rich corner of the Fe-Cr-Ni-C alloy system. For the austenitic stainless steels, chromium contracts the austenite field while nickel expands the region of stable austenite. The base composition of these highly corrosion-resistant stainless steels was decided upon as a result of phase diagram studies (during the period 1920–1930), since 8% by weight of the more expensive element nickel is the minimum amount that will give a nearly stable austenite at room temperature with 18% by weight of the element chromium, so that the high intrinsic corrosion resistance of both these elements is also utilized. The “18-8” stainless steels can lose their corrosion resistance by grain boundary precipitation of Cr_{23}C_6 . To overcome this, an addition of Ti or Nb is usually made, forming more stable TiC or NbC, so that no carbon remains for formation of the injurious chromium carbide at the grain boundary. As was previously mentioned, nickel forms no stable binary carbides from steel melts. In view of these facts, it is interesting that a recent (1966) investigation by Stadelmaier (320) reported unsuccessful attempts to form any ternary carbides in the nickel-rich corner of six ternary systems, which included Ni-Ti-C, Ni-Nb-C, and Ni-Ta-C. The corresponding cobalt-rich ternaries were also included. No ternary carbides were found in any of these twelve ternary combinations.

Although the high-speed steels were originally based upon the composition 18W-4Cr-1V-C-0.70 in % by weight, molybdenum has been so widely used, especially for the last 25 years, to replace part of the tungsten in such steels, that something about both Fe-W-C and Fe-Mo-C is necessary. In 1931 Grossmann and Bain (123) published a book *High Speed Steel*, which contained an admittedly tentative isothermal section and a “pseudobinary” section for Fe-W-C. However, 3 years later the monograph *Alloys of Iron and Tungsten* by Gregg (120) contained a 40-page chapter on the ternary Fe-W-C. This chapter was based largely on the work of Takeda (341); the chief criticism offered by Gregg was that Takeda’s diagram was too theoretical with insufficient experimental support. The work of Westgren on $\text{Fe}_4\text{W}_2\text{C}$ was also discussed by Gregg in this volume. The companion volume *Alloys of Iron and Molybdenum* by

Gregg (119), published in 1932, contained only a 5-page appendix for the ternary Fe-Mo-C, commenting on the work of Takei (342), also published in 1932. A later important review was published by Goldschmidt (114) in 1948, as was previously mentioned. Both binary and ternary carbides in alloy steels were reviewed, binary and ternary diagrams published, and a bibliography of ninety-three references was included. A description from the literature of the system Fe-V-C appeared, as well as schematic isothermal sections typifying Fe-W-C and Fe-Mo-C. The experimental results obtained by Goldschmidt (115), in the second part of his researches on the carbides of high-speed steels, have been discussed above. In this second paper, he included a perspective view of the quaternary Fe-Cr-W-C, showing the location and extent of the various binary and ternary carbide phases and the approximate location of the usual high-speed steel composition in the system. Vanadium and its carbides in high-speed steels were separately discussed.

The following year (1953) Kuo (183) published isothermal sections for both the stable (Fe-graphite-W) and metastable (Fe-W-Fe₃C) diagrams at 700°C. The carbides found in ternary space for the stable section were Fe₃C, WC, M₆C (composition limits Fe₃W₃C to Fe₄W₂C, structure face-centered cubic), and M₂₃C (also face-centered cubic, ideal composition Fe₂₁W₂C₆). These carbides all had analogs in the Fe-Mo-C system, which also contained (according to Kuo) two hexagonal forms of a molybdenum monocarbide "MoC"; this last controversial monocarbide need not be further discussed here. Kuo did not include isothermal sections for Fe-Mo-C in his paper, but his text amply covered the binary and ternary carbides of molybdenum-containing steels (Fe-Mo-C). Finally, in 1960 Campbell, Reynolds, and others (62) published a considerably expanded study of the Fe-Mo-C system. In general their findings agreed with those of Kuo and Takei; but, in the Campbell paper, isothermal sections for Fe-Mo-C were at 700, 925, and 1200°C, and eight vertical sections, five of varying molybdenum content (0.40, 0.80, 1.50, 3.0, and 6.0 wt. % Mo) and three of different carbon contents (0.40, 0.80, and 1.10 wt. % C), were included. The carbide phases found included Fe₃C or (Fe,Mo)₃C; (Fe,Mo)₂₃C₆, designated kappa carbide following Goldschmidt's notation; (Fe,Mo)₆C, called omega carbide; and Mo₂C, called theta carbide. The methods chiefly used were metallography by conventional light microscopy and heat treatment; some electron microscopy was performed, and X-ray diffraction was used to confirm identification of carbide phases. The alloy range was 0.05–1.3 % by weight carbon, 0.03–6.0 % by weight molybdenum, and the balance iron.

The references cited should be enough to show that extensive work has been done on ternary carbon-containing systems of ferrous alloys.

Literally hundreds of papers on high-speed steels have been printed in the last 40 years. In view of these facts, it is somewhat surprising to find a statement such as that made by Rassaerts, Kieffer, and others (266) in 1965 that no reference to the ternary system V-Cr-C could be found in the literature. It is true that this is not an iron-based ternary, but vanadium, chromium, and carbon are all important elements in the high-speed steels. The much greater complexities present in ternary and more complex alloy systems as compared to binaries, and in addition the fact that since high-speed steels have important practical applications much of the research is of an applied character, probably explain the absence of any prior publication on V-Cr-C.

2. Other Systems

Two principal areas of interest are ternary diagrams, centering mainly around uranium or plutonium carbides, and recent reinvestigations of ternary carbide systems, such as Hf-Ta-C and the paper on V-Cr-C just mentioned.

For nuclear fuels, the system U-Pu-C investigated by Dalton (73) is of considerable importance. Equilibrium phases between 50 and 60 atomic % carbon were studied by light microscopy and X-ray diffraction. Complete solid solubility of uranium sesquicarbide in plutonium sesquicarbide was observed. Another important and unsettled question is the effect of oxygen on uranium carbides, leading to a study of the system U-C-O. Two recent publications from the large number on this ternary system are one by Stoops and Hamme (322) and one by Anselin and others (9) on the system (U, Pu)(C, N, O) covering sintered carbides, carbonitrides, and oxycarbides. The constitution of the systems U-C-Mo, U-C-Re, U-C-W, U-C-Nb, and U-C-Y has been studied and reported by Chubb and Keller (65). Farr and Bowman (100) found a number of previously unreported ternary carbides of uranium in a partial phase diagram study. These carbides were of the type UMC_2 (where M is a metal atom). These included $UMoC_2$ (m.p. $2350^\circ \pm 30^\circ C$, orthorhombic) and UWC_2 (m.p. $2575^\circ C$, also orthorhombic). Lattice parameters for all the carbides they prepared were stated, as well as carbon-rich alloy eutectic temperatures for $UReC_2$ ($2115 \pm 30^\circ C$), $UCrC_x$ ($1770 \pm 30^\circ C$), and $UTeC_x$ ($1865 \pm 30^\circ C$). Only the lattice parameters that were stated to be of a preliminary nature will be given here. A second ternary technetium carbide $UTeC_2$ melted at approximately $1800^\circ C$; it was orthorhombic with $a = 5.4$, $b = 3.22$, and $c = 10.9$ Å. $UReC_2$ was orthorhombic with $a = 5.5489 \pm 0.0057$, $b = 3.2229 \pm 0.0004$, and $c = 10.7416 \pm 0.0086$ Å. This rhenium-containing carbide was also reported by Chubb and Keller. Tetragonal carbides containing iridium and rhodium were also reported by Farr and

Bowman. The formulas assigned were UIrC_2 and URhC_2 . The manganese carbide of this formula type UMnC_2 was orthorhombic, $a = 5.04 \pm 0.01$, $b = 3.172 \pm 0.0002$, and $c = 10.74 \pm 0.02$ Å.

Included in the systems and phase diagrams investigated or reinvestigated by Rudy, Nowotny, Benesovsky, and their associates (mainly refractory carbide systems), we mention first the investigation of the system Hf-Ta-C by Rudy and Nowotny (276) in 1963. The form of the system at 1850°C was examined by use of samples prepared by pressing and vacuum sintering. Ta_2C was found to dissolve more than 10 mole % hafnium carbide. The phase Ta_3C_2 (zeta) has a narrow hafnium concentration range. Rudy and Chang (277) published isothermal sections at temperatures of $1300^\circ\text{--}1900^\circ\text{C}$ for the following ternary systems: V-W-C, Nb-W-C, Ta-W-C, Cr-W-C, V-Mo-C, Nb-Mo-C, Ta-Mo-C, and Cr-Mo-C. Some of the data were obtained from the literature, some from their own experiments. Not over two isothermal sections, some of which were thermodynamically calculated, were shown for any single system. Later work on the ternary V-Cr-C by Rassaerts and others (267) has also been published. The homogeneity range of V_2C (hexagonal) was found to extend into ternary space to about $(\text{V}_{0.9}\text{Cr}_{0.1})\text{C}$, and of the orthorhombic form of V_2C to approximately $(\text{V}_{0.45}\text{Cr}_{0.55})\text{C}$.

VIII. Property Correlations

A. WITH PERIODIC TABLE

The fact that HfC and TaC have melting points higher than any metals is a classic example of the elementary rule that, if two elements combine chemically, the further apart they are vertically in the Periodic Table the greater the heat of formation and the higher the melting point of the resulting compound. Many of the rules and generalities attempting to show relations between carbides and position in the Periodic Table are of less value because of the existence of several known exceptions to the proposed rule. This is also the case with many of the empirical theories concerning bonding and structure (both electronic structure and especially crystal structure) of the transition metal carbides.

Goldschmidt (114) has proposed rules of this kind for binary and some transition metal ternary carbides, which have been quite widely quoted. For binary carbides, class 1 structures (cubic NaCl type) are formed by all the elements of Group IVA (TiC, ZrC, and HfC) as well as part of the elements of Group VA (VC, V_4C_3 , NbC, and TaC). However, in Group VIA and for some of the elements of Group VA, structures of class 2, hexagonal close-packed (Mo_2C , MoC, WC, and Ta_2C), are formed. Beyond

Group VIA the predominating structure type is orthorhombic (Fe_3C , Ni_3C , Co_3C). In Group VIA, chromium forms carbides of all three structures, Cr_{23}C_6 cubic, Cr_7C_3 hexagonal, and Cr_3C_2 orthorhombic. Goldschmidt classifies chromium as an intermediate or labile element. Manganese also forms Mn_3C orthorhombic, Mn_7C_3 hexagonal, and Mn_{23}C_6 cubic. All the structures listed here are those given by Goldschmidt in 1948. In explanation of this structure sequence, Goldschmidt cites Hagg's (128) radius ratio rules: if the ratio of the radius of the smaller nonmetal atom to the metal atom is below 0.59, cubic or hexagonal close-packed structures with coordination number 12 are to be expected. For radius ratios above 0.59, complex structures result. Extending these principles to iron-based ternary carbides, Goldschmidt proposes that elements (such as Fe-Co-Ni) forming orthorhombic carbides will be the least stable. Elements belonging to class 1 forming cubic carbides (such as TiC) will form no ternary carbides or solid solutions with iron. The greater chemical affinity or lower free energy of such carbides ties up all available carbon chemically combined with the element of Group IVA or VA. This is exactly what is done to prevent injurious grain boundary precipitation of Cr_{23}C_6 in austenitic stainless steels by formation of TiC.

If hexagonal carbides are formed (class 2), iron will form a cubic ternary carbide having limited solid solubility for iron (such as $\text{Fe}_3\text{Mo}_3\text{C}$ to $\text{Fe}_4\text{Mo}_2\text{C}$). With chromium, no ternary carbides containing iron are formed, but the primary carbides of both iron and chromium have considerable mutual solid solubility. Finally, the orthorhombic iron carbide Fe_3C is isomorphous and completely intersoluble with orthorhombic Mn_3C , Co_3C , and Ni_3C . Andrews and Hughes (7) have attempted to extend Goldschmidt's observations to hexagonal carbide and nitride phases of type M_2X , such as W_2C , Fe_3N to Fe_2N , and $\text{Ta}_2(\text{C}, \text{N})$. For twelve transition metals (Hf in Group IVA is omitted)—Ti, Zr (IVA); V, Nb, and Ta (VA); Cr, Mo, and W (VIA) plus Mn, Co, Fe, and Ni beyond Group VIA—Andrews and Hughes state that with the exception of cobalt: (a) elements forming a close-packed structure in the metallic state form only that interstitial phase (carbide or nitride) with the alternative close-packed arrangement of metal ions (i.e., face-centered cubic metal, hexagonal close-packed carbide), and (b) if the metal itself does not possess a close-packed modification (body-centered cubic Mo for example), both types of close-packed interstitial phase will occur (chromium is a possible but by no means certain exception). From a tabulation of twenty-three hexagonal carbide and nitride phases of " M_2X " type, hexagonal phases appear to be limited to appearing at or near such a composition ratio. If all the interstitial sites are not occupied, the hexagonal interstitial phase may extend to M_3X (25 at. % C or N). Thus, special importance attaches

to ratios of metal to carbon or nitrogen of 2:1 or 3:1. It is evident that the numerous exceptions that must be made lessen considerably the validity of such relations between crystal structure and position in the Periodic Table.

B. STRUCTURE AND BONDING

Bonding is generally understood to denote forces between atoms and, although in some cases the terms metallic, covalent, and ionic bond types are concepts somewhat at variance with reality, these terms are in common use and retained in the literature. Structure, on the other hand, is used in connection with the arrangement and location of electrons in atoms or molecules (electronic structure), as well as the space arrangements of atoms or groups of atoms (crystal structure). The crystal chemistry and crystal structures of carbides are dominated by a comparatively few isostructural types under which large numbers of individual carbides can be classified. A number of such structural types and the carbides belonging to them have been discussed. No mention has been made of the important part that octahedral structural units (in which a carbon atom is at the center of six metal atoms) play in the building up of the unit cells of these carbide structure types. As for bonding and bonding forces in carbides, two important types of theory or approach to the problem exist. One of these is the electron band theory (the approach of mathematical physics), while the other theories of bonding are marked by use of empirical assumptions in varying degrees. Empirical theories also vary widely in the extent of their application and prediction. Some are concerned with both electronic structure and crystal structure, while others are limited to one of these fields. A selection will be made among the many empirical theories of carbide bonding that have appeared during the last 25 years. Some of these, such as the proposals made by Rundle (280) in 1948, are still widely quoted and referred to in the literature. Other theories, such as that of Ubbelohde (350) attempting to use facts known about the palladium-hydrogen system to explain carbide bonding, are now mainly of historical interest. From the electron band approach to the problems of carbide bonding, two band structures for TiC have recently been published (in 1965 and 1966). Since TiC is an important transition metal monocarbide, having practical applications and with a considerable amount of information available with regard to its hardness, electrical resistivity, thermal conductivity, and elastic moduli, band theory can be applied. Most of the discussion of bonding will be limited to the "cubic carbides" having NaCl structure, typified by TiC. The so-called "saltlike" carbides, such as Al_4C_3 , are not of great interest at present, and can be largely explained by conventional chemical concepts.

For classification of binary carbides, we mention again Goldschmidt's (114) class 1 cubic (TiC), class 2 hexagonal close-packed (W_2C), and class 3 orthorhombic (Fe_3C). This scheme was also extended to iron-containing ternary carbides, such as the eta carbide series from $\text{Fe}_3\text{W}_3\text{C}$ to $\text{Fe}_4\text{W}_2\text{C}$. The structure determination for $\text{Fe}_3\text{W}_3\text{C}$ by Westgren (5) in 1933 was also mentioned previously. In 1965 Bojarski and Leciejewicz (41) published results of a neutron diffraction study of $\text{Fe}_3\text{W}_3\text{C}$. Their data confirm the earlier studies as to the position of the carbon atoms and the atomic parameters in the Fe-W-C system. The carbon atoms are in octahedral coordination with iron and tungsten.

Reference has also been made to the tabulation and classification of ternary carbides by Nowotny, Jeitschko, and others (247). In a somewhat more recent publication (248) the same authors extended their previous tables including over eighty ternary carbides to include newer members of each type. Crystal systems, type formulas, and typical examples for each class include: T_3MX (T = transition metal, X = carbon or nitrogen, M = lower melting metal or meta-metal), cubic perovskite carbides (Tb_3AlC), $\text{T}_3\text{M}_2\text{X}$ phases with a filled and ordered beta-manganese type structure ($\text{Mo}_3\text{Al}_2\text{C}$), the H-phases of type formula T_2MX (Nb_2SnC) belonging to the hexagonal system, the kappa carbides (following the designation by Kuo) hexagonal but with c/a ratios close to unity ($\text{W}_{10}\text{Co}_3\text{C}_4$) (270), and the eta carbides of type $\text{T}_4\text{M}_2\text{X}$ such as $\text{Zr}_4\text{Zn}_2\text{C}$. For the perovskite carbides, the carbon atom at the interior center of the face-centered cubic unit cell is octahedrally surrounded by six transition metal atoms at the face centers of the cube. This octahedral coordination is termed T_6X by Nowotny. For the beta-manganese type carbides, the T_6X octahedra are united at their corners. In the unit cells of the hexagonal H phases similar octahedra are joined by their edges, while in the eta carbides some of the T_6X octahedra are united by faces. For the perovskite carbides, which have a relatively simple face-centered cubic unit cell and structure, the Hagg radius ratio may have to have the upper limit extended from 0.59 to 0.65, more complex structures appearing above 0.65. The octahedra with carbon atoms at the center (T_6C) in both the perovskite and kappa carbide phases are united at their corners. Finally, as we move from $\text{T}_4\text{M}_2\text{X}$ to T_2MX to T_3MX , increasing the ratio of the transition metal T to the low melting metal M , we are also increasing a general tendency toward a closer packing of the parent metallic lattice.

Two principles of significance long recognized for carbide crystal structures are the Hagg radius ratio principle and Hume-Rothery's size factor rule. Hume-Rothery's favorable size factor rule states that complete solid solubility may be expected if the diameters of the two atoms

entering the solid solution are not over 15 % apart. Above this limit, solid solubility will be restricted. This principle applies to carbides, and the largest amount of information is available for the refractory monocarbides. For example, ZrC forms complete series of solid solutions with HfC, TiC, NbC, and TaC where size factors are favorable, but has only limited solid solubility with VC. In the application of these two rules, particularly the radius ratio rule, it is often difficult to determine or assign the proper atomic diameters, especially to the metal atom, as the observed interatomic distances in carbides and nitrides differ considerably from those in the metal. This problem of choice of proper atomic radii has been recognized for 35 years and is of considerable importance in theories of bonding.

At this point, we will briefly mention a number of empirical theories proposed to explain atomic and electronic bonding in carbides, but which need not be discussed at length. Umanski (351) assumed that the carbon of carbides was ionized. He ascribed the high hardness of such carbides as TiC and VC to a keying action on slip planes by the nonmetal atoms in a manner similar to early theories of precipitation hardening in alloys. According to Neshpor (241), the modern Russian ideas of Samsonov (282) are of the same general nature. Samsonov offers an explanation of carbide bonding in terms of the ionization potential I of the nonmetal atom, and the repulsive or acceptor ability of a transition metal atom with unfilled d - or f -electron shells. For this donor or acceptor ability, Samsonov uses an expression $1/Nn$ in which N is the principal quantum number of the unfilled d -electron level, and n is the number of electrons in this same unfilled electron level. In accord with predictions from this ratio, the superconductivity transition temperature of carbides of Group IVA (Ti, Zr, Hf) increases sharply as $1/Nn$ becomes smaller.

The proposals of Engel, originally published in Danish in 1949, were reviewed at length and summarized by Brewer (54) in 1963. Besides a short article, published in English by Engel (93) in 1954, two longer articles (94) outlining his theories were published bilingually in both English and German in the journal *Radex Rundschau* in 1956. Engel considered the very small atoms of the second period (e.g., carbon) as forming interstitial solid solutions and intermediate phases with the transition metal. In small amounts, the small interstitial atoms are just placed between the base metal atoms, without materially changing the bonding pattern or lattice of the transition metal. Electrons from the small atom left the outer levels and entered into the unfilled d levels of the transition metal. Thus, the small atoms were ionized and an ionic bond was created, in addition to what Engel terms "the electron field cancellation bond, generally called the covalent and metallic bond." Intermediate phases

such as carbides will be harder, stronger, and more difficult to melt because *d*-electron bonding, outer electron bonding, and ionic bonding add up to the most powerful bonding combination known. Some of the ideas proposed by Trost (347) were similar to those of Engel. The theory of Trost, the spatial electron concentration proposal by Schubert (289), and most of the other pertinent bonding theory on carbides and nitrides up to 1963 have been reviewed by Nowotny (246) in his article in the book *Electronic Structure and Alloy Chemistry of the Transition Elements* (29). In 1963 Dempsey (75) published what is essentially an empirical band theory for bonding in the refractory hard metals. A point to be noted from most of the empirical theories mentioned is the transfer of charge and electrons from the nonmetal to the metal, giving a bond of ionic character. By analogy with typical ionic solids, the brittleness of the cubic transition metal monocarbides is due to the presence of some ionic bonding. Somewhat at variance with theories emphasizing ionic character were the views of Kiessling (175) and Robins (272), who emphasized strong M-M (metal-metal) interaction based in part on the idea that cubic carbides show a close-packed metallic parent lattice. In his review article, Kiessling based his idea of strong metallic bonding in monocarbides upon plots made by Brewer and Krikorian (53) of the bonding energies of nitrides and carbides (MeX compounds), which were compared to the heat of sublimation of the pure metals. From the similarity in values, strong metallic bonding in carbides was inferred by Kiessling. Robins placed considerable importance upon resonance as a contribution to bond strength and crystal structure. For transition metals toward the center of the Periodic Table, a large number of hybrid (*spd*) bonding orbitals with comparable energy will be present. In such cases, the strength of bonding will depend upon a relationship between the electron concentration (N) and the effective coordination of the metal atoms (C). The maximum stability due to resonance is obtained when the number of bonding electrons per atom is approximately equal to half the effective coordination number. Robins emphasized transfer of electrons from the carbon atom to the unfilled *d* orbitals of the transition metal atom leaving singly ionized carbon atoms present. Considering TiC as an example, at room temperature titanium (according to Robins) has a distorted hexagonal close-packed structure, the distortion being due to the metal atoms (four valency electrons) reducing their effective coordination number below 12. Upon adding carbon, carbon atoms donate electrons to metal atoms, increasing the effective metallic valency. Carbon has so much donating power that addition of only a small amount of carbon causes change to a face-centered cubic lattice and a metallic coordination number of 12. We now have a new metallic phase (TiC) stabilized by the presence of carbon

and in which carbon has a wide range of solubility. Robins does not rule out the possibility of ionic type bonding due to electron transfer, but points out that resonance covalent and metallic type bonding is more important in the cubic (NaCl) carbides.

The explanation of carbide bonding advanced by Rundle (280), which is so widely referred to, was in turn based upon Pauling's metallic bond radii (253). Probably the most important idea of Rundle's theory, and one that constituted an extension of Pauling's concepts, was the idea of half-bonds. The conditions for forming half-bonds are stated by Rundle to be: (1) One element, A, must have more stable bond orbitals than valence electrons. Therefore A will generally be a metal. (2) Another element, B, must have relatively few bond orbitals. This will limit B to hydrogen and the first-row nonmetals, particularly carbon and nitrogen. (3) The electronegativities of A and B must not differ so much that the bond formed is essentially ionic. If the above conditions are met, compounds of A and B may be formed in which not all the bond orbitals of A are used for bond formation unless some orbital of B is used for more than one bond. Consequently, it will generally be better for B to form two half-bonds than one single bond. The requirement that the metal must have more stable bond orbitals than valence electrons limits the possible metals to transition metals (group A in the Periodic Table) with unfilled *d* shells. Furthermore, the alkalis and alkaline earths, although belonging to A groups in the Periodic Table, will be too electropositive in character. If the metal is beyond the fifth group of the Periodic Table, (MX) structures of NaCl type are not formed. Carbon has but four stable bond orbitals, but the octahedral configuration found in TiC, for example, requires six bonds. Pauling had explained this by supposing that four electron pairs resonated among the six bonds. According to Rundle, this was not sufficient to explain the brittleness of carbide structures or the preference of the light element for octahedral bonds. If the situation was formally stated in Rundle's terms, one orbital used with one electron pair formed two stable bonds, each of which was a half-bond or, in Pauling's terms, had bond number $\frac{1}{2}$. If *sp* orbitals were used, two of the six bonds formed by the light element would be ordinary electron pair bonds and resonance would make all six bonds equivalent. In contrast to the ideas of Hagg, Rundle believed that metal positions were appreciably changed from the metallic pattern in formation of carbides, and that radius ratio would not provide the necessary octahedral interstices for the carbon atoms in the rock salt type of carbide structure. From a table of the available structures of the transition metals themselves, and the structures of their carbides and nitrides, Rundle concluded that rearrangement of metal positions was necessary to provide octahedral interstices

for the nonmetal. To explain the unusual combination of brittleness with electrical conductivity, Rundle suggested that directional properties in bonding together with free electrons, a combination such as is found in graphite, were needed. Stated in other terms, directed but not localized bonds were needed. Preference for NaCl structure, high melting point, and hardness required metal-to-nonmetal bonds of considerable strength. Forming bonds with octahedral configuration through the half-bond concept explained formation of NaCl structure. Strong metal-to-nonmetal bonds could be partially due to a considerable amount of ionic character in the covalent and half-bonds. Rundle was aware of the increased distances between metal atoms in carbides as compared to metals, and that this would tend to weaken metal-to-metal atom bonds. He used Pauling's formulas for bond number and for metallic valence as well as Pauling's single-bond metallic radii to show that the monocarbides and mononitrides of most of the transition metals in the entire Periodic Table, which met Rundle's three requirements, had probable bond numbers of $\frac{1}{2}$ or $\frac{2}{3}$. Either of these bond numbers could be easily explained by Rundle's proposals. If the carbide had one third electron pair bonds and two thirds half-bonds, the electron density in the bond would be two thirds that of an ordinary single bond. Stated in Pauling's terminology, this would be a bond number of two thirds.

Hume-Rothery (155) made a number of criticisms of the theory of Rundle. He objected to use of Pauling's bond number rule without correction, on the ground that a shortening of apparent atomic diameter with decreasing coordination number is to be expected from the energy standpoint alone, without any consideration of a resonating valence bond theory. With regard to Rundle's suggestion that hardness and brittleness implied directed bonds, Hume-Rothery suggested comparison with ruthenium. This metal has a melting point of about 2550°C; it is metallic in properties with high electrical conductivity, so that the bond type must be essentially metallic, but ruthenium is also brittle enough to be ground to powder in an ordinary percussion mortar at room temperature. Therefore, why should the carbides that melted at even higher temperature, and thus were still further below their melting point at room temperature, be brittle because of directed bonds? Since the hexagonal close-packed structure possessed by many of the transition metals, such as titanium, possessed one octahedral interstice per atom, why should it be necessary for the metal atoms to change to a face-centered cubic structure in the carbide only to provide octahedral interstices? On this point, Hume-Rothery's conclusion is that, although formation of octahedral holes may be one factor, the face-centered cubic arrangement is favored by the metallic atoms in the carbide structure

because it provides them with mutually perpendicular bonds to six neighbors. If the octahedral interstices in a hexagonal close-packed system of spheres were filled, not all of the metal-to-nonmetal bonds would be perpendicular. The qualitative picture of carbide bonding for MX carbides of NaCl structure suggested by Hume-Rothery is that interatomic distances make it almost certain that covalent rather than ionic bonding is involved, as neither a C^{4+} or C^{4-} ion would fit and provide a stable structure. Each carbon atom tends to acquire a share in an octet of electrons. Since each carbon atom has four of its own electrons, it must obtain on the average two thirds of an electron from each of its six metallic neighbors, giving rise to resonating covalent bonds. This last suggestion is the same as that of Rundle. To explain conductivity in TiC, ZrC, and HfC having tetravalent metal atoms, which must use all four of the metallic electrons in forming the octet, Hume-Rothery suggests that conductivity arises from the fact that only some of the hybrid (*spd*) orbitals are filled.

Two recent calculations of the electronic band structure of TiC were mentioned previously. The first of these, by Ern and Switendick (96), was carried out by the augmented plane wave (APW) method and band structures for TiN and TiO were also calculated. Density of states, Fermi energy, and contours of constant energy were obtained for each of the three compounds. A charge distribution in the APW scheme was derived from the equivalent of thirty-two points in the Brillouin zone, and the admixture of bands was analyzed. The results were stated to be consistent with the experimental data.

A year later (1966) Lye and Logothetis (193) published the results of a study on optical properties and band structure of titanium carbide. Reflectivity measurements of TiC through the visible and vacuum ultraviolet gave additional data, which reduced the uncertainties connected with a calculation of the electronic band structure of TiC. The energy band calculation was carried out, using the tight binding approximation by the two-center method of Slater and Koster (315). The results of the two calculations for TiC differed widely. In addition to differences due to the method of calculation and to the use of optical data, Lye and Logothetis suggest other reasons that may account for the discrepancies, including (1) the core potentials, (2) the constant potential V_c between the APW spheres of Ern and Switendick, (3) the ionicity of each atom in the unit cell, and (4) the APW sphere radii (dependent upon the core potentials and the Madelung displacements). The differences between the two calculations may have been due to inapplicable assumptions with respect to one or more of the factors just listed. (Reference to the original papers should be made for further details.) Our purpose here is to discuss the

deductions made from Lye's calculation with respect to carbide bonding.

The energy band structure obtained by Lye showed a band structure for TiC having a high and rapidly varying density of states of *d*-like character, similar to the *d* states in the transition metals themselves. In addition, some net transfer of charge takes place from carbon atoms to titanium atoms, so that part of the binding is ionic; covalent bonding occurs not only between carbon and titanium atoms, but also between titanium atoms and between carbon atoms. The type of covalent bonding existing between the metal atoms is similar in origin to the band bonding of transition metals; this effect appears to account for the relatively high melting points of the transition metals. The high density of unfilled *d* states in the free atoms constitutes a relatively low energy reservoir for valence electrons of higher energy when the solid is formed, thus lowering the total energy of the system.

In commenting on the work of Lye, Williams (365) remarks that it is important to make clear what is new in this work, especially since so much has been written about the nature of bonding in the cubic carbides. The idea that charge is transferred from the nonmetal to metal in the carbide has been advanced by Umanski, Kiessling, Robins, and Dempsey, as was previously discussed. The work of Lye puts these ideas on a firmer basis and adds theoretical support. The presence of covalent bonding was emphasized by these earlier workers, as well as by Rundle. The calculation by Lye gives greater precision to this view. The work of Lye also emphasizes the complex influence of charge transfer on binding, a point not brought forth strongly in earlier work. There is a considerable ionic character in TiC bonding due to the presence of relatively few conduction electrons to act as a screen for the ionic interaction. The covalent bonds could be expected to be of a directed nature, leading to a large stiffness with respect to elastic carbide behavior in accord with observations. Both elastic and plastic deformation are also resisted by the ionic bonding.

IX. Summary

The binary metallic carbides available from the literature have been described. Methods for their preparation have been indicated. The occurrence and preparation of some ternary carbides have also been considered. Metals with no reported binary or ternary carbides include promethium among the rare earths, the transuranium elements beyond atomic number 94, francium, radium, actinium, polonium, antimony, tellurium, and bismuth. The extensive pioneer work of Moissan must be included in any

discussion of metallic carbides. Phase diagrams for a number of the important refractory metal-carbon systems have been discussed in some detail. A discussion of some of the problems of bonding in the cubic binary carbides of the transition metals is also included.

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SILICON HYDRIDES AND THEIR DERIVATIVES

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I. Introduction

The chemist who wishes to learn about the hydrides of silicon, the silanes, is fortunate in that a number of excellent reviews have appeared in the last decade. Two books, by Stone (253) and Ebsworth (113), were

published in 1962 and 1963, respectively, and between them cover many aspects of the topic. An earlier review by MacDiarmid (197) deals specifically with silicon hydrides, while more specialized treatments of preparative techniques have been provided by MacDiarmid (199) for halogen and pseudohalogen derivatives of silicon hydrides, and by Aylett (22) for silicon-nitrogen compounds, some of which contain Si—H bonds. Other useful recent sources include a general review of silicon-nitrogen chemistry (271), a survey of silicon-nitrogen polymers (23), and the proceedings of a meeting on organosilicon chemistry (in which hydrogen sometimes masqueraded as an organo group) in Prague (79). Principles of silicon chemistry are well expounded in Eaborn's book (112) and, finally, Parts B and C of Gmelin's treatise on silicon give a complete coverage of the literature up to the mid-1950's (154).

In view of this, it is certainly neither desirable nor possible to attempt to summarize here all aspects of silicon hydride chemistry. The treatment will be illustrative and not comprehensive, will concentrate on that recent work most interesting to the author, and will try to stimulate curiosity and dissatisfaction by pointing out some of the unsolved problems. Such a partial account will succeed most if it conveys that elusive thing—the feel of silane chemistry.

II. General Aspects of the Behavior of Silane Derivatives

A. HANDLING

Any discussion must necessarily begin by mentioning two not altogether unrelated points: the contribution of Alfred Stock, and the electronic configuration of silicon. As early as 1903, Stock published a paper on the technique of working with liquefied gases. In the following years he developed the high vacuum techniques that made it possible to study reactive volatile compounds, and also quantitative methods for determining the properties of extremely small amounts of such substances. A series of papers on silicon hydrides appeared between 1916 and 1926, and in these Stock enumerated most of the important modes of behavior of these substances; he later reviewed the field more generally (247). It is salutary for us to note how much was achieved without the use of infrared, ultraviolet, n.m.r. and mass spectrometers, without chromatographic methods, and without the interpretative background of quantum mechanics.

Today most preparative work on silanes and their derivatives is carried out in apparatus similar in principle to Stock's, although improvements in high vacuum taps and greases have made it normally un-

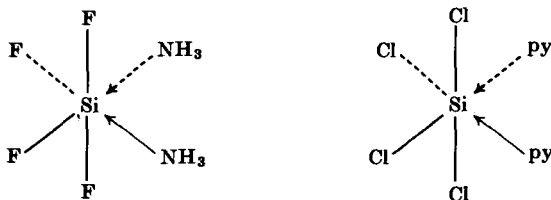
necessary to use mercury ventils as valves. Indeed, in some investigations the presence of mercury cannot be allowed (mercury reacts with iodosilanes and seems to catalyze the decomposition of some other derivatives), and special arrangements must then be made for measurements of pressure (e.g., 20).

Glove boxes are commonly used in the handling of less volatile derivatives, but it should be emphasized that extreme care is needed, both in desiccation and in removal of oxygen, if quantitative results are to be obtained. Technically, it seems perfectly feasible to construct a "hydride room," filled with ultra-dry nitrogen or argon. Workers would wear nonporous protective clothing with closed-circuit breathing equipment. If the atmosphere in such a small room contained only 1 ppm of water vapor, however, this would be sufficient to hydrolyze roughly a millimole of iodosilane.

B. BONDING CONSIDERATIONS

The extremely high reactivity of many silicon hydride derivatives, which necessitates the care in handling outlined above, can of course be related to silicon's electronic configuration. It is natural to compare silicon with carbon, and there is the obvious difference that, energetically above the highest filled levels in the valence state of silicon ($1s^2 2s^2 2p^6 3s^1 3p_x^1 3p_y^1 3p_z^1$), there lie five vacant $3d$ orbitals. Carbon in its valence state ($1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$) has $3s$ as the corresponding next available level. It is usually tacitly assumed that the energy separation $3p \rightarrow 3d$ is so much less for silicon than is the corresponding $2p \rightarrow 3s$ separation for carbon that the first gap is readily bridged while the second is not. Although this may be true when the atoms are combined in molecules, it is not obvious from the energy level separations for the free atoms (cf. 103, 204).

It is generally accepted that two different effects may be related to the availability of d orbitals on silicon; in both cases carbon is unable to act analogously. First, silicon may increase its coordination number in various complexes to [5] or [6]. This has long been known: such compounds as $\text{SiF}_4 \cdot 2\text{NH}_3$ and $\text{SiCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ are readily formed from their components at room temperature. Their probable structures are (56, 69):



In the case of other adducts (e.g., $\text{SiH}_3\text{X} \cdot \text{NMe}_3$), which are apparently five-coordinate, the position is not completely clear; this will be considered later (Section IV,C). Initial coordination by attacking nucleophiles such as OH^- and NH_2^- has often been postulated as an important step in reactions of substituted silanes, and Eaborn (112) has discussed how coordination of this kind may lower the activation energy of the process. We shall refer to such cases as involving an intermolecular use of d orbitals; it is accompanied by an increase in the number of σ -bonds formed by silicon.

Second, d orbitals may be involved in π -overlap with suitable filled orbitals on neighboring ligands. This effect, which is most marked with electronegative atoms or groups, has been increasingly invoked since two important papers, by Jaffé (176) and Craig *et al.* (94), showed theoretically that it was likely to be significant. Evidence for its occurrence has been reviewed by Stone and Seyferth (254) and more recently by Ebsworth (113); the most important facts fall under the following headings.

1. Change in Shape

Some of the more striking differences from carbon are shown in Fig. 1. A more detailed discussion of changes of this type will be given later, but

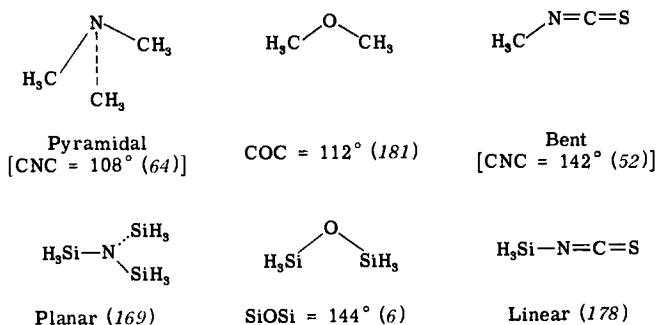


FIG. 1. Structures of corresponding methyl and silyl derivatives.

in general all can be rationalized in terms of optimum π -overlap. The structure alters in such a way that the lone-pair orbital(s) on nitrogen or oxygen develops increased p character, and thereby can overlap more effectively with silicon's d orbitals. The s character of the σ -bonds to silicon will at the same time increase. This change in shape can be demonstrated by various physical methods; in practice, vibrational and microwave spectroscopy and electron diffraction techniques have been mostly used.

2. Change in Reactivity

Amines and ethers behave as typical electron-pair σ -donors or Lewis bases. The corresponding silyl compounds interact either weakly or not at all with a range of Lewis acids. While a fuller discussion will be given later (Sections V,A,2 and VI,B), the data in Table I are typical. Amines are usually stronger bases than ethers, and the diminution of base strength is more noticeable in the case of silylamines.

TABLE I
COMPARISON OF LEWIS BASE STRENGTHS OF
CARBON AND SILICON ANALOGS

Base	Acid	Adduct combining ratio (base:acid)	Ref.
$(\text{CH}_3)_3\text{N}$	BMe_3	1:1 strong	(66)
$(\text{SiH}_3)_3\text{N}$	BMe_3	(no reaction)	(257)
$\text{CH}_2(\text{NMe}_2)_2$	BH_3	1:2 strong	(36)
$\text{SiH}_2(\text{NMe}_2)_2$	BH_3	1:2 weak	
$(\text{CH}_3)_2\text{O}$	SiH_3I	1:1 rather weak	(21)
$(\text{SiH}_3)_2\text{O}$	SiH_3I	(no reaction)	(19)

Not only is the electron-donor ability of nitrogen (or oxygen) in such compounds reduced, but the electron-acceptor ability of the attached silicon is simultaneously reduced also. Thus, although silyl halides react very readily with trimethylamine to yield solid adducts, there is no similar reaction between $(\text{SiH}_3)_3\text{N}$, $(\text{SiH}_3)_2\text{NN}(\text{SiH}_3)_2$, or $(\text{SiH}_3)_2\text{O}$ and trimethylamine.¹ These facts may be rationalized in the following rather naive way, taking trisilylamine, $(\text{SiH}_3)_3\text{N}$, as an example. If electron donation by nitrogen is to occur, electron density must be withdrawn from silicon's d orbitals, and a change in stereochemistry about nitrogen to an approximately tetrahedral arrangement must take place. The π -bonding between nitrogen and silicon is reduced, and evidently the gain in energy by complex formation is not sufficient to compensate for this. Also, involvement of silicon's d orbitals in π -bonding to nitrogen makes them less ready to accept electrons from outside, leading to a reduction in Lewis acid strength.

These changes in reactivity have in the main been demonstrated by means of phase studies, measurements of vapor pressures of mixtures, and heats of mixing. Infrared studies based on hydrogen-bonded interactions have also proved helpful. Kinetic studies are not usually feasible

¹ Slow reaction of a different kind does occur (see Sections V,A,4 and VI,B).

with silicon hydride derivatives, as reactions are extremely rapid, there is a considerable body of such information for organosilicon derivatives, however, which has been interpreted in terms of p_π - d_π interaction (see Eaborn, 112).

3. Change in Bond Length

Such evidence is always difficult to interpret, since it is not possible to switch π -bonding on and off in a particular bond; one must take a bond, with whatever multiple bond character that it possesses, as one finds it. However, the facts in Table II may be significant. The differences are so

TABLE II
BOND LENGTHS IN SILICON COMPOUNDS

Bond	Sum of covalent radii (Å)	"Corrected" sum ^a (Å)	Experimental bond length (Å)	Compound	Ref.
Si—N	1.87	1.76	1.73	(SiH ₃) ₃ N	(169)
			1.71	SiH ₃ NCS	(178)
Si—O	1.83	1.68	1.63	(Me ₃ Si) ₂ O	(278)
				(SiH ₃) ₂ O	(6)
Si—F	1.81	1.61	1.54	SiF ₄	(65)
			1.59	SiH ₃ F	(45)

^a By Schomaker-Stevenson equation (see text).

large, even after generous allowance has been made for electronegativity differences by some relationship such as the Schomaker-Stevenson equation, that it is hard to see how they can be interpreted except in terms of multiple bonding.

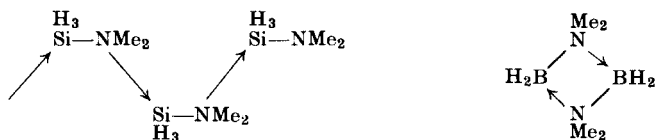
These three effects can thus be regarded as manifestations of p_π - d_π dative π -bonding, and we shall refer to this as intramolecular use of d orbitals. A few points may be noted at this stage. First, because several d orbitals are available around the σ -bond axis, no marked energy barrier to rotation will be expected; the situation is somewhat similar to that in the C \equiv C triple bond. Second, there is no evidence that dative π -bonding can occur in the absence of a σ -bond between the same two atoms; " π -only" interactions seem unlikely for steric reasons. Third, there is no theoretical reason why silicon should not be involved in dative d_π - d_π interactions, and indeed these were foreshadowed by Jaffé (176) and Craig *et al.* (94). It is only very recently, however, that they have been invoked in compounds containing a silicon-transition metal bond (see

Section VIII,B). Finally, evidence from a number of complex-forming and structural studies suggests that dative π -bonding decreases in importance in the following orders:



Particularly in trifluorosilyl derivatives σ -inductive effects are decisive, and such compounds generally behave as strong Lewis acids.

In any particular silane derivative, especially one in which silicon is linked to nitrogen or oxygen, there will be competition between inter- and intramolecular use of silicon's d orbitals. When a molecule is distant from its neighbors, in the gas phase for example, dative π -bonding will be important. In condensed phases, however, the molecules may tend to interact via intermolecular dative σ -bonding. Thus N,N -dimethylaminosilane, Me_2NSiH_3 , seems to be considerably associated in the solid phase (257). The infrared spectrum of the crystalline compound shows strong absorption around 500 cm^{-1} , which is attributed to $\text{Si}-\text{N} \cdots \text{Si}$ bridging (70)². It is known that N,N -dimethylaminoborane, Me_2NBH_2 , can exist as a dimer even in the gas phase because of similar intermolecular dative σ -bonding (68):



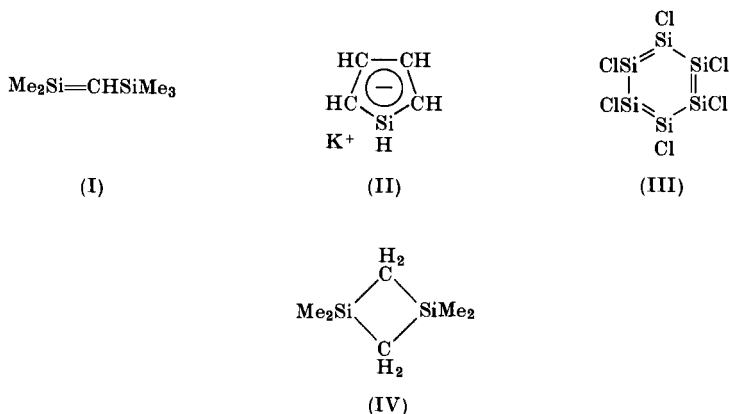
On the other hand, neither $\text{Me}_3\text{SiNMe}_2$ nor Me_2BNMe_2 shows evidence of intermolecular association, presumably because of steric repulsions. It has also been suggested that SiH_3NCS (196) and SiH_3N_3 (121) may be associated in the liquid phase; in the first case, this would probably be associated with nonlinearity of the heavy atoms (see Section IV,B).

Silicon is distinguished from carbon not merely by possession of d orbitals. Other differences significant in its hydride chemistry are its larger size (1.17 \AA as against 0.77 \AA) and its lesser electronegativity. The first has the effect of reducing steric repulsions, especially between hydrogens of silyl groups as compared with those of methyl groups. The exact value of silicon's electronegativity is still a matter of some dispute (e.g., see Allred and Rochow, 5; Drago, 106). It is quite certainly less than that of carbon—Pauling's scale gives values based on thermochemical data of 1.8 for Si and 2.5 for C—and this is doubtless a reflection of the

² X-Ray studies have now shown that solid Me_2NSiH_3 consists of cyclic pentameric units, with nitrogen atoms at the vertices of a regular pentagon, and planar SiH_3 groups at the mid-points of, and perpendicular to, the sides of the pentagon (227a).

increased efficiency of shielding of silicon's nuclear charge by its filled electron orbitals. The polarity of the $\text{Si}^{\delta+}\text{—H}^{\delta-}$ and $\text{Si}^{\delta+}\text{—P}^{\delta-}$ bonds, for example, is therefore different from that of the corresponding $\text{C}^{\delta-}\text{—H}^{\delta+}$ and $\text{C}^{\delta-}\text{—P}^{\delta+}$ bonds. Two estimates of the actual Si—H bond dipole are 1.25 D (80) and 1.6 D (46). Both these values seem high, but are consistent with the high observed intensities of infrared absorption associated with Si—H bonds.

It is significant that silicon does not seem able to form multiple bonds of the $p_{\pi}\text{—}p_{\pi}$ type. The three compounds (I–III) have all been reported in recent years (148, 60, 264, respectively), but (I) was found to be its



isomer (IV) (152), the evidence for (II) has been re-examined (59), and (III) has not been confirmed. Although hydrides of empirical composition SiH_2 , SiH , etc., may be made (e.g., 226, 235), these are undoubtedly polymeric and contain four-coordinate silicon. It is not clear why $p_{\pi}\text{—}p_{\pi}$ links are so reluctant to form; perhaps silicon is too large for effective sideways overlap of orbitals or, expressing the same idea in different terms, repulsions between nonbonding electrons on silicon and the neighbor atom are too severe. It should be noted that there is some evidence for the formation of $(\text{H}_2\text{Si}=\text{CH}_2)^+$ in a mass spectrometer (182); it could be argued that the positive charge has the effect of reducing electron-electron repulsions and hence the internuclear Si—C distance, making π -overlap feasible. (Orbital contraction effects may also be important—see later in this section.)

Mulliken (209, 210), in an important pair of papers, has suggested that when second-row elements combine with either first- or second-row elements, a small amount of mixing-in of d orbitals may occur. This can then lead to significant strengthening of σ -bonds and also provide addi-

tional bonding π -overlap. He suggests that Si—Si, Si—X (X = N, O, halogen), and even Si—H bonds, although written as single bonds, may in fact have an effective bond order of more than 1. This description accounts rather neatly not only for the lack of multiple bonds (since, for example, two Si—O “single-plus” bonds will be favored energetically over one Si=O bond), but also for the high observed bond energies of such putative single bonds, shown in Table III.

TABLE III
ENERGIES OF BONDS TO CARBON AND SILICON (IN KCAL MOLE⁻¹)

	H	F	Cl	Br	I	N	O
C ^a	99	116	78	68	51	73	86
Si (experimental) ^a	76	135	91	74	56	85 ^c	108
Si (predicted) ^b	(76)	89	60	52	39	56	66
Si (exptl.) — Si (predicted) Si (exptl.) × 100	0	34	34	30	30	34	39

^a Cottrell (86).

^b See text.

^c Estimated.

Let us assume (*pace* Mulliken) that the reduction in bond energy in going from C—H to Si—H represents the normal decrease in the absence of the d -mixing and π -overlap effects referred to above. We then can calculate a set of predicted Si—X single bond energies by decreasing the corresponding C—X bond energies in the same ratio. It can be seen, from the final row of figures in Table III, that the predicted values are consistently 30–40 % lower than the observed values, and moreover that the effect is greatest just for those bonds in which the greatest π -effects have been proposed.

Mulliken based his conclusions on calculations of overlap integrals between, for example, Si $3p\pi$ and Cl $3p\pi$ orbitals, and it is helpful to consider some aspects of overlap at this point. The usual picture of p_π - d_π overlap (Fig. 2) tacitly assumes that the orbitals will be of comparable size, and that overlap will be good. It turns out, however, that, if Slater (hydrogen-like) wave functions are used, the $3d$ orbitals are so diffuse that overlap is rather poor. Two ways out of this difficulty have been suggested. In the first (91), it is shown that electronegative ligands can bring about contraction of the d orbitals (by increasing the effective nuclear charge). In the second (96), use of a more sophisticated type of self-consistent field (SCF) wave function also results in a less diffuse d orbital. In both

cases, π -overlap will be improved. By a similar argument, d -mixing to enable silicon to increase its coordination number above 4 will be possible only if the d orbitals are comparable in size with the valence-shell s and p orbitals. Even a weakly electronegative ligand seems able to bring about d -mixing. Silane itself will not react with electron donors, but iodosilane readily does so (see Section IV,C).

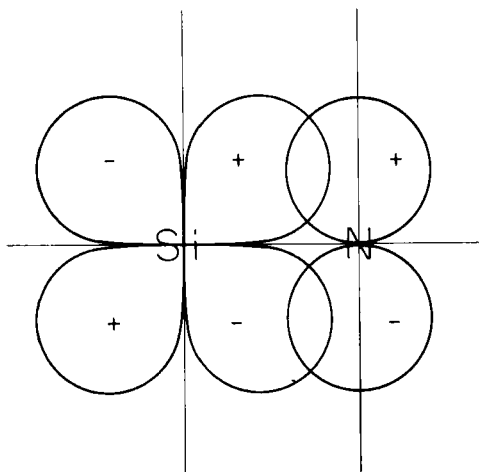


FIG. 2. Diagrammatic representation of d_{π} - p_{π} overlap of orbitals.

The qualitative ideas outlined so far have been put on a much firmer basis by some recent calculations of the π -electron distribution in $(\text{SiH}_3)_3\text{N}$ by Perkins (218). The results of this SCF-MO treatment suggest that the stabilization of the molecule attributable to π -bonding amounts to about 48 kcal mole⁻¹, and that there is appreciable electron delocalization onto the silicon atoms. It had been earlier pointed out by Ebsworth (114) that, when a molecule of this kind departs from planarity, the π -interactions are lessened but by no means vanish; as Randall and Zuckerman (221) were quick to point out, this tends to weaken arguments linking the occurrence of π -bonding with stereochemical changes. Perkins, in taking up this point, stresses that loss of planarity in $(\text{SiH}_3)_3\text{N}$ results in mixing of σ and π MO wave functions, and the resulting energy change is hard to estimate.

The simple picture shown in Fig. 2 will be further modified if more than one π -donating ligand is attached to silicon. In a compound such as $\text{SiH}_2(\text{NMe}_2)_2$, a number of different d orbitals can be involved, and their orientation with respect to the σ -framework and also the bond angle will

alter in such a way as to optimize the total σ - and π -overlap in the SiN_2 system. It may not be a sufficiently good approximation in such circumstances to consider π -overlap separately (cf. 95). The simple picture will also be modified if the π -donating orbital has some s character (e.g., in SiH_3NMe_2 , which probably has a nonplanar SiNC_2 skeleton) or some d character (which is possible in, e.g., Si—P compounds). Detailed calculations of overlap integrals in these more complex situations have not yet been performed; a clue to the results that may be obtained is provided by similar calculations on cyclic P—N systems (93), which show that, as the configuration changes, reduction in one type of overlap is often offset by increase in another. This is consistent with the flexibility (i.e., lack of strongly preferred orientation) of Si—O—Si and Si—N—Si chains.

These theories of π -interaction and d -orbital participation can be tested more effectively on derivatives of silane than on any other group of hydrides, because a much wider range of compounds is known. This is the justification for the somewhat extensive treatment given here. It may be noted that SiH_3 derivatives seem to manifest both inter- and intramolecular effects more than the corresponding trialkylsilyl derivatives (see Section IV,B). In the first case, this is probably a result mainly of steric effects, but it is not clear why π -interaction should be lessened. Possibly hyperconjugative effects between alkyl groups and silicon are responsible. Recently, too, it has been reported (4) that SiF_3 derivatives behave rather like corresponding SiH_3 compounds, although the Lewis acid function of the former is more marked.

C. BOND ENERGIES AND HEATS OF FORMATION

Values of the thermochemical bond energies $E(\text{Si—H})$ and $E(\text{Si—Si})$ have been discussed by Cottrell (86). His preferred values are quoted in Table IV; they will be altered somewhat by a recent change in the accepted value for the heat of sublimation of silicon (see Beezer and Mortimer, 57). More accurate values for the heats of formation of SiH_4 , Si_2H_6 , and Si_3H_8 have been obtained by Gunn and Green (160, 161); their method is a novel one involving explosive decomposition of the hydride, usually in the presence of stibine. Their value for $E(\text{Si—H})$ is very similar to the previous one, but $E(\text{Si—Si})$ proves to be appreciably smaller, in both di- and trisilane. Fehér *et al.* (141, 142) have also measured the heats of formation of $\text{Si}_n\text{H}_{2n+2}$ ($n = 1-4$) by a direct combustion method, but their values differ radically from those of Gunn and Green, and it seems likely that inherent difficulties of the technique (the heats of combustion to be measured are very small) may be responsible. No thermochemical studies on derivatives of silanes seem to have been reported, although they would be most valuable.

TABLE IV
HEATS OF FORMATION OF SILANES AND DERIVED BOND ENERGIES

Compound	ΔH_f (kcal mole ⁻¹)	$E(\text{Si—H})$ (kcal mole ⁻¹)	$E(\text{Si—Si})$ (kcal mole ⁻¹)	Ref.
SiH ₄	+7.3	76.5	—	(160)
	+7.8	72.6	—	(229)
	-11.3	—	—	(142)
Si ₂ H ₆	+17.1	76.5	46.4	(160)
	+15.1	72.6	39.7	(230)
	-35.8	—	—	(142)
Si ₃ H ₈	+25.9	76.5	46.9	(161)
	-54.1	72.6	—	} (142)
<i>n</i> -Si ₄ H ₁₀	-70.4	—	—	
		76	51	(86)

A number of groups have been active in determining bond-dissociation energies. These have been estimated by mass spectrometry, by measurement of appearance potentials for various ions. The appearance potential is the limiting energy just required to produce a particular ion (with no extra kinetic energy), and is not always easy to establish. Furthermore, the processes by which a certain ion is formed need to be assumed, but are sometimes ambiguous. Steele *et al.* (243) first studied silane and several alkylsilanes; from measurements of appearance potentials and a number of assumptions about the processes involved and the ions produced, they were able to deduce that the values of $D(\text{H}_3\text{Si—H})$ and $D(\text{H}_3\text{Si—SiH}_3)$ were 93 and 82 kcal mole⁻¹, respectively. In another study, Steele and Stone (242) examined disilane itself, and by more direct arguments established a value of 81 kcal mole⁻¹ for $D(\text{H}_3\text{Si—SiH}_3)$. Such large values were surprising; in particular, an earlier estimate of $D(\text{H}_3\text{Si—SiH}_3)$, based on measurements of the activation energy for the pyrolysis of disilane (133), was only 51 kcal mole⁻¹.

Similar electron impact experiments and measurements of appearance potentials have been carried out by Saalfeld and Svec (229, 230) (who used their results to derive values of the heat of formation of silane and disilane—see Table IV) and by Hess *et al.* (170, 171). Reasonable agreement between the different groups was obtained (see Table V).

Very recently, however, Connor *et al.* (81, 82) have remeasured some of the appearance potentials reported by Hess *et al.* They find appreciably lower values, and combine them with estimates of $D(\text{Me}_3\text{Si—SiMe}_3)$ to obtain the derived values shown in Table V. The Si—Si bond-dissociation energy was assumed to be equal to the measured activation energy for

TABLE V

BOND-DISSOCIATION ENERGIES (IN THE COMPOUNDS SHOWN)

$D(\text{Si—H})$ (kcal mole ⁻¹)	$D(\text{Si—C})$ (kcal mole ⁻¹)	$D(\text{Si—Si})$ (kcal mole ⁻¹)	Ref.
93 H ₃ Si—H Cl ₃ Si—H	65 Me ₃ C—SiH ₃	82 H ₃ Si—SiH ₃	(243)
		81.3 H ₃ Si—SiH ₃	(242)
83 Me ₃ Si—H		81 Me ₃ Si—SiMe ₃	(170)
88 Me ₃ Si—H	85 Me ₃ Si—CH ₃	86 Me ₃ Si—SiMe ₃	(171)
95 H ₃ Si—H		84 H ₃ Si—SiH ₃	(229, 230)
64–74 Me ₃ Si—H	59–69 Me ₃ Si—CH ₃	49, ^a 58 ^b Me ₃ Si—SiMe ₃	(81, 82)
84 Me ₃ Si—H	79 Me ₃ Si—CH ₃	69 Me ₃ Si—SiMe ₂ Et	(100, 101)

^a From molecular flow pyrolysis.^b From toluene carrier pyrolysis.

pyrolytic breakdown of hexamethyldisilane, either alone or with an excess of toluene, at about 700°. The fact that trimethylsilane was obtained in the latter case as a major product supports their contention that the primary breakdown produces SiMe₃· radicals.

Davidson and Stephenson (100, 101) have confirmed the lower value for the appearance potential found by Connor *et al.*, but suggest from their experiments on the pyrolysis of Me₃SiSiMe₂Et that $D(\text{Si—Si})$ should be 69 kcal mole⁻¹. This leads to higher values generally for $D(\text{Me}_3\text{Si—X})$.

The results of such studies, especially the value of $D(\text{Si—Si})$, are of great interest in connection with the chemistry of disilane; as will be seen (Section III,B), this compound often reacts via its Si—H bonds

TABLE VI
INFRARED STRETCHING AND DEFORMATION FREQUENCIES IN
SILYL DERIVATIVES

X in SiH ₃ X	Si—H stretch (cm ⁻¹)	SiH ₃ deformation (cm ⁻¹)	SiH ₃ rock (cm ⁻¹)	Ref.
H	2180s, 2183as	—	—	(187)
F	2189s, 2210as	991s, 929as	730	(49)
Cl	2201s, 2211as	945s, 952as	663	
Br	2200s, 2211as	930s, 947as	631	
I	2192s, 2206as	903s, 941as	592	(104)
CN	2205s, 2227as	920s, 941as	682	(192)
N ₃	2170	945	(690)	(121)
NCS	2200s, 2207as	949s, 950as	710	(129)
NCO	2300–2200	960	710	(118)
Me	2169s, 2166as	943	(539)	(48)
OMe	2150	982, 968	732	(245)
NMe ₂	2160, 2110	969s, 921as	695	(70)
PH ₂	2169	920, 904	—	(193)
AsH ₂	—	890	—	(107)
Co(CO) ₄	2160	906s, 947as	(600)	(27)
Mn(CO) ₅	2156, 2136	906	(609)	

rather than by cleavage of the Si—Si bond. Nevertheless, chemically, the lower estimates of dissociation energies seem more reasonable.

D. VIBRATIONAL SPECTROSCOPY

Infrared studies at various levels of sophistication have been carried out on a wide range of silicon hydride derivatives. Relevant data are summarized in Table VI (SiH₃X derivatives), Table VII (SiH₂X₂ and SiHX₃ derivatives), Table VIII [(SiH₃)₃M and (SiH₃)₂M derivatives], and Table IX (Si₂H₅X derivatives). It should be emphasized that, although Si—H stretching vibrations occur in a frequency region that is usually free from interference by other vibrations, severe coupling is possible among modes at lower frequencies. Because of this, terms like $\delta(\text{SiH}_3)$ rock are only approximate descriptions of the actual movement of the molecule that is responsible for a particular absorption. Where it is reasonably certain that such coupling is serious, values in the tables have been enclosed in parentheses. All these measurements refer to gas phase spectra, an indication of the volatility of most silane derivatives.

A number of correlations have been suggested between particular absorption frequencies in a related class of compounds and various

TABLE VII
INFRARED ABSORPTION FREQUENCIES IN SiH_2X_2 AND SiHX_3
DERIVATIVES

X in SiH_2X_2	Si—H stretch (cm^{-1})	SiH_2 scissors (cm^{-1})	SiH_2 wag (cm^{-1})	SiH_2 twist (cm^{-1})	Ref.
F	2246s, 2251as	982	903	730	(87)
Cl	2200	953	877	710	(126, 167, 168, 213)
Br	2206s, 2232as	925	828	688	(168)
I	—	925	791	—	(126)
Me	2145	961	(919)	—	(47, 126)
OMe	2180	933	—	—	(244)
NMe ₂	2136	953	(918)	—	(35)

X in SiHX_3	Si—H stretch (cm^{-1})	Si—H bend (cm^{-1})	Ref.
F	2315	—	(214)
Cl	2274	808	(153a)
Me	2123	—	(47)
OMe	2210	—	(244)
NMe ₂	2108	811	(35)

properties of the atom attached to silicon. Thus Kriegsmann (187) has suggested that the Si—H stretching vibration increases in frequency as the Pauling electronegativity of the other attached groups increases, and has related this to a reduction in the size of the $\text{Si}^{\delta+}\text{—H}^{\delta-}$ bond dipole. Smith and Angelotti (239) correlated Si—H stretching frequencies with a set of additive empirical parameters (E values); these were related, according to Thompson (259), to Taft's σ^* values of the substituents concerned. It was therefore argued that inductive effects were paramount. While it is true that these trends are followed in a rough and ready way, inspection of the tables will show many instances of anomalies. For example, the values of $\nu(\text{Si—H})$ for all the silyl halides are approximately equal, while the values for the compounds SiH_2X_2 decrease in the order $\text{X} = \text{Br} > \text{OMe} > \text{Me} > \text{NMe}_2$, which is certainly not an order of decreasing electronegativity. Only by certain arbitrary assumptions concerning the effect of π -bonding can such difficulties be avoided.

The symmetrical SiH_3 deformation frequency has been shown by Jolly (180) to increase roughly linearly with increase in electronegativity of the attached group, and Ebsworth *et al.* (126, 129) have suggested

TABLE VIII
INFRARED ABSORPTION FREQUENCIES IN DI- AND
TRISILYL DERIVATIVES

Compound	Si—H stretch (in cm^{-1})	SiH_3 deformation (in cm^{-1})	Ref.
$(\text{SiH}_3)_3\text{N}$	2167, 2140	944	(225)
$(\text{SiH}_3)_3\text{P}$	2165, 2154	939, 885 ^a	(99)
$(\text{SiH}_3)_3\text{As}$	2165, 2092	917, ^a 874	(11)
$(\text{SiH}_3)_3\text{Sb}$	2160	908 ^a , 853 ^a	
$(\text{SiH}_3)_2\text{O}$	2183, 2169	957	(195)
$(\text{SiH}_3)_2\text{S}$	2180	956, ^a 907 ^a	(127)
$(\text{SiH}_3)_2\text{Se}$	2185	932, 890	

^a Mean of two or more closely similar frequencies.

TABLE IX
INFRARED ABSORPTION FREQUENCIES IN DISILANYL COMPOUNDS

X in $\text{SiH}_3\text{SiH}_2\text{X}$	Si—H stretch (cm^{-1})	SiH_3 and SiH_2 deformation and/or rock (cm^{-1})	Ref.
H	2179, 2153 ^a	934, ^a 909, 844	(62, 163)
Cl	2190	942, ^a 883, ^a 807 ^a	(90)
Br	2190	944, 882, ^a 818, 788 ^a	(273)
I	2200, 2180	940, ^a 872, ^a 757 ^a	(272, 274)
OSi_2H_5	2155	937, 853, 808, 755	
$\text{N}(\text{Si}_2\text{H}_5)_2$	2150	931, 885, 849, ^a 808, 733	(274)
SSi_2H_5	2160	940, 878, 794, 764	

^a Mean of two or more closely similar frequencies.

similar correlations for SiH_2 "scissors" and "wagging" deformation modes in SiH_2X_2 derivatives, and for the SiH_3 rocking mode in simple SiH_3X compounds. Again, examples of these trends and exceptions to them may both be found in the tables. They often prove useful in a comparison of several closely similar compounds.

Relatively few Raman studies have been carried out, for obvious reasons; precision Raman spectrometers are not plentiful, and preparative chemists are reluctant to prepare the necessary amounts of samples. For instance, the author needed to carry out seventeen separate preparations of tetrasilylhydrazine in order to produce an acceptably large sample (see Section V,A,5). These limitations are now not so severe, and it seems

likely that soon Raman spectra will become semiroutine. It was feared at one time that photolysis of silane derivatives would produce cloudiness and spectra of poor quality, but this has proved to be overpessimistic. By working at low temperatures, good spectra have been obtained in a number of detailed studies; these will be referred to later.

E. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

A considerable amount of proton resonance data has been obtained, largely by Ebsworth and Turner (123, 124) and Van Dyke and MacDiarmid (267). A fairly complete selection of τ values and $J(^{29}\text{Si}-\text{H})$ coupling constants is assembled in Table X (SiH_3X , SiH_2X_2 , and SiHX_3 derivatives) and Table XI ($\text{Si}_2\text{H}_5\text{X}$ derivatives). In almost all cases, the natural abundance of ^{29}Si (4.7 %) was sufficient for splitting (due to its nuclear spin of $\frac{1}{2}$) to be observed. Other coupling constants, for example $J(^1\text{H}-^1\text{H})$, have been much less studied. Danyluk (98) has shown that the sign of the $^{29}\text{Si}-\text{H}$ coupling constant in Me_3SiHCl is negative.

Any general discussion of the significance of these values is beset with difficulties and pitfalls. It can be seen at once that the range of τ values is not very large, and also that there is a general inverse relation between the values of τ and $J(^{29}\text{Si}-\text{H})$. In general, too, the $\text{Si}-\text{H}$ protons become less shielded as H in SiH_4 is replaced by more electronegative groups. In the early halcyon days of such studies (before about 1963), it was widely believed that values of proton chemical shifts were a valid measure of the electron distribution in the molecule. Any deviations from the expected deshielding behavior of electronegative substituents were imputed to π -bonding effects. Thus the *increase* in proton shielding in passing from SiH_3F to SiH_2F_2 to SiHF_3 would be rationalized by assuming that $p_\pi-d_\pi$ donation increasingly outweighed inductive effects. Similarly, in the series of compounds $\text{CH}_3\text{SiH}_2\text{X}$, it was found that the methyl proton shielding *decreased* in the order $\text{X} = \text{H} > \text{N} > \text{O} > \text{F}$, an order consistent with the operation of inductive deshielding, but *increased* in the order $\text{X} = \text{I} < \text{Br} < \text{Cl} < \text{F}$, which might be rationalized in terms of steadily increasing $\text{X} \rightarrow \text{Si}$ π -donation.

Unfortunately, however, this kind of interpretation does not seem to be justified. In an important series of papers, Ebsworth and Turner (123, 124) and Ebsworth and Frankiss (115, 116) analyzed both chemical shift and coupling constant data in detail, and discussed possible mechanisms that could account for the trends observed. They pointed out *inter alia* that the behavior outlined in the previous paragraph, and attributed to π -bonding effects, was also observed in the case of corresponding $\text{CH}_3\text{CH}_2\text{X}$ β -proton chemical shifts, where no d orbitals can be invoked.

TABLE X

N.M.R. DATA FOR SiH_3X , SiH_2X_2 , AND SiHX_3 DERIVATIVES

Compound	τ (ppm) (± 0.01 unless otherwise stated)	$J(^{29}\text{Si}-\text{H})$ (c/s)	Ref.
SiH_4	6.80	202.5 ± 0.2	(123, 124)
SiH_3F	5.24	229.0 ± 0.6	
SiH_2F_2	5.29 ± 0.02	282 ± 3	
SiHF_3	5.49	381.7 ± 1.5	
SiH_3Cl	5.41	238.1 ± 0.2	
SiH_2Cl_2	4.60	288.0 ± 0.4	
SiHCl_3	3.93	362.9 ± 0.2	
SiH_3Br	5.83	240.5 ± 0.3	
SiH_2Br_2	4.83	289.0 ± 0.6	
SiH_3I	6.56 ± 0.03	240.1 ± 0.2	
SiH_2I_2	5.97	280.5 ± 0.2	
SiH_3CN	6.18	—	
SiH_3NCO	5.58 ± 0.02	231.5 ± 0.7	(118)
SiH_3NCS	5.54	240 ± 2	(123, 124)
SiH_3NCSe	5.52 ± 0.02	243.2 ± 0.4	(119)
SiH_3N_3	5.51	230.3 ± 0.5	(121)
SiH_3Me	6.42	194.4	(234)
SiH_2Me_2	6.18	190	
SiHMe_3	6.00	190	
$(\text{SiH}_3)_3\text{N}$	5.56 ± 0.02	212 ± 2	(123, 124)
$(\text{SiH}_3)_2\text{NMe}$	5.56 ± 0.02	212 ± 2	
SiH_3NMe_2	5.66 ± 0.04	208 ± 2	
$(\text{SiH}_3\text{N})_2\text{C}$	5.55	225 ± 1	
$(\text{SiH}_3)_2\text{O}$	5.39	221.5 ± 0.2	(123, 124)
SiH_3OMe	5.48	216.2	(267)
$(\text{SiH}_3)_2\text{S}$	5.64 ± 0.02	224.0 ± 0.3	(123, 124)
SiH_3SCF_3	5.58 ± 0.02	234 ± 1	(105)
$(\text{SiH}_3)_2\text{Se}$	5.88 ± 0.04	—	(123, 124)
$\text{SiH}_3\text{SeCF}_3$	5.70	—	(128)
SiHI_3	5.51	325.1	(75)
$\text{SiH}_2(\text{NMe}_2)_2$	5.62	217.6 ± 0.4	
$\text{SiH}(\text{NMe}_2)_3$	5.87	235 ± 1	
$\text{SiH}_2(\text{OMe})_2$	5.58	247.6 ± 0.6	
$\text{SiH}(\text{OMe})_3$	5.91	297.9 ± 0.3	
$\text{SiH}_2(\text{OSiH}_3)_2$	5.46 (SiH_2)	256.6 ± 0.3	
	5.33 (OSiH_3)		
$\text{SiH}(\text{OSiH}_3)_3$	5.82 (SiH)	316.0 ± 0.5	
	5.34 (OSiH_3)		
SiH_3PH_2	6.27	204 ± 1	(108)
SiH_3AsH_2	6.33	203 ± 1	

They therefore argued that, until a convincing mechanism of shifts and coupling constants can be put forward that accounts satisfactorily for the observed trends in silicon and carbon compounds, it is premature to single out certain changes and relate them to the presence of *d* orbitals on silicon.

Such considerations are relevant when considering an experiment described as an experimental test of Si—N π -bonding (222). The ^{15}N —H spin coupling in $\text{Me}_3\text{Si}^{15}\text{NHPH}$ was compared with that in (a) $^{15}\text{NH}_4^+$ and $\text{Ph}^{15}\text{NH}_2$ (both considered as examples of sp^3 hybridization), and

TABLE XI
N.M.R. DATA FOR DISILANYL COMPOUNDS^a

X in $\text{Si}_2\text{H}_5\text{X}$	τ (ppm)		$J(^{29}\text{Si—H})$	
	SiH_3	SiH_2	SiH_3	SiH_2
H	6.74	—	196.2	—
F	6.73	4.70	—	217.0
Cl	6.59	5.14	201.4	221.2
Br	6.41	5.70	202.6	225.8
I	6.14	6.61	204.6	224.4
OSi_2H_5	6.80	4.88	194.4	214.8
OSiH_3	6.78 ^b	4.87	192.8 ^b	210.6
$\text{N}(\text{Si}_2\text{H}_5)_2$	6.72	5.16	—	205.2
NMe_2	6.85	5.26	—	199.8

^a Van Dyke and MacDiarmid (267).

^b Refers to SiH_3 of Si_2H_5 group.

(b) $\text{C}_5\text{H}_5^{15}\text{NH}^+$ (sp^2 hybridization). It was argued that, if Fermi contact interaction were the dominant coupling mechanism, changes in *s* character in the bond from N to H would be observed as changes in $J(^{15}\text{N—H})$. In the event, the observed coupling was similar to examples (a) and distinctly different from (b). This means either that there is no significant Si—N π -bonding in Me_3SiNHPH or that $J(^{15}\text{N—H})$ is not an effective measure of such bonding, but it does not seem possible to say more at this stage.

The disilanyl compounds in Table XI show behavior somewhat similar, as far as the SiH_2 protons are concerned, to that of silyl compounds. The same inverse relationship between τ values and $J(^{29}\text{Si—H})$ values is roughly obeyed, and again there is no simple connection between chemical shift and electronegativity. The difference, Δ , given by $[\tau(\text{SiH}_3) - \tau(\text{SiH}_2)]$, between chemical shifts of the two different sets of

Si—H protons decreases with decreasing electronegativity of the substituent X; a similar effect is observed in $\text{CH}_3\text{CH}_2\text{X}$ and $\text{CH}_3\text{SiH}_2\text{X}$ compounds (97, 116). It is interesting that, in $\text{SiH}_3\text{SiH}_2\text{I}$, Δ is negative, i.e., the SiH_2 resonance is to high field of the SiH_3 resonance. Van Dyke and MacDiarmid (267), in an extensive discussion of these and other effects in disilanyl derivatives, suggest that this is compatible with a very low effective electronegativity of iodine in $\text{Si}_2\text{H}_5\text{I}$, which may be related to π -bonding effects in the Si—I bond. They also suggest that certain observed trends may indicate interactions across the Si—Si bond of a type not found in ethyl compounds. It is tempting to ascribe these to Si—Si π -interaction of the type suggested by Mulliken (see Section II,B), but in view of the discussion in the earlier part of this section, such suggestions must be viewed with some caution.

Most of the values in Tables X and XI refer to moderately dilute solutions, and it is found generally that dilution shifts are small. In particular, dilution shifts for both proton and ^{19}F resonances in the fluorosilanes $\text{SiH}_{4-x}\text{F}_x$ ($x = 1-3$) are almost within the limits of error for the determinations (124). This does not support the idea that association of these compounds in the liquid phase is significant (see Section II,G). An exception is found in the case of dimethylaminosilane, Me_2NSiH_3 , in which the proton dilution shift is considerable. There is other evidence for the association of this compound in condensed phases (see Section V,A).

Apart from studies of ^{19}F resonance where appropriate, very few other nuclei in silane derivatives have been studied by this technique. Holzman *et al.* (174) examined the ^{29}Si resonances of a number of compounds, but found that intrinsically weak absorption and severe quadrupole broadening were limiting factors. The latter effect was particularly troublesome when N, Cl, Br, or I was attached to silicon. It appears that only one study of ^{15}N attached to silicon (referred to earlier) and none of ^{17}O have been made, although the results would be of great interest.

F. USE OF OTHER PHYSICAL METHODS

Microwave spectroscopy has been of value in providing precise bond parameters for pseudohalides such as SiH_3NCS and SiH_3CN (see Section IV,B). Estimates of barrier heights to internal rotation have also been obtained; for example, Schwendeman and Jacobs (236) quote values (in kcal mole^{-1}) of 2.55 for $\text{SiH}_3\text{CH}_2\text{Cl}$ and 1.67 for SiH_3CH_3 .

Very few diffraction studies have been reported in recent years; the electron diffraction experiments on $(\text{SiH}_3)_3\text{N}$, $(\text{SiH}_3)_3\text{P}$, $(\text{SiH}_3)_3\text{As}$, $(\text{SiH}_3)_2\text{O}$, and $(\text{SiH}_3)_2\text{S}$ are referred to (Sections V,A,5, V,B,2, and VI,C),

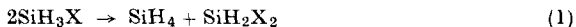
but no X-ray or neutron diffraction studies of silicon hydride derivatives have been carried out. The last-named method is of particular interest, because determination of hydrogen positions in solid silyl compounds, for example, could tell us much about the effects of intermolecular interactions on stereochemistry.

Dipole moments are often difficult to interpret, but the zero moment found for $(\text{SiH}_3)_3\text{N}$ (269) in the gas phase gives unequivocal confirmation of the planarity of the NSi_3 skeleton. The same authors in 1964 reported a similar study of $(\text{SiH}_3)_2\text{O}$ and SiH_3OCH_3 (270). The values found (0.24 and 1.17 D, respectively) were compared with the moment of $(\text{CH}_3)_2\text{O}$ (1.31 D) and discussed in terms of the bond angles in these compounds (see Section VI,C) and of p_π - d_π bonding between silicon and oxygen. The Si—H bond moment has been mentioned (Section II,B); measurements of the Si—N bond moment (which is small and variable) have been made by Schaarschmidt (232), and are consistent with a situation where the σ -inductive moment is opposed by a moment due to π -donation in the opposite direction.

Interesting information has recently been deduced by Bell and Walsh (58) from the vacuum ultraviolet spectra of silyl compounds. Although little detail could be seen, the spectra of SiH_3Cl , $(\text{SiH}_3)_2\text{O}$, $(\text{SiH}_3)_3\text{N}$, and $(\text{SiH}_3)_2\text{NMe}$ were all shifted to shorter wavelengths relative to those of the corresponding methyl compounds. It therefore appears that the silyl compounds possess higher first ionization potentials. Although this would not be expected from the relative electronegativities of silicon and carbon, it may be rationalized in terms of delocalization of lone-pair electron density onto silicon by d_π - p_π interaction.

G. DISPROPORTIONATION

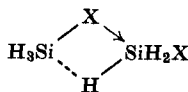
One of the most obvious and annoying features of the behavior of silyl compounds is their readiness to disproportionate. When almost any such compound is allowed to remain in the liquid phase, the following reaction occurs:



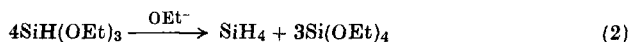
It may be slow, as in the case of SiH_3I at room temperature, or rapid, as in the case of SiH_3NMe_2 , SiH_3OMe , and SiH_3F ; of course other modes of decomposition may supervene, as in the case of SiH_3CN . Further decomposition may occur, giving rise to SiHX_3 and SiX_4 , if X is not too large. The reaction is generally extremely slow in the gas phase.

MacDiarmid (197) suggested that such reactions might involve a bimolecular complex of the type shown. Initial coordination of X to Si

would provide a relatively easy reaction path via the four-center intermediate shown; the ability of silicon to increase its coordination above 4, as discussed earlier, will not make it necessary for bond-breaking and bond-making processes to be synchronous (although they may be). The formation of a complex of this kind will clearly be more difficult (a) in the gas phase, and (b) if X is either of low electronegativity or is heavily involved in π -bonding with silicon.



This kind of reaction has been known for almost exactly 100 years; Friedel and Ladenburg (143) observed that triethoxysilane gave silane and tetraethoxysilane:

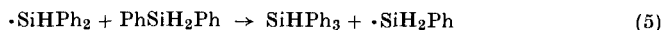
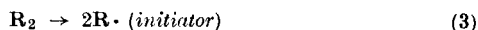


In their case, the reaction had to be catalyzed by a base, ethoxide ion, and it is now known that a wide variety of bases will catalyze the disproportionation of simple silyl compounds. A full discussion of this effect in relation to $(\text{SiH}_3)_3\text{N}$, $(\text{SiH}_3)_2\text{NR}$ ($\text{R} = \text{H}, \text{Me}, \text{Ph}$), $\text{Si}_2\text{H}_5\text{NMe}_2$, $(\text{SiH}_3)_2\text{O}$, and $(\text{SiH}_3)_2\text{S}$ will be given (Sections V, A, 4 and VI, B).

Acid catalysis of reaction (1) is also possible. Stock and Somieski (249) found that aluminum chloride greatly accelerated the disproportionation of chlorosilane, and more recently Russell (228) in a series of papers has thoroughly discussed the behavior of compounds of the type Me_3SiR ($\text{R} = \text{H}, \text{Et}, \text{Ph}$). A wide variety of conditions, solvents, and Lewis acids was employed, and it was concluded that aluminum halides were among the most effective catalysts, and that mechanisms involving siliconium ions or organometallic intermediates were unlikely. The most probable reaction intermediate was a complex involving two molecules of the substituted silane and one AlX_3 molecule. The formation of this complex could be assisted by the presence of a weakly donating solvent (e.g., benzene) or by small amounts of a basic co-catalyst (e.g., trimethylamine or water).

Free radical initiators may also speed disproportionation. Nelson *et al.* (212) found that diphenylsilane (which is reasonably stable thermally alone) could be attacked rapidly by ultraviolet radiation or by organic peroxides at 130° . They postulated a mechanism in which a silyl radical, formed either by $\text{Si}-\text{H}$ cleavage or by a hydrogen abstraction process,

rapidly abstracted hydrogen or phenyl from another molecule of Ph_2SiH_2 :



It may be noted that silyl radicals are extremely elusive, and have not so far been detected by methods appropriate for methyl radicals. As will be discussed (Section III,C), they appear to remove hydrogen extremely rapidly from various substrates.

Only by γ -irradiation of SiH_4 in an inert matrix at 4°K were Morehouse *et al.* (205) able to demonstrate the presence of trapped SiH_3 radicals by e.s.r. spectroscopy. It appears that, unlike CH_3 , the SiH_3 radical is pyramidal.

The three types of disproportionation catalyst referred to above are paralleled by the three types of catalyst that have been used to promote the addition of Si—H to multiple bonds. These are bases (61), metal salts (e.g., 50, 112), and free radical initiators (e.g., 237). The situation is often complicated by the fact that reaction seems to proceed simultaneously by more than one mechanism.

III. The Silanes, $\text{Si}_n\text{H}_{2n+2}$

A. PREPARATION AND SEPARATION

The classical method for the preparation of large quantities of silanes is by the action of dilute hydrochloric acid on magnesium silicide. In this way Stock and Somieski (248) prepared and characterized $\text{Si}_n\text{H}_{2n+2}$ ($n = 1-4$), and obtained a less volatile mixture of presumed isomers of Si_5H_{12} and Si_6H_{14} , which they were unable to separate. This method still represents a good way of making large quantities of the higher silanes;

TABLE XII
THE SILANES, $\text{Si}_n\text{H}_{2n+2}$

Compound	M.P.	B.P.	d (gm/ml)	ΔH_{vap} (cal mole ⁻¹)	ΔS_{vap} (e.u.)	Ref.
SiH_4	-185°	-111.9°	0.68 (-185°)	2982	18.4	(154, 280)
Si_2H_6	-132°	-14°	0.69 (-25°)	5200	20.1	(154)
Si_3H_8	-114.8°	53°	0.74 (0°)	6783	20.8	(154, 161)
Si_4H_{10}	- 84°	108°	0.79 (0°)	8260	21.7	(154, 208)

Fehér *et al.* (139) used an adaptation of it to prepare more than 300 ml of a liquid mixture of higher silanes. In the following paper (140), the same authors describe their most ingenious set of techniques for handling such reactive compounds. Special hypodermic syringes with protected needles are used to transfer the liquid silanes from one nitrogen-filled vessel to another via soft rubber septum caps that act as self-sealing closures. Attachments to the vacuum system that are sealed in the same way allow transfer of silanes to and from the usual fractionation line and storage vessels. Courage appears to be a prerequisite for such procedures.

Other metal silicides are known to contain varied arrangements of chains and rings of silicon atoms (276), and it seems likely that their hydrolysis would yield a rather different distribution of silanes from that afforded by Mg_2Si . In a preliminary note, Borer and Phillips (63) described the separation of twenty-one components derived from Mg_2Si and phosphoric acid; they used a vapor phase chromatography (v.p.c.) column containing silicone fluid on Celite, and showed that the products ranged up to Si_8H_{18} , and included a number of isomers of the higher members. Fehér and Strack (138) reported a similar separation, using a column filled with squalane on kieselguhr.

In a further report, Timms and Phillips (262) described the preparation of a mixture of silanes from silicon monoxide and 10% hydrofluoric acid. The products were again separated by v.p.c., and the distribution was shown to be rather different from that obtained before:

Relative amounts ($\text{Si}_3\text{H}_8 = 100$)					
Source of silanes	Si_3H_8	$n\text{-Si}_4\text{H}_{10}$	$i\text{-Si}_4\text{H}_{10}$	$n\text{-Si}_5\text{H}_{12}$	$i\text{-Si}_5\text{H}_{12}$
Mg_2Si	100	36	2.5	12	4.5
SiO	100	43	5.5	20	8

A most useful method for the production of higher silanes is that employing a silent discharge of the ozonizer type. Spanier and MacDiarmid (240) first used this to make Si_2H_6 , Si_3H_8 , and crude Si_4H_{10} from silane. Gokhale and Jolly (155) and Gokhale *et al.* (158) used a similar method to prepare n - and $i\text{-Si}_4\text{H}_{10}$, which were separated by gas chromatography. Evidence for silanes up to Si_8H_{18} was obtained. Finally, in a recent paper, Andrews and Phillips (14) describe in detail the separation of a mixture of silanes, germanes, and silicon-germanium hydrides, prepared by the action of a silent discharge on a mixture of SiH_4 , Si_2H_6 , and GeH_4 . Besides the mixed hydrides (discussed in Section VIII,A) they were able to identify $neo\text{-Si}_5\text{H}_{12}$, $n\text{-Si}_6\text{H}_{14}$, $n\text{-Si}_7\text{H}_{16}$, and

branched-chain Si_6 and Si_7 hydrides. Identification was based partly on a consideration of column retention times and partly on the behavior of the silane when passed into a 5-Å molecular sieve. Only straight-chain hydrides were removed.

Reduction of tetrachlorosilane by lithium aluminum hydride in ether remains the most favored way of making monosilane in the laboratory. Disilane (62) and trisilane (260) can be made similarly in quite good yields from the corresponding chlorosilane in a high-boiling ether. Commercial interest in monosilane (for the production of transistor-grade silicon by its pyrolysis) has led to a search for cheaper large-scale methods. Silica and lithium aluminum hydride give a 7% yield of silane when heated to 200° (275), while the high-pressure hydrogenation of a mixture of silica, aluminum, and aluminum chloride at moderate temperatures (175) produces yields up to 76%.

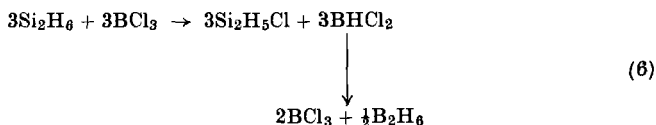
Like molecular sieves, the formation of clathrate compounds can be an effective way of differentiating between straight-chain and branched isomers. In an interesting paper by Müller and Meier (208), it is reported that both urea and thiourea form clathrate compounds with $n\text{-Si}_n\text{H}_{2n+2}$ when n is ≥ 3 . These derivatives become more stable toward oxidation and hydrolysis as n increases; the Si_5H_{12} -urea complex is stable in air at room temperature.

B. REACTIVITY

One of the few recent reports concerning the chemical properties of silane itself comes from Hagenmuller and Pouchard (165). They give a detailed description of the reaction of sodium and sodium hydride with silane under various conditions. Those reactions that lead to the production of NaSiH_3 are dealt with later (Section VIII,A), but it was also shown that sodium in liquid ammonia reacts with silane to give sodium amide and $\text{Si}(\text{NH})_2$ (a polymer). At 350°, a sodium film reacts with silane to form sodium hydride and NaSi .

A new, detailed study of the pyrolysis of silane has been reported by Purnell and Walsh (220). They show that an initial reaction accompanied by no overall pressure change yields hydrogen, disilane, and a trace of trisilane as the volatile products; its activation energy is 56 kcal mole⁻¹. Later, when 10–20% of the silane has decomposed, the pressure rises and the activation energy falls to 51 kcal mole⁻¹. The authors suggest that initially the formation of SiH_2 radicals derived from the unimolecular reaction, $\text{SiH}_4 \rightarrow \text{SiH}_2 + \text{H}_2$, may be an important step. In the later stages, loss of hydrogen from solid (polymeric) silicon hydrides may be the rate-determining process.

Even now, very little is known of the reactivity of disilane and the higher silanes. It seems fairly clear, however, that reaction often involves Si—H rather than Si—Si bonds, and that it proceeds more readily than with silane itself. When BCl_3 is mixed with silane there is no immediate reaction, although diborane may be produced by heating (131) or by introducing methyl radicals (233). Disilane and BCl_3 react together readily, however, to give diborane and disilanyl chloride (265):



PCl_3 behaves similarly, giving disilanyl chloride and phosphine (38), but BF_3 and PF_3 do not react with disilane under these conditions. The very mild conditions under which reaction (6) proceeds make it possible that other chloro derivatives of higher silanes may be prepared in this way.

Analogously, BBr_3 reacts with Si_2H_6 to give not only $\text{Si}_2\text{H}_5\text{Br}$ but also *sym*- and *unsym*-dibromodisilane and the more symmetrical tri- and tetrabromodisilanes (110). Heated silver halides have also been used by Hollandsworth *et al.* (173) to halogenate disilane.

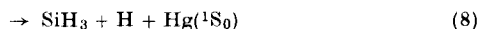
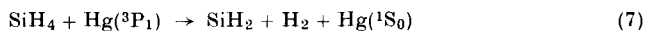
It is interesting that disilane, like hexahalodisilanes and many silyl derivatives, will undergo base-catalyzed disproportionation (cf. Section II,G). Morrison and Ring (206) have shown that hydride ions and even lithium chloride are effective catalysts in diglyme solution; they suggest that a silene intermediate may be involved.

Studies of vibrational spectra of the higher silanes have now become feasible; Spanier and MacDiarmid (240) reported the infrared spectrum of trisilane, while Fehér and Fischer (137) published infrared and Raman spectra of trisilane and *n*- and *i*-tetrasilane.

C. PHOTOLYSIS

In 1936 Emeléus and Stewart studied the photolysis of silane, and found that, in the presence of mercury, hydrogen and a solid of composition $(\text{SiH}_{0.91-0.48})_x$ were produced (134). This reaction has recently been re-examined with important results (215). Silane at 1-cm pressure and 25° , with a drop of mercury present, was irradiated with ultraviolet light (2537 \AA) from a helical source of high intensity. After 5 seconds, the products were led into a mass spectrometer and found to be hydrogen (3.8%), Si_2H_6 (1.7%), and Si_3H_8 (0.2%) together with traces of Si_4H_{10} and Si_5H_{12} . Simultaneously a film of solid was formed on the walls of the tube; with longer irradiation a stationary state was reached. If the tube

was then emptied of volatile products, filled with hydrogen, and re-irradiated, the film was removed and a mixture of volatile silanes was produced. The system seems to involve a number of radical chain processes; it is suggested that the primary steps are:



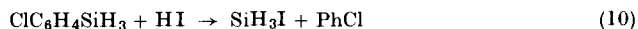
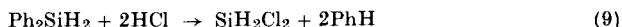
When an equimolar mixture of SiH_4 and SiD_4 was irradiated, the resulting hydrogen consisted approximately of H_2 (40%), HD (40%), and D_2 (20%). Addition of ethylene (up to 10% molar) hardly altered the yield of hydrogen or its isotopic distribution. This surprising result implies that silane is much more efficient as a radical scavenger than ethylene. This conclusion has been confirmed by extensive studies of the photolysis of SiD_4 and the methylsilanes by Nay *et al.* (211). In the same laboratory, Yarwood *et al.* (279) estimated that the radical-quenching cross section of silane is about 400 times that of methane. Furthermore, Kerr *et al.* (184, 185) measured the rate of hydrogen abstraction by methyl radicals from SiHCl_3 , etc., at various temperatures. They infer that the rapid quenching results from a high A factor in the Arrhenius equation rather than from an especially small activation energy.

If silanes are photolyzed in the presence of other substances, it may be possible to isolate silyl derivatives from the products. Thus, mixtures of SiH_4 with GeH_4 or MeI have been shown to yield SiH_3GeH_3 or MeSiH_3 in the presence of mercury vapor (153). The extension of such experiments to systems containing Si_2H_6 is an obvious step.

IV. Halogen and Pseudohalogen Derivatives of Silanes

A. HALIDES

From a preparative point of view, the recent development of routes to halosilanes that do not involve silane itself is of considerable importance. Both Fritz and Kummer (149–151) and Aylett and Ellis (28) have described preparations based on the cleavage of phenylsilanes, of which the following are typical:



The phenylsilanes are readily made from the corresponding Si—Cl compounds by reduction with lithium aluminum hydride; the chlorination of the phenyl ring in Eq. (10) is an important preliminary step, as otherwise the product mixture of iodosilane and benzene is very hard to separate completely.

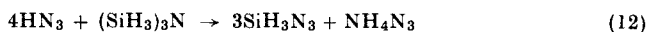
TABLE XIV
 PSEUDOHALIDE DERIVATIVES OF SILANE

Compound	M.P.	B.P.	d (gm/ml)	ΔH_{vap} (cal mole ⁻¹)	ΔS_{vap} (e.u.)	Ref.
SiH ₃ CN	+32°	49.6°	—	7169	22.2	(196)
SiH ₃ N ₃	-82°	26°	—	6680	22.3	(121)
SiH ₃ NCO	-89°	18°	—	6540	22.5	(118)
SiH ₃ NCS	-52°	84°	1.05 (20°)	8923	25.0	(196)
SiH ₃ NCS _e	-15°	111°	—	10,800	28	(119)
(SiH ₃ N) ₂ C	-75°	85°	—	8100	22.6	(117)

 TABLE XV
 STRUCTURAL STUDIES ON PSEUDOHALOGEN DERIVATIVES

Compound	Shape	Remarks	Method	Ref.
SiH ₃ CN	Linear SiCN	<i>n</i> -Cyanide	IR	(192)
SiH ₃ N ₃	Bent NNN Si	—	Microwave	(207, 238)
			IR	(121)
			Microwave	(130)
SiH ₃ NCS	Linear SiNCS	Si-N, 1.71 Å	Microwave	(177, 178)
SiH ₃ NCO	Linear SiNCO (probably)	—	IR/Raman	(129)
			Microwave	(130)
(SiH ₃ N) ₂ C	Linear SiNCNSi	Di-imide	IR	(118)
SiMe ₃ NCS	Bent SCN Si	Si-N, 1.78 Å	IR/Raman	(120)
SiMe ₃ NCO	Bent OCN Si	—	ED	(186)
			ED	

paration it is usually helpful and sometimes essential to dilute the halo-silane vapor with nitrogen when passing it over the metal salt. An exception is silyl azide—this was made by cleavage of a silylamine (Eq. 12) in dibutyl ether (121):



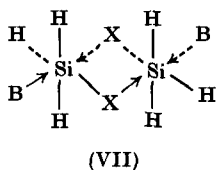
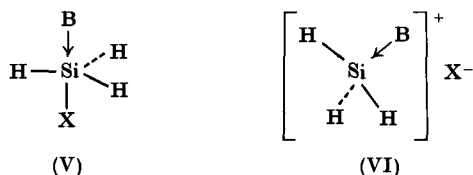
Structural studies on these compounds have attracted considerable attention; results are collected in Table XV. We may note that while silyl azide [like methyl azide (194)] is bent, silyl isocyanate and silyl

isothiocyanate [unlike their methyl analogs (52, 136)] have a linear skeleton. This can be thought of as a change in hybridization from sp^2 to sp at the nitrogen atom in SiH_3NCX ; the amount of energy for this process (which is not known accurately) must be provided as a result of increased p_π - d_π overlap between nitrogen and silicon. Linnett (190) has discussed these compounds in terms of the number of possible valence bond canonical forms that can be written for them. A restriction is imposed on the formal charges that may be placed on various atoms: nitrogen is limited to the range $+1$ to $-\frac{1}{2}$, while oxygen and sulfur may be in the range $+1$ to -1 . Silicon is allowed to form more than four electron-pair bonds, while carbon of course is not. He finds that there are four allowed linear forms for H_3SiNCX ($\text{X} = \text{O}, \text{S}$) but none for H_3SiN_3 . All but one of the forms for H_3CNCX and all for H_3CN_3 are bent. Linnett emphasizes that the difference between $-\text{NCX}$ and $-\text{NNN}$ is basically due to the lower nuclear charge of nitrogen as compared to oxygen, and nitrogen's unwillingness to accept a large excess negative charge.

It can also be seen that the trimethylsilyl derivatives, Me_3SiNCX , show less evidence of π -bonding than the hydride derivatives, SiH_3NCX . They are bent, not linear, and the $\text{Si}-\text{N}$ distances are larger.

C. ADDUCTS

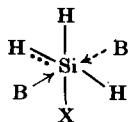
Halosilanes have been known for many years to form adducts with tertiary amines (41, 132), and it is interesting to consider various structural possibilities for such compounds. A 1:1 adduct, $\text{SiH}_3\text{X} \cdot \text{B}$ ($\text{B} =$



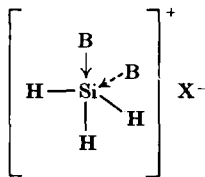
base), may be molecular and five-coordinate (V), ionic and four-coordinate (VI), halogen-bridged and six-coordinate (VII), or some more complex combination of these possibilities. A 1:2 adduct, $\text{SiH}_3\text{X} \cdot 2\text{B}$, may most simply be molecular and six-coordinate (in *cis* and *trans* forms)

(VIII), or ionic and five-coordinate (with various isomers) (IX). Similar possibilities for silicon tetrahalides have been discussed by Beattie (53).

Aylett and Sinclair (39) and Campbell-Ferguson and Ebsworth (73, 74, 74a) have recently provided a good deal of fresh information concerning these adducts. Pyridine and various 2-substituted pyridines reacted readily with iodosilane to form adducts $\text{SiH}_3\text{I} \cdot 2\text{B}$. No 1:1 adducts could be made. The pyridine compound dissolved in an excess of pyridine or in



[6] *trans*
(VIII)



[5] *axial-equatorial*
(IX)

acetonitrile to give conducting solutions, in which it behaved as a weak or a strong electrolyte, respectively. When the adduct $\text{SiH}_3\text{I} \cdot 2\text{coll}$ ($\text{coll} =$ collidine = 2,4,6-trimethylpyridine) reacted with trimethylamine, the substituted pyridine was displaced and, in the absence of solvent, $\text{SiH}_3\text{I} \cdot \text{NMe}_3$ was formed. When acetonitrile was present, a 1:2 adduct $\text{SiH}_3\text{I} \cdot 2\text{NMe}_3$ was formed. Both the 1:1 and 1:2 adducts gave conducting solutions in acetonitrile, while the 1:2 adduct gave a sublimate of the 1:1 adduct on gentle heating. α, α' -Bipyridyl and iodosilane gave a 1:1 adduct that behaved similarly to $\text{SiH}_3\text{I} \cdot 2\text{py}$.

With no solvent, trimethylamine formed a 1:1 adduct with SiH_3X ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and the extent of dissociation on heating increased from the iodide to the chloride (38). Thus the iodide forms the strongest adduct. When the 1:1 adduct with iodosilane was dissolved in acetonitrile, and the solvent subsequently removed, Campbell-Ferguson and Ebsworth noted that $\text{SiH}_3\text{I} \cdot 2\text{NMe}_3$ remained behind. They also reported *inter alia* that the infrared spectra of the solid adducts $\text{SiH}_3\text{X} \cdot 2\text{py}$ ($\text{X} = \text{Br}, \text{I}$) were closely similar in the region down to 250 cm^{-1} , implying that similar groupings were present in each.

All this evidence is consistent with the idea that the adducts can be formulated as $(\text{Me}_3\text{NSiH}_3)^+\text{I}^-$ and $(\text{B}_2\text{SiH}_3)^+\text{I}^-$, where $\text{B} = \text{NMe}_3$, pyridine, etc., and $\text{B}_2 =$ bipyridyl. In solution it seems probable that the mono- and bistrimethylamine cations exist in equilibrium. The true nature of the solids can be established only by diffraction experiments, however; a small amount of $\text{Si}^{\delta+} - \text{I}^{\delta-}$ charge separation in a structure still essentially that of a five- or six-coordinate molecular adduct might

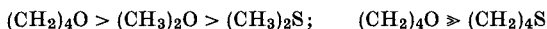
give rise to the behavior observed. In particular, ionization in donor solvents would be anticipated, and the Si—X infrared stretching frequencies could be shifted to such low values that they were not observed, particularly in the case of iodides.

The difficulties inherent in the use of infrared spectroscopy to establish adducts' structures are revealed in a salutary study by Beattie and Parrett (54). A simple valence force field (SVFF) calculation on the adduct $\text{SiH}_3\text{I} \cdot \text{NMe}_3$ showed that there are three vibrational frequencies, covering a range of more than 700 cm^{-1} , to which the Si—N stretch contributes. This mixing makes it hazardous or impossible to assign absorption bands to vibrations of particular bonds or groups.

The adduct $\text{SiH}_3\text{I} \cdot \text{bipyridyl}$ mentioned above deserves comment. Recently the analogous compound $\text{Ph}_3\text{SiI} \cdot \text{bipyridyl}$ was prepared by Corey and West (84), who refer to it as containing the siliconium ion $(\text{bipy} \cdot \text{SiPh}_3)^+$, with five-coordinate silicon. While this ion may indeed be present in solution (and perhaps in the solid), the name "siliconium ion" seems unfortunate; as Beattie and Webster (55) point out, ions of this kind are usually thought of as derivatives of quaternary N^+ , and by analogy $\text{H}_3\text{C} \leftarrow \text{NMe}_3$ is certainly not a conventional representation of the tetramethylammonium ion.

The ditertiary amine $\text{CH}_2(\text{NMe}_2)_2$ forms a 1:2 adduct with excess iodosilane, while an equimolar amount of iodosilane produces a 1:1 complex that may be chelate (36). The corresponding amine with no bridging methylene group, namely, tetramethylhydrazine, Me_2NNMe_2 , gives only a 1:1 adduct with iodosilane under the same conditions (18).

The interaction of much weaker bases, such as ethers and thioethers, with iodosilane has also been investigated by Aylett (21). It is found that the order of donor ability is:



Secondary reactions such as disproportionation of iodosilane and ether cleavage occur readily even at low temperatures, but it is clear that SiH_3I , unlike BH_3 , uniformly adopts so-called Class (a) behavior (3) and forms stronger complexes with oxygen than with sulfur. A similar conclusion can be drawn from earlier results (41), which show that toward iodosilane the order of donor strength of Group V donors is $\text{NMe}_3 > \text{PMe}_3 > \text{AsMe}_3$.

It will be seen that iodosilanes have received the most attention; however, it appears that bromosilanes show a similar tendency to yield ionic adducts, while fluorosilanes may produce molecular complexes. The behavior of chlorosilanes is not yet certain, but Campbell-Ferguson and Ebsworth (74a) have made the interesting suggestion that adducts of

SiH_3Cl and SiH_2Cl_2 may contain chlorine-bridged polymeric cations. When formation of halide ions and halogen bridging are both impossible, as in the case of the liquid adduct $\text{CHF}_2\text{CF}_2\text{SiH}_3 \cdot \text{NMe}_3$, a simple molecular species is formed (83).

V. Silane Derivatives with Group V Elements

A. SILICON-NITROGEN COMPOUNDS

1. Preparation

A wide range of silicon hydride derivatives containing Si—N bonds has now been prepared (Table XVI), and it is possible to make a number of interesting comparisons between them. While their boiling points are

TABLE XVI
SILICON HYDRIDE DERIVATIVES WITH NITROGEN

Compound	M.P.	B.P.	<i>d</i> (gm/ml)	ΔH_{vap} (cal mole ⁻¹)	ΔS_{vap} (e.u.)	Ref.
$(\text{SiH}_3)_2\text{NH}$	-132°	36°	—	5560	18.0	(33)
$(\text{SiH}_3)_3\text{N}$	-106°	52°	0.895/-106°	—	—	(250)
$(\text{SiH}_3)_2\text{NMe}$	-124°	32°	—	6770	22.2	(132)
$(\text{SiH}_3)_2\text{NEt}$	-127°	66°	—	—	—	
$(\text{SiH}_3)_2\text{NPh}$	-69°	189°	0.801/22°	8320	18.0	(32)
SiH_3NMe_2	+2.2°	19°	0.700/20°	6340	21.8	(29, 257)
SiH_3NEt_2	-149°	78°	0.751/20°	7410	21.2	(29)
$\text{SiH}_3\text{NC}_4\text{H}_8$	-46°	81°	0.810/20°	8860	25.0	(30)
$\text{SiH}_3\text{NC}_5\text{H}_{10}$	-109°	104°	0.775/20°	7780	20.6	
$\text{SiH}_2(\text{NMe}_2)_2$	-104°	93°	0.788/20°	7710	21.1	(35)
$\text{SiH}(\text{NMe}_2)_3$	-90°	142°	0.850/20°	9830	23.7	
$(\text{Si}_2\text{H}_5)_3\text{N}$	-97°	176°	0.873/0°	10,660	23.7	(274)
$\text{Si}_2\text{H}_5\text{NMe}_2$	<-134°	66°	—	8470	25.0	(1)
$(\text{SiH}_3)_2\text{NN}(\text{SiH}_3)_2$	-24°	109°	0.83/0°	8190	21.4	(17)

not particularly remarkable (apart from being rather low for compounds of such high molecular weight), melting points are uniformly very low, with one striking exception. This is dimethylaminosilane, already referred to (Section II,B) as a compound that seems to be associated in the solid phase.

The heat of association of SiH_3NMe_2 has been semiquantitatively assessed by Sujishi and Witz (257) and more recently by Aylett and

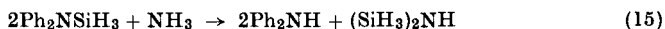
Emsley (29), using the following argument. The latter pair of workers measured both the heats of sublimation, ΔH_1 , and of vaporization, ΔH_2 , of the compound. It was then assumed that the heat of fusion of the hypothetical unassociated solid, ΔH_3 , was similar to that of trimethylamine. The last quantity is in any case rather small ($1.5 \text{ kcal mole}^{-1}$) so an error of up to 25 % will not be serious. The heat of association of solid SiH_3NMe_2 is now given by $\Delta H_1 - \Delta H_2 - \Delta H_3$, which turns out to be about $4.8 \text{ kcal mole}^{-1}$. This is comparable with the strength of hydrogen-bonding interactions in ice.

Methods of making these compounds have been discussed in detail (22). A halosilane is usually allowed to react under the mildest possible conditions with the corresponding N—H compound, either in the gas phase or in dilute solution at low temperature. Typical examples of such reactions are:



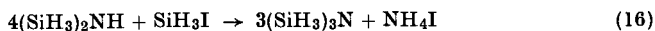
If the reacting base is a strong one (toward protons) and not too hindered sterically, an excess of base will result in a drastic lowering of yields because of base-catalyzed disproportionation, to be discussed later. If, on the other hand, the N-Si product is a fairly strong base, an excess of halosilane will also be harmful, since adducts such as $\text{SiH}_3\text{NR}_2 \cdot \text{SiH}_3\text{I}$ may be formed.

Because of the harmful effect of an excess of base, the amine exchange reaction that is so useful in organosilicon chemistry is of limited applicability. One interesting example of its use, however, is in the preparation of disilylamine, $(\text{SiH}_3)_2\text{NH}$, which cannot be prepared from ammonia and a halosilane, but is made in the following way (33):



A deficit of ammonia is used; diphenylamine is such a weak base that it does not catalyze the decomposition of the product.

The existence of disilylamine is important, because it was postulated by Stock and Somieski (250) as an intermediate in the preparation of trisilylamine by reaction (13) in a stepwise process. It has now been shown to react with iodosilane to give a high yield of trisilylamine,



which shows that the last step in Stock's process is feasible. It has not yet proved possible to isolate SiH_3NH_2 , however.

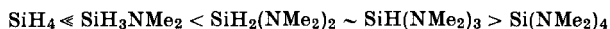
2. Base Strength

The reduction in base strength of Si-N compounds as compared with corresponding C-N compounds has already been commented on (Section II,B). Table XVII records a selection of published information on adducts

TABLE XVII
REACTIONS OF SILICON-NITROGEN COMPOUNDS WITH LEWIS ACIDS

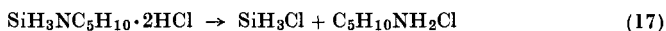
Acid	Base	Complex (base:acid)	Ref.	
BH ₃	(SiH ₃) ₃ N	(none)/-80°	(67)	
	(SiH ₃) ₂ NMe	1:1/-80°	}	(256)
	SiH ₃ NMe ₂	1:1/-80°		
	SiH ₂ (NMe ₂) ₂	1:2/-84°	}	(36)
	SiH(NMe ₂) ₃	1:2/-135°		
	Si(NMe ₂) ₄	1:1/-135°		
BMe ₃	(SiH ₃) ₃ N	(none)	(67)	
	(SiH ₃) ₂ NH	(interacts below -100°)	(33)	
	(SiH ₃) ₂ NMe	(none)	(257)	
	SiH ₃ NR ₂	1:1/-80°	}	(29, 257)
	SiH ₂ (NMe ₂) ₂	1:1/-84°		
	SiH(NMe ₂) ₃	(none)	(36)	
	SiH ₃ NC ₅ H ₁₀	1:1/-96°	(30)	
SiH ₃ I	(SiH ₃) ₃ N	(none)	}	(19)
	(SiH ₃) ₂ NMe	(none)		
	(SiH ₃) ₂ NN(SiH ₃) ₂	(none)	(17)	
	SiH ₃ NR ₂	1:1/-78°	(29)	
	SiH ₃ NC ₅ H ₁₀	1:1/-46°	(30)	
HCl	SiH ₃ NMe ₂	1:2/-96°	}	(29)
	SiH ₃ NEt ₂	1:3/-96°		
	SiH ₃ NC ₅ H ₁₀	1:2/-88°	(30)	

(or the lack of them) between simple silicon hydride amines and various Lewis acids. It will be seen that a compound containing three silyl groups attached to one nitrogen atom is a weaker base than one with two silyl groups attached to nitrogen, which in turn is weaker than a compound with only one silyl group on nitrogen. This is consistent with the picture of N → Si p_{π} - d_{π} donation already developed; this donation is more extensive when more silyl groups interact with a particular nitrogen atom. Furthermore, when more than one nitrogen atom is attached to a single silicon atom, the resulting compounds are stronger bases. In the series SiH_{4-x}(NMe₂)_x, the order of base strength with respect to borane has been shown by Aylett and Peterson (36) to be:



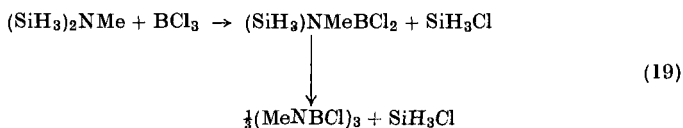
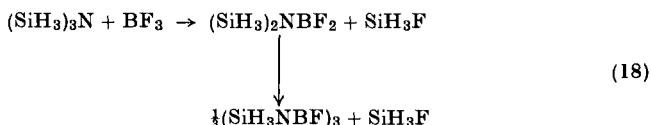
It will be noted that steric effects become predominant with the later members of the series; if a smaller reference acid could be used, it might be possible to demonstrate a continuous rise in base strength. Unfortunately, H^+ cleaves the Si—N bond in most such compounds (e.g., 35).

When warmed to room temperature, most of the adducts in Table XVII become fully dissociated. Some, however, may undergo further reaction, as follows (30):

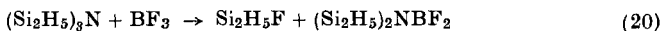


3. Cleavage Reactions

Boron halides have been shown to react in a similar fashion to Eq. (17) to produce silyl halides from Si-N compounds (67, 257, 258):



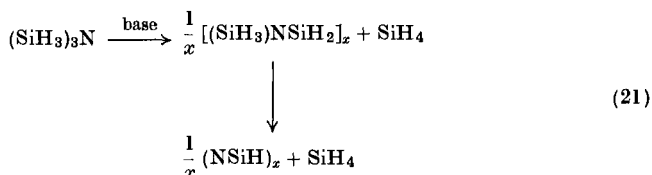
Disilanyl-nitrogen compounds also undergo similar cleavage with no breaking of the Si—Si bond (1):



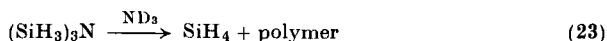
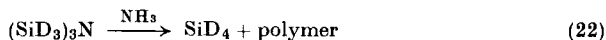
Probably other nonmetallic halides will be found to react in analogous ways; with organosilicon-nitrogen compounds they are known to do so (e.g., 102). A related reaction occurs when $(SiH_3)_3N$ is mixed with methanol or ROH ($R = MeCO, HCO, CF_3CO$); SiH_3OMe or silyl esters are formed, respectively (122).

4. Disproportionation; Polymers

The action of bases on silyl-nitrogen compounds has been investigated in some detail. Stock and Somieski (250) noted that excess ammonia reacted with trisilylamine to produce silane, and the outlines of base-catalyzed disproportionation have been presented (Section II,G). In an extensive study, Wells and Schaeffer (277) have shown how trisilylamine in the liquid phase reacts with a variety of bases to give silane:



The initial product shown was normally polymeric, but small amounts of a cyclic compound with $x = 3$ were also isolated. The species $(\text{NSiH})_x$ is of course highly cross-linked. Suitable bases included NH_3 , MeNH_2 , LiH in ether, and NMe_3 ; the last gave only slow reaction. By deuteration of either the trisilylamine or the added base, the authors were able to show that no base protons were incorporated in the silane produced, e.g.:

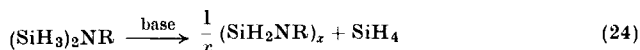


Kinetic studies at low temperatures showed that the activation energy for the process was about 4 kcal mole^{-1} , which is not much more than the value expected for a diffusion-controlled reaction. In general, the results were consistent with the ready formation of a bimolecular complex as reaction intermediate, although other possibilities could not be entirely eliminated.

It is interesting that the relatively stable compound $\text{Si}_2\text{H}_5\text{NMe}_2$ undergoes disproportionation to give disilane and unsymmetrical $\text{SiH}_3\text{SiH}(\text{NMe}_2)_2$. No silane and very little hydrogen appear to be produced in this reaction, so that presumably only one reaction path is important. Abedini and MacDiarmid (1) discuss this reaction in terms of nucleophilic attack by nitrogen, which preferentially occurs at a silicon atom already linked to nitrogen. This implies that σ -abstraction from this silicon outweighs π -donation to it.

Aylett (17) noted that tetrasilylhydrazine did not react rapidly with NMe_3 , and there was no evidence of complex formation. It was therefore inferred that π -bonding had greatly decreased the readiness of the SiH_3 group to form extra dative σ -bonds as compared with, say, iodosilane.

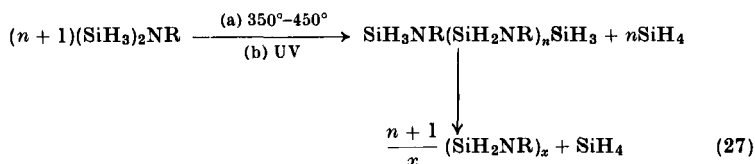
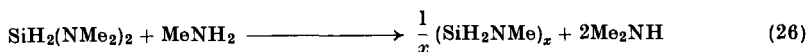
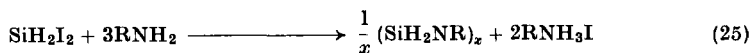
The base-catalyzed disproportionation of disilazanes has been reported recently by Aylett and Hakim (31). The authors studied the action of various bases on the compounds $(\text{SiH}_3)_2\text{NR}$ ($\text{R} = \text{Me}, \text{Ph}$) and found that, with any given base, the N-methyl compound reacted much more rapidly than the N-phenyl:



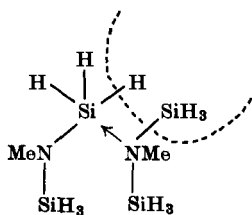
The order of catalyst efficiency for both compounds was $\text{NH}_3 > \text{NH}_2\text{Me} > \text{C}_5\text{H}_5\text{N} \sim \text{PhNH}_2 > \text{NMe}_3 > (\text{CH}_2)_4\text{O}$. It can be seen that for the nitrogen donors this order is based more on steric requirements than on proton affinity. Ammonia and methylamine reacted exceedingly rapidly in the initial stages, even below room temperature; the rate fell off markedly later, presumably because of the increasing viscosity of the

system. It has since been found that disilylamine is even more susceptible to this kind of attack (33).

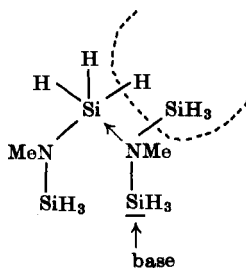
The polymers of composition $(\text{SiH}_2\text{NR})_x$ that are formed in reaction (24) have been prepared by a number of other routes (22, 23, 34, 43):



The first is a straightforward condensation reaction, the second is an amine exchange process, while the third, involving pyrolysis or photolysis in the gas phase, is noteworthy in that oligomers with $n = 1\text{--}3$ have been isolated in the case of the N-methyl derivative (37). No cyclic products of low molecular weight have ever been detected. The polymers possess considerable thermal and hydrolytic stability; for example, a sample prepared according to Eq. (25) suffered 3.5% weight loss after 12



(X)

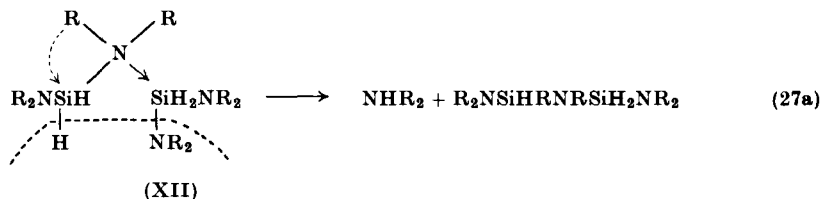


(XI)

hours at 400° , and dissolved only slowly in hot concentrated aqueous alkali. This stability may be thought of as arising from both electronic and steric factors; π -delocalization (cf. 92) along the polymer chain could logically confer resistance toward nucleophilic attack by decreasing silicon's electron-acceptor ability, while coiling of the polymer chains effectively shields silicon atoms from the outside world.

In accord with the previous discussion of disproportionation, the reaction intermediate for reaction (27) is probably a bimolecular complex (X). This can lose silane, as shown, in the first stage of an oligomerization reaction. Such a complex will be weak since, as was mentioned (Section V,A,2), the base strength of disilazanes is low (and their electron-acceptor power is also weak). The base strength will be enhanced, however, by electron donation from an added Lewis base (XI) because here the underlined silicon atom, in accepting σ -donated electrons, will π -bond less strongly to the central nitrogen atom. The nitrogen is thus enabled to donate electrons more effectively to another disilazane molecule. This is another manifestation of the intermolecular-intramolecular competition referred to (Section II,B).

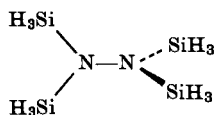
In the gas-phase pyrolysis of bis- and tris-dialkylaminosilanes (35) and of dialkylaminosilanes (29, 30), the major products derive from disproportionation processes. The presence of small amounts of dialkylamines, however, suggests that an alternative orientation of the bimolecular complex (X) and simultaneous alkyl migration (XII) may be significant:



5. Structures

Structural studies on simple derivatives have yielded important results. Hedberg (169) showed by electron diffraction techniques that $(\text{SiH}_3)_3\text{N}$ has a planar skeleton of heavy atoms. Three complete studies of the vibrational spectra of the same molecule (125, 188, 225) confirmed this result, and it was suggested that deformation from this planar arrangement was energetically quite easy; this leads to band broadening. Infrared and Raman spectra of $(\text{SiH}_3)_2\text{NMe}$ (71) and infrared spectra of SiH_3NMe_2 (70), together with their silyl-deuterated analogs, have also been reported. While it seems likely that the skeletal structure of $(\text{SiH}_3)_2\text{NMe}$ is almost planar and that of SiH_3NMe_2 is distinctly non-planar (and the observed absorptions were assigned on these bases), no definite information concerning molecular shapes could be deduced. In the case of tetrasilylhydrazine, an infrared and Raman investigation

suggested strongly that the molecule has a skeleton of D_{2d} symmetry (42):



Two planar NSi_2 units are connected at right angles. The adoption of this structure, rather than the all-planar D_{2h} arrangement, suggests that electron π -donation from N to Si is not sufficient to lessen appreciably the strong repulsions between essentially filled N $2p\pi$ orbitals. In N_2O_4 , which is planar, it is reasonable to suppose that there is considerable removal of electron density from the N—N region.

B. SILICON-PHOSPHORUS, SILICON-ARSENIC, AND SILICON-ANTIMONY COMPOUNDS

1. Preparation and Properties of Silicon-Phosphorus Compounds

Much less is known about these compounds (listed in Table XVIII) than about the corresponding Si-N derivatives, probably because they are more difficult to prepare. The field has recently been reviewed by Fritz (146).

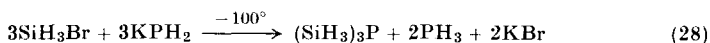
TABLE XVIII
SILICON HYDRIDE DERIVATIVES WITH PHOSPHORUS,
ARSENIC, AND ANTIMONY

Compound	M.P.	B.P.	d (gm/ml)	ΔH_{vap} (cal mole ⁻¹)	ΔS_{vap} (e.u.)	Ref.
SiH_3PH_2	$<-135^\circ$	13°	—	—	—	(144, 145)
$(\text{SiH}_3)_3\text{P}$	—	114°	—	8697	22.5	(11)
SiH_3PEt_2	—	$53^\circ/79 \text{ mm}$	—	—	—	} (146)
$\text{SiH}_2(\text{PEt}_2)_2$	—	$110^\circ/13 \text{ mm}$	—	—	—	
SiH_3PI_2	$<-2^\circ$	190°	$2.9/20^\circ$	9300	20.5	(41)
$(\text{SiH}_3)_3\text{As}$	—	120°	$1.201/20^\circ$	9798	24.9	} (11)
$(\text{SiH}_3)_3\text{Sb}$	—	255°	—	(7638)	—	

In 1953 Fritz reported that, when a mixture of silane and phosphine was heated at 450° – 500° , silylphosphine, SiH_3PH_2 , was formed in rather low yield (144). In subsequent publications, it was shown that SiH_3PH_2

reacted with a wide variety of protic reagents to give phosphine (145, 147). At about the same time, Aylett *et al.* (41) studied the reaction of iodosilane with white phosphorus in the temperature range 20°–100°. A mixture of products resulted, from which SiH_3PI_2 could be isolated. It seemed probable that trisilylphosphine, $(\text{SiH}_3)_3\text{P}$, was also formed, but it appeared to form a 1 : 1 adduct with iodosilane rather readily, and was not obtained in a pure state. The basic nature of Si-P compounds has also been demonstrated recently by the isolation of the liquid molecular adduct $\text{SiH}_3\text{PH}_2 \cdot \text{BH}_3$ (111).

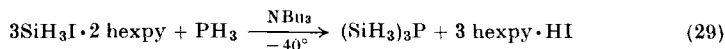
Trisilylphosphine was first obtained by Amberger and Boeters (9, 11) by the reaction of bromosilane with KPH_2 in dimethyl ether solution at low temperatures (yields of up to 55 % were reported):



It seems likely that SiH_3PH_2 is first formed and this, under the experimental conditions, then undergoes metal-hydrogen exchange with KPH_2 to form KPHSiH_3 . This reacts further with bromosilane to give $(\text{SiH}_3)_2\text{PH}$, and the process is repeated, yielding $(\text{SiH}_3)_3\text{P}$. Disproportionation does not seem to be excluded, however (13).

A discharge method has proved useful for making Si-P compounds. When a mixture of silane and phosphine was passed through an ozonizer-type discharge at -78° , SiH_3PH_2 , $(\text{SiH}_3)_2\text{PH}$, and $\text{Si}_2\text{H}_5\text{PH}_2$ but not $(\text{SiH}_3)_3\text{P}$ were formed (107, 156). In subsequent experiments, $\text{SiH}_4/\text{SiH}_3\text{PH}_2$ and $\text{Si}_2\text{H}_6/\text{PH}_3$ mixtures were subjected to a discharge; isomeric $(\text{SiH}_3)_2\text{PH}$ and $\text{Si}_2\text{H}_5\text{PH}_2$, respectively, were obtained in this way, each essentially uncontaminated by the other (157). A number of physical properties of these compounds, including infrared and n.m.r. spectra, were reported.

Aylett and Sinclair (38) have found that adducts of substituted pyridines and iodosilane react directly with phosphine in a suitable solvent to give trisilylphosphine:



where hexpy is 2-*n*-hexylpyridine. This method has the advantage that it avoids the preparation of a metal derivative of phosphine.

2. Structures of Silicon-Phosphorus Compounds

From a study of the infrared and Raman spectra of $(\text{SiH}_3)_3\text{P}$ and its deuterated analog, the very interesting structural conclusion was drawn that the PSi_3 skeleton is planar or nearly so (99). On the other hand,

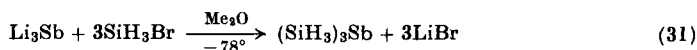
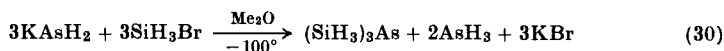
trigermylphosphine, $(\text{GeH}_3)_3\text{P}$, appears from similar evidence to be non-planar (87). Steric effects in the two molecules must be virtually the same, and the stereochemical difference was taken to imply that p_π - d_π donation from phosphorus to silicon is more pronounced than that from phosphorus to germanium.

An electron diffraction study, however, has now shown that $(\text{SiH}_3)_3\text{P}$ (also its arsenic analog) is definitely pyramidal, with a SiPSi bond angle of about 95° (51); its stereochemistry therefore affords no positive (or negative) evidence for π -bonding. It is interesting that the infrared/Raman selection rules are insensitive to such a large deviation from planarity. Presumably, as in the case of $(\text{SiH}_3)_2\text{O}$, the potential energy function for $(\text{SiH}_3)_3\text{P}$ shows only a low barrier to inversion (see Section VI,C).

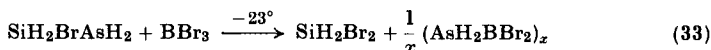
The infrared spectrum of silylphosphine has been reported (193). The molecule appears to be of low symmetry, and the observed absorption bands have been assigned in a similar way to those of CH_3PH_2 .

3. Silicon-Arsenic and Silicon-Antimony Compounds

Trisilyl-arsine and -stibine have been made by Amberger and Boeters (9-11) via the reaction of bromosilane with KAsH_2 and Li_3Sb , respectively:



The discharge method has also been used to make SiH_3AsH_2 and two Si_2AsH_7 isomers, which were identified mass spectrometrically (107). Little is known about their chemistry, but it seems that in at least one case the Si—H bond may be broken before the Si—As bond; SiH_3AsH_2 reacts with BBr_3 at low temperatures to give first $\text{SiH}_2\text{BrAsH}_2$, which then reacts further with Si—As cleavage (109):

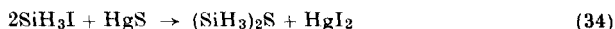


VI. Silane Derivatives with Group VI Elements

A. PREPARATION

Such derivatives (tabulated in Table XIX) have been prepared almost

always by means of the reaction between a halosilane and a silver or mercury salt, e.g. (135):



or by hydrolysis, e.g. (272):

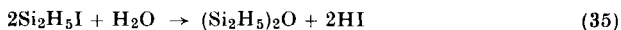
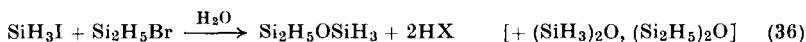


TABLE XIX

SILICON HYDRIDE DERIVATIVES WITH GROUP VI ELEMENTS

Compound	M.P.	B.P.	<i>d</i> (gm/ml)	ΔH_{vap} (cal mole ⁻¹)	ΔS_{vap} (e.u.)	Ref.
(SiH ₃) ₂ O	-144°	-15°	0.881/-80°	5630	21.8	(251, 252)
SiH ₃ OSi ₂ H ₅	—	43°	—	7500	23.8	(266)
(Si ₂ H ₅) ₂ O	-112°	95°	0.876/0°	8700	23.6	(90)
SiH ₃ OMe	-98°	-21°	—	6040	23.9	(244)
SiH ₂ (OMe) ₂	-100°	33°	—	7528	24.8	} (245)
SiH(OMe) ₃	-115°	81°	—	8782	24.8	
(SiH ₃) ₂ S	-70°	59°	0.929/10°	7740	23.3	(135)
(Si ₂ H ₅) ₂ S	-70°	144°	0.950/0°	11,380	27.3	(274)
SiH ₃ SH	-134°	14°	—	6200	21.9	(135)
SiH ₃ SMe	-117°	46.8°	—	7340	22.9	(246)
SiH ₃ SCF ₃	-127°	14°	—	6150	21.4	(105)
(SiH ₃) ₂ Se	-68°	85°	1.36/20°	8220	22.9	(135)
SiH ₃ SeCF ₃	-126°	35°	—	6700	22	(128)

Mixed compounds present more difficulty. Thus Si₂H₅OSiH₃ was made (266) in 18 % yield by the cohydrolysis of Si₂H₅Br and SiH₅I.



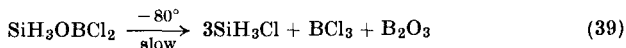
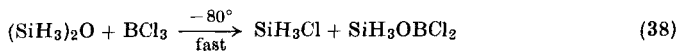
or by equilibration of (SiH₃)₂O/(Si₂H₅)₂O mixtures at 0° for long periods (32 % yield). Methoxysilanes were made from silane and methanol in the presence of copper (for derivatives with more than one methoxy group) or by the following reaction (244, 245):



B. CHEMICAL BEHAVIOR

The areas of interest in the chemistry of these compounds are similar to those of Group V derivatives and will be dealt with only in outline. Reported information is in any case sparser, and the interpretation of it follows the same lines. All those compounds that contain only one Group

VI atom are weak or negligible electron donors. Thus $(\text{SiH}_3)_2\text{O}$ does not interact with diborane (255) nor does SiH_3OMe (245). Also, $(\text{SiH}_3)_2\text{S}$ does not appear to form 'onium'-type adducts with either iodosilane or iodomethane (135). Lewis acids such as boron and aluminum halides cause cleavage of the Si—O bond (e.g., 189, 217):



It is interesting that $(\text{Si}_2\text{H}_5)_2\text{O}$ reacts more readily than $(\text{SiH}_3)_2\text{O}$ with BCl_3 , and also that $\text{Si}_2\text{H}_5\text{OSiH}_3$ is cleaved preferentially at the $\text{Si}_2\text{H}_5\text{—O}$ bond (266). These authors discuss this effect in terms of effective electron withdrawal from the α -silicon atom of the disilanyl group by means of possible $d_\pi\text{—}d_\pi$ interactions across the Si—Si bond.

Base-catalyzed disproportionation has been observed with both $(\text{SiH}_3)_2\text{O}$ and $(\text{SiH}_3)_2\text{S}$. Early work by Stock *et al.* (251, 252) suggested that $(\text{SiH}_3)_2\text{O}$ readily lost silane to give polymeric $(\text{SiH}_2\text{O})_x$, which was termed prosiloxane. This reaction has been recently re-examined by Campbell-Ferguson (72), who finds that $(\text{SiH}_3)_2\text{O}$ in the presence of various bases (e.g., water, acetonitrile, trimethylamine) or dihalosilanes and water yield $(\text{SiH}_2\text{O})_4$ and higher oligomers. MacDiarmid (200) has also reported that $(\text{SiH}_3)_2\text{O}$ in the presence of bases gives $\text{SiH}_2(\text{OSiH}_3)_2$ and $\text{SiH}(\text{OSiH}_3)_3$. It is possible that different reaction conditions lead to different products. Ammonia or trimethylamine also brings about the disproportionation of $(\text{SiH}_3)_2\text{S}$; in this case, silane and an adduct of approximate composition $(\text{SiH}_2\text{S} \cdot \text{base})_x$ are formed (198).

C. STRUCTURES

Structural studies have been confined to $(\text{SiH}_3)_2\text{O}$ and $(\text{SiH}_3)_2\text{S}$. Recent electron diffraction studies of high precision by the Oslo school have resolved the uncertainties that existed, particularly in relation to the first compound's structure; disiloxane has a bond angle (SiOSi) of 144° , while the corresponding angle in disilyl sulfide is 97° (6, 7). Infrared and Raman studies of $(\text{SiH}_3)_2\text{S}$ had strongly suggested a bond angle of about 100° (127, 191), but results on disiloxane were more conflicting. Early work by Lord *et al.* (195) had suggested that the skeleton was linear (or sufficiently close to linear so that the selection rules for D_{3d} symmetry were still obeyed). Later studies (15, 16, 202, 203, 261) seemed more consistent with a bent molecule, although it was not possible to estimate the bond angle with precision.

It is interesting to compare the forms of the potential energy function for various molecules as the bond angles change. The well-known double

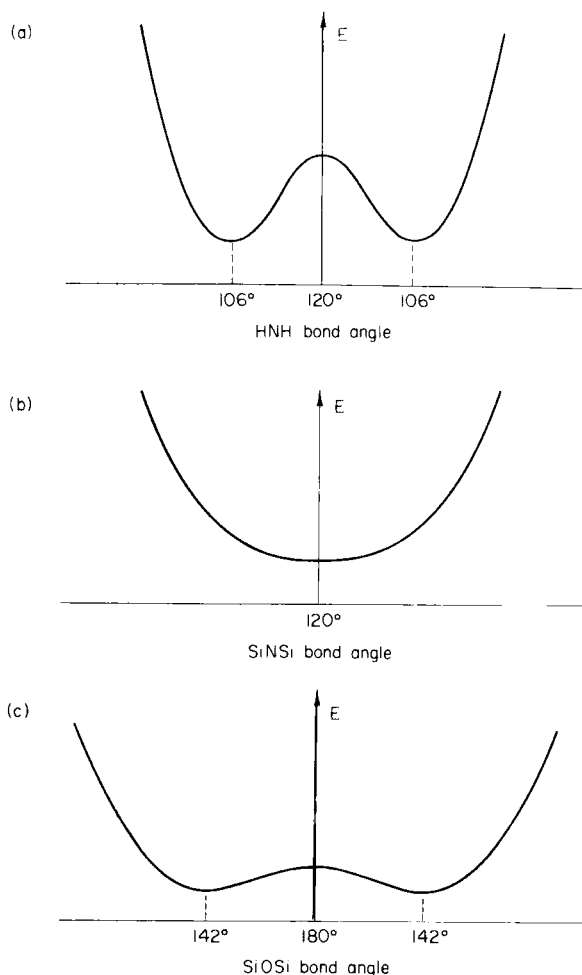


FIG. 3. Schematic potential energy functions for: (a) ammonia, (b) $(\text{SiH}_3)_3\text{N}$, and (c) $(\text{SiH}_3)_2\text{O}$.

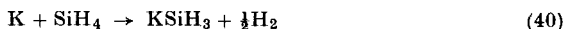
minimum curve for ammonia (Fig. 3a) represents a common situation in pyramidal molecules; the height of the potential barrier to inversion, about 6 kcal mole^{-1} , is a measure of the $sp^3 \rightarrow sp^2$ rehybridization energy. Trisilylamine can probably be represented by a curve with a shallow minimum (Fig. 3b), implying fairly easy out-of-plane bending. Disiloxane occupies an intermediate position (Fig. 3c); the curve has a shallow double minimum, and one analysis of the infrared data (15) suggests that the height of the potential barrier may be about $450 \text{ cal mole}^{-1}$. This leads to

very easy bending of the molecule, even at low temperatures. Trisilyl-phosphine is expected to have a curve that is a flatter version of Fig. 3a.

VII. Silicon-Metal Derivatives

A. NONTRANSITION METAL DERIVATIVES

Although various unsuccessful earlier attempts had been made to prepare silyl Grignard reagents and silyl-mercury compounds, the first silyl-metal compound to be isolated was potassium silyl, KSiH_3 . Ring and Ritter (223) prepared it either by the long reaction of silane or disilane with potassium metal in glyme (1,2-dimethoxyethane) at -78° , or by the reaction of potassium hydride with disilane in glyme at room temperature:



Potassium silyl proved to be remarkably stable thermally (up to 240°), but, while it reacted with chloromethane to give a quantitative yield of methylsilane, its behavior with other halides was disappointing. Thus with SiBr_4 no higher silanes were produced, but quantities of mono-silane. With SiD_3Br , extensive rearrangement occurred to give mixtures of all possible deuterated silanes and disilanes. Probably the use of glyme as a solvent in these reactions was harmful.

Recently, however, Amberger (8) reported that KSiH_3 reacts smoothly with a variety of halides in the absence of solvent to give some very interesting new compounds, e.g.:



Also Hagenmuller and Pouchard (165) have described the preparation of sodium silyl from silane and sodium in glyme at -30° ; formidable precautions were taken in handling the large quantities of silane required. Sodium silyl apparently reacts with AlCl_3 to give unstable aluminum trisilyl, $\text{Al}(\text{SiH}_3)_3$. In a further publication, Ring *et al.* (224) have presented evidence for the formation of KSi_2H_5 and KSi_3H_7 by the reaction of KSiH_3 with disilane.

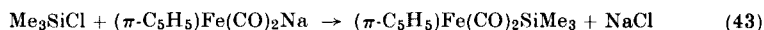
The earlier difficulties associated with the use of KSiH_3 in glyme have been partly overcome by Kennedy *et al.* (183). They find that, if the volatile products are allowed to escape rapidly, coupling reactions produce reasonable yields of Si_2H_6 (from SiH_3Br) and Si_3H_8 (from $\text{Si}_2\text{H}_5\text{Br}$). Their observation that lithium halides in glyme cause rapid disproportionation of Si_2H_6 , producing SiH_4 and a solid Si-H polymer, is probably

significant in this connection (cf. Section III,B). A different approach is to replace glyme by another donor solvent: Cradock *et al.* (88) find that hexamethylphosphoramide, $(\text{Me}_2\text{N})_3\text{PO}$, is very suitable both as a medium for the preparation of MSiH_3 ($\text{M} = \text{Li}, \text{Na}, \text{K}$) and for its further reaction with MeI , EtBr , and MeOCH_2Cl . The corresponding silyl derivatives were isolated in fair to high yields, especially from the potassium compound. (For the recent use of KSiH_3 to prepare Si-Ge and Si-B compounds, see Section VIII,A and B.)

Wurtz reactions can conveniently be considered at this point. Craig and MacDiarmid (89) successfully coupled iodosilane and methyliodosilane with liquid sodium amalgam to give reasonable yields of disilane and 1,2-dimethyldisilane, respectively. Less encouraging, however, was an attempted coupling of diiodomethane and iodosilane with sodium-potassium alloy in diglyme [bis(2-methoxyethyl) ether], which led to the formation of dimethylsilane (19)! Similar difficulties arose in the reaction of dibromosilane and potassium germynyl, KGeH_3 , in dimethyl ether, which gave germane as the only volatile product (11).

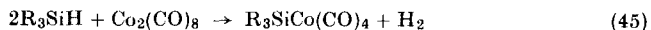
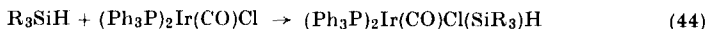
B. TRANSITION METAL DERIVATIVES

The first silicon-transition metal compound to be prepared was $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiMe}_3$ (219); it was made by the following reaction:



The compound proved to be thermally but not oxidatively stable. Some years later, Gorsich reported that $\text{Ph}_3\text{SiMn}(\text{CO})_5$ could be made similarly from Ph_3SiCl and $\text{NaMn}(\text{CO})_5$ (159).³

The first detailed study of organosilicon-transition metal compounds, however, was reported by Chalk and Harrod (76-78, 166). As part of an investigation into the catalysis of addition of Si-H compounds to olefins, it was found that the following reactions occurred quite readily:



The addition reaction (44) could be reversed on heating. Only rather electronegative substituents were successful in Eq. (44): R_3 was Cl_3 , EtCl_2 , PhCl_2 , or $(\text{OEt})_3$, but not alkyl or aryl. In Eq. (45), however, R may be an alkyl, aryl, or alkoxy group or chlorine. Furthermore, MacDiarmid and his co-workers (44, 164) have shown that $\text{Me}_3\text{SiCo}(\text{CO})_4$, $\text{MeSiH}_2\text{Co}(\text{CO})_4$, and $\text{F}_3\text{SiCo}(\text{CO})_4$ may be prepared analogously.

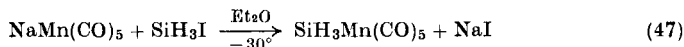
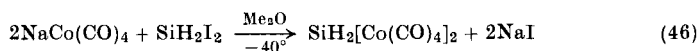
³ Jetz *et al.* (179) have recently made authentic $\text{Ph}_3\text{SiMn}(\text{CO})_5$ by another route, and find it to be different from Gorsich's product.

Independent studies by Aylett and Campbell (24–27, 40) have led to the preparation of the first unsubstituted silyl metal carbonyls (Table XX). These compounds were all made by the reaction of the appropriate

TABLE XX
TRANSITION METAL DERIVATIVES OF SILICON HYDRIDES

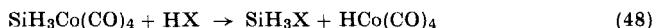
Compound	M.P.	B.P.	<i>d</i> (gm/ml)	ΔH_{vap} (cal mole ⁻¹)	ΔS_{vap} (e.u.)	Ref.
SiH ₃ Co(CO) ₄	–53.5°	112°	1.27/20°	8080	21.0	(24)
SiH ₃ Mn(CO) ₅	+25.5°	134°	—	9450	23.3	(26)
SiH ₂ [Co(CO) ₄] ₂	~15°	170°	—	9250	20.8	(25)
(SiH ₃) ₂ Fe(CO) ₄	52°	145°	—	10,470	23.3	(40)

iodosilane with sodium cobalt or manganese carbonyl in ether at low temperatures, e.g.:



In comparison with the corresponding alkyl metal carbonyls, these new derivatives are remarkably stable thermally. While CH₃Co(CO)₄ is reported to decompose above –30° (172), SiH₃Co(CO)₄ can still be recovered in 30 % yield after 30 minutes at 100°. The other products are hydrogen, carbon monoxide, cobalt carbonyl hydride, and a dark solid residue containing Co—Si bonds.

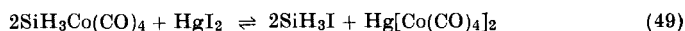
Silyl cobalt carbonyl reacts readily with protic reagents in the following way:



where X = Cl, OH, NH₂. The initial product reacts further in the case of water and ammonia attack to give (SiH₃)₂O and (SiH₃)₃N, respectively.

Further experiments on the cleavage of the Si—Co bond in Me₃SiCo(CO)₄ by Baay and MacDiarmid (44) have shown that it is broken at room temperature by water, methanol, Me₂AsCl [to give Me₂AsCo(CO)₃], and GeF₄ [to give F₃GeCo(CO)₄].

The equilibrium (49) lies well to the left at room temperature,



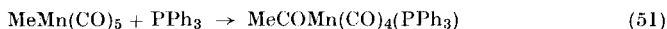
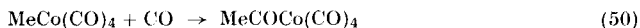
and hence Co(CO)₄ lies to the left of I in the conversion series (Section IV,A), and appears to be effectively less electronegative. Also, in so far as

correlations can legitimately be drawn between infrared absorption frequencies and electronegativity, it will be seen from Tables VI and VII that $\text{Co}(\text{CO})_4$ appears to be about as electronegative as iodine.

Trimethylamine and pyridine both form adducts of composition $\text{SiH}_3\text{Co}(\text{CO})_4 \cdot 2\text{base}$ with no displacement of carbon monoxide, and α, α' -bipyridyl gives a similar 1:1 product. The three most likely possibilities for the structures of these adducts are (a) a molecular compound of six-coordinate silicon, (b) an ionic compound, $(\text{SiH}_3 \cdot 2\text{base})^+\text{Co}(\text{CO})_4^-$, and (c) a situation intermediate between (a) and (b). An analogous problem has been discussed (Section IV,C). This time, however, we have a built-in probe that can help us to assess the degree of negative charge on the anion, namely, the carbonyl stretching frequency of the adduct. It is generally accepted that, as the negative charge on the metal atom in a carbonyl compound increases, the extent of π -donation outward to the carbonyl ligands also increases. Since this π -electron density must be accommodated in π^* antibonding orbitals of the ligands, the C—O bond is weakened and the carbonyl stretching frequency decreases (see, e.g., Cotton and Wilkinson, 85). In $\text{SiH}_3\text{Co}(\text{CO})_4$ itself, the mean $\nu(\text{CO})$ frequency is 2052 cm^{-1} , while that of fully ionized $\text{Co}(\text{CO})_4^-$ in solution is 1883 cm^{-1} . The corresponding values for the trimethylamine, pyridine, and bipyridyl complexes as nulls are 1870, 1882, and 1860 cm^{-1} , respectively, from which it can be seen that all the complexes have appreciable ionic character, and approximate very closely to type (b) above.

Silyl manganese pentacarbonyl (26) behaves somewhat similarly to the cobalt analog, but is generally less reactive, particularly with respect to cleavage of the Si—metal bond. Thus HCl at 75° causes substitution of H by Cl to yield $\text{SiH}_{3-x}\text{Cl}_x\text{Mn}(\text{CO})_5$ ($x = 1-3$). Its adducts with tertiary amines are weaker, but the same kind of infrared evidence as before suggests that they are essentially ionic in nature, viz. $(\text{SiH}_3 \cdot 2\text{B})^+\text{Mn}(\text{CO})_5^-$. On the other hand, the product of the reaction of an excess of NMe_3 with $(\text{SiH}_3)_2\text{Fe}(\text{CO})_4$, which can probably be represented as $(\text{SiH}_3 \cdot \text{NMe}_3)_2\text{Fe}(\text{CO})_4$ (40), has much less ionic character.

One notable feature of the chemistry of alkyl metal carbonyls is the ease with which they undergo carbonyl insertion reactions, e.g.:



Numerous attempts to bring about similar reactions with silyl metal carbonyls have been unsuccessful. Triphenylphosphine displaces CO from silyl cobalt carbonyl in a substitution reaction, giving $\text{SiH}_3\text{Co}(\text{CO})_3(\text{PPh})_3$, while direct carbonylation fails, even at high pressures. These facts, together with the considerable thermal stability of

these compounds, are consistent with the presence of d_{π} - d_{π} interaction between silicon and the metal; carbonyl insertion, by breaking this bond, would be an energetically unfavorable step.

Further evidence regarding d_{π} - d_{π} interactions comes from infrared data. Detailed studies of the $\nu(\text{CO})$ region for $\text{R}_3\text{SiCo}(\text{CO})_4$ species [including $\text{RSiH}_2\text{Co}(\text{CO})_4$] (164) and $\text{Ph}_3\text{SiMn}(\text{CO})_5$ (179) indicate that they approximate closely to C_{3v} and C_{4v} symmetry, respectively. A force constant analysis suggests in both cases that the silyl group is competing with the carbonyl group *trans* to it for the electrons in the metal's filled d_{π} orbitals.

VIII. Other Miscellaneous Derivatives

A. SILICON-GERMANIUM HYDRIDES

The hydrolysis of mixtures of metal silicides and germanides and also the action of a silent discharge on silane/germane mixtures have led to the production of complex mixtures of silicon-germanium hydrides. Higher silanes and germanes are of course produced simultaneously. Spanier and MacDiarmid (241) reported the preparation of SiH_3GeH_3 by the second route, while the Oxford group have shown how by the ingenious use of gas chromatography it is possible to separate and identify a wide range of mixed hydrides ranging up to mixed $(\text{Si}, \text{Ge})_6\text{H}_{14}$ species (14, 262, 263). Varma and Cox (268) have also described the preparation of SiH_3GeH_3 from KSiH_3 and chlorogermane.

Mass spectrometry was used by Royen and Rocktäschel (227) to show the presence of SiH_3GeH_3 , Si_2GeH_8 , and SiGe_2H_8 among the hydrolysis products of a mixed calcium silicide-germanide. Recently, too, measurements of the appearance potential (231) and heat of formation (162) of SiH_3GeH_3 have been reported. Values of its bond-dissociation energy and thermochemical bond energy were inferred to be 100 and 42.5 kcal mole⁻¹, respectively. This very large difference is as yet unexplained, and should be compared with the present uncertainty regarding the Si—Si bond energy, previously discussed (Section II,C).

As might be expected, the chemistry of SiH_3GeH_3 shows close resemblances to that of Si_2H_6 . Mackay *et al.* (201) have reported that it does not react under mild conditions with HCl or BF_3 , but yields HCl with AlCl_3 .

B. SILICON-BORON HYDRIDES

Various earlier attempts to make mixed unsubstituted boron-silicon hydrides (e.g., 216, 263), using such methods as the hydrolysis of boride-

silicide mixtures, were unsuccessful. There was some evidence that rapid disproportionation of the presumed products had occurred.

It has now been found by Amberger and Römer (12) that KSiH_3 will react with a variety of chloroboron compounds to yield Si-B derivatives such as $\text{SiH}_3\text{B}(\text{NMe}_2)_2$ and $\text{SiH}_3\text{BBu}(\text{NMe}_2)$. The adduct $\text{BH}_2\text{Cl} \cdot \text{NEt}_3$ gave rise to another adduct $\text{SiH}_3\text{BH}_2 \cdot \text{NEt}_3$; attempts to remove the amine led to decomposition. No compounds of the type SiH_3BX_2 ($\text{X} = \text{Cl}$, alkyl) or with more than one silyl group attached to boron could be isolated.

IX. Conclusion

Silicon hydride derivatives have many attractive features. They are usually volatile, and can therefore be conveniently handled in a high vacuum system; they are often small molecules, and thus are well suited to examination by various physical techniques; and they provide a convenient and varied set of systems in which theories of π -bonding and d -orbital use can be tested.

For these reasons, and because they offer a challenge to manipulative ingenuity and theoretical description, it seems very probable that these compounds will be much more widely studied in the next decade. Doubtless the second most abundant element holds plenty of surprises in store.

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SOME GENERAL ASPECTS OF MERCURY CHEMISTRY

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The element mercury, because of its ease of extraction from ores and its distinctive physical properties, has been known from the earliest times. Its fascination for the alchemists has found an echo in the continued interest of modern chemists in exploring the chemistry of the element. Since the number of publications concerning mercury must run to many thousands, it is impossible in a short review to do even rough justice to its detailed chemistry. We have therefore attempted to bring out certain features that seem to provide a framework on which the diverse studies of many disciplines can hang and be seen as a coherent whole.

I. The Mercury Atom

The mercury atom has the electronic ground state (Xe core)- $4f^{14}5d^{10}6s^2$. It may therefore be compared with Ba, (Xe core) $6s^2$, and the other Group IIB elements Zn, (Ar core) $3d^{10}4s^2$, and Cd, (Kr core) $4d^{10}5s^2$. The ionization potentials of the Group IIA, IIB, and IV elements are

shown in Fig. 1. Two features are at once apparent: the overall higher values of the ionization potentials of the B subgroup elements than of the A subgroup elements, and the contrast between the steady fall in ionization potential with increasing atomic number in the A subgroups and the minimum at the second long period shown in the B subgroups. In quantum mechanical terms, this can be rationalized by noting that in the A

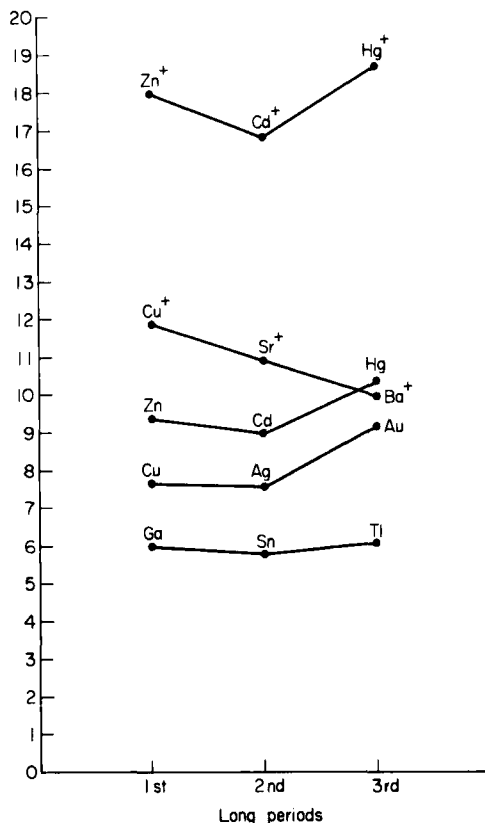


FIG. 1. Ionization potentials of Group IB, IIA, and IIB elements (C. E. Moore, Atomic Energy Levels, N.B.S., Washington, 1958).

subgroup the effect of increasing effective nuclear charge with atomic weight is a little more than offset by the increase in principal quantum number of the electron removed, leading to a steady but small decrease in ionization potential (I.P.) with atomic number. In going from Ca to Zn the $3d$ shell is filled. Because the radial distribution function of a $4s$ electron is such that it spends a portion of its time near the nucleus, while

the $3d$ electrons do not penetrate the Xe core to an appreciable extent, the $4s$ electrons in Zn experience a higher effective nuclear charge than in Ca and the first I.P. is 3.28 eV higher. Similarly, the first I.P. of Cd is 3.30 eV higher than that of strontium. However, between barium and mercury, in addition to the $5d^{10}$ electrons, there are the $4f^{14}$ electrons. The same arguments about the penetration of the $6s$ electrons through a $5d$ core apply to the $4f$ core, and the first I.P. of mercury exceeds that of Ba by 5.22 eV; indeed, the first I.P. of mercury is slightly greater than the

TABLE I
IONIZATION POTENTIALS AND VALENCE STATE PROMOTION ENERGIES
OF GROUP IIB METALS

	Zn	Cd	Hg
I.P. of $M \rightarrow M^+$ (eV)	9.4	9.0	10.4
I.P. of $M^+ \rightarrow M^{++}$ (eV)	18.0	16.9	18.7
$ns^2 \rightarrow ns^1p^1$ (kcal)	103.2	97.4	125.3

second I.P. of barium. This effect of tighter binding of the external electrons results in smaller atomic and ionic radii for the B subgroup elements than for their A subgroup partners with external electrons of the same principal quantum number, and is the cause of the "lanthanide contraction" referred to by chemists in the 1930–1950 period. These effects are major causes of the distinctive differences between A and B subgroup chemistry, and are especially important in the chemistry of the B subgroup elements of the third long period where they operate together.

The electron affinities of the Group IIB metals have not been measured directly and estimated values do not appear to be very reliable (45, 50). The high values of 1.2, 1.0, and 2.2 eV for Cu, Ag, and Au, respectively, suggest that the order should be $Hg > Zn > Cd$, which is the order of the electron affinities of Hg^+ , Zn^+ , and Cd^+ . However, addition of an electron to the uncharged atom is to the p orbital and, as will be seen later, this lies well above the s level for the Group IIB elements. It seems likely therefore that the electron affinities (E.A.) of the Group IIB atoms will be rather low. This means that the Mulliken electronegativity (I.P. + E.A.)/2 can be replaced by I.P. in making comparative studies in these cases. By this definition mercury is, after gold, the most electronegative metal.

Before mercury can form bonds to other elements it is necessary that the $6s^2$ ground state is reorganized to give $6s^16p^1$. The energies required for this promotion for the Group IIB elements are given in Table I. Just

as the ionization potentials are high for Group IIB metals so are these promotion energies, and this is particularly true for mercury. It has important consequences in the chemistry of covalent compounds of mercury; in particular, the high energy of promotion of electrons from $5d$ or $6s$ to $6p$ means that mercury tends to form two covalent bonds and further ligands are added only with difficulty. This theme, to be examined in more detail later, runs through the whole of the chemistry of mercury. In contrast to this high $s \rightarrow p$ promotion energy, the $5d^{10} \rightarrow 5d^9 6s^1$ transition in Hg^{++} requires very little energy, as can be seen from Table II. Dunitz and Orgel have shown that in these circumstances, an effect

TABLE II
PROMOTION ENERGY (eV) FOR GROUP IIB METALS

	Zn	Cd	Hg
$nd^{10} \rightarrow nd^9(n+1)s^1$	9.7	10.0	5.3
$nd^{10} \rightarrow nd^9(n+1)p^1$	17.1	17.3	14.7

related to a Jahn-Teller effect can operate to distort an octahedral environment in such a way that four bonds in a plane would be lengthened, and two bonds perpendicular to this plane shortened (21). This emphasizes that in an ionic environment, too, mercury, like Cu^+ , Ag^+ , and Au^+ , but unlike Zn^{++} and Cd^{++} , tends to have a special interaction with two ligands at 180° . The importance of the unit LHgL is therefore apparent in both the factors affecting reactivity of covalent compounds and the structure of crystalline ionic compounds.

II. Mercury Metal and Its Interaction with Other Metals

Mercury metal is unique in being a liquid at room temperature and is volatile and monatomic in the vapor. Nyholm (45) has suggested that this can be understood in terms of the high valence state promotion energy of mercury. If it is assumed that metals in their standard states exhibit their characteristic valency (i.e., 2 for the Group IIB metals), the effective binding energy of the metal is given by the sum of the heat of atomization and the valence state promotion energies. When this is done (see Table III), the "corrected" bonding energy is seen to follow the order of ionization potentials.

TABLE III
HEATS OF ATOMIZATION OF GROUP IIB METALS CORRECTED FOR
VALENCE STATE PROMOTION

Metal	Heat of atomization (kcal)	Valence state correction (kcal)	Corrected heat of atomization (kcal)	I.P. (eV)
Zn	31.2	103.2	134.4	9.4
Cd	26.8	97.4	124.2	9.0
Hg	15.3	125.3	140.6	10.4

The physical properties of mercury metal have been studied in great detail (and can be found in any of the standard compilations of physical data). Attempts have been made to understand these properties in terms of various models (32, 33).

It has already been noted that mercury is one of the most electro-negative metals and, although there does not appear to be a mercury equivalent of saltlike CsAu, mercury does react exothermically with the alkali metals to give stable compounds. With the metals of higher lattice energy and higher ionization potential, compound formation has been demonstrated at higher temperatures. [A summary of the available phase diagrams can be found in metallurgical texts (34).]

Mercury-mercury covalent bonds in mercurous compounds were the first, and for long the only known covalent metal-metal bonds. Recent research has greatly altered this picture and the conditions for metal-metal bond formation are better understood. It is thought that, as the formal positive charge on a complex having an odd number of electrons is reduced, it becomes more like a free radical (45). That is, the orbital becomes larger and effective overlap with another orbital becomes possible. In the case of mercury the known mercurous compounds are ionic in nature, with the possible exceptions of $(\text{CCl}_3\text{CO}\cdot\text{O})_2\text{Hg}_2$ (55) and $(\text{CH}_3\text{CO})_2\text{N}_2\text{Hg}_2$ (29). These two compounds appear to be in a class of their own, and preparative studies to delineate the stability range of such compounds would be very valuable.

The thermodynamic factors governing the disproportionation in solution of Hg_2^{++} into Hg^{++} and Hg will be discussed later. The disproportionation is strongly influenced by the nature of the ligands present, so that mercurous compounds of ligands that interact strongly with Hg^{++} are not known. It was thought at one time that all ligands would tend to bind more strongly to Hg^{++} than to Hg_2^{++} , and that no genuine complexes of Hg_2^{++} would exist. Recent work, however, has demonstrated that

ligands with oxygen as the donor atom do form complexes with Hg_2^{++} . The first evidence for mercurous complexes came from potentiometric studies on solutions containing Hg_2^{++} and NO_3^- , SO_4^- , ClO_4^- , and especially polyphosphate and oxalate. The first characterized compounds, however, contain ligands such as $(\text{C}_6\text{H}_5)_3\text{PO}$, $\text{C}_6\text{H}_5\text{NO}$, and $(\text{CH}_3)_2\text{SO}$ (49).

An interesting property of the Hg—Hg bond in the mercurous halides is the variation in bond length with the nature of the halogen (29):

	Hg_2F_2	Hg_2Cl_2	Hg_2Br_2	Hg_2I_2
$d(\text{Hg—Hg})$ (Å)	2.43	2.45	2.50	2.69

Various explanations have been advanced for this, but the most convincing is due to Ebsworth (22), who suggests that it is a lattice energy effect. For the small F^- ion, there is a large gain in lattice energy if the Hg—Hg bond is compressed. This factor becomes relatively less important as the size of the halogen increases. This factor could account also for the long Hg—Hg bond (2.90 Å) in $\text{Hg}_2\text{N}_2(\text{COCH}_3)_2$, which had always been a difficulty for the explanations based on electronegativity arguments. The importance of the coordination number of 2 in the chemistry of mercury compounds is shown in the structure of mercurous nitrate, in which the two water molecules of crystallization are positioned along the Hg—Hg axis (29),



as in the case of $[\text{CH}_3\text{HgOH}_2]^+$ the Hg—O stretching frequency can be detected in the Raman spectrum (25).

Compounds containing metal-metal bonds, in which one partner is a transition metal, occur mainly with transition metals in a low valency state, and particularly for d^6 , d^8 , and d^{10} systems. Mercury(II) is d^{10} and forms bonds to other d^6 , d^8 , and d^{10} systems. Some examples are shown in Table IV. King (39) and Hieber and co-workers (36) have prepared a number of derivatives of the type $\text{Hg}[\text{Mn}(\text{CO})_5]_2$, where the metal may be Mn, Fe, or Co and the CO group can be replaced (e.g., by NO or PPh_3). Compounds containing metal-HgX systems have been prepared by Nyholm and Vrieze (46), Lewis and Wild (41), and Gamorkan and Stiddard (26). The metals involved are Rh^{III} , In^{III} , Fe^0 , and W^{II} . It is probable that many more examples will be found. Examples are listed in Table IV.

TABLE IV
COMPOUNDS WITH MERCURY-METAL BONDS

Compound ^a	M.P. (°C)
Hg[Mn(CO) ₅] ₂	~155
Hg[Fe(CO) ₂ C ₅ H ₅] ₂	145-146
L ₃ Cl ₂ RhHgF	195
L ₃ Cl ₂ RhHgCl	205
[(Ph) ₃ P ₂ COCl ₂ IrHgCl	270
(CO) ₂ py ₂ FeHgCl ₂	>340

^a L = Ph₂AsMe.

III. Bond Energies of Mercury Hydrides, Halides, and Alkyls

As a result of spectroscopic (35) and kinetic (56) studies, the energies of a number of Hg—X bonds are known; these data are shown in Table V. The species exist as discrete molecules only in the gas phase. In Fig. 2 the

TABLE V
BOND ENERGIES OF HgX (g) → Hg (g) + X (g) (kcal)

HgF 41	HgCl 24	HgBr 17	HgI 8	HgCN 23 ± 6
HgCH ₃ 7 ± 3	HgC ₂ H ₅ 6 ± 4	HgCH=CH ₂ 19 ± 6	HgH 8.6	HgH ⁺ 53

bond energies of the compounds HgX (where X = halogen) are plotted against the sum (I.P. + E.A.) of the halogen. For comparison the bond energies of the corresponding HX are also shown. It can be seen that $\delta(\text{HX} - \text{HgX})$ increases from iodine to fluorine, and at fluorine the difference in kcal is only slightly less than the valence state promotion energy of 107 kcal for mercury. The mercury-to-fluorine bond is therefore quite similar to the H—F bond, while the Hg—I bond, after allowing for the valence state promotion energy, is much stronger than the H—I. This has important consequences in the solution chemistry of mercury halides.

Unfortunately the available data for ZnX and CdX are of low accuracy (14) and it is therefore difficult to make useful comparisons. Better data are available for the metal hydrides and alkyls, of which CH₃ can be taken as typical. These are shown before and after correction

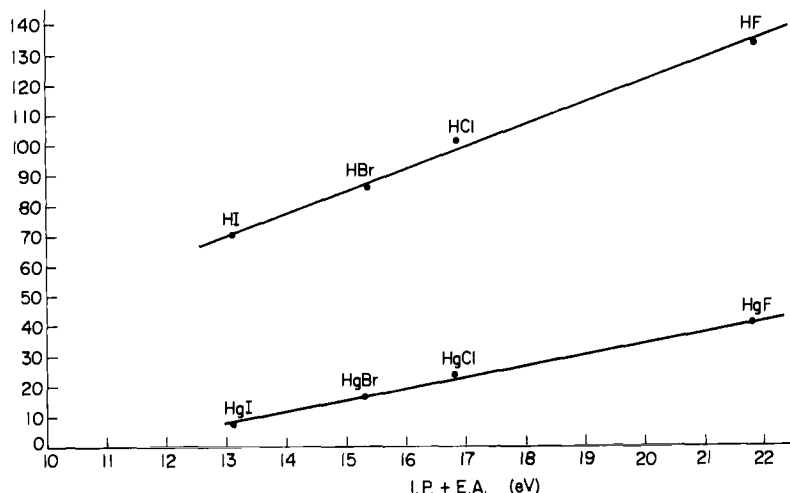


FIG. 2. Bond energies of mercury halides and hydrogen halides plotted against I.P. + E.A. of the halogen.

for valence state promotion in Table VI. The pattern of the corrected bond energies roughly follows the I.P.; a better comparison would be with I.P. + E.A., but E.A. data for Zn, Cd, and Hg are not available.

TABLE VI
COMPARISON OF BOND ENERGIES $M\cdot CH_3$ AND MH FOR GROUP IIB
METALS (kcal)

Metal	$M\cdot CH_3$	MH	Valence state promotion	Bond energy corrected		I.P. (eV)
				$M\cdot CH_3$	MH	
Zn	35	20	92	127	112	9.4
Cd	21	16	86	107	102	9.0
Hg	7	9	107	114	116	10.4

It is interesting to note that for Hg^+ , where no valence state promotion is needed, $D(HgH^+)$ at 53 kcal is much higher than $D(HgH)$ at 8.6 kcal. Indeed, $D(HgH^+)$ is of the same order as $D(MH)$, in which M is a Group IA or IB metal where the bond is also formed by the overlap of two s orbitals. An s^1-s^1 bond of this type must also exist in Hg_2^{++} , to be discussed in more detail later.

The heats of formation and bond energies of the covalent compounds

TABLE VII

HEATS OF FORMATION OF HgX_2 AND RHgX AS CONDENSED PHASES
AND VAPORS, AND BOND DISSOCIATION ENERGIES*

Compound	ΔH_f° (c)	ΔH_f° (gas)	$D_1 + D_2$	D_1	D_2	$\frac{D_1 + D_2}{2}$
$(\text{CH}_3)_2\text{Hg}$	14.0 ± 1	22.3 ± 1	58.4 ± 2	51.5 ± 2	6.9 ± 3	29
$(\text{C}_2\text{H}_5)_2\text{Hg}$	6.5 ± 1	17.2 ± 1	48.4 ± 4	42.5 ± 2	5.9 ± 4	24
$(n\text{-C}_4\text{H}_9)_2\text{Hg}$	-6.5 ± 2	6.6 ± 2	49.0 ± 4	—	—	—
$(i\text{-C}_3\text{H}_7)_2\text{Hg}$	-3.4 ± 1	9.3 ± 1	42.0 ± 4	27.0 ± 5	15 ± 7	21
$(\text{CH}_2=\text{CH})_2\text{Hg}$	—	—	67.4 ± 6	48.3 ± 1	19.1 ± 6	34
$(\text{C}_6\text{H}_5)_2\text{Hg}$	66.8 ± 1.5	93.7 ± 1.6	64.8 ± 4	—	—	32
HgCl_2	-55	-33.4	106 ± 2	81 ± 2	24	53
HgBr_2	-40.6	(-20)	89 ± 2	72 ± 2	17	45
HgI_2	-25.2	(-5)	69 ± 2	61 ± 1	8	35
CH_3HgCl	-27.8 ± 0.6	-12.3 ± 0.7	68.3 ± 2	64.3 ± 2	24	—
CH_3HgBr	-20.6 ± 0.6	-4.4 ± 0.7	78.8 ± 2	61.8 ± 2	17	—
CH_3HgI	-10.3 ± 0.6	5.25 ± 0.7	69.0 ± 2	59.0 ± 2	8	—
$\text{C}_2\text{H}_5\text{HgCl}$	-34.0 ± 0.7	-15.8 ± 1.0	84.3 ± 3	60.3 ± 2	24	—
$\text{C}_2\text{H}_5\text{HgBr}$	-25.9 ± 0.7	-7.6 ± 1.0	74.6 ± 3	57.6 ± 3	17	—
$\text{C}_2\text{H}_5\text{HgI}$	-15.9 ± 0.8	3.0	61.7 ± 3	53.7 ± 3	8	—
$\text{C}_6\text{H}_5\text{HgCl}$	0.0 ± 1.2	24.5 ± 1.5	90.5 ± 3	66.4 ± 3	24	—
$\text{C}_6\text{H}_5\text{HgBr}$	7.8 ± 1.2	—	80.6 ± 4	63.6 ± 4	17	—
$\text{C}_6\text{H}_5\text{HgI}$	17.6 ± 1.2	—	69.6 ± 4	61.6 ± 4	8	—
$(\text{CN})_2\text{Hg}$	62.5	88.5 ± 2	144 ± 2	123 ± 7	23 ± 6	72

* Skinner (56).

of divalent mercury of the types R_2Hg , RHgX , and HgX_2 (where R = organic group and X = halogen) are given in Table VII.

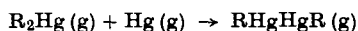
The most striking feature of the bond energies of these covalent mercury compounds is the large difference between the bond dissociation energies, $\text{HgR}_2 \rightarrow \text{HgR} + \text{R}$ (D_1) and $\text{HgR} \rightarrow \text{Hg} + \text{R}$ (D_2). The cause of this is the very high valence state promotion energy for mercury. In forming the first bond it is necessary to put in the whole of the promotion energy, but the second bond is formed without much further reorganization of the mercury orbitals. This effect is also observed with zinc and cadmium, but is less marked. Table VIII shows the data for $\text{Zn}(\text{CH}_3)_2$, $\text{Cd}(\text{CH}_3)_2$, and $\text{Hg}(\text{CH}_3)_2$. It can be seen that the energy $\text{M}(\text{CH}_3)_2 \rightarrow \text{MCH}_3 + \text{CH}_3$ (D_1) follows closely the I.P. of M without correction for valence state promotion, in contrast to that of $\text{MCH}_3 \rightarrow \text{M} + \text{CH}_3$ (shown in Table VI). It follows that $D_1 + D_2 +$ valence state promotion will also follow the I.P. order. It can be seen, however, that even after correction the $\text{Hg}-\text{CH}_3$ bond is weaker than might be expected.

TABLE VIII

BOND DISSOCIATION ENERGIES OF $M(\text{CH}_3)_2$ ($M = \text{Zn, Cd, AND Hg}$)

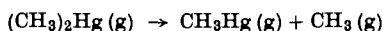
Metal	D_2 (kcal)	D_1 (kcal)	$D_1 + D_2$ (kcal)	Valence state promotion (kcal)	$D_1 + D_2$ corrected (kcal)	I.P. (eV)
Zn	35	47	82	92	174	9.4
Cd	21	46	67	86	153	9.0
Hg	7	52	59	107	166	10.4

There is an interesting consequence of the large difference between D_1 and D_2 for the mercury alkyls and the mercuric halides. Let us consider the reaction of a mercury alkyl with mercury,



using dimethylmercury as an example.

From the data in Table VII, $\Delta H = 52$ kcal for the reaction:



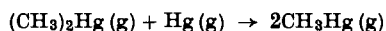
Since

$$\Delta H_f \quad (\text{CH}_3)_2\text{Hg}(\text{g}) = 22 \text{ kcal} \quad \text{and} \quad \Delta H_f \quad \text{CH}_3(\text{g}) = 32 \text{ kcal}$$

it follows that

$$\Delta H_f \quad \text{CH}_3\text{Hg}(\text{g}) = 42 \text{ kcal}$$

This means that $\Delta H = 62$ kcal for the reaction,



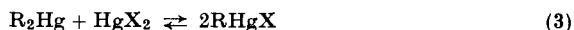
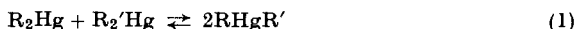
and therefore the heat of dimerization of CH_3Hg would need to be at least 62 kcal if a volatile mercurous dimethyl were to be stable to disproportionation. This explains why no volatile mercurous alkyls are known. If D_1 for dimethylmercury were 29 kcal, the mean bond energy, then ΔH_f of $\text{CH}_3\text{Hg}(\text{g})$ would be 19 kcal and the heat of reaction of dimethylmercury with a mercury atom would be only 14 kcal, and volatile mercurous alkyls would be stable to disproportionation for even a weak Hg—Hg bond. It is known that compounds corresponding to $(\text{RHg})_n$ are obtained in condensed phases, but nothing is known of their structure. Proceeding in the same way, it can be shown that Hg_2Cl_2 should not exist in the vapor phase or as a covalent liquid:



It is in fact found that the vapor in equilibrium with mercurous chloride, an ionic solid, is a mixture of mercuric chloride and mercury.

IV. Redistribution Equilibria of Mercury(II) Compounds

The experimental data up to 1964 have been reviewed by Lockhart (43), and some further reactions have been studied by Reynolds and Daniel (52). Much work has been done on the mechanism of these reactions, to be discussed later; attention here will be confined to the equilibria of the types



either in the vapor phase or in nonpolar solvents. For a single reaction of type (1), if the redistribution is statistical then the equilibrium constant $K = 4$. If K is < 4 the grouping on the left is preferred, while $K > 4$ implies a preference for the mixed product. Some experimental values are given in Table IX.

TABLE IX
REDISTRIBUTION OF EQUILIBRIA

$R_2Hg + R_2'Hg \rightleftharpoons 2RHgR' \text{ (at } 90^\circ)$		
R	R'	K
CH ₃	C ₂ H ₅	1.8
C ₂ H ₅	<i>n</i> -C ₃ H ₇	4.5
C ₂ H ₅	<i>i</i> -C ₃ H ₇	5.3
C ₂ H ₅	C ₆ H ₅	5.0
C ₂ H ₅	C ₂ H ₃	86
C ₂ H ₅	cyclo-C ₃ H ₅	130
<i>n</i> -C ₃ H ₇	<i>i</i> -C ₃ F ₇	$> 2 \times 10^3$
<i>i</i> -C ₃ H ₇	<i>i</i> -C ₃ F ₇	$> 2 \times 10^3$
C ₂ H ₃	cyclo-C ₃ H ₅	(did not redistribute)

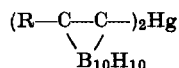
Data for the systems of type (2) where X = halogen are given in Table X. The data are expressed here as a heat of reaction to form the unsymmetrical products. As these reactions will have only a very small entropy change, these results indicate that all the reactions proceed essentially to completion.

For reactions of types (1) and (2) there are some examples in which it is difficult for kinetic reasons to establish the position of equilibrium. One example is given by Reynolds and Daniel (52), who found that

TABLE X
HEATS OF REDISTRIBUTION REACTIONS IN THE GAS PHASE

$R_2Hg + HgX_2 \rightarrow 2RHgX$		
R	X	$-\Delta H$ (kcal)
CH ₃	Cl	14
CH ₃	Br	10
CH ₃	I	8
C ₂ H ₅	Cl	15
C ₂ H ₅	Br	12
C ₂ H ₅	I	8
C ₆ H ₅	Cl	11

(CH₂=CH)₂Hg and (cyclo-C₃H₅)₂Hg did not redistribute under their conditions. Similarly, (C₆F₅)₂Hg (7), (C₆Cl₅)₂Hg (47), and organomercuric derivatives of barenes (62),



all react with HgCl₂ under only the most vigorous conditions and, similarly, compounds RHgX revert to R₂Hg only slowly if at all under the influence of reagents such as KCN and KI, which promote symmetrization by complex formation with the mercuric halide.

Quantitative studies on the third type of redistribution reaction, that between the individual mercuric halides, have been carried out by Marcus and Eliezer (44), and the results for the halides with no excess of halide ion present are shown in Table XI.

TABLE XI
REDISTRIBUTION EQUILIBRIA

$HgX_2 + HgY_2 \rightleftharpoons 2HgXY$	
Complex	log K
HgClBr	0.6
HgClI	1.0
HgBrI	0.5

Inspection of the figures in Table XI shows that the redistribution proceeds in favor of the unsymmetrical species whenever the two bonding atoms or groups differ appreciably in electronegativity. Marcus and Eliezer (44) attempted to give a quantitative account of this for the mercuric halides in terms of a simple electrostatic model. This correctly predicts the above trend but, as might be expected, such a simple model does not give very good quantitative agreement.

V. Compounds in Which Mercury Is Bonded to Nonmetallic Elements

Mercury reacts with the halogens and the Group VIB elements to form binary compounds, but is inert to the other nonmetallic elements. It is known to form bonds to boron, silicon, germanium, phosphorus, and arsenic in certain compounds only. With carbon, mercury compounds of many different types are known. Because of their relative lack of reactivity toward oxygen and water, these organomercury compounds have been employed by organic chemists in a wide range of synthetic and mechanistic studies.

A. MERCURY-BORON COMPOUNDS

The only known mercury-boron compound is the salt $(\text{Me}_4\text{N})_2-[(\text{B}_{10}\text{H}_{12})_2\text{Hg}]$, synthesized from the reaction of decaboranylmagnesium iodide with mercuric chloride (31).

B. MERCURY-CARBON COMPOUNDS

The extent of the research interest in organomercury compounds can be judged by the fact that King and Seyferth (40) in their *Annual Surveys of Organometallic Chemistry* list 95 references for the year 1965 alone. In the present article, only certain features of interest to inorganic chemists will be selected for discussion; reference will be made where possible to review articles in which specific information has been collected.

Mercury-carbon compounds can be subdivided into two classes: (a) R_2Hg and $\text{R}'\text{HgR}$, and (b) RHgX (where $\text{X} = \text{halogen}, \text{ClO}_4^-$, etc.). Examples of the former type are given in Table XII, and of the latter in Table XIII. The properties of both these classes are greatly influenced by the nature of R. Three separate types can be identified, although there are of course borderline examples. The first type can be defined as those mercurials where R is an aliphatic or aromatic hydrocarbon residue, the

TABLE XII
COMPOUNDS R_2Hg WHERE R IS MONOFUNCTIONAL

Compound	M.P. (°C)	B.P. (°C)
$Hg(CH_3)_2$	—	92
$Hg(C_2H_5)_2$	—	159
$Hg(CH=CH_2)_2$	—	59.5/20 mm
$Hg(C\equiv CH)_2$	—	—
$Hg(C_6H_5)_2$	125	204/10.5 mm
$Hg\left(\begin{array}{c} CH_3C-C \\ \quad \quad \quad \backslash \\ \quad \quad \quad B_{10}H_{10} \end{array}\right)_2$	167	—
$Hg(CF_3)_2$	163	—
$Hg(CF_2CF_3)_2$	106–107	—
$Hg(C_6F_5)_2$	142	—
$Hg(CCl_3)_2$	140	—
$Hg(CCl=CCl_2)_2$	72–73	—

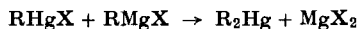
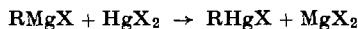
TABLE XIII
COMPOUNDS $RHgX$

Compound	M.P.
CH_3HgF	200
CH_3HgCl	167
CH_3HgBr	161
CH_3HgI	152
CH_3HgCN	93
CH_3HgOH	137
CH_3HgOAc	143
CF_3HgCl	76
CF_3HgBr	83
CCl_3HgCl	193
C_6F_5HgBr	155

second type where R is a group of the type $\text{>C=C<}X$ (where X is a reactive group such as OH, Cl, etc.), and the third type where R is a perhalo group, notably CF_3 , C_2F_5 , or C_6Cl_5 .

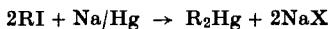
Although many reactions are known that lead to organomercury compounds (40), the principal reactions of preparative importance are given below.

(a) *Grignard reactions* (6, 38, 53):

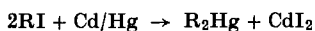


This is a general reaction.

(b) *Amalgam reactions* (1, 53, 57):

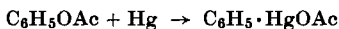


where R = alkyl, vinyl, aryl.

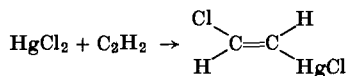
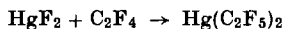


where R = perfluoroalkyl.

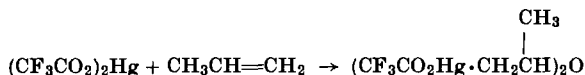
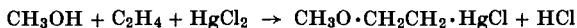
(c) *Mercuration* (18, 53), e.g.:



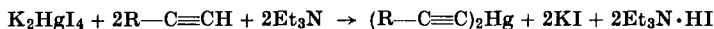
(d) *Addition reactions* (1, 57), e.g.:



(e) *Oxymercuration of olefins* (8, 24), e.g.:



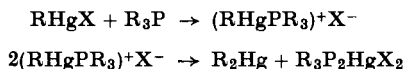
(f) *Acetylide formation* (19, 53):



The chemical reactions of organomercury compounds other than perfluoro derivatives have been reviewed by Reutov (51) and by Dessy and Kitching (18). The reactions of perfluoroalkyl and aryl mercurials are broadly similar, and follow the pattern expected for more electronegative groups. These reactions have been extensively studied by the techniques of physical organic chemistry; the classification of reaction types given below is essentially that of Dessy and Kitching.

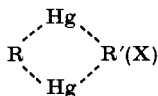
(a) *Subvalent organomercurials*: It has already been seen that RHgHgR would not be expected to be stable to disproportionation. However, by electrolytic reduction of RHgX in NH_3 , $\text{EtOH}/\text{H}_2\text{O}$, and $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$, a series of reduced species of empirical formula RHg have been obtained. These materials catalyze a number of reactions of organomercurials. No definite structural assignment has yet been possible.

(b) *Symmetrization reactions* $2RHgX \rightarrow R_2Hg + HgX_2$: These reactions are brought about by reagents that remove HgX_2 from the system, and hence displace the equilibrium that normally lies with $RHgX$. Typical reagents are halide ions, NH_3 , and R_3P . Recent work by Coates and Lauder (12) has shown by isolating the intermediates that this reaction, at least in some cases, proceeds by the mechanism:



In the case of the perfluoro compounds, derivatives of the type $(C_6F_5)_2Hg(bipy)$ and $[Hg(CF_3)_2I_2]^{2-}$ are sufficiently stable to be isolated (1, 57).

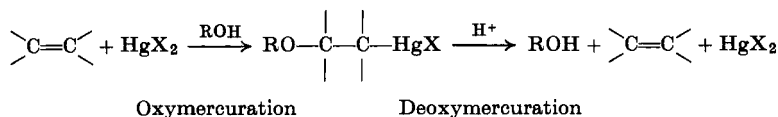
(c) *Exchange reactions*: Equilibrium data for reactions $R_2Hg + R'_2Hg \rightleftharpoons 2RHgR'$ have already been given. It has been shown that both R_2Hg and $RHgX$ undergo rapid isotope exchange with Hg metal, and a transition state of the type



is thought to be important.

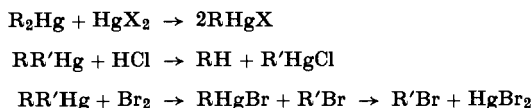
(d) *RHg^+ species*: Direct evidence for RHg^+ comes from the Raman studies of Goggin and Woodward on $RHgClO_4$ solutions (28). They observe that one species present is $RHgOH_2^+$. Stability constant data for the ion RHg^+ in water (where $R = CH_3$ and CF_3) have already been given. This concept has been used to interpret the kinetics of solvolytic reactions of $RHgX$ compounds.

(e) *Oxymercuration-deoxymercuration*:

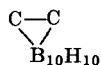


N.m.r. studies have shown that mercury-olefin adducts involve only σ -bonds. The details of the kinetics of both the above steps have received much study (18).

(f) *$\text{>C—Hg bond cleavage}$* : The most important examples of this class of reactions are:

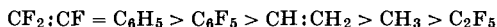


The first of these reactions proceeds readily where R is alkyl or aryl but, as has been noted, certain groups such as C_6F_5 and

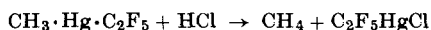
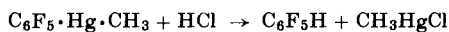


give rise to slow reactions.

The action of hydrogen chloride on $RR'Hg$ has been studied for a range of groups R and R' and a series established,

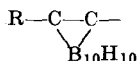


so that the further to the left in the series a group occurs, the greater is its tendency to be cleaved from Hg (57), e.g.:



This reaction has also been studied from a mechanistic viewpoint with optically active groups (18).

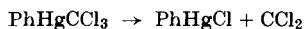
Bromination in general removes from mercury the same groups as HCl. The C_6F_5 and



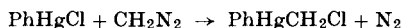
groups proved to be exceptions to this and it may well be that a different mechanism operates here. Certainly $(C_6F_5)_2Hg$ is unique in its ability to form stable adducts with R_3P , and coordination of a bromine molecule may be an intermediate step (57).

(g) *Radical reactions*: The thermal and photochemical decompositions of organomercurials proceed by radical mechanisms. These reactions and the fate of the radicals formed are reviewed by Bass (2).

(h) *Carbene formation*: Compounds having groups such as CCl_3 , CCl_2Br , etc., bonded to mercury decompose to give carbenes:

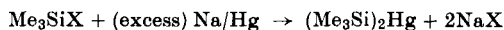


In some cases this is reversible:



C. COMPOUNDS IN WHICH MERCURY IS BONDED TO SILICON AND GERMANIUM

Wiberg and his co-workers (60) have isolated and characterized a stable mercury-silicon compound from the reaction:



This compound melts at 102°–104°C with decomposition and may be sublimed *in vacuo*. Attempts to extend this reaction to compounds containing Si—H bonds failed to produce compounds of the type $(\text{Me}_2\text{SiH})_2\text{Hg}$, but a polymeric compound Me_2SiHg was formed. The corresponding $(\text{Ph}_3\text{Si})_2\text{Hg}$ was obtained but was less stable than the methyl derivative.

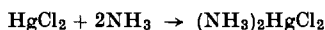
Bis(trimethylsilyl)mercury decomposes quantitatively on heating to give hexamethyldisilane and mercury, and with hydrogen chloride gives trimethylsilane, trimethylchlorosilane, and mercury.

The corresponding $(\text{Me}_3\text{Ge})_2\text{Hg}$ has also been obtained (27).

D. COMPOUNDS IN WHICH MERCURY IS BONDED TO NITROGEN, PHOSPHORUS, AND ARSENIC

A series of compounds containing Hg—N bonds are formed by the reaction of ammonia on mercuric chloride; these have long been known but only since the application of X-ray structure determinations have their chemical natures been understood (29):

(a) "Fusible white precipitate" or mercuric amines:



(b) "Infusible white precipitate" or mercuric amides and mercury imides:



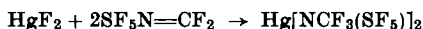
(c) Millon's base:



In the mercuric amines, the linear group $(\text{H}_3\text{N—Hg—NH}_3)^{++}$ [$d(\text{Hg—N}) = 2.10 \text{ \AA}$] is found in a statistical cubic structure of halide ions such that the mercury atom is the center of a face (i.e., with four nearest-neighbor chlorines), and the NH_3 unit is near the center of the cube. In the less stable py_2HgCl_2 , two chlorines lie at 2.34 Å from Hg and two more at 3.25 Å, while the Hg—N distance is 2.60 Å. In both cases the special position of two ligands, which runs through mercury chemistry, is again emphasized. In the mercuric amides, the main structural feature is a polymeric zigzag chain $\text{—NH}_2\text{—Hg—NH}_2\text{—Hg—}$; the imides have a layer structure, while Millon's base has a tetrahedral giant lattice.

The rather unstable compounds $(\text{RHgNH}_3)^+\text{X}^-$, as was previously mentioned, have been obtained by the action of NH_3 on RHgX , while the more stable $(\text{bipy})\text{Hg}(\text{C}_6\text{F}_5)_2$ has been isolated and characterized (7).

If nitrogen is bonded to electronegative groups, compounds of a different type are formed (58, 61):



The group $\text{N}(\text{CF}_3)_2$ behaves as a pseudohalogen.

Much less is known of compounds containing mercury bonded to phosphorus and arsenic. Mercuric salts react with PH_3 and AsH_3 , but nothing is known concerning the structure of the products (44a). The action of tertiary phosphines or arsines on mercuric halides or salts of halomercurate ions in ethanol leads to the formation of compounds of the type $(\text{R}_3)_2\text{P}_2\text{HgX}_2$, corresponding to the mercuric amines (17, 23). In general the reaction does not proceed beyond the stage L_2HgX_2 but, with the bidentate *o*-phenylenebisdimethylamine, HgL_2^{2+} is formed (42). The compounds $\text{Hg}[\text{P}(\text{CF}_3)_2]_2$ and $\text{Hg}[\text{As}(\text{CF}_3)_2]_2$ do not appear to be formed; when mercury reacts with $(\text{CF}_3)_2\text{PCl}$ the product formed is $[(\text{CF}_3)_2\text{P}]_2$.

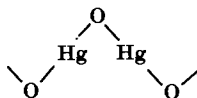
E. COMPOUNDS IN WHICH MERCURY IS BONDED TO OXYGEN, SULFUR, AND SELENIUM

Mercury reacts directly with oxygen, sulfur, and selenium to give compounds of the type HgX . The oxide and sulfide exist in two forms differing only slightly in energy:

		O	S	Se
$\Delta H_f \text{HgX}$ (kcal)	(a)	-21.68	-13.90	-5.1
	(b)	-21.56	-12.90	

These heats of formation follow the expected order. As in the case of the halogens, the order of stability constants in solution follows the inverse order. It is more difficult, however, to give a quantitative description in this case since, with divalent ions, species containing OH^- and O^{2-} are possible and direct comparisons are not always valid.

The simplest mercury-oxygen compound is the solid oxide HgO . This exists in two forms. In one form, the basic unit

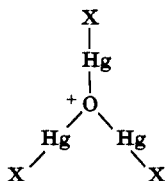


that is similar to that in amidomercuric compounds is planar and, in the other, is spiral in form. If the oxide is heated in a sealed tube with an alkali metal oxide, or better a peroxide, compounds M_2HgO_2 are formed

(37). These are colorless solids, which at once revert to mercuric oxide and alkali metal hydroxide with water. They contain the linear structural unit $[\text{O}—\text{Hg}—\text{O}]^{2-}$.

The tendency of the OH^- ion to form a strong covalent bond to mercury means that salts of oxy acids, except in strongly acidic media, are present as oxy salts, and even mercuric chloride and bromide give rise to a series of oxyhalides. This, like the mercury-halide-ammonia system, has long been known but was systematized only with the determination of structures by X-ray techniques. The main structural features occurring in these systems are as follows (29).

(a) Mercurioxonium cations,



where $\text{X} = \text{Cl}^-$, O^+ to give an extended lattice [e.g., $(\text{ClHgO})_3\text{Cl} = 2\text{HgCl}_2 \cdot \text{HgO}$, and $[\text{Hg}_3\text{O}_2]^{++}\text{SO}_4^{--} = \text{HgSO}_4 \cdot 2\text{HgO}$], in which the coordination about oxygen is a very flat pyramid. One HgX unit can also be replaced by H.

(b) Distorted tetrahedra: an example here is mercuric sulfite where two mutually normal planes, containing $\text{O}—\text{Hg}—\text{O}$ with bond angles 159° and 144° , are observed.

(c) Ionic lattices; e.g., $\text{K}_3\text{Hg}(\text{NO}_2)_4 \cdot \text{NO}_3$.

Combined oxygen is rather a poor ligand for the mercuric ion, as for mercury compounds. Compounds of the type $[\text{HgL}_6][\text{ClO}_4]$, however, have been observed, where $\text{L} =$ pyridine-*N*-oxide, dimethylsulfoxide, tetramethylene-sulfone, and thioxan oxide (5). Where the anion tends to form a covalent bond to mercury, the coordination number is reduced; thus $\text{HgCl}_2 \cdot 2\text{CH}_3\text{SO}$ is observed and is finally analogous to the HgCl_2L_2 compounds formed by Group VB donors.

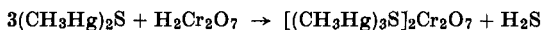
Although water is a poor ligand for Hg^{++} , it can be important in determining reactivity. In the mercuriation of aromatic rings a marked acceleration is observed by neutral salts such as sodium perchlorate. This has been interpreted as a lowering of the activity of H_2O and hence leaving Hg^{++} relatively free from solvation, in which form it is more reactive.

Although there are many formal similarities, mercury-sulfur compounds differ in many ways from their oxygen counterparts. In oxygen

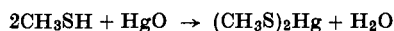
compounds, except where bonding is mainly ionic, the characteristic digonal coordination of mercury is dominant. In the corresponding sulfur compounds, marked distortion occurs and structures that may be thought of as distorted tetrahedra are common. The mercurioxonium structures, found in certain mercury oxyhalides, do have their counterparts in mercurisulfonium compounds, which are rather more stable.

Mercuric sulfide in the stable modification cinnabar has six sulfur atoms closer to mercury than the six of the van der Waals radii. Two of these are much closer (2.36 Å) than the other four, which are in two pairs (3.10 and 3.30 Å). The two nearest sulfur atoms make a bent S-Hg-S system with an angle of 172.4°. The black mercuric sulfide obtained on precipitation from solution has a zinc blende structure (29).

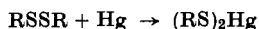
Although its solubility product is very low, mercuric sulfide will dissolve in concentrated solutions of sodium sulfide, and alkali metal salts M_2HgS_2 , formally analogous to M_2HgO_2 , can be obtained. Mercuric sulfide will also dissolve to some extent in concentrated solutions of mercuric salts. On heating these solutions the sulfide ion is oxidized by the mercuric ions. It is possible that the solution contains some type of mercurisulfonium species; Grdenić and Markusić (30) obtained and characterized a mercuric sulfonium species by the reaction:



The alkyl mercaptan derivatives of mercury, $(RS)_2Hg$, have long been known. They are obtained by the vigorous action of mercaptans on mercuric oxide (30):



The phenyl and perfluoroalkyl derivatives are obtained by the reaction (4):

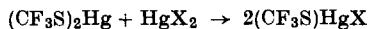


Examples are listed in Table XIV.

TABLE XIV
COMPOUNDS OF THE TYPE $(RS)_2Hg$

	M.P.	B.P.
$(CH_3S)_2Hg$	144	—
$(C_2H_5S)_2Hg$	76	(dec.)
$(i-C_3H_7S)_2Hg$	58	—
$(CF_3S)_2Hg$	39.4	182
$(C_7H_5S)_2Hg$	151.2	—

In their chemical behavior these compounds are very similar to the corresponding R_2Hg compounds. Thus they lead to derivatives $RSHgX$ when $X = \text{halogen}$, and where $R = CF_3$ the species $(CF_3S)_2HgX_2^{2-}$ can be obtained (20). The corresponding selenium derivatives $(CF_3Se)_2Hg$ have also been studied and are broadly similar (11). The equilibria in the reaction



have been studied by Raman spectroscopy in methanol (11) and the results are shown in Table XV.

TABLE XV
EQUILIBRIUM CONSTANTS FOR $Hg(SCF_3)_2 + HgX_2 \rightarrow 2CF_3SHgX$
AND THE CORRESPONDING SELENIUM DERIVATIVES

	HgX_2	$(CF_3S)_2Hg$	$(CF_3Se)_2Hg$
Cl	20 ± 10	20 ± 2
Br	2.3 ± 0.3	15 ± 10
I	1.67 ± 0.15	2.03 ± 0.02
SCN	1.35 ± 0.06	2.34 ± 0.06

Mercaptans will also react with mercuric halides to give solid complexes of the type $R_2S \cdot 2HgX_2$, $R_2S \cdot HgX_2$, and $(R_2S)_2HgX_2$. The structure of $R_2S \cdot HgX_2$ has been determined in the case of the complexes of diethylmercaptan with mercuric chloride and shown to be $[Et_2SHgCl]^+Cl^-$ (3).

F. MERCURY-HALOGEN COMPOUNDS

The bond energies of the mercuric halides have already been discussed, and the complexes formed between the mercuric halides and halide ions in solution will be discussed in more detail below (Section VI). This section will be concerned with the solid halides and halide complexes (29).

Mercuric fluoride has an ionic structure with each mercury atom having eight nearest-neighbor fluorines. The other mercury halides all have structures in which covalent bonding is important. In mercuric chloride, the basic unit is the linear $Cl-Hg-Cl$ with no other chlorine atoms closer than the run of the van der Waals radii. Mercuric bromide by contrast has a layer structure with six $Hg-Br$ distances less than the run of the van der Waals radii. Mercuric iodide has a structure based on HgI_4 tetrahedra that are corner-linked.

The mercuric halides other than fluoride are not dissociated in aqueous media. They are soluble in excess of alkali halide to give HgX_3^- and HgX_4^{2-} species. Interestingly, the sparingly soluble iodide is also soluble in excess of mercuric salts. Raman spectroscopic studies (10) have shown that the species present are HgCl^+ , HgBr^+ , and HgI^+ and also in the case of the iodide $[\text{Hg—I—Hg}]^{3+}$.

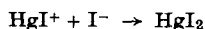
The ions HgX_3^- , HgX_4^{2-} , and more complex systems such as $\text{Hg}_2\text{X}_7^{3-}$ have been extensively used as precipitants for quaternary ammonium, phosphonium, and sulfonium salts. The chemistry and structural features of these compounds have been comprehensively reviewed by Deacon (16).

VI. Bond Energies and Equilibria in Aqueous Media

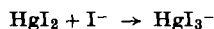
There is now a considerable body of data available on the equilibria between metals and ligands in aqueous solutions (56a). This has led to much discussion of the nature of metal-ligand bonding and a classification of metals into types A and B according to their tendency to form complexes whose stability is such that K (the stability constant) increases in the order $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ for type A, and the reverse order for type B (9). Mercury is a type B metal in this classification, while Cd is borderline and Zn, Cu, Sr, and Ba are type A. Mercury alone of the Group II metals can form salts based on the Hg_2^{++} ion in aqueous media, although Cd_2^{++} has been detected in NaAlCl_4 solution.

The data for the mercury halides will be discussed in some detail, as these illustrate rather well the unique position of mercury among the Group II elements. In Table XVII are given the thermodynamic data for the successive steps in complex formation between mercuric ions and halide ions (56a).

It can be seen that there is a marked break in both the stability constant and the heat of reaction at $n = 2$, corresponding to the formation of a neutral species HgX_2 . Thus, for the formation of iodo complexes, K_2 for the reaction



is greater by 10^7 than K_3 for the reaction



Conversely, K_1 and K_2 on the one hand and K_3 and K_4 on the other are of comparable magnitude. This expresses in numerical terms the statement, "Mercury tends to form two bonds at 180° and does not readily increase its coordination number". It will be shown later that this statement is less true for "hard" than for "soft" ligands.

TABLE XVI
THERMODYNAMIC DATA FOR COMPLEX FORMATION BY Hg^{++*}

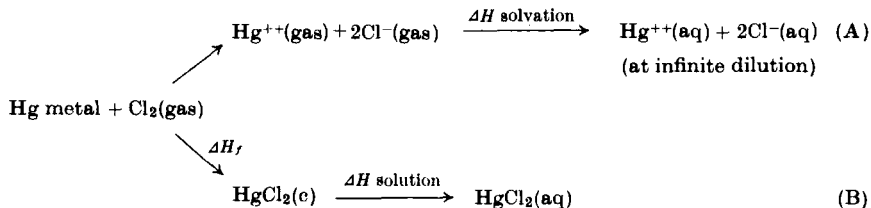
Ligand	log K				ΔH (kcal)				ΔS (e.u.)			
	K_1	K_2	K_3	K_4	ΔH_1	ΔH_2	ΔH_3	ΔH_4	ΔS_1	ΔS_2	ΔS_3	ΔS_4
OH ⁻	11.86	10.27										
CN ⁻	18.00	16.70	3.83	2.98	\longleftrightarrow 59.5 \longleftrightarrow				\longleftrightarrow -10 \longleftrightarrow			
SCN ⁻		16.43	2.71	1.98	\longleftrightarrow 35 \longleftrightarrow				\longleftrightarrow -20 \longleftrightarrow			
SeCN ⁻	\longleftrightarrow	26.4	\longleftrightarrow	2.47	\longleftrightarrow 46.5 \longleftrightarrow				\longleftrightarrow -20.8 \longleftrightarrow			
NH ₃	8.8	8.7	1.00	0.78	24.7		3.3	3.6	2.3	-6.4	-8.3	
NO ₂ ⁻	\longleftrightarrow 15 \longleftrightarrow											
NO ₃ ⁻	0.11	-0.1										
S ²⁻	50.23	(K_{80})										
S ₂ O ₃ ²⁻		29.27										
SO ₃ ²⁻		24.07										
SO ₄ ²⁻	1.42											
Se ²⁻	-59	(K_{80})										
SeO ₃ ²⁻		12.48										
F ⁻	1.03				-0.85				8			
Cl ⁻	6.74	6.48	0.85	1.00	5.9	6.9	2.2	0.1	11.1	6.3	3.0	5.1
Br ⁻	9.05	8.28	2.41	1.26	10.1	10.7	3.0	4.1	9	-5	-2	-2
I ⁻	12.87	10.95	3.67	2.37	17.6	15.0	3.6	4.0	\longleftrightarrow 13.7 \longleftrightarrow			
CH ₃ NH ₂	8.6	9.3	0.4									
NH ₂ CH ₂ CH ₂ NH ₂		14.3		9.0								
HO·CH ₂ CH ₂ NH ₂		8.51		8.81								
(NH ₂) ₂ CH(CH ₃)CH ₂	\longleftrightarrow		23.5	\longleftrightarrow								
CH ₃ O·CH ₂ CH ₂ NH ₂		9.19		8.65								
CH ₃ COOH		8.43										
EDTA ⁴⁻	\longleftrightarrow		21.78	\longleftrightarrow	\longleftrightarrow 18.9 \longleftrightarrow				\longleftrightarrow 35.5 \longleftrightarrow			

* The measurements (56a) are not all made under identical conditions, but the inaccuracies so caused are minor and do not invalidate the conclusions drawn in the text.

TABLE XVII
THERMODYNAMIC DATA FOR SUCCESSIVE STEPS IN COORDINATION
OF Hg^{++} BY HALIDE IONS

n :	$\log K_n$				$-\Delta H_n$				ΔS_n			
	1	2	3	4	1	2	3	4	1	2	3	4
Cl^-	6.74	6.48	0.85	1.00	5.9	6.9	2.2	0.1	11.1	6.3	3.0	5.1
Br^-	9.05	8.28	2.41	1.26	10.1	10.7	3.0	4.1	9	-5	-2	-2
I^-	12.87	10.95	3.67	2.37	17.6	15	3.6	4.0	$\longleftrightarrow 13.7 \longleftrightarrow$			

It is possible by e.m.f. and other measurements to relate the heat and free energy of formation of an aqueous ion to that of a solvated proton. If a value of the heat of hydration of a proton can be deduced, then it is possible to determine the absolute heat of formation of a metal ion, and hence the heat of solvation if the heat of formation of the gaseous ion is known. This has been done by Yatsimirskii (59), and enables all the heat terms in the diagram below to be evaluated:



Similar cycles for other metals and other halogens can obviously be written. Table XVIII shows the heat of formation of halides of Ca, Cd, and Hg as ionic solutions at infinite dilution, using the terms in (A), while Table XIX shows the calculation using the terms in (B). It can be seen that for both Ca and Cd the result obtained is the same in each case, showing, as is well known, that the halides of these elements dissolve to give ionic solutions at infinite dilution. By contrast, the values of $-\Delta H$ calculated by route (A) for HgX_2 are smaller than those calculated by route (B). This means that the actual heat of formation of $\text{HgX}_2(\text{aq})$ at infinite dilution (B) is greater than that calculated for an assembly of ions (A). The magnitude of this disparity increases from -17 kcal for HgCl_2 through -25 kcal for HgBr_2 to -37 kcal for HgI_2 , that is, in the order expected for increasing covalency. An interesting check on these calculations is that these difference figures should equal the observed

TABLE XVIII
HEATS OF FORMATION OF ION PAIRS AT INFINITE DILUTION FOR CaX_2 , CdX_2 , AND HgX_2 (kcal)

Ion	$\Delta H, \text{M}^{++}(\text{g})$	$\Delta H_{\text{solvation}}$	$\therefore \Delta H, \text{M}^{++}(\text{aq})$	$\Delta H, (\text{M}^{++} + 2\text{Cl}^-)(\text{aq})$	$\Delta H, (\text{M}^{++} + 2\text{Br}^-)(\text{aq})$	$\Delta H, (\text{M}^{++} + 2\text{I}^-)(\text{aq})$
Ca^{++}	464	-386	78	-206	-184	-156
Cd^{++}	627	-439	188	-96	-74	-46
Hg^{++}	690	-443	247	-35	-13	+15
	$\Delta H', \text{X}^-$	$\Delta H_{\text{solvation}}$	$\therefore \Delta H, \text{X}^-(\text{aq})$			
Cl	-58	-84	-142			
Br^-	-55	-76	-131			
I^-	-50	-67	-117			

TABLE XIX
HEATS OF FORMATION OF SOLUTIONS OF CaX_2 , CdX_2 , AND HgX_2 (kcal)

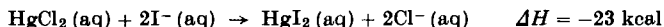
	$\Delta H_f(c)$			$\Delta H_{\text{solution}}$			$\therefore \Delta H \text{ MX}_2(aq)$		
	Cl	Br	I	Cl	Br	I	Cl	Br	I
Ca	-190	-161	-182	-18	-26	-28	-208	-187	-156
Cd	-93	-76	-48	-4	-1	+4	-97	-76	-44
Hg	-55.0	-40.5	-25.2	+3	+2	(est. +3)	-52	-38	(-22)

heat of formation of HgX_2 from $\text{Hg}^{++} + 2\text{X}^-$, that is, $\Delta H_1 + \Delta H_2$ in Table XVI. These figures in fact are -13 kcal for HgCl_2 , -21 kcal for HgBr_2 , and -33 kcal for HgI_2 .

The "class B" character of the mercuric ion in aqueous media must not be taken to imply that the order of the bond energies is $\text{HgI} > \text{HgBr} > \text{HgCl}$. Indeed, reference to Table VII shows that the reverse is true. From the data in Table XVIII it can be shown that



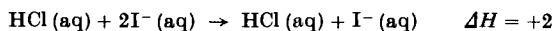
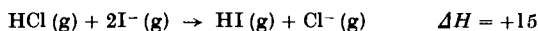
while from Table XVIII,



and

$$2(\Delta H_{\text{solvation Cl}^-} - \Delta H_{\text{solvation I}^-}) = -34 \text{ kcal}$$

It is reasonable to assume that the difference in solvation energy between the two un-ionized species HgCl_2 and HgI_2 will be small. It can be seen that the difference in reaction heat between gas phase and solution can be accounted for by the difference in solvation energy of the halide ions. A more elaborate but essentially similar treatment is given by Pöe and Vaidya (48). Similar calculations can be carried out for the hydrogen halides:



Once again the difference is close to the difference of the solvation of the halides, but there is no change of sign so that the stability order $\text{HCl} > \text{HBr} > \text{HI}$ is the same both in water and in the gas; this is "class A" pattern.

The "class B" behavior of mercury with halide ions is also shown in its behavior toward ligands of Group VI. For ligands such as NO_3^- and SO_4^{2-} , where binding is through oxygen, $\log K$ is small. Where binding is

TABLE XX
STABILITY CONSTANTS AND REACTION HEATS^a FOR
 $R \cdot Hg^+ + L^{A-} \rightarrow RHgL^{(A-1)-}$

Ligand	R = CH ₃			R = CF ₃
	log K	-ΔH	ΔS	log K
F ⁻	1.50	—	—	—
Cl ⁻	5.25	6.0	+3.6	5.78
Br ⁻	6.62	9.9	-3.6	7.24
I ⁻	8.60	—	—	9.63
OH ⁻	9.37	8.5	+13.7	10.76
S ²⁻	21.2	—	—	—
CN ⁻	14.1	22.1	-11.4	—
SCN ⁻	6.05	11.2	-10.6	—
CH ₃ HgSCN	1.65	—	—	—
NH ₃	7.60	—	—	—
S ₂ O ₃ ²⁻	10.90	11.7	+9.9	—

^a Schwarzenbach and Schellenberg (54).

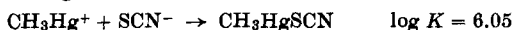
to sulfur as in S₂O₃²⁻, SO₃²⁻, and SCN⁻, log K is much larger and is even higher in SeCN⁻ than in SCN⁻.

The stability constants of a series of nitrogen bases have been determined by Davidson (15), who found that they could be expressed by the relation:

$$\log K_{Hg} = 0.93 \log K_R + 1.15$$

In this case, the reversal of the order of stability constants between mercury and hydrogen is not observed; the solvation energy of the neutral free base will be relatively small and does not have a major effect.

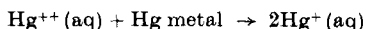
The ion CH₃Hg⁺ (Table XX) is very similar to Hg⁺⁺. As might be expected, the values of log K₁ for this ligand are similar to but smaller than log K₂ for Hg⁺⁺ with the same ligand. When CH₃ is replaced by the more electron-attracting CF₃, intermediate values are obtained. The ion CH₃Hg⁺ behaves essentially as acceptor for one ion only. This is illustrated by the two steps,



corresponding to a change between K₂ and K₃ for Hg⁺⁺ with SCN⁻ of ~8 to 2.7.

It is interesting in this context to consider the stability of the aqueous mercurous ion. This can be regarded either as a complex of a Hg atom

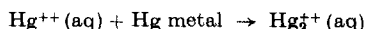
with Hg^{++} or as a compound of two Hg^+ ions, both of which can be regarded as $d^{10}s^1$ species. If it is assumed that the heat of hydration of Hg^+ is similar to that of Ag^+ at 117 kcal (Cu^{++} is very similar to Zn^{++} ; therefore we may assume that Ag^+ is similar to Cd^+ , and Cd^{++} very close to Hg^{++} ; this can also be deduced from theoretical calculations on heats of hydration), it is then possible to calculate $\Delta H_f \text{Hg}^+(\text{aq})$ from the first I.P. of mercury. The heat of reaction



is then

$$2(\Delta H_f \text{Hg}^+) - \Delta H_f \text{Hg}^{++}(\text{aq}) = 2(257 - 117) - 247 \text{ kcal} \\ = 33 \text{ kcal}$$

The observed heat of the reaction



is -0.82 kcal. This would imply an $^+\text{Hg}-\text{Hg}^+$ bond energy of 34 kcal if it is assumed that $\Delta H_{\text{hyd}} \text{Hg}^{++} = 2\Delta H_{\text{hyd}} \text{Hg}^+$. In view of the value $D(\text{Hg}^+-\text{H}) = 53$ kcal, this is not unreasonable. Proceeding in a similar way for cadmium, the heat of disproportionation of Cd^+ is -54 kcal, which is substantially higher than for Hg^+ . Further, the lower I.P. for Cd and Cd^+ than for Hg and Hg^+ indicates, as is observed in other cases, that bonds to cadmium will be less strong than to mercury. Quite small changes in solvation energies will, however, serve to alter greatly the stability of both Hg^+ and Cd^+ , and indeed Cd_2^{++} has been shown to exist in the compound $\text{Cd}_2(\text{AlCl}_4)_2$ in NaAlCl_4 solution (13).

A further limitation on the stability of mercurous compounds is provided by the value of the equilibrium constant

$$K = \frac{[\text{Hg}^{++}(\text{aq})]}{[\text{Hg mole}][\text{Hg}^{++}(\text{aq})]} \quad \log K = 1.92 \text{ at } 25^\circ$$

in relation to the stability constants of mercuric complexes. Any ligand for which $\log K$ is significantly greater than 1.92 will lead to disproportionation. Table XVI shows that stable soluble mercurous salts can be expected only for oxygen donors and for F^- in aqueous media. This is known to be the case. The well-known mercurous halides are all insoluble and their solubility products decrease in the order $\text{Hg}_2\text{Cl}_2 > \text{Hg}_2\text{Br}_2 > \text{Hg}_2\text{I}_2$, as they must if disproportionation is to be avoided.

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ALKYL DERIVATIVES OF THE GROUP II METALS

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I. Introduction

All the elements of Group II (with the exception of radium) are known to form alkyl derivatives. The compounds from magnesium and mercury are of very great interest and importance, the former because of their usefulness in synthesis, and the latter because of their physiological activity; as a consequence, so many of the compounds have been prepared and the literature on their properties is so extensive that a detailed account of their chemistry, even if confined to recent advances, is beyond the scope of a review article. Nevertheless, recent studies of the alkyl derivatives of all the Group II metals have revealed a pattern of structure and behavior that may make possible some rationalization of the properties and reactions of metal alkyls in general, and promise to lead to a greater insight into the nature of carbon-metal bonds.

Good accounts of the older chemistry of the alkyl derivatives of the Group II metals have been given in monographs on organometallic chemistry [e.g., Coates (95)]; it is the purpose of this article to attempt to systematize some of the mass of experimental data recorded during the past few years. The emphasis will be on the structural chemistry of the compounds. A detailed account of their reactions is not attempted, although the more important work on the influence of structure and solvation on reactivity is reviewed.

The Group II metals can form two covalent bonds, making use of the two electrons in their outermost *s* orbital. If one of the bonds is to carbon, and the other to another atom or group, the resulting compound may be written as R-M-X. (Throughout this review, any alkyl or aryl group is designated R; where an aryl group is specifically indicated, the symbol Ar is used.) In such a compound, as all the Group II metals are more electro-positive than carbon, the carbon-metal bond will have some polar character: $R^{\delta-}-M^{\delta+}-X$. The reactivity of the metal alkyls has often been considered (particularly by organic chemists) to lie in the partial carbanionic character of the alkyl group; the electron-deficient character of the metal has too often been overlooked. It is now becoming increasingly clear that the reactivity of the metal alkyls may be governed by the carbanionic character of the alkyl group, by the electron-deficient character of the metal, or by both (cf., e.g., 1, 138, 141-143, 215, 299).

In the case of the alkyl derivatives of the Group II metals, the electron deficiency of the metal in the simple compound R-M-X (which may in some cases have no more than transient existence) may be reduced by either intramolecular or intermolecular interactions. In the first case, electrons may be available from the groups R or X within the same mole-

cule; in the second case, electron-donating ligands may coordinate with the metal atom. The electron-donating ligands may be other R-M-X molecules, or other species such as solvent molecules. In the discussion below, the simple, unsolvated dialkyl derivatives of the metals are taken as a basis in examining the effect of other groups attached to the metal, and of the addition of other electron donors, on the structures and reactivities of the compounds.

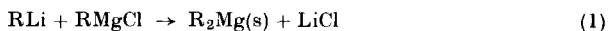
II. Compounds Containing the System C-M-C; the Dialkyl Derivatives of the Metals

A. SIMPLE, UNSOLVATED DERIVATIVES

1. Structure

a. Dialkylberyllium, -magnesium, -calcium, -strontium, and -barium Compounds. Although diethylzinc was the first true organometallic compound to be characterized (167), simple unsolvated derivatives of the more electropositive Group II metals have until recently been much less accessible, and those of calcium, strontium, and barium have not been prepared. (Bis(cyclopentadienyl)calcium is noted in Section II,D below.) The preparation of dimethylcalcium, -strontium, and -barium has been reported (340). However, the method described, which involved the reaction of the metals with methyl iodide in pyridine followed by prolonged extraction of the resulting solids with boiling pyridine, seemed suspect in view of the high reactivity of organocalcium compounds toward pyridine (80), and all attempts to repeat the preparation of dimethylcalcium led to materials superficially similar to those described, but which gave hydrogen, not methane, on hydrolysis, and appeared to be complexes of pyridine and bipyridyls with calcium hydride (78, 298).

It has recently been discovered that, in contrast to the Grignard reagents, dialkylmagnesium compounds prepared in diethyl ether may readily be desolvated (247) (and that dimethylmagnesium even crystallizes from diethyl ether without attached solvent) (112). A new general method for preparing unsolvated dialkylmagnesium compounds involves the reaction of an alkylolithium compound with the corresponding alkylmagnesium chloride in diethyl ether (Eq. 1), followed by desolvation (247):



Unsolvated alkylmagnesium halides, which are now readily accessible (see Section II,A,1 below), have been used as sources of unsolvated

dialkylmagnesium compounds (191), and may prove to be useful starting materials for the preparation of unsolvated dialkyl derivatives of other metals. For example, unsolvated di-*n*-butylberyllium has been prepared by the reaction of a solution of *n*-butylmagnesium iodide in benzene with beryllium chloride¹ (192).

Both dimethylberyllium (403) and dimethylmagnesium (459) have been shown by X-ray crystallography to exist in the solid state as long-chain polymers, with methyl groups forming bridges between the tetrahedrally coordinated metal atoms. The structure of diethylmagnesium is similar, with methylene bridges between the metal atoms (460). The magnesium compounds are involatile (459, 460), but dimethylberyllium may be sublimed and the vapor is believed to contain monomeric, dimeric, and trimeric molecules, with possibly higher polymers also (100). Diisopropylberyllium is reported to be dimeric both in benzene solution and in the vapor state (98); di-*n*-butylberyllium is dimeric in benzene (192). Recent determinations of the structure of di-*tert*-butylberyllium by infrared and Raman spectroscopy (114) and electron diffraction (201) have revealed that it is unique among the dialkylberyllium compounds in being monomeric, even in the liquid state (114). Di-*n*-pentylmagnesium is reported (191) to be largely dimeric in benzene.

The nature of the bonding in these polymeric molecules (and in the analogous aluminum compounds) has been extensively discussed [see Coates (95), pp. 57, 58, and 130], and it is generally accepted that they contain electron-deficient bonds, with two electrons in orbitals linking one carbon and two metal atoms (or possibly with four electrons in orbitals linking two carbon and two metal atoms) (451). In such a situation, although the molecule as a whole is electron-deficient, the deficiency on the metal atom is somewhat reduced, and it has attained a coordination number of 4. The observation that the higher beryllium alkyls show less tendency to polymerize than dimethylberyllium has been explained in terms of steric interference between the alkyl groups (460). The observations that di-*n*-pentylmagnesium is dimeric in benzene (191), and that dimethylmagnesium crystallizes from diethyl ether free from solvent (112), seem to indicate that the tendency of dialkylmagnesium compounds to form alkyl-bridged polymers is at least as great as that of the beryllium compounds.

The reactions of the simple, unsolvated derivatives of the more electropositive metals have been little studied; where the dialkyl derivatives are mentioned, it is almost invariably solvated complexes of the

¹ The conditions employed for this reaction are evidently fairly critical, as a similar experiment in which magnesium and magnesium halides were not removed from the reaction mixture failed to yield any di-*n*-butylberyllium (455).

simple compounds that are referred to. The action of heat, oxygen, and compounds containing "active" hydrogen on the dialkyl derivatives of the metals leads in certain cases to compounds of the formula $R-M-X$ (these reactions are reviewed in the appropriate sections below). It is reported that pyrolysis of dimethylmagnesium gives polymers with the composition $(MgCH_2)_n$ (500), and that dimethylberyllium similarly yields $(BeCH_2)_n$ (195).

b. Dialkylzinc, -cadmium, and -mercury Compounds. In contrast to the derivatives of the more electropositive Group II metals, the dialkylzinc, -cadmium, and -mercury compounds have little or no tendency to association, and are believed to have simple, linear structures [see Coates (95), pp. 63–82]; the mercury compounds show almost no indication of electron deficiency and, although the zinc and cadmium compounds readily function as electron acceptors (see Section II,B below), their electron deficiency is not reflected in their structures. [Crystallographic determinations have confirmed the linear configuration for diphenylmercury (502) and di-*p*-tolylmercury (267); the high dipole moment of diphenylmercury must be due to atom polarization (267).]

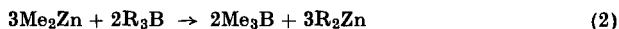
The simplicity of the structures of these compounds has prompted a number of studies of their physical properties (see, e.g., 66, 67, 207, 253, 428). In particular, the van der Waals volumes and radii of zinc, cadmium, and mercury have been calculated (67); values were chosen that yielded the correct number of external degrees of freedom per molecule (assuming free rotation about metal-carbon bonds), when linked with density and heat of vaporization data for the dimethyl derivatives. Similarly, analysis of the vibrational spectra of dimethylzinc, cadmium, - and -mercury [and of bis(trifluoromethyl)mercury] (253) gave values for the carbon-metal stretching force constants and carbon-metal-carbon bending force

TABLE I
CONSTANTS DERIVED FROM MEASUREMENTS ON DIMETHYL
DERIVATIVES OF GROUP II METALS

Compound	Van der Waals radius of metal (Å) (67)	Carbon-metal stretching force constant (md Å ⁻¹) (253)	Carbon-metal- carbon bending force constant (md Å ⁻¹) (253)
Me ₂ Zn	1.39	2.05	0.41
Me ₂ Cd	1.62	2.45	0.51
Me ₂ Hg	1.70	2.39	0.31

constants. The constants derived from measurements on the dimethyl derivatives are given in Table I.

With the classical methods of preparation (reaction of alkyl iodides with zinc, reaction of Grignard reagents with zinc chloride), it has been found difficult to obtain the less volatile dialkylzinc compounds free from halide and ether (426, 428); the pure compounds were obtained, however, by an alkyl-exchange reaction between dimethyl (or diethyl)-zinc and a trialkylboron compound:



The method should also be suitable for the synthesis of dialkylcadmium compounds (425, 426).

As in the case of the derivatives of beryllium and magnesium, the reactions of the dialkylzinc and -cadmium compounds have usually been studied in electron-donating solvents, and in addition the profound effect of other components of the systems has often not been realized. For example, standard textbooks on organic chemistry refer to the synthesis of ketones by the reaction of acyl chlorides with dialkylcadmium compounds. However, Kollonitsch (257) pointed out in 1960 that dialkylcadmium compounds, free from the magnesium salts and diethyl ether with which they are associated when prepared by the usual procedure, are unreactive toward acyl chlorides. Subsequent work by Kollonitsch (255, 256) and by French workers (122, 132, 152, 211, 226, 276, 293, 416) has emphasized the effect that metal salts can have on the reactivity of organocadmium and organozinc compounds (see Section IV,B,2 below).

In contrast to the derivatives of the more electropositive metals, dialkylmercury compounds do not normally interact with electron donors, and their chemistry has been intensively studied since they provide a particularly suitable subject for investigations on the mechanism of electrophilic substitution reactions. An excellent general account of such studies has been given (124), and some of the more important and interesting recent work is reviewed here (see particularly Sections II,B,2b and IV,A,4).

In addition to their electrophilic substitution reactions, the dialkyl derivatives of mercury (39) [and of zinc (173, 354) and cadmium (353)] undergo homolytic reactions, and are indeed well-known sources of alkyl radicals. For example, thermolysis or photolysis of dialkylmercury compounds has in recent years been used in the study of benzyl (38, 40), vinyl (387), and heptafluoroisopropyl (160) radicals. [Somewhat surprisingly, bis(nonafluoro-*tert*-butyl)mercury appears to decompose thermally by some route other than via perfluoro-*tert*-butyl radicals (160).]

B. COMPLEXES OF THE DIALKYL DERIVATIVES WITH ELECTRON DONORS

The interaction of the alkyl derivatives of the Group II metals with electron donors has in recent years aroused interest under three main headings: (a) correlation of the existence and stability of the complexes with properties of the metal and of the donor molecules, (b) the extent to which the polymeric structure of the beryllium and magnesium derivatives is broken down by electron donors, and (c) the effect of complex formation on the reactivity of the compounds. The chemistry of donor-acceptor complexes of beryllium, zinc, cadmium, and mercury derivatives has been reviewed (432).

1. Formation and Stability

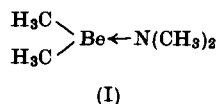
Dialkylberyllium compounds form complexes with diethyl ether, which are desolvated only with difficulty (95). On the other hand, simple dialkylmercury compounds do not normally form stable complexes even with strong electron donors, such as 1,4-dioxan (411, 432) or 2,2'-bipyridyl (102). (Complexes of perfluoroalkyl derivatives are discussed in Section II,C.) Derivatives of the other metals reveal wide variations within these limits. It would be convenient in considering the formation and stability of the complexes to have a list of electron donors in order of electron-donating capacity (Lewis basicity, nucleophilicity). Unfortunately very little quantitative information is available, partly because of the difficulty of defining a general parameter applicable in other than limited circumstances (359). Little attempt has yet been made to apply the concept of hard and soft acids and bases to these complexes, but this concept seems likely to be useful in this field.

Among the measures of electron-donating capacity that may be applicable to studies on the stability of donor-acceptor complexes are the following. (i) The heats of formation of the complexes between boron trifluoride and some ethers have been measured (70). (ii) More recently, the effect of various solvents on $J(^{119}\text{Sn}-^1\text{H})$ for trimethyltin bromide was investigated (182). The coupling constants were taken as a measure of the "nucleophilicity" of the solvents. (iii) The shift of the magnetic resonance due to the chloroform proton in various solvents has similarly been taken as a measure of the "basicity" of the solvents (283). The results of these determinations give some measure of electron-donating capacities, but the importance of steric factors in complex formation must also be emphasized. In particular, many bifunctional ethers, amines, etc. (e.g., 1,4-dioxan, *N,N,N',N'*-tetramethylethylenediamine, 2,2'-bipyridyl), function as exceptionally strong complexing agents.

Complex formation for each of the metals is considered below, and some aspects of the influence of solvation on reactivity are then discussed.

a. Complexes of Dialkylberyllium Compounds. Dialkylberyllium compounds, as was stated, are highly electron-deficient, and readily form complexes with ethers, amines, etc. In many cases the complexes are very stable, and the donor ligands are not easily removed. It is reported (105) that complexes are not formed between dimethylberyllium and donors such as trimethylarsine or dimethyl sulfide, although diphenylberyllium forms stable complexes with dimethyl sulfide (115). The comparatively "soft" sulfur and arsenic donors are apparently less able to break down the alkyl-bridging system to coordinate with the "hard" beryllium.

The structures of the dialkylberyllium complexes are of interest, because of their tendency to form polymers and because of the variable number of ligands attached. Dimethylberyllium forms 1:1 complexes with trimethylamine, trimethylphosphine, and dimethyl ether (105). The trimethylamine complex is volatile, and the vapor is largely monomeric, although there may be some association at lower temperatures and in the condensed phase. The structure I, in which beryllium is three-coordinate,

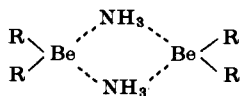


seems probable (105). The trimethylphosphine and dimethyl ether adducts are much less stable than the trimethylamine adduct. Stable 1:1 complexes are formed between diphenylberyllium and dimethyl ether, diethyl ether, dimethyl sulfide, trimethylamine, and trimethylphosphine (115).

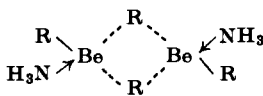
Apart from the simple 1:1 complexes, a number of adducts with other stoichiometries has been reported. Vapor pressure measurements on the dimethylberyllium-trimethylphosphine and dimethylberyllium-dimethyl ether systems gave indications of the existence of complexes such as $(\text{Me}_2\text{Be})_2 \cdot \text{L}_3$, $(\text{Me}_2\text{Be})_2 \cdot \text{L}$, and $(\text{Me}_2\text{Be})_3 \cdot \text{L}$ (105). Such complexes were not amenable to study and characterization, but it has proved possible to observe some dialkylberyllium-trimethylamine adducts in addition to the 1:1 compound. It was at first believed that, with an excess of trimethylamine and at temperatures below 10° , a complex with the composition $(\text{Me}_2\text{Be})_2 \cdot (\text{NMe}_3)_3$ was formed, and no indication of a complex $\text{Me}_2\text{Be} \cdot (\text{NMe}_3)_2$ was observed. However, it was shown (343) that a diethylberyllium-bis(trimethylamine) complex was stable below -35° , and a subsequent reinvestigation (50) of the dimethylberyllium-trimethylamine system disclosed that a bis(trimethylamine) adduct was formed be-

low 0° , rather than the 2:3 adduct previously reported. The earlier results were confused by the very slow uptake of trimethylamine by the 1:1 adduct. A stable dimethylberyllium-bis(pyridine) adduct, m.p. 91° – 92° , has also been reported (102). Similarly, tensimetric studies (115) revealed the existence of a number of 1:2 complexes of diphenylberyllium with electron donors. Those with dimethyl ether, dimethyl sulfide, and trimethylphosphine were stable at 0° (although the last two were partly dissociated in benzene), but those with diethyl ether and trimethylamine had appreciable dissociation pressures under similar conditions; steric factors are thought to account for the differences in stability.

At low temperatures, dialkylberyllium compounds form 1:1 complexes with primary and secondary amines (101, 158, 172) and ammonia (288), but at higher temperatures alkyl groups are displaced from beryllium (see Section VI,A below). Dimeric ammonia-bridged (II) or alkyl-bridged (III) structures have been proposed (288) for the complexes between ammonia and dimethyl- or diethylberyllium.

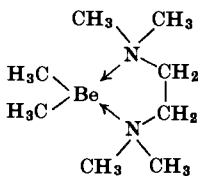


(II)

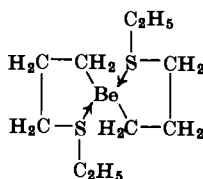


(III)

Dialkylberyllium compounds form stable and remarkably unreactive 1:1 complexes with a number of bidentate ligands, such as 1,2-dimethoxyethane, 2,5-dithiahexane, *N,N,N',N'*-tetramethylethylenediamine, *N,N,N',N'*-tetramethyl-*o*-phenylenediamine, and 2,2'-bipyridyl (50, 102, 115, 158). These complexes are monomeric in benzene solution (102), and so presumably is the complex between diethylberyllium and 1,4-dioxan (409). It seems likely that these complexes have structures such as IV, involving four-coordinate beryllium (102). Bis(4-thiahexyl)beryllium probably has the interesting chelated structure V, and the structure of bis(5-oxahexyl)beryllium is presumably similar (29).



(IV)



(V)

The complexes between dialkyl- and diarylberyllium compounds and 2,2'-bipyridyl are colored; for example, the diethylberyllium compound is red ($\lambda_{\text{max}} = 461 \text{ m}\mu$, $\epsilon = 3.7 \times 10^3$). It is argued (102) that the color of the complexes is due to transitions involving electron transfer from the beryllium-carbon bonds to the lowest unoccupied orbital of the bipyridyl.

Unstable complexes, of unknown structures, are reported (406, 408; cf. 480) to be formed between unsolvated diethylberyllium and various salts, including alkali-metal fluorides, potassium cyanide, and tetraalkylammonium chlorides; ionic rather than coordinated structures seem likely for these complexes (further details are given in Section II,E below).

b. *Complexes of Dialkylmagnesium Compounds.* In view of the tenacity with which Grignard reagents retain diethyl ether (95, p. 52; 412, 413), it is remarkable that dialkylmagnesium compounds are readily desolvated (247). The case of dimethylmagnesium, where alkyl bridging is apparently very strong, is particularly interesting. The compound is only sparingly soluble in diethyl ether, and is monomeric (and presumably solvated) in this solvent (223a, 435). It is reported, however, that it crystallizes as an unsolvated polymer (112). On the other hand, diphenylmagnesium forms stable, monomeric complexes, which may be crystallized, with two moles of diethyl ether (412, 413) or tetrahydrofuran (104), and di-*tert*-butylmagnesium forms a 1:2 complex with tetrahydrofuran (104a).

Stable 1:1 complexes between dialkylmagnesium compounds and bidentate ligands, such as 1,2-dimethoxyethane and *N,N,N',N'*-tetramethylethylenediamine, have been described (104, 104a, 489). These complexes resemble their beryllium analogs, being in many cases volatile, and monomeric in solution. No indication of the formation of compounds with six-coordinate magnesium has been observed (104).

c. *Complexes of Dialkylcalcium, -strontium, and -barium Compounds.* Simple dialkylcalcium, -strontium, and -barium compounds have not been authenticated, either unsolvated or as complexes with donor solvents (but see Section II,E below), although the small amount of triphenylacetic acid formed, when the product from the reaction of barium with triphenylmethane in liquid ammonia was carboxylated, indicated that some bis(triphenylmethyl)barium had been formed (185). It is of interest that tetrahydrofuran complexes of bis(triphenylgermyl)-strontium and -barium have been isolated (20).

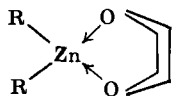
d. *Complexes of Dialkylzinc Compounds.* The formation of complexes by dialkylzinc compounds is uncomplicated by competing self-association of the organometallic compounds. Dimethylzinc and diphenylzinc

form complexes in solution with simple cyclic ethers (18, 419) (and it seems likely that similar complexes would be formed with acyclic ethers, although they have not been described). The complexes, as might be expected from the comparatively low electron-accepting capacity of zinc, are not highly stable. Thus, although the 1:1 dimethylzinc-ethylene oxide complex appeared to distill unchanged [419; but see Thiele and Zdunneck (432), p. 336], a study of the proton n.m.r. spectrum of the complex in cyclohexane solution showed that its heat of formation is only $-9.1 \text{ kcal mole}^{-1}$, and that it is partly dissociated in solution except at low temperatures (18). With tetrahydrofuran and pentamethylene oxide, dimethylzinc forms crystalline complexes containing a 1:2 zinc-to-ether ratio (419); it seems likely that steric factors are important in determining whether formation of a 1:2 complex is possible. With diethylzinc and longer-chain dialkylzinc compounds, no stable adduct could be isolated even with tetrahydrofuran, although there was interaction in solution (430).

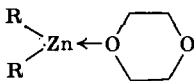
Dimethyl- and diarylzinc compounds yield stable complexes with tertiary amines, including trialkylamines and pyridines (292, 427, 430). Both a 1:1 and a less stable 1:2 complex are formed between dimethylzinc and trimethylamine; with triethylamine and pyridine only the 1:2 adducts were isolated (and these tended to dissociate in benzene solution) (421). A stable complex of diethylzinc with triethylamine has not been isolated, but the n.m.r. spectra of mixtures of the components reveal the presence of a 1:1 complex (414). The benzyl and higher-alkyl zinc compounds form stable complexes with pyridine, etc., but not with triethylamine (430). Complexes are also formed at low temperatures with secondary amines, but these tend to react further to give alkylzinc amides (see Section VI,C) (432, p. 339). [The complexes formed between dialkynylzinc compounds and ammonia (303) may also be mentioned here.]

Stable 1:1 complexes are formed between dialkylzinc compounds and a number of types of bifunctional electron donor, including diethers (18, 420), diamines (18, 329, 421, 427, 430), diphosphines (150, 318), and diarsines (318). Complex formation between diethylzinc or diphenylzinc and dioxan could be inferred from the high dipole moments of the zinc compounds in dioxan solution (234, 405, 410), and crystalline dioxanates of numerous dialkylzinc compounds have since been isolated (332, 392, 420). The dioxanates are 1:1 complexes, and are believed to have chelated structures (VI), rather than structures such as VII (18, 432, p. 337), and the complexes of many other diethers are presumably similar. However, 1,2-dimethoxyethane and 1,3-dimethoxypropane give bis-(etherates), which probably have structures such as VIII (420).

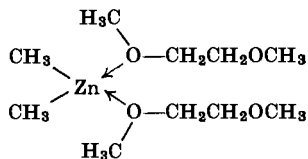
It seems likely that the 1:1 complexes of dialkylzinc compounds with diamines (430) and compounds such as tetramethyltetrazene, tetraphenylethylenediphosphine, and tetramethyl-*o*-phenylenediarsine (318) have chelated structures, such as IX. The constitution of the solid complex of diethylzinc with diazabicyclooctane (379) has not yet been established, but should be interesting. Tetraphenylethylenediphosphine gives a 2:1 adduct with diphenylzinc (318), and tetrakis(diphenylphosphino-methyl)methane gives monomeric 1:2 complexes with diethylzinc and



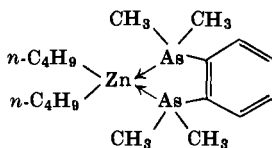
(VI)



(VII)



(VIII)

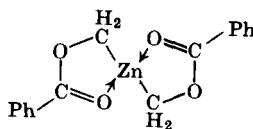


(IX)

diphenylzinc, but a polymeric 1:4 complex with dimethylzinc; a structure involving methyl bridges between zinc atoms has been suggested for the last complex (150). The interesting suggestion has been made (318) that the complexes of phosphorus- or arsenic-containing ligands may be stabilized by d_{π} - d_{π} back-bonding of electrons from the 3*d* orbitals of zinc to empty *d* orbitals of phosphorus or arsenic. However, such evidence as is available (e.g., the greater stability of diaryl than dialkyl complexes) indicates that any such back-donation is not of great importance in these complexes (but see below). Steric factors appear to be significant in the stabilization of complexes with bifunctional ligands, as no stoichiometric addition compounds of dimethylzinc and 1,3-dioxan could be isolated (420). It would be of interest to know whether the sulfur atom in the dimethylzinc-1,4-thioxan complex (420) is bonded to zinc, in view of the instability of complexes of dimethylberyllium with dialkyl sulfides.

Bis(benzoyloxymethyl)zinc probably has the structure X (476), and presents an interesting example of intramolecular coordination, somewhat analogous to the beryllium compounds noted under (a) above.

The complexes of dialkylzinc compounds with 2,2'-bipyridyl and 1,10-phenanthroline are of great interest because of their spectroscopic



(X)

properties. Coates and Green (102, 103) noted that the complexes of dimethylzinc with these ligands were colored, and the ultraviolet and visible absorption spectra of a number of complexes of this type were measured by Noltes and van den Hurk (319) and Thiele (429). It was observed that the long-wavelength absorption band of the complexes was at shorter wavelength and had higher intensity for more electro-negative alkyl groups. The data for the longest-wavelength absorption bands of some bipyridyl complexes are given in Table II. The data could

TABLE II
ABSORPTION BANDS OF COMPLEXES OF DIALKYLZINC COMPOUNDS
WITH 2,2'-BIPYRIDYL, IN TOLUENE SOLUTION (319)

R (in R_2Zn)	$\lambda_{max}(m\mu)$	$\log \epsilon_{max}$
iso- C_3H_7	480	2.63
C_2H_5	420	2.77
C_6H_5	350	2.91
C_6F_5	309	4.15

be explained very satisfactorily in terms of electron transfer from the organozinc component to the coordinating ligand. Transfer from the metal-carbon bonds (see Section II, B, 1a above) seems highly unlikely in this system, and it is most probable that the d orbitals of the zinc atom are concerned. Molecular orbital calculations do in fact indicate that the observed spectroscopic properties of the complexes can be explained in terms of interaction between the $3d$ orbitals of zinc and the highest filled and lowest unfilled orbitals of the ligands. [Similar considerations presumably also apply to the 1:2 complexes of dialkylzinc compounds with pyridine, quinoline, and isoquinoline (430).] The stabilities of some dialkylzinc-2,2'-bipyridyl complexes have recently been determined by a dielectric titration technique (316). The order of stability was *tert*-butyl > isopropyl > ethyl > methyl, the reverse of the order for the corresponding series of tetramethylethylenediamine complexes. It is thus apparent that d_{π} -bonding to zinc is important in the ground state of the bipyridyl complexes.

e. Complexes of Dialkylcadmium Compounds. As expected, dialkylcadmium compounds show less tendency than dialkylzinc compounds to form complexes with electron donors. Thus, although dimethylcadmium

forms crystalline 1:1 complexes with bifunctional ligands (1,4-dioxan, 2,2'-bipyridyl, etc.) (102, 332, 422), complexes with even strong monofunctional ligands (tetrahydrofuran, pyridine) dissociated so readily that they could not be purified (422). However, stable complexes, $R_2Cd \cdot (HMPT)_2$, have recently been isolated from the products of the reaction of alkyl iodides with cadmium in hexamethylphosphorotriamide (91). It has been noted that the dipole moments of diethylcadmium (411) and diphenylcadmium (405) in dioxan solution are less than those of the corresponding zinc and magnesium compounds. The interpretation of these results is not straightforward; the dipole moment could vary because of variations of the carbon-metal-carbon angle, or because of variations in the polarity of the carbon-metal bonds at a constant carbon-metal-carbon angle. Crystalline dioxanates of some diarylcadmium compounds were isolated, but were readily desolvated (331a). The 2,2'-bipyridyl and 1,10-phenanthroline complexes, like the corresponding zinc compounds, are colored (102, 422) and presumably have similar constitutions.

f. Complexes of Dialkylmercury Compounds. Simple dialkylmercury compounds normally show no signs of complex formation even with such powerful electron donors as 2,2'-bipyridyl (102), diazabicyclooctane (379), and hexamethylphosphorotriamide (455), although an oscillographic titration technique (346) and analysis of the 1H n.m.r. spectra (343a) gave some indication of interaction between diphenylmercury and donor ligands. However, the perfluoroalkylmercury compounds (see Section II,C below), where the electron density on mercury is reduced by the inductive effect of the highly electronegative perfluoroalkyl group, form complexes with strong electron donors such as pyridine oxide, sulfolane, piperidine, ethylenediamine (345, 346), 2,2'-bipyridyl (33), and 1,10-phenanthroline (119, 120); some of these complexes are sufficiently stable to be isolated and purified, and bis(tetrafluoro-4-pyridyl)mercury, with its exceptionally electron-withdrawing organic groups, forms a stable complex (m.p. 181°) with 2,2'-bipyridyl (89).

2. Influence of Coordination on Reactivity

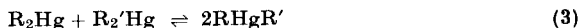
The influence of coordination in increasing the nucleophilic reactivity and in decreasing the electrophilic reactivity of metal alkyls has been discussed (141, 143, 454) (and see Section I), and a general review of the subject has been given (322). However, much more work has to be carried out on the nature of carbon-metal bonds and on the mechanisms of their reactions, and a full understanding of the role of coordination is still far from realization. Moreover, it has been pointed out (380) that, in many

reactions of alkyllithium compounds, the solvent may play a kinetic role in addition to its thermodynamic role in solvating the metal.

Two aspects of the problem are reviewed briefly here: first, the phenomenon of the exchange of alkyl groups between metal alkyl molecules (and the associated problem of the configurational stability of the alkyl groups); second, the influence of coordination on the reactivity of the alkyl derivatives in some representative reactions.

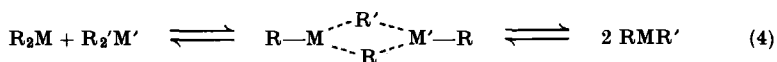
a. Alkyl-Group Exchange. When this subject was reviewed in 1965 (278), the information then available could be summarized as follows. The proton magnetic resonance spectra of simple dialkyl derivatives of magnesium, zinc, and cadmium indicated that alkyl groups were being exchanged at a rate faster than, or comparable with, the n.m.r. time scale (137, 292). The rates of exchange could be estimated in some cases, and were in the order cadmium < zinc < magnesium derivatives. For the corresponding mercury derivatives, and for mixtures of these with the zinc and cadmium derivatives, exchange was slow if it occurred at all (292). These results are incidentally difficult to reconcile with the reported (254, 331a) preparation of unsymmetrical dialkylzinc and dialkylcadmium compounds. However, it is true that exchange is slow for dialkylcadmium compounds in the absence of electron donors, and for dialkylzinc compounds in the absence of alkylzinc halides (64), and recent work (2, 391) provides unequivocal support for the original findings. The n.m.r. spectra of bis(perfluoroalkyl)mercury compounds showed ^{19}F — ^{199}Hg coupling, indicating that exchange was slow for these compounds (123).

At elevated temperatures, mixtures of dimethylmercury and bis(trideuteriomethyl)mercury gave rise to some of the mixed compound, CH_3HgCD_3 (137), and mixtures of dimethylmercury with diphenyl- or dibenzylmercury were in equilibrium with the appropriate mixed compounds (350). It appeared at first that a random distribution of organic groups was involved in these equilibria, but subsequent work, using a variety of dialkylmercury compounds, has demonstrated that the position of equilibrium depends on the nature of the groups (369). Thus, for example, whereas the equilibrium at 90° formulated as



lay largely on the left-hand side ($K_{\text{eq}} = 1.8$) when $\text{R} = \text{CH}_3$ and $\text{R}' = \text{C}_2\text{H}_5$, it lay largely on the right-hand side ($K_{\text{eq}} = 130$) when $\text{R} = \text{C}_2\text{H}_5$ and $\text{R}' = \text{cis-CH}_3\text{CH=CH-}$. As expected, the distribution of alkyl groups between dialkylmagnesium and dialkylmercury compounds could be correlated with the relative stabilities of the carbanions corresponding to the alkyl groups (139).

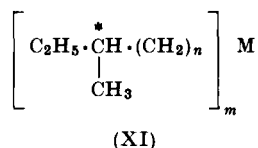
In the work reviewed earlier, little effect of the solvent polarity on the exchange rates was noted, and it was concluded that the exchange reaction proceeds by a nonionic mechanism, or one in which the transition state has little polar character. However, the donor strength of the solvent has some effect. For example, in solvent-free dimethylcadmium (137, 292) and diethylcadmium (69) and in their solutions in hexane, exchange is sufficiently slow for ^1H — ^{111}Cd and ^1H — ^{113}Cd spin-spin coupling to be observed. In donor solvents such as tetrahydrofuran (137) and pyridine (202, 292), however, exchange is rapid in the n.m.r. time scale. For mixtures of dimethylzinc and dimethylcadmium, in a series of solvents, the rate of exchange was significantly higher in donor solvents (292). On the other hand, it has recently been reported (223a) that the rates of exchange of alkyl groups between dialkylmagnesium compounds are retarded by solvents such as dimethoxyethane and tetramethylethylenediamine, but catalyzed by magnesium bromide. It has been suggested (292) that exchange of alkyl groups occurs by a mechanism involving an alkyl-bridged, four-center transition state (Eq. 4):



Such evidence as is available is in general consistent with this idea: (a) in the mixtures of dialkylmercury compounds, the mixed species RHgR' are produced, indicating that alkyl groups are transferred one at a time (137, cf. 350, 369), (b) the fact that rates of exchange are lower at higher dilution suggests a bimolecular rate-determining step (292), and it has been found that the exchange of methyl groups between dimethylmagnesium and methyl(cyclopentadienyl)magnesium is second order (first order in each reagent) (223a), and that the alkyl-exchange reaction between dialkylmagnesium and dialkylmercury compounds follows reversible second order kinetics (139), and (c) the effect of donor solvents could be to solvate the transition state (292). It has recently been observed (202) that methyl exchange in solutions of dimethylcadmium is strongly catalyzed by traces of alcohols or oxygen, and care must therefore be taken in interpreting many earlier results.

Besides being interesting and important in itself, the recent work on the configurational stability of the α -carbon atoms in alkyl derivatives of the Group II metals may furnish information on the mechanism of the alkyl-exchange reaction. Studies have also been made on the racemization of a series of optically active compounds of type XI, where $n = 1-4$ and $\text{M} = \text{Li}, \text{Mg}, \text{Be}, \text{Zn}, \text{Cd}, \text{B}, \text{Al}$ (273, 274). It was found that, except in the cases of beryllium, boron, and aluminum, racemization was not rapid

even at 100° (274). The behavior of the derivatives of the three exceptional metals may be ascribed to reactions of the type shown in Eq. (5), which are known to occur with these compounds (99). The case of the beryllium compounds is interesting, as the racemization observed in hexane solution is suppressed in dioxan solution, possibly because coordination of the metal prevents protophilic attack on the β -hydrogen atom

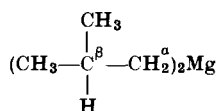


(274). These results seem to indicate that the reactions formulated in Eq. (5) are not in general important in alkyl-exchange reactions of the Group II metals.

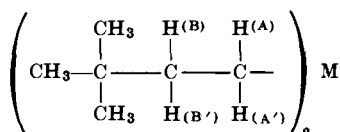


Although organomercury compounds with asymmetric α -carbon atoms are known (see, e.g., 220, 362), similar derivatives of the other Group II metals have not been authenticated,² save in the exceptional case of 2,2-diphenyl-1-methyl-1-cyclopropyl derivatives (124, p. 127; 456) where inversion at the α -carbon atom would be extremely difficult. However, recent studies on the proton magnetic resonance spectra of dialkyl derivatives of magnesium and other metals have shown that, even in systems where alkyl exchange might be expected to be rapid, and with alkyl groups where inversion at the α -carbon atom is not prevented, the α -carbon atom may be configurationally stable.

Studies have been made (164) on bis(2-methylbutyl)magnesium (XII) and bis(3,3-dimethylbutyl) derivatives (XIII). In the former compound



(XII)



(where M = Mg, Zn, or Hg)

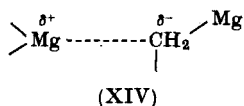
(XIII)

² When optically active bis(1,4-dimethylpentyl)mercury was allowed to react with the corresponding Grignard reagent, and the product carboxylated, the resulting acid was claimed to preserve a trace of optical activity (362).

(XII), the α -methylene protons are magnetically nonequivalent even when rotation about the $C^\alpha-C^\beta$ bond is fast, and at 0° in diethyl ether the proton magnetic resonance signal for the α -methylene protons corresponded to the AB portion of an ABX system. As the temperature was raised, the pattern changed to that for the A_2 portion of an A_2X system, and it was possible to calculate activation parameters for inversion at the α -carbon atom. Experiments on the dialkylmagnesium compounds in tetrahydrofuran or dioxan unfortunately gave inconsistent results, and reagents prepared from the Grignard reagent by precipitation with dioxan differed from those prepared from the dialkylmercury compound. However, all the data fitted the isokinetic relationship,

$$\Delta H^* = 370\Delta S^* + 19,400 \quad (6)$$

suggesting that there was a common inversion mechanism in all the solvents, and it was proposed that the kinetic data are best interpreted in terms of intermolecular electrophilic displacement on carbon (XIV). Unimolecular dissociation into free carbanions was ruled out for this system. Dineohexylmagnesium, -zinc, and -mercury (XIII) were studied



by Witanowski and Roberts (472). At 30° in diethyl ether, all three compounds had n.m.r. spectra of the $AA'BB'$ type. Dineohexylmercury preserved this pattern up to 150° , but at high temperatures the spectra for the other compounds coalesced to the A_2B_2 pattern. The activation energies for inversion at the α -carbon atom were calculated to be approximately $20 \text{ kcal mole}^{-1}$ for the magnesium compound and $26 \text{ kcal mole}^{-1}$ for the zinc compound. In contrast to Fraenkel's results, little difference was observed between the magnesium compound prepared from the Grignard reagent and that prepared from dineohexylmercury. Moreover, no change in inversion rate with concentration was observed, suggesting a unimolecular, S_E1 mechanism for inversion (or conceivably a reaction within a polymeric complex, whose degree of polymerization did not change over the concentration range studied).

Further information on the carbon-magnesium and carbon-zinc bonds comes from an analysis (268) of the proton magnetic resonance spectra of phenyllithium, diphenylmagnesium, and diphenylzinc in diethyl ether; the *ortho*-protons were, surprisingly, deshielded and this deshielding was accounted for in terms of the anisotropy of the carbon-metal bonds.

Clearly, more work remains to be carried out in this field. In particular, some attempt to correlate alkyl-exchange rates with rates of inversion would be valuable. [It has recently been reported (223*a*) that the rate of exchange of alkyl groups between 3,3-dimethylbutyl(cyclopentadienyl)magnesium and bis(3,3-dimethylbutyl)magnesium is substantially faster than the rate of inversion, and must therefore proceed with retention of configuration.] Some light may also be thrown on the n.m.r. studies by the results of more conventional investigations of the mechanisms of the reactions of metal alkyls [see (*b*) below].

b. Other Reactions. Three important types of reaction are briefly considered here: addition reactions (e.g., to carbonyl groups), electrophilic substitution reactions, and metallation reactions (which may be regarded as a special case of electrophilic substitution). All these reactions are affected by solvation, and the observed solvent effects have given valuable information on the reaction mechanisms. Unfortunately some results have to be treated with caution, as many trace impurities (especially metal halides and alkoxides) may have profound effects on reaction rates (e.g., see 202, 257, 454).

Although the addition of Grignard reagents to carbonyl compounds, nitriles, etc., has been intensively studied (24, 454) (see Section IV, B, 1*a* below), little quantitative work has been carried out on similar reactions of the dialkyl derivatives of the Group II metals. The reaction of di-*n*-butylmagnesium with acetone, methyl acetate, methyl trifluoroacetate, and *sec*-butyl crotonate was much slower in tetrahydrofuran than in diethyl ether (221, 223), which is consistent with the view (21, 27) that the rate-determining step in such reactions is displacement of a solvating molecule from the metal atom by the carbonyl oxygen. On the other hand, the reaction of di-*n*-butylmagnesium with azobenzene was somewhat faster in tetrahydrofuran than in diethyl ether.

No relevant studies of similar reactions of zinc and cadmium compounds have been made; in fact, pure dialkylzinc or -cadmium compounds do not normally react with carbonyl compounds, although they may do so in the presence of metal halides [86, 212; but see Chenault and Tatibouët (91)]. It may be relevant also that the complexes of dimethylzinc with 2,2'-bipyridyl, etc., are reported to be much less reactive toward oxygen than the uncomplexed reagents (102, 421).

In general, electrophilic substitution reactions involving dialkyl derivatives of the Group II metals proceed by bimolecular mechanisms. The classification of these mechanisms, as developed by a number of workers [leading references: (183, 232, 295)], has recently been refined and extended; Abraham and Hill (1) recently examined published data on a number of electrophilic aliphatic substitution reactions (including

metallation reactions), and classified them according to three mechanisms, which are designated S_E2 , S_Ei , and S_EC . The second of these (substitution, electrophilic, internal) could be further subdivided, as the reactions tended toward the other types of mechanism (substitution, electrophilic, bimolecular; substitution, electrophilic, via coordination). The crucial steps for the four types of mechanism are illustrated schematically in Fig. 1, where the reagent is represented as E-N. The appli-

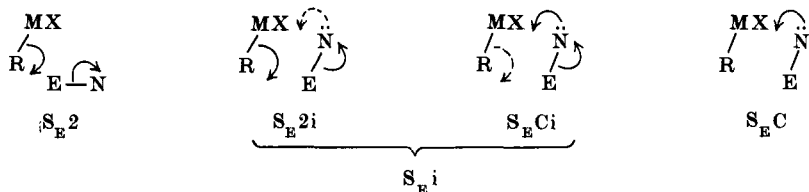


FIG. 1. Mechanisms of electrophilic aliphatic substitution reactions (cf. 1).

cation of this classification to the reactions of alkyl derivatives of the Group II metals is discussed below. However, a further mechanism, namely S_E1 , must first be mentioned. As even a benzyl derivative of an electropositive metal, magnesium, apparently gives rise to comparatively free carbanions only in a highly nucleophilic solvent, hexamethylphosphorotriamide (147), it might be expected that electrophilic analogs of S_N1 reactions will be rarely encountered. However, a few reactions of organomercury compounds have been found to proceed according to kinetics that indicate an S_E1 mechanism. These include the alkyl-exchange reaction between *p*-nitrobenzylmercuric bromide and mercuric bromide in dimethylsulfoxide (246), the reaction of β -chlorovinylmercuric chloride with iodine in dimethylsulfoxide (47, 48), and possibly the protolysis of dibenzylmercury [(46), see also (210a)] or phenylmercuric bromide (49) by hydrochloric acid in certain solvent systems. In these cases, ionization was favored by the nature of the organic groups and by the media, and the results have been interpreted (214) in terms of dissociation to an ion pair in the rate-determining step. [Some of these reactions could involve catalysis by halide ion (94) (Section VII,A below), and the present author suggests that the possibility should be considered that the rate-determining step in some of the reactions may conceivably involve dissociation of complexes between the organomercury compounds and the solvents.] In the one case where an S_E1 mechanism was claimed for a reaction of a simple dialkylmercury compound (the reaction between di-*sec*-butylmercury and diethylthallium bromide in dimethylformamide) (205, 232), it has now been shown that the original results were misinterpreted (238).

Numerous reactions of alkyl derivatives of the Group II metals may be cited as examples of the classification outlined above, but only a few representative ones are surveyed here. Most of the substitution reactions of alkylmercuric compounds proceed according to second order kinetics, and with retention of configuration. Further information on the mechanisms is obtained by a study of steric, polar, and solvent effects on the rate of reaction (1). For example, in the one-alkyl exchange reaction between alkylmercuric salts and mercuric salts, which proceeds according to these kinetics, added salts increased the rate constant (confirming an S_E2 mechanism), and the reaction rates were greatly influenced by the steric effect of the alkyl groups (227, 228). Polar solvents might lower activation energies for such reactions by solvating the transition states (1). On the other hand, in the reaction of dialkylzinc compounds with phenylmercuric chloride (leading to alkylphenylmercury compounds and alkylzinc chlorides), although the kinetics are as usual (first order in each reactant), it has proved difficult under some conditions to disentangle solvent, polar, and steric effects on the reaction rates (5). However, for the reaction in diethyl ether at 35°, the rate depended on the polar effect of the alkyl group, and the S_Ei (probably S_ECi) mechanism was proposed.

Very striking solvent effects have been observed in a number of metallation reactions. In general, these are accelerated by increasing solvation, suggesting that carbanionic attack is dominant, although, for some reactions of Grignard reagents with 1-alkynes, increasing solvation appears to decrease the rate of reaction³ (206, 481). Thus, Russian workers have found that methylmagnesium bromide is more reactive in metallating 1-alkynes in more strongly electron-donating solvents (492), that diethylzinc scarcely reacts with phenylacetylene in heptane but does react in strongly donating solvents (323), and that diethylcadmium reacts with phenylacetylene only slowly even in 1,2-dimethoxyethane but more rapidly in more strongly donating solvents (e.g., dimethylsulfoxide) and much more rapidly in the presence of complexing agents such as 2,2'-bipyridyl (324). Analogous phenomena have been noted (197) in the metallation of decaborane by dialkylzinc and -cadmium compounds: the rate of reaction depended on the solvating power of the solvent.

Investigations on metallation using one of the most strongly nucleophilic solvents known, hexamethylphosphorotriamide, have yielded very striking results. Hydrocarbons such as toluene are normally metallated

³ In these cases, the kinetics of the reactions were not straightforward, and the situation was complicated by the possibility that the solutions contained several types of organomagnesium species (see Section IV, B, 1a below).

only by organosodium and organopotassium compounds, but in "hexa-metapol" they undergo metallation even by Grignard reagents (126).

Metallation by Grignard reagents involving metal-halogen exchange (the above examples involving metal-hydrogen exchange) is also reported to be promoted by strongly electron-donating solvents (492).

C. BIS(PERHALOGENOALKYL) DERIVATIVES

The perfluoroalkyl and perfluoroaryl derivatives of the Group II metals have recently aroused particular interest, partly as a consequence of the general interest in fluoro-organic chemistry, and partly because of the influence of fluorine substitution in increasing the polarization of carbon-metal bonds. General reviews have been published on fluoro-carbon derivatives of metals (415, 438), on pentafluorophenyl derivatives of the elements (87), and on Grignard and organolithium reagents derived from di- and polyhalogen compounds (209).

No perfluoroalkyl derivatives of beryllium, calcium, strontium, or barium have been recorded. A number of perfluoro-organomagnesium compounds (generally the perfluoroalkylmagnesium halides) has been prepared as solutions in ethers, where they are presumably solvated (438, pp. 150-153; 87, pp. 281-282; 209). Polyfluorophenyl derivatives of magnesium are particularly readily accessible, as the hydrogen atom in a compound such as pentafluorobenzene is sufficiently acidic to be replaced by magnesium when allowed to react with an alkylmagnesium halide (204). The rate of exchange of pentafluorophenyl groups attached to magnesium is slow on the n.m.r. time scale in diethyl ether at 22° (see Section IV, B, 1a below), and thus it was possible to distinguish $C_6F_5Mg(hal)$ and $(C_6F_5)_2Mg$ species in solutions of pentafluorophenylmagnesium halides (153).

Very few perfluoroalkyl derivatives of zinc and cadmium have been reported (438, pp. 200 and 201; 87, p. 297). Those reported are perfluoroalkylmetallic halides, with the exception of bis(pentafluorophenyl)zinc and -cadmium. Both these compounds form stable complexes with ligands such as 2,2'-bipyridyl (319, 375a), and the zinc compound forms a moderately stable diethyl etherate (318). Bis(perfluoroalkyl)mercury compounds have been synthesized by a number of interesting routes, including the reaction of tris(perfluoroalkyl)phosphines with mercuric oxide (198), the addition of mercuric fluoride to perfluoroalkenes (13, 264, 294, 296, 482), pyrolytic decarboxylation of mercuric salts of perfluoro-alkanecarboxylic acids (118-120), and reaction of perfluoroaryl iodides with mercury (57, 117). In contrast to the unsubstituted dialkylmercury compounds, the perfluoro derivatives form complexes with strong electron donors (see Section II, B, 1e above). Bis(tetrafluoro-4-pyridyl)-

mercury, as expected for such exceptionally electronegative organic groups, forms a stable complex with 2,2'-bipyridyl (89). There is also evidence that bis(trifluoromethyl)mercury (which is soluble in water) forms labile 1:1 complexes with halide ions in aqueous solution (144, 145, 151) (see Section VII,A below).

The crystal structure of bis(pentafluorophenyl)mercury differs from that of the simple diarylmercury compounds in that the C-Hg-C angle is $176.2 \pm 1.2^\circ$ instead of 180° , and the rings are not coplanar (266). Bis-(pentafluorophenyl)mercury (88) is highly stable to heat and undergoes displacement of the *para*-fluorine atoms by certain nucleophiles (such as hydroxide and methoxide ions) without the carbon-mercury bond being affected (84) although, with halogens, hydrazine, and lithium aluminum hydride (84), cleavage of carbon-mercury bonds occurs. [Cleavage also occurs very readily with iodide ion in aqueous ethanol (129).] It does not readily undergo transmetallation reactions, and failed to react with zinc or cadmium (83).

The novel chemistry of the pentafluorophenyl derivatives of the metals has tended to overshadow studies of the corresponding pentachlorophenyl derivatives. Pentachlorophenyl derivatives of magnesium (341, 348) and mercury (130, 339) have been reported, however, and some of their reactions investigated, and there are already indications that the chemistry of the pentachlorophenyl compounds may differ considerably from that of the pentafluorophenyl compounds. For example, complexes of bis(pentachlorophenyl)mercury with 2,2'-bipyridyl or 1,10-phenanthroline could not be obtained (although an unstable complex with 3,4,7,8-tetramethyl-1,10-phenanthroline was isolated) (130). The interesting suggestion has been made (339) that, in pentachlorophenylmercury derivatives, intramolecular donor-acceptor interaction is possible between the *o*-chlorine atoms and mercury, and the nuclear quadrupole resonance spectra of pentachlorophenylmercuric chloride and bis-(pentachlorophenyl)mercury give some support to this idea (68a, 490).

It is convenient to mention at this point the extensive studies on the use of metallic derivatives of polyhalogen compounds in synthesis, especially as sources of reactive intermediates—arynes and carbenes. *o*-Halogenophenylmagnesium halides are widely used precursors of arynes (209, 210), and a number of α -halogenoalkyl derivatives of the Group II metals have been used as methylene-transfer agents. [The problem of establishing whether free carbenes are intermediates in some or all of these methylene transfer reactions (209, reference 44) will not be discussed here.] Leading references are as follows: (1) magnesium derivatives (209, 446, 447, 478), (2) zinc derivatives (61, 236, 275, 384, 395, 450, 479), and (3) mercury derivatives (60, 269, 270, 334, 368, 385, 386).

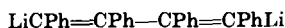
D. DIALKENYL DERIVATIVES

1. 1-Alkenyl Derivatives

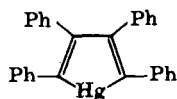
Compounds of the general formula $R \cdot CH=CH-M-X$ (where M represents a Group II metal) are of interest because of the possibility of interaction between the π -electrons of the C=C bond and vacant orbitals of the metal atom. Such interaction would be most apparent in the absence of electron-donating solvents, but, although many vinyl and other 1-alkenyl derivatives have been prepared, they have almost all been solvated. There is thus little evidence so far for such interactions, and in a related series, the ultraviolet (196) and n.m.r. (7a) spectra of arylmercury compounds show little or no evidence for resonance interaction between mercury and the π -system.

When the chemistry of vinylmetallic compounds was reviewed in 1962 (383), the only divinyl derivatives of the Group II metals that had been isolated were divinylzinc (36) and divinylmercury (34, 37, 308, 370). The synthesis of divinylcadmium from divinylmercury and cadmium has since been reported in a patent (163), although an earlier attempt, using vinylmagnesium bromide and cadmium chloride, was unsuccessful (35). Divinylmagnesium, -beryllium, -calcium, -strontium, and -barium have not been described. Dipropenyl- and diisopropenylmercury are known (301), and evidence has been obtained for a number of diallenic zinc compounds (177). A few more of the 1-alkenylmetallic halides have been reported (discussed in Section IV), but the structural chemistry of these compounds remains a potentially profitable field for investigation. The only detailed studies have been of the mercury derivatives, which proved particularly amenable to investigation by n.m.r. Exchange of alkyl groups in these compounds is slow on the n.m.r. time scale, and the spectra show splitting of the proton resonance signals by $^1H-^{199}Hg$ coupling. The spectra of divinylmercury (297) and of bis(*cis*-propenyl)-, bis(*trans*-propenyl)-, and bis(isopropenyl)mercury (301) have been analyzed. The spectra were consistent with simple, monomeric molecules, with chemical shifts of the orders predicted. In the cases of the propenyl derivatives, the $^1H-^{199}Hg$ coupling constants provided evidence for the absolute configurations of the molecules.

The claim (68) that the major product from the reaction of the dithio compound XV with mercuric chloride has the structure XVI seems to need further justification, particularly in view of the inconsistent molecular weight data (cf. 95, pp. 80 and 81); the first cyclic, monomeric organomercury compounds to be authenticated contain eleven-membered rings (28a).



(XV)



(XVI)

(Some aspects of reactions involving electrophilic substitution at unsaturated carbon are reviewed in Section IV.)

2. *Bis(allylic) and Bis(cyclopentadienyl) Derivatives*

These compounds are of great interest because several different types of bonding may be envisaged for them. Thus, for example, an allyl derivative could exist in an ionic form, with the allyl anion stabilized by charge delocalization; as a σ -bonded covalent compound; or as a π -bonded complex. In fact there is some evidence for all three types of constitution.

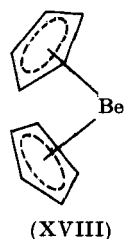
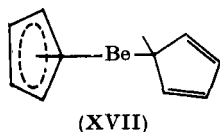
a. Allylic Derivatives. The diallyl derivatives of beryllium, calcium strontium, and barium have not been reported, and diallylmagnesium has been obtained only in solution (11, 467). The extensive work on allylmagnesium halides is reviewed (Section IV, B, 1b below), but as an example of one of the extremes of the possible structural types we mention here the recent evidence that, in very strongly electron-donating solvents (e.g., hexamethylphosphorotriamide), 2-butenylmagnesium bromide exists almost entirely as a salt of the *cis*-2-butenyl carbanion (8, 9). Several bis(allylic) derivatives of zinc (423, 426, 431) and cadmium (425) have been obtained as pure solids via the reaction of the dimethyl derivatives with tris(allylic)boron compounds. At room temperature, the proton magnetic resonance spectra of these compounds (and of diallylmagnesium) (467) indicated that the α - and γ -protons were magnetically equivalent (425, 431), and protolysis of the dicrotyl derivatives gave a mixture of 1- and 2-butenes (11, 177, 425). It was thus not possible to distinguish between π -allylic structures or rapidly equilibrating σ -bonded structures. (Ionic structures seem highly unlikely in these instances.) However, it has been reported (467, 468) that at -100° , the proton magnetic resonance spectrum of diallylzinc is that of a σ -allyl derivative, with no isomerization to the propenyl derivative. Furthermore, a recent analysis of the n.m.r. spectra of dicrotylzinc and bis(2-methylallyl)zinc revealed that the former compound had a spectrum of the ABX_3Y_2 type, corresponding to a σ -bonded crotyl derivative (423).

The protolysis of dicrotylmagnesium resembles that of the corresponding Grignard reagent (see Section IV, B, 1b), and gives a mixture of butenes in proportions depending on the nucleophilicity of the solvent (11). On the other hand, the proportions from the zinc and cadmium

derivatives were relatively unaffected by the solvating power of the solvent (177), and the unlikelihood of ionic structures for these reagents was thus confirmed. Although these protolysis studies gave little information regarding the possible solvation of the zinc and cadmium reagents, bis(allylic) derivatives of zinc (423, 424) and cadmium (425) do form stable complexes with 2,2'-bipyridyl.

Diallylmercury at ambient temperatures gives an n.m.r. spectrum corresponding to a "frozen" σ -allyl structure, but, on the addition of salts such as mercuric halides, rapid interconversion of allyl and propenyl groups occurs, leading to a spectrum of the AX_4 type (349).

b. *Cyclopentadienyl Derivatives*. Bis(cyclopentadienyl)derivatives of beryllium, magnesium, calcium, and mercury have been prepared. There is also a patent reference (71) to compounds of the formula C_5H_5ZnR (where $R = Et, Ph, tert-Bu$), but no information has been given on the structure or reactions of these compounds.



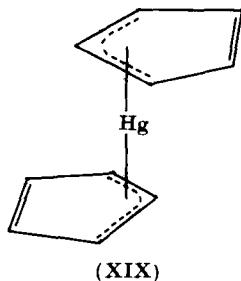
Bis(cyclopentadienyl)beryllium attracted interest from its first preparation (from cyclopentadienylsodium and beryllium chloride), because of its high dipole moment ($\mu_{25^\circ} = 2.46 \pm 0.06$ D in benzene, 2.24 ± 0.09 D in cyclohexane) (159). The infrared (169) and far-infrared (170) spectra of the compound were analyzed, in an attempt to reconcile them with structures such as XVII and XVIII that would account for the high dipole moment. However, it was subsequently found that in the crystal, bis(cyclopentadienyl)beryllium had a centrosymmetric molecular structure, with a lattice in the same space group as ferrocene (377); electron diffraction measurements on gaseous bis(cyclopentadienyl)beryllium confirmed that the molecule had a "sandwich" structure with planar, symmetrical, staggered C_5H_5 rings (19). The molecule was considered to be largely ionic, accounting for the high dipole moment. The electron diffraction study (19) further revealed the most interesting feature of the structure of the molecule: the beryllium atom occupies two alternative positions on the common axis of the rings, 1.485 ± 0.005 Å from one ring and 1.980 ± 0.010 Å from the other. The infrared spectra of

the solid and of solutions have now been reconciled with the structure found by electron diffraction (171).

Bis(cyclopentadienyl)magnesium is a well-known compound, being readily prepared from cyclopentadienylmagnesium halides (469) or by the direct reaction of magnesium with cyclopentadiene (30). However, although it appears to be similar to bis(cyclopentadienyl)beryllium in physical and spectroscopic properties (169, 170, 229), its molecular structure has not been determined. Bis(cyclopentadienyl)magnesium is a very valuable intermediate in the preparation of cyclopentadienyl derivatives of other metals (58, 360, 361), and bis(cyclopentadienyl)beryllium was used to prepare the first organometallic derivative of plutonium, tris(cyclopentadienyl)plutonium (42).

Bis(cyclopentadienyl)calcium has been prepared by the reaction of cyclopentadiene with calcium carbide (497, 498). A few reactions of this compound were reported, but its structure has not been investigated.

The constitution of bis(cyclopentadienyl)mercury, a somewhat unstable solid prepared from cyclopentadienylsodium and mercuric chloride (470), is a subject of controversy. It has been argued (470, 471) from the fact that the compound forms an adduct with maleic anhydride and from its spectroscopic properties (infrared, ultraviolet, n.m.r.) that it possesses a σ -bonded structure. However, the interpretation of both the chemical and the spectroscopic evidence has been questioned (309). A comparison of the proton magnetic resonance data recorded by the two groups of workers is instructive. Nesmeyanov and his co-workers record a singlet, with no signs of fine structure even at 200°K (146, 309), while Wilkinson and Piper (471) recorded a singlet at approximately -5.6 ppm relative to tetramethylsilane, with a broad shoulder at approximately -5.3 ppm.⁴ It is possible that the explanation for the observed discrepancies may lie in the effect of traces of mercury salts on the rate



⁴ The reference (471) gives chemical shifts of 1.5 and 1.8 ppm relative to the aromatic protons of toluene, which have here been taken as having a chemical shift of -7.17 ppm relative to tetramethylsilane.

of interconversion of different forms of the molecules (cf. 349). Besides a tautomeric σ -bonded system and a π -cyclopentadienyl structure, a third possibility involving π -allylic bonding (XIX) has been suggested (121). The problem remains unresolved, although a very recent communication (284a) reports that in sulfur dioxide at -70° , the n.m.r. spectrum of bis(cyclopentadienyl)mercury does show splitting consistent with a σ -bonded structure.

3. 1-Alkynyl Derivatives

Besides the acetylides and carbides (not discussed here), a number of noteworthy bis(1-alkynyl) derivatives of the Group II metals have been described.

It has recently been reported (342) that concentration of solutions of "phenylethynylmagnesium bromide" in tetrahydrofuran yields a mixture of two stereoisomers of a complex of bis(phenylethynyl)magnesium with four moles of solvent. A series of 1-alkynyl derivatives of zinc and cadmium has been described by Nast and his co-workers (303, 305). These include crystalline compounds of the formula $(\text{Ph}\cdot\text{C}\equiv\text{C})_2\text{M}$, prepared by the reaction of the diphenyl derivatives of the metals with phenylacetylene in liquid ammonia. Both the zinc and the cadmium compounds are soluble in liquid ammonia, and the zinc compound forms a crystalline complex, $(\text{Ph}\cdot\text{C}\equiv\text{C})_2\text{Zn}\cdot 2\text{NH}_3$ at -78° . Alkylethynyl-mercury compounds, $\text{R}\cdot\text{Hg}\cdot\text{C}\equiv\text{CH}$, have also been reported (259).

E. COMPLEX ORGANOMETALLIC ANIONS

It has long been recognized (95) that dialkylzinc compounds form complexes with alkyl derivatives of the more electropositive metals, and from the compositions of the complexes and their electrochemical properties they have been formulated as salts of alkylzinc anions. A largely ionic structure, $\text{Li}^+[\text{AlEt}_4]^-$, has been confirmed for the analogous lithium tetraethylaluminate (181), and the stability of the tetraethylaluminate anion has recently been manifested in the observation that the n.m.r. spectrum of the lithium salt in dimethoxyethane shows ^1H — ^{27}Al spin-spin coupling (327).

Complexes similar to the zinc derivatives are formed by some of the other Group II metals, and are described below. The more electropositive metals of the group (magnesium, calcium, strontium, barium) can also function as the positive counterions. Complexes of the type described here have been classified as "ate" complexes (473), and the importance of such complexes in the reactions of organometallic compounds is beginning to be realized (435, 474).

1. Alkylberyllium and Alkylmagnesium Anions

Both diphenylberyllium and diphenylmagnesium react with phenyllithium to form complexes, LiMPh_3 . The beryllium complex may be isolated as a crystalline etherate, but the magnesium complex dissociates in diethyl ether (477). In contrast, a study of the ^1H and ^7Li n.m.r. spectra of mixtures of methyllithium and dimethylmagnesium in diethyl ether suggests that species such as $\text{Li}_2\text{Mg}(\text{CH}_3)_4$ and $\text{Li}_3\text{Mg}(\text{CH}_3)_5$ are present, rather than the simple 1:1 complexes (381). In the analogous phenyl system, some of the complex Li_2MgPh_4 is present, but not the 3:1 complex (382). In the mixed systems, methyllithium plus diphenylmagnesium or phenyllithium plus dimethylmagnesium, mixed 2:1 complexes, $\text{Li}_2\text{MgMe}_{4-n}\text{Ph}_n$, were observed, and there was a tendency for the phenyl groups to be involved in these complexes, rather than in those of the type $\text{Li}_4\text{Me}_3\text{Ph}$ found in mixtures of methyllithium with phenyllithium (382a). Very recently, a crystalline 2:1 complex of methyllithium with dimethylberyllium (460b) and a liquid 1:1:1 complex of *n*-butyllithium, dimethylmagnesium and diethyl ether (104a) have been isolated; the crystal structure of the beryllium complex contains BeMe_4 groups, with the methyl groups at the corners of distorted tetrahedra (460b).

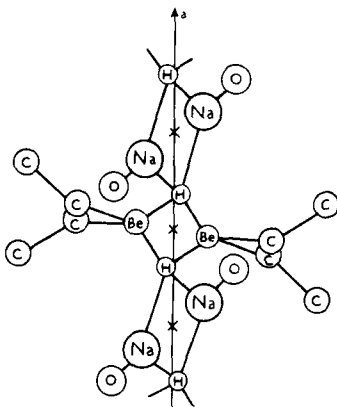


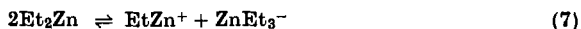
FIG. 2. Crystal structure of the etherate of sodium hydridodiethylberyllate. [Reproduced from Adamson and Shearer (7) by permission of the Chemical Society and the authors.]

Dialkylberyllium compounds also react with alkali-metal hydrides (96, 475) to form complex hydrides, which have been formulated as salts of $[\text{HBeR}_2]^-$ anions. However, in the solid state the etherate from the interaction of sodium hydride and diethylberyllium in diethyl ether has the dimeric structure shown in Fig. 2 (see Section III below) (7).

Complexes of diethylberyllium with various salts such as alkali-metal fluorides or cyanides and tetraalkylammonium salts have been described (406, 408). These are of variable composition (ratio of diethylberyllium to salt from 1:1 to 4:1 or higher) and unknown structure. Their solutions in ethers and in hydrocarbons conduct electricity⁵ (408), suggesting ionic structures. Electrolysis of the complexes results in deposition of beryllium carbide and beryllium at the cathode (407).

2. Alkylzinc Anions

Dialkylzinc compounds are particularly characterized by their tendency to form complex alkylzinc anions. In fact liquid diethylzinc itself has a slight electrical conductivity, consistent with ionization as represented in Eq. (7) (235), and a complex of ethylsodium and diethylzinc was among the earliest organometallic compounds known (457). The



ability of dialkylzinc compounds to form complexes of this type even in nonpolar solvents has recently been illustrated by an n.m.r. study of mixtures of ethyllithium and diethylzinc in benzene, which revealed the presence of the 1:1 complex, LiZnEt_3 (436).

From the large number of examples reported, it seems that complex formation is the general rule for combinations of the alkyl derivatives of the alkali metals, calcium, strontium, and barium, with dialkyl- and diarylzinc compounds. [Leading references to these complexes: (187, 190, 200, 230, 344, 457, 477).] The complexes of dialkylcalcium, -strontium, and -barium compounds are of interest (187, 190), as the uncomplexed derivatives of the alkaline earth metals are unknown (see Section II,A,1a above). With phenyllithium, diphenylzinc is reported (477) to form a second complex, $\text{Li}_3\text{Zn}_2\text{Ph}_7$, and n.m.r. studies (381) indicate that, in diethyl ether, complexes such as $\text{Li}_2\text{Zn}(\text{CH}_3)_4$ and $\text{Li}_3\text{Zn}(\text{CH}_3)_6$ may be formed. The complex, $\text{Li}_2\text{Zn}(\text{CH}_3)_4$, has very recently been isolated, and its crystal structure determined; the structure contains tetrahedral $\text{Zn}(\text{CH}_3)_4$ groups (460a). Lithium hydride reacts with diphenylzinc in diethyl ether to form a crystalline monoetherate of $\text{Li}[\text{HZnPh}_2]$, analogous to the beryllium complex [475].

3. Alkylcadmium and Alkylmercury Anions

Cadmium and mercury show much less tendency than zinc to participate in alkylmetallic anions. The only mercury compounds of this type

⁵ These results are in conflict with an earlier report (480) that the conductivity of solutions of dimethylberyllium in diethyl ether was not markedly increased by the addition of salts.

that have been characterized are 1-alkynyl derivatives, such as $\text{Ba}[\text{Hg}(\text{C}\equiv\text{C}-\text{R})_4]$ (304); similar derivatives of cadmium have been prepared (305). There is apparently little interaction between phenyllithium and diphenylcadmium in diethyl ether, although a crystalline complex was obtained on the addition of dioxan to the solution (477); ethyllithium and diethylcadmium form a solvated 1:1 complex in tetrahydrofuran, but not in benzene (436). It seems likely that there is complex formation between diphenylbarium and diphenylcadmium (186). No evidence has been obtained for the existence of complexes between phenyllithium and diphenylmercury (477).

It would be of interest to know whether complex formation takes place between organolithium compounds and bis(perfluoroalkyl)-mercury compounds.

4. Salts of Group II Metal Cations

Some calcium, strontium, and barium salts of tetraalkylzincate ions were mentioned above. Besides the Group II metals, several others are capable of participating in complex organometallic anions, and the alkaline earth metals and magnesium are sufficiently electropositive to function as the cations in "ate" complexes. Thus, for example, complexes such as $\text{Mg}[\text{AlMe}_4]_2$ (499) and $\text{Ca}[\text{AlEt}_4]_2$ (and the corresponding strontium and barium compounds) have been reported (277, 277a).

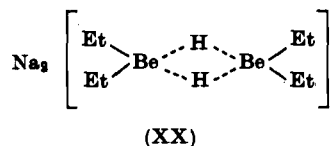
III. Compounds Containing the System C-M-H; the Alkylmetallic Hydrides

A number of alkylberyllium hydrides have been reported during the last few years, and these give indications of providing a promising field for study. Alkylmagnesium hydrides may also exist, although they have not yet been characterized, and one phenylzinc hydride has been reported.

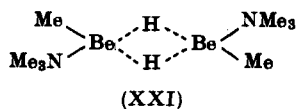
A. ALKYLBERYLLIUM HYDRIDES

In 1952 Wittig and Hornberger reported briefly that lithium hydride reacted with ethereal diphenylberyllium to give a crystalline complex, which they formulated as $\text{Li}[\text{BePh}_2\text{H}] \cdot \text{Et}_2\text{O}$ (475). Ten years later, Coates and Cox reported similar complexes, such as $\text{Na}[\text{BeEt}_2\text{H}]$, from diethylberyllium and sodium hydride (96). Complexes were also formed between dimethylberyllium and sodium hydride and between diethylberyllium and lithium hydride. Diethylberyllium did not react with magnesium hydride.

The sodium hydride-diethylberyllium complex was believed to be unsolvated, and a dimeric structure (XX) with hydrogen bridges was suggested. A subsequent X-ray crystallographic study has confirmed this hypothesis, except that the crystals did in fact contain two moles of ether in each dimeric unit, as illustrated in Fig. 2 (7).



Coates and his co-workers have now reported a range of alkylberyllium hydride derivatives. Treatment of the dialkylberyllium-sodium hydride complexes with ethereal beryllium chloride gave solutes with compositions corresponding to the formula $\text{Be}_3\text{R}_4\text{H}_2$ (53, 96). On evaporation of ether from a solution of " $\text{Be}_3\text{Me}_4\text{H}_2$," dimethylberyllium was lost, leaving hydride-rich residues (51, 53). When donor molecules were added to the solutions, mixtures of solvated dialkylberyllium compound and solvated alkylberyllium hydride were obtained (51, 53). The latter were dimers, with compositions such as $(\text{BeEtH} \cdot \text{Me}_3\text{N})_2$ (from ethylberyllium hydride and trimethylamine). Ethereal solutions of " RBeH " were also formed from dialkylberyllium compounds and trialkyltin hydrides (51) and from ethylberyllium bromide and lithium hydride (52). Hydrogen-bridged structures, such as XXI, were proposed for the dimers, and a comparison of the infrared (51) and n.m.r. (55) spectra of the complexes and of their deuterium analogs has confirmed

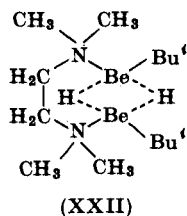


the hypothesis. The n.m.r. signals due to the methyl protons of $(\text{BeMeH} \cdot \text{Me}_3\text{N})_2$ showed splitting, which varied with temperature; this splitting was ascribed to *cis-trans* isomerism about the hydride bridge, and values of ΔH and ΔS were calculated for interconversion of the isomers (55). Some alkylberyllium hydride complexes may be prepared directly (116). Thus, the trimethylamine complex of phenylberyllium hydride is prepared in one stage from diphenylberyllium, beryllium chloride, sodium triethylborohydride, and trimethylamine, and is a

dimer, $(\text{BePhH} \cdot \text{Me}_3\text{N})_2$, in benzene (116); the analogous complex with trimethylphosphine in place of trimethylamine dissociates in benzene solution. Similarly, the trimethylamine complex of methylberyllium hydride is obtained by the reaction of dimethylberyllium, triethylstannane, and trimethylamine in the presence of diethyl ether.

Some reactions of the alkylberyllium hydride derivatives have been reported (52, 116). The simple etherates reduce carbonyl compounds (see also Section V, A below), and several of the hydrides (e.g., sodium diethylberyllium hydride, ethylberyllium hydride etherate) add to alkenes.

It seems likely (see Section II, B, 2a) that, on heating, dialkylberyllium compounds may decompose to beryllium hydride and alkenes via alkylberyllium hydrides, and pyrolysis of diisopropylberyllium does indeed give isopropylberyllium hydride (98). It has recently been reported (372) that thermal decomposition of di-*tert*-butylberyllium leads to isobutylberyllium hydride, which forms a 2:1 complex (XXII) with tetramethylethylenediamine. It has been suggested (194) that a polymeric substance with the composition $(\text{HBeCH}_2\text{CH}_2\text{BeH})_n$ is formed when diethylberyllium is pyrolyzed.



B. ALKYL DERIVATIVES OF OTHER GROUP II METAL HYDRIDES

It has been suggested (41) that the ethoxymagnesium hydride formed when diethylmagnesium in diethyl ether is treated with silane arises from fission of the solvent by ethylmagnesium hydride. It seems possible that alkylmagnesium hydrides may also be intermediates in the pyrolysis of dialkylmagnesium compounds (the end products including magnesium hydride and alkenes) (247, 466). Such compounds have not yet been isolated, and hence nothing is known about their structures.

The only other recorded member of this class of compounds is a crystalline product, formulated as $\text{Li}[\text{ZnPh}_2\text{H}] \cdot \text{Et}_2\text{O}$, from the interaction of lithium hydride with diphenylzinc in diethyl ether (475). It seems likely that this complex has a structure similar to that of the analogous beryllium complexes.

IV. Compounds Containing the System C-M-Halogen; the Alkylmetallic Halides

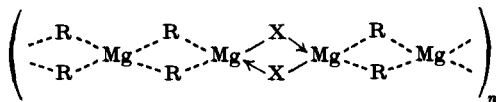
Representatives of this class of compound, the Grignard reagents, are of course the most familiar of all organometallic compounds. However, significant advances have been made in recent years in the study both of the Grignard reagents and of other compounds of the class.

A. UNSOLVATED ALKYLMETALLIC HALIDES

The Grignard reagents are *solvated* alkylmagnesium halides, from which it is almost impossible to remove solvent molecules (95, p. 52; 412, 413). Furthermore, alkylmetallic halide derivatives of the Group II metals often tend to disproportionate to the metal halide and the dialkyl derivative of the metal; thus, for example, the reaction of beryllium chloride with unsolvated *n*-butylmagnesium iodide led to di-*n*-butylberyllium (192). However, the alkylmercuric halides are well known, and unsolvated alkylmagnesium, alkylcadmium, and alkylzinc halides have been prepared and studied.

1. Alkylmagnesium Halides

The pioneering work of Bryce-Smith and his co-workers, followed by Zakharkin and his colleagues, on unsolvated alkylmagnesium halides has been reviewed (454). Their results may be briefly summarized as follows. Under carefully controlled conditions, *n*-alkyl- and arylmagnesium chlorides, bromides, and iodides may be readily prepared in nondonor



(XXIII)

solvents, by the direct reaction of magnesium with the alkyl or aryl halide (74-76, 79, 493, 494, 496). In general, the unsolvated reagents resemble the conventional Grignard reagents in their reactions, although some significant differences have been noted [see Wakefield (454)]. The compositions and structures of the unsolvated alkylmagnesium halides are so far ill-defined; they generally contain an excess of C-Mg over C-halogen bonds, and may have polymeric structures of type XXIII (74).

Since the review (454) referred to, little further has been published on the subject. *n*-Pentylmagnesium compounds have been prepared in benzene solution (191). Di-*n*-pentylmagnesium was soluble in this solvent, and the *n*-pentylmagnesium halides tended to disproportionate, depositing magnesium halide. In the case of the iodide, disproportionation did not proceed to completion, and the material remaining in solution was a polymer with the empirical formula R_5Mg_3I . Unsolvated alkylmagnesium halides (of unknown constitution) have also been prepared via adsorption of gaseous alkyl halides on magnesium films (180).

The crystal structure of material prepared by desolvation of some ethereal alkylmagnesium halides was found to be that of a mixture of dialkylmagnesium compound and magnesium halide (458); this finding does not necessarily apply to alkylmagnesium halides prepared in the absence of donor solvents.

In an investigation of the Wurtz-type side reaction occurring during the preparation of unsolvated alkylmagnesium halides, Bryce-Smith and Cox showed, by using cumene as a radical trap, that free radicals were formed in the reaction mixture (75). In a recent study (495), Russian workers found that thermal decomposition of unsolvated alkylmagnesium halides led to alkenes, but not to free radicals. In the presence of an alkyl halide, however, radicals derived both from the alkylmagnesium halide and from the alkyl halide were formed; homolytic reactions of this type were suppressed in donor solvents. Some alkyl-exchange reactions were also noted, *n*-butylmagnesium iodide and methyl iodide in heptane at 80° giving some methylmagnesium iodide.

2. Alkylzinc Halides

The classical synthesis of diethylzinc (167) involved the disproportionation of ethylzinc iodide. However, the disproportionation is apparently reversible (Eq. 8), as the reaction of zinc iodide with an excess of diethylzinc leads to a crystalline solid with the composition $EtZnI$ (235):



Ethylzinc bromide and ethylzinc chloride have recently been prepared via the reaction of diethylzinc with the zinc halides (65). The ethylzinc halides were crystalline, sharp-melting solids. The bromide and chloride gave clear solutions in hydrocarbon solvents, although ethylzinc iodide was soluble in nonpolar solvents only in the presence of diethylzinc; in its absence, the solutions deposited zinc iodide (64). [Ethylzinc iodide dissolves in diethylzinc to give a slightly conducting solution (235).] The preparation of unsolvated alkylzinc halides by removal of solvent from the solvated reagents has been described (174, 331), but no information

(apart from C and H analyses) was given on the constitution of the products.

Ethylzinc chloride and bromide are tetrameric in benzene solution, and a cubic arrangement of zinc and halogen atoms (Fig. 3) has been suggested for the tetramers (65).

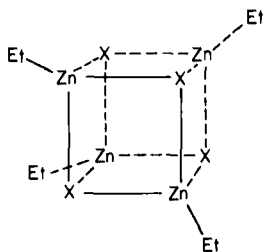


FIG. 3. Ethylzinc halide tetramers (X = Cl, Br) (65).

A recent determination (300) of the crystal structure of unsolvated ethylzinc iodide disclosed the presence of polymeric chains, with iodine bridges between the zinc atoms (Fig. 4).

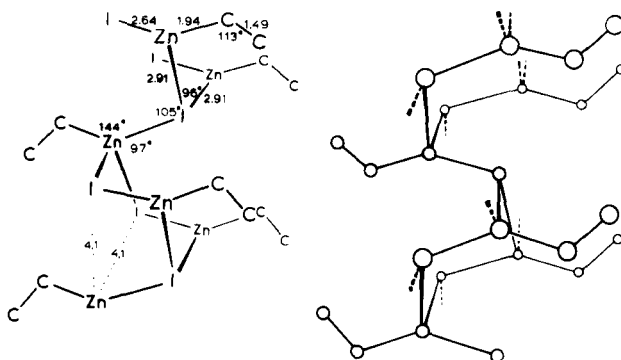


FIG. 4. Crystal structure of ethylzinc iodide. [Reproduced from Moseley and Shearer (300) by permission of The Chemical Society and the authors.]

Proton magnetic resonance studies on hydrocarbon solutions of the ethylzinc halides (64) showed that there was exchange of ethyl groups, and confirmed that in the cases of the chloride and bromide the equilibrium (Eq. 8) lay almost entirely to the right. For ethylzinc iodide, the situation was complicated by the precipitation of zinc iodide referred to above.

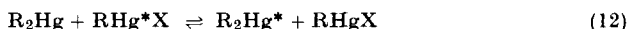
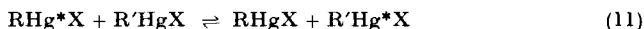
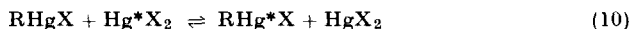
3. Alkylcadmium Halides

Few investigations comparable to those on the unsolvated alkylzinc halides have been carried out on the corresponding cadmium compounds. However, compounds with the composition of alkylcadmium halides (RCdX) have been isolated (390), although their structure has not been established.

Alkylcadmium halides are only sparingly soluble in diethyl ether and dioxan (254), and are thus presumably only weakly, if at all, solvated by these solvents. (However, the chemistry of solutions of "alkylcadmium halides" in donor solvents is reviewed in Section IV,B,2*d* below.)

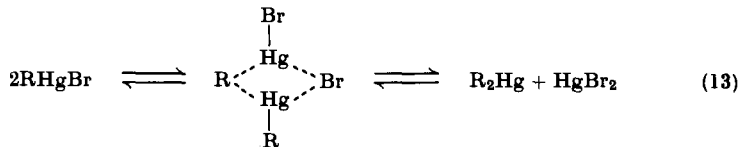
4. Alkylmercuric Halides

The simple alkylmercuric halides are well-known compounds, with properties consistent with largely covalent, monomeric structures (95). There is little in their structural chemistry that can be included under the heading "recent advances." However, certain aspects of their reactions continue to attract attention. These include the mechanisms of their substitution reactions, and the possible formation of complex salts of the alkylmercuric ion (see Section VII,A below for a discussion of the latter). A detailed survey of the extensive work on the mechanisms of the substitution reactions is beyond the scope of this article, and in any case this topic has been the subject of recent reviews (44, 124, 232, 364, 365) (see also Section II,B,2 above). However, in view of the current interest in the interactions between the alkylmetallic halide, metal halide, and dialkyl derivatives of the other Group II metals, some of the recent conclusions concerning the interactions of such mercury compounds are summarized here. These studies have been noteworthy for the difficulties involved in obtaining results from which unambiguous conclusions could be drawn, and indeed in obtaining reproducible experimental data. Reactions of the types shown in Eqs. (9–12) have been studied,

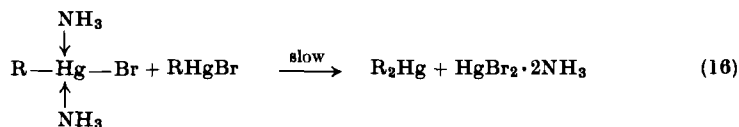
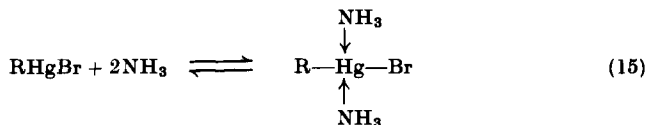


where X = halogen, and Hg^* represents labeled mercury. It seems to be generally agreed from studies using optically active alkyl groups [e.g., $\text{R} = \text{Ph} \cdot \text{CH}(\text{CO}_2\text{Et})$] that all these reactions proceed with retention of configuration (362, 363) and that they are in fact equilibria, although the position of equilibrium may lie or be displaced far to one side (350, 363,

365). Controversy has arisen, however, concerning the mechanisms of the reactions, and in particular concerning reactions of the type in Eq. (9), which are displaced to the left under the influence of ammonia on diphenylmercury. For the "symmetrization" of esters of α -bromomercuriphenylacetic acid by ammonia in chloroform, Reutov *et al.* (363, and references therein) have proposed the mechanism represented by Eqs. (13 and 14), where $R = Ph \cdot CH(CO_2Et)$:



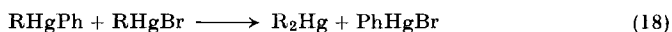
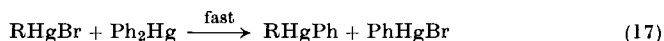
However, Jensen and Rickborn (241) have pointed out inconsistencies in the Russian workers' kinetic data, and have suggested alternative mechanisms involving complex formation between the alkylmercuric halide and ammonia, as represented by Eqs. (15 and 16):



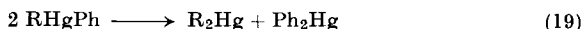
Both American and Russian workers have in fact obtained evidence for the formation of unstable donor-acceptor complexes between alkylmercuric halides and ammonia (241, 366), and the Russians now apparently accept a mechanism of the general type proposed by Jensen and Rickborn (365).

The same groups of workers have proposed alternative mechanisms for symmetrization by diphenylmercury. The Russian workers had proposed that the first stage of the reaction was represented by Eq. (13) (367). However, Jensen and Miller (239) demonstrated that in chloroform an initial, rapid reaction involving a 1 : 1 ratio of reactants occurred,

followed by a slow reaction leading to the symmetrical product, and proposed the scheme shown in Eqs. (17 and 18):



An alternative for the second stage was Eq. (19),



followed by another reaction as in Eq. (17). The Russian workers have since (45) obtained kinetic results consistent with these suggestions, and favoring the reaction corresponding to Eq. (19) as the second stage.

Yet another example of the difficulty in obtaining consistent experimental data for these reactions is provided by a reaction of the type shown in Eq. (9), but proceeding to the right. In the reaction between alkylarylmercury compounds (RHgAr) and ^{203}Hg -mercuric halides, leading to mixtures of alkylmercuric halide and arylmercuric halide, alternative claims were that (i) both products contained ^{203}Hg (140), and (ii) only the arylmercuric halide contained ^{203}Hg (310). The latter view has now been accepted by the American school (139).

It is evident that, in studies on the mechanisms of reactions of organo-mercury compounds, great attention has to be paid to the experimental conditions used. In particular, it has been pointed out that peroxides or combinations of mercury and mercury(I) salts (both of which could arise inadvertently) have a catalytic effect on a number of reactions (168, 231).

As in the case of the dialkylmercury compounds (see Section II,B,2a above), the rate of exchange of alkyl groups between alkylmercuric halide molecules is low, and ^1H — ^{199}Hg spin-spin coupling is readily observable. The proton magnetic spectra of compounds of the general formula RHgX have consequently aroused considerable interest. For a series of compounds, CH_3HgX and $\text{CH}_3\text{CH}_2\text{X}$, it has been found that $J(^1\text{H}$ — $^{199}\text{Hg})$ increases with increasing electronegativity of the group X (208). As alkenylmercuric halides are configurationally stable, the influence of the hybridization of the carbon atom attached to mercury and of the geometry of the systems on $J(^1\text{H}$ — $^{199}\text{Hg})$ has been investigated (461, 462). Compounds studied include the vinylmercuric halides, *cis*- and *trans*-2-chlorovinylmercuric halides, and methylethynylmercury. The spectra for a number of compounds of known stereochemistry were consistent with $J(^1\text{H}$ — $^{199}\text{Hg})$ of approximately 600 cycles sec^{-1} when H and Hg are *trans*, and approximately 100 cycles sec^{-1} when H and Hg are *gauche* (262).

Besides vicinal ^1H — ^{199}Hg coupling, long-range ^1H — ^{199}Hg coupling through four bonds has been reported for neopentylmercuric halides (397).

The proton magnetic resonance spectrum of methylmercuric iodide is of particular interest (162, 203, 208, 350). At higher temperatures in pyridine, the spectrum showed a single sharp band with no satellites; as the temperature was lowered, satellites appeared and became progressively sharper until at -35° their width was comparable with that of the main peak. However, the obvious explanation—exchange of methyl groups at the higher temperatures (cf. 208, 350)—is apparently untenable, as the line width of the main peak did not change with temperature (203). The spectra have now been interpreted (162, 203, 396a) in terms of a chain of relaxation effects involving transitions in the ^{199}Hg nucleus and rapid relaxation in the ^{127}I nucleus. It has also been observed (162) that the spectra of pure samples of methylmercuric thiocyanate in pyridine solution show no evidence for rapid methyl exchange (contrast Hatton *et al.* (208)).

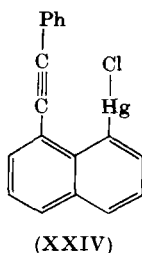
The mercury-chlorine and mercury-bromine stretching frequencies (near 320 cm^{-1} and near 230 cm^{-1} , respectively) for aryl-, alkyl-, and perfluoroalkylmercuric halides have been determined (109), and more recently the vibrational spectra of methylmercuric chloride, bromide, iodide, and cyanide have been analyzed, and force constants calculated (193); the carbon-mercury stretching force constant varied from $2.50 \times 10^5\text{ dynes cm}^{-1}$ for the iodide to $2.78 \times 10^5\text{ dynes cm}^{-1}$ for the cyanide (see Table I).

As was mentioned above, alkyl- and 1-alkenylmercuric halides are configurationally stable. The preparation and structural assignment of the *cis* and *trans* isomers of 4-methylcyclohexylmercuric bromide (237), 4-*tert*-butylcyclohexylmercuric bromide (16), and propenylmercuric chloride (93) have recently been reported. The crystal structure of *trans*-2-chlorovinylmercuric chloride has been determined, and its configuration confirmed (330).

Protolysis of allylmercuric halides leads to rearranged products (cf. the corresponding derivatives of the other Group II metals); crotylmercuric bromide, for example, leads almost exclusively to 1-butene on reaction with hydrochloric or acetic and perchloric acids (398). Protolysis of 1-alkenylmercuric halides generally proceeds without rearrangement, and with retention of configuration; the kinetics of acidolyses of a number of alkenylmercuric halides have been reported (307).

The problem of the structure of allylmercuric derivatives has been referred to above (Section II,D,2a). Further information on this subject has been provided by the ultraviolet spectrum of allylmercuric iodide

(263), which revealed interaction between the C=C and Hg—I chromophores; it was suggested that the mercury atom must be situated close to the double bond, so that, even if the compound does not have a π -allylic structure, the carbon-mercury σ -bond must be very long and easily deformed. On the other hand, and in contrast also to analogous alkyl-magnesium derivatives (see Section IV, B, 1*b* below), there is no sign of an interaction between the mercury atom and the multiple bond in 1-phenylethynyl-8-naphthylmercuric chloride (XXIV) (136) or in 3-butenylmercuric chloride (326).



B. SOLVATED ALKYLMETALLIC HALIDES

1. The Grignard Reagent

a. The Constitution of the Grignard Reagent. The state of knowledge on this subject was reviewed in 1966 (454) and in 1967 (24), and subsequent work has not materially affected the conclusion reached in the former review, namely, that the Grignard reagent is best represented by an extended equilibrium of the type formulated in Fig. 5. The later work has

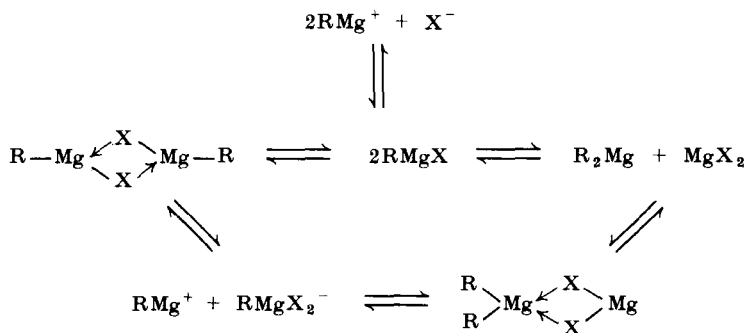
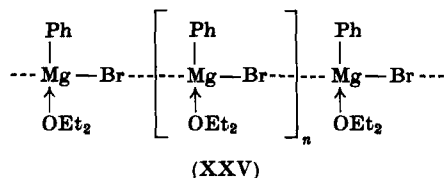


FIG. 5. Equilibria in Grignard reagents (X = halogen; solvent molecules omitted).

served to provide more conclusive evidence toward resolving some points of controversy, and to clarify the factors affecting the relative proportions of the various possible species in solution.

In the scheme shown in Fig. 5, association involving halogen bridging rather than alkyl bridging has been indicated. Arguments in favor of this formulation have been advanced (454), but powerful experimental evidence has now been provided by measurements of the variation in degree of association of various alkylmagnesium halides with concentration in diethyl ether (28). Association was least for alkyl groups favoring alkyl bridging (i.e., methyl, ethyl), and greatest for the compounds that might be expected to have the greatest positive charge on magnesium. For phenylmagnesium bromide, the graph of i against concentration was almost linear, with no marked change in slope near $i = 2$, and linear association of type XXV was proposed.



Further investigations on exchange reactions have been carried out by the Dutch school (56, 62). A study (62) of possible equilibria involving diethylmagnesium and ^{14}C -labeled ethylmagnesium bromide in diethyl ether was inconclusive, because of rapid statistical exchange of ethyl groups; but the observation that ^{28}Mg became statistically distributed, when labeled magnesium bromide was mixed with diethylmagnesium or ethylmagnesium bromide, indicated that all three species were involved in the equilibria (unless the exchange was catalyzed by impurities).

Smith and Becker have shown (399, 400), by measuring the heats of mixing of solutions of dialkylmagnesium compounds and magnesium halides in diethyl ether, that an almost instantaneous reaction takes place, involving a 1:1 ratio of the reactants and leading to a largely monomeric product. The conclusion was that for the systems studied ($\text{R} = \text{Et}, \text{Ph}$; $\text{X} = \text{Br}, \text{I}$; concentrations of the order of 0.1 M in diethyl ether), the equilibrium (Eq. 20) is rapidly established, and lies far to the right. On the other hand, the effect of the solvent on the constitution of the Grig-



nard reagent was illustrated by the observation (399a) that in tetrahydrofuran, although reaction was almost instantaneous, and the products largely monomeric, conversion to RMgX was incomplete. Similarly, while the polarographic behavior of some organomagnesium com-

pounds in 1,2-dimethoxyethane was consistent with the equilibrium (Eq. 20), it indicated that the equilibrium constant was of the order of 4 when $R = \text{PhCH}_2$, Ph , Me_2CH , or Et ; and $X = \text{Br}$ (347). [In view of the hypotheses that transient "magnesioid" species may be involved in some reactions of "nascent" organomagnesium compounds (63, 78, 298), the proposal that RMgX undergoes one-electron reduction at the mercury cathode to give $\text{RMg}\cdot$, which subsequently decomposes to $\text{R}\cdot$ and Mg , is of interest.] Similarly, the effect of the nature of the alkyl group on the constitution of the Grignard reagent has been illustrated by some n.m.r. studies. For ethereal solutions of pentafluorophenylmagnesium bromide and iodide, in which aryl-group exchange was slow on the n.m.r. time scale at room temperature, it was possible to distinguish two sets of signals in the ^{19}F n.m.r. spectrum (153). One set corresponded to bis(pentafluorophenyl)magnesium and the other to other pentafluorophenylmagnesium species (possibly $\text{C}_6\text{F}_5\text{MgX}$, although dimeric species were not ruled out, as the degree of association of the solutes was not determined); the chemical shifts of the two sets of signals varied with concentration, although the shifts for bis(pentafluorophenyl)magnesium alone were independent of concentration. Similar observations enabled the ratio $2[\" \text{RMgX} \"]/[\" \text{R}_2\text{Mg} \"]$ to be determined from the ^{19}F n.m.r. spectra of several fluoroaryl Grignard reagents (153a). Another system in which alkyl exchange was sufficiently slow for different alkylmagnesium species to be distinguished by n.m.r. involved mixtures of ethyl- and phenylethynylmagnesium compounds. For mixtures of ethyl- and phenylethynylmagnesium bromides, it was deduced (351) that the solutions contained mainly " RMgX " rather than " R_2Mg " species.

Further complexes of alkylmagnesium halides have been characterized. The 1:1 complex of *p*-fluorophenylmagnesium bromide with tetramethylethylenediamine is monomeric in benzene (153b), but the 1:1 complex of *tert*-butylmagnesium chloride with diethyl ether is monomeric (104a). The latter complex probably has a halogen-bridged structure, similar to that recently established for $[\text{EtMgBr}, \text{Et}_3\text{N}]_2$ by X-ray crystallography (435a).

The infrared spectra of solid methylmagnesium chloride and methylmagnesium bromide diethyl etherates showed bands corresponding to ether coordinated to dimethylmagnesium, to methylmagnesium halide, and to magnesium halide (220). The ether was so tightly bound as to exclude the possibility that the reagents were mixtures containing free magnesium halide. However, only very limited deductions about the structure of the reagents in solution may be made from such observations on the solids. A further attempt to differentiate between alkylmagnesium species in solution involved measuring the C—D stretching

frequencies for α -deutero-organomagnesium reagents (244). However, in every case, any difference in frequency between the dialkylmagnesium compounds and the corresponding Grignard reagents was insignificant. (On the other hand, the C—D stretching frequency for $(\text{CH}_2\text{D})_2\text{Hg}$ in chloroform was clearly distinguishable from that for $\text{CH}_2\text{D}\cdot\text{HgBr}$.)

Recent work on the configurational stability of Grignard reagents may lead to further insights into the nature of the carbon-metal bond in these compounds and into the mechanism of the alkyl-exchange reaction. The results of Roberts *et al.* (472) and of Fraenkel *et al.* (164) on the configurational stability of primary dialkylmagnesium compounds have been summarized (Section II, B, 2a). The results on the corresponding alkylmagnesium halides (164, 165, 464, 465) are qualitatively similar to those for the dialkylmagnesium compounds, the rates of inversion being slow on the n.m.r. time scale at low temperatures, and depending on the nature of the solvent and on the concentration of the reagent as well as on the temperature. In addition, the rate of inversion of the halides depends on the nature of the halogen; thus, 3-methylbutylmagnesium chloride undergoes inversion at the α -carbon atom much more rapidly than the bromide, and addition of magnesium bromide to a solution of the chloride slows its rate of inversion (464). Both groups of workers find that the inversion reaction exhibits a kinetic order greater than 1, and a bimolecular mechanism seems most likely. The observation (464) that the rate of inversion is lower in more strongly electron-donating solvents supports the view that electrophilic attack on the Grignard reagent (by species containing the grouping $-\text{MgX}$) is involved. A study of the relative rates of alkyl exchange and of inversion would be valuable.

Although many of the examples studied are atypical, in that they involve rigid ring systems, secondary alkylmagnesium halides in general appear to undergo inversion at the α -carbon atom comparatively slowly. Whitesides and Roberts (464) demonstrated this fact by observing the proton n.m.r. spectra of 3,3-dimethylcyclobutylmagnesium bromide and 2,3-dimethylbutylmagnesium bromide. Three groups of workers have studied the n.m.r. spectra of the norbornylmagnesium (216, 240, 265) and bornylmagnesium (216) halides. Preparation of these reagents from either the *exo*- or *endo*-halide affords a mixture of *exo*- and *endo*-Grignard reagents of similar composition. However, in contrast to the earlier studies involving carboxylation of the mixtures (373), the spectra indicate that the isomeric reagents are not rapidly interconverted.

Further studies have been reported on the mechanism of the reactions of Grignard reagents with ketones [addition (25, 220, 221, 223, 300a, 325, 400a, 401, 402), reduction (396b, 441, 449), condensation (439), other reactions (123, 483, 484), and general (23, 249, 251, 252b, 440, 442)], with

esters (222, 223), and with nitriles (148, 374), but these have not furnished major advances in our knowledge of the constitution of the reagents. It has been confirmed (401, 402) that ketone-Grignard complexes are intermediates in the reaction of methylmagnesium bromide with 2,4-dimethyl-4'-methylmercaptobenzophenone, and Holm (220-223) and Tuulmets (251) have interpreted the results of their investigations of the reactions of Grignard reagents with carbonyl compounds in terms of similar complexes. On the other hand, studies on reactions with methyl trifluoroacetate (222a) and with sterically hindered cyclobutanones (252a) indicate that addition to a carbonyl group can take place without the intermediacy of a ketone-Grignard complex. It has recently been suggested (24) that the reaction of methylmagnesium bromide with benzophenone may proceed by a termolecular mechanism. The difficulties in interpreting the many complexities of the kinetic data obtained for these reactions have been emphasized (24).

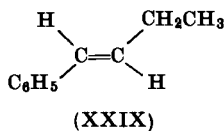
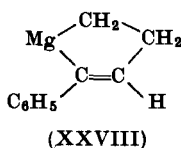
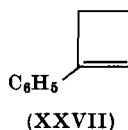
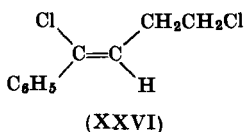
In the earlier review (454) it was emphasized that, in electron-donating solvents, solvent molecules form an integral part of the reagents, and later work has confirmed this generalization. Thus, the solvent effects in the reaction of ethylmagnesium bromide with benzonitrile are interpreted (374) in terms of specific solvent-Grignard complexes. Striking effects have been obtained by the use of extremely strong donors such as tetramethylurea (279) and hexamethylphosphorotriamide (HMPT) (126, 156, 166) as solvents for Grignard reagents; alkylmagnesium halides in HMPT enolize ketones (156) and even metallate hydrocarbons such as toluene (126). Grignard reagents form solid complexes with HMPT, but the complexes decompose on standing (166). An interesting example of the effect of coordination on reactivity involved the reaction of some substituted phenylmagnesium bromides with di-*tert*-butyl ketone (325): phenylmagnesium bromide itself did not react, *o*-methoxyphenylmagnesium bromide reacted smoothly (according to second order kinetics, first order in each reagent), and 2,6-dimethoxyphenylmagnesium bromide again failed to react. A recent interesting observation, and one that may have useful applications, is that optically active ethers show enhanced rotation when coordinated with Grignard reagents (448).

Further evidence has been obtained that radicals are involved in the formation of organomagnesium compounds from alkyl halides and magnesium. The reaction of several alkyl and aryl halides with magnesium in deuterated solvents led to deuterated products that indicated deuterium abstraction by radicals derived from the halides (15). However, in interpreting such results, the homolytic reaction between unsolvated alkylmagnesium halides and alkyl halides must be borne in mind (see Section IV,A,1 above) [cf. (488)]. A mechanism for the formation of Grignard

reagents involving the reaction of anion radicals and radicals on the surface of the metal has been proposed (22).

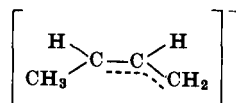
b. Alkenylmagnesium Halides and Related Compounds. The stereochemistry of vinylic Grignard reagents has been studied. Under suitable conditions, it is possible to prepare geometrically isomeric reagents from the corresponding 1-bromo-1-alkenes, such as the 1-bromo-1-propenes (306) and the β -bromostyrenes (486, 487). The reagents are apparently formed with retention of configuration (320), are configurationally stable, and react with mercuric chloride and carbon dioxide with retention of configuration. However, an n.m.r. study (282) on solutions of the Grignard reagents revealed that the apparent retention of configuration may not in fact be complete.

The reaction of *trans*-1,4-dichloro-1-phenyl-1-butene (XXVI) with magnesium in ether yields a variety of products, including 1-phenylcyclobutene (XXVII), whose formation is best rationalized in terms of the initial formation of the vinylic rather than the primary Grignard reagent (311), and *trans*-1-phenyl-1-butene (XXIX). The interesting suggestion has been made (242) that the intermediate leading to the formation of compound XXIX on hydrolysis is the cyclic magnesium compound (XXVIII).



It has long been known that allylic Grignard reagents react to give products derived from the allylic isomer as well as those corresponding to the original halide, and more recent proton magnetic resonance studies (463) have shown that ethereal allylmagnesium bromide is either a rapidly equilibrating mixture of σ -bonded isomers, or has a structure with magnetically equivalent allylic protons. Any equilibrium between crotyl- and butenylmagnesium bromide lay almost entirely on the crotyl side. A similar type of isomerization has recently been reported (312) in the indene series, the coupling reaction of the Grignard reagent from metallation of 3-methylindene with allyl bromide giving a 3:1 mixture of 1-allyl-3-methylindene and 1-allyl-1-methylindene.

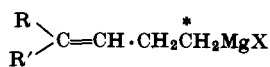
The constitution of allylic Grignard reagents has been further studied by French workers. Protolysis of crotylmagnesium halides (8, 9) or dicrotylmagnesium (11, 12) gave a mixture of 1-butene and *cis*- and *trans*-2-butene. The proportions of the products depended to some extent on the protolytic reagent, but varied relatively little with the halogen in the Grignard reagent. However, the nature of the solvent had a profound effect on the proportions of the products; in general, more strongly electron-donating solvents decreased the proportion of 1-butene, and increased the proportion of *cis*- to *trans*-2-butene. It has been suggested (8) that, in the more electron-donating solvents, the allylic group becomes more carbanionic in character, and in the strongest donors the reagent may be regarded as a salt of a *cis*-allylic carbanion (XXX). More recently



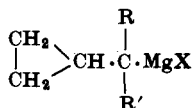
(XXX)

it has been reported (157) that the reaction of 1-methyl-2-butenylmagnesium derivatives with a number of electrophilic reagents gave mainly *cis*-alkenyl products. It was suggested that these reactions proceed by an S_E2' mechanism; in the transition state, the allylic group possesses considerable carbanionic character, and a preferred *cis* configuration.

Organomagnesium compounds do not generally react with isolated double bonds, although the addition of allyl- and benzylmagnesium bromide to the double bond of allylic alcohols has been reported (92, 149). However, numerous cases are now known of interactions between magnesium and double or triple bonds within the same molecule, but separated by two or more carbon atoms. In particular, it has been found by labeling experiments that allylcarbinyl reagents (XXXI) undergo a remarkable rearrangement, in which the α - and β -carbon atoms exchange positions (394). It was suggested that the rearrangement might take

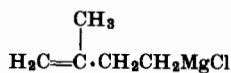
(a) $\text{R} = \text{R}' = \text{H}$ (b) $\text{R} = \text{R}' = \text{Ph}$

(XXXI)

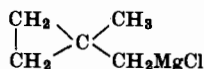
(a) $\text{R} = \text{R}' = \text{H}$ (b) $\text{R} = \text{R}' = \text{Ph}$

(XXXII)

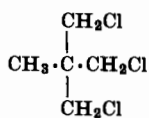
place via the cyclopropylcarbinyl intermediate (XXXII), which could be prepared at low temperatures, although it was present only in low concentrations in the equilibrium mixtures at room temperature (338). Subsequent studies (225, 280) have given further support to this hypothesis. Thus, although solutions of γ,γ -diphenylallylcarbinylmagnesium bromide (XXXIb) contained less than 0.3% of the isomeric cyclopropyl derivative, conditions giving more carbanionic character to the organic group (e.g., more strongly electron-donating solvents, substitution of potassium for magnesium) increased the proportion of the cyclopropyl derivative (XXXIb). A similar cyclopropylcarbinyl-to-allylcarbinyl rearrangement is involved in the formation of the Grignard reagents (XXXIII and XXXIV) as a result of the reaction of magnesium with 1,3-dichloro-2-(chloromethyl)-2-methylpropane (XXXV) (290, 291).



(XXXIII)

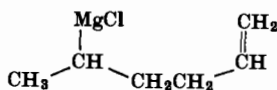


(XXXIV)

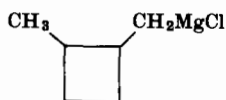


(XXXV)

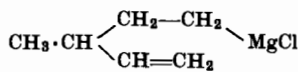
Some examples of the intramolecular reaction of magnesium with double bonds at the δ - and ϵ -positions have been reported. Thus, the isomerization of the Grignard reagent (XXXVI) from 5-chloro-1-hexene to the isomer (XXXVIII) probably proceeded via the cyclobutane derivative (XXXVII) (217, 218), and the Grignard reagent (XXXIX) from 6-chloro-1-heptene in tetrahydrofuran rearranged to give the cyclopentane derivative (XL) (371). These rearrangements are reported



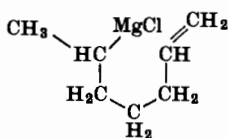
(XXXVI)



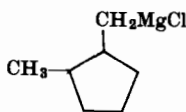
(XXXVII)



(XXXVIII)



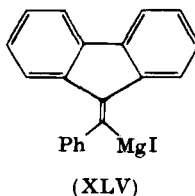
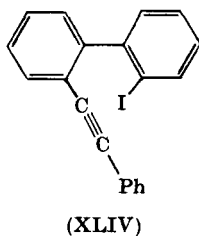
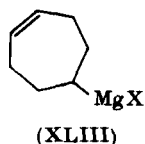
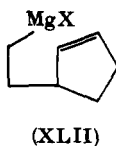
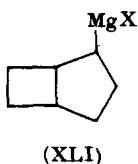
(XXXIX)



(XL)

(358) to proceed more rapidly in highly electron-donating solvents such as 1,2-dimethoxyethane and hexamethylphosphotriamide.

Some related ring-opening reactions have recently been reported, including the transformation of the reagent XLI to its isomers XLII and XLIII) (418).



An intramolecular reaction between magnesium and a triple bond has been demonstrated by Dessy and Kandil (136, 248); the reaction of 2-iodo-2'-(phenylethynyl)biphenyl (XLIV) with magnesium in tetrahydrofuran led to the rearranged derivative (XLV).

2. Solvated Alkylberyllium Halides

Compared with the Grignard reagents, the alkylberyllium halides have been very little studied. Dessy (134) observed no exchange of beryllium between mixtures of diphenylberyllium and ^7Be -beryllium bromide in diethyl ether or dioxan. However, there is apparently some interaction between dialkylberyllium compounds and beryllium halides in solution (134, 189), and mixtures of the two have been preferred to dialkylberyllium compounds alone in synthesis (52). A true alkylberyllium halide, *tert*-butylberyllium chloride, has recently been isolated as a 1:1 complex with diethyl ether; it is believed to have a dimeric structure containing Me_3CBeCl units linked by chlorine bridges (372). Evidence has also been obtained (25a) that when equimolar amounts of dimethylberyllium and beryllium bromide are dissolved in diethyl ether, the predominant species in solution is CH_3BeBr .

The preparation and some reactions of acylberyllium halides, $\text{R}\cdot\text{CO}\cdot\text{BeX}$, have been described (271). They are reported to give aldehydes on hydrolysis, and to couple to give α -diketones.

3. Solvated Alkylcalcium, -strontium, and -barium Halides

Somewhat surprisingly, in view of the abundance and reactivity of calcium, organocalcium compounds have been very little studied. This is largely because meticulous attention to the experimental conditions is required for even moderate yields of the alkylcalcium halides to be obtained from the reaction of calcium with alkyl halides (80, and references therein). The constitution of the alkylcalcium halides is largely unknown, although in simple cases (e.g., methylcalcium iodide) there is apparently an excess of carbon-calcium bonds over carbon-halogen bonds in solution. However, triphenylmethylcalcium chloride has recently been prepared in good yield in tetrahydrofuran (THF) solution, from which a crystalline product with the composition $\text{Ph}_3\text{CCaCl} \cdot 2\text{THF}$ was obtained (287); one mole of tetrahydrofuran was removed on heating *in vacuo*. The alkylcalcium halides are reported (80) to resemble alkyl-lithium compounds rather than Grignard reagents in their reactivity; their high reactivity toward pyridine is particularly noteworthy (80), and they are able to catalyze the polymerization of isoprene and butadiene (433).

Although the preparation of phenylbarium iodide was described in 1927 (188), very little has subsequently been published on the alkyl-strontium and -barium halides. However, triphenylmethylstrontium chloride and triphenylmethylbarium chloride resemble their calcium analog in forming complexes with two moles of tetrahydrofuran (285).

4. Solvated Alkylzinc Halides

The classical method for preparing alkylzinc iodides is the direct synthesis from alkyl iodides and zinc. It has generally been thought that alkylzinc bromides and chlorides could not be prepared similarly except from particularly reactive halides. However, methods have now been worked out (174, 176, 243, 491) for this direct synthesis of alkylzinc bromides and benzyl- and allylzinc chlorides (393) by the use of zinc or zinc-copper couples and strongly solvating solvents. The interaction of zinc with α -bromo esters in the Reformatsky reaction is well known. Solutions of the organozinc intermediates have recently been obtained (199, 393, 445, 501), and Reformatsky complexes from chloroacetic acid and ethyl chloroacetate (252) and from *N,N*-diethyl- α -bromoacetamide (125) have also been described. The constitutions of these solutions are complicated since, besides the possible types of species involved in simple alkylzinc halides, the Reformatsky complexes could involve species with zinc-oxygen instead of zinc-carbon bonds (125, 178, 179, 317, 445, 501).

Solutions of the simple alkylzinc halides in electron-donating solvents resemble in many respects the corresponding Grignard reagents. However, the zinc compounds are much less strongly solvated than the magnesium compounds, and there is not the striking difference between the solvated and unsolvated reagents noted above for the alkylmagnesium halides. Isolatable complexes of alkylzinc halides are in general formed only with strong electron donors such as dioxan (254, 332, 388, 389) or tetramethylethylenediamine (3, 4), although the isolation of arylzinc halide diethyl etherates has been reported (388, 389). The most thoroughly studied alkylzinc halide reagent is the solution of ethylzinc iodide in diethyl ether or tetrahydrofuran, and there is now overwhelming evidence that the predominant species in such solutions is monomeric EtZnI (presumably solvated). The evidence may be briefly summarized as follows.

(i) Mixtures of equimolar amounts of diethylzinc and zinc iodide in ether or tetrahydrofuran give, on standing, solutions indistinguishable from reagents prepared by the action of a zinc-copper couple on ethyl iodide in the same solvents (3, 4, 388).

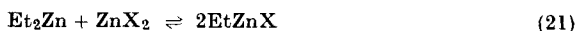
(ii) The species in such solutions are largely monomeric (i.e., EtZnI or mixtures of Et_2Zn and ZnI_2) (3, 4).

(iii) Addition of N,N,N',N' -tetramethylethylenediamine (TMED) to such solutions precipitates complexes with the composition $\text{EtZnI} \cdot (\text{TMED})$ (3, 4).

(iv) Addition of TMED to a freshly prepared mixture of diethylzinc and zinc iodide gives a complex with the composition $\text{ZnI}_2 \cdot (\text{TMED})$ (3, 4).

(v) The Raman and infrared spectra of solutions of ethylzinc iodide in diethyl ether show a strong band near 510 cm^{-1} , which is polarized in the Raman spectrum, and is assigned as the C—Zn stretching vibration. The C—Zn stretching frequency for diethylzinc is at 470 cm^{-1} , and this band is absent for the solutions of ethylzinc iodide (154a, 155).

It is thus concluded that the predominant species in solution is EtZnI , and that the position of any equilibrium (Eq. 21; $\text{X} = \text{I}$) lies far to the right. [It is apparently not possible to distinguish between Et_2Zn and EtZnI by proton magnetic resonance spectroscopy, probably because of rapid alkyl-group exchange in these systems (154).]



For ethylzinc bromide and ethylzinc chloride the situation is less well established since, although the solutions contain monomeric species, addition of TMED or 2,2'-bipyridyl gave precipitates of the zinc halide complexes (4, 135). In the case of the chloride, mixtures of ^{65}Zn -zinc

chloride and unlabeled diethylzinc in diethyl ether or tetrahydrofuran showed statistical exchange of ^{65}Zn (135). These results are probably best interpreted in terms of a rapid equilibrium (Eq. 21); $\text{X} = \text{Br}, \text{Cl}$). Unpublished work [D. F. Evans and I. Wharf, quoted in Abraham and Rolfe (4)] on the infrared spectra of mixtures of diethylzinc with zinc bromide or zinc chloride in tetrahydrofuran is also reported to support this interpretation [see also (154a)].

It has recently been reported (284; cf. 257) that certain reactions of dialkylzinc compounds are "activated" by metal halides in a similar manner to those of alkylcadmium compounds (see Section IV,B,2d below).

The alkenylzinc halides have been little studied, although allylic derivatives have been used in reactions with carbonyl compounds in preference to the corresponding Grignard reagents (295). The products of protolysis of crotylzinc halides have been compared with those from the corresponding magnesium and cadmium derivatives (q.v.) (9, 10). The proportions of the butene isomers were, in contrast to those from the Grignard reagents, relatively unaffected by the nucleophilicity of the solvent. It was concluded that solvation of the zinc reagents was comparatively weak, and that the allylic groups had little carbanionic character. The observation that the zinc derivatives gave a higher proportion of *cis*-2-butene than those of cadmium, and higher than those of magnesium in all but the most nucleophilic solvents, remains unexplained.

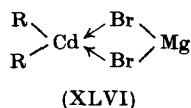
5. Solvated Alkylcadmium Halides

Although alkylcadmium halides are only weakly solvated, and stable complexes with donor molecules have not been isolated (91, 254, 331), the compounds have generally been prepared and studied in electron-donating solvents and are therefore considered here (rather than in Section IV,A,3 above).

Solutions of "alkylcadmium halides" have been prepared from the reaction of Grignard reagents with cadmium chloride, from the interaction of dialkylcadmium compounds with cadmium halides, and recently (90, 91) directly from metallic cadmium and alkyl halides in strongly donor solvents. It has been generally considered until recently that such reagents could be considered as solutions of dialkylcadmium compounds, with perhaps some loose complex formation between the dialkylcadmium compounds and cadmium halides. Thus, for example, mixtures of ^{115}Cd -diethylcadmium with inactive cadmium bromide or of inactive diethylcadmium with ^{115}Cd -cadmium bromide in tetrahydrofuran showed no exchange of activity after 21 days (175). However, the

enhanced solubility of diethylcadmium in the presence of cadmium bromide indicated that there was some interaction between the components, and precipitates with the composition RCdX have been prepared by the interaction of dialkylcadmium compounds with cadmium halides in diethyl ether (333, 390). Later studies have revealed a very striking effect of metal halides on the reactivity of dialkylcadmium compounds. Thus, Kollonitsch first pointed out (257) that pure dialkylcadmium compounds were unreactive toward acyl chlorides, in contrast to the reagents employed in the classical ketone synthesis, which contained magnesium halides. [A similar effect was noted for the corresponding zinc compounds, but this has received only little further attention (284).] Subsequent studies by Kollonitsch (255, 256, 258) and French workers (122, 132, 152, 211–213, 226, 276, 293, 416) have revealed many examples of the "activation" of organocadmium compounds by the addition of metal halides, and shown the usefulness of the activated reagents in synthesis. However, the mechanism of activation and the constitution of the solutions are still far from clear. Kollonitsch has emphasized that it is the *reactions* that are activated, and not necessarily only the organocadmium reagents. The activation has been rationalized in terms of complex formation between the metal halides (functioning as Lewis acids) and the acyl chlorides (293); zinc chloride and aluminum chloride are activating salts (293). However, activation by lithium bromide has been observed (226, 255), and magnesium iodide has been reported (255) to be more effective than magnesium chloride (although this order of effectiveness of the magnesium halides has been questioned) (226, 293). It has recently been proposed (133) that a complex, formulated as $[\text{CH}_3\text{CO}]^+[\text{CdCl}_3]^-$, is involved in the exchange of chlorine between acetyl chloride and cadmium chloride; this exchange was promoted by the addition of a quaternary ammonium salt. Activation of the alkylcadmium reagent may be involved, either instead of, or as well as, activation of the acyl chloride. There is in fact evidence that species containing both cadmium and the other metal involved are present in the solutions. Thus, whereas mixtures of dialkylcadmium compounds and cadmium halides in diethyl ether gave precipitates with the composition RCdX (333, 390), complexes with the composition $\text{RCdMgX}_3 \cdot 2\text{Et}_2\text{O}$ have been isolated from the solutions resulting from the reaction of Grignard reagents with cadmium chloride in diethyl ether (276), and complexes with the composition $\text{R}_2\text{Cd} \cdot (\text{MgX}_2)_2 \cdot (\text{HMPT})_n$ have been prepared via the interaction of Grignard reagents with cadmium chloride in hexamethylphosphorotriamide (91). Similarly, the infrared spectra of solutions of dialkylcadmium-magnesium bromide reagents show additional bands near 552 cm^{-1} , not present for either component alone, and attributed to

non-colinear cadmium-bromine bonds such as those in the hypothetical complex, XLVI (122).



Kinetic studies on the reactions of alkylcadmium reagents would be of interest; in the only one so far reported (152), it was found that the protolysis of diethylcadmium by isoamyl alcohol showed second order kinetics, and that the order was essentially the same when zinc chloride, aluminum chloride, or magnesium bromide was present, although the rates were increased by these halides.

Alkenylcadmium halides have been little studied. Protolysis of the reagent from crotylmagnesium chloride and cadmium chloride gave products little different from those from the corresponding zinc reagent (see Section IV, B, 2c above) (9). The exchange reaction between "crotylzinc bromide" (from crotyl bromide and zinc) and cadmium chloride in strongly donor solvents has been briefly reported (10); the equilibrium is stated to lie 64% on the side of the crotylcadmium reagent.

6. Solvated Alkylmercuric Halides

There is some evidence that, in contrast to the dialkylmercury compounds, alkylmercuric halides may form complexes with strong electron donors. Thus, although the addition of ammonia to solutions of alkylmercuric halides has little effect on the positions of the ultraviolet absorption maxima, it lowers their intensities (196, 366), and complexes of alkylmercuric halides with ammonia have been proposed as intermediates in symmetrization reactions (see Section IV, A, 4 above). Unstable complexes of alkylmercuric halides with trialkylphosphines have also been reported (106). Stable complexes are formed between perhalogenoarylmercuric halides and ligands such as 1,10-phenanthroline and 2,2'-bipyridyl (85a, 120a, 339) (see Section II, C above).

V. Compounds Containing the System C-M-O; the Alkylmetallic Alkoxides and Alkylperoxides

Alkylmetallic alkylperoxides and alkoxides have been suggested to be intermediates in the oxidation of the dialkyl derivatives of the Group II metals, and during the last few years many alkylmetallic alkoxide deriva-

tives of the Group II metals (except the alkaline earth metals) have been synthesized by various other routes. The chemistry of the compounds is of great interest, because of the possibility of back-donation of electrons from oxygen to the metals, or of intermolecular coordination of oxygen to the metals.

The chemistry of the alkylperoxides has recently been reviewed (404).

A. ALKYLBERYLLIUM ALKOXIDES AND ALKYLPEROXIDES

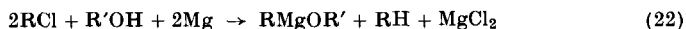
Although alkylberyllium alkylperoxides have not been characterized, evidence has been obtained (286) that methylberyllium methylperoxide, $\text{CH}_3\text{BeOOCH}_3$, is an intermediate in the oxidation of dimethylberyllium to beryllium methoxide by oxygen. Methylberyllium methoxide, which may also be a product of the oxidation of dimethylberyllium, has been prepared by the reaction of methanol with dimethylberyllium (101). It is soluble in benzene, in which it is dimeric,⁶ and disproportionates to dimethylberyllium and beryllium methoxide on heating. Other alkylberyllium alkoxides have been prepared by analogous reactions (115) and by the reaction of alkylberyllium hydrides with carbonyl compounds (52). Phenylberyllium methoxide and methylberyllium benzyloxide are tetrameric in benzene solution (52, 115), and may have cubane-type structures analogous to those of some of the alkylzinc alkoxides (see Section V,C below). However, the reaction of methylberyllium hydride with benzophenone in ether yields a crystalline complex, monomeric in benzene, which presumably contains three-coordinate beryllium and is formulated as $\text{Me}(\text{Et}_2\text{O})\text{BeOCHPh}_2$ (52). When phenylberyllium methoxide is prepared in the presence of diethyl ether the initial product contains some ether, and it thus seems that there is competition between internal and external coordination of oxygen to beryllium in the presence of donor solvents. The reaction of dimethylberyllium with compounds such as 2-methoxyethanol and 2-dimethylaminoethanol leads to products with various degrees of polymerization, and whose structures promise to be of considerable interest (97b).

B. ALKYL MAGNESIUM ALKOXIDES AND ALKYLPEROXIDES

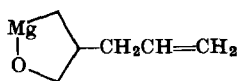
Although alkylperoxides may be involved in the autoxidation of organomagnesium compounds (286), and the product of the reaction of diethylmagnesium with a deficiency of oxygen in diethyl ether, at first presumed to be ethylmagnesium ethoxide (452), could possibly have been an alkylperoxide (453), no alkylmagnesium alkylperoxides have been isolated.

⁶ Professor Coates has reported in a lecture that a reinvestigation showed methylberyllium methoxide to be *tetrameric* in benzene solution.

Alkylmagnesium alkoxides have been prepared by a variety of methods, and are indeed readily available. They may be synthesized via the interaction of an alkyl chloride, an alcohol, and magnesium in a solvent in which magnesium chloride is insoluble (77, 82, 454) (Eq. 22 gives the overall equation for this group of related procedures); by the partial

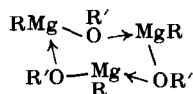


alcoholysis of dialkylmagnesium compounds (108; cf. 224); and via the addition of dialkylmagnesium compounds to carbonyl groups (108). Alkylmagnesium alkoxides may be involved as intermediates in the reaction of Grignard reagents with carbonyl compounds (396b, 454), and ethylmagnesium ethoxide is formed as a by-product of the pyrolysis of diethylmagnesium diethyl etherate (59). It has been suggested (92) that a cyclic alkylmagnesium alkoxide (XLVII) is a product of the reaction of an excess of allylmagnesium bromide with allyl alcohol.



(XLVII)

Like the beryllium compounds, the alkylmagnesium alkoxides are in general associated in solution (77, 108) and in some cases form stable diethyl etherates (108), although these are readily desolvated. Degrees of association from 3 upward have been reported for the unsolvated compounds: *n*-butylmagnesium isopropoxide is trimeric in benzene (77); ethylmagnesium isopropoxide, ethylmagnesium *tert*-butoxide, and isopropylmagnesium isopropoxide are tetrameric in benzene (108); and ethylmagnesium *n*-propoxide, isopropylmagnesium methoxide, and isopropylmagnesium ethoxide have degrees of association in the range 7–8.4 in benzene (108). Ethylmagnesium ethoxide may be trimeric in diethyl ether [(452); but see also Vreugdenhil (453)]. Structures of type XLVIII have been proposed for the trimers; these formally involve



(XLVIII)

three-coordinate magnesium, but the possibility of additional Mg—O π -bonding (i.e., back-donation from an occupied *n* orbital on oxygen to a vacant orbital on adjacent magnesium) must be taken into account (77). By analogy with the corresponding zinc compounds (see below), the

tetramers may have cubane-type structures (108). The ^1H n.m.r. spectra of some methylmagnesium alkoxides have been recorded, but yielded little information on the constitution of the reagents (223a).

C. ALKYLZINC ALKOXIDES AND ALKYLPEROXIDES

Methylzinc methoxide was recognized as an oxidation product of dimethylzinc over 100 years ago (85), and the process by which dialkylzinc compounds are oxidized to zinc alkoxides, via alkylzinc alkylperoxide and alkylzinc alkoxide intermediates, has been extensively studied (404, and references therein). The products of partial alcoholysis of dialkylzinc compounds are catalysts for the polymerization of alkene oxides, and have thus similarly aroused interest (73). Alkylzinc alkoxides also catalyze the trimerization of isocyanates, possibly by a mechanism involving a "template" coordination process (315).

Treatment of solutions of dialkylzinc compounds with the theoretical amount of an alcohol (or phenol) in general leads to solutions containing reagents with the composition RZnOR' (17, 110, 214). Cryoscopic measurements have indicated that many of the reagents (including the interesting compound with the grouping C-Zn-O-Si-C , from dimethylzinc and trimethylsilanol) (375) are tetrameric in benzene solution (110, 111), and methylzinc methoxide (6, 111) and ethylzinc *tert*-butoxide (289) crystallize in the form of tetramers, in which the zinc and oxygen atoms are arranged in the near-cubic form shown diagrammatically in Fig. 6.

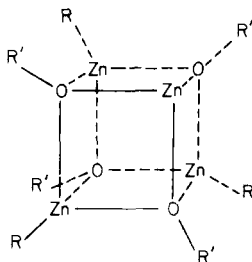
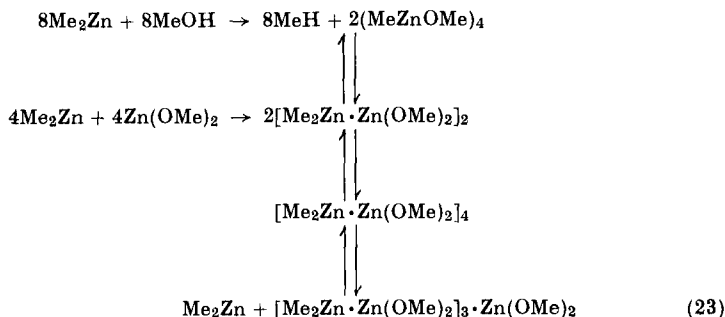


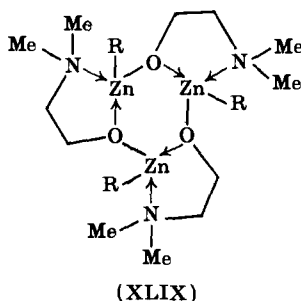
FIG. 6. Alkylzinc alkoxide tetramers: (i) $\text{R} = \text{R}' = \text{Me}$ (6, 111); (ii) $\text{R} = \text{Et}$, $\text{R}' = \text{Me}_3\text{C}$ (289).

Under certain conditions the cubic structure may persist in solution (111) even in the presence of pyridine, although the addition of 4-dimethylaminopyridine to a solution of methylzinc methoxide gives a crystalline adduct, $4-(\text{Me}_2\text{N})\text{C}_5\text{H}_4\text{N} \cdot \text{Zn}(\text{Me})\text{OMe}$, and methylzinc phenoxide tetramer gives a dimeric complex, $[\text{Me}(\text{py})\text{ZnOPh}]_2$, with pyridine (110). However, in some cases the constitution of the reagents in solution is not

straightforward. Bruce and his co-workers (17, 72) have demonstrated, mainly by proton magnetic resonance studies, that methylzinc methoxide and ethoxide and phenylzinc methoxide and ethoxide may contain complex equilibrium mixtures. Thus, the reaction of dimethylzinc with methanol or with zinc methoxide, to give solutions of "methylzinc methoxide," may be represented by the scheme:



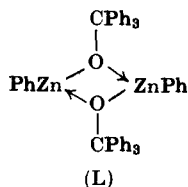
Monoalcoholyses of dimethylzinc and diphenylzinc with isopropanol, *tert*-butanol, and 2-methoxyethanol gave simpler reagents, containing species of the type $(\text{RZnOR}')_n$ (72; cf. 110). Reagents prepared by mixing dimethylzinc with zinc *tert*-butoxide (or zinc *n*-dodecoxide) were more complex than the corresponding reagents prepared by alcoholysis.



Although there is no evidence for chelation of the ether oxygen to zinc in methylzinc 2-methoxyethoxide (72, 111), chelation has been postulated (111) to account for the properties of the products from the reaction of dialkylzinc compounds with 2-dimethylaminoethanol and with acetoxime. The former gives trimers, $(\text{RZnOCH}_2\text{CH}_2\text{NMe}_2)_3$, for which the structure XLIX was suggested. Acetoxime gives a tetramer, $(\text{MeZnON}=\text{CMe}_2)_4$ (111), whose crystal structure has recently been determined (6). The four zinc atoms are at the corners of a tetrahedron, and above each face of the tetrahedron is an acetoximate group with the

oxygen attached to two zinc atoms, and the nitrogen to the third. The strength of the bonding maintaining the polymeric structure is sufficient to prevent its destruction by pyridine or 4-dimethylaminopyridine (111).

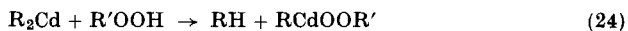
Although dimethylzinc does not react with benzophenone (except possibly to form a donor-acceptor complex), diethylzinc reacts with benzophenone to give ethylene and a trimer, $(\text{EtZnOCPh}_2)_3$, and diphenylzinc adds to the carbonyl group to give a *dimeric* product, $(\text{PhZnOCPh}_3)_2$ (113). *tert*-Butylzinc *tert*-butoxide, from di-*tert*-butylzinc and *tert*-butanol, has also been found to be dimeric in benzene (113). These dimeric and trimeric substances presumably have structures such as L, formally containing three-coordinate zinc (111). In the case of *tert*-butylzinc *tert*-butoxide, the dimeric structure is broken down by pyridine, and a monomeric complex, $\text{Me}_3\text{CZn}(\text{py})\text{OCMe}_3$, is formed (113).



An intermediate in the reaction of diethylzinc with water is thought to be ethylzinc hydroxide (214).

D. ALKYL CADMIUM ALKOXIDES AND ALKYL PEROXIDES

These cadmium derivatives in many respects resemble their zinc analogs. For example, the autoxidation of dialkylcadmium compounds proceeds by a mechanism similar to that of dialkylzinc compounds (404). However, alkylcadmium alkylperoxides, unlike alkylzinc alkylperoxides, may be prepared by the reaction of the dialkyl derivative of the metal with an alkyl hydroperoxide (127):



The reaction of two moles of dimethylcadmium with one mole of hydrogen peroxide probably gave the peroxide formulated as MeCdOOCdMe (127).

Alkylcadmium alkoxides are formed by monoalcoholysis of dialkylcadmium compounds, and are in several cases tetrameric in benzene (107, 375), like the corresponding alkylzinc alkoxides; methylcadmium methoxide is isomorphous with methylzinc methoxide (107). Methylcadmium *tert*-butoxide is exceptional, being dimeric in benzene solution

(107); its structure is presumably similar to that of phenylzinc triphenylmethoxide (L) (111). Methylcadmium *tert*-butoxide is remarkably unreactive, being only slowly hydrolyzed by water or even by 6 *N* sulfuric acid (107).

A recent paper (202) on the catalysis of methyl exchange in dimethylcadmium by traces of oxygen or methanol suggests that there may be complications in the methanolysis of dimethylcadmium, as the tetrameric methylcadmium methoxide was apparently not involved.

The alkylcadmium alkoxides show only weak acceptor properties, and only one crystalline donor-acceptor complex has been reported (107). This complex, Me(py)CdOPh, from methylcadmium phenoxide and pyridine, was partly dissociated in benzene solution.

E. ALKYL MERCURIC ALKOXIDES AND ALKYL PEROXIDES

Russian workers have studied the autoxidation of dialkylmercury compounds, and have rationalized the process in terms of alkylmercuric alkylperoxide and alkoxide intermediates (355, 356). Later the same school reported (352) the synthesis of phenylmercuric cumylperoxide, PhHg·OO·CMe₂·Ph, by the reaction of phenylmercuric chloride with the sodium derivative of cumene hydroperoxide. The synthesis of isopropylmercuric isopropoxide has been claimed (14) and described (357); the substance was formed as a low-melting solid, soluble in hydrocarbons, by the reaction of isopropylmercuric chloride with sodium isopropoxide, and was reactive and somewhat unstable. The synthesis of several phenylmercuric alkoxides has been accomplished by a similar route, and by the reaction of phenylmercuric hydroxide with alcohols; some of their reactions were investigated, including that with haloforms to give phenyl-trihalogenomethylmercury compounds (219).

Because of their instability, structural studies on the alkylmercuric alkoxides will be difficult. Phenylmercuric alkoxides have been reported (219) to be trimers in ethers or benzene, but solvated dimers in alcohols. In view of the very weak acceptor properties of alkylmercury compounds, the nature of the association in such systems merits investigation. Methylmercuric trimethylsiloxide is reported to be *monomeric* in benzene (376).

The alkylmercuric alkoxides and some related compounds (including sulfur analogs) appear to resemble the alkylzinc amides (see Section VI,C below) in undergoing insertion reactions with carbon dioxide, carbon disulfide, isocyanates, etc. However, no systematic investigation of these reactions has been reported, although the relevant references have been collated (272).

Most of the great number of organomercury compounds formulated with the system C-Hg-O are in fact largely covalent, although they are

often regarded as salts of alkylmercuric cations (e.g., "alkylmercuric acetates"). Certain aspects of the chemistry of some of these compounds are reviewed (Section VII,A below), but a comprehensive account is beyond the scope of this article.

VI. Compounds Containing the System C-M-N; the Alkylmetallic Amides

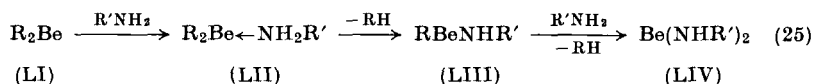
The compounds formed by the reaction of primary and secondary amines with the dialkyl derivatives of several of the Group II metals have been studied; the beryllium derivatives have attracted particular attention. No alkylcalcium, -strontium, -barium, or -cadmium amides have been described.

The alkylmetallic amides present certain features in common with the corresponding alkylmetallic alkoxides, and a comparison of the two series is of interest.

A second class of compounds containing the grouping C-M-N comprises the alkylmetallic azides, R-M-N₃. Methylmercuric azide was the only known Group II metal derivative of this type until recently, but some further alkylmercuric azides have now been reported (417), and some alkylzinc azides have been prepared by the reaction of dialkylzinc compounds with chlorine azide (302).

A. ALKYLBERYLLIUM AMIDES



Following the pioneering work of Coates and his co-workers (101) the reactions of dialkylberyllium compounds with primary or secondary amines have been extensively studied, and the constitution of the products examined. The reactions generally proceed in stages, as formulated in Eq. (25) for a primary amine. In several cases the intermediate products have been obtained; the coordination complexes (LII) are discussed (Section II,B,1a) above, and the beryllium amides (LIV) fall outside the scope of this article. The substances reviewed here are the alkylberyllium amides (LIII); some examples of these compounds are listed in Table III.



As indicated in Table III, the alkylberyllium amides that have been described have various degrees of association, but the majority of the compounds are dimeric or trimeric in solution in benzene. Structure LV has been proposed for the trimers, and structure LVI for the dimers (115). In general, it appears that trimers are formed when the substituents on

beryllium and especially nitrogen are small, and that dimers are formed when the substituents are large (97, 115). Both types of structure involve

TABLE III
ALKYLBERYLLIUM AMIDES

$\text{RBeN} \begin{array}{l} \text{R}' \\ \text{R}'' \end{array}$				
R	R'	R''	Degree of association ^a	Ref.
Me	H	H	polymer ^b	(288)
Me	H	Me	polymer ^b	(101)
Me	H	CH ₂ CH ₂ NMe ₂	2	(102)
Me	Me	Me	3 ^c	(101)
Me	Me	CH ₂ CH ₂ NHMe	2	}
Me	Me	CH ₂ CH ₂ NMe ₂	2	
Me	Et	Et	3	}
Me	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	2	
Me	Ph	Ph	2	
Me	Ph	CH ₂ Ph ^d	2	
Me			e	}
Me			e	
Et	H	H	polymer ^b	(288)
Et	Me	Me	3	(97)
Et	Me	NH ₂	polymer ^b	}
Et	Me	NHMe	polymer	
Et	Me	NMe ₂	4	
Et	Et	Et	2	}
Et	Ph	Ph	2	
Me ₂ CH	Me	Me	3	
Me ₃ C	Me	CH ₂ CH ₂ NMe ₂	1	
Ph	Me	Me	3	}
Ph	Me	CH ₂ CH ₂ NMe ₂	2	
Ph	Ph	Ph	2	

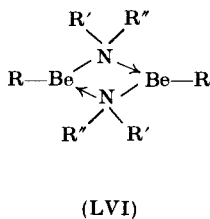
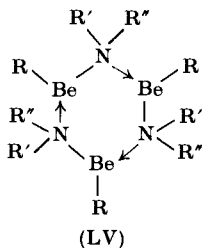
^a In benzene solution, unless otherwise indicated.

^b Insoluble; believed to be polymeric.

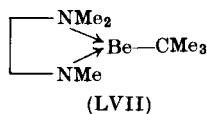
^c Trimeric in benzene and in vapor; probably polymeric glass at room temperature (54).

^d From methylberyllium hydride and benzylidene aniline (52).

^e Not recorded.



three-coordinate beryllium, except where chelation makes four-coordination possible (e.g., when $R' = \text{CH}_2\text{CH}_2\text{NMe}_2$) (115). The proton magnetic resonance spectrum of the methylberyllium dimethylamide trimer is consistent with structure LV ($R = R' = R'' = \text{Me}$), with rapid interconversion of conformations throughout the temperature range studied (-90° to $+25^\circ$) (54). The unique monomeric compound $\text{Me}_3\text{CBeN}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2$ presumably has the chelated structure (LVII) (97).



The alkylberyllium amide polymers involving three-coordinate beryllium are able to form complexes with pyridine or 2,2'-bipyridyl (97), although in some cases the situation is complicated by disproportionation processes. For example, the trimeric methylberyllium trimethylamide formed a dimeric 1:1 adduct, $[\text{Me}(\text{Me}_2\text{N})\text{pyBe}]_2$, or a monomeric 1:2 adduct, $\text{Me}(\text{Me}_2\text{N})\text{py}_2\text{Be}$, with the appropriate proportions of pyridine. The 2,2'-bipyridyl complex of methylberyllium dimethylamide rapidly underwent disproportionation, but both methylberyllium diphenylamide and ethylberyllium diphenylamide formed stable complexes; the ethylberyllium derivative, $\text{Et}(\text{Ph}_2\text{N})\text{bipyBe}$, was shown to be monomeric in benzene.

B. ALKYL MAGNESIUM AMIDES

Although the reaction of dimethylmagnesium with an equimolar amount of dimethylamine led to bis(dimethylamino)magnesium, several alkylmagnesium dialkylamides have been prepared by the reaction of other dialkylmagnesium compounds with secondary amines (104, 108, 112). The products are recorded in Table IV.

TABLE IV

ALKYLMAGNESIUM DIALKYLAMIDES

$\text{RMgN} \begin{array}{l} \nearrow \text{R}' \\ \searrow \text{R}'' \end{array}$			Degree of association ^a	Ref.
R	R'	R''		
Et	Me	CH ₂ CH ₂ NMe ₂	2	(104)
Et	Me	CH $\begin{array}{l} \nearrow \text{Et} \\ \searrow \text{Ph} \end{array}$ ^b	2	(108, 112)
Et	Et	Et	c	} (112)
Et	CHMe ₂	CHMe ₂	c	
Et	Ph	Ph	(polymer) ^{d,e}	
Et	$\begin{array}{c} \diagup \text{CMe}_2\text{---CH}_2 \\ \diagdown \text{CMe}_2\text{---CH}_2 \end{array}$	CH ₂	2	
CHMe ₂	CHMe ₂	CHMe ₂	2	(108, 112)
CHMe ₂	Ph	Ph	(polymer) ^{d,f}	(112)
CHMe ₂	Me	CH ₂ CH ₂ NMe ₂	2	} (104a)
CMe ₃	Me	CH ₂ CH ₂ NMe ₂	2	

^a In benzene solution, unless otherwise indicated.

^b From diethylmagnesium and benzyldiene aniline.

^c The product obtained from diethyl ether solution contained ether molecules, which could not be removed except by displacement by tetrahydrofuran.

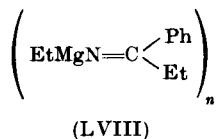
^d Insoluble; presumed to be polymeric.

^e Only weakly solvated by diethyl ether; addition of tetrahydrofuran gave monomeric EtMgNPh₂·(THF)₂.

^f Bis(ether) complex, Me₂CHMgNPh₂·(OEt₂)₂, dissociated in toluene to give unsolvated polymer.

It has been suggested (112) that the tendency of these magnesium derivatives to polymerize is due to the high stability of alkyl bridges between magnesium atoms. The polymeric structure may be broken down by solvation (footnote *e* in Table IV), by chelation (as in the case where R'' = CH₂CH₂NMe₂), or, most interestingly, where bulky groups are attached to nitrogen. In cases of the last type, the dimeric products could be formulated with alkyl or nitrogen bridges between the magnesium atoms; in either case, the otherwise unrecorded three-coordinate magnesium must be involved (108, 112).

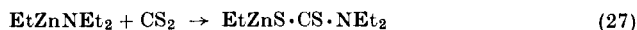
The reaction of diethylmagnesium with benzonitrile in diethyl ether is reported (112), to give a polymeric product, formulated as structure LVIII.



C. ALKYLZINC AMIDES

No methylzinc dimethylamide could be isolated from the product of the reaction of dimethylzinc with dimethylamine (110). However, a number of alkylzinc dialkylamides has been prepared by the reaction of dialkylzinc compounds (diethyl-, diisopropyl-, di-*n*-butyl-, and diphenylzinc) with secondary amines (diethylamine, diphenylamine, and *N,N,N'*-trimethylethylenediamine) (110, 313). The compounds from dimethylzinc and trimethylethylenediamine and from dimethyl- and diethylzinc and diphenylamine are all dimeric in benzene (110); the first of these presumably has a chelated structure with four-coordinate zinc, but the other two must be formulated with three-coordinate zinc (6, 110) (cf. the corresponding beryllium and magnesium compounds). Some *N*-alkylzinc diphenylketimines, from dialkylzinc compounds and diphenylketimine, are also reported to be dimeric in benzene (338a); in the case of *N*-methylzinc diphenylketimine, the dimeric structure was broken down by pyridine, to give a monomeric adduct, $\text{Ph}_2\text{C}=\text{N}\cdot\text{ZnMe}\cdot 2\text{py}$. The compounds formed by the reaction of dimethylzinc (and dimethylcadmium) with trimethylphosphinimide, $\text{Me}_3\text{P}=\text{NH}$, are tetrameric, and are formulated with cubane-type structures (375b).

The reactivity of the alkylzinc amides toward a second molecule of the amine is comparatively low (2, 159a), and in a number of cases they are stable in the presence of an excess of the amine (313). They undergo, however, interesting insertion reactions with, for example, isocyanates, isothiocyanates, carbon dioxide, and carbon disulfide, leading to further compounds containing the groupings C-Zn-N, C-Zn-O, and C-Zn-S (313). Some representative reactions are:



The reaction of alkylzinc dialkylphosphides with isocyanates and isothiocyanates also gives compounds formulated with the grouping C-Zn-N (e.g., $\text{EtZn}\cdot\text{NPh}\cdot\text{CO}\cdot\text{PPh}_2$) (314).

The insertion reactions with isocyanates described above have been formulated as involving addition across the C=N bonds, leading to compounds with the C-Zn-N grouping. However, Coates and Ridley found (111) that the reaction of diethyl- or diphenylzinc with phenyl isocyanate gave tetrameric products, and pointed out that, if, as seems very likely, the NCO group acts as a three-atom bridging group between zinc atoms in the polymers, speculation as to whether addition takes place across C=N or C=O bonds, or whether the products contain C-Zn-N or C-Zn-O groupings, becomes unprofitable. The reaction of pyridine with the adduct of diethylzinc and phenyl isocyanate yielded a crystalline complex, $\text{EtpyZn} \cdot \text{NPh} \cdot \text{COEt}$, which was evidently largely dissociated in benzene solution.

It has been suggested (315) that the trimerization of isocyanates by organozinc amides proceeds via coordination of three molecules of isocyanate to a molecule of a trimeric alkylzinc urea, which acts as a "template."

D. ALKYL MERCURIC AMIDES

Until recently, a lone example of this class of compounds was methyl *N*-phenyl-*N*-(phenylmercuri)carbamate, $\text{PhHg} \cdot \text{NPh} \cdot \text{CO}_2\text{Me}$, obtained by the reaction of phenyl isocyanate with phenylmercuric methoxide (128). However, a series of compounds of this class has now been made by the reaction of phenylmercuric hydroxide with secondary amines (260).

VII. Compounds Containing Other C-M-X Groupings

A. SALTS OF ALKYL MERCURIC CATIONS

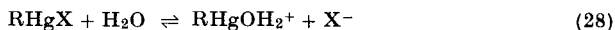
It is possible to consider the alkyl derivatives of the Group II metals, RMX , as salts of alkylmetallic cations, RM^+ , and in some respects it is convenient to formulate them in this way. Thus, for example, alkylzinc cations may be involved in the self-ionization of dialkylzinc compounds (235), and it is possible that alkylmagnesium cations are the reactive species in the reaction of Grignard reagents with ketones (26). The reagents formed by the reaction of magnesium with dimethyl sulfate (321) and with trimethyl phosphate (184) may be thought of in this way, although their constitutions are in fact unknown.

Although the above examples are somewhat exceptional, alkylmercury compounds are often conveniently regarded as salts of alkylmercuric cations, in spite of the fact that they are generally largely covalent, and that truly ionic constitutions are rarely encountered [the alkylmercuric perchlorates are one example (154)]. This is largely be-

cause, owing to the stability of the carbon-mercury bond toward hydrolysis, many alkylmercury derivatives may be studied by the normal methods of aqueous solution chemistry. The chemistry of alkylmetallic cations has recently been well reviewed (434), but some of the more important recent advances in the chemistry of alkylmercuric cations are surveyed here (some of the results discussed in Section IV,A,4 above are also apposite to this section).

Alkylmercuric cations have been studied from two main points of view: the stability of their complexes with various ligands has been compared with that of complexes of the proton, on the one hand, and of the mercuric ion, on the other; and their capacity to increase their coordination number to above 1 has been investigated.

The equilibrium

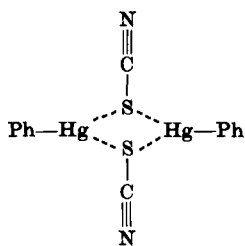


has been studied by a variety of methods, including polarography (396, 437), potentiometry (378), calorimetry (378), and absorption spectroscopy (93a, 378, 396). The simple equilibrium (Eq. 28) is complicated by a number of factors, including hydrolysis to alkylmercuric hydroxide, RHgOH , and formation of binuclear ions such as $(\text{RHg})_2\text{OH}^+$ (see below) (378). However, some clear generalizations may be made, particularly from the comprehensive work of Schwarzenbach and Schellenberg (378) on complexes of the methylmercuric cation. In many respects, the methylmercuric cation resembles the proton, generally having a coordination number of 1, and forming stable complexes with many donor ligands. For example, the degree of dissociation of methylmercuric nitrate in water is remarkably similar to that of nitric acid under comparable conditions (93a). However, the methylmercuric cation is a soft acid whereas the proton is hard (93a, 378), and this difference is reflected particularly in the high stability of complexes of the methylmercuric cation with sulfur donors, compared with the analogous proton complexes (378, 396). An approximately linear relationship has been observed between the logarithm of the stability constants of complexes of methylmercury with a number of ligands, and the nuclear spin-spin coupling constants, $J(^{199}\text{Hg}-^1\text{H})$, for the complexes (374a).

The formation of binuclear ions was mentioned above, and there is also evidence for the formation of trinuclear ions, such as $(\text{RHg})_3\text{S}^+$ (378) and $(\text{RHg})_3\text{O}^+$ (93a).

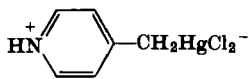
There is a growing body of information concerning the ability of alkylmercuric cations to achieve a coordination number of 2 or even 3. It was noted above (Section IV,B,6) that there is evidence for interaction between ammonia and alkylmercuric halides. With a strong, soft base,

such as a trialkylphosphine, some alkylmercuric salts in fact form isolatable complexes, which are liable, however, to disproportionation (106). Similarly, methylmercuric perchlorate forms with pyridine a complex formulated as $[\text{MeHgpy}]\text{ClO}_4$; the corresponding trimethylamine complex dissociates too rapidly to be isolated (106). There is evidence, from electrophoresis (31) and anion-exchange chromatography (32), for the presence of the ion $[\text{EtHg}(\text{SCN})_2]^-$ in solutions of ethylmercuric thiocyanate in aqueous potassium thiocyanate; a soft ligand is again involved. An analysis of the vibrational spectrum of phenylmercuric thiocyanate indicates that it is a dimer (LIX) (131), and thus provides another example of sulfur functioning as a donor to an organo-mercury group.

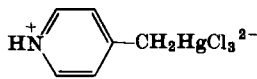


(LIX)

Several studies have been reported on complex formation between alkylmercuric halides and halide ions, particularly the iodide ion (another soft ligand). Complexes are evidently formed between allylmercuric iodide and iodide ion (261), and conductometric studies (151) suggest that, in the presence of potassium halides, trifluoromethylmercuric halides form complex ions such as $[\text{CF}_3\text{HgBrI}]^-$ and $[\text{CF}_3\text{HgI}_3]^{2-}$; the latter ion was reported to form salts with, for example, the zinc(II)-ethylenediamine complex. In related studies it was shown (144, 145) that, although there is some weak interaction between bis(trifluoromethyl)mercury and halide ions in aqueous solution, the evidence (from cryoscopic measurements) is not in favor of the formation of ions of the type $[\text{Hg}(\text{CF}_3)_2\text{X}]^-$. Strong arguments have been advanced (94) that decomposition of the ions LX and LXI is involved in the chloride ion-catalyzed acidolysis of the 4-pyridiomethylmercuric chloride ion.



(LX)



(LXI)

Two recently reported reactions of alkylmercuric salts probably involve one-electron reduction of the alkylmercuric cation to the alkylmercury radical; these are the reduction of alkylmercuric perchlorates with chromous ion (328), and the electrolytic reduction of alkylmercuric acetates in carbon tetrachloride (485).

B. OTHER COMPOUNDS

1. Sulfur Compounds

Several sulfur analogs of the alkylberyllium (97*a*, 101), alkylmagnesium (104*b*), alkylzinc (110), and alkylcadmium (107) alkoxides have been prepared by the reaction of the dialkyl compounds with thiols. These compounds in general have a higher degree of polymerization than the corresponding oxygen compounds. Thus, methylzinc methyl, *n*-propyl, and phenyl sulfides (110) and methylcadmium methyl and phenyl sulfides (107) are insoluble, and presumably polymeric. [Methylberyllium methyl sulfide was not characterized (101).] The degree of polymerization was not so great with bulky groups attached to sulfur. Thus, methylzinc isopropyl sulfide (110) and its cadmium analog (107) are hexamers in benzene, methylzinc and ethylzinc *tert*-butyl sulfides are pentamers (110), and methylcadmium *tert*-butyl sulfide is a tetramer (107). The pentameric structure of methylzinc *tert*-butyl sulfide persists in the solid state, and the crystal structure has been determined (6): the zinc atoms are all four-coordinate, but three, four-, and five-coordinate sulfur is involved. It has been suggested (107) that the hexamers may have structures based on two parallel six-membered rings of alternate metal and sulfur atoms. Several alkylberyllium alkyl sulfides (mostly with bulky groups attached to sulfur) are tetrameric in benzene (97*a*), as is ethylmagnesium *tert*-butyl sulfide (104*b*).

Some of the alkylzinc alkyl sulfides react with pyridine to give dimeric complexes, such as $(\text{MepyZnSCMe}_3)_2$ (see Section V,C above), and methylberyllium phenyl sulfide (97*a*) and some alkylmagnesium *tert*-butyl sulfides (104*b*) gave analogous complexes with ethers. In contrast, methylcadmium *tert*-butyl sulfide did not yield a pyridine adduct; the difference in behavior may be a consequence of the "softer" character of cadmium, resulting in preferential coordination to sulfur rather than to nitrogen.

The compounds formed by the reaction of carbon disulfide with alkylzinc amides (313) and phosphides (314) are formulated with the C-Zn-S system: $\text{RZn}\cdot\text{S}\cdot\text{CS}\cdot\text{NR}_2'$ and $\text{RZn}\cdot\text{S}\cdot\text{CS}\cdot\text{PR}_2'$.

The interaction of alkylmercuric cations with some sulfur ligands was mentioned above. A consequence of the tendency for the formation of

binuclear complexes is the ready formation of bis(methylmercuric) sulfide from methylmercuric thiol; the dipole moment of this sulfide has been measured and compared with its oxygen and selenium analogs (250).

2. Phosphorus Compounds

Some alkylzinc dialkylphosphides have been prepared from the dialkylzinc compounds and dialkylphosphines (110, 314). The compounds are polymeric (110, 314) and reported (314) to be very reactive. They undergo insertion reactions analogous to those of the corresponding amides (314) (see Section VI, C above), and ethylzinc diphenylphosphide forms a quaternary salt, $[\text{EtZn}(\text{PPh}_2)\text{Me}]\text{I}$, with methyl iodide (314).

The reaction of dimethylberyllium with dimethylphosphine leads to an uncharacterized polymeric product (101).

3. Miscellaneous Compounds

A solution presumably containing ethylmagnesium borohydride, EtMgBH_4 , resulted from the reaction of ethyllithium with chloromagnesium borohydride (43). It would be of interest to know whether other compounds containing the C-M-B system are formed as intermediates in the metallation of decaborane (197).

It seems likely (443) that compounds containing the system C-M-As are intermediates in the reaction of diethylmagnesium or diethylzinc with phenyl- or diphenylarsine.

Bis(methylmercuric) selenide has been prepared, and its dipole moment measured (250), and ethylberyllium ethylselenide has been obtained as a 1:2 complex with pyridine (97a).

The reaction of methylmercuric chloride with a solution containing the ion $[\text{Fe}(\text{CO})_4]^{2-}$ is reported (245) to give a complex with the composition $(\text{MeHg})_2\text{Fe}(\text{CO})_4$, which may well contain the trimetallic system C-Hg-Fe-Hg-C.

VIII. Salts of Aromatic Radical Anions

The more electropositive Group II metals are able, like the alkali metals, to transfer electrons to suitable aromatic systems to form compounds that may be regarded as charge-transfer complexes or as salts of aromatic radical anions.

Following the preparation of naphthalenemagnesium in liquid ammonia (233), similar magnesium derivatives of biphenyl, phenanthrene, and anthracene (in liquid ammonia) (281) and of anthracene, pyrene, and 1,1-diphenylethylene (in hexamethylphosphorotriamide)

(161) have been reported. The calcium derivative of acenaphthylene has been prepared in tetrahydrofuran (81), and the uncharacterized materials formed by the action of calcium on a variety of aromatic systems in liquid ammonia (444) are probably similar in nature.

Naphthalenemagnesium has been isolated from its solution in liquid ammonia and redissolved in dipolar aprotic solvents, notably hexamethylphosphorotriamide (336). Spectroscopic studies of magnesium-aromatic hydrocarbon systems have suggested that, in hexamethylphosphorotriamide, solvent-separated ion pairs may be present in some cases (335, 337).

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