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PROGRESS IN
INORGANIC CHEMISTRY

Volume 11

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PROGRESS IN
INORGANIC CHEMISTRY

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VOLUME II

1960

INTERSCIENCE PUBLISHERS, INC., NEW YORK
INTERSCIENCE PUBLISHERS, LTD., LONDON

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Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y.

For Great Britain, and Northern Ireland:

Interscience Publishers, Ltd., 88/90 Chancery Lane, London W. C. 2

PRINTED IN THE UNITED STATES OF AMERICA BY MACK PRINTING CO., EASTON, PA.

Preface to Volume II

I should like to state that neither the authors nor the publishers are responsible for a delay of a year in the publication of the article on solvent extraction by R. M. Diamond and D. G. Tuck. This article was written for Volume I, but because of its length and the unanticipated lengths of other articles in that volume, I appealed to the authors to permit me to defer it to Volume II, and they graciously acceded to this request. I do not believe that this has significantly diminished the value of the article in view of its fundamental rather than topical character.

I wish also to express my deep sorrow at the tragically premature death of Professor George Schaeffer. Inorganic chemistry has lost one of its most sincere and productive contributors. At the time of his death he was at work on a review of borohydride chemistry for this volume.

F. A. Cotton

Cambridge, Mass.
May 16, 1960

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Radioactivation Analysis in Inorganic Geochemistry

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I. Introduction

There is a new urgency to increase our knowledge of the distribution of the elements in the earth's crust and to formulate our knowledge in terms of chemical equilibrium and rate processes. Scientific research and technology are far advanced in understanding the properties and numerous uses of the elements. In sharp contrast, the geochemist has only a rudimentary understanding of the processes which govern the distribution of the elements in nature and for many elements lacks even empirical data on their distribution.

The need to understand the geochemistry of the elements in the earth's crust is particularly urgent at the present time as new demands for certain elements arise and as ore reserves dwindle. Ultimately we must mine and refine extremely low grade ores to maintain our industrial technology, and to this end fundamental knowledge of the behavior of the elements in the earth is of prime importance.

Brown (1) has emphasized the dependence of western civilization on its mineral resources and sources of energy. Should a catastrophe destroy our technological means of production, we could rebuild only

with great difficulty owing to the scarcity of easily accessible mineral deposits. Even today the vulnerability of industry to interruptions in the supply of raw materials makes mandatory an understanding of the occurrence of these materials.

The outlook for future energy production has already received close examination. Hubbert (2) warns that industrial energy production by fossil fuels must cease in a few decades because of exhaustion of supplies of petroleum, natural gas, and coal. Brown and Silver (3) have shown that the concentration of uranium and thorium in average granite is high enough to provide energy considerably in excess of that required to process the granite (assuming fission of all U^{235}, U^{238}, and Th^{232} recovered by acid leach of crushed granite). Weinberg (4) has shown that in principle energy may be produced profitably from average crustal material by any one of the following processes: deuterium fusion, fusion based on lithium reactions, fission of uranium and thorium in breeder reactors, and solar energy conversion. Theoretically, then, the earth's crust contains energy sources sufficient to maintain western industrial civilization for an indefinite length of time.

Of no smaller importance than the means for energy production is the need to insure supplies of mineral raw materials in future technology. Basic to this problem are the questions:

1. What are the abundances of the elements in the rocks of the earth's crust and in the oceans?

2. What is the chemical basis for the distribution of the elements in terms of thermodynamics and chemical reaction kinetics?

Any answer to the second question depends on the answer to the first, which is necessarily obtained by analysis of natural materials. At the present time even the first question is only partly answered. To gain insight into this problem, let us consider in some detail the abundances of the elements in crustal rocks, as they are known today.

II. Elemental Abundances in Rocks of the Earth's Crust

Vinogradov (5) has compiled analytical data up to 1955 for the contents of the elements in four categories of igneous rocks, in sedimentary rocks, and in the silicate phases of chondrite meteorites; his average values are reproduced in Table I. The final column is a weighted average of igneous rocks intended to have nearly the same

TABLE I

Abundances of the Elements in Silicate Rocks (5)

(In weight per cent)

Element	Silicate phase of stone meteorites (chondrites)	Ultrabasic rocks (dunites, peridotites, pyroxenites)	Basic rocks (basalts, gabbro, norites, diabases, etc.)	Intermediate rocks (diorites and andesites)	Acidic rocks (granites, liparites, rhyolites, etc.)	Sedimentary rocks (clays and shales)	Average igneous rock (2 parts of acidic rocks + 1 part of basic rocks)
Li	2.3×10^{-4}	2×10^{-4}	1.5×10^{-3}	2×10^{-3}	7×10^{-3}	6×10^{-3}	5×10^{-3}
Be	—	(2×10^{-5})	1.5×10^{-4}	—	5.5×10^{-4}	7×10^{-4}	4.2×10^{-4}
B	2.5×10^{-4}	(4×10^{-3})	1×10^{-3}	—	1.5×10^{-3}	1.2×10^{-3}	1.3×10^{-3}
C	4×10^{-2}	(1×10^{-2})	(1×10^{-2})	—	3×10^{-2}	1.2	2.3×10^{-2}
N	9×10^{-5}	—	—	—	3.6×10^{-3}	1×10^{-1}	(?)
O	41.02	43.00	44.80	46.10	48.66	51.84	47.3
F	—	(1×10^{-2})	3.7×10^{-2}	5×10^{-2}	8×10^{-2}	5×10^{-2}	6.6×10^{-2}
Na	6.7×10^{-1}	5.7×10^{-1}	1.94	3.0	2.77	0.66	2.50
Mg	15.82	14.10	4.50	2.18	0.56	1.34	1.70
Al	1.74	2.88	8.76	8.85	7.70	10.45	8.10
Si	20.57	20.20	22.80	26.00	32.30	24.8	29.1
P	1.6×10^{-1}	1.2×10^{-1}	1.4×10^{-1}	1.6×10^{-1}	7×10^{-2}	7.7×10^{-1}	9×10^{-2}
S	(1.8)	3×10^{-1}	2×10^{-1}	1×10^{-1}	4×10^{-2}	3×10^{-1}	9×10^{-2}
Cl	5×10^{-2}	(2×10^{-2})	2×10^{-2}	2×10^{-2}	2.4×10^{-2}	1.6×10^{-2}	2.3×10^{-2}
K	(2×10^{-1})	(5×10^{-1})	8.3×10^{-1}	2.31	3.34	2.28	2.50
Ca	1.97	7.70	6.72	4.65	1.58	2.53	3.30
Sc	5.3×10^{-4}	1×10^{-3}	2.4×10^{-3}	1.5×10^{-3}	7×10^{-4}	1×10^{-3}	1.3×10^{-3}
Ti	1.7×10^{-1}	3×10^{-1}	9×10^{-1}	8×10^{-1}	2.3×10^{-1}	4.5×10^{-1}	4.4×10^{-1}

(continued)

TABLE I (*continued*)

Element	Silicate phase of stone meteorites (chondrites)	Ultrabasic rocks (dunites, peridotites, pyroxenites)	Basic rocks (basalts, gabbro, norites, diabases, etc.)	Intermediate rocks (diorites and andesites)	Acidic rocks (granites, liparites, rhyolites, etc.)	Sedimentary rocks (clays and shales)	Average igneous rock (2 parts of acidic rocks + 1 part of basic rocks)
V	7×10^{-3}	1.4×10^{-2}	2×10^{-2}	1×10^{-2}	4×10^{-3}	1.3×10^{-2}	9×10^{-3}
Cr	3.9×10^{-1}	2×10^{-1}	3×10^{-2}	5.6×10^{-3}	$2\ 5 \times 10^{-3}$	$1\ 6 \times 10^{-2}$	1.17×10^{-2}
Mn	$2\ 96 \times 10^{-1}$	1.3×10^{-1}	$2\ 2 \times 10^{-1}$	1.2×10^{-1}	6×10^{-2}	6.7×10^{-2}	1.0×10^{-1}
Fe	(15.64)	9.85	8.56	5.85	2.70	3.33	4.65
Co	(4.5×10^{-2})	2×10^{-2}	4.5×10^{-3}	2×10^{-3}	5×10^{-4}	2.3×10^{-3}	1.8×10^{-3}
Ni	1×10^{-1}	1.2×10^{-1}	$1\ 6 \times 10^{-2}$	5.5×10^{-3}	8×10^{-4}	9.5×10^{-3}	1×10^{-2}
Cu	(1.5×10^{-4})	(8×10^{-3})	$1\ 4 \times 10^{-2}$	$3\ 5 \times 10^{-3}$	3×10^{-3}	5.7×10^{-3}	7×10^{-3}
Zn	$(\sim 10^{-3})$	5×10^{-3}	$1\ 3 \times 10^{-2}$	$7\ 2 \times 10^{-3}$	6×10^{-3}	8×10^{-3}	8×10^{-3}
Ga	—	4×10^{-4}	1.8×10^{-3}	2×10^{-3}	3×10^{-3}	4×10^{-3}	2.6×10^{-3}
Ge	(5×10^{-4})	—	1.5×10^{-1}	(1.5×10^{-4})	3×10^{-4}	7×10^{-4}	2×10^{-4}
As	3×10^{-5}	$2\ 8 \times 10^{-4}$	2×10^{-4}	$2\ 4 \times 10^{-4}$	1.5×10^{-4}	6.6×10^{-4}	2×10^{-4}
Se	—	—	—	—	—	6×10^{-5}	(10^{-6})
Br	6×10^{-4}	(1×10^{-4})	3×10^{-4}	4.5×10^{-4}	1.7×10^{-4}	6×10^{-4}	1.8×10^{-4}
Rb	5.5×10^{-4}	2×10^{-4}	$4\ 5 \times 10^{-3}$	7×10^{-3}	4×10^{-2}	4×10^{-2}	2.8×10^{-2}
Sr	2×10^{-3}	2.7×10^{-3}	$4\ 4 \times 10^{-2}$	8×10^{-2}	3×10^{-2}	4.5×10^{-2}	3.5×10^{-2}
Y	7×10^{-4}	4.5×10^{-4}	$1\ 8 \times 10^{-3}$	3×10^{-3}	2×10^{-3}	3.3×10^{-3}	2×10^{-3}
Zr	3.3×10^{-3}	3×10^{-3}	1×10^{-2}	2.6×10^{-2}	2×10^{-2}	2×10^{-2}	1.7×10^{-2}
Nb	5×10^{-5}	(1.5×10^{-3})	2×10^{-3}	3.5×10^{-4}	2×10^{-3}	2×10^{-3}	2×10^{-3}
Mo	(6×10^{-5})	(4×10^{-5})	1.4×10^{-4}	9×10^{-5}	1.9×10^{-4}	2×10^{-4}	1.7×10^{-4}
Ru	—	—	—	—	—	—	$(10^{-6}?)$

Rh	—	—	—	—	—	—	$(1 \times 10^{-7}?)$
Pd	—	$(1\ 5 \times 10^{-5})$	$(3\ 5 \times 10^{-6})$	—	(1×10^{-6})	—	(2×10^{-6})
Ag	—	(3×10^{-5})	(3×10^{-5})	—	(1.5×10^{-5})	(9×10^{-5})	(2×10^{-5})
Cd	—	—	$1\ 9 \times 10^{-5}$	—	1×10^{-5}	3×10^{-5}	$1\ 3 \times 10^{-5}$
In	(2×10^{-5})	$(1\ 3 \times 10^{-6})$	—	—	$1\ 2 \times 10^{-5}$	—	(10^{-5})
Sn	$4\ 5 \times 10^{-4}$	—	6×10^{-4}	—	$4\ 5 \times 10^{-3}$	3×10^{-3}	3.2×10^{-3}
Sb	1×10^{-5}	1×10^{-5}	$1\ 5 \times 10^{-5}$	2×10^{-5}	4×10^{-5}	1×10^{-4}	3×10^{-5}
Te	—	—	—	—	—	—	(10^{-7})
I	(1×10^{-4})	8×10^{-5}	5×10^{-5}	3×10^{-5}	4×10^{-5}	1×10^{-4}	4×10^{-5}
Cs	(1×10^{-6})	—	—	—	$1\ 9 \times 10^{-3}$	$1\ 2 \times 10^{-3}$	(1×10^{-3})
Ba	6×10^{-4}	$1\ 5 \times 10^{-3}$	2.7×10^{-2}	$6\ 5 \times 10^{-2}$	8.3×10^{-2}	8×10^{-2}	6.4×10^{-2}
La	2×10^{-4}	—	$2\ 7 \times 10^{-3}$	4×10^{-3}	4.6×10^{-3}	4×10^{-3}	4×10^{-3}
Ce	$2\ 3 \times 10^{-4}$	—	$\sim 10^{-3}$	3×10^{-3}	6×10^{-3}	3×10^{-3}	(4×10^{-3})
Pr	1×10^{-4}	—	$1\ 3 \times 10^{-4}$	—	1×10^{-3}	5×10^{-4}	7×10^{-4}
Nd	$3\ 5 \times 10^{-4}$	—	$(\sim 1 \times 10^{-3})$	2×10^{-3}	4×10^{-3}	$1\ 8 \times 10^{-3}$	3×10^{-3}
Pm	?	?	?	?	?	?	?
Sm	1×10^{-4}	—	$(1\ 5 \times 10^{-4})$	—	6×10^{-4}	5×10^{-4}	(4×10^{-4})
Eu	(3×10^{-5})	—	—	—	$(1\ 7 \times 10^{-4})$	(1×10^{-4})	$(\sim 10^{-4})$
Gd	(2×10^{-4})	—	(2×10^{-4})	—	(1×10^{-3})	5×10^{-4}	(7×10^{-4})
Tb	(6×10^{-5})	—	—	—	(2.5×10^{-4})	9×10^{-5}	$(\sim 10^{-4})$
Dy	(2×10^{-4})	—	(1.5×10^{-4})	—	(5×10^{-4})	4×10^{-4}	(4×10^{-4})
Ho	(7×10^{-5})	—	—	—	—	(1×10^{-4})	?
Er	(2×10^{-4})	—	1×10^{-4}	—	(2.5×10^{-4})	$2\ 5 \times 10^{-4}$	(2×10^{-4})
Tm	(3.5×10^{-4})	—	—	—	(2×10^{-4})	(2×10^{-5})	(1×10^{-4})
Yb	(2×10^{-4})	—	1×10^{-4}	—	(2×10^{-4})	2.2×10^{-4}	(2×10^{-4})
Lu	—	—	—	—	(2×10^{-4})	(2×10^{-5})	(1×10^{-4})
Hf	(6×10^{-5})	(6×10^{-5})	(2×10^{-4})	(5×10^{-4})	(4×10^{-4})	(4×10^{-4})	(3×10^{-4})

(continued)

TABLE I (*continued*)

Element	Silicate phase of stone meteorites (chondrites)	Ultrabasic rocks (dunites, peridotites, pyroxenites)	Basic rocks (basalts, gabbro, norites, diabases, etc.)	Intermediate rocks (diorites and andesites)	Acidic rocks (granites, liparites, rhyolites, etc.)	Sedimentary rocks (clays and shales)	Average igneous rock (2 parts of acidic rocks + 1 part of basic rocks)
Ta	5×10^{-5}	7.5×10^{-5}	1×10^{-4}	7×10^{-5}	3.5×10^{-4}	3.5×10^{-4}	2.7×10^{-4}
W	—	—	(1×10^{-3})	1×10^{-4}	—	—	?
Re	(8×10^{-8})	—	(6×10^{-6})	—	(6×10^{-7})	—	($\sim 10^{-7}$)
Os	—	—	—	—	—	—	(10^{-8}?)
Ir	—	—	—	—	—	—	(10^{-7})
Pt	(1×10^{-6})	—	—	—	—	—	(5×10^{-7})
Au	—	(1×10^{-5})	(3.5×10^{-6})	—	(1×10^{-6})	—	($\sim 10^{-7}$)
Hg	(1×10^{-6})	—	9×10^{-6}	—	4×10^{-6}	4×10^{-5}	6×10^{-6}
Tl	—	(6×10^{-6})	2×10^{-5}	(1.5×10^{-5})	2.5×10^{-4}	(2×10^{-4})	1.7×10^{-4}
Pb	(2×10^{-4})	—	8×10^{-4}	(1.5×10^{-3})	2×10^{-3}	2×10^{-3}	1.6×10^{-3}
Bi	(7×10^{-6})	—	—	—	(2×10^{-4})	(1×10^{-4})	($\sim 10^{-5}$)
Po	7.4×10^{-16}	2.2×10^{-16}	5.9×10^{-15}	1.3×10^{-14}	2.6×10^{-14}	2.4×10^{-14}	2×10^{-14}
Rn	2.2×10^{-17}	6.5×10^{-18}	1.7×10^{-16}	3.9×10^{-16}	7.6×10^{-16}	6.9×10^{-16}	6×10^{-16}
Ra	3.4×10^{-12}	1×10^{-12}	2.7×10^{-11}	6×10^{-11}	1.2×10^{-10}	1×10^{-10}	9×10^{-11}
Ac	2.1×10^{-15}	6.4×10^{-16}	1.7×10^{-14}	3.8×10^{-14}	7.4×10^{-14}	6.8×10^{-14}	5.5×10^{-14}
Th	1×10^{-4}	(6×10^{-4})	3×10^{-4}	7×10^{-4}	1.8×10^{-3}	1.1×10^{-3}	1.3×10^{-3}
Pa	3.5×10^{-12}	1×10^{-12}	2.7×10^{-4}	6.2×10^{-11}	1.2×10^{-10}	1.1×10^{-10}	9×10^{-11}
U	1×10^{-5}	(3×10^{-6})	8×10^{-5}	1.8×10^{-4}	3.5×10^{-4}	3.2×10^{-4}	2.6×10^{-4}

composition as sedimentary rocks with respect to the major elements. This average also has nearly the same composition with respect to most trace elements.

Included in this table are analytical data for 83 elements. Because of insufficient data the elements H, He, Ne, A, Kr, and Xe have been omitted, and values for Po, Rn, Ra, Ac, and Pa have been calculated assuming radioactive secular equilibrium with U and Th. All other data are based on reported chemical analyses of rocks by all analytical methods. Values in parentheses are open to question and need additional verification; where no value is given, data are entirely lacking or are insufficient to estimate an average. For some elements no values for any rock types are given, but a value for average igneous rock is estimated in the last column from meager data given elsewhere in the compilation (5).

We examine these data and note the following:

1. Eight elements—O, Si, Al, Fe, Ca, Na, K, and Mg—together comprise 99.15% of the weight of average igneous rock, and four others—Ti, Mn, S, and P—comprise 70% of the remaining elements.

2. Complete analytical data for all rock types are lacking for the majority of elements. This is most obvious for Se, Te, and the Pt group metals where practically no analyses are available. Data for the rare earths are based for the most part on spectrographic analysis by only three investigators, and ultrabasic rocks as a whole have been studied relatively little.

In Table II the abundance data for 76 elements (from the last column of Table I, excluding N, Pm, Po, Rn, Ra, Ac, and Pa) are arranged in concentration ranges from less than 0.1 to greater than 1000 parts per million (p.p.m.). From these data we observe the following:

1. For exactly half of these elements the average abundances are less than 10 p.p.m., and 11 elements lie below 0.1 p.p.m. Only 20 elements occur at average concentrations greater than 100 p.p.m., but most of these are no greater than 1000 p.p.m. (0.1%).

2. For most of the elements above 10 p.p.m. some analytical data exist for any of the rock types considered. However, for all elements which occur at less than 10 p.p.m., except for As, Ta, Sb, and I, data are completely lacking for some of the rock types.

It is essential for an adequate understanding of the geochemical behavior of the elements that we at least know their abundances in the

TABLE II
Abundances of the Elements in Average Igneous Rock

<0.1 p.p.m.	0.1–1 p.p.m.	1–10 p.p.m.	10–100 p.p.m.	100–1000 p.p.m.	>1000 p.p.m.
Se	Ag	Be	Li	C	O
Ru	Cd	Ge	B	F	Na
Rh	In	As	Sc	P	Mg
Pd	Sb	Br	V	S	Al
Te	I	Mo	Co	Cl	Si
Re	Bi	Pr	Ni	Cr	K
Os		Sm	Cu	Mn	Ca
Ir		Eu	Zn	Rb	Ti
Pt		Gd	Ga	Sr	Fe
Au		Tb	Y	Zr	
Hg		Dy	Nb	Ba	
		Ho?	Sn		
		Er	Cs		
		Tm	La		
		Yb	Ce		
		Lu	Nd		
		Hf	Pb		
		Ta	Th		
		W?			
		Tl			
		U			

principal types of rocks in the earth's crust. From the foregoing it is apparent that for the majority of elements this requirement is not fulfilled.

III. Analytical Sensitivity in Geochemical Analysis

There is a strong correlation between the amount of available analytical data and the abundance of an element. Analytical sensitivity limitations are the determining factor in studying the occurrence of the rarer elements, and the occurrence of most elements in many rocks has remained uninvestigated for want of a sensitive analytical method. To appreciate this problem, let us examine the sensitivity limits of the methods of analysis used in geochemistry.

Four general analytical methods are commonly employed in geochemistry: emission spectroscopy with a d.c. arc, X-ray fluorescence

spectroscopy, colorimetric analysis of solutions, and neutron activation analysis. (The methods of mass spectrometric isotope dilution analysis and electron probe microanalysis (6) are not included in this comparison. Each enjoys unique advantages over other analytical methods in certain cases, but to include them in the comparison would not invalidate the conclusions reached here.)

In Table III are listed values for the limits of sensitivity for detecting the elements by d.c. arc emission spectroscopy as given by Ahrens (7). Similar values are given by Wager and Mitchell (8). Using procedures commonly employed in silicate rock analysis, these limiting concentrations of elements are detectable by ignition of 50 mg. of sample in a carbon arc. For the 50 mg. sample a 20 p.p.m. limit corresponds to 1 μg. of the element on the electrode.

TABLE III

Direct Current Arc Emission Spectroscopy Sensitivity Limits for Silicate Analysis (7)

(Sample size 50 mg., in carbon electrode)

Element	Limit, p.p.m.	Element	Limit, p.p.m.
Na	0.3	V	3
K	2	Ni	3
Li	0.3	Co	3
Rb	1	Zr	10
Cs	2	Cr	1
		Sc	2
Ga	2	Y	10
Pb	5	Nd	10
Ag	0.5	La	10
Cu	1	Sr	3
Tl	1	Ba	3
In	1	Mo	3
Sn	10	Ti	10
Zn	100		
Ge	5	F	50
		Al	2
		Ca	2
		Mg	2
		Fe	5
		Mn	3
		Si	20

Examining Table III and comparing the results of Tables I and II, we observe that most elements exist on the average at or below the sensitivity limit for detection by emission spectroscopy. Only a few elements are sufficiently abundant to be studied by this method, especially at concentrations ranging down to 10% of the average.

Kemp (9) has reported the sensitivities attainable by measurement of X-ray emission spectra using the Applied Research Laboratories X-ray scanning quantometer. In Table IV these limits are given for high sensitivity operation (1 minute integration, low resolution). The data indicate no general improvement in sensitivity over emission spectroscopy.

TABLE IV

X-Ray Emission Limits of Detectability (9)

(Standard deviation at background, p.p.m.)

Element	Limit	Element	Limit	Element	Limit
$_{20}$Ca	60	$_{45}$Rh	8	$_{70}$Yb	8
$_{21}$Sc	40	$_{46}$Pd	10	$_{71}$Lu	10
$_{22}$Ti	10	$_{47}$Ag	10	$_{72}$Hf	10
$_{23}$V	8	$_{48}$Cd	20	$_{73}$Ta	10
$_{24}$Cr	5	$_{49}$In	20	$_{74}$W	10
$_{25}$Mn	3	$_{50}$Sn	30	$_{75}$Re	10
$_{26}$Fe	3	$_{51}$Sb	40	$_{76}$Os	10
$_{27}$Co	3	$_{52}$Te	50	$_{77}$Ir	15
$_{28}$Ni	3	$_{53}$I	70	$_{78}$Pt	15
$_{29}$Cu	3	$_{54}$Xe	100	$_{79}$Au	15
$_{30}$Zn	3	$_{55}$Cs	200	$_{80}$Hg	15
$_{31}$Ga	3	$_{56}$Ba	50	$_{81}$Tl	15
$_{32}$Ge	3	$_{57}$La	30	$_{82}$Pb	20
$_{33}$As	3	$_{58}$Ce	20	$_{83}$Bi	20
$_{34}$Se	5	$_{59}$Pr	10	$_{84}$Po	20
$_{35}$Br	5	$_{60}$Nd	10	$_{85}$At	20
$_{36}$Kr	5	$_{61}$Pm	10	$_{86}$Rn	20
$_{37}$Rb	5	$_{62}$Sm	8	$_{87}$Fr	30
$_{38}$Sr	8	$_{63}$Eu	8	$_{88}$Ra	30
$_{39}$Y	3	$_{64}$Gd	8	$_{89}$Ac	30
$_{40}$Zr	3	$_{65}$Tb	8	$_{90}$Th	30
$_{41}$Nb	3	$_{66}$Dy	8	$_{91}$Pa	30
$_{42}$Mo	5	$_{67}$Ho	8	$_{92}$U	30
$_{43}$Tc	5	$_{68}$Er	8	$_{93}$Np	40
$_{44}$Ru	5	$_{69}$Tm	8		

Sandell (10) has given sensitivity limits for colorimetric and fluorimetric methods of analysis, and these are summarized in Table V. The values given refer to the most sensitive test described by Sandell and refer to the minimum detectable amount of the element in grams per cm.^{2} of photometer light beam. (The minimum detectable amount of an element is defined as that when $\log_{10} I_0/I = 0.001$. Brief references made by Sandell to some new reagents, sometimes very sensitive, have not been considered in selecting the most sensitive test.)

The sensitivity of colorimetric analysis is considerably greater than either of the spectroscopic methods considered in Tables III and IV. Using a colorimeter cell of 1 cm.^{2} area, most of the 45 elements in

TABLE V

Colorimetric Sensitivities (10)

(Amount of element in units of 10^{-9} g./cm.^{2} corresponding to $\log_{10} I_0/I = 0.001$)

Element	Limit	Element	Limit
Li	1.2	Rh	9
Be	5.	Pd	5
Mg	1.1	Ag	5
Al	0.21	Cd	1.4
Ca	1.4	In	~10
Sc	6.	Sn	~100
Ti	2.6	Sb	2
V	9	Ba	1
Cr	1.2	Ce	25
Mn	5	Ta	40
Fe	2.	W	9
Co	1.9	Re	5
Ni	4	Os	0.5
Cu	0.8	Ir	3.9
Zn	1.6	Pt	2.9
Ga	~40	Au	3.
Ge	0.85	Hg	4.4
As	1.8	Tl	2.3
Sr	3.	Pb	3.1
Zr	4.	Bi	~10
Nb	2.4	Th	6.
Mo	10.	U	13.
Ru	~0.1		

Table V may be detected with sensitivities of 10^{-8} g. or better, and Al, Cu, Ge, Ru, and Os with sensitivities better than 10^{-9} g. Only Ga, Sn, Ce, and Ta have limits higher than 10^{-8} g. However, certain elements for which no satisfactory sensitive color reactions exist are not included in Table V, viz., the alkalies, the rare earths, Se, Te, the halogens, and the inert gases.

A brief comparison of Table V with Tables I and II suggests that in general sensitive colorimetric analysis permits accurate measurement of most elements at their average concentration in a 0.1 g. sample. (A sample of 0.1 g. is taken as the maximum desirable size for analysis of rocks and minerals because of ease both in separation of minerals from polymineralic rock for individual mineral analysis and in chemical processing in general.) However, to examine more rigorously

TABLE VI

Elements Having Acceptable Colorimetric Analytical Sensitivities

Element	Average abundance, p.p.m.	Colorimetric sensitivity limit, 10^{-9} g./cm.^{2}
Li	50.	1.2
Mg	1.70×10^4	1.1
Al	8.10×10^4	0.21
Ca	3.30×10^4	1.4
Sc	13.	6.
Ti	4400.	2.6
V	90.	9.
Cr	117.	1.2
Mn	1000.	5.
Fe	4.65×10^4	2.
Co	18.	1.9
Ni	100.	4.
Cu	70.	0.8
Zn	80.	1.6
Ge	2.	0.85
As	2.	1.8
Sr	350.	3.
Zr	170.	4.
Nb	20.	2.4
Ba	640.	4.
Ce	40.	25.
Pb	16.	3.1
Th	13.	6.

the question of sensitivity versus concentration of occurrence, let us impose the requirements that only 0.1 g. of sample is available for analysis and that an adequate analytical method must have a sensitivity limit one order of magnitude below the lowest concentration measured. Let the lowest concentration measured be 10% of the average concentration. The sensitivity limit of an acceptable analytical method must then be two orders of magnitude below the average concentration at which the element occurs.

Table VI lists those elements whose sensitivity limits according to Table V, assuming 0.1 g. of sample is analyzed, are two orders of magnitude below the amounts contained in average igneous rocks according to the last column of Table I, i.e., whose sensitivity limits in 10^{-9} g./cm.^{2} do not exceed the average concentration in parts per million. The surprising result is that of the 83 elements listed in Table I, only 23 have acceptable colorimetric procedures according to this criterion, and only 13 of these are heavier than Fe.

It is abundantly clear from the foregoing data that the geochemist, who is attempting to study the distribution of the elements in nature, is confronted with a formidable analytical problem.

IV. Sensitivity of Analysis by Neutron Activation

Analysis by neutron activation in a fission reactor is a highly sensitive and generally applicable method for determining the elements. Its principles have been described by Boyd (11), Smales (12), Leddicotte and Reynolds (13), and Meinke (14), and general radiochemical techniques upon which it is based have been described in textbooks, e.g., Friedlander and Kennedy (15) and Cook and Duncan (16). The sensitivities attainable by neutron activation analysis have been reported by Leddicotte and Reynolds (13), Meinke (14), and Schindewolf (17), and relevant nuclear data have been compiled by Koch (18) and Salmon (19). Reed (20) and Smales *et al.* (21) have summarized some recent applications to geochemistry. Activation analyses of geological materials published recently include studies of Th (22) and U (23) in meteorites; of cosmic spherules (24); of In in igneous rocks (25); of rapid Si, Al, and Na determination in silicate rocks (26); and of K–A age determination (27).

Like most methods of trace element determination, radioactivation analysis depends on a reaction of the element and on measurement of

some physical property of the reaction product, in this case its radioactivity. In neutron activation analysis one or more of the isotopes of the element are transformed into a new radioactive nuclide by a neutron reaction, and the amount of induced radioactivity is proportional to the amount of the element present. Usually the analytical procedure requires simultaneous irradiation of sample and standard, radiochemical separation and purification of the desired element, and counting of the induced radioactivity in a scintillation, proportional, or G-M counter.

For neutron activation analysis the slow neutron flux of a reactor is commonly used. Research reactors are now located within ready access to most laboratories in the United States (28), and irradiated samples may be shipped by air within a few hours after irradiation to the investigator's laboratory. The cost of irradiation is not the major cost of the analysis.

Neutron activation analysis is a general analytical method applicable to all elements heavier than neon and nearly always with high sensitivity. (Some of the elements neon and lighter may also be determined indirectly under certain circumstances.) Table VII is a compilation of the elements heavier than neon and their prominent radioactive thermal neutron reaction products. In the column labeled "Activity" are listed the most important species, with their half-lives, produced directly by neutron capture reactions, indirectly as daughter activities of the original reaction product, and in one case by (n, p) reaction (S^{35} from Cl). The corresponding measurable radiations are listed in the next column, viz., nuclear beta rays (β), nuclear gamma rays (γ), and atomic X-rays (x) and Auger and conversion electrons (e) if β and γ are absent.

In the final two columns of Table VII are given the sensitivity limits for detecting the elements when the corresponding radioactive species are measured. Each value is the weight of the element, W_{150} and W_1, in units of 10^{-9} g., which will give rise to 10 disintegrations per second when irradiated in a thermal neutron flux of 1×10^{13} n/cm.^{2} second for a maximum of either of two irradiation times, $t_{ir} = 150$ hours (6.25 days) and $t_{ir} = 1$ hour, respectively. The absolute values of these limits are significant to about 10%. Details on the calculation of sensitivity limits are given in the Appendix (pages 28–30).

TABLE VII

Neutron Activation Analysis Sensitivity Limits, W

(Flux = 1×10^{13} n/cm.^{2} sec.; A = 10 dis./sec.; t_{ir} = 150 hrs. and 1 hr.)

Element	Activity	Radiation		W_{150}, 10^{-9} g.	W_1, 10^{-9} g.
$_{11}$Na	14.97 hr. Na^{24}	β	γ	0.080	1.7
$_{12}$Mg	9.45 min. Mg^{27}	β	γ	13.	13.
$_{13}$Al	2.27 min. Al^{28}	β	γ	0.21	0.21
$_{14}$Si	2 65 hr. Si^{31}	β		14.	60.
$_{15}$P	14.22 day P^{32}	β		1.0	130.
$_{16}$S	87 day S^{35}	β		100.	$15. \times 10^3$
	5.04 min. S^{37}	β	γ	2.2×10^3	2.2×10^3
$_{17}$Cl	37 29 min. Cl^{38}	β	γ	0.43	0.64
	87 day S^{35}	β		8.5	1.2×10^3
$_{18}$A	110 min. A^{41}	β	γ	0.13	0.41
	35.0 day A^{37}	x	e	28	4.0×10^3
$_{19}$K	12 46 hr. K^{42}	β	γ	0.65	12.
$_{20}$Ca	57 min. Sc^{49}	β		33.	63
	8 8 min. Ca^{49}	β	γ	33.	33.
	164 day Ca^{45}	β		150.	$22. \times 10^3$
$_{21}$Sc	83 9 day Sc^{46}	β	γ	0.067	9.7
$_{22}$Ti	5.80 min. Ti^{51}	β	γ	11.	11.
$_{23}$V	3 76 min. V^{52}	β	γ	0.019	0.019
$_{24}$Cr	27 8 day Cr^{51}		γ	0.83	120.
	3.52 min. Cr^{55}	β		9.6	9.6
$_{25}$Mn	2.576 hr. Mn^{56}	β	γ	0.0069	0.029
$_{26}$Fe	44 3 day Fe^{59}	β	γ	310	$43. \times 10^3$
	2 60 yr. Fe^{55}	x	e	120.	$19. \times 10^3$
$_{27}$Co	5 24 yr. Co^{60}	β	γ	1.2	180.
	10.47 min. Co^{60m}		γ	0.0061	0.0062
$_{28}$Ni	2.564 hr. Ni^{65}	β	γ	5.8	25.
$_{29}$Cu	12.87 hr. Cu^{64}	β	γ	0.033	0.62
	5.10 min. Cu^{66}	β	γ	0.19	0.19
$_{30}$Zn	52 min. Zn^{69}	β		0.59	1 1
	13.8 hr. Zn^{69m}		γ	5.9	120.
	246 day Zn^{65}	β	γ	28.	4.1×10^3
$_{31}$Ga	14 3 hr. Ga^{72}	β	γ	0.047	0.98
	21.1 min. Ga^{70}	β	γ	0.14	0.16
$_{32}$Ge	82 min. Ge^{75}	β	γ	0.60	1.5
$_{33}$As	26.8 hr. As^{76}	β	γ	0.019	0.71
$_{34}$Se	18.2 min. Se^{81}	β		0.53	0.58
	2.30 hr. Br^{83}	β	γ	26	100.
	121 day Se^{75}		γ	17	2.4×10^3
$_{35}$Br	35.87 hr. Br^{82}	β	γ	0.070	3.4
	17.6 min. Br^{80}	β	γ	0.031	0.034
	4.38 hr. Br^{80m}		γ	0.090	0.61

(continued)

TABLE VII (*continued*)

Element	Activity	Radiation		W_{150}, 10^{-9} g.	W_1, 10^{-9} g.
$_{36}$Kr	114 min. Kr^{83m}	x	e	0.027	0.089
	4.36 hr. Kr^{85m}	β	γ	2.4	17.
$_{37}$Rb	17.8 min. Rb^{88}	β	γ	4.3	4.7
	18.68 day Rb^{86}	β	γ	0.96	130
$_{38}$Sr	2.80 hr. Sr^{87m}		γ	0 85	3.9
$_{39}$Y	64.4 hr. Y^{90}	β		0.15	11.
$_{40}$Zr	17.0 hr. Zr^{97}	β	γ	100	2.6×10^3
	65 day Zr^{95}	β	γ	180	26×10^3
$_{41}$Nb	6 6 min. Nb^{94m}	x	e	0 15	0 15
$_{42}$Mo	67.0 hr. Mo^{99}	β	γ	1 5	110
	14 61 min. Mo^{101}	β	γ	8.3	8 9
$_{43}$Tc					
$_{44}$Ru	4.45 hr. Ru^{105}	β	γ	1.3	8.9
	39.7 day Ru^{103}	β	γ	3.6	510.
	35.30 hr. Rh^{105}	β	γ	1.4	66.
$_{45}$Rh	4.4 min. Rh^{104m}		γ	0.014	0.014
	44 sec. Rh^{104}	β	γ	0.0012	0.0012
$_{46}$Pd	13.5 hr. Pd^{109}	β	γ	0.049	0.96
	7.6 day Ag^{111}	β	γ	11.	$1\ 3 \times 10^3$
$_{47}$Ag	2.3 min. Ag^{108}	β	γ	0.0078	0.0078
	253 day Ag^{110m}	β	γ	3.8	550.
	24.2 sec. Ag^{110}	β	γ	0.0033	0.0033
$_{48}$Cd	53 hr. Cd^{115}	β	γ	0.69	44.
	3.0 hr. Cd^{117m}	β	γ	1.6	8.0
$_{49}$In	53.99 min. In^{116m}	β	γ	0.0013	0.0024
$_{50}$Sn	27.5 hr. Sn^{121}	β		4.4	170.
	39 5 min. Sn^{123}	β	γ	26.	40.
	9.5 min. Sn^{125}	β	γ	16.	17.
$_{51}$Sb	2.80 day Sb^{122}	β	γ	0.036	2.7
$_{52}$Te	9.4 hr. Te^{127}	β		1.4	20.
	74 min. Te^{129}	β	γ	5.1	12.
	24.8 min. Te^{131}	β	γ	2.8	3.4
	8 08 day I^{131}	β	γ	6.7	780.
$_{53}$I	25.4 min. I^{128}	β	γ	0.038	0.046
$_{54}$Xe	9.13 hr. Xe^{135}	β	γ	10.	140.
	5 27 day Xe^{133}	β	γ	7.2	740
	3.9 min. Xe^{137}	β		16.	16
$_{55}$Cs	3.2 hr. Cs^{134m}		γ	13.	68.
	2.07 yr. Cs^{134}	β	γ	0.82	120.
$_{56}$Ba	84.0 min. Ba^{139}	β	γ	1.4	3.5
	12.0 day Ba^{131}		γ	66.	8.3×10^3
$_{57}$La	40.22 hr. La^{140}	β	γ	0.031	1 6

TABLE VII (*continued*)

Element	Activity	Radiation		W_{150}, 10^{-9} g.	W_1, 10^{-9} g.
$_{58}$Ce	33 hr. Ce^{143}	β	γ	2.4	110
	33.1 day Ce^{141}	β	γ	6.5	960.
	13.76 day Pr^{143}	β		8.6	1.1×10^3
$_{59}$Pr	19.2 hr. Pr^{142}	β	γ	0.022	0.60
$_{60}$Nd	12 min. Nd^{151}	β	γ	1.4	1.5
	2.0 hr. Nd^{149}	β	γ	1.1	3.9
	11.06 day Nd^{147}	β	γ	2.4	300.
	27.5 hr. Pm^{151}	β	γ	1.5	57.
	54 hr Pm^{149}	β	γ	1.3	88.
$_{61}$Pm					
$_{62}$Sm	47.1 hr. Sm^{153}	β	γ	0.0075	0.58
	23.5 min. Sm^{155}	β	γ	0.20	0.24
$_{63}$Eu	9.2 hr. Eu^{152}	β	γ	0.00038	0.0052
$_{64}$Gd	18.0 hr. Gd^{159}	β	γ	0.27	7.0
	3.6 min. Gd^{161}	β	γ	1.5	1.5
	6.88 day Tb^{161}	β	γ	3.2	360.
$_{65}$Tb	72.3 day Tb^{160}	β	γ	0.099	14.
$_{66}$Dy	139.2 min. Dy^{165}	β	γ	0.00046	0.0018
$_{67}$Ho	27.3 hr. Ho^{166}	β	γ	0.0047	0.18
$_{68}$Er	7.8 hr. Er^{171}	β	γ	0.21	2.4
$_{69}$Tm	129 day Tm^{170}	β	γ	0.065	9.6
$_{70}$Yb	101 hr. Yb^{175}	β	γ	0.024	2.2
	1.9 hr. Yb^{177}	β	γ	0.41	1.3
	6.75 day Lu^{177}	β	γ	0.86	96.
	31.8 day Yb^{169}		γ	0.15	20.
$_{71}$Lu	3.71 hr. Lu^{176m}	β	γ	0.0085	0.050
	6.75 day Lu^{177}	β	γ	0.0059	0.65
$_{72}$Hf	44.6 day Hf^{181}	β	γ	0.92	130.
	70 day Hf^{175}		γ	2.0	290.
$_{73}$Ta	115.1 day Ta^{182}	β	γ	0.19	28
	16.5 min. Ta^{182m}		γ	10.	11.
$_{74}$W	24.0 hr. W^{187}	β	γ	0.021	0.73
$_{75}$Re	16.7 hr. Re^{188}	β	γ	0.0073	0.18
	88.9 hr. Re^{186}	β	γ	0.0095	0.84
$_{76}$Os	30.6 hr. Os^{193}	β	γ	0.50	18.
$_{77}$Ir	19.0 hr. Ir^{194}	β	γ	0.0040	0.11
$_{78}$Pt	17.4 hr. Pt^{197}	β	γ	1.5	39.
	30 min. Pt^{199}	β	γ	1.2	1.5
	3.14 day Au^{199}	β	γ	1.6	130.
$_{79}$Au	2.697 day Au^{198}	β	γ	0.0043	0.32
$_{80}$Hg	24 hr. Hg^{197m}		γ	0.077	2.6
	65 hr. Hg^{197}		γ	0.096	7.2

(*continued*)

TABLE VII (*continued*)

Element	Activity	Radiation	W_{150}, 10^{-9} g.	W_1, 10^{-9} g.
$_{81}$Tl	4.19 min. Tl^{206}	β	4.8	4.8
	3.56 yr. Tl^{204}	β	14.	6.4×10^3
$_{82}$Pb	3.30 hr. Pb^{209}	β	1.1×10^3	5.9×10^3
$_{83}$Bi	5.013 day Bi^{210}	β	32.	3.2×10^3
$_{90}$Th	22.12 min. Th^{233}	β	0.053	0.061
	27.0 day Pa^{233}	β γ	0 36	49.
$_{92}$U	23 54 min. U^{239}	β γ	0 15	0 17
	2.346 day Np^{239}	β γ	0.17	12.
	12.80 day Ba^{140}	β γ	5 0	660.

To aid in comparing their sensitivities, the elements have been arranged in Table VIII in groups according to the lowest sensitivity limit given in Table VII. Of the 73 elements listed, 39 have sensitivity limits between 0.01 and 1 millimicrogram (mμg.) for the 150 hour irradiation time or 0.1 and 10 mμg. for the 1 hour time; 13 elements may be detected more sensitively, and only 21 less sensitively.

Let us now compare the elements for their abundances in average igneous rock (Tables I and II) and their neutron activation analytical sensitivities (Tables VII and VIII). Again (cf. Table VI), let us require for acceptable sensitivity a limit lower than 1% of the amount of the element contained in an average sample of 0.1 g. Therefore, sensitivity limits in mμg. which do not exceed the average elemental abundances in p.p.m. are acceptable. Table IX lists 55 elements which are acceptable according to this criterion and 3 inert gases for which there are no abundance data. The elements are grouped according to the ratio

R = Sensitivity limit (10^{-9} g.)

$\div$ Abundance in average igneous rock (p.p.m.)

TABLE VIII

Neutron Activation Analysis Sensitivities (Elements Arranged by Sensitivity Groups; in 10^{-9} g.)

(Flux = 1×10^{13} n/cm.^{2} sec.; A = 10 dis./sec.)

<0.001	0.001–0.01	0.01–0.1	0.1–1	1–10	10–100	100–1000	>1000
			Irradiation time t_{ir} = 150 hrs. (6.25 days)				
Eu	Mn	Na	Al	P	Mg	S	Pb
Dy	Co	Sc	Cl	Ni	Si	Fe	
	Rh	V	A	Mo	Ca	Zr	
	Ag	Cu	K	Ru	Ti		
	In	Ga	Cr	Sn	Bi		
	Sm	As	Zn	Te			
	Ho	Br	Ge	Xe			
	Lu	Kr	Se	Ba			
	Re	Pd	Rb	Ce			
	Ir	Sb	Sr	Nd			
	Au	I	Y	Pt			
		La	Nb	Tl			
		Pr	Cd				
		Tb	Cs				
		Tm	Gd				
		Yb	Er				
		W	Hf				
		Hg	Ta				
		Th	Os				
			U				
			Irradiation time t_{ir} = 1 hr.				
	Co	V	Al	Na	Mg	P	S
	Rh	Mn	Cl	Sc	Si	Ce	Fe
	Ag	Br	A	Cr	K	Hf	Zr
	In	Kr	Cu	Zn	Ca		Pb
	Eu	I	Ga	Ge	Ti		Bi
	Dy	Lu	As	Rb	Ni		
		Th	Se	Sr	Y		
			Nb	Mo	Sn		
			Pd	Ru	Xe		
			Pr	Cd	Cs		
			Sm	Sb	Tb		
			Ho	Te	Ta		
			W	Ba	Os		
			Re	La			
			Ir	Nd			
			Au	Gd			
			U	Er			
				Tm			
				Yb			
				Pt			
				Hg			
				Tl			

TABLE IX

Elements Having Acceptable Neutron Activation Analytical Sensitivities Grouped According to the Ratio:
R = Sensitivity limit (10^{-9} g.)/Avg. abundance (p.p.m.)

10^{-6}–10^{-5}	10^{-5}–10^{-4}	10^{-4}–10^{-3}	10^{-3}–10^{-2}	10^{-2}–10^{-1}	10^{-1}–1	?
Na	Si	Mg	P	Ni	S	A
Al	K	V	Cl	Br	Ge	Kr
Mn		Co	Ca	Ag	Zr	Xe
		Cu	Sc	In	Mo	
		La	Ti	I	Sn	
		Eu	Cr	Cs	Sb	
		Dy	Fe	Ce	Er	
			Zn	Nd	Hf	
			Ga	Gd		
			As	Tb		
			Rb	Tm		
			Sr	Yb		
			Y	Ta		
			Nb	W		
			Ba	U		
			Pr			
			Sm			
			Ho			
			Lu			
			Th			

It is notable that the majority of these elements may be detected adequately by several orders of magnitude.

Table X lists the 15 elements (excluding elements Ne and lighter) which are not acceptable according to this criterion. Only 7 of these are unacceptable by more than an order of magnitude. It is to be noted that some of the elements listed in Table X– viz., Rh, Ir, Au, Re, Pd, and Hg– may be detected with very great sensitivity, but at the same time these elements are extremely rare, and their detection sensitivities are not quite adequate according to our criterion.

We see that analysis by neutron activation is highly sensitive and is generally applicable to determining all elements heavier than neon. The sensitivity limits presented in Table VII are not to be regarded as ultimate sensitivity limits but only as limits for ordinary conditions of measurement. To increase the sensitivity of analysis, either the radiation counter background may be decreased by low level counting

TABLE X

Elements Not Having Acceptable Neutron Activation Analytical Sensitivities[a]

Element	Abundance, p.p.m.	Limit, 10^{-9} g.	
		t_{ir} = 150 hrs.	t_{ir} = 1 hr.
Se	(0.01)	0.53	0.58
Ru	(10^{-4}?)	1.3	8.9
Rh	(10^{-3}?)	0.0012	0.0012
Pd	(0.02)	0.049	0.96
Cd	0.13	0.69	8.0
Te	(10^{-3})	1.4	3.4
Re	($\sim 10^{-3}$)	0.0073	0.18
Os	(10^{-4}?)	0.50	18.
Ir	(10^{-3})	0.0040	0.11
Pt	(5×10^{-3})	1.2	1.5
Au	($\sim 10^{-3}$)	0.0043	0.32
Hg	0.06	0.077	2.6
Tl	1.7	4.8	4.8
Pb	16.	1.1×10^{3}	5.9×10^{3}
Bi	(~ 0.1)	32.	3.2×10^{3}

[a] Those elements with sensitivities unfavorable by more than a factor of ten are listed in *italic type.*

techniques, or the neutron irradiation may be carried out in a high flux reactor. For most elements either method may increase analytical sensitivity by an order of magnitude or more. Most of the elements of Table X may be determined with adequate sensitivity by a combination of high flux irradiation and low level counting.

A final highly important remark needs to be made in connection with activation analysis for exceedingly small amounts. Frequently the limiting factor in detecting traces of an element is not simply an inability to measure the desired property; rather, it may be the amount of the same element which is unavoidably introduced during processing for the analysis. For determining small amounts of the commoner elements, the contamination problem is more serious than for determining the rarer ones. Nevertheless, for most determinations below 1 p.p.m. contamination must be carefully controlled.

Neutron activation analysis usually enjoys a tremendous advantage with respect to contamination over any other analytical method requiring solution chemistry, e.g., colorimetry or mass spectrometric isotope dilution. As the analysis is ordinarily carried out, the entire sample is irradiated and after irradiation is chemically processed.

In this way, the only serious contamination that may be introduced after irradiation must be itself radioactive, and this is relatively easy to control. Indeed, large nonradioactive amounts of the element to be determined are usually added (as a "carrier") during chemical processing to assist in separations. Only contamination contained on or in the sample before irradiation need be controlled with care. Where colorimetric or other methods fail because of high contamination background, even if they have the required sensitivity, it is possible to carry out reliable analyses for extremely small amounts by neutron activation.

V. Major Element Determination by Neutron Activation Analysis

The neutron activation analysis sensitivity limits presented in Tables VII and VIII indicate both that the trace elements are detected with unusually high sensitivity and that many of the abundant elements are detected with unusually poor sensitivity. In addition, the abundant elements frequently give rise to short-lived radioactive species which die quickly after irradiation, e.g., 2.27 min. Al^{28}, 9.45 min. Mg^{27}, 57 min. Sc^{49} (from Ca), and 5.80 min. Ti^{51}. For trace element determination this is a fortunate circumstance. A mineral sample may be given an intense irradiation for high sensitivity trace element analysis, and, after a moderate cooling time, the total sample radioactivity is not so great as to be hazardous in laboratory chemical processing.

Two major elements which have low sensitivity limits are Na and K. Because of this, most common silicate minerals, given brief slow neutron irradiation followed by a 1–2 day cooling time, are radioactive predominantly with 14.97 hr. Na^{24} and 12.46 hr. K^{42}. Procedures for the rapid analysis of silicates for Na and K may be based upon this fact.

A procedure for the determination of K in biotite and other minerals has been described (29). The radiation emitted by 12.46 hr. K^{42} is predominantly energetic 3.55 m.e.v. β which penetrates several hundred mg./cm.^{2} of Al absorber with reasonable efficiency. In the procedure for the analysis of biotite for K, 30 mg. specimens are irradiated simultaneously with equal portions of suitable standards for a few minutes in a reactor. After cooling for 24–36 hours, they are then counted using an end-window proportional or G-M counter and

Al absorbers of 800 and 2000 mg./cm.^{2}. The thinner absorber serves to shield out low energy β radiation from 14.97 hr. Na^{24} and other species in the sample, but enough 12.46 hr. K^{42} β radiation is passed to be counted with good efficiency. The thicker absorber shields all β rays and passes only γ rays from 14.97 hr. Na^{24} and other species, counted with about the same (low) efficiency for any absorber thickness in the range 0–2000 mg./cm.^{2}. The latter counting rate is subtracted, as a small correction, from the former to obtain the net K^{42} β counting rate. Comparison of the sample and standards leads to the analytical result. The procedure requires no chemical processing and may be rapid and highly accurate.

A similar procedure for determining Na has been suggested (30). During the radioactive decay of 14.97 hr. Na^{24} an energetic 2.754 m.e.v. γ ray is emitted which may be counted with good efficiency by a scintillation counter. Lower energy γ rays from 12.46 hr. K^{42} and other species may be discriminated against electronically, and the Na^{24} γ activity may be counted without interference. Comparison of simultaneously irradiated sample and standards leads to the analytical result.

Brownell *et al.* (26) have determined Si, Al, and Na in silicate rocks by irradiation with fast and slow neutrons using a polonium–beryllium neutron source. Fast neutrons produce 2.27 min. Al^{28} in proportion to the content of Si by the reaction $Si^{28}(n, p)Al^{28}$. Neutrons from the same source, moderated with paraffin, produce 2.27 min. Al^{28} and 14.97 hr. Na^{24} in proportion to the contents of Al and Na in the sample by neutron capture reactions. By measuring the decay of radioactivity following separate fast and slow neutron irradiations, the contents of Si, Al, and Na are calculated.

Bradley and Bradley (31) have determined Na, K, and Ca in single crystals of feldspar by pile neutron irradiation and counting induced 14.97 hr. Na^{24}, 12.46 hr. K^{42}, and 164 day Ca^{45} radioactivity using a G-M counter and Al absorbers.

VI. Isotopic Abundance Determination by Neutron Activation

A radioactive nuclide produced by slow neutron reaction with an element always arises from a single isotope of the element. Thus, if we determine K by measuring slow-neutron-induced 12.46 hr. K^{42} radio-

activity, we in fact are determining the amount of the isotope K^{41}. By assuming the relative isotopic abundance of K^{41} to be the same in sample and standard, we may compute the content of K in the sample. The result will agree with a gravimetric or other chemical analysis only if the isotopic composition is as assumed. A discrepancy may indicate different isotopic compositions of the sample and standard.

Most analysis of the elements for their isotopic composition has been with the mass spectrometer, and the isotopic composition of gases can now be made with great precision. Interesting variations in the isotopic composition of the elements H, C, N, O, and S have been measured by mass spectrometry of gaseous compounds, and these variations have been related to the geological history of the elements. Epstein (32) reviews some oxygen isotope geochemistry.

Solid source mass spectrometry does not so readily give the precision necessary to detect variations in the isotopic composition of "solid" elements. In certain of these cases, however, neutron activation analysis combined with chemical gravimetric analysis may be sufficiently precise to detect isotopic variations of 1% or less.

For isotopic abundance measurement by combined activation analysis and chemical analysis, four elements, Ca, Li, Si, and Ni, are particularly favorable. The isotope which gives rise to the principal radioactivity in each case is not abundant, and the ratio of its mass to that of the most abundant isotope is great. Because of this, gravimetric analysis and activation analysis are essentially measures of the abundant and the rare isotopes, respectively, and measurably large natural variations in isotopic composition may be associated with the large mass ratio of the two isotopes.

Calcium, 96.97% Ca^{40}, gives rise on neutron activation predominantly to the decay chain 8.8 min. Ca^{49}–57 min. Sc^{49}–stable Ti^{49} from neutron capture by the rare isotope 0.185% Ca^{48}. The Ca^{48} content of normal Ca may be determined by irradiating submilligram aliquots of purified and accurately weighed Ca and measuring the decay of the 57 min. Sc^{49} 2.05 m.e.v. β radiation with a proportional or G-M counter. Analysis of replicate aliquots may lead to a precision error on activity measurement of less than 1%, and Sr impurity may be determined by scintillation counting of 2.80 hr. Sr^{87m} γ activity also produced in the neutron irradiation.

Lithium, 92.58% Li^7 and 7.42% Li^6, may be determined indirectly by thermal neutron activation (33). In a dilute aqueous solution of Li^+,

energetic tritons, produced by the reaction $Li^6(n, \alpha)H^3$, react with O^{16} to produce the positron emitter 112 min. F^{18} in proportion to the concentration of Li^6 (34). The isotopic composition may be determined by comparing precision radioactivity measurements with accurate chemical determination of total Li.

In a similar manner, the Si^{30} content of silicon, 92.18% Si^{28}, may be determined by precise measurement of the 1.47 m.e.v. β radioactivity of 2.65 hr. Si^{31}.

Finally, the Ni^{64} content of nickel, 67.76% Ni^{58} and 26.16% Ni^{60}, may exhibit natural variations great enough to be detected by measuring β or γ radioactivity of 2.56 hr. Ni^{65}.

Isotope abundance ratios may sometimes be obtained from the relative amounts of two different radioactive species induced by neutron reactions with different isotopes. A particularly interesting case in point is argon. The data of Table VII show that both 110 min. A^{41} and 35.0 day A^{37} are produced in good yield by neutron activation. They may be measured individually by filling a counter with the irradiated gas and counting the radioactivity soon after irradiation and again later after 110 min. A^{41} has decayed. Stoenner and Zähringer (27) have described age determination of meteorites by determining K and A by neutron activation.

VII. Other Methods of Radioactivation Analysis

For several elements analysis by slow neutron activation may be difficult because of an inconveniently short half-life of the active species, a long half-life making positive identification of the radioactivity difficult, radiations such as X-rays or low energy electrons and β rays which are not easily measured efficiently and precisely, or merely a very low neutron capture cross section. For one or another of these reasons determinations of the ten light elements H to Ne are accomplished with difficulty in most materials, and sometimes analysis for the elements Mg, Al, S, Ti, Fe, Nb, Tl, Pb, and Bi may require special techniques. For the determination of some of these, nuclear reactions other than slow neutron capture may be used to produce more easily measured radioactive species.

Fast pile neutrons may be used to induce radioactivity by (n, p), (n, α), and $(n, 2n)$ reactions. Reed (35) has presented analyses of meteoritic material for Tl and Pb using the fast neutron reactions,

$$Pb^{204}(n, 2n)Pb^{203},\ t_{1/2} = 52 \text{ hr.}$$

$$Tl^{203}(n, 2n)Tl^{202},\ t_{1/2} = 12 \text{ days}$$

Because fast neutron reaction cross sections are small and reactor fluxes decrease rapidly with increasing neutron energy, analytical sensitivity by fast neutron activation is less favorable than by thermal neutron activation. In certain difficult cases, however, fast neutron reactions may be practical. Some other fast neutron reactions useful in activation analysis are:

$$Mg^{24}(n, p)Na^{24},\ t_{1/2} = 14.97 \text{ hr.}$$

$$Al^{27}(n, \alpha)Na^{24},\ t_{1/2} = 14.97 \text{ hr.}$$

$$S^{32}(n, p)P^{32},\ t_{1/2} = 14.22 \text{ days}$$

$$Ti^{48}(n, p)Sc^{48},\ t_{1/2} = 44 \text{ hr.}$$

$$Fe^{56}(n, p)Mn^{56},\ t_{1/2} = 2.576 \text{ hr.}$$

The light elements present a special problem. Li may be determined in aqueous solution by slow neutron irradiation and measuring the secondary reaction product 112 min. F^{18}, as described in Section VI. The same series of reactions may be used to determine oxygen and has been described by Osmond and Smales (33) and others (36,37). Any of the light elements in surface layers may be determined by bombarding in low energy accelerators and counting particles emitted from the sample during irradiation. The determination of F and other elements using a 2 m.e.v. Van de Graaff generator has been described (38).

Charged particle activation analysis using a classical cyclotron is now being studied by Winchester (39) for determining C, O, and Si using 15 m.e.v. deuterons, the strontium isotopes Sr^{86}, Sr^{87}, and Sr^{88} using 7.5 m.e.v. protons, and Nb using 30 m.e.v. alpha particles. Although charged particle activation analysis requires rather special conditions of irradiation, and its sensitivity is not in general so great as that for slow neutron activation analysis, it finds some unique applications.

VIII. Summary and Conclusions

It has been shown that the limiting factor in studying the natural occurrence of most of the elements of the periodic system has been

analytical sensitivity. Neutron activation analysis is the only general analytical method which gives the required sensitivity and is superior to colorimetric, emission spectrographic, and X-ray methods of analysis. In addition to its high inherent sensitivity, neutron activation analysis also offers great freedom from contamination background and is well suited to analysis at extremely low concentrations. It is the most promising analytical method in trace element geochemistry.

At the same time, activation analytical procedures are usually no less time-consuming than any procedures involving "wet chemistry." Therefore, in those samples where the sensitivity of other more rapid analytical methods is adequate, no advantage is gained by employing activation analysis. In any particular geochemical problem the relative merits of all analytical methods should be considered in light of the requirements of the problem. The point to be made here, however, is that neutron activation analysis is a powerful method which may profitably be employed widely in geochemistry.

Some areas of investigation now opened up by neutron activation analytical methods have been implied in the text. In general, the entire field of the distribution of trace elements in rocks and minerals is now amenable to study by analysis of natural materials. In the first place, the variations in trace element concentrations among different rock types may be examined with precision. More important, the distribution of the elements among the mineral phases coexisting in a single rock may be studied. This problem, scarcely examined up to the present,* is fundamental to understanding the chemical basis for the equilibrium and rate processes of the elements in nature. Because of the high sensitivity of activation analysis, small single mineral crystals, or even sections from crystals, may be analyzed for many trace elements. In this way, concentration gradients and distribution coefficients between minerals may be accurately measured, and a detailed picture of trace element behavior may be obtained.

The rare earth elements are especially interesting. Because of the great similarity in their chemical properties they are usually found in nature associated with each other. However, systematic differences in their chemical properties, related to the lanthanide contraction in ionic radius with increasing atomic number, are reflected in variations

* One study of this type has been reported by Wager and Mitchell (8).

in the relative abundances of the rare earths contained in minerals of different composition and history. Such variations may be interpreted in more quantitative chemical terms than the natural variations in occurrence of any other group of elements. Heretofore determined only with difficulty by any analytical method (hence the name "rare" earth), they are determined especially well by neutron activation analysis.

The advantages of determining some major elements and certain isotope ratios by neutron activation analysis have been discussed, and activation by other nuclear particles may in certain cases usefully extend radioactivation analysis. Only after testing these possibilities may the scope of activation analysis be assessed. The method nevertheless appears at the present time to warrant extensive application.

Acknowledgments. The author is grateful to the Oak Ridge Institute of Nuclear Studies and the Oak Ridge National Laboratory for appointment as a University Research Participant during which part of this work was accomplished, and to the National Science Foundation for a reseach grant to the Massachusetts Institute of Technology, from which some of the support for this work was derived. Helpful comments by G. W. Leddicotte, S. A. Reynolds, J. W. Irvine, Jr., E. J. Green, and S. Lindenbaum are gratefully acknowledged.

APPENDIX
Neutron Activation Analysis Sensitivity Calculation

The sensivitity of analysis by thermal neutron activation depends on the neutron flux available and the activation cross section for the radioactive species measured, as well as the length of irradiation time if the activity is long-lived. Experimentally, the ultimate sensitivity attainable in a particular case depends also on the method chosen for counting the radioactivity and, especially, on the type of chemical separation required to effect the analysis. Frequently, a very short half-life of the induced radioactivity precludes careful chemical processing or accurate counting, and sometimes two elements in the same sample interfere by producing the same radioactivity or activities of nearly the same decay characteristics. Finally, the determination of a trace element of low cross section (poor analytical sensitivity) in a high cross section material may be difficult merely because of the need to separate very small amounts of radioactivity of the desired element from the overwhelming activity of the matrix.

Examples of difficult determinations may include the following: Ag in a silicate rock by counting 2.3 min. Ag^{108} (short half-life) or 253 day

Ag^{110m} (low sensitivity and half-life too long to establish by observing decay), S in NaCl by measuring 87 day S^{35} (more of radioactivity produced from Cl than from S) or 5.04 min. S^{37} (short half-life), Au in Pt by measuring 2.697 day Au^{198} (interference of 3.14 day Au^{199} produced from Pt), Nb by measuring 6.6 min. Nb^{94m} (short half-life and poorly detected X-rays and Auger electrons) or 20,000 yr. Nb^{94} (long half-life), and Pt in Ga (similarity of half-lives of 17.4 hr. Pt^{197} and 14.3 hr. Ga^{72} and hazard of overwhelming Ga radioactivity). On the other hand, because of convenient half-life, high neutron capture cross section, and energetic radiation, determinations of many elements, including Na, Mn, Cl, In, several rare earths, Cu, Ga, As, and W, are straightforward, and often no chemical separations at all following irradiation are required.

Although the experimental sensitivity depends greatly on the particular analysis, still it is a useful guide to calculate the amount of an element which will give rise to a fixed disintegration rate under certain irradiation conditions. The magnitude of such a quantity, referred to as a "sensitivity limit," is arbitrary because it does not consider the problems of chemical separation or radiation detection, but it is useful if the values for half-lives and the types of emitted radiation are also borne in mind.

The data presented in Table VII are based on isotopic abundances, half-lives,* and radiations given by Strominger, Hollander, and Seaborg (41), chemical atomic weights given by Wichers (42), and thermal neutron activation cross sections given by Lyon (43) and by Hughes and Schwartz (44).** In most cases absolute cross section values are uncertain by about 10%, and calculated sensitivity limits are therefore significant to no more than 10%.

The sensitivity limits were calculated according to the equation

$$A = \phi a \sigma N [1 - \exp(-\lambda t_{ir})] \exp(-\lambda t_d)$$

where

A = radioactivity of sample after times t_{ir} and t_d, in disintegrations per second

*Half-life values used for Ru^{105} and Rh^{105} are those given by Winchester (40).

**In all cases, cross section values given by Lyon (43) are within a factor of 1.5 of those of Hughes and Schwartz (44) except for production of Ge^{75}, Ge^{77}, Zr^{97}, Ag^{110m}, Sb^{122}, Ba^{139}, and Ta^{182} where the values are in agreement by about a factor of 2.

t_{ir} = irradiation time
t_d = decay time following end of irradiation before activity is measured
λ = decay constant, 0.693/half-life
ϕ = neutron flux, in n/cm.^{2} sec.
a = fractional isotopic abundance of the reacting isotope
σ = cross section for neutron reaction with the reacting isotope to produce the radioactive nuclide of interest, in cm.^{2}/atom
N = number of atoms of target element present in sample for irradiation

All sensitivities were calculated for irradiation in a neutron flux of 1×10^{13} n/cm.^{2} sec., and 10 dis./sec. has been chosen as a limiting measurable activity for all nuclides. Two irradiation times have been selected for sensitivity calculation: 1 hour, corresponding to a minimum cost irradiation in some reactors, and 150 hours (6.25 days), corresponding to a typical week of reactor operation.

Under these conditions, the minimum weight of element detectable in mμg. (10^{-9} g.) is

$$W = (N_{satn}/F)(\text{at. wt.}) \times 10^{-3}$$

where

N_{satn} = $1/0.602a\sigma$, in $\mu\mu$mole (10^{-12} mole)
σ = cross section, in barns (10^{-24} cm.^{2}/atom)
F = $1 - \exp(-\lambda t_{ir})$
(at. wt.) = atomic weight, in grams/mole

and all activities are computed for the end of irradiation, $t_d = 0$. In the case of daughter activities longer-lived than their parents produced in the neutron reaction, the asymptotic values at long times t_d extrapolated exponentially to time $t_d = 0$ have been computed, e.g., 57 min. Sc^{49}. The symbols with subscripts, W_{150} and W_1, have been used to distinguish between the two irradiation times.

The sensitivity limits are conservative values attainable with ordinary radiochemical methods. In a sense they are more conservative than the limits of the other three analytical methods discussed here, for the neutron activation limits may be improved more readily by refined techniques. In this sense they should not be regarded as ultimate limits.

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Halides and Oxyhalides of the Elements of Groups Vb and VIb

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I. Introduction

The interest shown in the halides and oxyhalides of Groups Vb and VIb elements during the last few years makes appropriate a review of the general state of knowledge concerning these compounds. It is intended that this article provide an acquaintanceship with the known compounds in these groups, review briefly their general properties, and be illustrative of current activity, particularly with respect to synthetic and structural aspects, in this subject.

II. Nitrogen Halides

The best known of the binary halogen compounds of nitrogen are the trihalides; the nonexistence of pentahalides of nitrogen is related, of course, to the lack of bonding orbitals sufficiently low lying to participate in the required hybridization for a pentacovalent nitrogen atom. Also to be considered in this section are the halogen azides and several additional binary compounds of nitrogen and fluorine, each possessing a nitrogen–nitrogen bond.

A. PREPARATION

Of the trihalides only the bromide has not been isolated as a pure substance;* only an ammine of the bromide is known. Efforts to prepare NX_3 compounds by direct synthesis from X_2 and N_2 are unsuccessful because of the great strength of the $N{\equiv}N$ bond in N_2.

The trifluoride may be prepared by electrolysis at 125°C. of ammonium hydrogen fluoride, NH_4HF_2. The resulting mixture of gases, including H_2, N_2, HF, etc., is separated by a combination of chemical and physical means (1). Difficulties attending the separation of products are diminished if a simple compound of nitrogen, perhaps NH_3, is fluorinated (2).

Nitrogen trichloride, NCl_3, is prepared in similar fashion by reacting aqueous ammonia and chlorine (3), or by the electrolysis of a solution of NH_4Cl in HCl (4). A convenient laboratory procedure utilizes

* Very recently the first mixed halide of nitrogen, chlorodifluoroamine, NF_2Cl, has been reported (437).

the reaction of Cl_2 with a cold aqueous solution of $(NH_4)_2SO_4$ and subsequent extraction of the NCl_3 with CCl_4 (5).

Glow discharge experiments yielded no indication of any compound when N_2 and Br_2 were employed as reactants. If NH_3 is substituted for N_2, however, a red compound, characterized from its decomposition products as $NBr_3 \cdot 6NH_3$, is formed on cooling. Reaction of Br_2 and NH_3 in the absence of the glow discharge results in the same compound (6). The ammine also forms in the reaction of BrCNO with NH_3 in ethyl chloride solution (7).

Nitrogen triiodide may be prepared from the reaction of the polyhalide salt, $KIBr_2$, and ammonia (8):

$$3KIBr_2 + 4NH_3 \longrightarrow 3KBr + 3NH_4Br + NI_3$$

The ammine of NI_3 is formed in the interaction of I_2 and NH_3 at room temperature (9). The amount of ammonia in the compound increases as the temperature of the reaction decreases; above $-25°C.$ the monoammine is obtained, but at lower temperature the NH_3/NI_3 ratio can reach 12.

For each of the four principal halogen elements an azide, XN_3, has been reported. The action of iodine on silver azide in cold, ethereal solution gives IN_3. Bromine azide may be prepared similarly from sodium or silver azide, but the chlorine compound is obtained by the action of ammonia on sodium hypochlorite. The most recently prepared halogen azide, FN_3, results, together with NH_4F and N_2, when a stream of hydrazoic acid and N_2 is treated with fluorine (10). The decomposition of FN_3 leads to the compound difluorodiazine, FN_{22}:

$$2FN_3 = 2N_2 + N_2F_2$$

N_2F_2 has also been isolated in small yields from the products of the electrolysis of NH_4HF_2 (416,417).

Tetrafluorohydrazine, N_2F_4, has been reported as resulting from the reaction at 375°C. of NF_3 with various metals such as stainless steel, copper, arsenic, etc (11):

$$nNF_3 + M \longrightarrow {}^{n}/_{2}\, N_2F_4 + MF_n$$

The reaction of ammonia and fluorine in a packed copper reactor has been reported to give small amounts of N_2F_4 (418).

B. STRUCTURE AND PROPERTIES

Some physical properties of these compounds are listed in Table I. Detailed structural information for this group of compounds has been obtained only for NF_3 and N_2F_2. The pyramidal NF_3 molecule is best regarded as derived from sp^3 hybridization of the nitrogen bonding orbitals. The effect of this hybridization on bond angles, bond distances, and dipole moments for NF_3 (dipole moment = 0.235 D.) and other Group Vb trihalides has been discussed (13).

TABLE I
Physical Properties of Nitrogen Halides

	Melting point, °C.	Boiling point, °C.	ΔH_{vap}, kcal./mole	ΔH_{form}, kcal./mole	Density, g./ml.
NF_3	−208.5	−129	2.77	29.7	1.537 (−129°C.)
N_2F_2 (*cis*)	−195	−105.7			
N_2F_2 (*trans*)	−172	−111.4			
N_2F_4		−73	3.17		
FN_3	−154	−82			
NCl_3	< −27	71		51.7 (in CCl_4)	1.65 (20°C.)
BrN_3	~ −45				
$NBr_3 \cdot 6NH_3$	d. > −67				
$NI_3 \cdot NH_3$				35	

The initial structural parameters estimated from infrared examination placed the N—F distance and F–N–F angle at 1.45 A. and 110 degrees or larger, respectively (15). More recent electron diffraction (16) and microwave (17) investigations refine these values to 1.37 A. and 102.1 degrees.

Electron diffraction also provides evidence for the *cis*- and *trans*-configuration of N_2F_2 with N—F, 1.44 A.; N=N, 1.25 A.; and N—N—F angle, 115 ± 5 degrees. The substantial shortening of the nitrogen–nitrogen distance implies the expected double bond character (18).

The microwave spectrum of N_2F_4 suggests a hydrazine-like molecule with angle F—N—F = 108 ± 3 degrees, angle N—N—F = 104 degrees, and the dihedral angle 65 ± 3 degrees (419).

If nitrogen trichloride has a pyramidal structure similar to NF_3, the vibrational spectrum should show four fundamentals. The only reported study of the NCl_3 spectrum is inconclusive in regard to this requirement (19).

A common characteristic of the binary nitrogen-halogen compounds, with the exception of NF_3, and perhaps N_2F_2 and N_2F_4, is their relatively great tendency toward thermal decomposition, chemical reactivity, or both. The three compounds of high thermal stability owe this, at least partially, to the enhancement of the N F bond strength by ionic resonance contributions. This factor is of far less influence in the N—Cl, N—Br, and N– I bonds. Thus, while NF_3 is almost chemically inert at moderate temperatures, the chloride vapor is decomposed by thermal pulse (20), supersonic wave (21), or electric spark (22). When frozen in liquid air and then thawed *in vacuo*, it is reported to explode spontaneously (23). In anhydrous organic solvents NCl_3 is moderately stable (24), but hydrolysis of NCl_3 gives NH_3 and HOCl (25), indicating a partial negative charge on the N atom.

The decomposition of the nitrogen triiodide monoammine has been carefully studied, and it is suggested that the NH_4I product is a secondary one arising from the reaction of iodine atoms and ammonia molecules (26). The fact that ammonia strongly retards the rate of reaction indicates deammoniation as the initial step, followed by fast decomposition of free NI_3. The small inhibiting effect of N_2 or water vapor is considered to be the result of interference with escaping NH_3 molecules in the rate-controlling step. Agents which promote the decomposition, such as light, electrons, neutrons, alpha particles, or X-rays, are effective because of thermal effects (27); in the so-called photodecomposition reaction, for example, the explosive reaction occurs after, not during, the exposure (28).

At −78°C. in liquid ammonia NI_3 reacts with K or Na amide to give N_2, I^-, and NH_3. However, silver amide gave a dark, insoluble compound, $NI_3 \cdot NH_2Ag$, stable in liquid NH_3 (29).

The unshared pair of electrons on the N atom in NX_3 molecules suggests possible electron donor properties. Efforts to prepare an addition compound of NF_3 with the Lewis acid B_2H_6 in the gas phase under high pressure were unsuccessful. In the liquid phase violent explosions resulted (30).

Fluorine azide at pressures under 200 mm. and at room temperature decomposes slowly to N_2 and N_2F_2, but does so very rapidly at 100°C. (10). The other three halogen azides hydrolyze rapidly to give mixtures of hydrazoic and hypohalous acids. Iodine azide is decomposed to its constituent elements when dissolved in nonaqueous media. Reduction with metallic Na gives NaI and NaN_3 or, if less than the required amount of Na is used, NaN_3 and I_2. A sodium arsenite solution decolorizes both chlorine and iodine azides, forming sodium arsenate and NaN_3 (31).

III. Nitrogen Oxyhalides

Compared to the halides the oxyhalides have received a substantial amount of attention and their properties are relatively well understood. This group of compounds includes the nitrosyl fluoride, chloride, and bromide, XNO; the nitryl fluoride and chloride, XNO_2; and the less well-known nitroxyl halides or halogen nitrates, XNO_3. A comprehensive review dealing with ClNO is available (12).

A. PREPARATION

Nitrosyl fluoride was initially prepared by Pt-catalyzed reaction of ClNO vapor and silver fluoride (14). Another procedure involves the double decomposition at 300°C. of NaF and $NOBF_4$, the latter obtained from the reaction of N_2O_3 with concentrated HBF_4 (32). The direct vapor phase fluorination of NO has also been employed to prepare the substance (33), but, like the other methods cited, is limited in its applicability by the reactivity of FNO toward the quartz apparatus used in the purification procedure. Recently, using a poly(chlorotrifluoroethylene) reaction vessel, the vapor-liquid fluorination of NO at −160°C. was found to proceed smoothly and afford the desired product in greater than 90% yield (34).

A wide variety of methods have been employed for preparing ClNO. This substance occurs, of course, as a product of the reaction of concentrated hydrochloric and nitric acids, or from the interaction of metal chlorides with nitric acid or N_2O_4. The difficulty in separating the ClNO from the accompanying Cl_2 makes such procedures less than satisfactory for preparative purposes.

The third-order, homogeneous gas phase reaction between NO and Cl_2 proceeds smoothly at room temperature with but small, reversible

decomposition of the product; operation at elevated temperature accelerates both forward and back reactions comparably (35). Charcoal and alumina catalysts have been used at 40–50°C. to accelerate the attainment of equilibrium with excellent results (12). The reaction of organic and inorganic nitrites is also useful; $AlCl_3$, for example, when heated with sodium nitrite gives good yields of ClNO (36). Recommended laboratory procedures for ClNO preparation include the reaction of nitrosylsulfuric acid and HCl (37) and the treatment of $NaNO_2$ with HCl (38).

Like ClNO, nitrosyl bromide is obtained by a third-order gas phase reaction between NO and Br_2. The equilibrium favors the reactant side somewhat more than in the case of ClNO, and appreciable concentrations of reactants are therefore present even at 0°C.

The lack of reports concerning the existence of INO is presumably a reflection of the relative strengths of NO^+ and I^- as oxidizing and reducing agents, respectively.

Nitryl fluoride, FNO_2, is prepared in better than 90% yield by the fluorination of NO_2 in a static system (34). This reaction is first order in each reactant and independent of FNO_2 pressure. The activation energy is given as 10.5 kcal./mole (39). Yields approaching theoretical may be obtained from the action of a stream of fluorine on dry sodium nitrite; the desired product is separated from excess F_2 and nitrogen peroxide by condensation and fractionation (40). The compound can also be obtained by passing a stream of nitryl chloride, $ClNO_2$, over AgF at 240°C. in a platinum tube; the yield, however, is only 5% (41). The reaction of NO_2BF_4 and NaF, similar to that employed for FNO, has also been used.

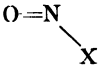
Although attempts to prepare $ClNO_2$ by the direct reaction of NO_2 and Cl_2 have been unsuccessful, the compound is obtainable by several other approaches. Ozone rapidly oxidizes ClNO to give $ClNO_2$ in high yields (42). A continuous stream of the substance is formed by the dropwise addition of chlorosulfonic acid to anhydrous nitric acid (43). N_2O_5 and PCl_5 also react to yield $ClNO_2$ (44). The compounds $BrNO_2$ and INO_2 have not been reported; the reason for the failure to prepare these compounds is probably the same as that previously suggested for the nonexistence of INO.

Nitroxyl fluoride, NO_2F, is prepared by bringing cold fluorine, diluted with a nonreactive gas such as N_2, into contact with cold, dilute (about 3*N*) nitric acid (45). Nitroxyl chloride, $ClNO_2$, has

recently been prepared by reacting ClO_2 or Cl_2O with NO_2 or N_2O_5 (433). The rather unstable compounds $BrNO_3$ and $Br(NO_3)_3$ have also been reported (434).

B. STRUCTURE AND PROPERTIES

The bent, unsymmetrical configuration of the nitrosyl halides



is well established. The required three fundamental vibrations have been identified in the infrared spectrum of each of the three molecules, FNO (46,47), ClNO (48, 49) and BrNO (49). The molecular dimensions derived from infrared, electron diffraction (ClNO and BrNO), and microwave spectra (ClNO and BrNO) are listed in Table II.

TABLE II
Bond Distances, Bond Angles, and Dipole Moments of Nitrogen Oxyhalides

	N—X, A.	N—O, A.	X....O, A.	X—N—O, angle, deg.	O—N—O angle, deg.	Dipole moment, D.
FNO	1.52	1.13		110		
ClNO	1.95	1.14	2 64	116		1.830
BrNO	2.14	1.15	2 81	114		1.870
FNO_2	1.35	1 23			125 (assumed)	
$ClNO_2$	1 79	1 23			125 (assumed)	

The N—X distances exceed the sum of the covalent single bond radii; 1.73 and 1.88 A. for N—Cl and N—Br, respectively. This has been ascribed, assuming spherical symmetry and a radius of 1.40 A. for the NO^+ ion, to resonance between the covalent structure and the NO^+X^- form (50). Averaging the calculated N—X distance in pure ionic and pure covalent structures indicates the N—X bond to be about 50% ionic for both N—Br and N—Cl. The N—F bond in FNO is also longer than the sum of covalent single bond radii (1.34 A.) and presumably the same explanation could apply.

The dipole moments calculated from dielectric constant measurements also support the resonance structure idea; pure covalent ClNO and BrNO have been calculated to have dipole moments of 0.3 and 0.4 D., respectively (50).

The vibrational spectra of FNO_2 (51) and $ClNO_2$ (52) support the XNO_2 arrangement. Further support for this formulation and proof of a planar structure of C_{2v} symmetry are obtained from the results of microwave measurements on $ClNO_2$ (53) and FNO_2 (54). These structures are thus obtained from the planar nitrate ion by replacement of an oxygen atom by an F or Cl atom (55).

An electron diffraction study of gaseous NO_3F suggests a hypofluorite structure in which the fluorine atom attached to oxygen is out of the plane of the nitrogen and oxygen atoms (56). The proposed parameters are:

N—O: 1.29 ± 0.05 A.
N—O′ (F attached): 1.39 ± 0.05 A.
O′—F: 1.42 ± 0.05 A.
O—N—O: 125 ± 5 degrees
N—O′—F: 105 ± 5 degrees

As suggested by the data given in Table III, all compounds in this group exist as gases at room temperature. Colorless nitrosyl fluoride

TABLE III
Physical Properties of Nitrogen Oxyhalides

	Melting point, °C.	Boiling point, °C.	ΔH_{vap}, kcal./mole	ΔH_{form}, kcal./mole	Density, g./ml.
FNO	−132 5	−59 9	4 6	−15 8	1.326 (b.p.)
ClNO	−- 61 5	− 5 8	6 0	12 6	1 592 (b.p.)
BrNO	− 55 5	~ 0		19 6	
FNO_2	−166	−72 1	4.3		1.494 (−73°C.)
$ClNO_2$	−145	−15	5 0		1.41 (b.p.)
FNO_3	−181	−45.9			1 507 (b.p.)
$ClNO_3$	−107 (vac.)	18	7 3		

is rapidly hydrolyzed to give nitric oxide and hydrofluoric, nitric, and nitrous acids. FNO is vigorously reactive toward most substances; incandescence results when boron, silicon, or red phosphorous is treated with FNO at room temperature. Reactions with metals, leading to NO and metal fluoride, are of variable speed. Thus, sodium and tin are rapidly attacked, but copper and lead react only slowly. P_2O_5 gives POF_3 and N_2O_3 when treated with FNO, but an unidentified condensation product results from the action of FNO on liquid SO_2.

The chemical properties of nitryl fluoride have been the subject of a recent detailed examination (40). Most metals—Na, K, Zn, Cd, Al, Ti, etc.,—form both metallic oxides and fluorides when reacted with FNO_2; a few—Cr, Mo, W, and U—give oxyfluorides; while a number—Be, Mg, Ca, and Au—undergo no reaction up to 300°C. With nonmetals solid nitronium salts such as $(NO_2)_2SiF_6$, $(NO_2)PF_6$, and $(NO_2)SeF_5$ are the usual result. Toward organic compounds nitryl fluoride behaves as a nitrating agent of somewhat greater activity than nitryl chloride (57).

Colorless nitroxyl fluoride is thermally unstable (432), but may be handled at room temperature. It is appreciably soluble in water with slow evolution of oxygen and liberates I_2 from KI solution or solid KI. With KOH solutions O_2 is rapidly generated. Detonation in air gives NO_2 as one product. Mechanical shock may produce explosive decomposition even when NO_3F is in the solid state at liquid air temperatures (58).

Nitrosyl chloride engages in chemical reaction in several general ways. Two important types are (*1*) the double decomposition in which ClNO forms a chloride with the other reactant and the NO group may either undergo further reaction or be evolved as the nitric oxide molecule and (*2*) the simple addition reaction through which compounds such as $ClNO \cdot AlCl_3$ are formed. In this latter case the formula as written is intended to be noncommittal with respect to the true formulation; such compounds may be either donor-acceptor or ionic substances.

Several examples of first type of reaction may be mentioned. In the presence of water ClNO hydrolyzes to give hydrochloric and nitrous acids. The latter, in concentrated acid solution, may disproportionate to give nitric oxide and nitric acid. Certain metals—K, Ag, Cd, etc.—react with ClNO to give the corresponding chloride and NO. Other metals—Cu, Zn, Al, Fe, etc. form chlorides which react in turn with excess ClNO to form addition compounds. Nonmetals such as S, Se, and I_2 interact with ClNO to free NO and produce S_2Cl_2, Se_2Cl_2 and ICl.

Compounds react in a variety of ways with NOCl (59):

$$AgClO_4 + ClNO = NOClO_4 + AgCl$$

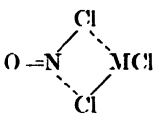
$$AgI + ClNO = NO + {}^1/_2I_2 + AgCl$$

$$AgNO_2 + ClNO = AgCl + NO + NO_2$$

With Na_2SiO_3 an exchange reaction occurs, but the nitrosyl silicate is unstable and quickly decomposes on slight warming to N_2O_3 and SiO_2 (60).

The second mode for ClNO reaction is the direct formation of addition compounds without preliminary oxidation. Complexes such as $CuCl \cdot ClNO$, $BCl_3 \cdot ClNO$, and $SbCl_5 \cdot ClNO$ are obtained from the corresponding metal or nonmetal chloride. Many ClNO addition compounds are certainly ionic with NO^+ cations and chloro complex anions present in the substance. X-ray examination suggests $NO^+AlCl_4^-$ for the adduct with AlCl (61), but the results of Raman spectroscopic investigation indicates the structure to be intermediate between the ionic and covalent arrangements (62).

Exchange of Cl^{36} between solvent ClNO and several adducts provides information concerning the structure of the complexes (63). $ClNO \cdot AsCl_3$, $ClNO \cdot FeCl_3$, and $ClNO \cdot SbCl_5$ in such a system undergo complete exchange, and the ionic structure is therefore proposed. The arsenic chloride complex could be formulated with either $AsCl_2^+$ or $AsCl_4^-$ ions. Rapid exchange of Cl^{36} has also been observed for the insoluble complexes of the chlorides of Zn, Cd, and Hg in contact with liquid ClNO. This is explained on the basis of an $NO^+MCl_3^-$ structure; a reasonable choice over a



configuration and the unlikely bonding of two chlorine atoms to one nitrogen.

The most widely used criterion for the presence of NO^+ in a ClNO complex is the electrical behavior of a liquid ClNO solution. While the chloride ion is little solvated, resonance in the $[NO(ClNO)]^+$ structure encourages strong solvation of the NO^+ ion (64). Thus, alkali chlorides are insoluble in ClNO, but ClNO complexes, with their potentially solvated NO^+, are soluble. Electrolysis of $[NO^+][FeCl_4^-]$ gives nitric oxide at the cathode and chlorine at the anode. Conductance studies also support the ionic nature of many adducts in liquid ClNO.

The ionizing solvent characteristics of liquid ClNO are not surprising, of course, since its dielectric constant is 19.7 at $-10°C$. (65).

Using Cl^{36} exchange rate data on the $POCl_3$–ClNO system to derive the free Cl^- ion concentration, the ion product $[NO^+][Cl^-]$ has been calculated as 10^{-16} (66).

In the area of miscellaneous ClNO reactions those involving strong fluorinating reagents, ClNO, and another reactant are of interest. The conversion of PBr_5, B_2O_3, and GeO_2 to the FNO complexes of PF_5,BF_3, and GeF_4, respectively, has been described (67).

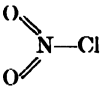
Finally, the large number of reactions of ClNO with organic substances has been classified in several groups depending upon the character of the organic compound and the reaction conditions (12). The general types of reactions are chlorination, nitrosation, chloronitrosation, oxidation, and diazotization.

Contrary to expectations based on analogy with the hydrolysis of ClNO, the ammonolysis reaction of the nitryl compound yields chloramine and ammonium nitrite as principal products instead of the anticipated ammonium chloride and nitramide. Hydrazine and NH_4Cl do appear as minor secondary products. It has been proposed that this result implies that the proper formulation of $ClNO_2$ must be as nitrosyl hypochlorite, O=N–O–Cl (44). Further examination of the chemical properties of $ClNO_2$ has suggested an alternative view in accord with the results of structural determination previously mentioned. It is pointed out that owing to the presence of another oxygen attached to nitrogen, the N—Cl bond in $ClNO_2$ is not as polar as that in ClNO, and the $ClNO_2$ consequently behaves as a source of negative chlorine only with very strong Lewis acids. Thus, complexation reactions of $ClNO_2$ do not occur unless oxidations providing Cl^- takes place first. $SnBr_4$ is oxidized to give Br_2, and $(NO_2)_2SnCl_6$ is readily formed; but $SnCl_4$, since it is nonoxidizable by $ClNO_2$, does not form a complex. With the very strong electron acceptor SO_3, however, a crystalline adduct of empirical formula $ClNO_2 \cdot 2SO_3$ is obtained. This product could be formulated as nitryl chlorodisulfate, $NO_2(ClS_2O_6)$ (68).

$SiCl_4$ and BF_3 did not react with $ClNO_2$, but exothermic reaction occurs with PCl_3 (68). In liquid chlorine $ClNO_2$ and $SbCl_5$ form the complex NO_2SbCl_6 which indicates, in light of previous interpretation, that $SbCl_5$ in this solvent is an extremely strong Lewis acid (69). It would be interesting to examine the behavior of $ClNO_2$ and the strong electron acceptor BCl_3.

Unexplained is the observation of the failure of SO_2 to react with $ClNO_2$ after 36 hours of refluxing. With metallic Bi, Zn, or Mg the chlorides are formed on reaction with $ClNO_2$ at -30°C., but no reaction was observed with Cu, Mg, Fe, Al, or Sn (68).

Further chemical evidence against the nitrosyl hypochlorite formulation for $ClNO_2$ and in favor of the



structure is found in the observed stoichiometry of reaction between $(CH_3)_4NN_3$ and $ClNO_2$:

$$2ClNO_2 + (CH_3)_4NN_3 = (CH_3)_4NNO_3 + N_2 + N_2O + Cl_2$$

The azide ion is a sensitive reagent for the NO^+ group via the reaction:

$$XNO + X_3^- = N_2 + N_2O + X^-$$

Since no hypochlorite is observed, $ClNO_2$ is indicated to be the acid chloride of nitric acid. The products NO_3^-, N_2, N_2O, and Cl_2 are believed to result from the decomposition of $ClNO_2$ to N_2O_4 and Cl_2 followed by oxidation of N_3^- by N_2O_4 (70).

The behavior of $ClNO_2$ with organic compounds, particularly aromatics, has been examined. In the presence of HF, $AlCl_3$, or BF_3 as catalyst $ClNO_2$ is a good nitrating agent (71). In the absence of catalysts and in polar solvents, however, the compound will chlorinate alkylbenzenes (72). Addition of $ClNO_2$ to olefinic compounds in diethyl ether also occurs (71).

The chemical behavior of nitrosyl bromide, the only accepted oxybromide of nitrogen, has not been examined in any detail, but should be patterned after that of ClNO with allowance made for the greater ease of oxidation of the bromide ion.

IV. Phosphorus Halides

The variable valence of phosphorus and the existence of mixed halides result in a large number of phosphorus halides. Each halogen is represented by a compound of formula PX_3; all except iodine form PX_5; chlorine and iodine give P_2X_4; and many mixed halides, few

of which are well characterized, have been reported for phosphorus in both +3 and +5 oxidation states.

A. PREPARATION

These compounds may, for the most part, be prepared by direct synthesis. White phosphorus reacts vigorously with each of the halogens to give a mixture of PX_3 and PX_5 and, in the case of chlorine or iodine, small amounts of P_2X_4. The regulation of conditions and relative amounts of reactants may assist in obtaining a preponderance of one product, but purification steps are always necessary if this preparative approach to a desired compound is used. The presence of small amounts of water, for example, results in the formation of oxychlorides. Red phosphorus is somewhat less reactive with the elemental halogens.

In the commercial process for PCl_3 liquid P is chlorinated directly at the boiling point of PCl_3 (74°C.) in order to establish reflux conditions. The escaping volatile mixtures from this process usually contains about 1% phosphorus which can be chlorinated again in another vessel. Oxychlorides and other impurities are removed by fractional distillation, and over-all yields of 95% or higher are obtainable.

The usual procedure for the preparation of the pentachloride is chlorination of PCl_3 in CCl_4 solution, the white crystalline PCl_5 precipitating from solution. A suggested laboratory scale operation for the production of PCl_5 involves a two-step chlorination of red P in CCl_4; about 7 hours is required for the preparation of 1 kilogram of PCl_5 (73).

Diphosphorus tetrachloride, P_2Cl_4, is best prepared by the action of a silent electrical discharge on a mixture of PCl_3 and H_2 (74).

The colorless liquid phosphorus tribromide and the pale yellow solid pentabromide may be prepared using procedures similar to those employed for the chlorides. Thermal analysis of the P–Br_2 system suggests that PBr_5 can react further with Br_2 to give the polyhalides PBr_7, red crystals decomposing into two liquid layers at 106.5°C. (m.p. of PBr_5), and PBr_{17}, a solid melting at 14.5°C. (75).

The two iodide compounds are formed in the reaction of red or white phosphorus in CS_2 solution with the stoichiometric amount of iodine. Depending on the I/P ratio the dark red crystalline PI_3 or

the orange P_2I_4 results. The pentaiodide is not known, possibly because of steric effects associated with the large iodine atom.

Phosphorus trifluoride is prepared most easily by the action of AsF_3 or ZnF_2 on liquid PCl_3 (76). It occurs together with mixed chlorofluorides when PCl_3 is treated with SbF_3 in the presence of $SbCl_5$ (Swarts reaction), or with CaF_2 (77). Calcium fluoride also reacts with P_2O_5 to yield some PF_3 (78).

The gaseous pentafluoride results from treatment of PCl_5 with AsF_3 and may also be obtained from the decomposition of the mixed halide, PF_3Br_2 (79), and by pyrolysis of KPF_6.

B. PREPARATION OF MIXED HALIDES

With the exception of mixed fluoroiodides several examples of each of the possible combinations of two different halogens with phosphorus are known. Evidence has also been offered for a chlorobromofluoride of phosphorus, PFBrCl, based on the Raman spectrum of a mixture of $PFCl_2$ and $PFBr_2$ (80); isolation has not been effected, however. Of the mixed compounds the best characterized are the chlorofluorides and bromofluorides of phosphorus in the +3 oxidation state. The Swarts reaction, the interaction of PCl_3 vapor with hot CaF_2, the hot tube equilibration reaction of gaseous PCl_3 and PF_3 (77), and the treatment of PCl_3 with NH_4F (81) all yield PF_2Cl and $PFCl_2$ in variable amounts. Similar procedures applied to PBr_3 give PF_2Br and $PFBr_2$ (82).

Mixtures of PCl_3 and PBr_3 (83), the chlorination of PBr_3 (84), and bromination of PCl_3 (85) have been reported to yield a number of products, $PClBr_2$ and PCl_2Br among them. The isolation and characterization of these as anything but highly unstable species is doubtful even though Raman evidence for the existence of these substances has been given (83,86).

The +5 oxidation state of phosphorus has proven most fruitful in preparing mixed halides. The compound PF_3Cl_2 has been obtained in two strikingly different forms. The gaseous covalent molecule is formed when PF_3 and Cl_2 (gas or liquid) react (87), but a white hygroscopic solid of this composition, clearly ionic in nature, results when PCl_5 is treated with AsF_3 (88). Transformation of the covalent to the ionic form has been reported to occur in acetonitrile (89). Paralleling the dimorphic character of PF_3Cl_2 is the behavior of PF_3Br_2. Passage of a stream of PF_3 into liquid Br_2 produces an easily

decomposed liquid, PF_3Br_2; however, treatment of PBr_5 with AsF_3 in CS_2 or CCl_4 solution yields a salt-like ionic substance of the same empirical composition (90). The reaction of PBr_2F and bromine has been shown to yield either the ionic (i.e., $PBr_4^+F^-$) or molecular form of PBr_4F depending upon temperature conditions (420).

The ionic forms of PF_3Cl_2 and PF_3Br_2 have been used to prepare other mixed halides. Heating the chlorofluoride *in vacuo* gives PCl_4F, a liquid at room temperature and a poor electrical conductor, and PF_5 (91), but if the parent compound is heated in $AsCl_3$ suspension, there forms a solution from which solid PCl_4F, an electrical conductor in CH_3CN solution, precipitates. The molecular weight determination for this solid in glacial acetic acid yields a lower result than would be expected for ionic PCl_4F, however.

In $AsBr_3$ or PBr_3 a suspension of ionic PF_3Br_2 decomposes to PF_5 and PBr_4F, and the latter compound is itself partially decomposed to PBr_5 (90).

Mention of compounds involving phosphorus(V), bromine, and chlorine is widespread in the literature, but there is little agreement on the composition of these substances. During the last decade several groups of researchers have attempted to determine the nature of the solid products formed in the reaction of PCl_3 and Br_2. Study of melting point versus composition curves and electrical conductance for the liquid mixtures by a Russian group indicated compounds of composition PCl_3Br_4 and PCl_3Br_8 (92). Both were isolated, and melting points 37.7 and 24.6°C., respectively, determined. On the basis of viscosity studies on the same system, this group of workers later reported the compound PCl_3Br_8, but did not isolate the substance (93). It is hypothesized that the preparation of each of these compounds results from an oxidation of PCl_3 to PCl_3Br_2 which ionizes to PCl_3Br^+ and Br^-. In the ionic state polybromides, $Br(Br_2)_n^-$, are formed, resulting in the aforementioned species of general formula $PCl_3 \cdot (Br_2)_n$. These compounds are acknowledged to be of limited stability, but, in contrast to the small electrical conductivity of PCl_3 or PBr_3, a high conductivity is observed. This rises with temperature to 40–50°C., then falls off as decomposition becomes significant.

The formation of PCl_3Br_2 as an intermediate is agreed upon by another group, but their results from a spectrophotometric study of the PCl_3-Br_2 reaction were interpreted as indicating the disproportionation of this intermediate to an unstable aggregate $PCl_3Br_{5.7}$ (94).

This aggregate, under reduced pressure, formed a stable mixed halide, $PCl_{4.67}Br_{0.33}$. Isolated and subjected to X-ray examination this proved to be a single-phase crystal. Attempts to isolate the compounds reported by the Russian investigators were unsuccessful. In CCl_4 or $PhNO_2$ no complex formation between PCl_3 and Br_2 was observed.

A third group of researchers have recovered light yellow crystals of composition $PCl_{4.5}Br_{0.5}$ (closely approximating $PCl_{4.67}Br_{0.33}$ noted above) from an $AsCl_3$ solution of PCl_3 and Br_2 in 1 : 1 mole ratio (95). A structure $PCl_4^+PCl_5Br^-$ is proposed. It is suggested that $PCl_{4.67}$-$Br_{0.33}$ is a decomposition product of $PCl_{4.5}Br_{0.5}$.

Finally, English investigators have examined the cryoscopic behavior of PCl_3 and Br_2 in nitrobenzene (96). The results are fully described by two reactions:

$$PX_3 + X_2 = PX_5$$

and

$$PX_3 + 2X_2 = PX_7$$

Attempts to obtain solid phases from CCl_4 solution gave materials containing CCl_4 of crystallization. The uncertainty of the analytical data for Cl and Br permits speculation that these solids might be members of a $PCl_3(Br_2)_n$ series. However, a careful attempt to prepare PCl_3Br_4 according to the procedure already cited was unsuccessful (96). It is obvious that considerable effort is required to resolve these apparently conflicting data.

The uncertainty and controversy surrounding the P–Cl_2–Br_2 system are in marked contrast to findings regarding iodine-containing mixed halides. No indication of compound formation involving P^{III} was observed after a variety of experimental approaches had been employed on the systems PCl_3–I_2, PBr_3–I_2, and P_2I_4–I_2 (97). Size considerations have been invoked to explain this lack of reactivity (98), just as in explaining the nonexistence of PI_5.

With pentavalent phosphorus, however, iodine is found to yield the solid phases PCl_6I (97) and PBr_6I, the former being isolated in the pure state. Compounds of this composition are also obtained from the reaction of PX_3 with IX (99) or of PX_5 with IX (100,101), where X is Cl or Br. These complexes dissociate in CCl_4 solution to PCl_5 and ICl and to PBr_3, IBr, and Br_2, respectively (102). Finally,

two compounds containing Cl, Br, and I have been reported as the product of the following reactions in CCl_4 solution:

$$PBr_5 + ICl = (PBr_4)^+(BrICl)$$

$$PCl_5 + IBr = (PCl_4)^+(BrICl)^-$$

Electrical conductivity in $PhNO_2$ suggests the ionic formulation. These compounds may be recrystallized from hot CCl_4 and have well-defined melting points (103).

C. STRUCTURE

The structures of the tri- and pentahalide compounds have been examined by a number of techniques. The P^{III} halides, chiefly covalent compounds but with some ionic contribution in the P–X bonds, have a triangular-based pyramidal form with the P atom at the apex and an unshared pair of electrons attached thereto. This configuration indicates that phosphorus uses a set of bonding orbitals in the range between p^3 and sp^3.

Table IV summarizes structural parameters determined by a variety of procedures.

TABLE IV
Bond Distances, Bond Angles, and Dipole Moments of Phosphorus Halides

	P—X, A.	X—P—X angle, deg.	Dipole moment, D.
PF_3	1.546 ± 0.008	104 ± 3	1.03 ± 0.01
PCl_3	2.043 ± 0.003	100.1 ± 0 3	1.00 ± 0.01
PBr_3	2.23 ± 0.01	100 ± 2	0 52 ± 0.01
PI_3	2.52 ± 0.01	98 ± 4	
P_2I_4[a]	2.475	102.3	
$PFCl_2$	2.02 ± 0.03	102 ± 3[b]	
PF_5	1.57 ± 0 02	(90, 120, 180)	
PCl_5	P—apical Cl: 2 19 ± 0 06	(90, 120, 180)	
	P—equatorial Cl: 2.04 ± 0.06		
PF_3Cl_2	P–F: 1.59 ± 0.03	F–P–F: 120	
	P–Cl: 2.05 ± 0.03	Cl–P–Cl: 180	

[a] P—P, 2.212 A.; I–P–P angle, 93.9 degrees.
[b] Cl—P—Cl angle, 102 ± 3 degrees.

The pentavalent phosphorus-halogen compounds in the gaseous or liquid states may be considered to be, like the trihalides, covalent substances. Hybridization of the sp^3d type would permit the observed trigonal bipyramidal structure, symmetry D_{3h}, for these molecules.

Until recently there has been no evidence of any association of the pentahalide molecules in the vapor state. Although vapor density measurements give no results suggestive of association, a careful examination of the mass spectra of PCl_5 vapor shows peaks assigned to ions of the species P_2Cl_9, P_2Cl_7, P_2Cl_5, etc. (104). It is argued that these do not result from combination of fragments in the instrument, but are caused by the presence of a small amount of P_2Cl_{10} in equilibrium at room temperature with solid $PCl_4^+ PCl_6^-$. Evaporation of ion pairs then produces P_2Cl_{10} molecules. Although detailed structural information is unavailable at present, it is suggested that two

TABLE V
Physical Properties of Phosphorus Halides

	Melting point, °C.	Boiling point, °C.	ΔH_{vap}, kcal./mole	ΔH_{form}, kcal./mole	Density, g./ml.
PF_3	−151.5	−101 5	3.49	−189 (g)	
PCl_3	−111.8	74.2	7.8	− 79.4 (l)	1.56 (21°C.)
P_2Cl_4	− 28	~180			
PBr_3	− 40.5	172.8	11.6	− 16.5 (l)	2.85 (15°C.)
PI_3	61 2	d. >200		− 10.9 (s)	
P_2I_4	124.5	d.		− 19.8 (s)	
PF_5	− 93.7	− 84.5	4.11		
PCl_5		subl. 167	15.5 (subl.)	−106.5 (s)	
PBr_5	<100	d. >106	13.6	− 60.6 (s)	
PF_2Cl	−164.8	− 47.3	4.2		
$PFCl_2$	−144.0	13.9	5.95		
PF_2Br	−133.8	− 16.1	5.45		
$PFBr_2$	−115	78.4	7.34		2.18 (0°C.)
$PFBr_4$ (ionic form)	87				
PF_3Cl_2		d. >70			
PF_3Br_2	− 20	d.			
$PFCl_4$					
Covalent form[a]	− 63	67			
Ionic form[a]		subl. 175			

[a] See text.

PCl_5 groups are joined via a 2-chlorine atom bridge, thus providing each phosphorus atom with an octahedral configuration.

Studies of the isotopic exchange rate of Cl^{36} between PCl_5 and Cl_2 in CCl_4 solution show the three shorter-bonded equatorial Cl atoms of the PCl_5 molecule to exchange much more rapidly than the apical Cl atoms (105). The addition of Cl_2 to PCl_3 is therefore considered to occur mainly in the equatorial plane, a *cis* reaction. The greater chemical reactivity of the equatorial positions is also shown by the preferential removal of chlorine from these positions by mercury.

In the solid state PCl_5 and PBr_5 are present in ionic form. Thus, crystallized from nitrobenzene PCl_5 is composed of PCl_4^+ (tetrahedral) and PCl_6^- (octahedral) units arranged as in the CsCl structure (106,107). The P—Cl distances in the two units are calculated from the X-ray data (106) to be 1.97 A. in the PCl_4^+ and 2.04 and 2.08 A. in PCl_6^-.

Solid PBr_5 is composed of Br^- and PBr_4^+ units, the P—Br distance in the latter being about 2.13 A. (108). The Raman spectrum of the solid suggests that PBr_4^+ has a regular tetrahedral structure (109). In the vapor state PBr_5 is fully dissociated to PBr_3 and Br_2 (435).

D. GENERAL PROPERTIES

In general the phosphorus (III) halides hydrolyze readily in water to phosphorous and hydrohalic acids. In slightly basic solution PCl_3 is found, by chromatographic and iodometric analyses, to give $H_2P_2O_5^{2-}$ and HPO_3^- as the principal hydrolysis products, with smaller amounts of $HP_2O_5^{3-}$, $H_2P_2O_7^{2-}$, HPO_4^{2-}, and other phosphorus-containing ions and molecules (110). In more basic solution less $H_2P_2O_5^{2-}$ is present, while the yield of other products, notably HPO_3^-, is increased. A somewhat different distribution of hydrolysis products was observed for PBr_3 and PI_3; the less polar the P—X bond, the greater the tendency to form hydrolysis products containing P—P linkages. The rate of the hydrolysis is also inversely related to the P—X bond polarity.

The solvolysis of PCl_3 in liquid ammonia, followed by thermal decomposition, proceeds through a series of compounds having P—N bonds, and ends with the polymeric paranitride $(PN)_x$ (111).

Oxygen, sulfur, and the halogens generally oxidize the trihalides to the corresponding POX_3, PSX_3, or PX_5 compounds. A mixture of fluorocarbons, principally CF_4 and C_2F_4, is obtained from the Ni-catalyzed high temperature reaction of PF_3 and carbon (112).

The trihalides may behave as weak Lewis bases, a tendency expected to increase with the atomic number of the halagon. Thus, while PF_3 or PCl_3 forms no complexes with BF_3, BCl_3, or $AlCl_3$, both PCl_3 and PBr_3 will form addition compounds with the stronger Lewis acid BBr_3 (114). In addition, such complexes as PF_3BH_3 (m.p. $-116°$C.) (113), $(PF_3)_2PtCl_2$ (76), and $Ni(PX_3)_4$ (115,116) where X is F, Cl, or Br, are formed. That PCl_3 and PBr_3 may act as Lewis acids is established by the formation of weak complexes with trimethylamine (114).

The trihalides self-ionize only to an extremely limited extent. Liquid PF_3 at $-113°$C. has a specific conductance of 4.2×10^{-10} ohm^{-1} $cm.^{-1}$. No combination of liquid PF_3 with KF was observed during a contact period of 3 months. When a KF–gaseous PF_3 mixture is heated above 200°C. a red product, presumably the result of the disproportionation of PF_3 to $P + PF_5$, is observed. The PF_5 so formed can then combine with KF (117).

Commercially, PCl_3 and PBr_3 are important as halogenating agents in a variety of organic reactions, particularly the conversion of acids to acid chlorides and bromides. PCl_3 and PBr_3 behave somewhat differently toward alcohols: the former yields phosphite esters, the latter alkyl bromides. Each also has some catalytic properties.

The phosphorus pentahalides are less stable than the trihalides, and this thermal instability increases from chloride to bromide. While PF_5 is thermally stable, PCl_5 is completely dissociated above 300°C. to PCl_3 and Cl_2, and PBr_5 is dissociated to a small degree in the liquid state or in nonaqueous solvents even at low temperatures (118).

The pentahalides are rapidly hydrolyzed to phosphoric and hydrohalic acids. With limited amounts of water, however, oxyhalides will result. The ammonolysis of PCl_5, like that of PCl_3, gives as a final product $(PN)_x$ (111). Solvolysis reactions for the pentahalides are generally quite exothermic.

The electrical conductances of solutions of PCl_5 in $POCl_3$, PhCOCl, $PhNO_2$, PhCN, or MeCN have been measured, and the results in each of these polar solvents suggest ionization to PCl_4^+ and PCl_6^-. This conclusion is proven by electrolysis of PCl_5 in MeCN or $PhNO_2$ in which products are formed at the appropriate electrode according to the equations (119):

$$PCl_6^- = PCl_5 + {}^1/_2Cl_2 + e^-$$

$$2PCl_4^+ + 2e^- = PCl_3 + PCl_5$$

Phosphorus pentachloride, in its complex formation reactions, most frequently yields substances containing the PCl_4^+ ion. Chlorides of tri-, tetra-, and pentavalent metals (Al, Fe, Tl, Sb; Sn, Zr, Se, Pt; and Sb, Mo, W, for example) react in liquid $POCl_3$ with PCl_5 to give the corresponding complex of the tetra-chlorophosphonium ion. Alternatively, the same results may be achieved by reacting PCl_3 with a solution of the metal chloride in $SOCl_2$. The PCl_3 is oxidized to PCl_5 by the solvent, and the complex then formed (120).

Efforts to prepare isolable PCl_6^- complexes other than $PCl_4^+PCl_6^-$ have been unsuccessful; KCl, CsCl, and Me_4NCl could not be made to react with PCl_5 either directly or in appropriate solvents. However, in iodine monochloride the results of conductometric titration of PCl_5 with KCl have been interpreted in terms of $KPCl_6$ compound formation (121). This conclusion has been criticized as being based upon unproven assumptions of the amphoteric character of PCl_5 in ICl. Subsequent X-ray study of $PCl_5 \cdot ICl$ shows PCl_4^+ and ICl_2^- to be present (122).

The possibility of stabilizing PCl_6^--containing systems by solvents has been proposed, and transport number and electrolysis experiments on the HCl–PCl_5–nitrobenzene system have been interpreted in favor of the formulation $[(CH_3CN)_nH^+][PCl_6^-]$ (123).

The stability of hexafluorophosphate is, in contrast to that of PCl_6^-, very high. Thus, PF_6^- containing substances may be prepared directly from the halide salt and PF_5, but indirect procedures, such as the treatment of metal chloride dissolved in liquid HF with PCl_5, are more convenient (124).

V. Phosphorus Oxyhalides

Oxyhalides of phosphorus are known only for the element in the +5 oxidation state. The known compounds of this type are POF_3, $POCl_3$, $POBr_3$, and a number of mixed halides.

A. PREPARATION

PX_3 compounds are susceptible to oxidation, and the direct reaction with O_2 is an important commercial method for the preparation of

$POCl_3$. The action of a deficiency of water on PX_5 suffices to form any one of these compounds, but in the laboratory $POCl_3$ is more readily obtained by the action of PCl_5 on oxalic acid:

$$PCl_5 + H_2C_2O_4 = POCl_3 + 2HCl + CO_2 + CO$$

or on P_2O_5:

$$3PCl_5 + P_2O_5 = 5POCl_3$$

Treatment of dihydroxydifluoroboric acid, $H_3BF_2O_2$, with PCl_5 also leads to $POCl_3$:

$$3PCl_5 + 3H_3BF_2O_2 = BPO_4 + 2POCl_3 + 2BF_3 + 9HCl$$

$POBr_3$ is obtained by a similar reaction using PBr_5, but PCl_3 undergoes no reaction even at the boiling point. Phosphorus triiodide is apparently completely hydrolyzed with the P_2O_3 or H_3PO_3 forming a "boron phosphite" residue with the B_2O_3 product (125).

A laboratory procedure for $POBr_3$ is the reaction of PBr_5 with P_2O_5, but difficulties may be encountered because of the tendency of PBr_5 to sublime along with the volatilized $POBr_3$ product (126). A final purification step involving fractional crystallization and removal of volatile impurities has been recommended as valuable to this procedure (127).

Reaction between acetic acid and PBr_5,

$$CH_3COOH + PBr_5 = POBr_3 + HBr + CH_3COBr$$

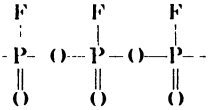
has been demonstrated to yield a very pure product. Hydrogen bromide may be avoided by using *tert*-butyl alcohol in ether solution (128):

$$2C_4H_9OH + PBr_5 = 2C_4H_9Br + POBr_3 + H_2O$$

The oxyfluoride has been prepared from $POCl_3$ via the Swarts reaction, by vapor phase fluorination using CaF_2 pellets, and through interaction with liquid HF (129). Reaction of P_2O_5 with either IF_5 (130) or HSO_3F (131) also gives POF_3.

A polymeric species of phosphorus oxyfluoride is produced by passage of PF_3 and O_2 through an electrical discharge at $-75°C$. The initial product, $P_7O_{10}F_{15}$, a white solid, undergoes decomposition on warming to 0°C. giving POF_3, PF_5, $P_2O_3F_4$, and a hygroscopic, easily

hydrolyzed polymer, $(PO_2F)_n$ (132). The structure of this substance is suggested to be:



The mixed chlorofluorides, $POClF_2$ and $POCl_2F$, also occur in the fluorination of $POCl_3$ by SbF_5 or CaF_2. Similar reactions give the corresponding bromofluorides (133). Other mixed halides, $POCl_2Br$ and $POClBr_2$, are reported as products of the reaction of acetic acid with PCl_3Br_2 or mixtures of PCl_5 and PBr_5. From a warmed mixture of $POClBr_2$ and SbF_3 the isolation of $POFBr_2$, $POFClBr$, and $POFCl_2$ has been carried out (134). No indication of reaction was found when $POCl_3$ and $POBr_3$ were mixed (135).

A pyrophosphoryl chloride, $P_2O_3Cl_4$, and a tetraphosphoryl chloride, $P_4O_4Cl_{10}$, are produced in small amounts from the low temperature reaction of PCl_3 and N_2O_4 (136). To account for these species a complex mechanism involving radicals has been proposed:

$$N_2O_4 = 2(NO_2\bullet)$$

$$NO_2\bullet + PCl_3 = Cl_3PONO$$

$$Cl_3PONO = \overset{\bullet}{Cl_2PO} + NOCl$$

$$\overset{\bullet}{Cl_2PO} + \bullet ONO = Cl_2PO(ONO)$$

$$Cl_2PO(ONO) + \overset{\bullet}{Cl_2PO} = P_2O_3Cl_4 + NO$$

$$2\ \overset{\bullet}{Cl_2PO} + 2\ POCl_3 = 2\overset{\bullet}{P_2O_2Cl_5} \longrightarrow P_4O_4Cl_{10}$$

Pyrophosphoryl chloride was first discovered as a product of the partial hydrolysis of $POCl_3$ by a current of moist air (137). This product may also be obtained by the sealed tube reaction of $POCl_3$ and P_2O_5 at 200°C. (421).

B. STRUCTURE AND PROPERTIES

POX_3 molecules are tetrahedral in shape and are similar in the double bond character of the P—O linkage. It has been noted that the 3*d* orbitals of phosphorus probably play some part in the bonding just as they do in PX_5 (138).

TABLE VI

Bond Distances, Bond Angles, and Dipole Moments for Phosphorus Oxyhalides

	P—O, A.	P—F, A.	P—Cl, A.	P—Br, A.	X—P—X angle, deg.	Dipole moment, D.
POF_3	1.45 ± 0.03	1 52 ± 0 02			102.5 ± 2	1 69
$POCl_3$	1 45 ± 0.03		1 99 ± 0 02		103 6 ± 2	2.40
$POBr_3$	1.41 ± 0.07			2 06 ± 0 03	<108 ± 3	
POF_2Cl	1.55	1 51	2 01		(all angles: <106)	
$POFCl_2$	1 54	1.50	1 94		(all angles: <106)	

Early electron diffraction studies (139) gave results which have been subsequently refined by microwave investigation (140,141) and more recent electron diffraction determinations (142). These values are reported in Table VI. Raman spectra of phosphoryl halides and mixed halides have been reported and are in full accord with the tetrahedral structure (134,135,143,144). The expected diamagnetism of POX_3 molecules has been observed for $POCl_3$ (145).

The Raman spectrum of $P_2O_3Cl_4$ suggests the molecule to consist of two $-P(=O)Cl_2$ groups connected by an oxygen bridge (422).

The existence of phosphoryl chloride as a liquid through a temperature range similar to that for liquid water has attracted interest to $POCl_3$ as a proton-free ionizing solvent. The density, 1.648 g./ml. at 20°C., is found to decrease normally with increasing temperature but the specific electrical conductance has a maximum at 88°C.

TABLE VII

Physical Properties of Phosphorus Oxyhalides

	Melting point, °C.	Boiling point, °C.	$\Delta H_{vap.}$, kcal./mole	$\Delta H_{form.}$, kcal./mole	Liquid density, g./ml.
POF_3	− 39 1	− 39 8	5 55	−260 (g)	
$POCl_3$	1 3	105 1	9 5	−143 8 (l)	1.712 (0°C.)
$POBr_3$	56	192.0	15 ($\Delta H_{sub.}$)	−110 1 (s)	
POF_2Cl	− 96.4	3.1	6 09		1.656 (0°C.)
$POFCl_2$	− 80.1	52.9	7 40		1.593 (0°C.)
$POFBr_2$	−117.2	110.1	7.52		
POF_2Br	− 84.8	30.5	7.09		
$POCl_2Br$	11 0	137.6			
$POClBr_2$	~30	165			
POFClBr		~80			
$P_2O_3Cl_4$		65			
$P_4O_4Cl_{10}$	37	105			

This behavior is ascribed to the temperature-dependent character of the self-ionization mechanism (146):

$$2POCl_3 = POCl_2^+ + POCl_4^-$$

However, no compound containing discrete $POCl_4^-$ ions in the solid state has been isolated. Aluminum halides and the chlorides of Sb, Ti, Sn, Te, Zr, B, Mo, and Mg form solid solvates or addition

compounds from $POCl_3$ solutions. Several oxides—CaO, MgO, and ZnO—and hydroxides $Ca(OH)_2$, $Mg(OH)_2$, and $Ni(OH)_2$ also yield isolable solids. Other compounds give conducting solutions in $POCl_3$ but no recoverable solid solvates, viz., $HgCl_2$, ICl, PCl_5, $AsCl_3$, etc. Finally, PBr_3, PCl_3, $SOCl_2$, and $SiCl_4$ are soluble, but produce no effect on the electrical conductivity of the solvent (147, 148).

The observed conductivity increase for many of the above solutions, and the results of electrolysis experiments on $AlCl_3$–$POCl_3$ and $SbCl_5$–$POCl_3$ systems, are explained in terms of the ions $POCl_2^+$ and $AlCl_4^-$ and $POCl_2^+$ and $SbCl_6^-$ (149,150). A Raman investigation proved the presence of $SbCl_6^-$ ions in solutions of the latter system, but interpretation of Raman data in favor of the presence of these ions in the solid recovered from the solution is probably incorrect (151). A single crystal X-ray study of $SbCl_5$–$POCl_3$, the only crystal structure reported for any of these solid solvates, clearly shows the substance to be built up from $Cl_3PO \rightarrow SbCl_5$ donor-acceptor molecules (152). Since $SbCl_5$ is of very high Lewis acid strength, as shown by potentiometric titration in $POCl_3$, it is reasonable to assume that the other solid solvates are also molecular in form. In solution, of course, the solvent effect of a large excess of $POCl_3$ molecules promotes dissociation and ionization of the adduct. The electrical conductivity of the $GaCl_3$–$POCl_3$ complex in the molten condition has been interpreted in terms of the ionic formulation, $POCl_2^+GaCl_4^-$ (153).

While most compounds examined behave as acids in liquid $POCl_3$, the presence of $POCl_4^-$ ions in $POCl_3$ solution and the corresponding amphoteric character of this solvent are demonstrated by neutralization reactions of $POCl_3$ solutions of VCl_5 and PCl_5:

$$PCl_5 + POCl_3 = PCl_4^+ + POCl_4^-$$

$$VCl_4 + 2POCl_3 = 2POCl_2^+ + VCl_6^{2-}$$

and

$$2PCl_4^+ + VCl_6^{2-} = (PCl_4)_2\,VCl_6$$

Such complexes may be isolated as insoluble salts or by solvent evaporation. Although of limited solubility R_4NCl and $ZnCl_2$ also behave as bases in $POCl_3$ (154). The high solubility of $(CH_3)_4NCl$ and $(C_2H_5)_4NCl$ in $AsCl_3$ and $SeOCl_2$, as contrasted to their limited solubility in $POCl_3$, indicates $POCl_3$ to be very low in acidic, i.e., chloride ion–acceptor, properties (155).

The series of solid compounds formed by $ZrCl_4$ and by $HfCl_4$ with $POCl_3$, $POCl_2F$, $POClF_2$, and POF_3 have been examined (156).

When one of the mixed oxyhalides is involved, the composition of the solid product is determined by the contact time of solvent and MCl_4. A sufficiently long period permits complete halogen exchange to occur between phosphoryl molecules, and $2POCl_3 \cdot MCl_4$ is obtained. If the solid is removed after brief mixing, the mixed phosphoryl halide will be present in the crystalline phase.

A phase study of the $POBr_3$–$GaBr_3$ system shows the existence of a 1:1 complex melting at 154°C. (127). Compared to the electrical conductivity of the pure reactants that of the molten complex is high and implies the presence of $POBr_2^+$ and $GaBr_4^-$ ions, a finding in accordance with that for the $POCl_3$-$GaCl_3$ system mentioned above.

Complex formation has also been observed with the tetraphosphoryl chloride. It reacts with $SnCl_4$ to give $[P_4O_4Cl_8^{2+}][SnCl_6^{2-}]$; hence two of its chlorides are relatively easily ionized (136). Both $SnCl_4$ and $SbCl_5$ have been found to form addition compounds with $P_2O_3Cl_4$ (423).

VI. Halides and Oxyhalides of Arsenic, Antimony, and Bismuth

A. PREPARATION

Direct action of the halogens on elemental As, Sb, or Bi leads to the formation of the trihalides, a complete series of which is known for each of these elements. Certain of these compounds also result from the displacement reaction of a halogen on the appropriate oxide or sulfide, as products of the treatment of the trioxide with a halogen acid, or by the exchange reaction of a trihalide with an alkali halide salt in which the halogen differs from that in MX_3.

The older literature contains numerous claims for lower valence halides of these elements, but of those reported only BiCl has been clearly isolated and characterized (157). At temperatures below 323°C. $BiCl_3$ is reduced with excess Bi to give a 75% yield of BiCl. Purification to the 98–99% level is achieved through sublimation or extraction with benzene. The black product is stable in air at room temperature, but decomposes above 323°C. to Bi and $BiCl_3$.

X-ray examination of reported BiX_2 preparations (158) reveal these to possess the same crystal structure as BiX_3, thus suggesting a mixture of Bi and BiX_3 (159).

The occurrence of pentahalides of these elements is apparently governed by two factors. The increasingly favorable steric factor in the series As, Sb, Bi is offset by the increasing oxidizing power of M^V in this series. As a result arsenic forms only a pentafluoride, anti-

mony a fluoride and chloride, but bismuth only a fluoride. The arsenic and antimony pentafluorides are prepared by reaction of the element at 300–350°C. with fluorine, but bismuth requires a more drastic method (204). The recently developed direct synthesis requires a temperature of 600°C. or greater and approximately 2 atmospheres fluorine pressure (160).

A few mixed pentahalides have been described; SbF_3Cl_2 is obtained by reacting SbF_3 and Cl_2 at 135°C. under some pressure (161). Treatment of $SbCl_5$ with AsF_3 is reported to produce $SbCl_4{}^+F^-$ (dec. >83°C.), described as a strong electrolyte in liquid AsF_3 (162). In the presence of a small amount of water AsF_3 reacts with Cl_2 or NCl_3 to give impure tetrachloroarsenic(V) hexafluoroarsenate, $AsCl_4{}^+$-$AsF_6{}^-$ (163,164). The assumed oxyhalide impurity is removed by chlorination of the impure product in liquid $AsCl_3$. It is interesting that no reaction between anhydrous AsF_3 and Cl_2 is observed, nor is the mixed halide product obtained when quantities of water equimolar with, or greater than, the amount of AsF_3 are used. Attempts to add Br_2 or I_2 to AsF_3 were unsuccessful (165). Raman evidence suggests the presence of equilibrium mixed halides in the $AsCl_3$–$AsBr_3$ system, but no new species are believed present in an AsF_3–$AsCl_3$ mixture (166).

The systems $SbCl_5$ I_2, $SbCl_5$–ICl, and $SbCl_3$–ICl all give evidence (viscosity, conductance, and freezing point diagram) for the existence of compound(s) best formulated as $I^+[SbCl_6]^-\cdot nICl$, where $n = 1$ or 2 (167).

The oxyhalides will be discussed in connection with the properties of the halides (see page 63).

B. STRUCTURE

Election diffraction and microwave studies of various MX_3 molecules show them to be uniformly pyramidal in shape with the X–M–X angle close to 100 degrees in all cases (13,168–171). Table VIII summarizes these values. Raman spectra (172) and NMR measurements (173) are in accord with this configuration. Crystal structure investigations of the solid tribromides and triiodides of As and Sb (174), $SbCl_3$ (174), and SbF_3 (175) show these to be molecular crystals with a structure based upon the pyramidal MX_3 molecule. Solid BiF_3, on the other hand, is isostructural with YF_3 (176,177).

A linear structure, Cl–Bi=Bi–Cl, has been suggested for the structure of BiCl (424).

The high viscosity (178) and surface tension (179) of SbF_5 suggest a polymerized material, and this is supported by NMR measurements; a chain structure based upon fluorine bridging is proposed (180). Electron diffraction patterns of gaseous $SbCl_5$ (181) indicate that the molecule possesses a trigonal bipyramid structure, symmetry D_{3h}. Solid $SbCl_5$ is a molecular compound with the trigonal bipyramidal structure of the gaseous molecule retained. The equatorial Sb—Cl distance is the same in the solid as in the gas, but the apical Sb—Cl distance is shortened by 0.05 Å. (182). X-ray diffraction patterns (160) indicate solid BiF_5 to be isostructural with the body-centered tetragonal α-form of UF_5 (183).

TABLE VIII
Structural Parameter for As, Sb, and Bi Halides

	M—X, A.	X—M—X angle, deg.	Dipole moment, D. (in dioxane)
AsF_3	1.712 ± 0.005	102 ± 2	
$AsCl_3$	2.161 ± 0.004	98.4 ± 0.5	3 11
$AsBr_3$	2.33 ± 0.02	100.5 ± 1.5	2.90
AsI_3	2.55 ± 0.03	101 ± 1 5	1.83
SbF_3	2.03	88	
$SbCl_3$	2.325 ± 0.005	99 5 ± 1.5	5.16
$SbBr_3$	2.51 ± 0 02	97 ± 2	5 0
SbI_3	2.67 ± 0.03	99 ± 1	
$BiCl_3$	2.48 ± 0.02	100 ± 6	
$BiBr_3$	2.63 ± 0 02	100 ± 4	
$SbCl_5$	2.31; 2.43 ± 0 06		

Crystal structure study of antimonyl chloride, SbOCl, shows this substance to be composed of infinitely extending sheets of $(Sb_6O_6Cl_4)^{2+}$ ions held together by the remaining Cl^- ions (184). Thus, both covalently and ionically bonded chlorine atoms are present. Isomorphous $Sb_4O_5Cl_2$ and $Sb_4O_5Br_2$ are described as layers of Sb—O sheets connected by halogen sheets. In the Sb—O sheets are zigzag chains of Sb and O (185).

Infrared and Raman data support a trigonal bipyramidal structure for AsF_5 (186).

C. GENERAL PROPERTIES

The trends noted in the properties of an AsX_3–SbX_3–BiX_3 series, where X is the same halogen for each compound, are essentially related to the increase in metallic character of the group Vb elements

TABLE IX
Physical Properties of As, Sb, and Bi Halides and Oxyhalides

	Melting point, °C.	Boiling point, °C.	ΔH_{vap}, kcal./mole	ΔH_{form}, kcal./mole	Density, g./ml.
AsF_3	−5.95	62.8	8.57 (b.p.)	−198 (l)	2.67 (0°C.)
$AsCl_3$	−13	130	8.70 (25°C.)	− 71.5 (l)	2.16 (20°C.)
$AsBr_3$	35	220	10.0 (220°C.)	− 43.1 (l)	
AsI_3	146	403	19.2	− 13.6 (s)	
SbF_3	292	subl. 319		−216 (s)	
$SbCl_3$	72.9	221	10.9 (125°C.)	− 91.4 (s)	2.44 (178°C.)
$SbBr_3$	96.6	280		− 60 (s)	
SbI_3	167	401		− 23 (s)	
BiF_3	725				
$BiCl_3$	232	447	23.2 (25°C.)	− 90.6 (s)	
$BiBr_3$	218	460			
BiI_3		subl. 439		− 24.0 (s)	
$AsOF_3$	−68.3	25.6			
AsF_5	−79.8	−53.2	5.00 (b.p.)		3.4 (−73°C.)
SbF_5	7.0	150			2.99 (23°C.)
$SbCl_5$	5	~140	11.5 (76.5°C.)		2.35 (20°C.)
BiF_5	<160	230	14.9		5.4 (25°C.)

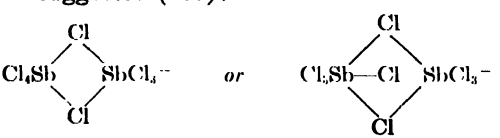
with increasing atomic number. Thus, in the trichloride series the hydrolysis of $AsCl_3$ to H_3AsO_3, or $As_2O_3 \cdot nH_2O$, is capable of reversal in contrast to the irreversibility of the same reaction with PCl_3. Antimony and bismuth trichlorides form insoluble intermediate oxyhalide species readily reconverted to the halide by an excess of the appropriate halogen acid. Besides the well-known SbOX and BiOX compounds, the previously noted $Sb_4O_5X_2$ (X is Cl or Br) has been isolated and identified (185). Also, when heated above 700°C., BiOCl and BiOBr transform to complex oxyhalide structures (187). Only one oxyhalide of arsenic has been prepared; the reaction of elementary fluorine with an equimolar mixture of $AsCl_3$ and As_2O_3 results in the compound $AsOF_3$ (188).

Similar trends in the solubility characteristics of the trifluorides in polar and nonpolar nonaqueous media are observed. Thus, AsF_3 is quite soluble in liquid HF (189), in benzene, or ether, while BiF_3 dissolves to only a very limited extent in these solvents. A study of the solubility of SbF_3 in a variety of organic liquids suggests that SbF_3 is a nonelectrolyte and that the relatively high solubility found for SbF_3 in alcohols and ketones may be related to hydrogen bond formation (190). As expected, SbF_3 is much less soluble in organic solvents than $SbCl_3$ or $SbBr_3$.

The ability of AsF_3 to act as a fluoride ion acceptor is evident in its exothermic reactions with the fluorides of K, Rb, Cs, and Tl to form the tetrafluoroarsenate salts, $MAsF_4$. The importance of the size and polarizing power of the cation in such a complex is indicated by the failure of Li and Na fluorides to form such complexes (191).

Isotopic exchange reactions involving MX_3 compounds have received considerable attention. The exchange of bromine atoms between radioactive Br_2 and $AsBr_3$ in CCl_4 at room temperature is very rapid (192). Use of I^{131} demonstrates that AsI_3 and SbI_3 experience complete exchange with molten I_2 or I_2 vapor in less than 2 hours. With labeled KI, however, SbI_3 underwent total exchange, while AsI_3 exchanged only to a limited extent (193), a reasonable result considering the relative ionicity of the bonds. The exchange of Cl_2 with $AsCl_3$ is catalyzed by HCl, suggesting an $HAsCl_4$ intermediate for the reaction (194). A study of the RCl_3—R^*Br_3 system, in which R^* is radioactive As or Sb, showed complete exchange to occur in 10 minutes (195).

Isotopic exchange between Sb^{III} and Sb^{V} has been investigated in both CCl_4 and aqueous HCl system. With the tri- and pentahalides in the former the exchange is homogeneous, accelerated by light, and apparently proceeds by two paths, one first order in $SbCl_5$, the other first order in $SbCl_3$ and second order in $SbCl_5$. A rate law expression is given and a possible mechanism discussed (196). In the HCl system the evidence suggests $SbCl_6^-$ and $SbCl_3$ as the exchanging Sb^{V} and Sb^{III} species, respectively. While the identity of the transition state is very much in doubt, chlorine bridging between $SbCl_3$ and $SbCl_6^-$ has been suggested (197):



The attractively wide and convenient liquid range of arsenic trichloride has suggested its use as a nonaqueous solvent medium. Conductometric titration of $SbCl_5$, among other acids in the system, with Me_4NCl (base) gives a typical neutralization reaction with the formation of Me_4NSbCl_6. In addition, the acid $AsCl_2^+SbCl_6^-$ may be prepared (198).

An addition compound is probably formed by $AsCl_3$ and $SiCl_4$, but CCl_4, $GeCl_4$, and $SnCl_4$ give no evidence of such combination (199). Nor is any compound formation observed in the $AsBr_3$–BBr_3 system (200).

In chloride-containing aqueous systems Bi^{III} forms complex ions $BiCl_n^{3-n}$, where $n = 1, 2, 3, 4$, and 5 (201). The addition of variable amounts of Cl^- and Br^- to a perchloric acid solution of Bi^{III} gives the complex ions $BiBr_4Cl^{2-}$, $BiBr_2Cl_3^{2-}$, and $BiBrCl_4^{2-}$ with smaller amounts of $BiBr_3Cl_2^{2-}$ in equilibrium with $BiBr_5^{2-}$ and $BiCl_5^{2-}$(202).

The pentahalides are more volatile than the corresponding trihalides, are readily hydrolyzable, and possess good halogenating properties. The observed ability of molten BiF_5 to oxidize Br_2 to BrF_3, BrF_3 to BrF_5, and Cl_2 to ClF shows it to be one of the most powerful fluorinating agents known. Bismuth pentafluoride, like SbF_5 and AsF_5, is a good fluoride ion acceptor and readily forms BiF_6^- with alkali fluorides. The stabilities of these hexafluorobismuthates decrease with decreasing size of the cation (see AsF_3 complexes, page 64); hence, variation in oxidizing strength of these compounds should be obtainable by changing the cation (160). In liquid BrF_3 bismuth pentafluoride behaves as an acid (203). The hydrolysis products of BiF_5 include ozone, BiF_3, and Bi_2O_5 (204).

The solubility of AsF_5, SbF_5, and $SbCl_5$ in liquid HF promotes the formation of the solvent cation H_2F^+ (205,425). SbF_5 dissolved in IF_5 increases the electrical conductivity of the solution by formation of IF_4^+ and SbF_6^- ionic species (206). The compound $IF_4^+SbF_6^-$ (m.p. 103°C.) is recoverable from solution. A phase study of the BrF_3–SbF_5 system indicates several compounds: $3BrF_3{\cdot}SbF_5$ (dec. −16°C.), $3BrF_3{\cdot}2SbF_5$ (dec. −30.8°C.), $BrF_3{\cdot}SbF_5$ (m.p. 129.8°C.), and $BrF_3{\cdot}3SbF_5$ (m.p. 33.5°C.) (207). SbF_5 also forms addition compounds with S, Se, Te, SO_2, NO_2 (208), AsF_3, and SbF_3 (178). AsF_5 fails to combine with SO_2, but forms $AsF_5{\cdot}NO_2$ similar in charac-

ter to the $SbF_5 \cdot NO_2$ compound (208). The specific electrical conductance of SbF_5 is quite low (1.2×10^{-8} ohm^{-1} cm.$^{-1}$ at 25°C.) compared to that of AsF_3 (2.4×10^{-5} at 25°C.), a difference paralleling the viscosity differences (460 centipoises at 20°C. for SbF_5; 1.17 centipoises at 8°C. for AsF_3) of the compounds (178).

VII. Oxygen Halides

A rigorous definition of oxygen halides would include only the oxygen fluoride compounds, since the compounds formed by oxygen with chlorine, bromine, or iodine are more properly halogen oxides. However, for the sake of contrast between the properties of the various compounds and for uniformity of coverage all binary oxygen-halogen compounds will be considered.

A. PREPARATION

There are three well-characterized oxygen fluorides: oxygen monofluoride, O_2F_2, ozone fluoride or trioxygen difluoride, O_3F_2, and oxygen difluoride, OF_2. The first of these, a yellow solid, is obtained by subjecting an equimolar mixture of O_2 and F_2 at -180°C. to an electrical discharge (209). Ozone trifluoride, for the most part unrecognized or unaccepted until recent confirmatory work (210), was first reported to result from the action of ultraviolet radiation on a liquid mixture of O_2 and F_2, or from the reaction between liquid OF_2 and liquid O_2 in the silent electrical discharge (211,212). Oxygen difluoride, the best known of the compounds, is prepared by reacting fluorine with aqueous sodium hydroxide in a continuous process. The final product is a mixture of OF_2 and oxygen, the latter resulting from the interaction of OF_2 with the hydroxide ion. The removal of most of the oxygen is best accomplished by applying vacuum to the solution cooled to -195°C.; the OF_2 content of the mixture is thereby increased to 95% (213).

Four binary chlorine-oxygen compounds are known: Cl_2O, ClO_2, Cl_2O_6, and Cl_2O_7. Chlorine monoxide, Cl_2O, results when freshly precipitated and dried HgO is treated with Cl_2:

$$2Cl_2 + 2HgO = HgCl_2 \cdot HgO + Cl_2O$$

The vigor of the reaction is such that inert material may be mixed with the HgO to slow the reaction. Excess chlorine may be removed

from the product by condensation of the Cl_2O (214). The monoxide also is formed by the reaction of Cl_2 with a solution of potassium hypochlorite.

The dioxide, which has attracted much attention because of its commercial uses, is usually prepared in the laboratory by the reaction of Cl_2 and silver chlorate at 90°C. (215) or by reaction of Cl_2 with solid $NaClO_2$ (216). The latter procedure is essentially that used in commercial production of the material; another important industrial process involves the electrolysis of solutions of NaCl and $NaClO_2$ (217).

The interaction of ozone and ClO_2 at low temperature (218), followed by purification by distillation, and the exposure of ClO_2 to strong ultraviolet radiation (219) have been used to prepare Cl_2O_6.

The anhydride of perchloric acid, Cl_2O_7, is obtained by the dehydration of the acid with P_2O_5 followed by suitable distillation of the oily product (220). Chlorine heptoxide is also formed when Cl_2 and O_3 are irradiated with ultraviolet light (221).

Three bromine oxides, Br_2O, BrO_2, and Br_3O_8, are generally accepted. The recent proposal of a fourth, BrO_3, raises doubt about the authenticity of Br_3O_8. All, of course, are relatively unstable.

The monoxide is prepared in a manner similar to that employed for Cl_2O; bromine vapor is passed over mercuric oxide at 50–60°C. (222). The same reaction carried out in CCl_4 solution at room temperature produces Br_2O in superior yields (223).

The electrical discharge technique is employed to convert mixtures of bromine vapor and oxygen at −190°C. to bromine dioxide, BrO_2 (224). Yields up to 80% were reported; ozone formed in the reaction is separated from the solid BrO_2 by pumping and, after warming to −30°C., the excess Br_2 is sublimed from the BrO_2.

Claims for tribromine octaoxide, Br_3O_8, result from the formation of a substance by bromine and ozone at 0°C. in the proportion 10–15 parts of ozone to 1 part of bromine (225). Explosion hazards of the reaction are avoided by maintaining low temperature and low partial pressure of the reactants. The question concerning the identification of Br_3O_8 arises from several repetitions of this reaction using Br_2/ozone ratios of 1:50, the only ratio at which any bromine oxide was formed. No product other than BrO_3 was observed. Bromine trioxide is also

produced in the glow discharge at 0°C. from a mixture of Br_2 and excess oxygen (226).

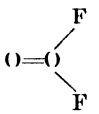
Of the three binary iodine-oxygen compounds only one, I_2O_5, is a true oxide; the others, I_2O_4 and I_4O_9, appear to be salt-like iodates. The first is prepared by oxidizing the element with fuming HNO_3 or N_2O_5 or by thermal dehydration of iodic acid at about 200°C. Iodine tetroxide, I_2O_4, is formed as a crystalline material when iodine and concentrated H_2SO_4 are warmed and then permitted to stand at room temperature for several days (227). While the substance obtained by careful washing of the oxidation product of I_2 in this solution is commonly represented as iodyl iodate, IO^+IO^{3-}, there are no structural data or, for that matter, molecular weight data in support of this structural proposal.

The behavior of the compound I_4O_9 suggests that it is best considered as iodine(III) iodate, $I(IO_3)_3$. The compound is obtained by treating iodic acid with concentrated H_3PO_4; I_2 and O_2 are also products (228).

I_4O_9 may also be obtained from the reaction of ozone with iodine in either the gaseous state or in CCl_4 or other organic solvent (229).

B. STRUCTURE

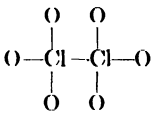
Direct evidence for the structures O_2F_2 and O_3F_2 is lacking, but the mode of decomposition of the former, kinetically unimolecular, suggests an



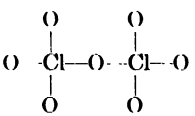
structure rather than a F—O—O—F arrangement. For oxygen difluoride the spectroscopic (230) and electron diffraction (231) data indicate a bent model having an O—F distance of 1.418 A. and an F—O—F angle of 103.2 degrees.

Electron diffraction data (232–234) and infrared information (235,236) are available for Cl_2O and ClO_2. In addition, the microwave spectrum for Cl_2O has been reported (237). For Cl_2O the measured Cl- -O distance is 1.70 ± 0.02 A., and the Cl—O—Cl angle is 110.8 ± 1 degrees; the corresponding values for ClO_2 are 1.49 ± 0.01 A. and 116.5 ± 2.5 degrees (233). The extreme shortness of the Cl—O bond in ClO_2 argues for considerable double bond character, a

suggestion supported by infrared data (235). The importance of polar contributions to the over-all structure of ClO_2 is indicated by the unusually large dipole moment of 1.70, a much higher value than that expected from the electronegativity difference of O and Cl. The ionicity of the Cl_2O molecule corresponds to a 25% contribution of each of the possible Cl^+OCl^- structures (237). Specific information for the other two chlorine oxides is not available; however, the change from diamagnetism to a small paramagnetism when solid Cl_2O_6 melts or is placed in aqueous solution suggests the breaking of Cl:Cl bond to give the odd electron ClO_3 species (238). A reasonable structure might then be an ethane-like arrangement:



The thermal decomposition of Cl_2O_7, a homogeneous, unimolecular reaction, is interpreted in terms of the primary products ClO_3 and ClO_4; a structure



is indicated. The bond energy of the central Cl—O linkage has been estimated as 48 kcal. (239).

The thermal instability of the bromine oxides has been an obstacle to collection of structural data; it is not unreasonable, however, to expect molecular shapes similar to those of the analogous chlorine compounds.

There is also a dearth of structural information on the iodine oxides (see page 68). The molal susceptibility of I_2O_4 in the solid state has been measured, and the diamagnetic nature observed contradicts the presence of IO_2 units in the structure; the assumption of $IO^+IO_3^-$ would agree with this result (240).

C. GENERAL PROPERTIES

In Table X are listed some physical properties of these compounds.

Gaseous OF_2 is slightly soluble, with decomposition, in water, acids, and alkalies. The hydrolysis reaction is slow at moderate temperatures, but becomes explosive at steam temperature. Although

possessing strong oxidizing properties, OF_2 requires a fairly high activation energy for decomposition or reaction; this explains its nonreactivity with H_2, CH_4, or CO unless sparked. These oxidizing properties have suggested its use in liquid form as a propellant component; in this respect it is somewhat more expensive than liquid O_2, ozone, or N_2O_4, as well as posing special handling problems (241).

Endothermic ozone fluoride is a strong oxidizing agent and undergoes quantitative decomposition to O_2 and O_2F_2 at about −158°C. Gaseous fluorine, activated by an electrical discharge, also converts

TABLE X
Physical Properties of Halogen Oxides

	Melting point, °C.	Boiling point, °C.	$\Delta H_{vap.}$, kcal./mole	ΔH_{form}, kcal./mole	Density, g./ml.
OF	(−224?)	(−185?)			
O_3F_2	−164	− 57	4.57	4.7	1.734 (−156°C.)
O_3F_2	−190	−157		6.2	1.80 (−190°C.)
OF_2	−224	−145	2.65	7.6	1.66 (−173°C.)
Cl_2O	−116	2	6.20	18.3	
ClO_2	− 59	11	6.52	23.5	1.64 (0°C.)
Cl_2O_6	3 5	~203	9.50		2.02 (3.5°C.)
Cl_2O_7	− 91.5	80	8.29	63.4	1.86 (0°C.)
Br_2O		d. > − 40			
Br_3O_8		d. > − 80			
BrO_2		d. > − 40		12.5	
BrO_3		d. > − 70			
I_2O_5		stable to 300			
I_4O_9		d. > 75			
I_2O_4		d. > 85			

O_3F_2 to O_2F_2. Liquid O_3F_2, at −183°C., reacts vigorously with solid anhydrous NH_3, liquid methane, solid hydrazine, red phosphorus, sulfur, charcoal, bromine, and iodine. Solid ethyl alcohol did not react at this temperature, but exploded when the mixture was warmed (210).

Above the boiling point of O_2F_2, −57°C., the red liquid undergoes rapid decomposition to O_2 and F_2. This reaction has been interpreted as leading to a compound OF (209,242), and, although subsequent investigation (243,244) tended to rule out this species, recent

electron impact studies on OF_2 have revived the opinion that it is stable, if only for a transitory period, during the exothermic decomposition to O_2 and F_2 (245,246).

Both chlorine monoxide and chlorine dioxide are extremely reactive materials toward even mild reducing agents. Dissolved in water Cl_2O produces hypochlorous acid, while ClO_2 in water or bases disproportionates to give chlorite and chlorate mixtures. The stability of either compound is very limited; Cl_2O may explode at or above its boiling point or on exposure to a strong light source. Pure ClO_2 may detonate spontaneously in the gas phase, and mixtures with air are unsafe when the ClO_2 partial pressure exceeds 30 mm. (217). In CCl_4 solution the rate of decomposition is slow; storage of the substance in this solution maintained in the dark is thus possible for short periods. The photochemical and thermal dissociations of these two chlorine oxides have been extensively studied and mechanisms, requiring the existence of a radical ClO, devised to explain the observed rates and products (247).

The observed behavior on mixing Cl_2O_6, the least volatile of the chlorine oxides, with water is varied; with gaseous H_2O crystals of the perchloric acid monohydrate may be obtained, but violent reaction results with liquid water. The thermal decomposition of Cl_2O_6 suggests that initial formation of ClO_3 is followed by reaction to ClO_2 and O_2, ClO_2 and ClO_4, or Cl_2 and O_2; the activation energy for each being about 12 kcal./mole. The ClO_4 is invoked as an intermediate species to explain the observed formation of Cl_2O_7. If fluorine is present in the decomposition mixture, much of the ClO_2 forms ClO_2F. At higher temperature ClO_2 tends to decompose more rapidly, and hence the Cl_2/ClO_2F ratio in the products increases (248). The reaction of Cl_2O_6 with acid anhydrides or acid chlorides yields metal perchlorates or oxyperchlorates (249).

Chlorine heptoxide, Cl_2O_7, is less reactive than ClO_2 and Cl_2O, but is still very thermal and shock sensitive. As previously noted, the decomposition intermediates are ClO_3 and ClO_4 which immediately undergo further reaction to simpler molecules. ClO_4 is not believed to be capable of more than transitory existence (250).

As indicated in Table X, all the bromine oxides are very unstable, and decomposition begins at low temperatures and proceeds to the elements, Br_2 and O_2. Stabilized in cold CCl_4 bromine monoxide reacts with alkalies to give hypobromite (251).

Bromine dioxide is capable of oxidizing iodide to iodine and yields bromide and bromate on alkaline hydrolysis. The reaction of Br_3O_8 with water apparently produces HBr, $HBrO_3$, and oxygen (225). Since BrO_3, with small amounts of BrO_2 impurity, can produce a similar group of hydrolysis products, there is further reason for uncertainty regarding the true existence of Br_3O_8. At $-40°C$. BrO_2 forms a solid complex with nitrogen dioxide, $BrO_2 \cdot 3NO_2$ (252). Similar compounds with CO, SO_2, NH_3, and SeO_2 could not be prepared, the BrO_2 acting as a strong oxidizing agent in each case. The complex was also prepared from a mixture of O_2, Br_2, and N_2 at low pressure in a glow discharge at $-195°C$. Attempts to prepare similar complexes using O_2, N_2, and Cl_2, or O_2, N_2 and I_2, were unsuccessful.

The anhydride of iodic acid, I_2O_5, is a strong oxidizing agent capable of oxidizing CO (253), H_2S, and NO (254), but does not react with $ClNO_2$ (68). Bromine trifluoride reacted with I_2O_5 yields IF_5, Br_2, and O_2 (255). IF_5 and I_2O_5 react to give a mixture of oxyfluorides of iodine, IOF_3 and IO_2F (256).

The difficulty in characterizing iodine tetroxide has already been noted; molecular weight data have not been obtained because of the compound's failure to dissolve in a suitable solvent and lack of volatility. The assumption of $IO^+IO_3^-$ as ions in the structure would imply relatively high solubility in H_2O; the substance is actually only very slowly soluble even in basic solutions, however, the products being I^- and IO_3^- ions.

Unlike iodine tetroxide, I_4O_9 is very hygroscopic. On reaction with water HIO_3 and HI can form and then further react to yield iodine. This behavior is consistent with the formulation of the compound as iodine(III) iodate.

VIII. Sulfur Halides

Binary sulfur-halogen compounds are limited to those of the three lighter halogens; claims for sulfur iodides are probably incorrect and involve only solid solutions of sulfur and iodine.

The well-characterized fluorides of sulfur are three in number, SF_4, SF_6, and S_2F_{10}. A lower fluoride, S_2F_2, (257,258), although accepted for many years, has not yet been satisfactorily characterized. Examination of the infrared spectrum (259) of what was believed to be S_2F_2 suggests that this material was improperly identified because

of preparative difficulties (260) and is actually just thionyl fluoride, SOF_2. Further, a reported detection (261) of S_2F_2 and the difluoride, SF_2, in the electrical discharge decomposition products of SF_6 has subsequently been withdrawn (262). The analytical data (263) supporting the compound are probably faulty. Re-examination of the preparation, purification, and properties of S_2F_2, and of SF_2, is thus in order.

A. PREPARATION

Of the many procedures suggested for the preparation of SF_4, the two most useful appear to be direct synthesis at −75°C. under very dry conditions (264) and the reaction of SCl_2 with NaF suspension in acetonitrile at 70–80°C. (265,426). One distillation in the latter procedure gives SF_4 of greater than 90% purity.

The very stable SF_6 is the principal product of any direct fluorination of sulfur at other than very low temperatures (266). For the preparation of the very toxic S_2F_{10} the nonclassified literature lists only the tedious procedure of separation of tiny amounts of the substance from the products of direct fluorination of sulfur at ordinary temperatures (267).

The monochloride, S_2Cl_2, and dichloride, SCl_2, of sulfur are both products of the reaction between sulfur and chlorine (268). They also result from the interaction of H_2S and chlorine (269). The substance S_3Cl_2 has been reported as a decomposition product of S_2Cl_2 (270). Reaction of hydrogen polysulfide, H_2S_n, with SCl_2 or S_2Cl_2 yields several chlorosulfanes, S_3Cl_2, S_4Cl_2, and S_5Cl_2 (271), the compositions of which were confirmed by cryoscopic determination of molecular weights and Raman spectra. Other chlorosulfanes of much higher S/Cl ratio are formed by S_2Cl_2 and H_2 using a hot-cold tube method (272). Sulfur tetrachloride, prepared by chlorinating S, S_2Cl_2, or SCl_2 below −30°C., is unstable and decomposes at its melting point, −30°C. The red liquid resulting from the fusion of the yellow solid SCl_4 has been shown to be a mixture of SCl_2 and Cl_2 (273,274).

Only one simple bromide, S_2Br_2, is recognized. This is obtained by heating Br_2 with excess sulfur in a sealed tube (275). Purification is accomplished by distillation under reduced pressure. A series of bromosulfanes, analagous to the chlorosulfanes, may be prepared by the action of HBr on the corresponding S_nCl_2 or of H_2S_n on S_2Br_2 (276).

The only known mixed halide of sulfur, SF_5Cl, results from the reaction of Cl_2 and S_2F_{10} at elevated temperature (277), or from the fluorination of SCl_2 at $-10°C$. (427).

B. STRUCTURE

Sulfur tetrafluoride has been examined using infrared, Raman (278), and NMR (279,280) spectroscopic techniques and clearly possesses irregular tetrahedral symmetry, C_{2v}. The ten valence electrons can be regarded as hybridized in an sp^3d manner to give a trigonal bipyramid configuration to the molecule with the unshared pair of electrons being present in the equatorial plane of the bipyramid. The NMR spectrum for the liquid at room temperature shows rapid exchange of fluorine atoms, probably by a fluorine bridge mechanism, with an activation energy of 4.5 ± 0.8 kcal./mole (280).

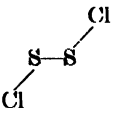
For SF_6 the regular octahedral structure, based on a sp^3d^2 hybridization of sulfur orbitals, is supported by all structural techniques. Halogen exchange studies of fluorine atoms between SF_6 and gaseous HF indicate a small degree of ionicity of the S—F bond (281).

The most reasonable structure for the S_2F_{10} molecule consists of two sulfur atoms joined by a covalent bond with each sulfur surrounded by five fluorine atoms, all bond angles being 90 degrees. This structure is confirmed by electron diffraction (282). The length of the S—S bond, compared to the covalent sum of 2.08, suggests the free rotation model makes an important contribution to the overall structure. The equivalence of the selection rules for both staggered (D_{4d}) and eclipsed (D_{4h}) molecules, as well as for the molecule having free rotation, prevents the determination of this structural detail from vibrational studies (283,284). Neither SF_6 nor S_2F_{10} possesses any dipole moment (285).

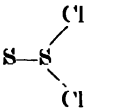
TABLE XI
Bond Distances, Bond Angles, and Dipole Moments for Sulfur Halides

	S—X, A.	S—S, A.	X—S—X angle, deg.	X—S—S angle, deg.	Dipole moment, D.
SF_6	1.58 ± 0.03		90		0
S_2F_{10}	1.56	2.21	90	90	0
S_2Cl_2	1.99 ± 0.03	2.05 ± 0.03		103	1.0
SCl_2	2.02		100.3		0.6

According to electron diffraction results (286) S_2Cl_2 is a chain structure with a chlorine attached to each sulfur atom, the Cl—S—S angle being 103 degrees. Infrared examination (287) gives results in accord with this arrangement and, together with the diffraction data, suggests a structure of C_2 symmetry and excludes the *cis* (C_{2v}) or *trans* (C_{2h}) configurations. An internal rotation barrier of about 8 kcal./mole has been suggested based upon Raman observations (288), but other examinations of Raman spectra fail to reveal the torsional fundamental on which this is based (289). The appearance at −170°C. of previously absent Raman lines has been interpreted as resulting from a fundamental change in structure from the



configuration to (290)



Raman spectra of SCl_2 indicate the molecule to be bent as might be expected (291). Infrared (292) and electron diffraction (286) are in agreement with this structure assignment.

The chain structures assumed for the halosulfanes are supported by observations on the molar volume, molar refraction, and parachor (293). For S_nCl_2, with $n = 1, 2, 3$, and 4, approximately constant increments in these properties are observed through the series.

C. GENERAL PROPERTIES

Physical properties of these halides are listed in Table XII. Sulfur tetrafluoride is a good fluorinating agent and has found specific application in the replacement of carbonyl oxygen with fluorine in carboxylic acids, aldehydes, ketones, and quinones (265,428).

The reaction of SF_4 with compounds containing carbon-nitrogen multiple bonds yields organoiminosulfur difluorides, a previously unknown compound type (429). The SF_4 molecule, soluble without reaction in CCl_4, toluene, cyclohexane, and other organic solvents (280), is easily hydrolyzed to SOF_2 and slowly to SO_2 and HF. The

TABLE XII
Physical Properties of Sulfur Halides

	Melting point, °C.	Boiling point, °C.	ΔH_{vap}, kcal./mole	ΔH_{form}, kcal./mole	Density, g./ml.
SF_4	−121	− 40.4	6.32	−172	1.919 (−73°C.)
SF_6	− 51	subl. − 65	4.08	−262	2.51 (s, m.p.)
S_2F_{10}	− 55	29	6.15	−461	2.08 (0°C.)
S_2Cl_2	− 80	138	8.61	− 14.3	
SCl_2	− 78	d. 59		− 12.0	
SCl_4		d. − 31		− 13.7	
S_2Br_2	− 46	d. 90		− 4.0	

slow room temperature reaction with glass produces SiF_4 and SOF_2. With fluorine SF_4 is converted to SF_6 at room temperature and above. No reaction with Cl_2, O_2, or liquid BrF_3 was observed (295).

With BF_3 an addition compound is formed, but BCl_3 is fluorinated by SF_4 (295). The products of this latter reaction are dependent upon the SF_4/BCl_3 reactant ratio. If SF_4 is in excess:

$$7SF_4 + 4BCl_3 = 4SF_4 \cdot BF_3 + 3SCl_2 + 3Cl_2$$

If BCl_3 is in excess:

$$3SF_4 + 8BCl_3 = 3SCl_2 + 3Cl_2 + 4BF_2Cl + 4BFCl_2$$

A small amount of SF_4BF_3 is formed in the second reaction also. The failure of SF_4 to form an adduct with BCl_3, considering that BCl_3 is a stronger Lewis acid than BF_3 (294), suggests that SF_4 has little tendency to behave as a Lewis base by donating its unshared electron pair, and, together with other reasoning (295), indicates the $SF_4 \cdot BF_3$ adduct is best represented by an ionic formulation, $SF_3^+BF_4^-$, rather than the donor-acceptor type structure, $F_4S \rightarrow BF_3$. Infrared evidence in support of the ionic structure has been offered (436). However, an intermediate structure with F bridges is also possible. The great fluoride acceptor strength of AsF_5, and SbF_5, each of which forms a 1:1 complex with SF_4 (296,436), suggests that these, too, are ionic substances.

Sulfur tetrafluoride reduces IrF_6 and forms, when SF_4 is in excess, a complex of composition $SF_4 \cdot IrF_5$, the structure of which has not been determined. Iridium tetrafluoride is also reduced to IrF_3 by the action of SF_4 at 350–400°C. (414).

The behavior of SF_4 as a Lewis acid is demonstrated by the formation of adducts of SF_4 and various tertiary amines. The NMR spectrum for the adduct with pyridine suggests an octahedral structure with the fluorine atoms in the equatorial plane and the pyridine molecule and sulfur's unshared electron pair above and below the plane (415).

The outstanding characteristic of SF_6 is its extreme nonreactivity. Thus, no reaction with water, hydrogen, fused alkali, ammonia, oxygen, or most metals at red heat is observed, although boiling sodium will decompose the molecule (297). Since thermodynamic calculation shows the hydrolysis reaction of SF_6 to SO_3 and HF to be decidedly exothermic (298), the failure of hydrolysis to occur must be related to a very high energy of activation for the reaction. In high intensity electrical fields SF_6 is relatively inert, hence its use as an insulating gas in electrical apparatus. Only under extreme conditions and after long use are decomposition products, SF_4, SOF_2, etc., observed (261).

Sulfur dichloride is somewhat unstable and slowly decomposes according to:

$$2SCl_2 = S_2Cl_2 + Cl_2$$

For this decomposition the equilibrium constant has been determined as 0.013 at room temperature (270). Ultraviolet spectra study of the rate of this decomposition using freshly distilled SCl_2 showed the decomposition to proceed to about one-fourth of its equilibrium value in one hour (299).

Although the hydrolysis reactions of these two lower chlorides of sulfur are complicated by their decomposition tendencies and the attending secondary hydrolysis reactions, the principal intermediates in the hydrolysis of S_2Cl_2 and SCl_2 appear to be thiosulfurous acid, $S_2(OH)_2$, and sulfoxylic acid, $S(OH)_2$, respectively (300). The course of succeeding reaction is largely determined by pH. In the basic hydrolysis of SCl_2 the end product is chiefly thiosulfate; an acidic hydrolysis yields mainly pentathionate (301). S_2Cl_2 gives principally polythionic acids on hydrolysis (302). The heat of hydrolysis of S_2Cl_2 has been reported as 35 kcal./mole at 24.88°C. (303).

Studies of the hydrolysis of S_2Cl_2 and SCl_2 in the presence of sulfurous and thiosulfuric acids have been carried out, and the results are in agreement with the $S(OH)_2$ and $S_2(OH)_2$ intermediates pro-

posed (302). Thus, the observed products of the over-all reaction for SCl_2 could result from the "neutralization" of the $S(OH)_2$ intermediate:

$$S(OH)_2 + 2H_2SO_3 = S(SO_3H)_2 + 2H_2O$$
Trithionic acid

and
$$S(OH)_2 + 2H_2SO_3 = S(S_2O_3H)_2 + 2H_2O$$
Pentathionic acid

Similar reactions are suggested for S_2Cl_2.

It has been suggested that the charge distribution in the sulfur chlorides is such that SCl_2 should be considered a dichlorine sulfide. It is reasoned that hydrolysis produces H_2S and HOCl; subsequent oxidation of H_2S by HOCl gives the ultimate products (304). In refutation of this suggestion, however, the similarity of the reaction of SCl_2 to $S(NR_2)_2$ and $S(OEt)_2$ has been pointed out. Further, experiments with pure H_2S and HOCl failed to yield any trace of the observed products of the hydrolysis of SCl_2 (301).

The reaction of S_2Cl_2 with a wide variety of oxides has been examined (305). Chlorides and/or sulfides of the metals, combined with SO_2 and S, may result; in a few instances sulfates formed. The oxides of Ba, Cd, Ag, Hg, and Pb reacted violently at room temperature with evolution of much heat, but temperatures of 100–120°C. were required to obtain good reaction with those of Cu, Mg, Ca, Zn, and Sr. Al_2O_3 and Pb_3O_4 reacted very slightly even after prolonged heating.

The very slow room temperature exchange of sulfur between S_8 and S_2Cl_2 becomes measureable at 100°C. (306). The rate is proportional to S_8 concentration; the rate-determining step

$$S_8 = S_6 + S_2$$

is followed by the rapid reversible reaction:

$$S_2 + S_2Cl_4 = 2S_2Cl_2$$

The decomposition of SCl_4 to SCl_2 and Cl_2 at its melting point hinders investigation of its chemical properties. Nevertheless, a number of complexes have been reported involving SCl_4: $SCl_4 \cdot BCl_3$ (m.p. −23°C.) (307); $FeCl_3 \cdot 2SCl_4$ (308); and $SbCl_5 \cdot SCl_4$ (subl. 125°C.), $SCl_4 \cdot 2AsF_3$, $SCl_4 \cdot AsCl_3$, $2SCl_4 \cdot SnCl_4$, and $SCl_4 \cdot TiCl_4$ (309). Knowl-

edge of the structure of these complexes would be of interest in light of previous comments on SF_4 complexes. It has been suggested that solid SCl_4 is composed of SCl_3^+ and Cl^- ions (310).

Sulfur monochloride and sulfur dichloride react with ammonia to give cyclic S_4N_4 (311). Condensation of S_2Cl_2 or SCl_2 with $C_2H_5NH_2$ gives ring compounds. A very recent study of the reaction of SCl_2 with methylamine in hexane solution has shown the formation of a polymeric material of composition $(CH_3NS)_n$, a crystalline $(CH_3NS)_4$, and two crystalline isomers of formula $(CH_3N)_3S_5$ (299). Structural examination of these materials by X-ray and NMR indicates a chain structure for the polymer and ring structures for the crystalline products.

The chloro- and bromosulfanes are quite susceptible to decomposition and/or hydrolysis; however, S_3Cl_2 can be maintained at 0°C. for several weeks with no evidence of decomposition if moisture is rigorously excluded (312). These halosulfanes, as shown by their molar volume, molar refraction, and Raman spectra, are long chain structures similar to the alkanes; the greater reactivity of the —S- S—S ·· structure relative to the —C—C- -C— arrangement may be due to the exposed nature of the sulfur atom as compared to the H atom protection afforded the carbon atoms.

IX. Sulfur Oxyhalides

The oxyhalides of sulfur include three principal classes; thionyl or sulfur(IV) oxyhalide, SOX_2; sulfuryl or sulfur(VI) oxyhalides, SO_2X_2; and pyrosulfuryl halides, $S_2O_5X_2$. In addition there are a number of sulfur oxyfluorides of more complex composition.

A. PREPARATION

1. Thionyl Compounds

The colorless liquid $SOCl_2$ is prepared in a variety of ways, the most important of which are the reactions of PCl_5 with SO_2 and of Cl_2O with sulfur. A recent preparation of $SOCl_2$ is the charcoal-catalyzed air oxidation of S_2Cl_2 (313). The accompanying sulfuryl choride impurity, SO_2Cl_2, is removed by refluxing with sulfur and redistilling (314).

The other thionyl compounds are most easily derived from the chloride. Thionyl fluoride, for example, is prepared by catalytic

fluorination (SbF_3 and $SbCl_5$) of $SOCl_2$ (315); fractional distillation separates the SOF_2 from the mixed thionyl chlorofluoride, SOClF, also formed. The latter compound also results from treatment of $SOCl_2$ with IF_5 (316). Direct reaction of SO_2 with zinc fluoride also gives SOF_2. Thionyl bromide is obtained from $SOCl_2$ by treatment with HBr gas at 0°C. (317), or by reaction of $SOCl_2$ with KBr dissolved in liquid SO_2 (318). The bromofluoride may be prepared in like manner to SOClF by treatment of $SOBr_2$ with IF_5 (316). Attempts to prepare SOI_2 in stable form have been unsuccessful (319,320).

2. *Sulfuryl Compounds*

The fluoride is obtained most conveniently through the thermal decomposition of barium fluorosulfonate (321). It is also formed in the direct reaction of SO_2 and F_2, by the fluorination of SO_2Cl_2 with KF or NaF at 400°C. (322), and by the reaction at elevated temperature of fluorine and sodium sulfate or sodium sulfite (323). Sulfuryl chloride is prepared by the catalyzed reaction of SO_2 and Cl_2 (324). The mixed halide, SO_2ClF, is obtained by subjecting SO_2Cl_2 to a Swarts reaction (SbF_3 + $SbCl_5$) (325) or by treating the SO_2Cl_2 with other fluorinating agents such as AgF_2 (326), IF_5 (327), CoF_3, or MnF_3 (328).

Sulfuryl bromide and iodide are not known, but a mixed bromofluoride, SO_2BrF, has been obtained from the reaction of SO_2 with a mixture of BrF_3 and Br_2 (316).

3. *Pyrosulfuryl Compounds*

Pyrosulfuryl chloride, $S_2O_5Cl_2$, is readily prepared from SO_3 and CCl_4, or S_2Cl_2 may be substituted for the CCl_4. The interaction of P_2O_5 and chlorosulfonic acid also gives the compound.

The corresponding fluoride, $S_2O_5F_2$, results from the treatment of refluxing SO_3 with SbF_5 (329). Recently it has been obtained by treating CaF_2 at 100–300°C. with excess SO_3 followed by addition of 70–98% H_2SO_4 (330). A suggested sequence of reactions is:

$$CaF_2 \xrightarrow{SO_3} Ca(S_2O_6F)_2 \xrightarrow{H_2O\ (\text{in } H_2SO_4)} CaSO_4 + H_2SO_4 + S_2O_5F_2$$

The mixed chlorofluoride is prepared by reacting $S_2O_5Cl_2$ with AgF at 80–90° for 2 hours; some sulfuryl chlorofluoride also may be formed.

No success has been experienced in the preparation of this mixed compound using AgF, AgF with HF, or AgF_2 with $S_2O_5Cl_2$ (331).

4. Other Oxyfluorides

The passage of a stream of SOF_2 together with elemental fluorine over AgF_2 at 200°C. results in the formation of thionyl tetrafluoride, SOF_4, in small yields and pentafluorosulfur hypofluorite, SF_5OF, in larger amounts (333). SOF_4 is more commonly prepared by the reaction of SOF_2 and F_2 on a Pt surface at 150°C. (332). SO_2F_2 fails to react further with F_2 under catalytic influence, but SO_2 may be fluorinated to SF_5OF (333). Fluorine fluosulfonate, SO_3F_2, is prepared by the AgF_2-catalyzed fluorination of SO_3 at 220°C. (334). A small by-product of this reaction is $S_2O_6F_2$, but at lower temperatures, about 100°C., this latter substance is obtained exclusively (335). The properties of this compound of composition $S_2O_6F_2$ differ considerably from those of the compound having the same empirical composition obtained by passing an electrical discharge through a 1:1 mixture of SOF_2 and O_2 at low temperature (336). The electrical discharge technique also yields $S_2O_5F_4$ in addition to thionyl and sulfuryl fluoride.

Trisulfuryl fluoride, $S_3O_8F_2$, is obtained when a boron trifluoride–saturated solution of sulfur trioxide is treated with 70% H_2SO_4 (337). The addition of SO_2 to $S_2O_6F_2$ has also been used successfully for the preparation of this substance (338). The corresponding chloride, $S_3O_8Cl_2$, has been prepared by the reaction of CCl_4 with SO_3 at 80°C. (339,340).

In the room temperature fluorination of sulfur small traces of O_2 may act to form the compound $S_2O_2F_{10}$ in small yields (341).

B. STRUCTURE

Electron diffraction structural determinations for SOF_2 (342), $SOCl_2$ (286,342), and $SOBr_2$ (343) show these molecules to be pyramidal with S at the apex. This symmetry, C_s, is supported by infrared (344), Raman (345), and microwave (346) data for SOF_2, and by Raman (347,348) and infrared for $SOCl_2$ (349).

The sulfuryl fluoride and chloride molecules possess a somewhat irregular tetrahedral structure, symmetry C_{2v}. Electron diffraction (286,350) and infrared (349,351) data are available for both SO_2F_2

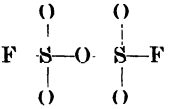
TABLE XIII

Bond Distances, Bond Angles, and Dipole Moments for Sulfur Oxyhalides

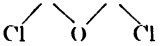
	S—X, A.	S—O, A.	X—S—X angle, deg.	O—S—X angle, deg.	Dipole moment, D.
SOF_2	1.585 ± 0.001	1.412 ± 0.001	92.8 ± 0 1	106.8 ± 0.1	1.618
$SOCl_2$	2.07 ± 0.03	1.45 ± 0.02	114 ± 2	106 ± 1	1.60
$SOBr_2$	2.27 ± 0.02	1.45 (assigned)	96 ± 2		1.47
SO_2F_2	1.530 ± 0.003	1.405 ± 0.003	96.1 ± 0 1	(O—S—O: 124 0 ± 0.2)	1 10
SO_2Cl_2	1.99 ± 0.02	1.43 ± 0 02	111 ± 2	(O—S—O: 119.8 ± 0.5)	1 795
$S_2O_2F_{10}$	1.56 ± 0.02	1 66 ± 0 05			
		(O—O: 1 47 ± 0.03)		(S—O—O: 105 ± 3)	

and SO_2Cl_2. Raman (345) and microwave (352,361) data have been given for the fluoride. A peroxide-type structure is assigned to $S_2O_2F_{10}$ on the basis of electron diffraction results; an angle of 107 ± 5 degrees between the planes specified by $S_1O_1O_2$ and $O_1O_2S_2$ is indicated (341). Table XIII summarizes known structural parameters.

Interatomic distances and bond angles for the other oxyhalides have not been reported, but the general atomic arrangement within the molecule has been determined for some. The infrared (355) and NMR spectra (330) of $S_2O_5F_2$ are in accord with the structure

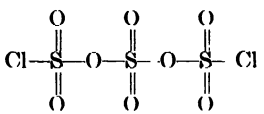


for the substance, although the S—O—S angle is not specified. Pyrosulfuryl chloride has C_{2v} symmetry based upon two symmetry planes at right angles to each other, and a two-fold axis (353). A structure



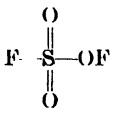
in which each S atom is surrounded tetrahedrally by 1 chlorine and 3 oxygen atoms is proposed. Although the rotation of the $-SO_2Cl$ groups around the central S—O bond is probably hindered, only one molecular species is observed by Raman examinations; the concentration of the other structural form must be very small.

Chemical evidence (340) indicates the structure of $S_3O_8Cl_2$ to be somewhat similar to the preceding compound; thus:

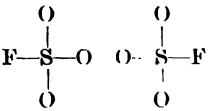


The configurations of SO_3F_2 (334), SOF_4 (333), SOF_6 (333), and $S_2O_6F_2$ (335) have been inferred from chemical properties and infrared examination. Further support for these structures has been provided by observation of the F^{19} magnetic resonance spectra (354). The presence of two equal absorption peaks in the fluorine fluoro-

sulfonate NMR spectrum supports the assigned hypofluorite arrangement



The single F^{19} resonance peak for SOF_4 indicates equivalent environment for the fluorine atom and a structure $F_4S{=}O$. The intensity ratio 5:1 for the two resonances of SOF_6 is best interpreted in terms of an octahedral arrangement of 5 fluorine atoms and a hypofluorite group around a central sulfur atom. Similar considerations suggest a peroxide structure



for peroxydisulfuryl fluoride (335).

C. GENERAL PROPERTIES

Increasing molecular weight in the thionyl halide series is accompanied by decreasing thermal stability. While SOF_2 is very stable, $SOCl_2$ begins to decompose above 150°C., and $SOBr_2$ is decomposed well below its estimated boiling point, distillation under reduced pressure being required in the purification of the substance (318). The chlorofluoride is intermediate to $SOCl_2$ and SOF_2 in its stability and tends to decompose slowly to the difluoride and dichloride at elevated temperatures (315).

A similar trend is in evidence with respect to the hydrolysis behavior of these compounds. Thionyl fluoride reacts slowly with water to give SO_2 and HF, but rapidly with alkali hydroxide solutions. The readiness with which $SOCl_2$ reacts with water is responsible for its application as a dehydrating agent in the preparation of numerous anhydrous metal halides. Thus, $MgCl_2$, $SnCl_2$, $SnCl_4$, $CuCl_2$, $FeCl_3$, $CoCl_2$, and $NiCl_2$ are easily obtained from their hydrates by refluxing with $SOCl_2$ (356,357).

The pattern of thermal stability and hydrolysis for the sulfuryl halides is similar. SO_2F_2 is extremely stable and undergoes few reactions at oridnary temperature (it is not decomposed by hot water)

TABLE XIV
Physical Properties of Sulfur Oxyhalides

	Melting point, °C.	Boiling point, °C.	ΔH_{vap}, kcal./mole	ΔH_{form}, kcal./mole	Density, g./ml.
SOF_2	−110	− 43.8	5.18		3.0
$SOCl_2$	−104.5	78 8	7.48	− 58.5	1.656 (14.5°C.)
$SOBr_2$	− 49.5	d. 59	10.40		2.67 (25°C.)
SOClF	−139.5	12.2	5.90		1 576 (0°C.)
SO_2F_2	−136.7	− 55.4	4.79		
SO_2Cl_2	− 54.1	69.1	6.70	− 93 3	
SO_2ClF	−124.7	7.1	6.34		
SO_2BrF	− 86 5	40			2.17 (0°C.)
$S_2O_5Cl_2$	− 37.5	152.5	13.2	−166.6	
$S_2O_5F_2$	− 48	51	7 6		1 75 (0°C.)
S_2O_5ClF	− 65	100 1	8 1		1 797 (20°C.)
SOF_4	− 99.6	− 49	5 1		1 82 (−49°C.)
SOF_6	− 86 0	- 35 1	5 2		2.04 (−73°C.)
SO_3F_2	−158 5	− 31 3	5 4		1 78 (−74°C.)
$S_2O_6F_2$	− 55	40[a]; 67 1[b]			
$S_2O_5F_4$	− 95	d. − 20			
$S_3O_8F_2$	− 67.2	120	8 6		1.83 (25°C.)
$S_3O_8Cl_2$	18.7	61 (3 mm.)	11.0		1.90 (20°C.)
$S_2O_2F_{10}$	− 95	49			1.82 (20°C.)

[a] Reference 336.
[b] Reference 335.

while SO_2Cl_2 vapor is partially decomposed to SO_2 and Cl_2 at 100°C. and is easily hydrolyzed to hydrochloric and sulfuric acids. Sulfuryl fluoride is reluctant to react as a fluorinating agent (neither it nor SO_2ClF will react with hydrocarbons, phenol, etc., even in the presence of a catalyst), but SO_2Cl_2 is an excellent chlorinating and/or sulfonating agent for organic compounds when heated or under catalytic influence (358). The mixed chlorofluoride is again intermediate to SO_2F_2 and SO_2Cl_2 in reactivity. Above 320°C. SO_2BrF decomposes to SO_2, SO_2F_2, and Br_2 (316).

The ability of $SOCl_2$ to transform metal oxides to chlorides or oxychlorides at elevated temperatures and pressure has been demonstrated (359). In addition to metathesis-type reactions these conversions may be accompanied by reduction

$$2UO_3 + 6SOCl_2 = 2UCl_5 + 5SO_2 + SO_2Cl_2$$

or by oxidation

$$3WO_2 + 7SOCl_2 = 3WOCl_4 + S_2Cl_2 + 5SO_2$$

Certain sulfates, $BaSO_4$, for example, also may be converted to chlorides by thionyl chloride (360).

Sulfuryl chloride is likewise effective in converting metallic oxides to chlorides and sulfates (362) and sulfides to chlorides (363). The solvent properties of liquid SO_2Cl_2 have been examined (364); $SbCl_5$ is the strongest acid in the system followed by $SbCl_3$, $AsCl_3$, $TiCl_4$, etc. The best bases are R_4NCl, PCl_5, $TeCl_4$ and C_5H_5N in that order.

Fluorine fluorosulfonate, a highly reactive oxidizing agent, reacts with cold alkali solutions according to:

$$SO_3F_2 + 2OH^- = SO_3F^- + F^- + H_2O + {}^1/_2O_2$$

Reaction of SO_3F_2 with KI solution liberates two equivalents of iodine for every mole of SO_3F_2 consumed:

$$SO_3F_2 + 2I^- = SO_3F^- + F^- + I_2$$

and suggests the presence of a hypofluorite group in the molecule (334). The reactions of fluorine fluorosulfonate with SO_2, SOF_2, and I_2 have also been studied (430).

The reactions of thionyl tetrafluoride and pentafluorosulfur hypofluorite with cold alkali solutions proceed as follows (333):

$$SOF_4 + 4OH^- = SO_3F^- + 2H_2O + 3F^-$$

and

$$SOF_6 + 6OH^- = {}^1/_2O_2 + 5F^- + 3H_2O + SO_3F^-$$

Both compounds liberate iodine from KI solution and form sulfuryl fluoride as one product in each case. The reaction of SOF_6 follows the stoichiometry:

$$SOF_6 + 2I^- + H_2O = SO_2F_2 + 2HF + I_2 + 2F^-$$

The reaction of SOF_4 with iodide solution is not entirely clear; iodine is first produced in substantial amount, but disappears within a few seconds to give a colorless acidic solution and gaseous SO_2F_2 (333). Complex formation between SOF_4 and BF_3, AsF_5, and SbF_5 has been observed (436).

Pyrosulfuryl fluoride is more stable toward hydrolysis than the chloride, but reacts with hot water or room temperature alkali solutions (329). The chloride behaves toward metals, including some of the less reactive ones such as Au and Pt, as a chlorinating agent.

The chemical properties of the second form of peroxydisulfuryl difluoride, $S_2O_6F_2$, have been studied (338). The substance reacts with SO_2 (see above), with NO to give nitrosyl fluorosulfonate (m.p. 156–157°C.), and with NO_2 to evolve O_2 and yield a 1:1 mole ratio of $NOSO_3F$ and nitryl fluorosulfonate, NO_2SO_3F. The reactions with the halogens are of interest; with fluorine at 200°C. in a nickel tube:

$$S_2O_6F_2 + F_2 = 2SO_3F_2$$

Bromine and iodine yield substances apparently containing halogen in a positive oxidation state:

$$\underset{\text{(excess)}}{Br_2} + 3S_2O_6F_2 = 2Br(SO_3F)_3 \quad \text{(m.p. 59°C.)}$$

$$\underset{\text{(excess)}}{Br_2} + S_2O_6F_2 = 2BrSO_3F \quad \text{(b.p. 120.5°C.)}$$

$$I_2 + 3S_2O_6F_2 = 2I(SO_3F)_3 \quad \text{(m.p. 32.2°C., dec. 114/3 mm.)}$$

No iodine compound corresponding to $Br(SO_3F)$ was found. Chlorine undergoes no reaction with $S_2O_6F_2$; it is suggested that the high dissociation energy of the Cl_2 molecule may be responsible for this lack of reactivity (338).

Trisulfuryl chloride, $S_3O_8Cl_2$, decomposes at 116°C. into $S_2O_5Cl_2$ and SO_3 (340). Its reaction with ammonia is via ammonolysis of the S—O—S linkage rather than through amide formation. Freshly distilled $S_3O_8Cl_2$ fumes in air and hydrolyses slowly in cold water. Trisulfuryl fluoride is somewhat more stable than $S_3O_8Cl_2$, decomposition being slow at its boiling point (337). Hydrolysis of the fluoride with aqueous KOH gives KSO_3F and H_2SO_4. Both $S_3O_8Cl_2$ and $S_3O_8F_2$ are insoluble in concentrated H_2SO_4.

Disulfur decafluorodioxide, $S_2O_2F_{10}$, is similar to S_2F_{10} in its physical and chemical behavior. Thus, it is resistant to acids and bases and undergoes no decomposition when stored in glass for long periods of time (341).

X. Halides and Oxyhalides of Selenium and Tellurium

A. PREPARATION

Monohalides are known only for selenium. The chloride (365) and bromide (366) are formed in the direct reaction of the halogen

with selenium and the more stable Se_2Cl_2 by reduction of $SeCl_4$ with PCl_3. The bromide is known only as a constituent of the condensation products of gaseous $SeBr_2$; in the vapor state and in CCl_4 it undergoes decomposition.

Of the dihalides, $SeCl_2$ (367) and $SeBr_2$ (366) exist only in the vapor state; condensation promotes decomposition, the extent of which is governed by the equilibrium (368):

$$2SeBr_2 = Se_2Br_2 + Br_2$$

$K = 0.0252$ for this reaction and is comparable to that reported for SCl_2 in the liquid phase without solvent (see SCl_2, page 77).

Tellurium dichloride is obtained by synthesis from the elements, by reduction of $TeCl_4$ with Te, and by treatment of molten Te with CF_2Cl_2 (369). It is moderately stable in the pure form regardless of aggregation state. Similar considerations apply to the other dihalide, $TeBr_2$ (370); reaction at 500°C. of molten Te with CF_3Br gives a mixture from which $TeBr_2$ can be separated by distillation (371).

All tetrahalides except the iodide of selenium have been prepared. Relatively impure samples of the vigorously reactive SeF_4 were first reported to result from fluorination of Se in a copper boat and later by reactions of AgF with $SeCl_4$ at 50°C. Recently, a direct synthesis using low temperature and a thin Se sublimate (similar to SF_4 synthesis) has given high yields of material easily purified by trap-to-trap distillation (372).

Regarding tellurium tetrafluoride it appears that early claims (373–375) of the compound's preparation are in error and that the products were actually a complex tellurium oxyfluoride and/or TeF_6. However, a time-consuming reduction of TeF_6 with finely powdered Te at elevated temperature has produced the crystalline material (376,377). A far simpler procedure has been recommended; TeO_2 is reacted directly with SeF_4 at 80° according to:

$$TeO_2 + 2SeF_4 = TeF_4 + 2SeOF_2$$

Volatile $SeOF_2$ and excess SeF_4 are removed by pumping to leave the solid TeF_4 (378).

The tetrachlorides of Se and Te may be prepared by the chlorination of the element using elementary Cl_2 or some other chlorinating agent (379,380).

Selenium tetrabromide has been shown to exist in the solid state, but is is fully dissociated in the gaseous state or when dissolved in nonpolar solvents such as CCl_4 (368).

A variety of procedures have been employed to prepare $TeBr_4$; besides direct synthesis the substance is obtained from the reaction of TeO_2 with HBr solutions, by oxidation of Te with HNO_3 in an HBr solution, and by treatment of Te^{IV} in HCl solution with KBr (381).

The only definitely proven iodide of S, Se, or Te is TeI_4 obtained by direct reaction of the elements, by reaction of $TeBr_4$ with ethyl iodide in a sealed tube at 100°C. or by sealed tube reaction of Te and cyanogen iodide (382).

Two mixed halides of tellurium(IV) have been reported. Evaporation of an ethereal solution of $TeBr_2$ and iodine gave red crystalline $TeBr_2I_2$ (371). Bromine also reacts with $TeCl_2$ to give the yellow powder $TeCl_2Br_2$ (369). Efforts to prepare this latter product by oxidation of $TeBr_2$ with Cl_2 gave only $TeCl_2$ and $TeCl_4$ (371).

The only hexavalent halides of Se and Te are, as in the case of sulfur, the fluorides. The stable end product of the reaction of fluorine and the element is, in each instance, the hexafluoride, MF_6 (375). Ditellurium decafluoride, Te_2F_{10}, is prepared in better than 20% yield by the fluorination of Te in the presence of CaF_2 (383). The yield has been more than doubled by mixing TeO_2, instead of CaF_2, with Te and diluting the F_2 stream with oxygen (384). The existence of Te_2F_{10} and S_2F_{10} suggests that careful examination of fluorination products of selenium might yield evidence for the corresponding selenium compound.

The well-defined oxyhalides of Se and Te are relatively few in number. Selenium oxychloride, $SeOCl_2$ results from the interaction of SeO_2 and $SeCl_4$ in CCl_4 solution. It is also prepared by forming an addition compound of SeO_2 and HCl and then dehydrating with concentrated H_2SO_4 and treating with Cl_2 (385). $SeOBr_2$ may also be prepared by the reaction of SeO_2 with $SeBr_4$.

The oxyfluoride, $SeOF_2$, is usually prepared by halogen exchange between $SeOCl_2$ and AgF or HgF_2 (386). It also is formed in the reaction of elementary F_2 (372) or ClF_3 (387) with SeO_2, and as a by-product of the conversion of TeO_2 to TeF_4 using SeF_4 (378) (see page 88).

Several other selenium oxyfluorides have been prepared recently. By warming a mixture of barium selenate and fluorosulfonic acid the volatile SeO_2F_2 is obtained in 92% yield (388). Pentafluoroselenium hypofluorite, F_5SeOF, and diselenium decafluorodioxide, $Se_2O_2F_{10}$, both compounds having sulfur analogues, have been prepared in small yields by treating SeO_2 or $SeOCl_2$ with elementary F_2 (389). There was also indication of an oxyfluoride containing 3 atoms of Se per molecule, possibly $Se_3O_2F_{14}$.

The increasing basicity of the group VIb elements with increasing atomic number is evident in the lack of oxyhalides of tellurium in oxidation state IV. However, the fluorination of a 1:1 ratio of Te and TeO_2 gives in small yields substances which have been tentatively identified as $Te_3F_{14}O_2$ and $Te_6F_{26}O_5$ (384).

B. STRUCTURE

Raman examination of liquid Se_2Cl_2 and Se_2Br_2 reveals that each has six fundamental vibrations in accord with the requirements of C_{2v} or C_2 symmetry (390). Electron diffraction study of $TeBr_2$ indicates a triangular structure (391); the value of the angle X—Te—X cited in previous work (392) is much too large. Tellium tetrachloride, in the vapor state, possesses a distorted trigonal bipyramid shape with an unshared pair of electrons occupying one of three equatorial positions; the molecular symmetry is therefore C_{2v} (393). In contrast, however, the Raman spectra of liquid and solid $TeCl_4$ and $SeCl_4$ suggest a strong structural similarity of these compounds with $SbCl_3$ and $AsCl_3$ (394). These chlorides of Te and Se are therefore represented as $TeCl_3^+Cl^-$ and $SeCl_3^+Cl^-$ in condensed aggregation states with Te and Se atoms at the apex of the pyramidal structure of the complex cations. This ionic formulation is supported by the large dipole moment (2.570) observed for $TeCl_4$ and its suggestion of a strongly polar Te - Cl bond (395,396). Crystallographic data are available for the orthorhombic TeI_4 (397). Raman examination (398) of SeF_4 supports C_{2v} symmetry in confirmation of the results obtained by electron diffraction (399) and NMR (280).

Conclusions from the infrared spectra of the hexafluorides concur with the expected regular octahedral structure, O_h, for SeF_6 (400) and TeF_6 (401). Analysis of the vibrational spectrum of Te_2F_{10} as determined by infrared and Raman indicates the substance to be isostructural with S_2F_{10} (284). The only oxyhalides for which infor-

mation is available are $SeOCl_2$ and $SeOF_2$. The gaseous molecule of the former is of the same configuration as $SOCl_2$ (342), and Raman examination of the latter was not conclusive with respect to molecular shape (402).

Table XV summarizes known molecular dimensions.

TABLE XV

Bond Distances, Bond Angles, and Dipole Moments of Se and Te Halides and Oxyhalides

	M—X, A.	X—M—X angle, deg.	Dipole moment, D.
$TeBr_2$	2.51 ± 0.02	98 ± 3	
$TeCl_2$	2.36 ± 0.03	(150-80?)	2.54
$TeCl_4$	2.33 ± 0.02	93 ± 3; 90-120	2 570
SeF_4	1.765 ± 0.025	120 ± 10; 104 5 ± 4 5	
SeF_6	1.70 ± 0.03	90	
TeF_6	1.84 ± 0.03	90	
$SeOCl_2$	~1.7 (M-O: 1.61)	~106 (X—M-O: ~114)	2.62

C. GENERAL PROPERTIES

The limited range of stability of the mono- and dihalides of selenium limits the information available concerning the chemical and physical behavior of these compounds. Thus, the monohalides decompose on warming the liquid substance; the dihalides are unstable in any but the vapor state.

Somewhat greater stability is found for the tellurium dihalides, although $TeCl_2$ (369) undergoes decomposition to Te and $TeCl_4$ in in Et_2O, Bu_2O, and dioxane, and the decomposition (371) of $TeBr_2$ to Te and $TeBr_4$ is catalyzed by traces of moisture. Reactions of F_2 and Cl_2 convert the dihalides to TeF_4 and TeF_6 and to $TeCl_4$, respectively. Bromine adds to $TeCl_2$ to give the mixed Te^{IV} compound and converts the dibromide to $TeBr_4$. In etheral solution I_2 and $TeBr_2$ form $TeBr_2I_2$, but no $TeCl_2I_2$ could be prepared. Ammonia forms a complex, $Te(NH_3)_2Br_2$, at room temperature, but at $-50°C$. the reaction with liquid NH_3 results in Te nitride, Te, and NH_4Br.

Pyridine accelerates the disproportionation of $TeCl_2$ and forms a complex with one of the products; Te and $(py)_2TeCl_4$ are obtained. With the mixed halides pyridine forms $(py)_2TeCl_2Br_2$ and $(py)_2TeBr_2I_2$. The latter, dissolved in hot concentrated HX, where X is Cl or Br, forms the orange solid $(C_5H_5NH)_2TeBr_2I_2X_2$. Further

TABLE XVI
Physical Properties of Se and Te Halides and Oxyhalides

	Melting point, °C.	Boiling point, °C.	$\Delta H_{sap.}$, kcal./mole	ΔH_{form}, kcal./mole	Density, g./ml.
Se_2Cl_2				− 20	
Se_2Br_2					
$SeCl_2$				− 10	
$SeBr_2$		d. 227			
$TeCl_2$	208	328			
$TeBr_2$	210	339			
SeF_4	− 9.5	106	11.2		2.75 (18°C.)
TeF_4	129.6		8.2		
$SeCl_4$		subl. 191		− 46.1	
$TeCl_4$	225	390	18.4	− 77.4	2.56 (232°C.)
$SeBr_4$	d.				
$TeBr_4$	380 ± 6	414–27		− 49.3	
TeI_4	259 (s.t.)	d. 100			
$TeBr_2I_2$					
$TeCl_2Br_2$	292	415			
SeF_6	− 34.6	subl. − 46.6	6.6 (ΔH_{subl})	−246	2.26 (−35°C.)
TeF_6	− 37.8	subl. − 38.9	6.7 (ΔH_{subl})	−315	
Te_2F_{10}	− 34	53	9.44		2.88 (25°C.)
$SeOF_2$	15	126			2.80 (21.5°C.)
$SeOCl_2$	10.9	177	10.2		2.42 (22°C.)
$SeOBr_2$	41.7				3.38 (50°C.)
SeO_2F_2	− 99.5	− 8.4	6.77		3.05 (−73°C.)
$SeOF_6$	− 54	−29			
$Se_2O_2F_{10}$	− 62.8	76.3			

treatment with HI gives $(C_5H_5NH)_2TeI_6$. The preparation of the latter suggests the stability order for Te^{IV} complex ion formation of $Cl^- < Br^- < I^-$. The existence of these mixed halide anions presents interesting isomeric possibilities.

The hydrolysis of either $TeCl_2$ or $TeBr_2$ is accompanied by disproportionation and gives the products Te, H_2TeO_3, and HCl or HBr.

The tetrahalides, with the exception of the fluorides, form complex halides of the type M_2TeX_6. Thus, $SeCl_4$ dissolved in concentrated HCl and treated with an alkali chloride gives, on cooling to 0°C., the anhydrous M_2SeCl_6 (403). Similar procedures have been applied to $SeBr_4$, $TeCl_4$, $TeBr_4$, and TeI_4; the hydrolysis tendency of the

tellurium compounds is, of course, somewhat less than that of the selenium halides.

Complexes of $SeCl_4$ and $TeCl_4$ with $AlCl_3$ (404) and PCl_5 (120) have been examined via Raman spectroscopy and are best described in terms of ionic formulations, $SeCl_3^+ AlCl_4^-$, $TeCl_3^+PCl_6^-$ (62,405), etc. $SeCl_4$ and $SeBr_4$ hydrolyze to H_2SeO_3 and HX in aqueous solution; the corresponding Te compounds initially form hydrated halides which are slowly transformed to TeO_2.

No tellurium tetrafluoride complexes have been reported, but SeF_4 forms fluoride complexes of the composition $MSeF_5$, where M is Na, K, Rb, Cs, and Ti. Unstable fluoro complexes are formed with Ba and Ag. As a strong fluorinating agent SeF_4 reacts vigorously with H_2O, P_2O_5, V_2O_5, CrO_3, and P. It dissolves Br_2, I_2, S, and Se and is itself miscible in all proportions with H_2SO_4, IF_5, etc. (371). Tellurium tetrafluoride is similarly unstable in the presence of moisture and attacks glass, copper, and silver at 200°C. and Pt at 300°C.

Nuclear magnetic resonance spectra of group VIb tetrafluorides in nonaqueous solution show the presence of fluorine exchange, the rate of which increases in the order $SF_4 < SeF_4 < TeF_4$. This order is in accord with increasing molecular association suggested by the melting and boiling points and supports exchange mechanisms involving bridging fluorine atoms (280).

The hexafluoride of Se is substantially more reactive than the inert SF_6. Ammonia is oxidized at 200°C., and hot sodium amylate solution quantitatively hydrolyzes SeF_6. A slow reaction with mercury forms Hg_2F_2, and a solution of NaI in acetone is rapidly oxidized. No attack on Pyrex is observed up to 500°C. (406). SeF_6 acts toward anhydrous alkali salts as a strong fluorinating agent:

$$SeF_6 + 6KCl \xrightarrow{500°} 6KF + SeCl_4 + Cl_2$$

$$2SeF_6 + 12KBr \xrightarrow{300°} 12KF + Se_2Br_2 + 5Br_2$$

$$SeF_6 + 6KI \xrightarrow{25°} 6KF + Se + 3I_2$$

In the presence of H_2O no reaction is observed with KCl or KBr; however, the reaction with KI under these conditions:

$$SeF_6 + 6KI + 2H_2O = 6KF + SeO_2 + I_2 + 4HI$$

has been suggested as an analytical method for SeF_6 (407).

Tellurium hexafluoride, TeF_6, is moisture sensitive and is fully hydrolyzed in 24 hours. The increasing reactivity noted in the series SF_6, SeF_6, and TeF_6 is related to the increasing ease of molecular polarization, a trend demonstrated by dielectric constant (408) and refractive index (409) measurements. The ready availability of the orbitals required for hybridization enables TeF_6 to form complexes with fluoride ion donors (410) and with Lewis bases (411). Formation of the former type was achieved by reacting a metal fluoride, CsF, RbF, or KF, with excess TeF_6 at 250°C. in a pressure vessel. Slow cooling and the release of excess TeF_6 enabled the recovery of a crystalline product. With each of these three alkali metal complexes X-ray lines not characteristic of the alkali halide starting material were observed. The inability of TeF_6 to donate fluoride ions is responsible for the failure of AsF_3 or BF_3 to form complexes with the tellurium compound. The fluorotellurates formed react with water to evolve TeF_6 and dissolve the metal fluoride.

The weak Lewis acid character of TeF_6 is indicated by the formation of $2R_3N \cdot TeF_6$ addition compounds with trimethyl- and triethylamine. Each is a solid, but the trimethylamine complex appears to be somewhat more stable. The structure of these amine complexes at −180°C. has been investigated using NMR and an equilibrium mixture of three geometrical isomers proposed; amine molecules are positioned in 1-2, 1-3, and 1-8 locations in a cubic arrangement around a central Te atom. At higher temperatures the rapid exchange of amine molecules between ligand sites makes the three isomers indistinguishable.

Efforts to prepare analogous SeF_6 fluoride and amine complexes were unsuccessful.

Ditellurium decafluoride is somewhat more reactive than S_2F_{10}; in contact with 20% aqueous NaOH it is unaffected in 18 hours, but undergoes a slight hydrolysis on several months exposure. Like S_2F_{10} it will oxidize the iodide ion of an acetone solution of KI. At its boiling point Te_2F_{10} slowly attacks Hg, but S and Se are unaffected. Its high toxicity is similar to that of S_2F_{10} (384).

For the oxyhalides of formula $SeOX_2$ the usual stability trend is observed; $SeOF_2 > SeOFl_2 > SeOBr_2$. The oxyfluoride is a strong fluorinating agent, reacting violently with phosphorus and water. The small specific electrical conductance of $SeOCl_2$, 2×10^{-5} ohm^{-1} $cm.^{-1}$ at 25°C. suggests self-ionization of the liquid, possibly to

$[SeOCl \cdot SeOCl_2]^+$ and Cl^- (412). Complexes of $SeOCl_2$ with $SnCl_4$, $TiCl_4$, and $FeCl_3$ have been prepared but no compound with $SiCl_4$ was formed (413). Surprisingly, a weak complex is formed with CCl_4. Infrared determination of the Se—O stretching frequencies in the complexes with $SnCl_4$ and $TiCl_4$ is in agreement with the proposal of bond formation via donation from the oxygen to the metal atom.

The hydrolysis of SeO_2F_2 proceeds rapidly in moist air to give selenic acid and fluoroselenic acid, $HSeO_3F$. In alkali solution the quantitative hydrolysis products are selenate and fluoride ions. The reaction of SeO_2F_2 with gaseous ammonia is violent, with red Se being deposited; however, in CCl_4 solution the same reaction gives NH_4F and probably selenamide and related compounds. SeO_2F_2 does not react with glass, Fe, Cu, or brass at moderate temperature, but mercury is attacked slowly with the formation of $SeOF_2$ (388).

Pentafluoroselenic hypofluorite, $SeOF_6$, is sensitive to traces of water vapor and liberates oxygen from water or alkali solutions. The main reaction for this is:

$$2SeOF_6 + 16KOH = 2K_2SeO_4 + 12KF + 8H_2O + O_2$$

In an acid solution iodide ion reduces selenium in this oxyfluoride to a variety of oxidation states including zero, hence the difficulty in making use of this reaction in quantitative analysis. Diselenium decafluorodioxide, in contrast, is almost inert toward water, concentrated acids, or bases. Reaction with KI solution is slow. The decomposition products (200°C. in a closed tube) include SeF_6 among unidentified substances (389).

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Extraction of Inorganic Compounds into Organic Solvents

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I. Introduction

It has been known for a number of years that many substances will partition between two immiscible liquids in a manner which is related to their solubilities in the individual phases. The use of this behavior for purification and separation has long been a fundamental technique for the organic chemist (310), but there has been less interest in solvent extraction in the field of inorganic chemistry until recently. This was true although the extractability of several inorganic compounds was early established; the extraction of uranyl nitrate from aqueous solution by ether, for example, was discovered in 1842 (252). During and since World War II, however, the advent of atomic energy programs in a number of countries has brought about the use of liquid-liquid extraction on a large scale for inorganic materials. Typical uses might include the separation of uranium

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from its ores, the removal of plutonium from irradiated material, and the final repurification of uranium. More recently, solvent extraction processes have been suggested for the production of some of the rarer metals such as zirconium and niobium in the high state of purity required for reactor use.

Since solvent extraction permits clean and rapid separations, it has also become an important and useful technique for the analytical chemist. The applications of extraction in analysis have been thoroughly discussed in the recent book by Morrison and Freiser (223), and in a series of reviews in *Analytical Chemistry* (46,225). For the radiochemist, too, the production of carrier-free tracers of high specific activity is simplified considerably by the neat separations possible with this method (281). Conversely, the use of radioactive tracers has been invaluable in the investigation of solvent extraction systems, both in reducing the analytical problems involved and in permitting studies at extremely low concentrations. For a variety of reasons, then, a considerable interest has arisen in recent years in the investigation of the extractive behavior of inorganic compounds and in the mechanism of the extraction process itself. A knowledge of the principles governing such behavior can clearly increase the usefulness and specificity of solvent extraction, both in the laboratory and on the industrial scale, and, of course, the physical and inorganic chemistry involved is of interest for its own sake.

In this review we shall be concerned almost exclusively with the extraction of inorganic species under varying conditions, with special emphasis on the mechanism of the extraction process and on the general behavior of extraction systems. No attempt will be made to give a comprehensive coverage of recent work in the field, but it is hoped to make a somewhat critical survey.* The results discussed relate mainly to equilibrium conditions. There appear to have been few attempts to study the rate at which equilibrium is achieved; no doubt valuable information could be obtained from such kinetic measurements. The primary aim will be to display and discuss some of the factors which govern the equilibrium condition of a two-phase liquid-liquid extraction system. Reference should be made at this point to the earlier reviews of the subject by Irving (147) and Kuznetsov (187).

* The literature survey covered in this review is up to Summer, 1958.

A. TYPES OF EXTRACTION SYSTEMS

There are a number of different ways in which the experimental data on the solvent extraction of inorganic compounds can be organized for review. Any scheme is an arbitrary one, and nature provides examples which seem to fit simultaneously into more than one category. Bearing this in mind, and realizing that the naming of the classes is even more arbitrary, we have organized extractable compounds into the following six classes: simple molecules, pseudomolecular species, coordinately unsolvated salts, mineral acids, complex metal acids, and coordinately solvated salts. This arrangement is roughly in order of increasing complexity of the extraction process.

We have chosen to discuss first those systems in which the extracted species exists in both phases principally as the same simple molecule, such as I_2. This is followed by a discussion of systems in which the species of interest is (partially) ionized in the aqueous phase and is a molecular compound in the organic phase. For want of a better name, we are calling this group "pseudomolecular." The weak acids and bases and, more importantly, the metal chelates provide examples of this class. In general, extraction of these molecular substances is not markedly dependent on the particular solvent used. Next are treated compounds consisting of ions large enough that they do not bind the water or solvent around them in a primary solvation shell or coordination sphere; for classification purposes these have been named "coordinately unsolvated salts." They extract and exist in the organic phase as ionized, though not completely dissociated, salts. Their extraction is somewhat dependent upon the nature of the solvent, and especially upon its dielectric constant.

The remaining systems discussed in this review involve species which pass into the organic solvent by virtue of their ability to coordinate with the organic molecules to form some type of solute-solvent complex. This may be a hydrogen-bonded complex or one in which the solvent molecule is actually bonded to the metal atom or to its primary hydration sphere. The extraction of such systems is characterized by a strong dependence on the properties of the solvent used, particularly on its basic strength and the steric availability of the donor atom, and on the nature of the aqueous phase. The simplest of such systems are the mineral acids, in which

the coordination of the solvent molecule is primarily to the (hydrated) hydrogen ion. The same type of solvent complex is involved with the complex metal acids, but there are additional complications arising from the formation of the complex anion in the aqueous phase in the presence of a mineral acid which also extracts; this may result in ionic interactions in the organic phase.

Finally, the last section, on "coordinately solvated salts," treats those salts which extract with coordination, particularly of the cation, to the solvent molecules. If the solvent is basic enough, identifiable complexes result, as with pyridine and a number of phosphoryl compounds. With less basic solvents, such as the ethers, the interaction is usually too weak for the isolation or definite complexes, but it is nevertheless one of the principal features of the extraction. With hydroxylated solvents, such as the alcohols, solvation of the extracting anion may also become important. The extraction of uranyl nitrate is discussed in some detail since there is already a large literature on this compound and yet there still appears to be some uncertainty as to the solute-solvent interactions involved. In a final paragraph we note briefly some information on the extraction of the heteropoly acids and partition in fused salt systems and other topics on which there is, as yet, only fragmentary information.

B. DEFINITION OF TERMS

It will be as well to define here the terms to be used in this discussion. One finds in the literature a number of terms such as distribution ratio, extraction coefficient, partition constant, etc., with an equally individualistic set of symbols. We shall use the following more for the sake of consistency than because of any belief in their superiority over those employed by other authors. For the over-all ratio, which is generally the most easily obtainable experimental quantity, we shall use the term distribution ratio, D,

D = total concentration of species A in all chemical forms in the organic phase ÷ total concentration of species A in all chemical forms in the aqueous phase

$$= [(A_1)_o + (A_2)_o + \ldots (A_i)_o]/[(A_1) + (A_2) + \ldots (A_j)]$$

where $(A_1)_o$ and (A_1) imply concentrations in the organic and aqueous phases, respectively. For simpler systems in which the distributing

species has one and the same form in both phases, this reduces to the partition coefficient,

$$P_1 = (A_1)_o/(A_1)$$

This is, in fact, the well-known "partition law." Other symbols have their usual meaning unless otherwise stated.

C. THE PARTITION LAW

The fundamental law governing solvent extraction is that found empirically by Berthelot and Jungfleisch (15) some 80 years ago, namely, that for the equilibrium distribution of a species A between two immiscible solvents 1 and 2 at constant temperature,

$$P = (A)_1/(A_2) = \text{constant}$$

provided that the chemical nature of the solute species is the same in both phases. This law has been derived thermodynamically by Nernst (238). At constant pressure and temperature, it follows by definition that, at equilibrium, the partial molal free energy of the solute is the same in each phase (imposing the restriction just mentioned as to chemical identity). For the chemical potentials then

$$\mu_1 = \mu_2 \tag{1}$$

Making the substitution

$$\mu = \mu^\circ + RT \ln a$$

where μ° is the chemical potential in the standard state (usually taken as a hypothetically ideal 1 molal solution) and a is the activity of the solute at the actual concentration, one has

$$\mu^\circ_1 + RT \ln a_1 = \mu^\circ_2 + RT \ln a_2 \tag{2}$$

Equation 2 can be rearranged to

$$a_1/a_2 = \exp \{[\mu^\circ_2 - \mu^\circ_1]/RT\}$$

i.e.,

$$P = (A)_1/(A)_2 = [\gamma_2/\gamma_1] \exp \{[\mu^\circ_2 - \mu^\circ_1]/RT\} \tag{3}$$

For the simplest possible system in which the two solvents are completely immiscible under all circumstances the exponential term is a constant, K, so

$$P = (A)_1/(A)_2 = K\gamma_2/\gamma_1 \tag{4}$$

TABLE I
The Partition Coefficient of Bromine Between Water and Carbon Tetrachloride at 25°C. (157)

Br_2 concentration, g./liter		
In H_2O	In CCl_4	P
14.42	545.2	37.82
7.901	252.8	32.01
5.651	172.6	30.54
2.054	58.36	28.41
0.7711	21.53	27.92
0.5761	15.72	27.26
0.4476	12.09	27.02
0.3803	10.27	27.00
0.2478	6.691	27.00

Measurements of the partition coefficient of a species then yield both the activity coefficient in the organic solvent (if the aqueous phase activity coefficient can be independently determined) and the value of K. The latter is the limiting value of P at infinite dilution, when $\gamma_2/\gamma_1 \rightarrow 1$, and can be determined by extrapolation from measurements at low concentrations. Table I lists values of P found by Jakowkin (157) for the distribution of bromine between water and carbon tetrachloride; it will be seen that at low concentrations a reasonably constant value is obtained, indicating the anticipated constancy of K for such immiscible liquids. At higher concentrations, P increases, but the changes in γ_2/γ_1 are relatively small, and, in fact, in the absence of chemical reactions in either phase, only moderate variations in the activity coefficient ratio are to be expected for simple covalent molecules. Subject to the restrictions already stated, such solutes should obey the partition law to a good approximation. With ionizable species, however, marked deviations may occur, depending upon the solvent. For example, Grahame and Seaborg (117) found that the distribution ratio of gallium chloride between diethyl ether and $6M$ HCl was constant from 10^{-12} to $10^{-3}M$ gallium, but more recent work has revealed that the same substance shows very large changes in D between bis(2-chloroethyl) ether and $6M$ HCl over the same range of metal ion concentrations (128). Care must be exercised in applying the partition law to such systems, as will be seen in Section VI.

II. Simple Molecules

The first extraction system we shall discuss involves the partition of a simple covalent molecule between an aqueous solution-organic solvent pair. These are the simplest systems, and although essentially different from those described later, they illustrate several factors common to all extraction systems. There is a large literature on the extraction of organic compounds, the vast majority of which fall into the present class; although the discussion will be for the most part of inorganic species, organic compounds will be used as examples in some cases.

The simplest system one can imagine involves the distribution of a relatively inert molecule between two immiscible solvents. Under such circumstances the Nernst partition law holds and the activity coefficient ratio will be close to unity. For such an ideal system, the partition coefficient over the whole range of concentrations should be near the ratio of the saturated solubilities of the solute in each phase. (Since the organic solvent and water are not completely immiscible, one should take the solubilities when each phase is already saturated with the other; this correction must become significant with solvent pairs of appreciable mutual solubility.) One of the best-known examples of this type of system is the distribution of molecular iodine between water and a nonpolar organic solvent. Gwynne and Davies (117a), for example, have recently discussed the partition of iodine between water and carbon tetrachloride; the ratio of the solubilities is 89.6 and the partition coefficient at indefinitely dilute solution is 89.9 at 25°C.; P is slightly dependent on iodine concentration. Gwynne and Davies also showed that the temperature dependence of the partition coefficient is that to be expected from the heats of solution. For the process I_2(solid) → I_2(CCl_4 solution), one finds +6920 ± 380 cal./mole, and for the corresponding dissolution in water +6150 ± 100 cal./mole. The experimentally determined heat of extraction is +490 ± 25 cal./mole, and that calculated from the individual heats of solution +770 ± 480 cal./mole, in agreement within experimental error. A number of earlier examples of this type have been reviewed by Hill (135).

For systems approximating to the idealized conditions defined above, then, the main reason for the extraction of covalent species into the organic phase, and the main factor influencing the numerical

value of the partition coefficient, is the difference in the solubilities. The solubility of nonelectrolytes in various media has been extensively discussed by Hildebrand and Scott (131). Ignoring any specific solute-solvent interactions, the solubility of such molecular species in organic solvents is generally at least an order of magnitude higher than in water. This emphasizes the preference of the covalent solute molecules for the disordered organic solvent into which they can fit with little or no energy barrier over the comparatively highly ordered aqueous phase. The solute-water interaction may be comparable with, or even stronger than, the solute–organic solvent interaction, but the solvent-solvent interactions in water arising from hydrogen bonding are considerably stronger than the corresponding interactions in the organic solvent. The structure of water consequently tends to force the solute molecule into the organic phase unless the solute has functional groups which bond strongly to water. Furthermore, since the degree to which the water structure must be broken down in order to insert a solute molecule depends on the latter's size, molecular size is clearly an important factor in partitions involving water and an organic solvent. Data are lacking to illustrate this point unambiguously for inorganic compounds, although later evidence will show it well by inference. We can see the order of this effect, however, from data on the partition of a number of aniline derivatives between benzene and water (Table II); only those compounds whose basic strengths are of the same order of magnitude have been chosen. This group of compounds cannot

TABLE II
Partition of Aniline Derivatives Between Benzene and Water (81)

Compound	P	Base constant ($\times 10^{-10}$)
Aniline	10	5.3
n-Toluidine	19	2.9
β-Naphthylamine	279	2.0
p-Chloroaniline	83	1.5
p-Bromoaniline	132	1.04
p-Nitrosomethylaniline	3.3	1.63
p-Nitrosodimethylaniline	51	1.95

perhaps be considered as a whole, but within the three subdivisions the larger molecules have the greater partition coefficients in each case. The halogen compounds probably have higher coefficients than their size would predict because of the possibility of interaction of the halogen atom with the organic solvent.

Another example is to be found with the inert gases, for which P can be calculated from the data given by Friedman (93) for the solubilities in a number of solvents. The calculated partition coefficients will differ from the actual experimental values because of the appreciable mutual solubilities of water and solvent, but this need not concern us here. For nitromethane and water, the calculated values are

	P
He	5.5
Ne	6
Ar	12
Kr	19
Xe	28

The interpretation of the solubilities of the inert gases in various solvents is outside the scope of this review (75), but it is clear that the effect of increasing atomic volume is to cause the element to move out of the water into the organic phase where solvent-solvent interactions are smaller. For helium, and to a lesser extent neon, these effects are perhaps not so sharply identified since the atomic volume of these elements is such as to allow them to fit into the vacancies in the water structure without too great an energy barrier.

The effect of size is also apparent in the studies of Collander (42) on the distribution of various classes of organic compounds between water and diethyl ether. It was found that the extraction increased by a factor of 2–4 for each new CH_2 group introduced into the molecule in a homologous series. This work also shows the effect of specific group interactions; aldehydes, ethers, and ketones, for example, had distribution ratios lower than the corresponding hydrocarbons by factors of 5–150. Such molecules can form hydrogen bonds with water and so are more acceptable in that phase than the inert hydrocarbons.

Changes in the chemical nature of the solvent will also affect the distribution of simple molecules, but since a major factor in their

distribution is the disruption of the water structure, the nature of the organic solvent is not of critical importance unless it, too, has a structure or possesses groups capable of specific interactions with the solute. The distribution ratios for a simple covalent molecule between water and a variety of solvents, such as the aliphatic and aromatic hydrocarbons, their halogenated derivatives, ethers, etc., will not generally show a spread of more than an order of magnitude or two. This is an important and distinctive feature of this class of extraction systems, in contrast to systems involving ionic species. The latter do not extract appreciably into nonbasic, low dielectric solvents and consequently show large variations in the values of D with different solvents. In fact, if the extraction of a substance takes place approximately as well with solvents such as chloroform or carbon tetrachloride as with basic solvents such as the ethers, one can be almost certain that the partition of a neutral covalent molecule is occurring.

Of course, even in such systems there will be variations in behavior due to varying solvent-solute interactions. There is a considerable literature on the nonideal solutions formed by iodine, for example, in various organic solvents, revealed by changes in the absorption spectrum of the solute. Hildebrand and Scott (134) have studied the properties of such solutions, and there is now increasing evidence on the formation of complexes between iodine and many organic solvents by various types of acid-base or charge-transfer interactions (58,124,162). Estimates of the heat of complexing have been made (121). The existence of such interactions does not alter the basic premise that the partition coefficient is the ratio of the solubilities in each phase, since it is merely the solubility in the organic phase which is affected. It does mean, however, that the partition coefficient for iodine between water and an organic solvent depends to some extent on the chemical nature of the solvent chosen.

The addition of another solute to the aqueous phase may affect the distribution in a number of ways. Long and McDevit (193) have reviewed the physico-chemical factors involved in the "salting-out" of nonelectrolytes from aqueous solution, and we shall not discuss this topic. The salting-out of electrolytes is discussed in Sections VI and VII. Of greater importance than salting-out are those chemical changes which affect directly the concentration of the distributing species. Again, the extraction of iodine provides

an almost classical example (158); addition of iodide ion results in the equilibrium

$$I_2 + I^- \rightleftharpoons I_3^-$$

in the aqueous phase, so that the distribution ratio is given by

$$D = (I_2)_o/[(I_2) + (I_3^-)]$$

The formation constant, K, of the I_3^- ion in the aqueous phase can then be found from measurements of D in the presence and absence of iodide, since

$$D = P/[1 + K(I^-)]$$

where P is the partition coefficient for I_2. Similar experiments have been carried out for the formation of $CuSO_4 \cdot 4NH_3$ (53) and for the naphthol-picric acid complex (185).

We shall now give a number of examples of the extraction of covalent molecules, mostly into nonpolar solvents, illustrating the factors just discussed. The distribution of both iodine and bromine has been studied (15), and, as one might predict from the size of the molecules, iodine is extracted better than bromine; for water–carbon disulfide, under the same conditions, $P_{I_2} \approx 400$ and $P_{Br_2} \approx 80$. The covalent halides of a number of metals also extract into organic solvents as nonelectrolytes. One of the earliest examples is the work of Hantzsch and Vagt (120) on the extraction of mercuric chloride into toluene or benzene. Other molecules of this type studied include SbI_3 (257), $AsCl_3$ (7,30,87), $AsBr_3$ (30), $GeCl_4$ (30,87, 275), InI_3 (122), and HgI_2 (227). Irvine and his co-workers (30) have shown that the extraction of $AsCl_3$ occurs with a variety of organic solvents and that, for a given aqueous solution, the distribution coefficient into CCl_4, $CHCl_3$, benzene, bis(2-chloroethyl) ether, and diisopropyl ether is virtually independent of solvent. From this work, and that of Arcand (7), it appears that partially hydrolyzed $AsCl_3$ species may also be involved in the extraction. A number of the studies have been concerned with the effect of changes in the composition of the aqueous phase on the formation of the distributing species. For example, addition of iodide ion to aqueous solutions of mercuric iodide causes the following two equilibria to be set up

$$HgI_2 + I^- \rightleftharpoons HgI_3^-; \text{ equilibrium constant } K_1$$
$$HgI_2 + 2I^- \rightleftharpoons HgI_4^{2-}; \text{ equilibrium constant } K_2$$

Moser and Voigt (227) have shown that the distribution ratio is then given by

$$D = P\,[1 + K_1(1)\gamma_1/\gamma_2 + K_2(1)^2\gamma_1^2/\gamma_3]^{-1}$$

With the activity coefficients for I^-, HgI_3^-, and HgI_4^{2-} in the aqueous phase, γ_1, γ_2, and γ_3, estimated from the Debye-Hückel expression, the resulting values of K_1 and K_2 were in good agreement with results from other types of experiments.

The solubility of the aluminum halides in benzene is well known, the solute existing as a molecular dimer (78,79,115). No extraction studies have been possible, however, because of the rapid hydrolysis of these compounds in aqueous solution. Most metal halides do not dissolve in organic solvents; ferric chloride is only slightly soluble in diisopropyl ether (190) and gold(III) bromide is said to be insoluble in ether in the absence of water (105). These metal halides can be extracted as ionic species, namely the acid HMX_4, into basic solvents (see Section VI).

The tetroxides of osmium and ruthenium have been shown to extract into carbon tetrachloride. In the work of Anderson and Yost (6), $(OsO_4)_4$ molecules were postulated to account for deviations in the vapor pressure of solutions of OsO_4 in CCl_4, but Hildebrand and Scott (132) have pointed out that the results can be understood in terms of the different internal pressures of the two liquids. Martin (205) found no evidence for polymeric RuO_4 species. It was shown that change in pH affected the distribution of this compound because of possible acid and base dissociations, i.e.,

$$\begin{array}{ccc} & & H^+ + HRuO_5^- \\ & \nearrow\!\!\!\nearrow & \\ RuO_4 + H_2O & \rightleftharpoons & H_2RuO_5 \\ & \searrow\!\!\!\searrow & \\ & & HRuO_4^+ + OH^- \end{array}$$

Another oxide which extracts into nonpolar solvents is chlorine dioxide (52). An interesting example of the distribution of an atomic species is the extraction of mercury from aqueous solution into a

solvent such as hexane in which the element is more soluble than in water (226).

We shall finally note in this class the extraction of the fatty acids into solvents such as benzene. The transfer of a neutral molecule is involved, since these substances are virtually undissociated in aqueous solution at moderate concentrations. These compounds illustrate the variation in D which may arise from chemical reactions in the organic phase, for it has long been known that in low dielectric solvents the fatty acids exist as dimers. Considering the equilibria

$$2A_{(o)} \rightleftharpoons A_{2(o)}; \quad K = (A_2)_o/(A)_o^2$$

$$A \rightleftharpoons A_{(o)}; \quad P = (A)_o/(A)$$

The distribution ratio becomes

$$D = [(A)_o + 2(A_2)_o]/(A) = P + 2KP(A)$$

The distribution depends upon the concentration of acid and upon the value of K, the dimerization constant. Obviously, from measurements of D, the value of K can be obtained. The variation in this constant with solvents of differing dielectric constant and basicity will be discussed in Section VI. Slightly more complicated expressions for the distribution ratio can be derived for acids whose ionization in the aqueous phase cannot be neglected (136).

The extraction of the fatty acids also illustrates the effects of molecular size and chemical interaction quite clearly. Using methyl isobutyl ketone, Vogt and Geankoplis (304) have shown that the distribution ratio goes up in the order formic < acetic < propionic. A more extensive investigation has been reported by Pagel and McLafferty (243) using tri-*n*-butyl phosphate, which was found to be a much better extractant for organic acids than ethyl or isopropyl ether, benzene, toluene, or chloroform, as one might expect from its strongly basic character (Section VII). The extraction of acids increased with chain length in the order acetic < propionic < butyric < valeric, and for the dibasic acids malonic < succinic; the presence of a phenyl group also increases D. On the other hand, the addition of hydroxy groups increases the hydrophilic nature of the acid by enhancing the solvation in the aqueous phase, so that hydroxy acids do not extract as well as their normal analogues; i.e., acetic > glycollic, propionic > lactic, and succinic > malic > tartaric. In keep-

ing with this, gluconic acid with its five hydroxy groups is extracted only very slightly (at 0.1N solution $D = 0.083$; cf. $D = 2.34$ for acetic acid at the same concentration). Similarly, monobasic acids extract better than dibasic acids of the same chain length. Solvation effects in the aqueous phase also explain the failure of formic acid to extract into paraffinic or halogenated solvents (i.e., $D \sim 10^{-2}$–10^{-3}). This acid is slightly stronger than its higher homologues, but is also much more hydrophilic in nature than, e.g., acetic acid. The acid extracts quite well into ethers and ketones (e.g., $D \sim 0.4$ at low concentrations for diethyl ether). In this respect, formic acid behaves like the mineral acids; the importance of solvation effects in both phases will be discussed in connection with the extraction of these compounds (Section V).

III. Pseudomolecular Systems

On general principles, ionic compounds would not be expected to extract into organic solvents from aqueous solution because of the large loss in electrostatic solvation energy which would occur. This may be seen by using the Born equation (29) to calculate the free energy of transfer, ΔF_t, of a bare ion of radius r and charge Ze, from water (dielectric constant ϵ_w) to an organic solvent of dielectric constant ϵ_o,

$$\Delta F_t = Z^2e^2/2r(1/\epsilon_o - 1/\epsilon_w)$$

Normally, $\epsilon_o < \epsilon_w$, so that a positive free energy change results. For example, for the transfer of one mole of a 1-1 electrolyte with $r_1 = r_2 = 2$A. into a solvent with $\epsilon_o = 10$ and taking $\epsilon_w = 80$, one finds $\Delta F_t = +14.5$ kcal./mole. The order of magnitude, and certainly the sign, of this free energy change remain the same even if the effect of ion pairing in the organic phase is considered. From the theory of Bjerrum (22) and of Fuoss and Kraus (97), the value of the association constant, K, of a pair of oppositely charged ions can be calculated as a function of the dielectric constant ϵ_o, the ionic charges Z_1 and Z_2, and the distance of closest approach of the ions, $r_1 + r_2$. The free energy of ion pairing is then $\Delta F_{ip} = -RT \ln K$, and for the example taken above, $\Delta F_{ip} = -6.5$ kcal. This is certainly appreciable, but only about one-half the difference in the electrostatic solvation energies, so that a considerable positive free

energy of transfer remains. Furthermore, from this treatment, the extraction of a polyvalent ion is predicted to be more difficult, and this is confirmed experimentally; ReO_4 can be extracted from MoO_4^{2-} (290), and MnO_4^- from MnO_4^{2-} (141).

Unfortunately, this use of the Born and Bjerrum-Fuoss-Kraus equations to calculate the energy of transfer of an ionic species is a gross oversimplification of the process. Both assume a continuous medium of uniform dielectric constant, which is, of course, not valid for any liquid, but is especially far from reality for water with its relatively open, but highly hydrogen-bonded structure. More important is the fact that only the electrostatic free energy is accounted for, and it is well known that ions in water, or any other strongly electron-donating and/or accepting solvent, may form (chemical) bonds with the nearest neighbor solvent molecules. Perhaps the most often quoted example of an aquo ion is the $Cr(H_2O)_6^{3+}$ ion studied by Hunt and Taube (144), but all other small polyvalent ions must possess similar structure, though their rate of water exchange may be much more rapid. The solvent extraction of a hydrated species, when this is possible, is itself evidence for the existence of such aquo ions (see Section V). For the purposes of this paper, such solvation involving solvent bonding will be called primary or coordinate solvation, to distinguish it from all other secondary solvation. For ions, this secondary solvation involves principally the electrostatic orientation and polarization of the solvent, but also includes interactions due to dispersion forces, which may become important for large ions. Although most small ions are coordinately hydrated, large ions may not be; for example, Bu_4N^+ and Ph_4B^- certainly do not bind their nearest water molecules. One would therefore expect the extraction of these two classes of ions to show a different dependence on the nature of the solvent. Coordinately hydrated ions will extract best into those solvents capable of bonding to the ions or to the water molecules of the hydration shell, and the coordinately unhydrated ions will extract better the higher the dielectric constant of the solvent.

The electrostatic energy argument against the extraction of ions into low dielectric constant solvents still holds, however, and so the most obvious way to make an aqueous ionic species extractable is to destroy its charge. This can be done by combining the ion of interest with an ion, or ions, of opposite charge to form a neutral

molecular species. The larger and bulkier and more hydrophobic the resulting molecule, the better will be its extraction.

A simple example is furnished by the anion of a weak acid. By association with a hydrogen ion to form the neutral acid, extraction can be increased by several orders of magnitude. Since the fraction of extractable molecular species in the aqueous phase depends on the hydrogen ion concentration, the distribution ratio will show a dependence on the latter, in contrast to those cases where *only* the same molecular species exists in both phases. The nature of this dependence is easily shown. Consider the equilibria

$$H^+ + A^- \rightleftharpoons HA \qquad K_{HA} = (HA)/(H)(A)$$

$$HA \rightleftharpoons HA_{(o)} \qquad P_{HA} = (HA)_o/(HA)$$

where $(HA)_o$ and (HA) stand for the equilibrium organic and aqueous phase concentrations, respectively; for simplicity, charges are not shown. K_{HA} is the acid association constant, and P_{HA} its partition coefficient. The distribution ratio is then

$$D = (HA)_o/[(HA) + (A)] = P_{HA}/[1 + 1/K_{HA}(H)] \qquad (5)$$

and

$$\log D = \log P_{HA} - \log [1 + 1/K_{HA}(H)] \qquad (6)$$

As an illustration, Figure 1 is a plot of log D vs. pH for the case $K_{HA} = 10^{10}$, $P_{HA} = 10^2$. It can be seen that when $K_{HA}(H) << 1$, (that is, (HA) << (A)) $\log D \backsimeq \log P_{HA}K_{HA} + \log (H)$, and the plot is a straight line of unit slope. At higher (H), HA) is no longer negligible, and so the slope decreases until, when (HA) >> (A), or $K_{HA}(H) >> 1$, $\log D \backsimeq \log P_{HA}$. Molecular HA is then the dominant species in both phases, and a constant value of D is to be expected.

Such distribution behavior has been observed experimentally for a number of weak acids; for example, various phenols (113,242) dithizone (148,151,269), acetylacetone (264), 8-quinolinol (68), cupferron (68), salicylic acid (138), cinnamic acid (138), 3,5-dinitrobenzoic acid (138), and tropolone (70), partitioning between water and solvents such as benzene, chloroform, cyclohexane, and methyl isobutyl ketone. It may be noted that the determination of D at several well-chosen hydrogen ion concentrations gives the value of P_{HA} as well as values for K_{HA}, the acid association constant in water

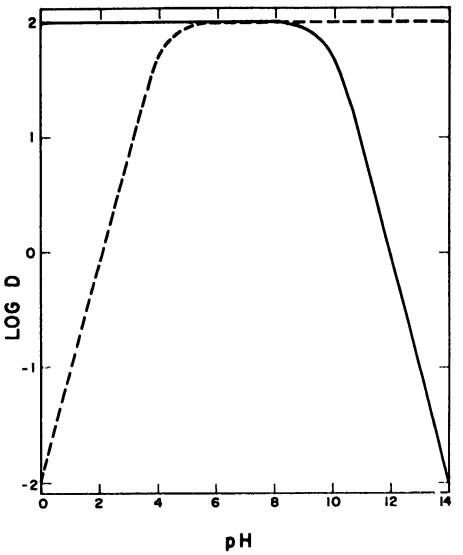


Fig. 1. Log D vs. pH for a weak acid with $K_{HA} = 10^{10}$, $P_{HA} = 10^2$ (———) and for a weak base with $K_B = 10^{10}$, $P_B = 10^2$ (– – – –).

saturated with the organic solvent. Such a method, involving the distribution between water and benzene, was used in 1901 by Farmer to determine the acid strength of hydroxyazobenzene (80) and has also been used for various phenols (113,242) and dithizone (148,157).

An exactly analogous situation is furnished by weak bases, such as the amines. Here one has

$$D = (B)_o/[(B) + (BH)] = P_B/[1 + 1/K_B(OH)]$$

$$= P_B/[1 + (H)/K_B K_W] \quad (7)$$

$$\log D = \log P_B - \log [1 + (H)/K_B K_W] \quad (8)$$

where P_B is the partition coefficient of the base, K_B its association constant, and K_W is the water ion product. Such behavior is illustrated by the dashed curve in Figure 1 for a weak base with $K_B = 10^{10}$ and $P_B = 10^2$. This time the region of constant D, where $D = P_B$, occurs when (H) is very small; i.e., $(H) << K_B K_W$. When (H) gets larger, so that the concentration of BH^+ is no longer negligible, the plot of log D vs. log (H) has a negative slope, eventually of -1. Again, such behavior has been observed experimentally

for the distribution between water and chloroform or cyclohexane of certain methyl-substituted pyridines and quinolines and used for calculating their base constants (112). The base constants of a series of aniline bases were obtained as long ago as 1904 by Farmer and Warth from the difference in the distribution between water and benzene of the free bases and their hydrochloride salts (81); some of these are listed in Table II.

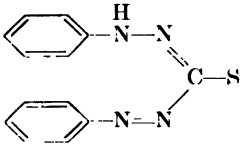
An amphoteric molecule would show both of the previous types of behavior. If the acid and base association constants were both 10^{10}, and $P = 10^2$, the combined full and dashed curve in Figure 1 illustrates the variation in the distribution of an amphoteric substance with change in (II). Such behavior is observed experimentally for 8-quinolinol distributing between water and chloroform (188).

By far the most important and useful examples of this type of system are the neutral metal chelate complexes. These consist of a metal cation combined with sufficient chelate anions to form a neutral molecule; the anions possess two, or more, coordinating groups and so are bound to the metal in a cyclic structure. These groups must be so spaced as to make a stable ring, usually five- or six-membered, and usually have as the basic atom nitrogen, sulfur, or oxygen.

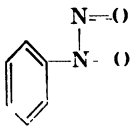
Although metal chelate complexes may be cationic, neutral, or anionic, and all types have been used in extraction systems, only the neutral ones will be considered in this section. Since for many polyvalent cations the coordination number is twice the charge, the appropriate number of bidentate uninegative anions will both neutralize the metal ion charge and completely destroy the primary hydration shell, transforming the hydrated ion into an unhydrated organic molecule,

$$M(H_2O)_{2n}^{n+} + nC^{-} \rightleftharpoons MC_n + 2nH_2O$$

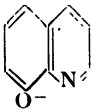
Examples of some of the more important bidentate anions (derived from the weak acid parent chelating reagent) are dithizonate (I),



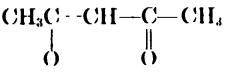
(I)



(II)



(III)



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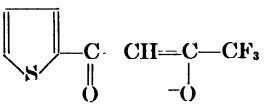

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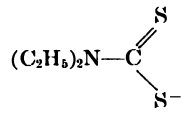


(VI)

cupferrate (II), 8-quinolinolate (III), acetylacetonate (IV), thenoyltrifluoroacetonate (TTA, V), and diethyldithiocarbamate (VI). There are, of course, many more such reagents (270,311), and some of them have been found to chelate with almost any polyvalent metal cation, under the proper conditions.

If all the polar groups of a chelating reagent are bound into the metal cation, so that the molecule presents an essentially hydrocarbon-like surface, it will be almost insoluble in water and soluble in nonpolar organic solvents. On the other hand, if the resulting chelate complex has polar groups exposed, it will be more soluble in water, and less so in solvents such as chloroform, benzene, and carbon tetrachloride. However, the solubility in solvents containing polar groups, such as ethers, ketones, etc., may be high due to the specific interactions of the groups in the complex and in the solvent molecules, just as with the extraction of simple molecules.

The extraction of a metal chelate depends not only upon its own structure and upon the nature of the solvent, but also upon the process of forming the complex. Expressions describing the extraction behavior of metal chelate systems were given at least as early as 1941 by Kolthoff and Sandell (183) and applied to the extraction of zinc dithizonate into chloroform. Later, these expressions were generalized by Irving and Williams (156) and by Furman, Mason, and Pekola (98). In its simplest form, the theory assumes that (*1*) the chelating agent, HC, and metal chelate, MC_n, are the only species in the organic phase; (*2*) the metal ion forms no appreciable amount of hydrolyzed, polymeric, or complex products in the aqueous phase; that is, it exists there mainly as the aquo ion, M^{n+}; and (*3*) concentrations may be used instead of activities in the expressions. The following equilibria must then be considered:

$$H^+ + C^- = HC \qquad K_{HC} = (HC)/(H)(C)$$

$$M^{n+} + nC^- = MC_n \qquad K_{MC_n} = (MC_n)/(M)(C)^n$$

$$HC = HC_{(o)} \qquad P_{HC} = (HC)_o/(HC)$$

$$MC_n = MC_{n(o)} \qquad P_{MC_n} = (MC_n)_o/(MC_n)$$

and the distribution ratio

$$D = (MC_n)_o/(M) = P_{MC_n}K_{MC_n}(C)^n \tag{9}$$

$$D = P_{MC_n}K_{MC_n}(HC)_o^n/P_{HC}{}^n K_{HC}{}^n (H)^n = K(HC)_o^n/(H)^n \tag{9'}$$

This simple expression predicts that the value of D for a neutral chelate complex of a metal ion, of charge $n+$, varies directly as the nth power of the *equilibrium* chelate reagent concentration in the organic phase (not on the total or initial HC concentration) and inversely as the nth power of the equilibrium hydrogen ion concentration in the aqueous phase. A plot of log D vs. $-$log (H) at constant $(HC)_o$, or vs. log $(HC)_o$ at constant (H) should yield a straight line of slope $+n$. These predictions have been verified in several studies: the extraction of zinc by dithizone into chloroform (149,183) and into carbon tetrachloride (149), iron(III) (271) and copper(II) (98) by cupferron into chloroform, zirconium and hafnium by thenoyltrifluoroacetone (142) and by acetyltrifluoroacetone (274) into benzene. It should be noted that it has proved simplest to test this expression using radioactive metal tracers, since in this way a negligible proportion of the reagent is complexed, so that $(HC)_o$ does not depend upon the metal concentration and the degree of extraction. Conversely, such straight line log-log plots give experimental evidence as to the nature (charge) of the metal species in the aqueous phase and the formula of the organic phase complex under the conditions studied (11,44) (but see pages 131–134).

Equation 9′ shows that a high distribution ratio depends upon $K_{MC_n}/K_{HC}{}^n$, that is, upon a large association constant for the metal complex and upon a small one for the acid reagent. Although a discussion of the factors involved in determining the magnitude of these constants is beyond the scope of this review, four generalizations can be made.

1. The value of K_{MC_n} usually increases with increasing charge and decreasing size of the ion, so that for a given chelating agent, the value

of K does likewise. Thus, for some TTA complexes distributing between water and benzene, Irving (147) lists values of K as Sr^{II}, 9×10^{-10}; Y^{III}, 10^{-7}; Zr^{IV}, 9.4×10^{7}; Ra^{II}, very small; Ac^{III}, 8×10^{-12}; Th^{IV}, 5; Pb^{II}, 8×10^{-6}; Bi^{III}, 2.5×10^{-4}; Po^{IV}, 4×10^{-2}. Apart from this intrinsic difference in K for cations of different charge, the separation of such ions can be enhanced by varying the hydrogen ion and reagent concentrations. (Actually, although a given increase in the organic phase reagent concentration is equivalent in its effect to the same proportional decrease in the aqueous hydrogen ion concentration, usually the latter is varied because of its greater ease of determination and adjustment.) The degree of separation possible in the extraction of two metals, 1 and 2, is usually represented by the separation factor, β_2^1,

$$\beta_2^1 = D_1/D_2 = K_1 (HC)_o^{n_1-n_2}/K_2 (H)^{n_1-n_2}$$

Thus a change of one pH unit causes a $10^{n_1-n_2}$ variation in β_2^1, so that metals of different charge type (which form extractable chelate complexes) can often be separated under the proper conditions of pH. An example is the separation and purification of actinium produced by the neutron irradiation of radium, as described by Hagemann (118). The actinium is extracted away from the target radium with TTA in benzene at pH 6, returned to the aqueous phase with $6M$ acid, and subsequently separated from thorium and polonium by TTA extraction of the latter at pH 1.

2. Metal cations of the same charge and coordination type usually show a similar order for their ease of extraction, independent of the nature of the solvent and of the chelating agent. There is little dependence of the order on the solvent because the exterior of the bulky chelate complex of any such metal ion closely resembles that of any other, if the hydration shells have been destroyed, so that the complexes have similar partition characteristics. The order of extraction depends, then, upon the order of complex formation, that is, upon K_{MC_n}. It has been found by several investigators that these constants have an order which, neglecting steric factors, is usually independent of the nature of the chelating agent (204,208). For some of the divalent transition metals the order of decreasing strength of complex formation is Pd > Cu > Ni > Pb > Co > Zn > Cd > Fe > Mn > Mg, and for the rare earths, alkaline earth, and alkali metal series the order is that of increasing size. These series, then,

should also give approximately the order of extraction of the metals with any given chelating agent, and as far as this has been investigated, it seems to be true (155). However, steric factors may destroy this relationship, as bulky substituents near the coordinating groups of the chelating reagent will hinder reaction with small metal cations, particularly if several of the anions are involved in the complex. Thus it was observed that Al did not form a tris-2-methyl-8-quinolinolate complex (precipitate) as it did with the nonmethylated reagent (209), and this was shown to be characteristic of the 2-substituted reagents, and quite reasonably ascribed to steric interference (150). A comparison of the 2- and 4-methyl-8-quinolinolate complexes (the parent reagents are of comparable acid strength) verified this and showed that the bis-complex (planar?) of the 2-methyl compound with Ni was weaker than that with Co or Zn, and hence out of the expected order (164).

3. As the chelating agent is varied, using a particular metal ion, K_{MC_n} tends to be larger or smaller as K_{HC} is larger or smaller. That is, changes in these two constants tend to run parallel (21,154,204), although there are exceptions when the chelates are not of the same general type (71,165) or when steric factors interfere. *A priori*, then, it is difficult to predict the change in $K_{MC_n}/K_{HC}{}^n$ when the reagent is varied. Experimentally, however, it seems that the net effect on D is that indicated by the change in K_{HC} itself; that is, the chelate reagent which is the stronger acid forms the weaker metal complex, but nevertheless gives the higher value of D. It seems that the enhanced extraction of La^{III}, Th^{IV}, and U^{VI} with 5,7-dichloro-8-quinolinol over that with the nonhalogenated reagent is due primarily to this effect (74), and this is possibly also true for the extraction of Er^{III} and Nd^{III} with these reagents (215).

4. Equation 9′ shows that the value of D for a particular metal also depends upon the ratio $P_{MC_n}/P_{HC}{}^n$. Again, any change in the nature of the chelating agent, or in this case, of the organic solvent as well, usually changes both of these constants in the same direction, but the change in P_{MC_n} is usually smaller than that in $P_{HC}{}^n$. Thus a change in the reagent or in the solvent to yield a higher value of P_{HC} (all other conditions the same) will also result in a larger value of P_{MC_n}, but (usually) in a lower value of D. For example, dithizone has a larger partition coefficient into chloroform than into carbon tetrachloride (157), and so does zinc dithizonate (149), but for a

given value of $(HC)_o^2/(H)^2$ the zinc is extracted more completely into the latter solvent, and this is also true of other metal dithizonates. Similarly, isovaleroyltrifluoroacetone has a larger partition coefficient between water and benzene than between water and *n*-hexane, but the extraction of Zr and Hf is more complete into the latter solvent under comparable conditions (143). Th^{IV} and Pu^{IV} acetylacetonates show larger K's with methyl isobutyl ketone than with chloroform, although acetylacetone and the metal chelates both have larger partition coefficients into the latter solvent. This is not an absolute rule, however, since U^{IV} has about the same K with chloroform as with the ketone (266).

Equation 9′ was derived with the simplifying assumption that the metal species in the aqueous phase is principally present as the uncomplexed aquo ion. This assumption may well not be true. For example, the concentration of the extractable metal chelate complex may not be negligible in the aqueous phase, so that a term in (MC_n) must be included in the denominator of the expression for D. More generally, the formation of this neutral chelate species in the aqueous phase undoubtedly proceeds stepwise through lower complex cations at small chelate concentrations and may continue to anionic complexes, MC_p^{n-p}, at high reagent concentrations. Equation 9′ can be modified to include all these complexes by considering the additional equilibria (265)

$$M^{n+} + iC^- \rightleftharpoons MC_i^{n-i} \qquad K_{MC_i} = (MC_i)/(M)(C)^i$$

$$D = (MC_n)_o/\sum_{i=0}^{p} (MC_i)$$

$$= [P_{MC_n}K_{MC_n}(HC)_o^n/P_{HC}^nK_{HC}^n(H)^n][1 + \sum_{i=1}^{p} K_{MC_i}(C)^i]^{-1}$$

$$= [K(HC)_o^n/(H)^n]\ [1 + \sum_{i=1}^{p} K_{MC_i}\ (HC)_o^i/P_{HC}^iK_{HC}^i(H)^i]^{-1} \quad (10)$$

If the concentration of the chelate complexes in the aqueous phase is negligible compared to (M^{n+}), equation 10 reduces to equation 9′, but if they are significant, as when $K_{MC_i}(C)^i > 1$ or $K_{MC_i}(HC)_o^i > P_{HC}^iK_{HC}^i(H)^i$, D is no longer a function of the nth power of $(HC)_o/(H)$, but of the $\bar{n}$th power, where $\bar{n}$ is the average charge on the metal complexes in the aqueous solution or $(n - \bar{n})$ is the average number

of univalent chelate anions complexed with the metal in the aqueous phase. As either log $(HC)_o$ or $-\log (H^+)$ is increased, holding the other constant, a plot of log D vs. log (C) will show a slope of $\bar{n}$, which gradually decreases to zero as MC_n becomes the principal aqueous phase metal species. From that point, $D = P_{MC_n}$ = constant, as the system is then that of a single molecular species distributing between water and the organic solvent, unless anionic complexes are also possible in the aqueous phase. In the latter case, log D will pass through a maximum and then decrease with increasing log (C) as the nonextracting anionic complexes form. The slope of the curve, $\bar{n}$, will now be negative, and still indicates the average charge on the aqueous phase metal species, while $(n - \bar{n})$ still gives the average ligand number. Hence the study of the variation in the distribution ratio of a metal ion as the known aqueous phase chelate anion concentration is varied by varying either $(HC)_o$ or (H^+) allows the determination of the values of the partition and association constants, P_{MC_n} and K_{MC_n}, of the metal species if P_{HC} and K_{HC} have already been determined. This distribution method has indeed been used in the determination of some stepwise chelate formation constants (69,267,280) and also for the study of other complex equilibria in aqueous solution.

However, if other complexing agents, represented by X^-, are present, the metal complexes involving them must also appear in the distribution ratio expression. In the usual cases, where X^- stands for halide, thiocyanate, sulfate, etc., these complexes are soluble only in the aqueous phase, and so

$$D = (MC_n)_o / \sum_{i=0}^{p} \sum_{j=0}^{q} (MC_iX_j)$$

$$= K[(HC)_o^n/(H)^n] \left[1 + \sum_{i=0}^{p} \sum_{j=0}^{q} K_{MC_iX_j}(C)^i(X)^j\right]^{-1} \qquad (11)$$

(both i and $j \neq 0$)

making allowance for the possibility of mixed complexes. At a fixed value of (X), D depends upon (C) or $(HC)_o/(H)$ as before, but with constant $(C) = (HC)_o/(H)K_{HC}$. D now depends upon the concentration of X^-. Such a result was found in the extraction of iron cupferrate into chloroform from HCl–NaCl solutions (271); the value of D decreased with increasing chloride concentration.

In not too complicated cases, the values of $K_{MX_{\bar{m}}}$ can be determined by studying this variation of D with (X^-), as $-\partial \log D/\partial \log (X) = \bar{m}$ = the average number of anions, X^-, complexed with the metal species at that concentration. This method was employed by Connick and McVey to study the complexes of zirconium with SO_4^{2-}, F^-, Cl^-, and NO_3^-, using TTA extraction into benzene (44), and similar studies have been made on the complexes of Th^{IV} (56), U^{IV} (17,57), and U^{VI} (55).

A use for such competitive complexing by another nonextracting agent has been found in analytical separation schemes. Since, as already mentioned, cations of the same charge and coordination type seem to have an order to their chelate association constants which is independent of the nature of the reagent, two metals which have a small separation factor, β, with one chelating agent, might not be expected to be much more separable with any other such reagent. But if an appropriate second complexing agent, X^-, is added to the system to form water-soluble complexes with the metals, in competition with the extracting agent, usefully large values of β may result. If the added "masking" agent is not a chelating agent, but is F^-, CN^-, $S_2O_3^{2-}$, etc., good separations may be possible because of their different orders of complexing. For example, the addition of $S_2O_3^{2-}$ and CN^- selectively holds back Hg, Cu, Bi, Ag, Pb, Ni, and Co in the dithizone extraction of Zn (85), and the complexing of Co, Cu, Ni, Zn, and Cd by CN^- permits the sole extraction of Al by 8-quinolinol (104). If the added substance is a chelating agent which forms water-soluble metal complexes, β may still become large, even though both agents have the same metal-complexing order, because the competition for the metal ions enhances the effect of small differences in complexing order. Ethylenediaminetetraacetic acid is frequently used as such a masking agent, for example, to hold back Fe, Cu, Ni, and Co in the 2-nitroso-1-naphthol extraction of Pd into toluene (39), and to hold back Cu in the dithizone extraction of Hg (91).

A special type of aqueous metal ion complexing is represented by association with OH^-, that is, by hydrolysis of the metal ion. This possible complication to the simple extraction scheme represented by equation 9′ was considered by Kolthoff and Sandell (183), who added a correction term to the denominator to represent the hydrolyzed species. Connick and McVey (44) in their study on the

distribution of Zr^{IV} between water and benzene in the presence of thenoyltrifluoroacetone, considered the possibility of mixed complexes as given by equation 11 with $X^- = OH^-$ and used the variation in the value of D with changing (OH^-) to determine the amount of average hydrolysis. That is, $\partial \log D/\partial \log (OH^-) = -\partial \log D/\partial \log (H^+) = n - \bar{I}$, where $\bar{I}$ is the average number of OH^- per metal cation, provided that there is no significant formation of chelate complexes in the aqueous phase. In the latter case it would be more difficult, but not impossible, to evaluate the parts of the hydrogen ion dependence due to aqueous chelate formation and to hydrolysis (267).

Another type of aqueous phase reaction that can be studied to advantage by determining the variation in D it causes is polymerization of the metal species, which for many polyvalent cations occurs simultaneously with hydrolysis. Connick and Reas (45) showed that in the TTA extraction of Zr into benzene from 1 or 2M $HClO_4$ solutions, the only metal species in the benzene phase was monomeric $Zr(TTA)_4$, and thus the decrease in D with increasing aqueous phase metal ion concentration was due to aqueous phase polymerization of the hydrolyzed zirconium, first to a dimer, and then to higher polymers as the metal ion concentration approached 0.1M. If neutral metal chelate polymers are also possible in the organic phase, it would become very much more difficult to unravel the metal ion concentration dependence.

With the use of basic solvents, complex formation or coordination with the solvent may also occur. This is possible with basic oxygen-, nitrogen-, or sulfur-containing solvents and, in fact, plays a major part in the extraction of ionic compounds, as discussed in Sections VI and VII. It has been observed even with chelate complexes: Rydberg reports mixed thorium complexes of acetylacetonate and methyl isobutyl ketone in the system, thorium(IV)–H_2O acetylacetone–methyl isobutyl ketone (267).

In all the cases mentioned so far it has been assumed that only the metal species MC_n exists in the organic phase. This has been confirmed in several cases by showing experimentally that D has an nth power dependence on $(HC)_o$ and on $1/(H)$, but is not always true; Rydberg (267) has shown, in fact, that in the extraction of UO_2^{2+} into chloroform with acetylacetonate, symbolized A^-, both UO_2A_2HA and UO_2A_2 extract. The former species probably carries

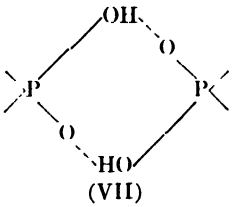
one water, and the latter two waters, of hydration, in order to give the UO_2^{2+} its usual coordination number of six toward oxygen. It is interesting to note that the partition constant for the dihydrate is only 3.3 compared to 22 for the monohydrate. Water of hydration is a handicap to good extraction into nonbasic solvents because the normal coordination energy of this water with other water molecules is lost on extraction; substitution by the acetylacetone molecule provides the first shell coordination for the UO_2^{2+} ion, while making the resulting complex even bulkier and more hydrocarbon-like and so less hydrophilic. This aspect of extraction involving coordinate solvation of the extracting species will be discussed again in Section VII, but it might be emphasized as a general phenomenon for those chelates whose coordination number is greater than twice their charge. For example, the alkaline earth ions usually have a coordination number of six, and so, although they form oxinate complexes in aqueous solution, these retain two water molecules in their first solvation shell and do not extract into chloroform. Luke and Campbell (196) found that Mg oxinate would extract into a butyl Cellosolve-chloroform mixture; presumably the Cellosolve oxygens have displaced the water molecules. Using 1*M* solutions of 8-quinolinol (HOx) in chloroform, Dyrssen (72) found that Sr would extract as $Sr(Ox)_2(HOx)_2$, the reagent molecules displacing the remaining two first-shell water molecules. Jankowski and Freiser (159) report that other alkaline earth ions can also be extracted with concentrated oxine solutions. Yet another possibility for extracting ions with coordination numbers greater than twice their charge is to use singly charged tridentate chelating groups or mixtures of singly charged and neutral bidentate reagents.

We shall now consider a class of extractants which is an important development of the last ten years. As early as 1949, it was recognized that the monobutyl and dibutyl phosphoric acids would extract uranium as well as, or better than, the neutral ester, tributyl phosphate. Dilute solutions of dibutyl phosphoric acid in dibutyl ether, containing some residual monobutyl acid, extract Zr^{IV} and In^{III} quantitatively, and Y^{III}, Nb^{V}, Sn^{IV}, Ta^{V}, and Mo^{VI} partially, from aqueous solutions 1*M* in nitric or sulfuric acid (272). Phosphoric acids containing larger alkyl groups, such as bis(2-ethylhexyl)phosphoric acid, have a lower water solubility and a smaller emulsifying tendency, and the corresponding phosphonic acids, $R(HO)_2PO$ and

$R(R'O)(HO)PO$, and phosphinic acids, $R_2(HO)PO$, show equally good extraction characteristics.

The mechanism of metal ion extraction into dilute solutions of these acids in kerosene, carbon tetrachloride, chloroform, benzene, or other nonpolar solvent is a cation exchange process, just as with the chelate systems already described, and may be considered formally analogous to the cation resin exchange process, although the analogy should not be carried too far, since the low dielectric constant kerosene phase, containing effectively no water, is quite dissimilar to an (aqueous) resin phase, even though the latter is ~50% hydrocarbon matrix.

A minor complication over the previous systems is that the dialkyl phosphoric (10,73,246) and phosphinic (184) acids appear to be dimeric in the nonpolar solvent, with a bridged structure (VII), and

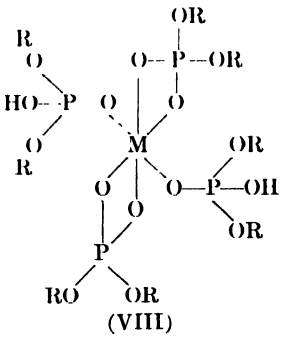


(VII)

so, presumably, are the dialkyl phosphonic acids. The monoalkyl phosphonic acids are probably still more highly associated. For example, in the extraction of uranium(VI) at low concentrations with bis(2-ethylhexyl)phosphoric acid, the value of the distribution ratio depends directly on the second power of the organic phase concentration of the (dimeric) acid an inversely on the second power of the aqueous phase hydrogen ion concentration (10). This indicates that the reaction can be written as

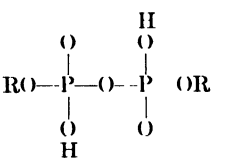
$$UO_2^{2+} + 2[(RO)_4P_2O_2(OH)_2]_{(o)} \rightleftharpoons UO_2[(RO)_4P_2O_3(OH)]_{2(o)} + 2H^+$$

The extracting species is possibly VIII, where M represents UO_2^{2+} with the two uranyl oxygens above and below the plane of the paper. The two phosphate anions are chelated to the cation, and to complete the usual six coordination of UO_2^{2+} toward oxygen, two more molecules of the acid are involved in primary solvation. This is very similar to the acetylacetonate case described earlier, except that both water molecules have been displaced. When the uranium concentra-



(VIII)

tion becomes appreciable compared to that of the phosphoric acid, there is no longer sufficient acid for each UO_2^{2+} to bond the two anions and two acid molecules. The two solvating acid molecules then exchange their hydrogens for uranyl ions, building up polymeric complexes in the organic phase. These tend to a limiting structure with two acid anions per uranyl ion; the six coordination of the latter is satisfied by sharing other oxygens in the bound phosphate anions. The dialkyl pyrophosphates (IX) show still higher extrac-



(IX)

tion for U^{VI} and especially for U^{IV} (194), possibly because a more stable complex results with six-membered chelate rings.

The extraction of several other metal cations has been reported for solutions of the mono- and dialkyl phosphoric acids in nonpolar solvents. Examples are Ti^{IV}, Zr^{IV}, Hf^{IV} (23), and Y^{III}, La^{III}, and the rare earths (250), as well as Bk^{IV} (251). Since all these cations have coordination numbers twice their charge, it is unlikely that additional molecules of acid are involved beyond the anions necessary to form the neutral complex. In all these cases, anions such as PO_4^{3-}, F^-, and Cl^- which form aqueous complexes with the cations hinder the extraction by competing with the alkyl phosphate anions. The possibility of studying such aqueous phase phenomena is indicated, as in the TTA studies mentioned earlier.

Under appropriate conditions the alkyl phosphoric acids also can extract the alkaline earth ions and even the alkali metal ions; in these cases it is perhaps not meaningful to talk of chelate complexes, but the extraction still probably has more in common with chelate complex extraction than with that of the coordinately unsolvated salts discussed in Section IV.

In conclusion, mention should be made of the carboxylic acid systems. These reagents may or may not form (four-membered) chelate complexes in the sense that both oxygens of the carboxylate group occupy a position in the first solvation shell of the metal ion, but again the mechanism of extraction is closer to that of the chelate systems than to that of the large, unhydrated salts. For example, the extraction of UO_2^{2+} by dilute solutions of salicylic acid in methyl isobutyl ketone corresponds to that by acetylacetone in chloroform even to the formation of both UO_2C_2 and UO_2C_2HC complexes in the organic phase (C stands for either the acetylacetonate or salicylate anion). The first compound presumably has two molecules of water; the second, one. Methoxybenzoic acid in methyl isobutyl ketone extracts only the UO_2C_2 species, but this is probably due to the difficulty in forming the UO_2C_2HC complex because of steric hindrance by the methoxy groups (139). These carboxylic acids, as well as 3,5-dinitrobenzoic acid and cinnamic acid, extract Pu^{IV} (123), Th^{IV} (140), and presumably other polyvalent cations.

Similarly, benzoic acid extracts Fe^{III}, Al^{III}, Sc^{III}, Ga^{III}, In^{III}, and Be^{II} into ethyl acetate or butyl or amyl alcohol (163). Sodium or ammonium butyrate extracts Cu, Mn, and Fe from neutral solutions into benzene; with butyraldehyde or ethyl acetate as solvent, butyrate also extracts Co and Ru (314). With 20% butyric acid in chloroform or ethyl acetate, Al and Fe (12) extract completely above pH 4 and Be (283) extracts around pH 9.7. Similarly, capric acid extracts Pd and Ru (314). There appears to be little information on the nature of the extracted species and on whether or not molecules of acid and/or water are involved in solvation of the cations.

The use of perfluorocarboxylic acids also allows extraction into diethyl ether (212). With perfluorobutyric acid, trivalent cations, e.g., Fe^{III}, Al^{III}, Cr^{III}, and also UO_2^{II} and Be^{II}, can be extracted from mono- and divalent cations, and with the larger perfluorooctanoic acid, divalent cations, e.g., Ca^{II}, Mg^{II}, Fe^{II}, Pb^{II}, and Zn^{II}, can also be extracted. Distribution into the organic phase increases with

increasing acid concentration and with higher pH. Optimum extraction occurs at a pH just below that at which the cation would precipitate as the hydroxide. From analyses of crystalline products obtained on evaporating the ether extracts, it seems that basic salts of the acids are formed, containing waters of hydration. Ether molecules may also be involved; here again more work is necessary before these systems can be properly described.

IV. Coordinately Unsolvated Salts

In the earlier discussion of the factors involved in the extraction of an ionic species into an organic solvent, it was noted that any significant change in either the primary or secondary solvation of an ionic species extracting into a less polar and/or lower dielectric constant medium is of prime importance. Obviously, if there is a large loss in solvation energy, extraction will be poor. In the cases already discussed (with the possible exception of the carboxylate systems), only uncharged molecular species are involved in the organic phase. The formation of such a neutral complex destroys both the ionic first shell hydration and the electrostatic secondary solvation, but this energy loss is compensated for by that gained in complex formation, and the resulting disturbance of the water structure by the (hydrophobic) complex leads to the complex being forced into the organic phase.

If the organic phase species themselves are to be ionic, as in the majority of the systems yet to be discussed, other means must be employed to ensure that the losses in primary and secondary solvation energies on entering the organic phase are small. Such will be the case if the hydration energies themselves are small. So we shall start by considering the extraction of large ions such as Ph_4As^+, Ph_4P^+, Bu_4N^+, and Ph_4B^-. The size and structure of these ions are such that they do not have a primary hydration shell in the sense we have defined, i.e., no coordinate bonding to the nearest waters.

Furthermore, the secondary orientation and polarization energy of an ion decreases with increasing ionic size (as $Z^2/2r$, by the Born equation). The bulk of the ion disrupts the hydrogen-bonded water structure at a cost of 4–6 kcal./hydrogen bond; and the larger the ion, the greater the amount of disruption and the greater the tendency for the ion to be pushed into the organic phase. With the exception

of hydroxylated solvents such as the alcohols, organic solvents do not possess a (hydrogen-bonded) structure, and the attractive interactions of the solvent molecules which must be displaced are van der Waals' interactions of the same order of magnitude as those between the ion itself and the nearest solvent molecules. But since the solvation energy in the organic phase is primarily electrostatic in nature, it will be greater the higher the dielectric constant of the solvent. As a general rule, then, for these systems, and in contrast to the simple molecules, we might expect the extraction to vary markedly from solvent to solvent, showing at least a rough correlation with dielectric constant.

Such large ion extraction systems have become useful in the separation and analysis of anions, as the larger singly charged ones, especially the oxy-ions such as ReO_4^-, MnO_4^-, ClO_4^-, IO_4^-, etc., fulfill the requirement of no primary hydration shell. Hence they extract well into organic solvents with equally large, or larger, cations such as Ph_4As^+, Ph_4P^+, Ph_3MeAs^+, Bu_4N^+, etc. It should be emphasized that these species extract as ions; they do not react chemically to form a neutral molecule, although in low dielectric constant solvents they may associate to ion pairs or higher aggregates. An expression for the distribution ratio can be derived for such large ion systems by considering the equilibria involved. With B^- the large ion of interest, and a large cation-containing reagent as the chloride, A^+Cl^-,

$$A^+ + B^- \rightleftharpoons A^+_{(o)} + B^-_{(o)} \qquad P_{AB} = (A)_o(B)_o/(A)(B)$$

$$A^+_{(o)} + B^-_{(o)} \rightleftharpoons A^+B^-_{(o)} \qquad K_{AB} = (AB)_o/(A)_o(B)_o$$

$$A^+ + Cl^- \rightleftharpoons A^+_{(o)} + Cl^-_{(o)} \qquad P_{ACl} = (A)_o(Cl)_o/(A)(Cl)$$

$$A^+_{(o)} + Cl^-_{(o)} \rightleftharpoons A^+Cl^-_{(o)} \qquad K_{ACl} = (ACl)_o/(A)_o(Cl)_o$$

Larger ion associations in the organic phase are also possible, charged as well as uncharged. We shall consider only the uncharged quadrupolar species as examples; the extension to larger aggregates is obvious.

$$2A^+_{(o)} + 2B^-_{(o)} \rightleftharpoons A^+B^-A^+B^-_{(o)}$$

$$K_{A_2B_2} = (A_2B_2)_o/(A_o^2)(B)_o^2$$

$$2A^+_{(o)} + B^-_{(o)} + Cl^-_{(o)} \rightleftharpoons A^+B^-A^+Cl^-_{(o)}$$

$$K_{A_2BCl} = (A_2BCl)_o/(A)_o^2(B)_o(Cl)_o$$

and so

$$D = [(B)_o + (AB)_o + (A_2B_2)_o + (A_2BCl)_o]/(B) \quad (12)$$

where charges have been left out for simplicity. With low dielectric constant solvents such as have usually been employed in these extraction systems, the first term in the numerator, that involving the concentration of dissociated B^- in the solvent, is negligible, and so (neglecting any charged aggregated species in the organic phase also) this can be transformed into

$$D = K_{AB}P_{AB}(A) + K_{A_2B_2}P_{AB}^2(A)^2(B) + K_{A_2BCl}P_{AB}P_{ACl}(A)^2(Cl) \quad (13)$$

The resulting expression has a fairly involved dependence on the concentration of several ions, including B^-, due to the ionic aggregates in the organic phase. If the concentration of B^- is small, as is usually the case, the second term on the right becomes negligible, and if the reagent concentration in the organic phase is also not too high, the last term drops out, so that A^+B^- is the only important organic phase species of B^- and

$$D = K_{AB}P_{AB}(A) \quad (14)$$

or

$$D = K_{AB}P_{AB}(ACl)_o/K_{ACl}P_{ACl}(Cl) \quad (14')$$

These expressions are similar to the simplified ones for chelate extraction systems, as they should be, for although no molecular species is present in the organic phase as with the chelate complex, the undissociated ion pair, A^+B^-, behaves thermodynamically as a molecule. Both formulations 14 and 14′ are valid, of course, but if the reagent is mainly in the aqueous phase so that its total concentration $\approx$ (A), there is no chloride dependence, since (Cl) and $(ACl)_o$ increase together, and equation 14 is the more useful. If the reagent is predominantly in the organic phase so that its total concentration $\approx (ACl)_o$, equation 14′ is the form more easily applied, and there will be an inverse dependence of D on the aqueous chloride concentration. (Exactly the same situation holds for the hydrogen ion dependence of D in chelate extraction systems.)

Equations 14 and 14′ were derived by Tribalat and tested on the extraction of ReO_4^- into $CHCl_3$ by $Ph_4As^+Cl^-$, where they held over a range of reagent and added chloride concentrations (290).

In similar fashion ReO_4^- is extracted into chloroform with Ph_4P^+ (291) and with triphenylbenzylphosphonium chloride (292). In fact, ReO_4^- should be extracted by any large cation, e.g., alkyl- or aryl-substituted ammonium, phosphonium, arsonium, stibonium ions, etc. Any other large anion such as TcO_4^- (293), MnO_4^- (293), or IO_4^- could replace ReO_4^-. In fact, for analytical purposes, this lack of specificity is something of a handicap, as any relatively large, unhydrated univalent cation will extract any such large univalent anion. On the other hand, polyvalent ions, because of their greater hydration energy, are not so easily extracted; hence good separations are possible between ReO_4^-, MnO_4^-, or TcO_4^- and MoO_4^{2-}, WO_4^{2-}, or CrO_4^{2-}, for example.

Of course, the procedure may equally well be used to extract a large univalent cation with a large univalent anion as reagent. For cations such as Ph_4As^+ or Bu_4N^+ this works well into chloroform with, say, $K^+MnO_4^-$, but with smaller cations such as Me_4N^+, or more importantly, the (hydrated) alkali metal ions, extraction is too poor to be useful. Extraction can be improved by using a higher dielectric constant solvent, such as bis(2-chloroethyl) ether ($\epsilon = 21.2$), nitrobenzene ($\epsilon = 34.8$), or nitromethane ($\epsilon = 35.9$), or by using still larger anions, such as Ph_4B^-, or both. Thus the alkali cations can be extracted into nitromethane with the reineckate ion, $Cr(NH_3)_2(SCN)_4^-$ (94). The order of extraction increases as expected from lithium to cesium, that is, in the order of increasing size and decreasing hydration. With the smaller ReO_4^- ion, the extraction is much poorer, but the order of cations the same (94). With the larger Ph_4B^- ion, still better extraction into nitrobenzene ensues, being essentially quantitative for cesium (88). Similarly, as was demonstrated at the turn of the century, the alkali cations can be extracted into nitrobenzene with polyiodide ions, the order of extraction increasing from lithium to cesium to $(CH_3)_4N^+$ (54); and the larger the polyiodide ion, the better the extraction (27). Nitrobenzene or nitromethane is better than diethyl ether or other lower dielectric solvents.

However, if solvents of high dielectric constant are used to improve the extraction, the resulting specificity of the system is reduced, as all ions, including divalent and small ones, become more extractable. More importantly, dissociation of the ion pairs in the organic phase occurs, especially at low concentrations. This means that the first

term in the numerator of equation 12 is now the most important, i.e.,

$$D = (B)_o/(B) = P_{AB}(A)/(A)_o \qquad (15)$$

The expression of electroneutrality in the organic phase, $(A_o) = (B)_o + (Cl)_o$, can be used to transform equation 15 into

$$D = P_{AB}\{(A)/[P_{AB}(B) + P_{ACl}(Cl)]\}^{1/2} \qquad (15')$$

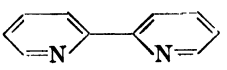
This indicates a more complicated dependence of D on ionic concentrations than when the extracting species was ion-paired. For example, when $P_{AB}(B) < P_{ACl}(Cl)$, there is no dependence of D on the concentration of the ion of interest, B^-, but when $P_{AB}(B) \gtrsim P_{ACl}(Cl)$, D decreases with increasing (B), eventually as $(B)^{-1/2}$. This decrease occurs even though no polymerization of B^- is involved in either phase, which is quite a different situation from that in the systems discussed so far where a dependence of D on the concentration of the species of interest indicates such polymerization. In the present case, this is strictly the result of a "common ion" effect acting through A^+ when the aqueous phase concentration of A^+ is determined by one compound, A^+Cl^-, and the organic phase concentration of A^+ is dominated by a different one, A^+B^-. Also, even in the limiting cases, D now shows a smaller dependence upon the concentrations of A^+ and Cl^-, i.e., $(A)^{1/2}$ and $(Cl)^{-1/2}$, rather than the first-power dependence of equation 14'. Perhaps the greatest change in the nature of the extraction process when dissociated ionic species are involved in both phases is the possibility of variation in the distribution ratio of the ion of interest when the concentration of any ionic species that extracts into the organic phase is altered. This effect does not show in equation 15' because in its derivation no other ions were assumed to be present in the solvent. But if ions M^+ and X^- are present, they must be included in the equation expressing the electroneutrality of that phase, $(A)_o + (M)_o = (B)_o + (Cl)_o + (X)_o$, and so equation 15 becomes

$$D = P_{AB}/P_{ACl}^{1/2}\{[P_{ACl}(A) + P_{MCl}(M)]/[P_{AB}(B) + P_{ACl}(Cl) + P_{AX}(X)]\}^{1/2} \qquad (15'')$$

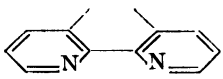
Thus D may depend upon the concentration of any ion present in the system. Since very little work has been done to examine these variations in the case of the large ion systems (63), further discussion

of this point will be postponed to the treatment of the complex metal acids where the effect was first described (60,268) and where experimental evidence is available.

The discussion given holds well for the commoner univalent anions, especially the oxygenated ones, since they fulfill the requirement of no primary and little secondary hydration. Most cations of interest, however, with the exception of the heavier alkali metal and substituted ammonium ions, do not meet this requirement, being polyvalent as well as small. They cannot, in general, extract into the organic phase because of the too great loss of solvation energy involved, unless they are suitably modified. One way to do this is to make the cation very large and hydrocarbon-like. Certain chelate reagents having two uncharged basic groups such as α,α'-dipyridyl (X) and 1,10-phenanthroline (XI) form cationic complexes with



(X)



(XI)

some metal ions such as Cu^{I} and Fe^{II}, but even so the resulting chloride salts do not extract appreciably into chloroform or similar solvents. From the previous discussion it might be anticipated that by using larger anions and/or higher dielectric constant solvents, good extraction could be obtained. This has been shown experimentally; tris(phenanthroline)iron(II) perchlorate extracts moderately well into chloroform and quite well into nitrobenzene (202), and by using still larger anions, such as long chain alkyl sulfate or sulfonate ions, the dipyridyl complex can be essentially completely extracted into $CHCl_3$ (256).

Alternatively, still larger chelating reagents can be used, such as alkylated or arylated phenanthrolin, e.g., 2,9-dimethyl-1,10-phenanthroline and 4,7-diphenyl-1,10-phenanthroline. The complex cations formed by these with Fe^{II} and Cu^{I} extract well into the water-insoluble alcohols such as amyl and hexyl alcohols (277,278) or into chloroform–ethyl alcohol mixtures (100); presumably their perchlorate salts would extract even better into higher dielectric constant solvents. Dimethylphenanthroline is rather specific for Cu^{I}, since the two methyl groups near the nitrogens block the formation of the tris(phenanthroline)iron(II) complex (100,195).

As a last example of making a cation large and extractable by transforming it into a chelate cation, the bis(2,2′,2″-terpyridyl)-cobalt(II) cation will be noted. This extracts as the ClO_4^- salt into a variety of organic solvents (211); of those tested (benzene, diethyl ether, carbon tetrachloride, chloroform, hexyl and isoamyl alcohols, and nitrobenzene), nitrobenzene is the best, in line with the present discussion. Extraction is better with ClO_4^- than with the smaller I^- or SCN^- ions, which, however, are better than Cl^- and CN^-.

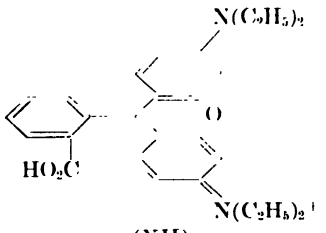
Another general method for making small, polyvalent metal cations extractable is to transform them into large complex anions. One way is to form chelate complexes, but this time negatively charged ones. For example, the colored, water-soluble complex formed by three molecules of 8-iodo-8-quinolinol-5-sulfonic acid (ferron) with one Fe^{III} ion is extractable with Bu_3HN^+ into isoamyl alcohol in the pH range 2–7.5 (324). The sulfosalicylate complex of titanyl ion can be extracted with Ph_4As^+ or Bu_3HN^+ into chloroform in the pH range 2.4–4.6 (323). Still another example is the formation of an anionic complex of UO_2^{2+} with 8-quinolinolate ion (or with benzoin-2-oxime, cupferron, hydroxylamine, peroxide, or pyrogallol); this is extractable into ketones, alcohols, diethyl ether, chloroform, etc., in the presence of a large tetraalkylammonium cation (40).

The expression for the distribution ratio for these systems, as well as for the preceding complex cation cases, is slightly more complicated than equation 14 or 15, since allowance must be made in the denominator for the various aqueous phase complex ions. Thus, in the last example,

$$D = [(UO_2Ox_3)_0 + (R_4NUO_2Ox_3)_0 + \text{higher ion associations}]/[(UO_2) + (UO_2Ox) + (UO_2Ox_2) + (UO_2Ox_3)]$$

where Ox represents the 8-quinolinolate ion. Depending upon the dielectric constant of the solvent, this would lead to an expression like 14′ or 15′, but with an additional factor of $[1 + K_{UO_2Ox}(Ox) + K_{UO_2Ox_2}(Ox)^2 + K_{UO_2Ox_3}(Ox)^3]^{-1}$ bringing in the dependence on the complexing agent.

Another way of converting some of the transition metal ions into large, coordinately unhydrated anions is to form their halide or pseudohalide complex anions. Thus, Webster and Fairhall (309) have shown that the large amine dye cation Rhodamine B (XII) will extract Sb^V from aqueous 6*M* HCl into benzene to give



(XII)

a violet-colored organic phase (useful for photometric analysis). Kuznetsov (186) pointed out that this was due to a compound formed by the dye cation and an Sb^V anion, insoluble in water but extractable into the solvent. Other complex metal chlorides give similar precipitates with Rhodamine B, and reduced antimony does not extract. The extractable Sb^V anion is most likely $SbCl_6^-$, even though in the aqueous 6*M* HCl the principal species may well be a partially hydrolyzed one, e.g., $Sb(OH)Cl_5^-$ (239); it should be remembered that the principal organic phase species does not have to be the same as the principal aqueous phase one. Ramette and Sandell (258) have shown that *D* for extraction into benzene varies linearly with the equilibrium aqueous phase dye concentration, at constant aqueous HCl concentration, as indicated by equation 14, and have discussed the fact that small amounts of orange-colored $RH(SbCl_6)_2$ and $RHClSbCl_6$ (where R is the Rhodamine B cation) may also extract at high HCl concentrations where the dye cation becomes protonated. It seems possible that the decrease in *D* observed with increasing HCl concentration above about 3–4*M* may be due to the increasing proportion of the dye in the protonated (and thus more highly charged and less extractable) form.

Feigl, Gentil, and Goldstein (82) have shown that Tl^{III} as $TlCl_4^-$ or $TlBr_4^-$ is extractable with the Rhodamine B cation from aqueous hydrohalic acid solution into benzene, ether, $CHCl_3$, or amyl alcohol, as are $SbBr_6^-$, $FeCl_4^-$, $FeBr_4^-$, $AuCl_4^-$, $AuBr_4^-$, NCS^-, and mercury (II). Similarly, Onishi and Sandell (241) studied the extraction of $GaCl_4^-$ into benzene with Rhodamine B; over the limited range studied, the distribution ratio was shown to be independent of the Ga concentration and to increase with increasing HCl concentration. The increase in *D* with increasing HCl, up to about 6*M* acid, is due to the increasing fraction of gallium in the extractable $GaCl_4^-$ form, and the subsequent decrease is probably due to the increasing protona-

tion of the dye cation. In contrast to Ga^{III}, Au^{III} forms the $AuCl_4^-$ complex so readily that even at a few tenths molar HCl the complex is the predominant species in both phases, and the value of D falls continuously with increasing acid (201). Similarly, SbI_4^- extracts into benzene with Rhodamine B (313), and the extraction of BiI_4^- with $(C_{16}H_{33})_4N^+$ (106) has been used in analytical chemistry for over 30 years.

In fact, it can be expected that any uninegative halometallic complex anion should be extractable into a variety of organic solvents by a variety of large organic cations. If the organic cation is a dye, this permits photometric determination of the extracted salt, although all the other extractable anions will interfere unless held in the aqueous phase in some manner. Thus, methyl violet extracts Sb^V from $6M$ HCl ($SbCl_6^-$) into benzene (160), as does malachite green (19), the cation of anthraquinone-1-azo-4-dimethylaniline (186), and a large number of other amine cations, such as those derived from *p*-aminoazobenzene, its methylated and ethylated derivatives, etc. (20). Although such procedures have not been described in the literature, the corresponding salts with the other uninegative halometallic anions must likewise extract. Nor are such large dye cations necessary; the smaller alkyl- and aryl-substituted ammonium, phosphonium, and arsonium cations, e.g., Ph_4P^+ and Ph_4As^+, give chloroform-extractable precipitates with the uninegative chloro and bromo complex anions of Fe^{III}, Ga^{III}, Au^{III}, etc., and are said to extract the dinegative halo complexes of Ir^{IV}, Os^{IV}, Pt^{IV}, and Pd^{II} as well (235,236).

Complex anions formed with the larger, pseudohalide ions, such as thiocyanate, are often stronger than the chloride ones and, being larger, are more extractable, so that the polyvalent complex anions may extract. Ziegler and Glemser (321,322) have noted the extraction of $Co(SCN)_4^{2-}$ and $Co(CNO)_4^{2-}$ with Bu_3HN^+ into a number of solvents. Ellis and Gibson (76) have shown that Cu^{II} extracts as the $Cu(SCN)_4^{2-}$ complex with Ph_3MeAs^+ into $CHCl_3$, CH_2Cl_2, and (best) into *o*-dichlorobenzene, as does Co^{II}. Dwyer and Gibson (66) studied the extraction of Fe^{III} from thiocyanate solutions with Ph_3MeAs^+ into *o*-dichlorobenzene and also prepared the crystalline salt $(Ph_3MeAs)_3Fe(SCN)_6$ (67). The spectrum of this salt dissolved in *o*-dichlorobenzene was slightly different from that in extract solution; the absorption maximum shifted to longer wavelengths.

They ascribed this behavior to the dissociation of the salt into $Ph_3MeAsSCN$ and lower complexes of iron, i.e., $(Ph_3MeAs)_2Fe(SCN)_5$ and $Ph_3MeAsFe(SCN)_4$. Ziegler, Glemser, and Petri (325) report similar observation with $(Bu_3NH)_3Fe(SCN)_6$ in isoamyl acetate, and much earlier Rosenheim and Cohn (260) noted this behavior for alkali hexathiocyanatoferrate salts in diethyl ether. This dissociation is probably enhanced in the low dielectric constant organic solvents where highly charged species are disfavored; Bock (24) finds that the iron thiocyanate species in the diethyl ether phase after extraction from aqueous ammonium thiocyanate is, in fact, the tetrathiocyanate complex, $Fe(SCN)_4^-$.

Finally, as a last example of coordinately unsolvated salt systems, the use of high molecular weight secondary and tertiary alkylammonium salts in relatively nonpolar solvents should be mentioned. Such systems have become important in the last few years in connection with uranium process technology and show promise of wider application in metal ore processing and in analytical chemistry, as well as being of interest because of the organic, inorganic, and physical chemistry problems involved. The virtually complete extraction of simple strong acids, such as HCl, H_2SO_4, and HNO_3, and the partial extraction of some weak acids by chloroform or nitrobenzene solutions of long chain amines such as methyldioctylamine was shown by Smith and Page (276) in 1948. Such acid extraction will be discussed in Section V, but Smith and Page also recognized that once the acid had extracted, the resulting ammonium salt behaved somewhat like an anion exchange resin and could exchange its anions with others in the aqueous solution. This formal analogy with anion exchange resins is of great practical help to the analytical and process chemist in working out separation schemes, but should not be overstressed. The extraction (or exchange) of anions from the aqueous phase by an organic solution of the substituted ammonium salt gives, in general, the expected order, namely, that the less the hydration of the anion—i.e., the lower the charge, the larger the size, and the more hydrophobic the structure of the anion—the better the extraction.

A number of investigators have studied the extraction properties of substituted ammonium salts (4,5,32,48–50). Although the free amines themselves are quite soluble in organic diluents, their salts are much less so, generally showing a decreasing solubility in the order sulfate, acid sulfate, chloride, and nitrate and in the order tertiary, secondary,

and primary ammonium salt. Branching in the alkyl groups of the amines increases solubility, and aromatic diluents allow greater concentrations than aliphatic solvents. The extraction of a metal from the aqueous phase by the amine salt solution takes place when the metal ion is an anionic oxo species, e.g., V^{V} and Mo^{VI}, or forms a complex ion with sulfate, chloride, etc., in the aqueous phase, e.g., Fe^{III} and U^{VI}. The distribution ratio for the metal will be independent of its concentration if the metal species are all monomeric; for polymers, D will increase or decrease with metal concentration depending upon whether the polymeric species are more or less extractable than the monomeric ones. From aqueous sulfate solutions, U^{VI} and Fe^{III} provide examples of constant D, while V^{V} and Mo^{VI} show an increasing D with increasing metal concentration (41). The hydrogen ion concentration may also have an effect on the distribution ratio through reaction with the complexing anion, e.g., $SO_4^{2-} + H^+ \rightleftharpoons HSO_4^-$, or by influencing metal ion hydrolysis. These effects are all as would be expected, but the dependence of D on the amine salt concentration appears rather unusual. Simple considerations of the equilibria involved, as used in deriving equation 14′, lead to the expectation of an nth power dependence of D on the organic phase amine salt concentration, where n is the number of amine groups involved per metal anion. From saturation experiments, the number of ammonium cations per metal anion in the organic phase species has been determined for several metal sulfate complexes and appears to be 2 for Fe^{III} and 4 or 6 for U^{VI}, depending upon the amine (41). A 2nd, 4th, or 6th power dependence is to be expected, but in each case a direct dependence of D on the alkylammonium concentration is observed. This can be explained most simply by the assumption that the amine salts in the organic diluent are associated into colloidal aggregates of nearly constant composition, but light-scattering and isopiestic measurements have shown that some, but not all, of the amine salt solutions are aggregated. The influence of the structure of the amine on the distribution is also somewhat obscure. Some metals, e.g., Fe^{III}, the rare earths, Ti^{IV}, Zr^{IV}, Th^{IV}, and U^{IV} extract best from sulfate solutions into the salts derived from primary amines, worse into secondary amine derivatives, and poorest into those derived from tertiary amines. The extraction of other metals, such as U^{VI} and V^{V}, is practically independent of amine class. In either case branching of the alkyl

groups near the nitrogen usually lowers D, presumably a steric effect, but the effect of branching is tied in with the nature of the hydrocarbon diluent used. For example, with chloroform, U^{VI} extraction with either secondary or tertiary amine salts generally is in the order straight chain > branched chain, but with kerosene the order reverses. Obviously, more work is in order for the complete unravelling of the mechanism of this extraction process.

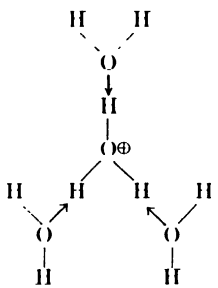
V. Mineral Acids

A separate discussion of the distribution of the simpler inorganic acids between two immiscible solvents illustrates a number of factors characteristic of the extraction of hydrated ionic species, especially in contrast to the behavior of covalent molecules. It was noted earlier that in general the extraction of a covalent molecule from aqueous solution is possible with essentially any organic solvent which is immiscible with water, although specific effects modify the partition coefficient in certain cases. Small ionic species, however, are relatively strongly solvated in aqueous solution by the highly polar water molecules, to an extent depending on their charge density and chemical properties. There is consequently little tendency for them to extract into nonpolar, noncoordinating solvents which cannot compensate for the resulting loss of hydration energy. Similar reasons, of course, account for the insolubility of ionic crystals in such solvents. Only those solvents which can provide primary solvation and/or a high dielectric medium can overcome the forces which hold the crystal together.

The solubility of salts in organic solvents will be discussed in Section VII, and it will be shown that for some solvents (the alcohols) and for certain types of salts, the solvation may be large enough to cause appreciable solubility. For the present discussion it will be sufficient merely to note that many organic solvents possess functional groups which confer basic properties upon the parent molecule. Oxygenated solvents such as ethers, ketones, and esters have such properties, for example, by virtue of the availability of a pair of electrons of the oxygen atom for donor-acceptor bonding. The basicity of the amines is a well-known example of the effect of the lone pair of the nitrogen atom. The basicity of these and other organic compounds has been discussed by Gordy and Stanford (114).

Water itself is, of course, an amphoteric solvent which can bind to other water molecules and to other suitable species by hydrogen bonding and/or induced dipole interactions. In a two-phase system containing ions which can be solvated, basic organic solvents must compete then with water for coordination with these ions. If the properties of the organic solvent are suitable, the result may be the formation of a complex species which is sufficiently solvated by the nonaqueous solvent to allow it to pass into the organic phase. This is in contrast with the behavior of molecular species for which, in general, the chemical nature of the solvent is not a critical factor.

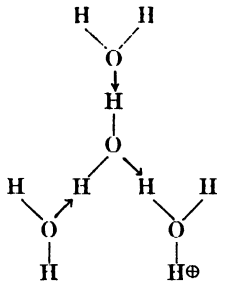
The hydrogen ion possesses properties which make it especially suitable for this coordinate solvation. The unique behavior in aqueous solution arises from its high charge density. There is now increasing evidence (13,107,109,302,308,317) that in water the H_3O^+ ion has three water molecules hydrogen-bonded to it in the primary hydration shell to give the symmetrical species XIII



(XIII)

These water molecules are bound more strongly than might be expected from the size of the hydronium (H_3O^+) ion (similar to potassium ion), because the positive charge is not distributed over the surface of the ion, but is concentrated at the three hydrogens, causing strong hydrogen bonding to the three water molecules. This hydrated structure is further solvated either by more water molecules or by the basic organic molecules, the oxygen (or nitrogen) of the solvent molecule bonding to the first-shell water molecule through one of the latter's hydrogens. This secondary solvation is more favorable for H_3O^+ than for any other small cation, since the positive charge concentrated on the (inner) hydronium hydrogens can shift to the (outer) hydration water hydrogens by the vibration jump

mechanism responsible for the high equivalent conductivity of H_3O^+ in water. That is, one of the inner protons can jump over to one of the hydration shell water molecules leading to a structure (XIV)



(XIV)

in which one of the hydration shell waters becomes, temporarily, the center of positive charge. The hydrogens of this molecule, carrying a partial positive charge, can now hydrogen-bond more strongly to the basic oxygen of the solvent molecule than the less polarized water molecule in the hydration shell of, say, a lithium ion (63a). Structure XIV indicates, of course, only one of three equivalent locations of the positive charge. This proton jump process in the hydrated hydronium ion is unique among cations and obviously cannot occur with the alkali or other cations; along with the stronger first-shell hydration already mentioned, it should contribute to a larger solvation energy in the organic phase for the acids than for salts of the same anion. These arguments, then, suggest reasons for the much higher extraction of the acids of both the simple and complex metal anions compared with the alkali metal salts. With strongly basic solvents, salts may extract because the solvent can displace a water molecule from the first hydration shell and so form a stable extractable species. These are, however, somewhat specialized circumstances and are discussed in Section VII.

An effect of solvation in the organic phase is illustrated by the extraction and dimerization of the lower molecular weight fatty acids discussed in Section II. The published data on the extraction of the chloroacetic acids have been re-examined by Brown and Mathieson (31) who have shown that the data can be fitted to a two-parameter equation. The two factors involved are dimerization in the organic phase and the possibility of interaction between the acid

monomer and the solvent. In aqueous solution, the (bound) acidic hydrogen of a fatty acid molecule is almost certainly solvated by at least one water molecule. The largest part of the molecule, however, is the hydrophobic alkyl group which tends to force the molecule into the organic phase in a two-phase system. In this process the original hydration energy of the acid proton must be compensated for in some way, either by dimerization or by solvation by the organic solvent, depending on the nature of the solvent used. In nonhydrogen-bonding solvents of low dielectric constant the acids exist largely as dimers, and in any given solvent of this type the more highly chlorinated acids are the more highly associated. With a basic solvent, the ability to interact with the acid by hydrogen bonding brings about the dissociation of the dimers. It appears that the more highly chlorinated acids, which are, of course, the stronger acids, hydrogen-bond the more strongly with the basic solvents. This treatment emphasizes the importance of solvation in the organic phase in the extraction of acidic species. In this connection, it is worth noting the effect of basicity on the solubility of water in organic solvents (133). The solubility in hydrocarbons in typically equivalent to a mole fraction of 10^{-3}–10^{-4}; in ethers, on the other hand, the solubility is orders of magnitude higher than this, and it seems clear that this is due to the basic character of these solvents. In the case of strongly basic phosphoryl compounds, the solubility of water corresponds to the complete formation of a 1:1 complex such as TBP·H_2O (3,218,296). In keeping with this acid-base interaction, the corresponding complex with hydrogen peroxide has a larger formation constant (297); the latter is, of course, a stronger acid than water.

As an extreme example of the effect of solvation on the extraction of minerals acids, one may cite the work of Smith and Page (276) who showed that long chain aliphatic amines will bring about the extraction of hydrochloric acid into chloroform. With a 5% solution of methyldioctylamine in this solvent, they achieved almost complete extraction of chromic, hydrochloric, nitric, oxalic, succinic, sulfuric, and *p*-toluenesulfonic acids; even phosphoric acid, which is strongly hydrated in aqueous solution, was 50% extracted from 0.1*N* solution.

The evidence for the formation of hydrogen-bonded complexes between basic solvents and acid molecules relates almost entirely to mineral acids, and in particular to nitric acid. Sutton (284) was

probably the first to interpret the extraction of nitric acid into diethyl ether in terms of the equilibrium,

$$HNO_3 + Et_2O_{(o)} \rightleftharpoons Et_2O \cdot HNO_{3(o)} \qquad (16)$$

although this system is in fact complicated by the appreciable solubility of ether in aqueous nitric acid. Glueckauf (108) has pointed out that the formation of such a hydrogen-bonded complex is a common feature of all ternary systems involving ethers in equilibrium with nitric acid and water. The heat of hydrogen bonding in the organic phase has also been reported by this author as approximately -7 kcal./mole. A mass action treatment of the extraction of nitric acid in dibutylcarbitol has been given (294), and it has been shown to be necessary to write the equilibrium constant for equation 16 in the form

$$(R_2O \cdot HNO_3)/(R_2O) = \text{constant} \times a_{HNO_3}$$

where $(R_2O \cdot HNO_3)$ and (R_2O) are the concentrations of complexed and uncomplexed ether in the organic phase, and a_{HNO_3} is the activity of nitric acid in the equilibrium aqueous phase. This is obeyed satisfactorily up to the point at which addition of nitric acid to a second oxygen atom of the solvent molecule begins to occur. A similar effect has been noted in the extraction of nitric acid into tri-*n*-butyl phosphate which possesses two different types of oxygen atom; the ethereal oxygens of the butoxy group are much less basic in character than the strongly polar P—O group (296). As a result, there is a marked change in the behavior of the system once the formation of the 1:1 complex is complete. Alcock *et al.* (2) have shown that with very concentrated nitric acid and in the presence of a diluent in the organic phase, a third phase appears; the composition of this phase corresponds to $TBP \cdot HNO_3$. The behavior of this solvent is further complicated by the appreciable solubility of water in the organic phase so that one has to consider the two equilibria

$$H_2O + TBP_{(o)} \rightleftharpoons TBP \cdot H_2O_{(o)}$$

$$HNO_3 + TBP_{(o)} \rightleftharpoons TBP \cdot HNO_{3(o)}$$

Confirmation of hydrogen bonding in such systems by physical methods has not been reported in many cases. The ultraviolet spectrum of nitric acid–butyl ether extract solutions has been investigated

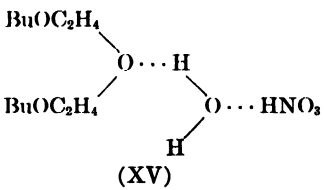
by Vdovenko, Lipovskii, and Kuzina (303) who find spectral changes corresponding to hydrogen bonding. Changes have been noted in the infrared spectrum of dibutylcarbitol in the presence of nitric acid (294), and of tri-*n*-butyl phosphate on the addition of one molar equivalent of water (2). There seems to be opportunity for more work on this aspect of the subject.

We shall discuss the nature of the extracted species in the organic phase later in this section and note here the differences in the extraction of the inorganic acids. Nitric acid extracts into basic solvents better than the other mineral acids which have been studied. The extraction into diethyl ether has been known for many years and more recently solvents such as methyl isobutyl ketone (255), dibutylcarbitol (294), pentaether (199), diisopropyl ketone (295), and a number of others (181) have been reported. Nitric acid is weak (K_{diss} = 23 (259)) compared with the hydrogen halides and shows appreciable covalent character in the pure state. With ethers and ketones, the extraction of hydrogen chloride and bromide is poor, with values of D typically around 0.02; with alcohols, D increases ten-fold, reflecting the stronger solvating properties of these solvents (47). Tributyl phosphate will also extract the hydrogen halides to about the same extent as the higher alcohols (300). Perchloric acid, on the other hand, will extract into ethers and ketones nearly as well as nitric acid (e.g., $D \sim 0.3$ at moderate concentrations) (64,295). It is interesting to note that for the hydrogen halides there is evidence of the solubility of basic organic solvents in their aqueous solutions (37,191,203,298). This implies that the hydrogen halides do in fact interact with the solvents, as one might expect, but that the resultant complex does not readily extract into the organic phase.

Sulfuric acid does not extract into ketones, ethers, or esters, but does extract into alcohols (295,316). Phosphoric acid likewise does not extract into diisopropyl ketone (295). These facts illustrate the competition between water and the organic solvent. Both these acids are known to have strong primary hydration in aqueous solution; for sulfuric acid this arises from the presence of two oxy and two hydroxy groups which can hydrogen-bond water molecules very strongly. Extraction into alcohols is possible, of course, since such solvents can solvate the anion, but with nonhydroxylated solvents the competition strongly favors the aqueous phase. Similar arguments apply to phosphoric acid. It is significant that anhydrous sulfuric

acid is soluble in ether (254), and that aqueous solutions of both sulfuric and phosphoric acid dissolve appreciable quantities of this solvent (179,203) so that the poor extraction does not arise from any inability to interact with the solvent. It is worth recalling the similar effect of anionic hydroxy groups on the extraction of organic acids (243).

Information on the chemical state of the extracted acid species in the organic phase is now becoming available. For the very strong acids, there appears to be some unity of behavior in this respect. We have noted earlier the unique properties of the proton and the way in which they lead to the formation of a tetrahydrated species $H_9O_4^+$ in aqueous solution. Recent evidence by the present authors (300) suggests that this configuration is maintained in the extraction of strong acids into certain basic solvents. For perchloric acid into dibutyl cellosolve and diisopropyl ketone, a hydration number of $\sim$4 was found. Hydrochloric and hydrobromic acids do not extract sufficiently into ethers and ketones for similar experiments to be carried out, but tri-*n*-butyl phosphate extracts these acids quite appreciably. Here, again, the results indicate that for these acids and for perchloric acid, four water molecules accompany each acid molecule into the organic phase. The competition of the organic solvent and water under these circumstances must be for the coordination positions of the $H^+(H_2O)_4$ species. For weaker acids, however, the situation is much less clear-cut. Most of the experimental data relate to nitric acid, and there are obvious differences of opinion on the interpretation of the results. Glueckauf (108) and McKay (199) believe that water can pass into the organic phase by interaction with any donor species, including the nitric acid–solvent complex, so that no true hydrates are formed. Results from experiments with a different analytical method (294), however, suggest that with dibutyl carbitol the extracted species is $H_2O \cdot HNO_3$, which may exist in the solvent phase as a complex (XV). A different type of behavior is shown with tri-*n*-butyl phosphate for which there is evidence that



(XV)

the extraction is the result of the formation of a complex TBP·HNO_3, which is unhydrated (2,296). Addition at the less basic ester oxygens, however, seems to involve $H_2O \cdot HNO_3$ species once more. On this basis one can expect hydration numbers less than unity by formation of both $R_2O \cdot H_2O \cdot HNO_3$ and $R_2O \cdot HNO_3$ species in amounts depending on the basicity and chemical nature of the solvent; values greater than unity might arise by combination of one or both of these with $R_2O \cdot H(H_2O)_4NO_3$. It is clear that these problems will have to be resolved before a satisfactory picture of solvation processes in the organic phase can be presented, and the use of physical methods of investigation should give much helpful information. It is worth noting in this respect that trichloroacetic acid has been recently studied (64) and behaves in much the same way as nitric acid, suggesting that acid strength may be a critical factor in determining the nature of the extraction complex. This acid extracts into dibutyl Cellosolve with ~1 mole of water per mole of acid, as does nitric acid.

One thing that does seem agreed is that such acids are only weakly dissociated in the organic phase. McKay and his co-workers (2) have published data on the conductivity of solutions of nitric acid in tri-*n*-butyl phosphate over a wide range of concentrations and have made estimates of the dissociation, which is always below ~1% even at $10^{-3}M$ acid.

From this review of the extraction of the mineral acids, the following tentative suggestions may be advanced to explain the order of the distribution ratio for a given ethereal or ketonic solvent. It appears that at least three factors must be considered:

1. Acid strength, which divides the monobasic acids investigated so far into two groups; $HClO_4$, HI, HBr, and HCl are very strong acids and CCl_3COOH and HNO_3 are weaker ones. One would expect the second group to extract well because of the greater ease of formation of the neutral molecule.

2. Within these two groups, the effect of molecular size would give the order $HClO_4 > HI > HBr > HCl$ and $CCl_3COOH > HNO_3$.

3. Solvation. With nonhydroxylated solvents, the anions cannot receive primary coordinate solvation. However, they may be solvated in aqueous solution; hydration numbers have been estimated by Glueckauf (107) as $ClO_4^- = 0.3$, $Cl^- = Br^- = I^- = 0.9$, and $NO_3^- = 0$. This implies that the halides will be bound more strongly into

the aqueous phase than the perchlorates. This effect of anion solvation has already been discussed in connection with sulfuric and phosphoric acids and a number of the organic acids.

Combining this effect with the first two leads to an extraction order: $CCl_3COOH > HNO_3 > HClO_4 > HI > HBr > HCl > H_2SO_4 > H_3PO_4$. This is certainly in agreement with the experimental findings, but further work is obviously needed to establish this whole argument more firmly.

VI. Complex Metal Acids

Probably more important as extraction systems than the mineral acids discussed in the preceding section are the complex metal acids formed by some of the transition metals with the halide and pseudohalide (CN^-, SCN^-, etc.) ions. They show all the properties of the simple strong acids, with the added complication that the extractable complex has to be formed by reaction of the metal cation with the appropriate number of halide ions. Thus, large amounts of the hydrohalic acid are necessarily present and extract simultaneously into the organic phase. This leads to peculiarities in the extraction behavior of the metal due to "common ion" effects between the acids.

One of the earliest known examples of this type, and one of the best studied, is the ferric chloride–hydrochloric acid–diethyl ether system. In 1892, Hanriot (119) and Rothe (262) showed that Fe^{III} extracted very well from strong (6*M*) HCl solutions into diethyl ether, and this fact was soon put to use in analytical work for separating this element from many others (178,189,240,279). Since then some, or all, of the halides of Ga^{III}, Au^{III}, Fe^{III}, In^{III}, Tl^{III}, Mo^{VI}, Sb^{V}, As^{III}, Ge^{IV}, Hg^{II}, Nb^{V}, Pt^{II}, Po^{II}, Pa^{V}, Sc^{III}, Sn^{II}, Sn^{IV}, Sb^{III}, Cd^{II}, and Pb^{II} have been found to extract into basic solvents. (See, for example, the papers on fluoride systems by Bock and Herrmann (26), on chloride systems by Mylius and Hüttner (230); on bromide systems by Wada and Ishii (305), Bock, Kusche, and Bock (28), and Denaro and Occleshaw (59); and on iodide systems by Kitahara (180) and Irving and Rossotti (153).) Most of these extract as complex acids, although some distribute as neutral molecules, e.g., $AsCl_3$ and $HgCl_2$. It is with the acid systems that this section is concerned, and Fe^{III} will be used as an illustrative example.

Although it was found that the similar extraction of Au^{III} into diethyl ether from hydrochloric acid solutions appeared to involve the

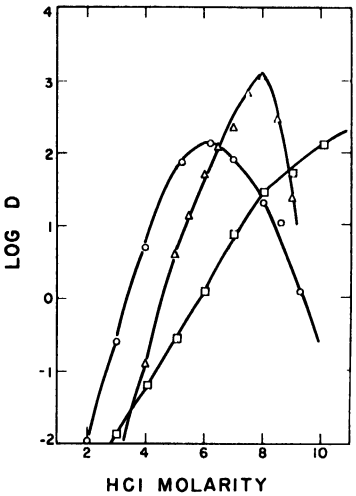


Fig. 2. Log D vs. HCl molarity for the extraction of Fe^{III} into diethyl ether (O · O), into diisopropyl ether (Δ——Δ), and into bis(2-chloroethyl) ether (□——□).

known species $HAuCl_4$ (230), it was generally assumed that the iron species passing into the ether phase was $FeCl_3$. The initial rise in D with increasing HCl concentration (Fig. 2) was ascribed to the transformation of the aquo Fe^{III} ion to the neutral species with increasing chloride concentration, and the decrease in D above $6M$ HCl was ascribed to the formation of still higher, nonextracting, anionic chloro complexes. But these considerations had to be modified when it was found that $FeCl_3$ was not the distributing species. Kato and Ishii (169), as a result of analytical studies, gave the formula $HFeCl_4 \cdot 4.5H_2O$ for the extracting compound. Nekrasov and Ovsyankina (237) reported that at high initial HCl concentrations the ratio of Cl to Fe in the extracted compound increased, reaching 5.38 for an aqueous solution initially $10M$ in HCl and $1M$ in $FeCl_3$. Similarly, Nachtrieb and Conway (231) determined that $HFeCl_4$ was the species extracting into diisopropyl ether from aqueous solutions below $8M$ in HCl, but that from more concentrated acid solutions additional HCl appeared to extract, although the absorption spectrum of the extracted iron species remained the same. (In all the analytical studies, correction has been made for the amount of acid which extracts into the solvent in the absence of iron.) Axelrod and Swift

(9) showed that the species extracted by bis(2-chloroethyl) ether was $HFeCl_4$ with 4–5 molecules of water, and that the ratio of Cl to Fe remained 4 in extractions from HCl solutions up to 11*M* in concentration. A possible explanation for the differences in HCl coextracted under these differing conditions will be suggested later in this section; the important feature common to these systems, at least below about 7–8*M* HCl, is that the extracting species has been shown to be (a solvate of) $HFeCl_4$. Spectrophotometric studies (169,210,231) showed that the absorbing species in the ether extracts also exists in concentrated aqueous HCl, and more detailed studies by Friedman showed this to be the $FeCl_4^-$ anion (92). He compared the absorption spectra of thin layers of solid $KFeCl_4$ with those of Fe^{III} in concentrated HCl and in the ether extract from the HCl solution, and with those of solutions of $KFeCl_4$ in anhydrous diethyl ether and ethylene bromide, and found them to be the same. Since the spectrum of the iron species did not vary with the nature of the solvent, this was a strong indication that the solvent was not coordinated directly to the iron. In the case of the similarly extracting indium(III) complex acid, $HInBr_4$, Raman spectra studies (318) of diethyl ether and methyl isobutyl ketone extracts have shown that the metal is indeed tetrahedrally coordinated to the four bromine atoms, thus ruling out direct metal-solvent bonding. Similarly, the lack of dependence of the absorption spectra on the nature of the cation associated with the $FeCl_4^-$ anion, whether in the solid or in the organic phase, suggests that the proton is not chemically bound to the anion in the organic phase, but that $HFeCl_4$ is a strong acid, completely ionized, although not necessarily fully dissociated, in the solvent. Conductivity studies of diisopropyl ether extracts show that although such ether solutions of the complex iron acid conduct poorly, the conductivity is much greater than that of HCl solutions of comparable concentration, indicating that the chloroferric acid is stronger than hydrochloric (36). In fact, the results are similar to those obtained by Friedman and Taube for the salt NH_4GaCl_4 in anhydrous ether (95). Certain variations in the distribution ratios of these complex metal acids with changes in metal concentration and with the addition of perchloric acid, discussed later in this section, also indicate that the complex metal acids are strong, comparable to $HClO_4$.

An important reason for the relatively high extraction of these metal anions is that they have no primary hydration shell in water (indium-

(III) chloride may be an exception; it certainly has a surprisingly low extraction); the metal is buried in the halogens, and these latter interact only weakly with the surrounding water. Except for the fact that they carry a single negative charge, these anions resemble CCl_4 in their disruption of the water structure and tendency to be forced out of the water phase into any structureless organic solvent. The charge does lead to a secondary (electrostatic) solvation which favors the higher dielectric constant medium, water, in preference to the organic solvent, but the complex anion is so large that this latter effect is relatively small, compared with that for the chloride ion. This is not true for polyvalent anions and is undoubtedly the main reason why the otherwise similar complexes $CoCl_4^{2-}$, $ZnCl_4^{2-}$, etc., show negligible extraction into ether and relatively poor extraction into better solvents.

The large size and relatively weak interaction with water of the MX_4^- anions is not sufficient in itself to yield high extraction; the accompanying cation must also be considered. If it, too, is a large univalent ion, such as Ph_4As^+ or $(Bu)_4N^+$, the ejection of the pair of ions into the organic phase will readily occur, and the more so, the higher the dielectric constant of the solvent, as discussed in Section IV. On the other hand, small or polyvalent cations with considerable primary hydration do not readily transfer into an organic phase, and extraction with such cations would be poor. But the special characteristics of the hydrogen ion, discussed in Section V, which lead to its unusually strong solvation by basic organic molecules, cause it to give, in general, very good extraction of the complex anions into basic organic solvents. Exactly as with the simple acids, the extraction is higher the more basic the solvent and the more available, sterically, the solvent molecule's donor atom (234).

Now, knowing what is the extracted species, the shape of the distribution curve of Fe^{III} into diethyl ether as a function of HCl concentration (Fig. 2) can be considered again. The steep rise in the value of D with increasing initial aqueous HCl concentration is certainly due in great part to the increasing proportion of the aqueous iron transformed into the extractable $FeCl_4^-$ complex with the increasing chloride concentration. (The different complexing abilities of the various metals cause this increase in D to take place at different hydrogen halide concentrations with the different complex acids.) Partly it is due to the decrease in the water activity with increasing

HCl concentration, as this decrease in "free" water makes more important solvation by the organic molecules, and hence causes greater extraction of all species, and particularly those involving the highly solvated hydrogen ion. But the origin of the maximum in the extraction into ether and the subsequent decrease with increasing initial aqueous HCl concentration cannot be due to the formation of more highly charged, nonextracting iron species, as no higher chloro complex of iron than $FeCl_4^-$ is known. Also, the maximum with diisopropyl ether is at a higher initial HCl concentration, and there is no maximum with bis(2-chloroethyl) ether (Fig. 2). What happens with diethyl ether is that, as the initial aqueous HCl concentration is increased, more and more of the ether gets pulled into the aqueous phase to solvate the hydrogen ion there, reducing the need for the acids, HCl and $HFeCl_4$, to extract. With concentrated HCl solutions, so much of the ether passes into the aqueous phase that marked phase volume changes occur, and the aqueous HCl concentration is decreased by the dilution. In fact, the equilibrium HCl concentration itself passes through a maximum around 7*M* initial aqueous HCl and then decreases at higher initial acid concentrations. With the larger, more hydrocarbon-like diisopropyl ether, less solvent dissolves in the acid phase and the phase volume changes are smaller. So the maximum in the acid distribution ratio occurs at a higher HCl concentration, as do those of the metal complex acids. With the still less soluble dibutyl and bis(2-chloroethyl) ethers, relatively little solvent dissolves even in concentrated HCl, so that the aqueous phase remains near its original volume and is essentially undiluted, and there are no maxima in the HCl distribution ratio or in those of complex acids. Diethyl ether–HBr and diethyl ether–HI solutions show the same type of behavior, but with still greater phase volume changes (153), and the maximum in the acid distribution ratio is at progressively lower HBr and HI concentrations. In general, the maxima in the distribution ratios of the metal complex acids into diethyl ether are also at correspondingly lower HBr and HI concentrations, but this is modified by the different complex-forming ability of the various metals with Cl^-, Br^-, and I^-.

Another feature of the extraction of the complex metal acids into diethyl and diisopropyl ethers which does not appear to occur with the larger ethers is the formation of a second ether phase at high HCl and metal ion concentrations. This heavier ether phase contains

most of the extracted metal and was reported for the iron–diisopropyl ether system by Dodson, Forney, and Swift (65), and for the gallium–diisopropyl ether system by Nachtrieb and Fryxell (232). The explanation for this behavior has not been given, but it must not be restricted to the acids or to systems containing water, as Friedman and Taube (95) report the formation of two ether phases with diethyl ether in contact with solid NH_4GaCl_4, NH_4FeCl_4, NH_4AlCl_4, and $LiGaCl_4$.

A general expression for the distribution ratio of iron(III) chloride (taken as a model for the metal acids) into a basic organic solvent would be

$$D = \frac{[(FeCl_4)_o + (HFeCl_4)_o + (\text{ion associations})_o]}{[(Fe) + (FeCl) + (FeCl_2) + (FeCl_3) + (FeCl_4)]} \quad (17)$$

$(HFeCl_4)_o$ represents the organic phase concentration of ion pairs $H^+FeCl_4^-$ (97), and $(\text{ion associations})_o$ represents all higher ionic aggregates in that phase, i.e., ion triplets, quadruplets, etc. (97,228, 233). Extraction from acid solutions is being assumed, so no hydrolyzed or polymeric iron species are being considered in the aqueous phase.

With low dielectric constant solvents such as the aliphatic ethers, the concentration of dissociated $H^+FeCl_4^-$ is usually negligible, so that the first term in the numerator of equation 17 may be neglected. Symbolizing all the ion aggregates by the ion quadruplet, $H^+FeCl_4^-H^+FeCl_4^-$, for simplicity's sake, and making use of the following equilibrium expression

$$2H^+FeCl_{4\,(o)} \rightleftharpoons H^+FeCl_4^-H^+FeCl_{4(o)}$$

$$\delta_{HFeCl_4HFeCl_4} = (HFeCl_4HFeCl_4)_o/(HFeCl_4)_o^2$$

one finds

$$D = [(HFeCl_4)_o + \delta_{HFeCl_4HFeCl_4}(HFeCl_4)_o^2]/\sum_{i=0}^{4}(FeCl_i) \quad (18)$$

It can be seen that when the organic phase iron concentration becomes high enough so that ion quadruplets form, the value of the distribution ratio will become concentration dependent, increasing with increasing iron concentration. This type of deviation from the Nernst distribution law was observed in the iron(III)–diethyl ether and

–diisopropyl ether systems by Dodson, Forney, and Swift (65), in the gold(III)–diethyl ether system by Mylius and Hüttner (230), and in the gallium(III)–diisopropyl ether system by Nachtrieb and Fryxell (232), and the explanation was advanced by Myers, Metzler, and Swift (229) (although much earlier, Dodson, Forney, and Swift (65) quote unpublished work by Dodson indicating this explanation) and supported by isopiestic and other experimental studies by Myers and Metzler (210,228).

Such ion associations also furnish an explanation for the varying $HCl/FeCl_3$ ratios found in the ether phase species at high HCl and $FeCl_3$ concentrations (231,237). Under such circumstances, mixed ion associations such as $H^+FeCl_4^-H^+Cl^-$ could occur and are the more likely the higher the HCl concentration, thus raising the $HCl/FeCl_3$ ratio of the extracting species. With higher dielectric constant media such as bis(2-chloroethyl) ether ($\epsilon = 21.2$), such ion aggregates are negligible and the Cl/Fe ratio should remain 4 up to concentrated HCl solutions, as is observed.

In fact, with such solvents of higher dielectric constant, even the ion pairs dissociate, so that the expression for D becomes

$$D = [(FeCl_4)_o + (HFeCl_4)_o] / \sum_{i=0}^{1} (FeCl_i) \qquad (19)$$

Using the condition for electroneutrality in the organic phase,

$$(FeCl_4)_o + (Cl)_o \rightleftharpoons (H)_o$$

and the following equilibria,

$$H^+ + Cl^- \rightleftharpoons H^+_{(o)} + Cl^-_{(o)}$$
$$\alpha_{HCl} = (H)_o(Cl)_o/(H)(Cl)$$

$$H^+ + FeCl_4^- \rightleftharpoons H^+_{(o)} + FeCl_4^-{}_{(o)}$$
$$\alpha_{HFeCl_4} = (H)_o(FeCl_4)_o/(H)(FeCl_4)$$

$$H^+_{(o)} + FeCl_4^-{}_{(o)} \rightleftharpoons HFeCl_{4(o)}$$
$$\delta_{HFeCl_4} = (HFeCl_4)_o/(H)_o(FeCl_4)_o$$

this becomes

$$D = \Big(\alpha_{HFeCl_4}(FeCl_4)\{(H)/[\alpha_{HCl}(Cl) + \alpha_{HFeCl_4}(FeCl_4)]\}^{1/2} + \alpha_{HFeCl_4}\delta_{HFeCl_4}(H)(FeCl_4)\Big) / \sum_{i=0}^{4} (FeCl_i) \qquad (19')$$

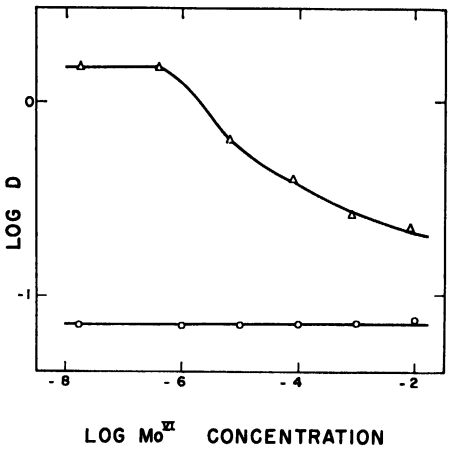


Fig. 3. Log D vs. log Mo^{VI} concentration for extraction into dibutyl ether (O——O) and into bis(2-chloroethyl) ether (Δ——Δ) from 8.1M HCl.

The value of D may now depend upon the metal ion concentration, even though no polymerized species are present. When the metal ion concentration in the organic phase is small compared to that of chloride, $\alpha_{HCl}(Cl) \gg \alpha_{HFeCl_4}(FeCl_4)$ and D is independent of the metal concentration. However, when $(FeCl_4)_o \gtrsim (Cl)_o$, or $\alpha_{HFeCl_4}(FeCl_4) \gtrsim \alpha_{HCl}(Cl)$, the first term in the numerator becomes dependent on the metal concentration. In the limiting case, $D \propto (FeCl_4)^{-1/2}$. There is ample experimental evidence for this feature of the complex metal acid extraction systems with solvents of moderate dielectric constant (61,128). Figure 3 shows plots of log D vs. log metal concentration for Mo^{VI} chloride into dibutyl and bis(2-chloroethyl) ethers from 8M HCl (61). For the former, the value of D is a constant; for the latter, it falls off above $10^{-6}M$ molybdenum until the ion-paired species predominates in this organic phase. That is, the first term in the numerator in equation 19′ decreases until the second term becomes dominant; D then becomes constant again, but at a lower value than at very small metal concentrations. The explanation for this behavior was first given by Saldick (268), and was amplified by Diamond (60) and by Poskanzer (253). It is a particular case of the behavior possible whenever the extractable species under consideration is ionic and dissociated in the organic phase as well as in the aqueous one, and the concentration of an ion common to both

the metal species and another electrolyte present in the system is furnished predominantly by one species in one phase and the other species in the other phase (60). In the case under dicussion, the common hydrogen ion is furnished predominantly by the HCl in the aqueous phase and, at Mo^{VI} concentrations $>10^{-6}M$, by the metal species in the organic phase. In this Mo^{VI} concentration range, doubling the metal concentration in the aqueous phase raises it by only $\sqrt{2}$ in the organic phase, as the hydrogen ion concentration is also increased there by $\sqrt{2}$. The extraction of all acids present, that is, both HCl and the metal complex acid, is repressed as can be seen very simply by considering the equilibria involved. Neglect of this feature of ionic extraction systems invalidates the use of the general extraction expressions of Irving, Rossotti, and Williams (152) for ionic systems showing dissociation in the organic phase and restricts their application to chelate systems or to ionic systems involving low dielectric constant solvents such as the ethers.

Of course, a dependence of D on the metal concentration may also be caused by polymerization of the metal species in one phase or the other. The ion aggregation in organic solvents of low dielectric constant is one example, and formation of nonextracting polymeric species in the aqueous phase is another possibility. Such aqueous phase dimerization would cause the slope of the log-log plot of D vs. metal concentration again to approach $-1/2$, but can easily be distinguished from the previous "common ion" case by comparing the behavior when using another solvent of quite different dielectric constant. The polymerization would be independent of the nature of the organic solvent, and so should always cause a decrease in D at about the same aqueous metal concentration. The common ion effect, however, occurs only in solvents of high enough dielectric constant to allow dissociation of the ionized species and so may, or may not, occur, depending upon the solvent (Fig. 3). For example, the extraction of Mo^{VI} chloride from $4M$ HCl into bis(2-chloroethyl) ether shows a decrease in D with increasing metal concentration above about $10^{-3}M$ (Fig. 4), but unlike the case at $8M$ HCl shown in Figure 3, the same decrease also occurs with diethyl ether (61), (and also with 2-ethylhexanol and methyl isobutyl and methyl amyl ketones). At $4M$ HCl, this decrease is due to the formation of aqueous phase polymers, as has also been shown in other ways.

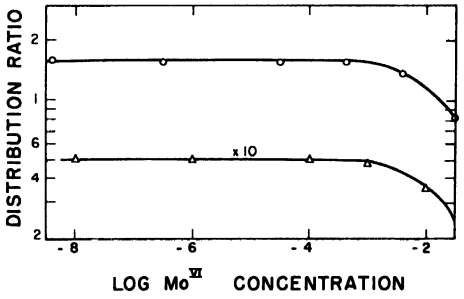


Fig. 4. D vs. log Mo^{VI} concentration for extraction into diethyl ether (O - O) and into bis(2-chloroethyl) ether ($D \times 10$) (Δ - Δ) from 4.1M HCl.

There are other interesting peculiarities in the extraction of ionic species in the presence of a second ionic compound. With low dielectric constant solvents, just as an increase in D is observed at high metal concentrations due to association of the $H^+FeCl_4^-$ into ionic aggregates, high values of D can also be obtained by the addition of other strong acids which extract well. These produce mixed ion aggregates, containing the metal species of interest, in the organic phase. For example, a small amount of $HClO_4$ added to a tracer metal complex–HCl–ether system extracts and so produces a high concentration of ion-paired $H^+ClO_4^-$ in the organic phase. These further associate to larger aggregates, incorporating some of the small amount of $H^+MCl_4^-$, and thus increasing the latter's extraction through the formation of new species, e.g., $H^+ClO_4^-H^+MCl_4^-$. Figure 5 shows the increase in In^{III} extraction into dibutyl ether which results upon the gradual substitution of 10M $HClO_4$ for 10M HCl (62). Another factor helping to increase the value of D is that the substitution of $HClO_4$ lowers the water activity, and this tends to increase the extraction of hydrated ionic species into basic organic solvents in order to solvate there.

But with decreasing chloride concentration, the proportion of metal in the extractable chloro complex must decrease in favor of lower complexes and the aquo ion, so that eventually the value of D reaches a maximum and then falls with further replacement of HCl. Upon substitution of HNO_3 for the HCl, the increase in D is less marked than with $HClO_4$ (Fig. 5) both because HNO_3 is weaker and probably forms some molecular acid as well as ion aggregates and

because its addition raises the water activity (for the same reason) and decreases the tendency of ionic species to extract.

With higher dielectric constant solvents in which the extracted ionic species are mainly dissociated, a lowering of D occurs upon the addition of a strong acid through the operation of a common ion effect analogous to the dependence of D on the metal concentration. For upon the substitution of HCl by the better-extracting $HClO_4$ or HNO_3, a much higher hydrogen ion concentration is produced in the organic phase which represses the extraction of the complex metal acid. By including the additional anion, Z^-, in the electroneutrality condition,

$$(Cl)_o + (MCl_4)_o + (Z)_o = (H)_o$$

the expression for D can be derived (60,253,268) which clearly shows this behavior, e.g.,

$$D = [(MCl_4)_o + (HMCl_4)_o]/\sum_{i=0}^{4}(MCl_i)$$

$$= \left(\alpha_{HMCl_4}(MCl_4)\{(H)/[\alpha_{HCl}(Cl) + \alpha_{HZ}(Z) + \alpha_{HMCl_4}(MCl_4)]\}^{1/2} + \alpha_{HMCl_4}\delta_{HMCl_4}(H)(MCl_4)\right)/\sum_{i=0}^{4}(MCl_i) \quad (20)$$

For $HClO_4$ and HNO_3, $\alpha_{HZ} \gg \alpha_{HCl}$, so that with solvents such as bis(2-chloroethyl) ether where there is considerable dissociation (the first term in the numerator predominates), the replacement of even a few per cent HCl by $HClO_4$ or HNO_3 causes a dramatic drop in the distribution ratio of the metal acid (provided it is not present in greater amounts than the $HClO_4$ or HNO_3 added). An example is shown in Figure 5 of the values of D for the extraction of In^{III} chloride into the chloroether from solutions $6M$ in total acid, but with varying proportions of HNO_3 or $HClO_4$ (62). (HNO_3 causes a less steep decrease in D because it is a weaker acid, although of somewhat higher extractability.) After an appreciable amount of HCl has been replaced, the addition of more $HClO_4$ or HNO_3 gives a differing behavior. The plot for HNO_3 continues to decrease, but that for $HClO_4$ passes through a minimum D and then increases, perhaps to values as high as with the original HCl solution alone, before eventually turning down again when there is not enough chloride left in the system to form the extractable chloro complex. This

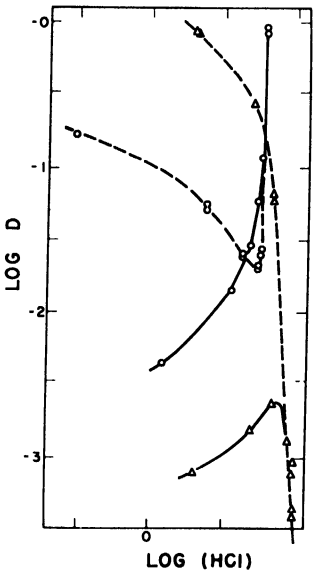


Fig. 5. Log D vs. HCl concentration for In^{III} tracer into dibutyl ether from 10M acid, the total ionic strength held constant with $HClO_4$ (Δ- - -Δ) and with HNO_3 (Δ——Δ); same, but into bis(2-chloroethyl) ether from 6M acid, the total ionic strength held constant with $HClO_4$ (O- - -O) and with HNO_3 (O——O).

difference is probably due, at least partly, to the effect of the change in water activity, $HClO_4$ decreasing it and HNO_3 increasing it, and possibly to the formation of ion associations even in solvents such as the chloroether when the ion concentration in that phase becomes great enough.

The replacement of HCl by $HClO_4$ or HNO_3 can also be considered as a special case of "salting" effects, although the more usual meaning is restricted to the replacement by, or addition of, salts. Since the salts have negligible extraction in the systems under the conditions normally used, they have little effect on the organic phase, directly, but can increase or decrease the extraction of a distributing species by several aqueous phase effects. Different salts, and in particular their cations, tie up differing amounts of water in their hydration shells, and so the availability of water to solvate the metal species of interest (especially the hydrogen ion of the complex acids) varies greatly. Small polyvalent cations tie up water to the greatest ex-

tent and so help force ionic species into the organic phase to solvate there, while large univalent ions will lower the extraction. Actually, hydrogen ion is about as good a dehydrating agent, per equivalent, as the small polyvalent cations such as Al^{III}, Mg^{II}, and Ca^{II}, so that in extraction from hydrogen halide solutions, there is little to be gained from this effect, and most salts, such as the alkali halides, will depress the extraction (63a,222). For complex metal acid systems, this lowering in D is due both to the raising of water activity and to the decrease in concentration of the hydrogen ion, one of the constituents of the extracting species. But for those solvents in which the acid is very soluble, or which dissolve readily in the acid phase, the consequent lowering of the aqueous acid and complexing anion concentrations may be great enough to diminish the extraction of the metal species, and in such cases the replacement of part of the acid by a strongly hydrated (but nonextracting) salt will improve the metal distribution. This is especially true when salts with coordinate solvation rather than acid species are being extracted (so that no hydrogen ion is needed for the distributing species), and it is in such salt systems (discussed in Section VII) that salting agents are most useful and most commonly used. In favorable cases, such as the ether extraction of uranyl nitrate from nitric acid solution, even the use of the poorly dehydrating ammonium nitrate (99,127) gives enhanced extraction, although the corresponding lithium, calcium, or aluminum salts would be much better (99). Bock and Bock's study of the salting-out effects in thorium nitrate extraction (25) illustrates this very well, if due allowance is made for the different concentrations of the nitrate salts in their saturated solutions.

Those elements that have two or more oxidation states may show very different extraction behavior depending upon the oxidation state involved. For example, Fe^{III} extracts well into oxygenated solvents from HCl or HBr solutions, but Fe^{II} does not. The lower oxidation state does not form a uninegative complex halide ion; in fact, it does not form anionic halide complexes at all. The much better extraction of Sb^{V} chloride or bromide over that of Sb^{III} is possible due to a similar cause; Sb^{V} probably forms the anion SbX_6^- in strong acid, while that of Sb^{III} is possibly higher charged. The reverse situation is true with arsenic, where the III state extracts much better than the V. As^{III} appears to extract as a neutral chloro molecule, while As^{V} possibly remains a hydrophilic oxygenated acid.

Most of what has been said has to do with chloride, bromide, and iodide systems, so a few comments on the fluoride systems may be in order. First, not many metals seem to extract well as fluoride complexes. Bock and Herrmann (26) in a study of diethyl ether extractions from HF solutions 1–20*M* in acid found only Nb^{V}, Ta^{V}, and Re^{VII} extracted better than 50%. They also observed only a small extraction of Sn^{II} and Sn^{IV}, as well as of As^{III}, As^{V}, Te^{IV}, Ga^{IV}, Hf^{IV}, P^{V}, Se^{IV}, V^{III}, V^{IV}, Sb^{III}, and Mo^{VI}. Probably a major reason why so few metals extract, or extract well, is that their fluoride complexes are polynegative anions. With fluoride the metals reach their maximum coordination number, and so Fe^{III} becomes FeF_6^{3-} in contrast to the chloro and bromo complex ions, FeX_4^-. The more highly charged the ion, the poorer the extraction, as noted earlier. Also the uninegative fluoro complexes that can form are smaller than the other corresponding halide complexes; they disturb the water structure less and so have a smaller tendency to be pushed into the organic phase. Lastly, because of the weakness of hydrofluoric acid, the water activity is greater in an aqueous HF solution than in a corresponding HCl, HBr, or HI solution, which again tends to yield a lower extraction. It should be noted that the identity of few of the extracting species has been determined, so that not all of the partially extracting metals necessarily do so as complex fluoroacids; they may not be acids, and/or they may not even contain fluorine.

By going to better solvents than diethyl ether, however, essentially complete extraction can be obtained for some metals. This is true for Ta and Nb, which do not extract well from the other halogen acids and are more easily kept in fluoride solutions in order to prevent hydrolysis. For example, Ta and Nb can be extracted into methyl isobutyl ketone from an aqueous phase of 10*M* HF + 6*M* H_2SO_4 + 2.2*M* NH_4F (213). Nb (and presumably Ta) can be similarly extracted into diisobutylcarbinol (217). From a solution 6*M* in H_2SO_4 and only 0.4*M* in HF, Ta can be extracted into diisopropyl ketone and separated from Nb; by increasing the HF concentration to 9*M*, the Nb can also be extracted (282).

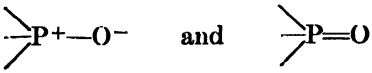
VII. Coordinately Solvated Salts

It has been mentioned that in order to transfer a hydrated ionic species from aqueous solution into an organic solvent, any possible loss in solvation energy must be compensated for in the organic phase.

For the hydrogen ion there is a unique mechanism for this solvation, but with other cations there is no such specific concentration of charge at any point on the surface of the hydrated ion. The solvation forces are therefore correspondingly weaker. This comparatively poor primary solvation which weakly basic solvents offer small ionic species is reflected in the low solubility of the latter in such solvents. The influence of the chemical nature of the solvent itself has been investigated by Garwin and Hixson (102) using nickel and cobalt (II) chlorides. The solubility of these salts in nonpolar, noncoordinating solvents and in aliphatic ethers was negligible; in aliphatic esters, acids, and ketones and in aromatic aldehydes, a slight solubility was found (e.g., in ethyl acetate: $CoCl_2$ 1.08% (*w/w*)a nd $NiCl_2$ 0.02%). With aliphatic alcohols, however, this solubility is increased more than 20-fold, with the exact value depending on the molecular weight and structure of the solvent. The authors suggested that $NiCl_2$ and $CoCl_2$ only dissolve in solvents which contain an actual or potential —OH group, thereby explaining the negligible solubility in ethers. An alternative explanation seems more reasonable, however. Ethers must have less chance of solvating a comparatively small cation because of the considerable steric hindrance arising from the difficulty of arranging these molecules around the ion. With ketones, esters, and acids, however, the basic oxygen atom is much more readily accessible by virtue of its attachment to a carbon atom by a double bond, so that solvation can occur more readily than with ethers of equal or greater basicity. The high solubility of these halides in the aliphatic alcohols arises from the ability of these solvents to solvate both anion and cation (see later). But even with the high solubility, the distribution ratios for the two phase system are very low ($D \sim 10^{-3}$), since water can provide the necessary primary solvation much more easily than the organic solvent. In general, then, with weakly basic solvents, the extraction of most salts is negligible.

There is, however, a class of organic solvents which shows remarkable solvating properties for inorganic compounds and will serve to illustrate some of the principles involved in the solvent extraction of salts. These are the esters of orthophosphoric acid and a number of related compounds, whose essential functional group is the semipolar phosphoryl bond, which has a basic oxygen atom with good steric availability. The mono- and dialkyl esters show a number of differences from the trialkyl compounds in their extraction behavior, and

have been discussed earlier. Before passing to a detailed consideration of these solvents, one might note the high electric moment of the phosphoryl group (3.3 ± 0.1 units (77)) implying that of the two limiting structures



there is a large contribution to the resonance state from the former, so that the structure can be justifiably written as

The corresponding

bond has a similar moment, 3.0 ± 0.1 units, although there seem to have been no studies of the interactions of such compounds with inorganic species.

The properties of the P→O bond should give good solvating (and hence extracting) properties. Tri-*n*-butyl phosphate (TBP) has been extensively used in solvent extraction on both the laboratory and the industrial scale and may be taken as a typical compound containing the P→O bond. We have already noted the extraction of a number of acids into this solvent. The hydrogen halides (300) and sulfuric acid extract much more readily into it than into ethers and ketones (for 3*M* H_2SO_4, $D \approx 0.11$ (299)), emphasizing the strongly basic character of TBP.

The first description of the use of TBP in extracting inorganic compounds seems to have been published by Warf (306). Although a great deal of work has appeared since, much of it has emphasized industrial more than theoretical aspects. A number of papers at the 1955 Geneva Conference reported various methods of using TBP for the extraction of uranyl nitrate (34,51,89,198,289), notably in its separation from fission products. In many cases, and especially in large-scale work, the solvent is diluted with some inert hydrocarbon in order to reduce the viscosity and density of the organic phase and so improve the separation of the two phases.

The solubilities of a number of hydrated inorganic nitrates in TBP have been measured by Wendlandt and Bryant (312) and by Healy and McKay (125). The latter authors have shown that for highly

soluble salts, the composition of the saturated solutions corresponds to the formation of definite solvates. There is particular evidence that the solubility of uranyl nitrate is due to the formation of a complex $UO_2(NO_3)_2 \cdot 2TBP$ which has a sharp melting point at $-6°C$. This 2:1 ratio has also been reported by Karpacheva, Khorkhorina, and Rozen (168). Unlike the solvates formed by uranyl nitrate in ethers and ketones, the complex with TBP is completely anhydrous; in fact, if any water is initially present in the solvent (as $TBP \cdot H_2O$), two molecules are displaced for every uranyl nitrate which dissolves. The behavior of plutonium(IV) nitrate underlines the difference between the phosphoryl solvents and the ethers. In TBP the species present is $Pu(NO_3)_4 \cdot 2TBP$, the absorption spectrum of which is unaffected by the addition of nitric acid (125). In aqueous solution, at high nitrate concentrations, the tetranitrate complex goes to the anion $Pu(NO_3)_6^{2-}$ (137), while in extract solutions in dibutylcarbitol there is evidence (301) that in the presence of strong nitric acid the species present is a solvated acid $H_2Pu(NO_3)_6$; the absorption spectrum of both of these hexanitrates is strongly dependent on the nitric acid concentration.

This evidence, then, suggests that the solvation of salts by phosphoryl solvents occurs by direct bonding of the solvent to the cation of the salt rather than to any primary solvation sheath of water molecules. The strong donor properties of the solvent are partially responsible for this behavior. Healy and McKay (126) have noted the effect of substitution of C_6H_5 for C_4H_9 in TBP on the extraction of uranyl nitrate. The extraction decreases in the order $Bu_3 > Bu_2Ph > BuPh_2 > Ph_3$; with decreasing donor activity in the solvent, the mode of interaction begins to change and water is found to accompany $UO_2(NO_3)_2$ into the organic phase, suggesting that the solvent is now behaving like the ethers and ketones (see later). A more thorough investigation of the effect of basicity has been carried out by Burger (35) for a series of organic phosphates, phosphonates, phosphinates, and phosphine oxides. The effect of electrophilic substituents in the alkyl group is to lower the electron density at the phosphoryl oxygen, thus lowering the basicity and reducing D for $UO_2(NO_3)_2$. Each group of phosphorus compounds has a characteristic infrared absorption frequency, indicative of the basicity of the P→O group, and this has been shown to correlate well with the extraction of $UO_2(NO_3)_2$ into typical members of the group.

The distribution laws applicable to the extraction of inorganic nitrates into TBP have been discussed by Hesford and McKay (129).

Following the mechanism suggested by Moore (218) for $UO_2(NO_3)_2$, they take the fundamental equilibrium as

$$M^{p+} + pNO_3^- + qTBP_{(o)} \rightleftharpoons M(NO_3)_p \cdot qTBP_{(o)}$$

Neglecting activity coefficients one can write a mass action constant

$$K_1 = (M(NO_3)_p \cdot qTBP)/(M^{p+})(NO_3^-)^p(TBP)^q$$

and

$$D = K_1(NO_3^-)^p(TBP)^q$$

The effects of variations in nitrate and nitric acid concentrations are considered, as is the effect of complexing the metal. More important for determining the solvation state of the salt in the organic phase is the result of changes in the concentration of TBP in that phase, brought about by diluting the organic phase with some inert solvent such as CCl_4. For constant aqueous phase conditions and low concentrations of TBP, activity coefficients in the organic phase can be neglected and one finds the limiting law

$$D \propto (TBP)^q$$

$$\partial \log D/\partial \log (TBP) = q$$

which gives the solvation number directly. Deviations from this limiting situation may occur at higher TBP concentrations. Using this approach, the formulas of the following solvated salts have been established:

Trisolvates: $M^{III}(NO_3)_3$, where M = Y, Ce, Eu, Tb, Tm, Lu, Am

Disolvates: $M^{IV}(NO_3)_4$, where M = Zr, Th, Np, Pu

$MO_2(NO_3)_2$, where M = U, Np, Pu

One may note that Levitt and Freund have found $ZrCl_4 \cdot 2TBP$ by similar arguments (192).

Because of the pth power dependence of D on (NO_3^-), extractions of this type show strong salting-out effects. For example, sodium nitrate and aluminum nitrate are both very effective salting-out agents for plutonium(IV) nitrate (16,116). Both these salts are themselves only slightly soluble in TBP. Extractable nitrates, however, do not salt-out as well; in fact, by competing for the available TBP

molecules for solvation in the organic phase, they can reduce the extraction of the molecule of interest.

Like uranium, thorium nitrate extracts well into TBP (249); using the extraction from concentrated nitric acid, a separation scheme for Sc, Th, and Zr has been evolved. Thorium is more readily extracted than the rare earths, but less so than plutonium (IV); at low acidities, hydrolysis may cause a fall in the distribution ratio (130). Best, McKay, and Woodgate have investigated the extraction of the three plutonium nitrates (16). Plutonium(III) nitrate is only poorly extracted even from 5*M* nitric acid, but plutonium(IV) nitrate extracts well; plutonyl nitrate also extracts readily but less so than the uranyl compound. In addition to the nitrates, extraction of the heavy elements from hydrochloric acid solutions has been studied. Peppard, Mason, and Gergel (248) have separated Th, Pa, and V by extraction into TBP from HCl. Bagnall and Robertson (11) have shown that polonium can be extracted from HCl solution, forming a complex that is probably $PoCl_4 \cdot 2TBP$.

Peppard and co-workers have studied the extraction of the trivalent rare earth elements into TBP from both hydrochloric and nitric acid media. In both cases, from concentrated acid solution, an increase in extractability with atomic number was found, paralleling the order of decreasing basicity (245). With dilute ($\sim 0.3M$) aqueous nitric acid, the order of the distribution ratios is reversed; no explanation has been offered for this inversion. Peppard, Gray, and Markus (247) have drawn attention to the analogous solvent extraction behavior of the lanthanides and the actinides, for both of which log *D* is a linear function of atomic number from concentrated HCl or HNO_3. More recently Peppard *et al.* (244) have shown that for tracer concentrations of the rare earths in nitric acid, the plot of log *D* against atomic number is actually two straight lines of different slope intersecting at $Z = 64$. The slopes depend somewhat on the nitric acid concentration and on the concentration of TBP in the organic phase. The effect of changing nitric acid concentration on *D* for the rare earths is due to a number of factors, including salting-out by nitrate ion, formation of nitrate complexes, activity changes, and the competition of nitric acid itself for the organic solvent (273).

The nitratonitrosyl complexes of ruthenium have been studied by means of their extraction into TBP, and estimates made of the proportion of the various nitrate complexes at different nitric acid con-

centrations (33,161). Zirconium nitrate (3) and chloride (192) have been shown to extract into TBP. Chatelet and Nicaud (38) have discussed the extraction of $CoCl_2$ into TBP in terms of the dimer said to be formed at high concentrations (Wormser (319); but see Katzin and Gebert (175)). Only at high concentrations does the extraction become appreciable ($D \sim 0.03$). Nickel chloride is only slightly extracted, but $CuCl_2$ extracts as well as $CoCl_2$. Quantitative extraction of Fe^{III} from $4M$ HCl solution has been achieved with tributyl phosphine oxide (261); this compound also extracts Cr^{VI} from HCl solution (315), as does tributyl phosphate (64).

Despite the poorer, primary solvating properties of ethers, ketones, esters, etc., there are a number of inorganic nitrates which will extract into these solvents. The best known of these is probably uranyl nitrate, the importance of which in nuclear engineering was noted earlier as one of the reasons for the present interest in solvent extraction. Other nitrates whose extraction into ethereal solvents has been studied include Am^{VI} (8), Ce^{IV} (25), Np^{VI} (182), Pu^{VI} (110), Pa^{V} (207), Th^{IV} (25), and Zr^{IV} (25). The extraction of uranyl nitrate can be taken as an (extreme) example of such systems and is certainly the most thoroughly studied.

One must first note that there is evidence that uranyl nitrate is incompletely dissociated in aqueous solution. The formation constant for the reaction

$$UO_2^{2+} + NO_3^- \rightleftharpoons UO_2NO_3^+$$

has been estimated as 0.21 (1) and 0.5 (18) under different conditions, and further association is possible to the anion $UO_2(NO_3)_3^-$ which has been identified both in crystals and in solution (167). Consequently, it seems that in aqueous solution one can have appreciable amounts of the neutral salt; since the salt is insoluble in nonpolar solvents, however, the extraction must clearly involve solvation by basic solvents.

Glueckauf and McKay (110) were the first to suggest that the high extraction of the uranyl ion and its analogues was related to the use of the $5f$ orbitals in the solvation complex, but Katzin (170) has pointed out that a number of inorganic nitrates can be solvated by basic organic solvents, so that uranyl nitrate is by no means unique. Qualitatively this is undoubtedly correct, but the difference seems rather large, as under comparable conditions the distribution coef-

ficients for Mn, Co, Cu, and UO_2 nitrates into ether are in the ratios $0.1:1:2:10^7$. Connick and Hugus (43) suggest that because of the structure of the uranyl ion the uranium atom carries essentially a charge of +4 and that this high charge may be responsible for the strong interaction with basic solvents. In agreement with this solvation of the cation, uranyl perchlorate is said to extract into ethyl ether (166).

Whatever the exact mode of solvation, there is no doubt that solvated uranyl nitrate complexes do exist; we have already noted those formed with tributyl phosphate. Mixed solvates of the type $UO_2(NO_3)_2 \cdot 3H_2O \cdot S$, $UO_2(NO_3)_2 \cdot 2H_2O \cdot 2S$, $UO_2(NO_3)_2 \cdot 2H_2O \cdot S$, etc., have been reported for a number of solvents (177,206). With alcohols, anhydrous solid phases such as $UO_2(NO_3)_2 \cdot 4i\text{-BuOH}$ have been identified. There has been some disagreement over the role of water in the solvation process in the organic phase. Katzin (171) believes that for many ethereal and ketonic solvents the species is a solvate of $UO_2(NO_3)_2 \cdot 4H_2O$, with evidence in some cases for $UO_2(NO_3)_2 \cdot 6H_2O$, although the results of Gardner, McKay, and Warren (101,199) are somewhat different. The Harwell group have published a number of papers on the thermodynamics of this extraction. The number of organic molecules solvating uranyl nitrate is estimated as 2–7, although the alcohols behave anomalously (111). Deviations from the simple partition law are ascribed to activity effects in the organic phase, although no account is taken of deviations arising from the complexing of the solvent (197).

A rather different series of extractable salts are the metal thiocyanates, which resemble in some ways the complex halometallic acids already described. The use of these compounds in the colorimetric analysis of a number of metals is well established (224). Bock (24) surveyed the extraction of various metal thiocyanates into diethyl ether from NH_4SCN solutions slightly acid with HCl. He found that Be^{II}, Zn^{II}, Co^{II}, Sc^{III}, Ga^{III}, In^{III}, Ti^{III}, Fe^{III}, Sn^{IV}, and Mo^{V} extract well and that Al^{III}, V^{IV}, and U^{VI} do so to a smaller degree. The same variety of basic solvents may be used to extract these species as with the halometallic acids (307), and again the presence of an electron-donating atom in the solvent molecule is necessary. The metal thiocyanate complex ions are much larger than the corresponding halides, so that they disturb the water structure more and have a greater tendency to be ejected into the organic phase. This means

that dinegative anions also may extract (e.g., $Co(SCN)_4^{2-}$, $Zn(SCN)_4^{2-}$, and $Sn(SCN)_6^{2-}$) and that not only acid species extract, but also the corresponding alkali (and substituted ammonium) salts. As with the halide complexes, the extraction of the alkali metal thiocyanate complexes into ethers, esters, ketones, and alcohols usually decreases in the order Li > Na > K > NH_4 (307); extraction is favored with solutions of lowest water activity and of the most hydrated cations. Extraction from acid solutions probably involves the acid metal thiocyanate complex, but such extractions have a difficulty which leads to poor distribution ratios. Thiocyanic acid itself extracts very well, so that the addition of acid to a thiocyanate salt solution results in the practically complete extraction of the hydrogen or thiocyanate ion, whichever is in lowest concentration, leaving its aqueous concentration essentially zero. This removes one of the components necessary for the formation of the desired metal thiocyanate complex acid, and low values of D are obtained. Thus very little acid can be tolerated in the thiocyanate systems. On the other hand, basic solutions are also ruled out because of metal ion hydrolysis, and thus optimum extraction is obtained over a relatively narrow pH range, the limit increasing somewhat with higher thiocyanate concentration. This was first observed by Fischer and Bock in their study of the diethyl ether extraction of scandium(III) with NH_4SCN (86). As a result of this feature of thiocyanate extraction systems, useful (optimum) extraction takes place from only slightly acid solutions, and the extracting species is actually the metal thiocyanate complex salt, rather than the acid. For example, Bock (24) has found that $(NH_4)_2Zn(SCN)_4$ and $NH_4Fe(SCN)_4$ are the species extracting into diethyl ether from NH_4SCN solutions, and Watkins, Welt, and Diamond (307) have shown that $Na_2Co(SCN)_4$ is the cobalt species distributing between aqueous NaSCN solutions and methyl amyl ketone. However, as with the halometallic species, the nature of the extracting species of a metal may change with the conditions and the solvents, and there is still room for definitive experiments. The case of Fe^{III} thiocyanate is a good example. Bock found, by analysis, $Fe(SCN)_4^-$ to be the extracting species into diethyl ether (24), Mitchell and MacDonald found $Fe(SCN)_3$ by ebullioscopic methods in the same solvent (214), and several workers have described the extraction of $Fe(SCN)_6^{3-}$ with large cations, as mentioned in Section IV.

In any case, extraction of the metal thiocyanate complex salts shows all the variations and complications described already for the complex halometallic acids, including variations in D with increasing metal concentration and depression of the appropriate highly extracting salt with a common cation (307). The use of the basic solvent pyridine to extract metals in the form of compounds such as $Cu(py)_2(SCN)_2$ should also be noted (145,216). These extraction complexes appear to be similar to those formed by TBP with halides and nitrates.

Finally in this section we shall discuss the extraction of salts into the higher aliphatic alcohols, a group of organic solvents which are immiscible with water and yet which possess the basic functional group (—OH) associated with many of the physical and chemical properties of water. Furthermore, this group is in a favorable steric position to show both its donor and acceptor character. These solvents can solvate both cationic and anionic species, as does water. This presents an essential difference from the solvents discussed previously in this section, and is illustrated by the extraction by these solvents of those acids whose anions are solvated in aqueous solution (see page 155), such as sulfuric acid (D into ether, 0.0006; D into n-butanol, 0.146 (316)) and hydrochloric acid (D into isobutanol, 0.63 (47)).

The solvation of salts by aliphatic alcohols has been discussed by Katzin, with special emphasis on cobalt(II) salts; the cation is generally regarded as existing as $Co(H_2O)_6^{2+}$ in dilute aqueous solution. The ternary diagrams of systems such as $CoCl_2$–H_2O–t-C_4H_9OH and $Co(NO_3)_2$–H_2O–t-C_4H_9OH have been constructed and solid phases corresponding to $Co(NO_3)_2 \cdot 4H_2O \cdot 2BuOH$, $Co(NO_3)_2 \cdot 3H_2O \cdot 3BuOH$, and $Co(NO_3)_2 \cdot 2H_2O \cdot 4BuOH$ identified (172,174). Stable alcoholates of $CoCl_2$ are also known for this and a number of other alcohols (174). The detailed properties of such systems have been discussed in terms of the hexacoordination of the cobaltous ion, but for the purposes of the present discussion the importance of these results is their illustration of solvation in alcoholic solution. This behavior is, of course, far from characteristic of all salts; potassium chloride, for example, is much less soluble in ethyl alcohol than is cobaltous chloride (83,90). It seems, however, that all salts which have strong primary solvation in aqueous solution will be solvated by alcohols, and by similar interactions.

Katzin and his co-workers (84,173,176) have also published some interesting data on the heats of solution of certain hydrated salts, again emphasizing the similar solvating properties of water and the alcohols. For the various hydrates of $UO_2(NO_3)_2$, $Co(NO_3)_2$, $CoCl_2$, and $Th(NO_3)_4$, it was found that the heat of solution into i-C_4H_9OH was always lower than that into ethyl ether, even though the basicities of the two solvents are very similar. Katzin, Simon, and Ferraro (176) have suggested that this is due to the absorption of energy in processes involving the formation of higher solvates. According to these authors, the normal processes of dissolution in the solvent involve the loss of some of the water molecules and the acceptance of solvent molecules (not necessarily equal in number to the lost water molecules), and the heat of solution is the heat evolved in these exchanges. For alcohols one can expect maximum coordination of the solvent with the metal, involving the separation of anion and cation in order to accommodate the extra solvating molecules With ethers, the anions retain coordination sites allowing for fewer solvent molecules. The former process, then, absorbs energy which would otherwise appear as heat, leading to an anomalously low heat of solution with respect to solution in ether.

Despite the high solubility noted earlier, the extraction of $CoCl_2$ from aqueous solution by 2-octanol is poor even for almost saturated solution; a 35% solution gives $D \sim 10^{-3}$ (102). For $NiCl_2$, D, in the absence of other salts, is even smaller. The salting-out effect of a number of salts was investigated, and HCl and $CaCl_2$ found to be among the most effective (103); these results were discussed in terms of the differing solvation of the Co^{2+} ion as shown by the color of the solution. It has been pointed out, however, by Moore *et al.* (219), that the order of effectiveness in salting-out—HCl > LiCl > $CaCl_2$ > $AlCl_3$ or $(CH_3)_4NCl$—is in fact the order of extraction of these compounds. They suggest that if the salting-out agent is itself extracted, the formation of the extracting neutral salt of interest will be enhanced in the alcohol phase by a mass action effect. But one must also note the effect of the water activity of the aqueous phase on the extraction of a salt into an alcohol; if sufficient water molecules are tightly bound by (say) $CaCl_2$, the water available for hydration of $CoCl_2$ will be decreased, forcing the latter to seek solvation by the alcohol. The effect of molecular size shows up neatly in the extrac-

tion of Co^{II} salts into alcohol, with the order $CoCl_2 < CoBr_2 < Co(ClO_4)_2$.

Zinc chloride has been shown to be soluble in 2-octanol; a separation can be made from $CdCl_2$, which is about 10^3 less soluble (221). For $ZnCl_2$ and a number of other chlorides which extract into 2-octanol, the water/salt ratio in the alcohol phase has been investigated (320). After allowing for the solubility of water in the solvent, which varies with the activity of water in the aqueous phase, one should then find the number of water molecules extracted with each molecule of salt. The hydration numbers derived in this way do not seem unreasonable (e.g., 2.9 for $CaCl_2$), but there is a curious feature in these results. A graph of water concentration against salt concentration for (say) $ZnCl_2$ is linear up to ~0.5 molal (slope 2.2), but at this point there is a sharp change of slope (to 0.6). The reason for this is by no means clear; a fall in hydration number at high concentration is to be expected, but in a smooth fashion rather than by a series of discrete changes.

The extraction of perchlorates into alcohols was noted earlier, with larger distribution ratios than for the corresponding chlorides. As with the chlorides, other perchlorates increase the extraction of the Co^{II} and Ni salts (220). One rather surprising feature is the large hydration numbers found for these salts in the organic phase—14.7 for $Co(ClO_4)_2$ and 10.9 for $Ni(ClO_4)_2$ (320).

Templeton and his associates have investigated the extraction of nitrates into alcohols. Among those nitrates which extract into *n*-hexanol are Th^{IV}, La, Ce^{III}, Pr, Nd, Sm, Al, Ca, Mg, Ni, and Co^{II}. For the rare earths, at any given aqueous phase concentration, the distribution coefficients are in the order Sm > Nd > Pr > La > Ce (285); for these elements, and for Th^{IV} (263), a linear relationship was found between log (mole fraction of the cation in the aqueous phase) and log (mole fraction of the salt in the organic phase). On this basis the process

$$R^{3+} + 3NO_3 \rightleftharpoons R(NO_3)_{3(alc)}$$

was suggested as being the step responsible for the linearity; for the rare earths a slope of ~4.5 was found. The linear log-log relation also holds for the system $Al(NO_3)_3$–H_2O–*n*-hexanol (286). Using the method outlined earlier, an apparent hydration number of 8.9 was derived, but it was not possible to correlate the distribution coefficient

with a_w. Both (Al^{3+}) and (NO_3^-) affect the concentration in the organic phase to the 3rd power, indicating a very complicated situation. For Zn, Mg, Ca, Ni, and Co^{II} nitrates (287), the linearity of the log-log plot disappears and there is no simple relation between solute activity and the organic phase salt concentration. Plots of H_2O molality against nitrate molality in the alcohol phase are also not linear; for Co, Ni, Mg, and Zn, the slope is between 4.0 and 5.3, and for La, 3.4. For $Ni(NO_3)_2$, a value of 3.8 is given in a later paper reporting the ternary diagram for $Ni(NO_3)_2$–H_2O–*n*-hexanol (288). Further investigation of these nitrate systems appears to be required.

VIII. Miscellaneous Systems

Finally we shall note two extraction systems for which there is as yet little published information on the factors which govern the distribution. Of particular interest to the analyst is the extraction of the heteropoly acids of elements such as Mo, As, P, W, V, and S. Some of the experimental details have been discussed by Morrison and Freiser (223); in keeping with the acidic character of the extracted species, basic solvents are required. There appears to have been no attempt to study the extraction process itself, doubtless because the aqueous solution chemistry of these acids is incompletely understood. More attention has been given to the partition of elements in fused salt and fused metal systems. A brief review of the work published up to 1957 is given in ref. (225). The possible use of such systems in the treatment of neutron-irradiated uranium, for example, suggests that they have great potential industrial importance, but their behavior is somewhat beyond the scope of this review.

Acknowledgment. This work was supported in part by the U. S. Atomic Energy Commission.

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Some Fluorine Compounds of the Transition Metals

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I. General Introduction

In recent years knowledge of the fluorine compounds of the transition metals has increased considerably, mainly because fluorine itself has ceased to be a laboratory curiosity as a result of simplification in its preparation and handling. New materials and improved techniques have also made the older preparative methods more effective, but it is certainly true that a surprising amount of new work in the field can still be done with a polyethylene bottle, a polyethylene breaker, and a platinum dish.

Since an excellent comprehensive review has recently been written by Dr. A. G. Sharpe (1), the author has been selective in his choice of topic. The lanthanides and actinides (i.e., the *f* block elements) have been more than adequately covered already (2) and only very recent work is included here. References have been cut down to an essential minimum, and, where convenient, data have been transferred to tables.

The author is indebted to Drs. D. W. A. Sharp and A. G. Sharpe for reading the manuscript and suggesting improvements.

II. Fluorine Compounds of the Transition Metals

A. INTRODUCTION

Fluorine is characterized by its extreme electronegativity and small ionic size, so that few of its compounds, especially those of the transition elements, resemble other halides, and parallels are to be sought rather among oxides and hydrides. Like oxygen it brings out

high valencies, e.g., Pt^{VI} and Cu^{III}, though not necessarily the highest, e.g., CrF_5 but CrO_3, OsF_6 but OsO_4. Lower valency fluorine compounds, especially of the second and third period *d* block transition elements are often unstable and difficult to prepare; e.g., no AuF or ReF_3 is known.

The common fluorine covalency or coordination number is six. Four covalency would be expected, but has not been confirmed, for chromium tetrafluoride in the vapor state; it probably occurs in the complex salts $KAgF_4$ and $KAuF_4$, which should have square planar $[MX_4]^-$ ions. Covalences of seven and eight are known in some complex salts of Groups IV and V, and for the lanthanides and actinides.

B. UNIVALENT FLUORIDES

The only true univalent transition metal fluoride is that of silver, but mercurous fluoride, Hg_2F_2, may also be included here. Argentous fluoride is yellow when pure (3), not white as is sometimes stated, and is peculiar chiefly for its large solubility in water and the formation of a subfluoride, Ag_2F. The absence of monofluorides of copper and gold has excited some interest, and it is becoming evident that if these compounds exist at all they disproportionate easily into metal and higher fluorides. It has been shown that cuprous fluoride is thermodynamically unstable (4); but the experiments of Wartenberg (5) are interesting in that they suggest that cupric fluoride dissociates at high temperatures into CuF and F_2. If this is so, it might be possible to prepare cuprous fluoride as a metastable entity at low temperatures in the absence of catalysts such as moisture or hydrogen fluoride. One possible approach is to reduce the higher fluoride with a nonmetal.

Mercurous fluoride (20), like AgF, is very soluble in water but is easily hydrolyzed by it. Neither Ag^I nor Hg_2^I forms stable complex fluorides.

C. BIVALENT FLUORIDES AND THEIR COMPLEXES

A few of the difluorides (Table I) can be obtained directly from aqueous solution, but most require anhydrous hydrogen fluoride or elementary fluorine in their preparation. They are high-melting solids; most are stable to the atmosphere, but those of Pd, Ag, and

TABLE I
Difluorides

	Preparative method	Color	Structure	M—F distance A.	Magnetic moment, BM	Ref.
Cr	HF and $CrCl_2$ at 25°	Green	Rutile (dis)	Two at 2.43 Two at 2.01	4.3	11
	HF and Cr at red heat	White		Two at 1.98		
Mn	Aqueous precipitation	Pink	Rutile (dis)	Two at 2.13 Four at 2.10	5.98	13,15
Fe	HF and Fe HF and $FeCl_2$ (anhyd.)	White	Rutile (dis)	Two at 1.99 Four at 2.12	5.59	13,16
Co	HF and $CoCl_2$ (anhyd.)	Pink	Rutile (dis)	Two at 2.03 Four at 2.05	4.6	13,17
Ni	HF and $NiCl_2$ F_2 and $NiCl_2$	Yellow	Rutile (dis)	Two at 1.99 Four at 2.02	2.85	13,17
Cu	F_2 on Cu or CuCl	White	Rutile (dis)	Two at 2.27 Four at 1.93	—	12
Zn	Dehydration of hydrate	White	Rutile	Two at 2.02 Four at 2.04	—	13
Pd	$PdF_3 \cdot BrF_3$ adduct and SeF_4 at 150°	Violet	Rutile	Two at 2.17 Four at 2.15	1.84	18
Ag	F_2 on Ag, $AgNO_3$, or AgX at 150–200°	Brown	—	—	1.0	19
Cd	Aqueous precipitation	White	Fluorite	—	—	21
Hg	Hg salts and F_2 Hg_2F_2 and Cl_2	White	Fluorite	—	—	20

Hg are readily hydrolyzed and must be handled in closed systems. These three compounds, however, are the most interesting chemically. Impure palladous fluoride was originally prepared from the trifluoride by reduction with a variety of agents including hydrogen, iodine, sulfur dioxide, and palladium metal itself (7), but has recently been made in high purity by reducing the trifluoride with either sulfur tetrafluoride or selenium tetrafluoride (8). For mercuric fluoride the best starting material is mercurous fluoride, which disproportionates on being heated into HgF_2 and Hg. An elegant synthesis is to warm Hg_2F_2 in a stream of chlorine; volatile $HgCl_2$ distills over, leaving HgF_2 behind as a white crystalline residue (9). Argentic fluoride requires elementary fluorine in its preparation; the usual starting material is one of the halides other than AgF (10). It is a dark brown paramagnetic solid which attacks glass slowly; the course of the reaction can be followed by the change of color from brown to yellow starting along and spreading from the striations in the glass. Argentic fluoride is a powerful oxidizing agent; some idea of its strength may be gained from the fact that it is not normally formed by action of bromine trifluoride on silver, although this reagent will oxidize rhodium to Rh^{IV}.

The omissions in Table I are interesting. One would not expect to find difluorides of Mo, W, Zr, Hf, Nb, or Ta, although dichlorides of these elements are known, and the behavior of IrF_3 makes it unlikely that IrF_2 will be prepared, but there is every reason to suppose that fluorides of Au, Rh, Ru and Ti should be isolatable under the proper conditions. If PtF_2 can be made, it will no doubt be the only paramagnetic salt of Pt^{II}, as PdF_2 is of Pd^{II} (8).

Difluorides with large cations crystallize with the fluorite structure, but the rest are of the rutile type. Small departures from ideality (Mn, Co, Pd) may be real or may perhaps be due to slight variations in composition; many of these salts cannot be easily recrystallized. Large distortions (Fe, Cr, Cu) must be due to more fundamental causes. The M—F distances in CuF_2 and CrF_2 have been accounted for in terms of ligand field predictions (11,12), but those of FeF_2 (13) are difficult to explain and so far no attempt has been made. In view of the recent work relating the structure of AgO to CuO (14) it seems likely that AgF_2 will also prove to be of the rutile type.

The complex fluorides AMF_3 (Table II) of cadmium and of the first period (A is K, Rb, Cs, or NH_4) are generally obtained by the

TABLE II
Complex Fluorides AMF_3

	Preparation method	Cation	Color	Structure	Magnetic moment, BM	Ref.
Cr	CrAc + KHF_2 under petroleum ether	K	Pale blue	Perovskite (dis)	—	23
Mn	Aqueous precipitation	K, Rb, NH_4, Cs	White	Perovskite	4.89; antiferromagnetic	25,26
Fe	Aqueous precipitation	K	White	Perovskite	4.17; antiferromagnetic	25
Co	Aqueous precipitation	K	Pink	Perovskite	4.03; antiferromagnetic	25
Ni	Aqueous precipitation	K	Pale yellow	Perovskite	2.07; antiferromagnetic	25
Cu	Aqueous precipitation	K	White	Perovskite (dis)	1 46; antiferromagnetic	23,25
Zn	Aqueous precipitation or melts	K, Rb, Na, Cs	White	Perovskite Perovskite (dis)	Diamagnetic	25
Pd	$CsF + PdF_2$ in SeF_4	Cs	Brown or violet	—	—	22
Cd	Aqueous precipitation or melts	K	White	Perovskite	—	25

action of a concentrated solution of alkali fluoride on a solution containing the bivalent transition metal; for example, $KCoF_3$ is made from potassium fluoride and cobaltous chloride. Only the cesium salt is known for the series $APdF_3$; it is made by selenium tetrafluoride reduction of the bromine trifluoride adduct $PdF_3 \cdot BrF_3$ in the presence of cesium fluoride at 200° (22).

The NH_4, K, and Rb salts which have been examined by X-ray diffraction (Table III) have been shown to have the perovskite lattice, sometimes with slight modifications. The chromium and copper salts, which are very difficult to obtain pure, have tetragonal distortion of the cubic perovskite cell: there are four longer and two shorter M—F bonds in each unit cell (23). This is in accordance with the predictions of the ligand field theory. Although the perovskite lattice is usually looked on as a typically ionic assemblage of A^+, M^{2+}, and X^- ions, the infrared spectra (24) of the fluorides suggest that there is appreciable covalent character to the M—F bond.

TABLE III
Bond Lengths and Infrared Absorption Frequencies of Complex Fluorides KMF_3 (23–26,190)

	Unit cell size, A.	M- F distance, A.	Frequency, cm. $^{-1}$
Cr	$a = 4.27$; $c = 4.01$	Four at 2.14; two at 2.01	481
Mn	$a = 4.19$	Six at 2.10	407
Fe	$a = 4.11$	Six at 2.06	431
Co	$a = 4.07$	Six at 2.04	439
Ni	$a = 4.01$	Six at 2.01	445
Cu	$a = 4.13$; $c = 3.92$	Four at 2.07; two at 1.96	489
Zn	$a = 4.05$	Six at 2.03	437

As with the difluorides, some of the difficulties associated with the X-ray work may well stem from the preparative methods, as none of the salts can be satisfactorily recrystallized. Consequently, nearly every worker in this part of the field has obtained slightly different unit cell sizes for the compounds (cf. 25), and as a result recent preparative work has stopped short at the K and Rb salts.

TABLE IV
Complex Fluorides A_2MF_4

	Preparative method	Cation	Color	Structure	Ref.
Fe	Aqueous precipitation or melts		—	—	
Co	Melts	K	Pink	Tetragonal with distorted $[CoF_6]$ octahedra	30
Ni	Melts	Li	Yellow	Fluorospinel	31
		K	Yellow	K_2CoF_4	32
Zn	Melts	K	White	K_2COF_4	31
Cu	Melts	K	White	K_2CoF_4	28
Pd, Pt	-	K	Yellow	- -	33

The complex fluorides A_2MF_4 (Table IV) have been but little investigated. The structures have been explained in terms of $[MF_6]$ octahedra and are thus quite different from the chlorides such as K_2CoCl_4 where the transition element is four-covalent (185). In K_2CuF_4 there are four long Cu···F bonds and two shorter ones in each $[CuF_6]$ octahedra as predicted by ligand field theory (28).

The complex fluorometallate ions do not appear to persist when the salts AMF_3 and A_2MF_4 are dissolved in water (29).

D. TERVALENT FLUORIDES AND THEIR COMPLEXES

Trifluorides (Table V) are widely distributed among the transition elements; like the difluorides, they are high-melting solids. Excepting those of Mn, Co, Pd, and Au they are comparatively inert and when well crystalline are practically insoluble in water.

Most of the preparations (Table V) are straightforward, but one or two call for comment. Pure manganese trifluoride is difficult to obtain; the action of fluorine on $MnCl_2$ leads to a product which still contains MnF_2, and the BrF_3 method is unsatisfactory because the product invariably contains bromine. The difficulty has been overcome by heating the BrF_3 adduct $(BrF_3)_2 \cdot MnF_4$ in fluorine at 300–500° (34). Ruthenium trifluoride is best obtained by the reduction of the pentafluoride with iodine (35); here the iodine is converted to iodine pentafluoride. Iridium trifluoride is also obtained by the reduction of a higher fluoride, this time the hexafluoride, IrF_6, by iridium metal (35). Although RhF_3 has so far always been made by the action of fluorine on a trihalide, it should be possible to avoid elementary fluorine and use hydrogen fluoride gas instead. In mak-

ing RhF_3 it is necessary to limit the supply of fluorine to avoid conversion of this compound to the tetrafluoride (36).

The structures of the *d* block fluorides, except for YF_3, are derived from that of ReO_3 and have been discussed in terms of the close packing of the fluorine atoms (35). Manganese trifluoride, in which the manganese has a d^4 electronic configuration, is distorted in accordance with ligand field theory predictions (34). The structure of AuF_3 is not yet known in detail.

Both ruthenium and iridium trifluorides show variations in composition (35) which have been attributed to admixtures of small amounts of other valency states. This phenomenon is probably more widespread than is generally realized and is worth looking into, especially when samples can be obtained by more than one preparative method.

The structures of the lanthanide (and actinide) trifluorides are similar to that of lanthanum trifluoride itself (37). The metal atom is not six-coordinate, as in the ReO_3 structure, but has five near fluorine neighbors and six more a little further away. Yttrium trifluoride has nine-coordinate metal atoms (38).

The trifluorides of manganese, cobalt, palladium, and gold are hydrolyzed immediately by water. Ruthenium trifluoride is stable in a moist atmosphere for some time, but eventually it appears to absorb moisture and changes in color from brown to red. A reactive yellow form of RuF_3 is produced by the action of carbon monoxide on the pentafluoride at 140° (39); this material dissolves in water (with hydrolysis) to give a red-brown solution which seems to be the same as that formed when Ru^{3+} is dissolved in hydrofluoric acid. Rhodium trifluoride forms a crystalline hydrate ($+9H_2O$); however, this is not prepared from the inert anhydrous salt, but by an indirect method (40); presumably it should be written as the aquo-salt $[Rh(H_2O)_6]F_3 \cdot 3H_2O$.

Tervalent complex fluorides are numerous and of several different kinds. They form a difficult group that has not been investigated at all thoroughly, but it is clear that in most of them the transition metal is six-coordinate. As a result of Brosset's work on the fluoroaluminates (48), it would be surprising if more of them are not found to show nonstoichiometry.

1. Compounds with Ionic Lattices

These are formed by the larger transition metal cations of yttrium, the lanthanides, and the actinides (49). They have the empirical

TABLE V
Trifluorides

	Preparative method	Color	Structure	M—F distance, A.	Magnetic moment, BM (25°)	Ref.
Sc	Dehydration of hydrate in HF gas stream F_2 + metal or anhydrous halides at 300–600°	White	MoF_3	Six at 1.95	—	46
Ti	Hydride + HF at 700°	Violet	VF_3	Six at 1.97	1.75[a]	43,44
V	Anhydrous trichloride + HF at 300–500°	Green	VF_3	Six at 1.94	2.55	45,47
Cr	Dehydration of hydrate in HF gas stream Anhydrous trichloride + HF at 300–500° F_2 + metal or anhydrous halides at 300–600°	Green	VF_3	Six at 1.90	3.8	35,47
Mn	F_2 + metal or anhydrous halides at 300–600° Decomposition of BrF_3–trifluoride adducts	Purple	VF_3 (dis)	Two at 2.09 Two at 1.91 Two at 1.79	4.94	34,47

Fe	Dehydration of hydrate in HF gas stream Anhydrous trichloride + HF at 300–500° Fe + metal or anhydrous halides at 300–600°	White	VF_3	Six at 1 92	—	35
Co	F_2 + metal or anhydrous halides at 300–600°	Brown	VF_3	Six at 1.89	2.46	35,47
Y	Dehydration of hydrate in HF gas stream	White	YF_3	Eight at 2.3 One at 2.6	—	38
Nb	Hydride + HF at 700°	Blue	MoF_3	Six at 1.95	0.7	42
Mo	Anhydrous trichloride + HF at 300–500°	Brown	MoF_3	Six at 1.95	—	41
Ru	Reduction of higher fluorides	Brown	VF_3	Six at 1 98	—	35
Rh	F_2 + metal or anhydrous halides at 300–600°	Red	PdF_3	Six at 1 98	—	35
Pd	F_2 + metal or anhydrous halides at 300–600° Decomposition of BrF_3–trifluoride adducts	Chocolate	PdF_3	Six at 2 04	2.0	35,47
La (rare earths)	Precipitation from aqueous solution	White	LaF_3	Six at 2 70 Five at 2.36	—	37
Ta	Metal + HF at 600°	Grey	MoF_3	Six at 1.95	1.4	41,47
Ir	Reduction of higher fluorides	Black	PdF_3	Six at 2 01	—	35
Au	F_2 + metal or anhydrous halides at 300–600° Decomposition of BrF_3–trifluoride adducts	Yellow	AuF_3	—	—	46

[a] θ = 0 degrees.

formula AMF_4, but do not contain complex ions, being crystal aggregates of A^+, M^{3+}, and F^- ions. The salts (e.g., $KLaF_4$) are made either by precipitation from aqueous solution or by extraction from fluoride melts. The curious compound $NaCaCdYF_8$ can be placed under this heading: it has a fluorite lattice with the metal ions distributed among the calcium positions of CaF_2 (51). The double fluoride $NaYF_4$ also has the fluorite structure, a consequence of the similarity in the ionic radii of sodium and yttrium, 0.98 and 0.93 Å., respectively (57).

2. Four-Covalent Compounds

These are formed by Ag and Au and again have the formula AMF_4. Here one would expect to find square planar $[MF_4]^-$ complex ions, and it appears likely that $KAuF_4$ will prove to be isostructural with the corresponding fluorobromate(III), $KBrF_4$ (52,53). The $[MF_4]$ ion is, of course, isoelectronic with $[PtCl_4]^{2-}$; and, as expected, both $AAgF_4$ and $AAuF_4$ are diamagnetic. The silver compounds are easily prepared by the action of fluorine on a mixture of ACl and $AgNO_3$; they are light yellow and, like AgF_2, attack glass and fume in moist air (52). The gold salts are made by the action either of bromine trifluoride on a suitable mixture of alkali chloride and gold powder (54) or of fluorine gas on the chloroaurates. Both sets of salts are decomposed immediately by water.

3. Cryolite-like Compounds

The complex fluorides A_3MF_6 (Table VI) (A is alkali metal; rarely Li, Na) contain discrete $[MF_6]^{3-}$ ions in the solid, but with one possible exception there is no evidence that these persist in solution. The cryolites are distributed throughout the central portion of the *d* block; their stability at the scandium end is evidently governed by ionic size. At the copper group end of the periodic table, copper itself forms K_3CuF_6, but silver and gold, with their increasing tendency to form inner orbital complexes, are limited to four covalency.

It is doubtful whether any of the cryolites can be obtained in a pure state directly from aqueous solution; usually hydrates such as $A_2MF_5 \cdot H_2O$ are precipitated. The fluorine reactions all go easily at about 300°; the chief difficulty is to find suitable compounds or mixtures for starting materials.

TABLE VI
Complex Fluorides A_3MF_6

	Preparative method	Cation	Color	Structure	Magnetic moment, BM (25°)	Ref.
Sc	Aqueous precipitation	NH_4, K	White	Cubic	—	57
	KHF_2 melt	K	White	Tetragonal	—	39
Ti	Aqueous precipitation	NH_4	Pale violet	—	—	
	Heat K_2TiF_6 in H_2 at 700°	K	Pale violet	Tetragonal	1 70	61
	Electrolytic reduction of K_2TiF_6 in KCl melt	K	Pale violet	Tetragonal	—	62
V	$K_2VF_5 \cdot H_2O$ and KHF_2 melt	K	Green	Cubic	2.74–2.79	39,47
Cr	F_2 + (3ACl + $CrCl_3$)	K	Green	Cubic	3.8–3.9	57,61
	KHF_2 melt	K	Green	Tetragonal	—	55
Fe	F_2 + (3ACl + FeX_3)	K, Rb	White	Cubic	—	57
	KHF_2 melt	K	White	Tetragonal	—	55
Co	CoF_3 + KF in HF	K	Blue	—	4.26	63
	F_2 + $A_3Co(CN)_6$	K, Rb, Cs	Blue	Cubic	5.1–5.3	64
Ni	F_2 + (3KCl + $NiCl_2$)	K	Violet	Cubic	—	57
Cu	F_2 + (3KCl + CuCl)	K	Pale green	Cubic	2.8	56,65
Y	F_2 + (3ACl + YU_3)	K, Rb, Cs	White	Tetragonal	—	57
Mo	K_3MoCl_6 + KHF_2 melt	K	Brown	Cubic	3.2	39
Ru	$RuCl_3$ + KHF_2 melt	K	Dark grey	Tetragonal	1.25	39,58
Rh	$K_3Rh(NO_2)_6$ + KHF_2 melt	K	Buff	Tetragonal	Diamagnetic	40,58
Ir	$(NO_2)_2IrF_5$ + carbonate	Na, (NaK_2)	Grey	—	—	66
				Cubic (K_2Na salt)	—	
Mn	KHF_2 melt	K	Bluish violet	Tetragonal	4.95	55

The structures of the transition metal cryolites seem to follow those of the parent aluminum compounds, A_3AlF_6. Few crystallographic data have been reported for sodium salts. The other alkali and ammonium salts have structures derived from the antifluorite structure; they usually have cubic symmetry when prepared at high temperatures, but specimens prepared at lower temperatures may have a slight tetragonal distortion. K_3MnF_6, like MnF_3 itself, shows a much larger distortion as a result of the Jahn-Teller effect. It is possible that some of the phase changes may also be associated with changes of composition in the same way as those observed by Brosset for the fluoroaluminates, but so far there is no evidence on this point.

The cryolites, except for the Mn^{III}, Ni^{III}, and Cu^{III} compounds, are relatively unreactive. They are stable to air, but are slowly attacked by water. K_3MnF_6 is rapidly attacked by water with the formation of hydrated manganese sesquioxide (55), and the Ni^{III} and Cu^{III} salts are hydrolyzed by water with oxygen evolution (56,57). The ruthenium and rhodium complexes are inert to water, but are soluble in dilute acid (58); the latter are completely decomposed in solution, but the ruthenium compounds are unusual inasmuch as the $[RuF_6]^{3-}$ ion appears to be retained in solution (39).

4. Complexes $A_2MF_5 \cdot xH_2O$

Hydrated precipitates of the composition $A_2MF_5 \cdot xH_2O$ ($x \leq 1$) seem to be the normal products when a solution of the tervalent transition element of the first period is added to an alkali fluoride solution (59). Salts $A_2MF_5 \cdot H_2O$ (M = V, Cr, Mn, Fe) are known; some have the antifluorite structure and doubtless contain $[MF_5 \cdot H_2O]^{2-}$ anions. Dehydration leads to the anhydrous compounds, which presumably contain condensed $[MF_6]$ octahedra. Compounds with divalent cations e.g., $BaFeF_5$ (which is formed from $BaFeO_3$ and fluorine) (39)—are known and would presumably contain similar condensed anions.

5. Other Complexes

The hydrated salts $KMoF_4 \cdot H_2O$ and $KWF_4 \cdot H_2O$ were mentioned a long time ago (60), but no subsequent work has been reported. Vanadium(III) gives salts such as $KVF_4 \cdot 2H_2O$ which might be ex-

pected to contain the $[VF_4(H_2O)_2]^-$ anion. Not much is known about anhydrous salts, but Hoppe (26) has recently made the manganese compounds $AMnF_4$ (A = K, Rb, Cs) by reducing the corresponding quadrivalent compounds, $AMnF_5$, in hydrogen at 250°.

Polynuclear complexes such as $(NH_4)_3Mo_2F_9 \cdot 2H_2O$ have been mentioned (60), but again there is no recent work.

It is clear, as remarked above, that much remains to be done in this part of the field. For instance, it would be interesting to know the properties of the complex fluorides of Ta^{III}, of PtF_3, and of K_2PdF_5 and K_2PtF_5 in which the platinum metal could be five-covalent. None of these materials has yet been isolated.

E. QUADRIVALENT FLUORIDES AND THEIR COMPLEXES

The quadrivalent fluorides, in conformity with Fajans' rules, show a decrease in ionic character compared with the tervalent compounds. None of the anhydrous salts can be obtained the wet way, and the methods used to prepare them have been almost as numerous as the fluorides themselves; however, they all begin either with anhydrous hydrogen fluoride or with elementary fluorine itself.

The tetrafluorides show physical properties which depend on the position of the particular transition metal in the Periodic Table. In the first period, titanium tetrafluoride is volatile (b.p. 284°), and chromium tetrafluoride probably sublimes at a similar temperature, but vanadium tetrafluoride disproportionates on sublimation (>325°) to VF_3 and VF_5. The other tetrafluorides have high melting and boiling points, with the curious exception of iridium, which has similar properties to the pentafluorides, especially to MoF_5, although recent work (67) has confirmed the formula IrF_4.

Most of the tetrafluorides, and especially the more volatile members, are hygroscopic substances which are completely decomposed by water, but ZrF_4 and HfF_4 form hydrates and TiF_4 gives the fluoro acid H_2TiF_6(aq). Well-crystalline PtF_4, in contrast to $PtCl_4$, is not decomposed rapidly by water and can be handled for a short time in the open air without perceptible decomposition.

The chemical properties of the tetrafluorides are little known. The unit cell sizes, but not the detailed structures, of the isomorphous Zr, Hf, Ce, Tb, Th, U, Pu, Am, and Cm compounds have been reported (69,70). The least certain compound in Table VII is that of man-

TABLE VII
Some Tetrafluorides

	Preparative method	Color	Other properties	Ref.
Ti	HF + $TiCl_4$ at 25° F_2 + TiO_2 at 300°	White solid Colorless liquid	B.p. 284°	74
V	HF + VCl_4 at 0–20°	Brown solid	Subl. 325; dec. into VF_3 and VF_5	75
Cr	Cr or $CrCl_3$ + F_2 at 300°	Brown solid Blue vapor	V.p. 3 mm. at 200°	76
Mn	Mn, $KMnO_4$, or $MnCl_2$ + F_2	Red-brown	Existence only suspected (see text)	
Zr	HF + $ZrCl_4$ at 300° Heat $(NH_4)_2ZrF_6$; ZrO_2 + F_2 at 300°	White solid Colorless liquid	Subl. red heat	77
Mo	Heat Mo_2F_9 (from Mo$(CO)_6$ + F_2 at −60°), residue is MoF_4	Green solid	Not volatile below 300°	71
Rh	$RhCl_3$ + F_2 at 500° BrF_3 + $RhCl_3$, heat adduct	Blue solid	Volatile at red heat in F_2	36 72
Hf	HF + $HfCl_4$ at 300°; heat $(NH_4)_2$ HfF_6; HfO_2 + F_2 at 300°	White solid	Subl. red heat	77
W	C_6H_6 + WF_6 at 110°	Red-brown solid		73
Re	Heat ReF_5	Blue solid	Subl. >300°	68
Os	$W(CO)_6$ + OsF_6	Yellow solid	M.p. 230° (d.)	108
Ir	IrF_6 + Ir at 200°	Yellow solid and liquid	M.p. 106°; b.p. 300°; liquid supercools readily	67
Pt	F_2 + $PtCl_4$; BrF_3 + Pt, heat adduct	Orange solid	Volatile in F_2 at high temp.	72

ganese. The bromine trifluoride adduct of this compound has been made, but the only evidence for MnF_4 itself is the red-brown smoke formed when almost any Mn compound is heated in F_2 (33,39).

The complex salts derived from the quadrivalent fluorides are better known than the binary compounds, mainly because they are more easily handled.

1. Compounds with Ionic Lattices

Like the tervalent compounds, these are usually formed by large cations of the actinides and lanthanides. Thus, K_2UF_6 has a disordered fluorite structure containing K^+, U^{4+}, and F^- ions (49).

The lanthanide compounds (of Ce, Pr, Tb, and perhaps Dy also) have only been described very recently (26,33); they appear to be isostructural with the fluorouranates(IV) and to show the expected magnetic properties. It has been shown that a similar type of compound may be formed by *d* block elements providing they are matched with suitable cation; e.g., $CaMnF_6$ has the VF_3 structure and is said to contain Ca^{2+}, Mn^{4+}, and F^- ions (78). This conclusion seems unlikely; $BaMnF_6$ contains MnF_6^{2-} ions, and it would be surprising if the Mn—F bond suddenly became ionic in the Ca salt. Clearly, discussion of the bonding in these compounds should await more information, and should at least be postponed until the nature of the bonding in the binary fluorides is known.

2. *Compounds* AMF_5

Only the manganese salts have been investigated in any detail. They are made by the action of fluorine on the perovskites $AMnF_3$ at 400 500° (26) or by the action of bromine trifluoride (79) or selenium tetrafluoride (86) on alkali permanganates. They are reddish brown salts readily hydrolyzed by water (contrast K_2MnF_6). The infrared spectrum of $KMnF_5$ is almost identical with that of K_2MnF_6 (24), which suggests that $[MF_6]$ octahedra are present in the crystal structure.

3. *Compounds* A_2MF_6

These are fairly widely distributed, although there are still some omissions. Only those of Ti, Zr, Hf, and Mn can be made directly from aqueous solution; the rest require dry methods or the use of nonaqueous solvents. The summary of preparative methods (Table VIII) shows the remarkable success of medium temperature fluorination by fluorine at 300° and the versatility of bromine trifluoride as a fluorinating agent. The preparation of the complex fluorides of ruthenium, osmium, and iridium is discussed in Section II-E. For purposes of discussion the A_2MF_6 complexes are best divided into three sections: (*a*) those with the Group IV valency (Ti, Zr, Hf), (*b*) the compounds in Groups V and VI, and (*c*) the compounds in Groups VII and VIII

(*a*) *Group IV Complexes.* The titanium complexes differ from the others in forming hydrates (e.g., $K_2TiF_6 \cdot H_2O$), which are, however,

TABLE VIII
Complex Fluorides A_2MF_6

	Preparative methods	Cation	Color	Structure	Magnetic moment, BM	Ref.
Ti	Aqueous solution	K	White	K_2SiF_6, K_2GeF_6, K_2MnF_6	—	1,93
		NH_4, Rb, Cs	White	K_2GeF_6	—	94
		Ba, $Mg{\cdot}5H_2O$	White	$BaSiF_6$	—	
		Na	White	Na_2TiF_6	—	
V	F_2 + V^{III} complexes	K	—	—	—	95
Cr	F_2 + (2ACl + $CrCl_3$)	K, Rb	Flesh	K_2SiF_6, K_2MnF_6	—	95
		Cs	—	K_2SiF_6	—	
Mn	Aqueous solution	K	Yellow	K_2SiF_6, K_2GeF_6, K_2MnF_6	—	1,93
	BrF_3 + (KCl + $KMnO_4$)	K	—	—	—	94
	F_2 + ($MnCl_2$ + 2ACl)	K, Rb, Cs	Yellow	K_2GeF_6	3.8–3.9	78,104
	F_2 + ($MnCl_2$ + 2ACl)	Na	Yellow	Na_2TiF_6	—	
	F_2 + manganites	Ca, Mg	Yellow	VF_3	—	
	F_2 + manganites	Sr, Ba	Yellow	$BaSiF_6$	—	78,104
	Aqueous solution	NH_4	Yellow	K_2GeF_6	—	1
Co	Cs_2CoCl_4 + F_2 at 300°	Cs	Yellow	K_2SiF_6	2.97 (calc.)	64
Ni	F_2 + ($NiCl_2$ + 2ACl) at 300°	K, Rb, Cs	Red	K_2SiF_6	Diamagnetic	96

Zr	Aqueous solution	K, NH_4, Tl	White	8-coordinate Zr	—	81,97
		Ca, Ba	White	ReO_3	—	26
		Rb, Cs	White	K_2GeF_6	—	81,97
Ru	H_2O on AMF_6	K, Cs	Yellow or pink	K_2GeF_6	2 9 (300°K.)	86,105
	F_2 + ($BaCl_2$ + $RuCl_3$)	Ba	Blue	$BaSiF_6$	—	88
	$K_2Ru(NO_2)_4(NO)(OH)$ + KHF_2 melt	K	Pink	K_2SiF_6	—	89
Rh	BrF_3 + ($RhCl_3$ + 2ACl)	Na	Yellow	Na_2TiF_6	1.7–1.9	47,72
	F_2 + $RhCl_3$ + 2ACl	K, Rb, Cs	Yellow	K_2GeF_6	—	88
Pd	A_2PdCl_4 + BrF_3	K	Yellow	K_2MnF_6	Diamagnetic	99
	A_2PdCl_4 + F_2	Rb, Cs	—	K_2SiF_6	—	98
Hf	Aqueous solution	K, NH_4, Tl	White	K_2ZrF_6	—	81,97
		Ca, Ba	White	ReO_3	—	26
		Rb, Cs	White	K_2GeF_6	—	81,97
Re	HF + A_2ReBr_6 at 300°	K, Rb, Cs	White	K_2GeF_6	—	83
	AHF_2 + A_2ReI_6	K, Rb, Cs	White or pale pink	K_2GeF_6	3 3–3 4 (25°) θ = 40 deg. (K salt)	84,105
	From K_2ReF_6 in aqueous solution	Na	Bluish	Na_2ReF_6 tetragonal modification of K_2SiF_6	—	83,84
		Ba	White	$BaSiF_6$	—	
		NH_4	White	K_2GeF_6	—	
		$[Co(NH_3)_6]^{3+}$	—	—	—	
		$[Ni(NH_3)_6]^{2+}$	—	—	—	

(continued)

TABLE VIII (*continued*)

	Preparative methods	Cation	Color	Structure	Magnetic moment, BM	Ref.
Os	Alkali + AMF_6	K, Cs	Cream	K_2GeF_6	1.48 (300°K.)	85,87,105
	From K_2OsF_6 in aqueous solution	Ba	White	$BaSiF_6$	—	
		Na	—	Na_2TiF_6	—	
		NH_4	—	K_2GeF_6	—	
Ir	H_2O on AMF_6	K, Cs	Cream or pink	K_2GeF_6	—	85,87
	From K_2IrF_6 in aqueous solution	Ba	—	$BaSiF_6$	—	
		Na	—	Na_2TiF_6	—	
		NH_4	—	K_2GeF_6	—	
	$K_3Ir(NO_2)_6$ + KHF_2 melt	K	Pink	K_2GeF_6	–	89
Pt	F_2 + K_2PtCl_6	K	Yellow	K_2GeF_6	—	
	BrF_3 + A_2PtCl_6	Na	Yellow	Na_2TiF_6	—	47,72
		K, Rb, Cs	Yellow	K_2GeF_6	—	98,99
	F_2 + Pt (foil) + AF_3	—	Yellow	—	—	100–103
	Rare earths	—	—	—	—	
	Other salts by ion exchange	—	—	—	—	

easily dehydrated. There is also an acid salt, Na_3HTiF_8. The structures of the complexes A_2MF_6 have been discussed in considerable detail by Sharpe (1); it is sufficient to note here that K_2ZrF_6 and K_2HfF_6 are unique in exhibiting eight coordinations of the transition metal (81), although the Cs and Rb salts are six-coordinate. It would be interesting to know whether the Nb, Ta, Mo, and W compounds follow the same structural pattern; these have not yet been isolated, though it should be possible to prepare them.

(*b*) *Group V and Group VI Complexes.* Only the V and Cr salts are known, the former very imperfectly. They are immediately hydrolyzed by water; the Cr salts disproportionate at the same time into Cr^{III} and Cr^{VI}. In both $[VF_6]^{2-}$ and $[CrF_6]^{2-}$ there are empty *d* orbitals; presumably these offer a point of attack for water molecules if one assumes an S_N2 mechanism. This tendency to rapid hydrolysis leads to practical difficulties in the attempted preparation of A_2MoF_6 and A_2WF_6 which have not yet been overcome. For example, the interaction of MoF_4 with KHF_2 should give K_2MoF_6, but the isolation of pure complex salts from the melt has so far proved impossible (39).

(*c*) *Group VII and Group VIII Complexes.* These are characterized by the occupation of each nonbonding *d* orbital by at least one electron. Technetium and iron salts are absent, the former because no attempts have been made to prepare them.

In the first period, the stability of the $[MF_6]^{2-}$ ions is presumably in the order Mn > Ni > Co > Fe. The nickel salts are evidently stabilized to some extent by the filling *d* shell in octahedrally bonded Ni^{IV}; for Co^{IV} only the caesium salt (64) is known, which suggests that the critical factor in the stability of the quadrivalent cobalt complexes is lattice energy. All attempts to prepare fluorine compounds of Fe^{IV} have failed, presumably because the extra stability conferred upon Fe^{III} by the half-filled *d* shell is enough to prevent stabilization of $[FeF_6]^{2-}$ in the crystal even by a very large cation.

Nearly all the salts have magnetic moments which fall within the expected range, but the reported data on Cs_2CoF_6 are peculiar and require confirmation.

Only the $[MnF_6]^{2-}$ ion exists in aqueous solution, and it appears to undergo a slow, irreversible decomposition even in hydrofluoric acid solution, so that the isolation of fluoromanganates from aqueous solution (e.g., in the reduction of permanganate by ether or Mn^{2+} in

hydrofluoric acid) requires practice and a rapid technique if a good yield is to be obtained. The main decomposition products are Mn^{III} (which remains in hydrofluoric acid solution) and hydrated manganese dioxide. The cobalt and nickel salts are decomposed at once by water with the liberation of oxygen.

In the second period, the fluororuthenates(IV) exist in pale pink, pale blue, or cream variants according to the color of the quinquevalent salts from which they were prepared. They decompose slowly in moist air, and cold aqueous solutions precipitate hydrated ruthenium dioxide on standing. Hot or alkaline solutions decompose rapidly. Addition of hydrochloric or hydrobromic acid to the cold solution gives the corresponding haloruthenate(IV); the course of this reaction can be followed by the color change. The salts are soluble in pyridine to give green complexes of unknown composition (39). The fluororhodates and fluoropalladates are completely and irreversibly hydrolyzed by water.

In the third period, all the salts are relatively inert toward water. The fluororhenates(IV) are colorless or pale pink as a rule, but the sodium salt is bluish (83,84). They are affected neither by alkali, unless very concentrated, nor by halogen acid, except by 40% hydrofluoric acid which, rather surprisingly, decomposes them. The fluoroosmates(IV) (85,87) are nearly as stable to alkali, but are readily attacked by halogen acid. The fluoroiridates(IV), which exist in cream or pale pink varieties, are inert to alkali and to hydrochloric acid, but hydrobromic acid reduces them to Ir^{III}. There is some evidence that in strong alkali the species $[IrF_5(OH)]^{2-}$ is formed reversibly (87). The fluoroplatinates, which are pale yellow, are attacked readily by halogen acid and apparently by alkali also.

The behavior of these compounds toward water is interesting. It is certain that thermodynamically all should be hydrolyzed; but in fact some (the third period compounds) are not, some (Mn, Ru) are hydrolyzed slowly, and the others (Co, Ni, Rh, Pd) are decomposed immediately. It is easy to understand why compounds with unoccupied, nonbonding *d* orbitals should be hydrolyzed; obviously, a first stage would be the attachment of a water molecule to a vacant orbital (S_N2 mechanism). This easy addition is not available in the present case, so that an S_N2 mechanism would involve either the formation of two "half-bonds" in the transition state or the promotion of electrons to higher orbitals. An S_N1 mechanism would involve

the removal of a fluorine ion from the complex (the rate-determining step) followed by addition of water. Rapid hydrolysis in water occurs only for compounds in which the transition metal is in a high oxidation state; $[CoF_6]^{2-}$ and $[NiF_6]^{2-}$ are sufficiently powerful oxidizing agents to liberate oxygen from water. $[RhF_6]^{2-}$ and $[PdF_6]^{2-}$ are decomposed to give precipitates of hydrated oxides of M^{IV}, but it would still be quite possible here for a hydrolysis mechanism to involve lower oxidation states.

Another interesting problem is the behavior of the less labile salts, i.e., those of rhenium, osmium, iridium and platinum, toward hydrochloric acid. $[OsF_6]^{2-}$ and $[PtF_6]^{2-}$ are attacked, but $[ReF_6]^{2-}$ and $[IrF_6]^{2-}$ are not.

4. Complexes of Higher Coordination Number

For quadrivalent metals these are formed by the Group IV elements Zr and Hf, and by uranium. Complexes A_3MF_7 are precipitated when solutions of Zr^{IV}, Hf^{IV}, and U^{IV} are added to excess of alkali fluoride solution (A = K, Rb, Cs); when sodium fluoride is used, complexes such as Na_5ZrF_9 can be obtained as well. The $[MF_7]^{3-}$ ion has the pentagonal bipyramid shape (27,90,91); the structure of Na_5ZrF_9 is unknown. How far these fluoro ions retain their identity in solution is uncertain; in very dilute solution Zr has been shown to be present as the (presumably hydrated) ZrF_3^+ ion (92).

Complexes of high covalency will only be formed while there are spare *d* orbitals to bond with the extra fluoride ions, so one would expect for M^{IV} a maximum of nine in Group IV decreasing to six in Groups VII and VIII. Covalencies greater than six are only realized in Group IV and for uranium, but this situation may be due more to experimental difficulty than to any fundamental reason.

F. QUINQUEVALENT FLUORIDES AND THEIR COMPLEXES

Not many pentafluorides are known (Table IX), and none can be made from aqueous solution even as a hydrate. Niobium, tantalum, and uranium pentafluorides have been made by the action of anhydrous hydrogen fluoride on the pentachlorides, but they and the remaining compounds are conveniently prepared by reactions involving elementary fluorine. A little MoF_5 is obtained when molybdenum sponge is heated in a defective supply of fluorine (39), but it

TABLE IX
Pentafluorides

	Preparative method	Color	M.p., °C.	B.p., °C.	Magnetic moment, BM (25°)	Ref.
V	$V + F_2$ at 300–350°	White solid Straw-colored viscous liquid	19.6	48.4	- -	106,111,112
Cr	Cr or $CrCl_3 + F_2$ at 300°	Fire red	Vol. at 100			76,113
Nb	Nb, Nb_2O_5, or $NbCl_5 + F_2$ at 300–500°	White solid Colorless liquid and vapor	80	234.9	- -	107,149,151
Mo	$MoF_6 + Mo(CO)_6$ at 25°	Yellow solid and liquid Colorless vapor	70.0	209.9	-	39,71,186
Ru	$F_2 + Ru$ or RuO_2 at 300° $BrF_3 + Ru$ at 25° heat adduct	Green solid and liquid Colorless vapor	115	270–275	-	86,172
Ta	Ta or $Ta_2O_5 + F_2$ at 300°	White solid Colorless liquid and vapor	95.1	229.2	- -	107,149,151
Re	$ReF_6 + W(CO)_6$ at 20°	Yellow solid and liquid	48.0	208.5 (dec. to $ReF_4 + ReF_6$)	1.41; θ = 578 deg.	68,186
Os	OsF_6 + UV light	Grey-green solid	70.0	225.5	2.06; θ = 80 deg.	108,162,186
	$OsF_6 + I_2$ in IF_5	Green liquid at 70°C.; blue liquid at 225°C.				
	$OsF_6 + W(CO)_6$	Colorless vapor				
Pt	$PtCl_2 + F_2$	Dark red	76	>300	Paramagnetic	181,187

is better to allow a fluorine stream well diluted with nitrogen to interact with molybdenum hexacarbonyl at −75°. This reaction yields Mo_2F_9, which decomposes in a vacuum at 150° to give a mixture of MoF_5, which distills off, and MoF_4, which remains behind as a nonvolatile residue (71). Another method is to warm molybdenum carbonyl with excess molybdenum hexafluoride (39):

$$5MoF_6 + Mo(CO)_6 \rightarrow 6MoF_5 + 6CO$$

The older and more tedious method of making vanadium pentafluoride was by disproportionation of the tetrafluoride (75).

Rhenium pentafluoride has recently been obtained by the action of rhenium or tungsten carbonyls on ReF_6, and OsF_5 either by the reduction of OsF_6 by a solution of iodine in iodine pentafluoride or by the action of tungsten carbonyl on OsF_6.

It is convenient to mention here the various "mixed valency" compounds. These are best known for uranium (114) and lie in between the compositions UF_4 and UF_5, e.g., U_2F_9 and U_4F_{17}. They are made by the action of UF_6 on UF_4 at low pressure, by thermal decomposition of UF_5, or by the interaction of UF_4 and UF_5. Such compounds are probably also formed by some of the transuranic elements. Their properties are those of "mixed valency" compounds, i.e., equivalence of the U atoms and strong color. The behavior of Mo_2F_9 (71) suggests that it should be represented as the salt $(MoF_3)^+$-$(MoF_6)^-$.

The pentafluorides of the first period (V and Cr) are easily volatile, but the others in the *d* block melt between 79 and 150° and boil at 200–300° (the f block pentafluorides are more salt-like and tend to disproportionate into MF_4 and MF_6 when strongly heated). All are very reactive, being hydrolyzed by water with a considerable evolution of heat, and should therefore be handled in closed systems. Glass apparatus can be used in the preparation and handling of pentafluorides provided special care is taken to dry starting materials and to maintain anhydrous and HF-free conditions: it is very difficult to free pentafluoride from traces of moisture and only VF_5 and perhaps CrF_5 can be dried over sodium fluoride.

Not a great deal is known about the physical and chemical properties of the *d* block compounds. Vanadium pentafluoride, which has

TABLE X
Complexes AMF_6

	Preparative method	Cation	Color	Structure	Magnetic moment, BM	Ref.
V	VF_5 + AF under pressure	K, Rb, Cs	White	$BaSiF_6$ or $KOsF_6$; rhombohedral distortion of CsCl		115
	BrF_3 + ACl or ACl_2 + VCl_3	Ag	White	CsCl		
		Ca, Sr, Ba	White	—		
		Li	White	?$NaOsF_6$ (hexagonal)		115
Nb	Aqueous solution	Na	White	NaCl		115
	BrF_3 + [Nb_2O_5 + 2ACl]	K	White	$KNbF_6$		117
		Rb, Cs (NH_4)	White	$BaSiF_6$ or $KOsF_6$; rhombohedral distortion of CsCl		115
Mo	MoF_6 + AI + SO_2	Na	White	NaCl		118–120
	MoF_6 + AI + IF_5	K	White	$KNbF_6$		
		Rb, Cs	—	$BaSiF_6$ or $KOsF_6$; rhombohedral distortion of CsCl	1.3 (25°); θ = 66° (K salt)	
Ru	$RuCl_3$ + ACl + F_2 at 300°	K, Rb, Cs	Blue	$BaSiF_6$ or $KOsF_6$; rhombohedral distortion of CsCl	3 6–3.8 (25°)	88
	BrF_3 + Ru + ACl	K, Rb, Cs	Pink or white	$BaSiF_6$ or $KOsF_6$; rhombohedral distortion of CsCl	3.6–3.8 (25°)	86
		Ag	Pink or white	—		
		Ca, Sr, Ba	Pink or white	—		
	BrF_3 + $RuCl_3$ + ACl	Na, Li	—	$NaOsF_6$ (hexagonal)		183

Ta	Aqueous solution	Li	White	?$NaOsF_6$ (hexagonal)		115
	BrF_3 + [Ta_2O_5 + 2ACl]	Na	White	NaCl		115
		K	White	$KNbF_6$		117
		Rb, Cs (NH_4)	White	$BaSiF_6$ or $KOsF_6$; rhombohedral distortion of CsCl	—	115
W	WF_6 + AI + SO_2	Na	White	$KNbF_6$	0.5 (25°) (K salt); antiferromagnetic	118–120
		Rb, Cs	White	$BaSiF_6$ or $KOsF_6$; rhombohedral distortion of CsCl	—	
Re	ReF_6 + AI + SO_2	Na	White	NaCl	—	120.121
	ReF_6 + AI + IF_5	K	White	$KNbF_6$	1.85 (25°); θ = 58° (K salt)	
		Rb, Cs	White	$BaSiF_6$ or $KOsF_6$; rhombohedral distortion of CsCl		
Os	$OsBr_4$ + ACl + BrF_3	Li, Na, Ag	Cream	$NaOsF_6$ (hexagonal)	—	85,87
	2$OsBr_4$ + $AClO_3$ + BrF_3	K, Rb, Cs	Cream	$BaSiF_6$ or $KOsF_6$; rhombohedral distortion of CsCl	3.25–3.3 (25°); θ = 0° (K salt)	105.122
		Ca, Sr, Ba	Cream	—		
Ir	$IrBr_3$ + ACl + BrF_3	Na	Pink	$NaOsF_6$ (hexagonal)	—	85.87.122
	2$IrBr_3$ + ACl_2 + BrF_3	K, Rb, Cs	Pink	$BaSiF_6$ or $KOsF_6$; rhombohedral distortion of CsCl	1 2	
		Ca, Sr, Ba	Pink	—	—	

been the subject of recent studies, is viscous like SbF_5 at 25°, and on basis of conductivity measurements the autionization

$$2VF_5 = VF_4^+ + VF_6^-$$

has been postulated (106). VF_5 is a powerful fluorinating agent and will convert SO_2 to SOF_2. NbF_5 and TaF_5 are feeble fluorinating agents, and, instead of fluorinating SO_3 to pyrosulfonyl fluoride as VF_5 does, combine with it to form stable adducts (107). Osmium pentafluoride, which is probably the same material as Ruff's "OsF_6" (108), has been shown to form adducts with SeF_4 (109). ReF_5 disproportionates above 200° to ReF_4 and ReF_6; the reaction is rapid at its boiling point (110). Attempts to prepare IrF_5 (e.g., by reduction of IrF_6 with iodine (67)) have been unsuccessful, although again the SeF_4 complexes are known (109). Very recently indications have been obtained of the existence of PtF_5 (181), and details of the properties of this compound are awaited with interest.

1. Complexes AMF_6

In this group (Table X) only the complexes of Nb and Ta can be isolated from aqueous solution, and the method is tedious. Probably the most useful reagent in this part of the field is BrF_3; it has been used to make V, Nb, Ta, Ru, Os, and Ir salts. The choice of starting materials may be important; for instance, osmium sponge is oxidized rather easily to OsF_6 by BrF_3 so that it is better in this case to use $OsBr_4$. In making the Ru salts by the medium temperature fluorination method, particular care must be taken to start with dry reactants; otherwise, Ru is lost as volatile ruthenium tetroxide.

Since molybdenum, tungsten, and rhenium are oxidized to the sexivalent state by both fluorine gas and bromine trifluoride, these reagents cannot be used in the preparation of quinquevalent complexes of these elements. These complexes are best made by the reaction of the hexafluorides by alkali iodide in an indifferent solvent such as liquid sulfur dioxide

$$MF_6 + AI \rightarrow AMF_6 + I$$

but the rhenium and molybdenum salts may also be made in iodine pentafluoride solution; here the solvent can hardly be considered

indifferent and the reducing agent must be either iodine liberated from the iodide by reaction with the solvent

$$5AI + IF_5 \rightarrow 5AF + 3I_2$$

or a species of polyhalide ion such as $[IF_4]^-$.

The complexes AMF_6 (except the silver salts) are white or slightly colored materials. The color in some cases seems to depend on the method of preparation; for example, specimens of $KRuF_6$ prepared by the high temperature fluorination method are pale blue, but those from bromine trifluoride solution may be pale pink or cream. The colors are probably due to trace impurities, and no doubt the slight brownish tint of specimens of KWF_6 and $KReF_6$ is due to the same cause. Structures have been discussed in detail by Sharpe (1) and by Cox (115).

Chemical properties are governed to some extent (as with M^{IV}) by the availability of *d* orbitals. For M^V the dividing line comes between Group VII and Group VIII.

(*a*) *Group VIII Complexes.* In these the $[MF_6]^-$ ion has at least one electron in each spare *d* orbital. The fluororuthenates and fluoroiridates dissolve in water with the evolution of oxygen and are themselves reduced to $[RuF_6]^{2-}$ and $[IrF_6]^{2-}$. Side reactions result in a little ruthenium tetroxide and iridium dioxide being formed, respectively, the former through hydrolysis of $[RuF_6]^{2-}$ to $RuO_2 . nH_2O$ followed by oxidation of the ruthenium dioxide to tetroxide by $[RuF_6]^-$.

The redox potentials for the reaction $MF_6^- + e \rightarrow MF_6^{2-}$ have been estimated for both RuF_6^- and IrF_6^- from the chemical behavior of the compounds; they have about the same value, $E^\circ \simeq 2.1$ volts. The solution becomes acid as each equivalent of M^{IV} fluoro acid ion gives two M^V fluoro acid ions (182).

The salts $AOsF_6$ dissolve in water without apparent reaction, although the solution, as commonly occurs with nearly neutral osmium solutions, smells slightly of OsO_4. When the pH of the solution is raised above 7 by addition of alkali, oxygen is evolved and quadrivalent $[OsF_6]^{2-}$ is formed. This means that $[OsF_6]^-$ is a less powerful oxidizing agent than $[RuF_6]^-$ or $[IrF_6]^-$. The redox potential for the reaction

$$OsF_6^- + e \rightarrow OsF_6^{2-}$$

has been estimated from the chemical behavior of the salts to be about $E^\circ \simeq 0.6$ volt (cf. RuF_6^- above).

(*b*) *Group VI and Group VII Complexes.* Here the $[MF_6]^-$ ion has at least one spare orbital unoccupied. The salts are hydrolyzed immediately by water, and the molybdenum and tungsten salts are so sensitive to traces of moisture that they could be used as irreversible color indicators (change: near white to deep blue). The hydrolysis products are complicated, probably including oxyfluorides (very easily oxidized with tungsten) and mixed-valency hydrated oxides. The rhenium salts turn black on exposure to moist air; with water they give brown, hydrated rhenium dioxide, hydrofluoric acid, perrhenic acid, and a small proportion (about 20%) of fluororhenate(IV). The yield of fluororhenate(IV) can be made quantitative if the quinquevalent salt is fused with an acid fluoride such as KHF_2 and the cold melt dissolved in water (39); presumably in this case the empty *d* orbital is occupied temporarily by F^- ions or HF molecules so that it is clear that the mechanism which operates for the fluoroosmates(V), fluoroiridates(V), and fluororuthenates(V) is still significant for rhenium. There is no evidence of quadrivalent fluoromolybdates and fluorotungstates in the products of hydrolysis of $AMoF_6$ and AWF_6; if they are formed at all, they would have an unoccupied *d* orbital in the transition metal fluoro ion and so would be expected to undergo further ready hydrolysis.

(*c*) *Group V Complexes.* The vanadium salts are hydrolyzed to give oxyfluoride complexes, but with quinquevalent niobium and tantalum the hydrolysis of the fluoro ions is reversible. With tantalum the equilibrium is more toward the fluoride side than with niobium, sufficiently so to provide a means of separating Nb and Ta. The NbF_6^- and TaF_6^- ions almost certainly do not exist as such in aqueous solution, as the tendency toward higher covalencies is very strong.

2. *Complexes A_2MF_7 and A_3MF_8*

These are formed (116) by Nb and Ta. The salts A_2TaF_7 (A = K, Rb, Cs) are easily made from the alkali carbonate, tantalum pentoxide, and excess of hydrofluoric acid; they are only slightly soluble in the cold in aqueous solution. The corresponding niobium salts are more difficult to make; they require a high fluoride ion concentration or the use of anhydrous hydrogen fluoride. The usual

products obtained from aqueous solution are the salts $A_2NbOF_5 \cdot H_2O$. The compounds A_3MF_8 appear to be formed in the presence of a large excess of alkali fluoride; only the sodium salt is well known.

As with the quadrivalent complexes, the question of higher covalency or coordination number is bound up with the *d* orbitals in M^V. It would be expected therefore that compounds A_2MF_7 and A_3MF_8 should also be formed by molybdenum and tungsten, and A_2MF_7 by rhenium. There are signs that the salts K_3MoF_8 and K_3WF_8 can be isolated, but the chief difficulty in preparing such compounds is solubility. If nonaqueous solvents are used, there is no certain way of knowing in advance whether the products will be the desired salts A_3MF_8 or A_2MF_7 or merely mixtures of AF and AMF_6. For example, although it is easy to obtain heptafluorotantalates(V) from aqueous solution, they cannot be isolated from bromine trifluoride solution, presumably because the hexafluorotantalates(V) are less soluble and so crystallize out first.

G. HIGHER FLUORIDES AND COMPLEX FLUORIDES

Apart from the hexafluorides, only the newly discovered rhenium heptafluoride comes in this section. ReF_7 is a pale yellow solid, m.p. 4°, which is less volatile than ReF_6. It is formed by the action of fluorine on rhenium hexafluoride under pressure at 400° (188.)

Tungsten and uranium hexafluorides can be made without elementary fluorine; the first by the action of anhydrous hydrogen fluoride, arsenic trifluoride, or antimony pentafluoride on tungsten hexachloride, and the second from uranium pentachloride and anhydrous hydrogen fluoride. However, all the hexafluorides are conveniently made in the laboratory by the action of elementary fluorine on either the metal (Mo, W, Re, Os, and Pt) or a lower fluoride (U). Most of the preparations are easy, but a good supply of fluorine is essential, especially for IrF_6 and PtF_6. Platinum hexafluoride is somewhat unstable and requires special apparatus and reaction conditions. Some of the fluorides can be made by the action of bromine trifluoride on the elements (Mo, W, Re, and Os), but as it is difficult to separate them from the bromine which is formed at the same time, this method is not recommended (Table XI).

In view of their considerable reactivity, the hexafluorides are best handled in closed systems. They attack glass in the presence of even

TABLE XI
Hexafluorides

	Preparative method	Color	M.p., °C.	B.p., °C.	Magnetic moment, BM (25°)	Ref.
Mo	Metal + fluorine at 300°	White solid Colorless liquid and vapor	17.5	35		128–130
W	Metal + fluorine at 300°	White solid Colorless liquid and vapor	2.3[b]	17.1		131–133
Re	Metal + fluorine at 300°[a]	Yellow solid and liquid Colorless vapor	18.8[b]	35.6	1.05 (25°)	134–136 186,188
Os	Metal + fluorine at 300°[a]	Yellow-green solid Yellow liquid Colorless vapor	32.1	47.0	1.5; θ = 66 deg.	123.125 186
Ir	Metal + fluorine at 300°	Yellow	44.4	53	3.3; θ = 0 deg.	125.137, 139
Pt	Pt + F_2 under special conditions	Black solid Brown vapor	56.7	—		138

[a] When ReF_6 and OsF_6 are prepared using fluorine derived directly from an electrolytic cell special precautions must be taken to guard against volatile impurities passing into the reaction zone. The presence of these, which may contain traces of Cl_2, leads to orange specimens of ReF_6 and dark green specimens of OsF_6 (39).

[b] WF_6 and ReF_6 have solid transition points at −8.2 and −4.8°C., respectively (186).

traces of moisture, but can be handled in it provided the surface has first been baked in a vacuum and then "pickled" by temporary exposure to the fluoride. When storing *d* block compounds in glass for any length of time it is advisable to have a little dry sodium fluoride in the system to act as a "keeper"; its function is to combine with any hydrogen fluoride or transition metal oxyfluoride which may be present. Uranium hexafluoride, however, combines with sodium fluoride and so cannot be kept pure in this way.

X-ray studies on the solid hexafluorides have shown the presence of molecular MF_6 units in the crystal (123), a result consonant with the low melting and boiling points. The vapors have also been shown to be monomeric from vapor density measurements (cf. 123).

The chemical properties of the hexafluorides are not well known. Molybdenum hexafluoride is easily reduced to the quinquevalent state and attacks organic materials, though little is known about the products. It is vigorously hydrolyzed by water to give completely soluble products; the reduction is complicated, and when only small quantities of moisture are present a little Mo^V may be formed. Tungsten hexafluoride is as reactive toward water, but is less easily reduced and appears to be less reactive toward organic materials; e.g., it gives a red solution in benzene and is miscible with other hydrocarbons (124).

Rhenium hexafluoride disproportionates on hydrolysis into the hydrated dioxide and perrhenic and hydrofluoric acids, but slow decomposition in a slightly moist glass apparatus yields white oxyfluorides and a little of the blue oxyfluoride, $ReOF_4$ (108).

The three platinum metal hexafluorides are less stable than the foregoing. Osmium hexafluoride is very like the rhenium compound in appearance and physical properties; its magnetic moment varies in the way expected for an Os^{VI} $d\epsilon_2$ compound (125). It easily forms a lower fluoride (OsF_5) when irradiated in a silica tube with ultraviolet light (with the liberation of fluorine) and is also reduced by iodine. The hydrolysis of OsF_6 is not simple; it seems to parallel that of the isoelectronic $[ReF_6]^-$ ion, and the products are osmium tetroxide, hydrofluoric acid, and a complex fluoro ion, probably $[OsF_6]^-$. When dissolved in alkali the hexafluoride gives a little tetroxide (10%), but the greater quantity goes to $[OsF_6]^{2}$. It is odd that although a *d* orbital is still available in Os^{VI} for coordination, the decomposition goes largely by the electron transfer mechanism whereby Os^{VI} acquires an extra electron to become $[OsF_6]^{--}$.

Iridium hexafluoride, with its bright yellow vapor, decomposes slowly in daylight, apparently to the quadrivalent IrF_4, so that it presumably absorbs in the blue or violet region of the visible spectrum. It is reduced to IrF_4 by ultraviolet light and heat (170° in nitrogen). Its hydrolysis yields oxygen, hydrofluoric acid, and hydrated iridium dioxide. One would expect, since it is isoelectronic with $[OsF_6]^{--}$, that the hydrolysis would give some $[IrF_6]^{2-}$, but this has not been observed, perhaps because the conditions used have been too vigorous. IrF_6 undergoes an interesting reaction with liquid N_2O_4 (126), giving $NO_2^+IrF_6^-$ which, on being heated, is degraded to $(NO_2)_2IrF_5$, an Ir^{III} compound.

The remaining hexafluoride in the *d* block, that of platinum, has only recently been discovered and characterized, although it is fairly certain that it must have been previously observed (and overlooked) by several workers. All the more credit must go to Weinstock and Malm (123) for isolating the first compound in which platinum undoubtedly has a valency of six. Not much is yet known about its properties; it is stable in nickel at 25°, but decomposes slowly in Pyrex or silica vessels, presumably by photolysis. It is a very strong oxidizing agent and will oxidize neptunium(IV) to NpF_6. Thermally it appears to be unstable (c.f. IrF_6).

The sexivalent complex fluorides, except for those of uranium, are little known. Recent studies have shown that they are formed by combination between the alkali (K, Rb, Cs) fluorides and the hexafluorides of the *d* block elements molybdenum, tungsten, and rhenium in the presence of a suitable ionizing solvent such as iodine pentafluoride (119,140). The compounds (stable to 150°) have the formulae K_2MF_8, $RbMF_7$ (apparently isostructural with K_2MF_8), and $CsMF_7$. They present some puzzling features; e.g., the X-ray evidence suggests that in the K and Rb salts the covalency of the transition metal does not rise above six. The salts are hydrolyzed by water, and it is noticeable with those of rhenium that the green color of Re^{VI} presists in solution for several days in the cold, although it appears only transiently when ReF_6 itself is hydrolyzed.

III. Oxyfluorides, Complex Oxyfluorides, Mixed Halides, and Coordination Compounds

A. OXYFLUORIDES

Owing to the similarity in size (ionic radii F^- = 1.36 A., O^{2-} = 1.40A.; covalent radii F = 0.64 A., O = 0.66 A.), oxygen and fluorine

can replace one another without causing a large structural distortion, so that in physical properties some transition metal oxyfluorides are similar to binary fluorides of similar empirical formulas (e.g., molybdenum oxytetrafluoride has the melting and boiling points of a pentafluoride) and others to oxides (e.g., TaO_2F is nonvolatile like ReO_3, and ReO_3F has a boiling point near that of OsO_4). Since each successive replacement of a fluorine atom by an oxygen atom leads to a unit increase in the oxidation number of the transition metal ion, it may be expected that (*1*) oxyfluorides will be more covalent than the parent fluorides and (*2*) the coordination number of the transition metal may also change. Each of these factors will affect the structure and volatility of the compound. Thus, although CrF_4 probably has six-covalent chromium in the solid state like the complex K_2CrF_6, the volatile CrO_2F_2 probably has a molecular structure in the solid with four-coordinate chromium.

1. Oxyfluorides MOF (69,141,142,144,145)

These are known for yttrium, the lanthanides, and two actinide elements, actinium and plutonium. They are prepared either by partial hydrolysis of the trifluorides at 800° or by the high temperature combination of the tervalent oxides and fluorides. Most of those which have been examined by X-ray diffraction have been shown to possess the ionic fluorite type of structure, with a random distribution of O^{2-} and F^- among the fluorine positions. Molybdenum is said to form a hydrated oxyfluoride, $MoOF \cdot 4H_2O$, corresponding to the oxychloride, $MoOCl \cdot 4H_2O$ (146).

2. Oxyfluorides MOF_2 and MO_2F

Like the trifluorides, these are high-melting solids. Titanium oxydifluoride is a white, stable substance made by the partial hydrolysis of titanium tetrafluoride (150). The neighboring vanadium oxydifluoride VOF_2 is a yellow solid prepared by the action of gaseous hydrogen fluoride on vanadium oxydibromide, $VOBr_2$ (75). Niobium dioxyfluoride, NbO_2F, a white compound, is made by heating to 250° the hydroxyfluoride obtained from niobium pentoxide and aqueous hydrofluoric acid, and tantalum dioxyfluoride, TaO_2F, is prepared by a similar method starting from tantalum metal and hydrofluoric acid (148). Tungsten oxydifluoride is a grey powder obtained by the action of hydrogen fluoride on tungsten dioxide at

500° (73). Thorium oxydifluoride is prepared by the action of hydrogen fluoride at 800° on the hydrated salt, $ThF_4.4H_2O$ (143). Uranium oxydifluoride is known only as the hydrate, $UOF_2.2H_2O$, prepared from aqueous solution (e.g., U_3O_8 and 30% HF) (152). It is probable that other compounds such as $ReOF_2$ have actually been made, but their preparation and properties require confirmation (153).

The oxyfluorides which have been investigated by X-ray diffraction, $TiOF_2$, NbO_2F, and TaO_2F, have been shown to be isostructural with ReO_3 and hence with the trifluorides of Nb, Ta, and Mo; the oxygen and fluorine atoms have a random distribution among the oxygen positions of rhenium trioxide (148,150).

3. Oxyfluorides MOF_3, MO_2F_2, and MO_3F

Some of the oxyfluorides, MX_4, have been reinvestigated quite recently; others, such as MoO_2F_2 and WO_2F_2, have not been studied since the pioneer work of Ruff (Table XII).

Vanadium oxytrifluoride was first described by Ruff. His product, however, was considerably less volatile than that obtained by

TABLE XII
Oxyfluorides MX_4

	Preparative method	Color	M.p., °C.	B.p., °C.	Ref.
VOF_3	$F_2 + V_2O_5$	Pale yellow		Subl. 110	107,112
	$BrF_3 + V_2O_5$				
CrO_2F_2	$HF + CrO_3$	Reddish violet solid	a	Subl. 29.6	76,154
	$HSO_3F + CrO_3$				
	CrO_3 or $K_2Cr_2O_7 + SeF_4$	Brown vapor			158
	$CrO_3 + IF_3$				
	$CrO_3 + CoF_3$				155
MnO_3F	$HSO_3F + KMnO_4$	Green	−38	Volatile	159
	$IF_5 + KMnO_4$				158
MoO_2F_2	$HF + Mo\ O_2Cl_2$	White		Subl. 270	128
WO_2F_2	$WOF_4 + H_2O$	White		?	128
ReO_3F	$HF + ReO_3Cl$	Yellow	147	164	159
	$IF_5 + KReO_4$				161
$ReOF_3$	$ReF_5 + SiO_2$ at 250°	Black solid			68

[a] White polymeric form of CrO_2F_2 melts at about 200°.

recent workers, and one wonders whether in fact he actually got a polymeric form similar to that given by chromyl fluoride.

Chromyl fluoride exists in two forms. The product obtained from the several methods of preparation is a red-brown vapor, easily visible in small concentrations, which condenses to reddish violet crystals. Under the influence of light the red vapor polymerizes to a white solid whose properties are not well defined. Chromyl fluoride is said to attack glass and silica, but it is likely that under rigorously anhydrous conditions it could be handled in these materials. Since it does not combine with alkali fluoride, sodium fluoride can be used as a "keeper" (cf. the hexafluorides). Solutions of chromyl fluoride in iodine pentafluoride and selenium tetrafluoride are handled quite conveniently in Pyrex vessels. Chromyl fluoride gives the chlorofluoride, CrO_2ClF, with CrO_2Cl_2 and combines with potassium bifluoride to form the complex salt, $KHCrO_2F_4$ (154,155).

Permanganyl fluoride, MnO_3F, is a green compound unstable above 0°; at 25° it decomposes, sometimes explosively, into MnF_2, MnO_2, and O_2. At low temperatures it is more stable and can be stored indefinitely at −60°. Its intense green vapor, visible, like CrO_2F_2 vapor, at low concentrations, is photosensitive, but its solution in iodine pentafluoride is stable up to the boiling point of the solvent (98°); when this is boiled the oxyfluoride is vigorously decomposed by water.

Vanadium oxytrifluoride, chromyl fluoride, and permanganyl fluoride form a related triad; the next three compounds, MoO_2F_2, WO_2F_2, and $ReOF_3$, form another selected group with completely different physical properties. This change presumably reflects an increase in coordination number from four (cf. 156,157) to six in the solid state. However, none of the four has yet been adequately investigated, and little is known about them beyond the fact that they are all readily hydrolyzed by water. Rhenium trioxyfluoride has only recently been prepared, though its existence was suspected by Ruff. It is more like OsO_4 than the other MX_4 oxyfluorides in its physical properties and is said to be less stable than the other oxyfluorides of rhenium.

4. Oxyfluorides MOF_4, MO_2F_3, and MO_3F_2

Molybdenum and tungsten oxytetrafluorides were originally made by the action of hydrogen fluoride on the corresponding oxychloride.

TABLE XIII
Oxyfluorides MX_5

	Preparative method	Color	M.p., °C.	B.p., °C.	Ref.
$MoOF_4$	HF and $MoOCl_4$ F_2 and Mo oxides	White solid Colorless liquid and vapor	97.1	184.4	128,186
WOF_4	HF and $WOCl_4$	White solid Colorless liquid and vapor	110	185	163
$ReOF_4$	ReF_6 and $W(CO)_6$	Blue solid Blue liquid Colorless vapor	106.9	171.1	110,186
ReO_2F_3	F_2 and ReO_2	White solid Colorless liquid and vapor	90	213	134,186
OsO_3F_2	F_2/O_2 and Os BrF_3 and OsO_4	Orange solid Volatile above m.p.	170	-	164
$PtOF_4$		Red solid Black liquid bromine-colored vapor	260	Subl. 150	181,187

$MoOCl_4$, but they are also formed when the elements are heated in an oxygen fluorine stream and when the oxides are heated in fluorine.

When dry they do not attack glass and can be readily purified by vacuum distillation. These two oxytetrafluorides are white, crystalline solids which melt to colorless, sticky liquids. As the temperature is raised, the liquids become mobile and eventually boil to give colorless vapors. They are not so reactive as the hexafluorides and differ from them in combining slowly with dry sodium fluoride. Molybdenum oxytetrafluoride is easily reduced by organic matter and probably also by traces of moisture, since it produces bluish fumes when exposed to the atmosphere. It dissolves in a little water to give a pale blue solution which becomes colorless on dilution.

The blue rhenium oxytetrafluoride is one of the products formed when ReF_6 decomposes on moist glass; it is best prepared by the action of tungsten carbonyl on the hexafluoride. In appearance and properties, except for the color, it much resembles the foregoing tungsten and molybdenum compounds. On hydrolysis it gives perrhenic acid, hydrofluoric acid, and hydrated rhenium dioxide.

Rhenium dioxytrifluoride appears to be the same compound as Ruff's ReO_2F_2. It is more stable than the trioxyfluoride, ReO_3F,

and can be distilled without decomposition in Pyrex at atmospheric pressure. With water it gives a colorless solution containing perrhenic and hydrofluoric acids.

Osmium trioxydifluoride, OsO_3F_2, is the only certain oxyfluoride of the platinum metals, though there are indications (39,162) that another oxyfluoride of osmium, probably $OsOF_4$, also exists. OsO_3F_2 is an orange solid, with a surprisingly high melting point, which dissolves in water to give a colorless solution containing Os^{VIII}.

5. Oxyfluorides MOF_5

Only one compound is known, the septavalent rhenium oxypentafluoride, $ReOF_5$ (134). It is the major product formed when rhenium dioxide is burned in fluorine, and is also formed (together with the dioxytrifluoride and a little rhenium hexafluoride) by the action of a fluorine-oxygen mixture on rhenium metal sponge. Rhenium oxypentafluoride has the physical properties of a hexafluoride, m.p. 40.8°C., b.p. 72.8°C. (186); it is probably the compound said by Ruff to have the composition $ReOF_4$. With water it is hydrolyzed vigorously to give a colorless solution containing perrhenic and hydrofluoric acids; toward most reagents it behaves superficially in the same way as molybdenum hexafluoride.

The absence of a stable osmium oxyfluoride such as OsO_2F_4 is probably a measure of the decreasing stability of the six-covalent state of osmium as the charge on the ion increases.

B. COMPLEX OXYFLUORIDES

This field is not particularly rewarding or inspiring, except perhaps to the crystallographer, and the study of complex oxyfluorides has been neglected. The number of compounds described is formidable, and it would be out of place in this review to do more than show their relationship to other complex fluorides. Classification depends on the possibility of isomorphous replacement of fluorine by oxygen within the complex ion.

1. Ionic Compounds

Since the replacement of a fluorine atom by an oxygen leads to a unit increase in the oxidation number of the transition metal, fewer compounds of this kind are to be expected. In fact none has been reported, but it is possible that the green double salt, NH_4UOF_5,

said to be formed on electrolysis of a solution of uranylammonium carbonate in hydrofluoric acid, falls into this category.

2. *Four-Coordinate Compounds*

The only certain four-coordinate compounds are the fluorochromates, $ACrO_3F$, prepared from dichromates and hydrofluoric acid. The potassium and cesium salts have the scheelite ($CaWO_4$) structure with tetrahedral $[CrO_3F]^-$ ions (165). Thermal studies (166) have not given any indication of equivalent molybdenum and tungsten compounds; neither are any complexes known with planar $[MX_4]^-$ ions.

3. *Five-Coordinate Compounds*

None has been reported; the oxyfluorides AMX_5 and A_2MX_5 probably contain condensed MX_6 octahedra.

4. *Six-Coordinate Compounds*

The large majority of complex oxyfluorides probably contain octahedral ions, simple (e.g., $[NbOF_5]^{--}$) or condensed like those in the fluoro complexes $TlAlF_4$ and Tl_2AlF_5 (167, 171). They can be classified in much the same way as the oxygen-free compounds, but there is less X-ray evidence available and most of the divisions are purely by analogy.

(*a*) *Derivatives of* MX_2. From thermal studies on the system WO_3–KF the phase K_3WO_4F has been isolated (166). No X-ray data have been reported, although the compound gave a characteristic powder photograph.

(*b*) *Derivatives of* MX_3. The anhydrous AMX_4 compounds have not been reported, but the type A_2MX_5 is known; e.g., for vanadium there are the salts $BaVO_2F_3$ and K_2VOF_4. Cryolite-like compounds A_3MX_6 are known for vanadium (e.g. $(NH_4)_3VO_2F_4$), for molybdenum (e.g., $K_3MoO_3F_3$), and for tungsten (e.g., $K_3WO_3F_3$) (160,168,170, 173,174).

(*c*) *Derivatives of* MX_4. AMX_5 slats are known for vanadium (174) and chromium. The latter, which contain quniquevalent chromium, have the formula $ACrOF_4$ and are made by the action of bromine trifluoride on the dichromates (79). This is one of the few cases in

which bromine trifluoride acts as a reducing agent. The A_2MX_6 type of compound is more frequent; it is known for vanadium (e.g., K_2VOF_5), for niobium (e.g., K_2NbOF_5), for molybdenum (e.g., K_2MoOF_5 and K_2MoOF_4), for tungsten (e.g., K_2WOF_5 and $K_2WO_2F_4$), and for osmium (e.g., $K_2OsO_4F_2$) (160,168,173,174). The tungsten compound K_2WOF_5 (140) has not been fully characterized, and the osmium work (169), in view of the change in the status of other osmium-fluorine compounds, needs to be repeated.

(*d*) *Derivatives of* MX_5. Six-coordinate complexes are not numerous; sexivalent complexes, $AMOF_5$, of molybdenum, tungsten, rhenium, and probably osmium have been isolated through interaction of the appropriate hexafluoride with alkali fluoride under slightly moist conditions using iodine pentafluoride as solvent (39,119,140); they appear from unit cell measurements to be isostructural with the AMF_6 fluoro complexes. Salts of octavalent osmium (e.g., $CsOsO_3F_3$) have been prepared from the action of BrF_3 on OsO_4 and an alkali metal fluoride (164).

5. *Seven-Coordinate Compounds*

These are restricted to niobium in the *d* block and to uranium, although there seems to be little doubt that they will eventually be found for other elements as well.

$K_3UO_2F_5$ and the low temperature form of K_3UF_7 have pentagonal bipyramidal $[MX_7]^{3-}$ complex ions. K_3NbOF_6 and the high temperature form of K_3UF_7 have the K_3ZrF_7 structure, where the fluorine atoms in the $[MX_7]^{3-}$ ions have a random distribution instead of being in special positions (90,91).

6. *Hydrates*

In some complexes water may replace oxygen or fluorine in the octahedral ion, and hydrates such as $NH_4 \cdot WO_2F_3 \cdot H_2O$ are probably better represented with the water molecule in the ion, i.e., $NH_4 \cdot [WO_2F_3 \cdot H_2O]$. Salts of this kind seem to be especially numerous for vanadium. There is the possibility that in some salts the water molecule, as in $K_2AlF_5 \cdot H_2O$ (171), is contained in interstices in the lattice. Hydrates of the type $A_2MX_6 \cdot H_2O$ have been shown by X-ray crystallography to contain $[MX_6]^{2-}$ ions and not seven-coordinate $[MX_6 \cdot H_2O]^{2-}$ ions; e.g., the compound K_2NbOF_5 contains

$[NbOF_5]^{2-}$ ions just as $K_2TiF_6 \cdot H_2O$ contains $[TiF_6]^{2-}$ ions (175). Water molecules may also be associated with the cation, e.g., $Cu(H_2O)_4 \cdot MoO_2F_4$ (168).

7. *Peroxy Compounds*

These are formed by molybdenum, tungsten, and uranium, and probably by other elements as well. Only those of molybdenum and tungsten have been isolated as solids; the action of hydrogen peroxide on a solution of $K_2MoO_2F_4 \cdot H_2O$ yields two compounds, $K_2MoO_3F_4 \cdot H_2O$ and $K_2MoO_4F_2 \cdot H_2O$; for tungsten a similar preparative technique gives $K_2WO_3F_4 \cdot H_2O$ (173). The formulas do not distinguish between true peroxy groups (O_2), which could occupy one position in the octahedral complexion, and hydrogen peroxide, which could be present either as one of the ligands in the octahedral ion or as hydrogen peroxide of crystallization.

Much of this work was reported at the beginning of the century and provides a difficult, though potentially fruitful, field for future study by modern methods.

8. *Salts of Polyacids*

Vanadium, molybdenum, tungsten, and uranium form compounds of more complex composition than those just described, e.g., $K_3V_3O_3F_{14}$ and $K_3Mo_4O_{13}F \cdot H_2O$ (170). No structural work has been done on such materials, and although it is tempting to seek parallels with known structures such as those of the paramolybdates or metatungstates, little advantage is to be gained by so doing.

9. *Double Salts*

Some complex fluorides and oxyfluorides form addition compounds with KHF_2 and similar substances. The few compounds which have been examined by X-ray photography have been shown to be double salts; e.g., K_3NbOHF_7 is an aggregate of K^+, $[NbOF_5]^-$, and $[HF_2^-]$ ions (175,189).

C. MIXED HALIDES

Mixed compounds, in which one or more fluorine atoms have been replaced by another halogen, are common with *p* block elements. Only three certain transition metal compounds have been reported; they are the mixed chlorofluorides $TiClF_3$ and $UClF_3$ and the iodotet-

rafluoride OsF_4I. Titanium chlorotrifluoride is prepared by the action of chlorine on titanium trifluoride. It is yellow powder said to be more volatile than titanium tetrafluoride; it is hydrolyzed in the air to give $TiOF_2$ (176). Uranium chlorotrifluoride does not appear to have been made pure; the best preparation is from the interaction of uranyl fluoride and carbon tetrachloride (177). It is a green crystalline compound which sublimes in a vacuum at between 550 and 560°. Osmium iodotetrafluoride, OsF_4I, is a dark green or black nonvolatile solid made by the action of excess iodine on osmium hexafluoride (108).

It seems likely that other mixed halides will be prepared; for instance, examination of the early reports of Ruff in the literature shows that he undoubtedly prepared an impure molybdenum chlorofluoride during investigations of the properties of molybdenum fluorides.

D. COORDINATION COMPOUNDS

1. Carbonyls and Nitrosyls

There have been no reports of carbonyl fluorides, and so far attempts to make them have been unsuccessful; e.g., the reaction between rhenium carbonyl iodide, $Re(CO)_5I$, and iodine pentafluoride yields only the dimeric tetracarbonyl iodide $[Re(CO)_4I]_2$ (178), and the action of fluorine itself on molybdenum carbonyl yields lower fluorides (71). It seems that metallic carbonyls will find a place in preparative fluorine chemistry as starting materials for the lower fluorides; e.g., molybdenum carbonyl dissolves in molybdenum hexafluoride to yield molybdenum pentafluoride (39). The behavior of gaseous carbon monoxide toward metal fluorides has been little studied, but ruthenium pentafluoride is reduced at 200° to a yellow, finely divided, and reactive form of trifluoride, which dissolves in water with hydrolysis (39).

Scarcely any investigations have been made of nitrosyl complexes, but one possible approach looks promising, at least for platinum metal compounds. The platinum metals all form stable complex nitrites, e.g., $K_2Pt(NO_2)_4$, $K_2Rh(NO_2)_6$, and $K_2[Ru(NO)(NO_2)_4(OH)]$. These dissolve in 40% hydrofluoric acid with the evolution of nitrous fumes; $K_2Pd(NO_2)_4$ gives the hydrated oxide and $K_2[Os(NO)(NO_2)_4(OH)]$ is oxidized to the tetroxide, but the others retain nitrogen even after repeated evaporations with hydrofluoric acid. A preliminary experi-

ment suggested that a platinum compound, $(Pt(NO)(NO_2)F_2$, is one of the products from $K_2Pt(NO_2)_4$ (39).

2. *Phosphorous Trifluoride Complexes*

Phosphorous trifluoride is in some instances able to replace carbon monoxide as an electron donor, e.g., in Wilkinson's $Ni(PF_3)_4$ (179); this suggests that Moissan's platinum compound should be written as $(PF_3)PtF_2$ with divalent platinum. Recently Hair and Robinson (180) have investigated the action of phosphorous trifluoride on some higher metal fluorides and found that the compounds $(PF_3)OsF_2$, $(PF_3)IrF_2$, $(PF_3)PdF_2$, and $(PF_3)CoF$ are formed. Of these, $(PF_3)PdF_2$ and $(PF_3)CoF$ are diamagnetic. The palladium result is in contrast to the paramagnetism of palladous fluoride itself; the diamagnetism of $(PF_3)CoF$ suggests monovalent cobalt. Unfortunately, none of these materials is sufficiently crystalline to give Debye X-ray photographs, and they have not been examined by any other physical method (180).

3. *Other Coordination Compounds*

Since phosphorous trifluoride forms complexes so easily, arsenic trifluoride might be expected to do the same, but its behavior toward transition metal fluorides has scarcely been investigated.

The three other fluorine-containing solvents which are known to promote ionization, SeF_4, IF_5, and BrF_3, form adducts with a number of transition metal fluorine compounds. A selection is given in Table XIV. Some of these may be true coordination compounds, but others, such as the adduct $BrF_3.AuF_3$, are generally considered without any clear evidence to be salts such as $BrF_2^+AuF_4^-$. The available chemical evidence sometimes serves to distinguish between the possibilities; for example, the adduct $IrF_5.SeF_4$ dissolves in water to give fluoroiridate ion and is therefore held to be the salt $SeF_3^+IrF_6^-$, but the adduct $IrF_5.SF_4$ dissolves in water to give hydrated IrO_2 and is therefore supposed to be a true coordination compound. The question arises as to the "basicity" or "acidity" of solvent and solute according to the Lewis definitions of these terms.

Bromine trifluoride forms very stable adducts (dec. >200°) with the alkali fluorides (e.g., $KBrF_4$), but the "acid" adducts such as $BrF_2^+AuF_4^-$ are less stable to heat and usually break up at

TABLE XIV

Some Adducts of the Transition Metal Fluorides[a]

Formula	Color	M.p., °C.	Other properties[b]	Ref.
		BrF_3 Adducts		
$NbF_5 \cdot BrF_3$	White		Stable at 30°; dec. slowly at 50°; rapidly at 150°	127
$TaF_5 \cdot BrF_3$	White		Stable at 10°; dec. slowly at 100°; rapidly at 150°	127
$?RhF_4 \cdot 2BrF_3$	Pink		Dec. at 25° to RhF_4; not isolated	54
$RuF_5 \cdot BrF_3$	Buff	120 (d.)	All BrF_3 lost at 180° → RuF_5	86
$OsF_5 \cdot BrF_3$	Pale blue			22,109
$IrF_5 \cdot BrF_3$	Yellow		On heating → $(IrF_5)_2BrF_3$ which retains BrF_3 on distillation	109 182
$PdF_3 \cdot BrF_3$	Brown		Dec. rapidly at 180° to PdF_4	54
$PtF_4 \cdot 2BrF_3$	Red		Dec. rapidly at 200° to PtF_4	54
$AuF_3 \cdot BrF_3$	Lemon yellow		Dec. at 120° to AuF_3	54
		SeF_4 Adducts		
$NbF_5 \cdot SeF_4$	White	80		181
$TaF_5 \cdot SeF_4$	White	120	B.p. 320°/760 mm.	108
$OsF_5 \cdot SeF_4$	Pale blue	130	Dec. at m.p. to $(OsF_5)_2SeF_4$ which retains SeF_4 on distillation	109
$IrF_5 \cdot SeF_4$	Buff	130	Dec. at m.p. to $(IrF_5)_2SeF_4$ which retains SeF_4 on distillation	109
$PtF_4 \cdot 2SeFr$	Light orange		Dec. at 300° to Pt black	22
$AuF_3 \cdot SeF_4$	Yellow	210 (d.)		22
$PdF_3 \cdot SeF_4$	Buff	—	Dec. at 150° to PdF_3; at 200° in air to PdF_2	8
$VOF_3 \cdot 2SeF_4$	Cream	—	Dec. >60°	80
$MoO_2F_2 \cdot SeF_4$	Cream	70–71		22
		SF_4 Adducts		
AuF_3	—	—	No adduct formed	22
PdF_3	—	—	Reduced to PdF_2 at 200°	8
$OsF_5 \cdot SF_4$				109
$IrF_5 \cdot SF_4$	Buff	130–135	Dec. at m.p. to $(IrF_5)_2SF_4$	109
$?RuF_5 \cdot SF_4$	Pink	150 (d.)		22

[a] IF_5 does not appear to form any transition metal fluoride adducts.

[b] Decomposition temperatures *in vacuo*.

120–150°. Solvolysis certainly occurs in bromine trifluoride; one interesting example has been observed during the preparation of the fluororuthenates(V) and fluoroosmates(V) (85,86). A solution of $KRuF_6$ in BrF_3 assumes the red-brown color characteristic of a solution of RuF_5 in BrF_3; when the solution is evaporated *in vacuo* at 25°, the dry solid which appears retains this color, losing it only above 100° where it becomes cream, the color of the pure salt. A solution of $KOsF_6$ in BrF_3 is not strongly colored, and on being cooled throws out the pure complex salt. Clearly, RuF_5 is a weaker "acid" in BrF_3 than OsF_5.

Iodine pentafluoride forms stable salts with alkali fluorides (e.g., KIF_6 is stable to 150°), but the "acids" break up very readily, and few, if any, of the possible transition metal compounds have been isolated; for example, OsF_5 gives a green solution in IF_5, the same color as the pentafluoride itself, but all the IF_5 comes off in a good vacuum at 60°. Only the strongest "acids" such as SbF_5 form stable adducts with IF_5, and on the whole the evidence suggests that IF_5 is a more "acidic" solvent than BrF_3.

Selenium tetrafluoride forms the salts $ASeF_5$ with alkali fluorides, but these are very reactive and no reliable estimate of their stability has been made (80). No indication has so far been found of the salts A_2SeF_6, which suggests that SeF_6^{2-} is not important in the SeF_4 solvent system. The acid adducts are often very stable indeed (see Table XIV), and in the compounds $IrF_5 \cdot SeF_4$ and $(IrF_5)_2SeF_4$ the quinquevalent state of iridium is stabilized (IrF_5 does not exist). It is interesting to note that two of the SeF_4 adducts, those with OsF_5 and IrF_5, have been shown to lose SeF_4 on being heated giving 2:1 complexes, which are more covalent in character than the 1:1 complexes; e.g., $(OsF_5)_2SeF_4$ is hydrolyzed to OsO_2, etc., while $OsF_5 \cdot SeF_4$ gives the fluoro ion OsF_6^-. This suggests that although the 1:1 complex should be written as $SeF_3^+OsF_6^-$, the 2:1 complex should not be represented as $SeF_2^{2+}2OsF_6^-$. In conclusion, it seems best to represent SeF_4, when considering the autionization $2SeF_4 \rightleftharpoons SeF_3^+ + SeF_5^-$, as a "basic" solvent.

Sulfur tetrafluoride forms compounds with similar formulas to SeF_4 adducts, but they seem to be nonionic (see Table XIV). It is certain that adducts should be formed by other halogen fluorides, such as BrF_5 and ClF_3, and also by TeF_4 so that much work remains to be done in this field (cf. 184).

Little is known about other adducts, such as those formed by pyridine, SO_2, and SO_3, beyond the formulas. One or two of the SO_3 complexes (e.g., $IrF_4.3SO_3$) could prove to contain S_3O_9 ring systems, and others (e.g., $WF_2(SO_3F)_4$) are fluorosulfates.

4. Amino Compounds, etc. (Werner Compounds)

These are not nearly so well known with fluorine as with the other halogens. Mixed compounds such as $[Crpy_3F_3]$ and $[Cr(NH_3)_5F]F_2$ only appear to be formed by first-period transition elements; in the second and third periods amino compounds such as the very soluble white $[Pd(NH_3)_4]F_2$ are formed, but have been little studied. Recently Matoush and Basolo (82) have studied some of the fluorocobaltamines, and in particular they have succeeded in resolving optically active isomers of $[Coen_2F_2]NO_3$ in agreement with a *cis* configuration.

The boundary between the Werner salts and the type of complex described in the preceding section is not clear cut, and it will be interesting to see the results when some of the work now actively in progress on the behavior of transition metal chlorides toward ammonia has been extended to include volatile fluorides.

IV. Preparative Methods and Techniques

A. IDENTIFICATION AND CHARACTERIZATION

The chief methods of characterization, after a full analysis has been carried out, are vapor density (volatile fluorides), X-ray powder photography (mainly for complex fluorides), magnetic measurements, and infrared absorption spectra. Of these X-ray powder photography is undoubtedly the most useful because, even if it is impossible or undesirable to proceed to a full structural determination, comparison may be made with X-ray photographs of known materials. In connection with this it is worthwhile knowing that one frequent impurity in complex fluorides, K_2SiF_6, seldom gives a good X-ray spectrum. Since many fluorides are hygroscopic, the writer has found that specimens are conveniently photographed in thin-walled Pyrex glass capillaries. To avoid the inconvenience of a dry box, a device such as in Figure 1A is used; the bulb is sealed from the main preparative line under vacuum. The glass beads take the place of pestle and mortar.

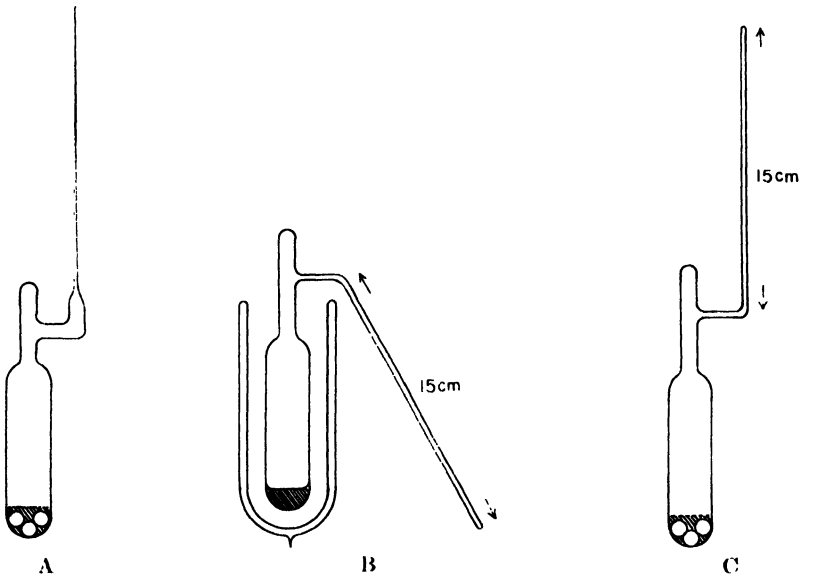

Figure 1. Devices for handling hygroscopic fluorides.

Magnetic measurements at a single temperature are really only of use for first-period transition elements, though they may be a pointer in other cases. Measurements made over a temperature range may be very valuable, since they usually give a clear indication of valency state with fluorine compounds, e.g., for osmium hexafluoride (125). In Figure 1B is shown a typical device for filling a tube with a volatile fluoride; in Figure 1C is shown a similar device for a complex or nonvolatile fluoride. The glass beads serve the same function as for X-ray powder specimens and indeed it is often convenient to adapt the apparatus so that specimens for different physical measurements may be prepared at the same time.

The diameter of the magnetic specimen tube is not critical; the writer has found it convenient to use about 1 g. of material so that with volatile fluorides about 0.2–0.3 ml. is needed and with nonvolatile fluorides about 0.2–0.4 ml.

The use of infrared spectra as a means of characterization is a recent development. Stretching frequencies of a selection of transition metal fluorides are now known (γ from about 800–300 cm.$^{-1}$),

so that qualitative information about structure and valency may be obtained (24). Nujol mulls are less apt to contain moisture than KBr discs and hence are more useful for hygroscopic materials. It is interesting to note that measurements so far made show that there is little difference in M- -F stretching frequencies between "loose" complex ions (e.g., ScF_6^{3-}) and "ionic" lattices (e.g., $KLaF_4$).

B. PREPARATIVE METHODS

The chief preparative methods for inorganic fluorine compounds will have been evident from the foregoing sections; some examples are summarized in Table XV.

TABLE XV
Preparative Methods

Starting material	Reaction conditions	Product
	Preparations Using Anhydrous Hydrogen Fluoride	
$KMnO_4$	Liquid HF at 10°	MnO_3F
$K_2Cr_2O_7$	Liquid HF at 10°	CrO_2F_2
$CrF_3 \cdot 6H_2O$	Gaseous HF at 300°	CrF_3
$MoCl_3$	Gaseous HF at 300°	MoF_3
$TiH_{0.7}$	Gaseous HF at 700°	TiF_3
	Preparations Using Potassium Biflouride	
$K_2FeF_5 \cdot H_2O$	Heat to 400°; extract acetone-water (10:1)	K_2FeF_6
K_2ReI_6	Heat to 400°; extract water and recrystallize	K_2ReF_6
	Preparations Using Elementary Fluorine	
3KCl and $CoCl_2$	300°	K_3CoF_6
W	Powder pretreated in H_2 at 100; F_2 at 100–300°	WF
K_2PtCl_6	300°	K_2PtF_6
Ta_2O_5	300–500°	TaF_5
	Preparations Using Bromine Trifluoride	
TiF_6^{2-}	VF_6^- $CrOF_4^-$ MnF_6^{2-} MnF_5^- MnF_3	
	NbF_6^- RuF_6^- RhF_4 PdF_3	
	RuF_6^{2-} RhF_6^{2-} PdF_6^{2-}	
	TaF_6^- $ReO_2F_4^-$ OsF_6^- IrF_6^- PtF_4 AuF	
	OsF_6^{2-} IrF_6^{2-} PtF_6^{2-} AuF_4^-	
	$OsO_3F_3^-$	

Nonaqueous solvents have been playing an increasingly important part in the field. Bromine trifluoride (b.p. 127°) has been the most used insofar as it is a powerful fluorinating agent, but it suffers from the limitation that only high valency compounds are obtained. The other two useful solvents, iodine pentafluoride (b.p. 98°) and selenium tetrafluoride (b.p. 102°), are weaker in their fluorinating action, but may be used in combination with reducing agents. These three solvents attack glass slowly even when dry and for accurate work are best handled in silica. Anhydrous hydrogen fluoride (b.p. 19°) (160) is an excellent solvent, but has the drawback that the only transparent material it can be handled in, polytrifluoroethylene, is still very expensive. Recent work has shown that it may eventually be replaced by fluorosulfuric acid (6) and trifluoroacetic acid (50). Water as a solvent has a limited application in the field as preparative work in it is effectively restricted to insoluble compounds. Methyl alcohol dissolves ammonium fluoride and has been used for the preparation of $(NH_4)_3FeF_6$ (147). Both the alkali fluorides and bifluorides have been used as fluorinating agents in the form of their melts; the latter has several applications (Table XV).

The so-called medium temperature fluorination method has been extensively used for the preparation of simple and complex fluorides. A good supply of fluorine, free from HF and SiF_4 is required, and most of the reactions can be carried out in nickel apparatus of the simple kind, since they go at temperatures of about 300°. The usual method of purifying fluorine is to pass it over sodium fluoride pellets and then through a liquid oxygen (not liquid nitrogen) trap; in the writer's experience the design of the liquid oxygen trap is worth attention because small quantities of HF and SiF_4 tend to pass on as an aerosol. Very dry conditions are essential for the preparation of volatile fluorides, whether with fluorine itself or bromine trifluoride; a preparation embodying most of the useful techniques is given below. Hexafluorides, VF_5, and CrO_2F_2 can be dried subsequently over sodium fluoride, but this is not a substitute for careful drying of starting materials and apparatus. The choice of starting materials is important, especially for complex fluorides.

Preparative methods depending on reduction of high valency compounds are becoming increasingly important; for noble metal fluorides iodine is effective as a reducing agent; for others, hydrogen, metals, tungsten carbonyl, and even glass itself have been used.

Electrolytic reductions in anhydrous HF and other fluoro solvents will prove useful.

C. PREPARATION OF POTASSIUM FLUORORUTHENATE(V)

The apparatus (Fig. 2) is constructed of borosilicate (Pyrex) glass except for the reaction vessel (*D*), which should preferably be of silica, the copper sodium fluoride trap (*M*), and the copper inlet tubes (*N* for fluorine and *P* for nitrogen). The fluorine source is an electrolytic cell capable of delivering about 6 liters of fluorine per hr. The trap (*B*) contains bromine standing over phosphorus pentoxide.

Before beginning the experiment, the apparatus, stoppered at *R*, is evacuated through *G* and is thoroughly flamed out. Dry nitrogen is admitted via *G*, and J is unsealed to allow a mixture of ruthenium sponge and potassium bromide (1:1) to be poured into the reaction vessel. *J* is sealed by drawing off at *Q*, and the apparatus is again evacuated and flamed out. After dry nitrogen has been admitted, traps *A* and *F* are cooled in liquid oxygen and the apparatus is flushed out by a stream of nitrogen (about 2 liters/hour) admitted through *P* and *R*. The magnetic seal *L* is broken, and sufficient bromine is distilled from *B* into the reaction vessel to provide a five-fold excess by volume over the powdered mixture of ruthenium and potassium bromide. *B* is now removed from the apparatus by drawing off the inlet tube above *L*. A stream of fluorine (4 liters/hour) is admitted through *N;* the nitrogen stream is maintained at 2 liters/hour. The reaction vessel (*D*) is kept at about 25° by a cold

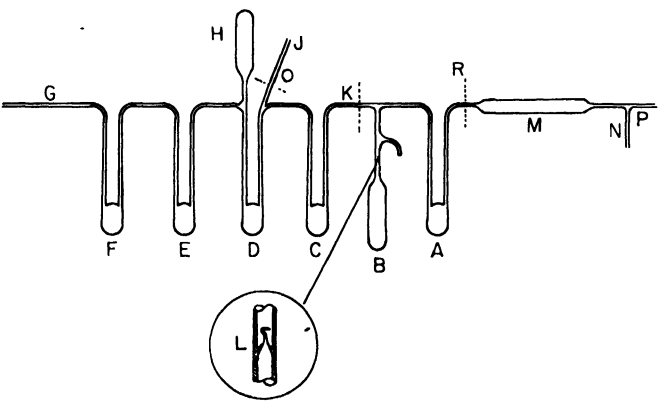

Figure 4. Reaction line for a preparation involving bromine trifluoride.

water bath; it is shaken gently at intervals to bring bromine above the bromine trifluoride which forms the upper layer. When the reaction is complete (this is best determined by warming the reaction vessel a little and noting whether any bromine vapor appears above the liquid surface), the fluorine is stopped and the nitrogen stream is increased to between 4 and 6 liters/hour. *D* is now cooled in an alcohol–solid carbon dioxide bath, and when all the fluorine has been flushed away the apparatus is sealed at *K* and is evacuated through *G*. The alcohol–solid dioxide bath is transferred to *E*, and *D* is warmed very gradually to 200° to remove the bromine trifluoride. Potassium fluoruthenate(V), $KRuF_6$, remains behind in *D* as a white powder and is transferred into *H* for storage, either under vacuum or in dry air or nitrogen.

The technique described is superior to that whereby bromine trifluoride itself is allowed to come into contact with ruthenium metal, as these two materials interact with explosive violence. Excess of bromine trifluoride must be destroyed in carbon tetrachloride, not in water.

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Intensities of Spectral Bands in Transition Metal Complexes

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I. Introduction

Any valid theory concerned with the electronic structures of chemical compounds must at the very least be capable of giving a correct description of the various electronic ground states of the compounds under discussion. If, further, the theory predicts the properties and energies of the excited states, we have every reason to be pleased. This, of course, is because a solution of the Schrödinger equation for all but the most simple molecules is a major undertaking, and, as a consequence, simplifications have to be introduced to render the problem soluble in a reasonable time. But it is clear that the greater the number of approximations, the more we must satisfy ourselves with a final result which is only a qualitative description of the true situation.

Because of the intrinsic complications, most electronic theories are semiempirical; that is, we make use of quantities which are measured (but in principle calculable), and then by means of the theory we calculate other properties of the system. A well-known example is the simple molecular orbital (MO) treatment of the π-electron system in

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benzene (1). From experiment it is possible to estimate the so-called "exchange integral β," and from this quantity to make new predictions via the theory. Virtually the exact same situation as the one just described exists also in the ligand field theory of transition metal complexes. Here it is a quantity called Dq which is taken from experiment and put into the theory, and the spectra, magnetism, and related phenomena are calculated in terms of this parameter for complexes of the transition metals (2).

Let us therefore assume that we are in the happy situation of possessing a theory *in casu*, a set of wave functions describing correctly the energy differences between the ground state and the excited states. The question then arises: Will these wave functions, constructed in some semiempirical manner to fit the positions of the absorption bands, also describe, e.g., the intensities of the bands? We may anticipate that this would indeed be a happy coincidence.

This very point is clearly demonstrated by the ligand field theory, by the use of which we can, without excessive labor, construct a set of wave functions which will predict the position of the absorption spectra of the complex ions with an accuracy of a few hundred wave numbers. However, an attempt to calculate the intensities of the absorption bands with these same wave functions leads to predicted intensities of zero. Thus we have to augment our wave functions in a manner such as *not* to alter the energy of the levels very much, while at the same time introducing such new features as to assure that the absorption bands will have some intensity. It is clear, however, that this will introduce new parameters into an expression already involving a parametric approximation. Nevertheless, at the very least we can attempt to understand the source of intensity, even though the exact numbers predicted by the theory must be viewed with some caution.

II. Theory

Given the observed molar extinction coefficient, ϵ, of a certain absorption band as a function of the frequency, ν (assumed to be measured in wave numbers, cm.$^{-1}$). It is then convenient to define the oscillator strength, f, of the measured band as

$$f = 4.32 \times 10^{-9} \int \epsilon_\nu d\nu$$

that is, a constant times the area of the absorption band. Many bands have a shape like that of a gaussian error curve. If we approximate the actual shape of the band with such a function and define $\nu_{1/2}$ as the width of the band (in cm.$^{-1}$), where $\epsilon_\nu = {}^1/_2\epsilon_{max}$, we obtain as an expression for f:

$$f = 4.60 \times 10^{-9}\epsilon_{max}\nu_{1/2}$$

This expression gives a good estimate of f in nearly all cases of interest.

If a band is seen to be composed of more than one absorption peak, it is customary to resolve the band into two or more gaussian curves and to give the f number for each peak. It is not always easy to achieve such a resolution because of the uncertainty as to the exact position of the maxima and as to the values of the half-widths of the bands. However, it can usually be done with a little patience.

Theoretically, we have the following expression for f:

$$f = 1.085 \times 10^{-5}\ \nu\ [\mathrm{av_I} \textstyle\sum_{II} \left| \int \psi_I^* \vec{r} \psi_{II} d\tau \right|^2]$$

Here ψ_I and ψ_{II} are the wave functions for the initial and final states, ν is the frequency of the band, and $\vec{r}$ is the vector $\vec{r} = \boldsymbol{i}x + \boldsymbol{j}y + \boldsymbol{k}z$. The $\mathrm{av_I}$ and $\sum_{II}$ have the following meanings: suppose that our ground state is, say, three-fold degenerate and that the upper state is two-fold degenerate. That is, there are three independent wave functions all with the same energy, E, which make up the ground state and two which compose the upper state (see Fig. 1). To calculate f we must evaluate the integrals

$$\int \psi_1^* \vec{r} \psi_2 d\tau$$

for all transition combinations, in the case cited $3 \times 2 = 6$. These six values of the integral are then squared, added together, and divided by 3. We have then summed over the excited states II and averaged this sum over the initial states I.

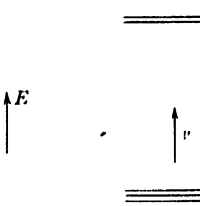

Fig. 1. Splitting of the d-orbitals in a cubic crystalline field.

III. Octahedral Complexes

The electronic absorption bands of octahedral complexes can be divided into three classes, a distinction between them being given by the value of the molar extinction coefficient, ϵ. If ϵ for the band is greater than 1, but less than 200, the chances are that there is a "spin-allowed band"; if ϵ is less than 1, then it is known that the band in question is a "spin-forbidden band"; and, finally, for $\epsilon > 200$ the band is probably a "charge transfer band" (2). We shall treat these three cases in the above order, but will first digress briefly in order to introduce some very useful symmetry concepts.

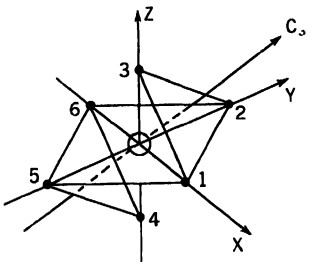

Fig. 2. Model of an octahedral complex, indicating one of the three-fold axes.

Suppose that we have a molecule composed of a metal ion, having one $3d$-electron outside a closed argon shell (Ti^{3+}), surrounded by six water molecules arranged in a regular octahedron around the central ion (Fig. 2). We know that the $3d$-electron is five-fold degenerate and that the five wave functions can be expressed as the product of a common radial part times the angular dependence, this latter consisting of the five functions (xz), (yz), (xy), $(x^2 - y^2)$, and (z^2) (1,2). Let us place the ligands (the water molecules) on the coordinate axes. The charge distributions of the five d-orbitals are seen in Figure 3, and it is observed that the (xz), (yz), and (xy) orbitals are directed out "between" the ligands, whereas the (z^2) and $(x^2 - y^2)$ orbitals are directed "against" the ligands.

Thinking of the ligands as being negative charges (or dipoles with their negative ends pointing toward the metal ion), we infer that the d-electron will, in a teleological sense, try to avoid the directions where the negative electric field density is greatest. Consequently the five

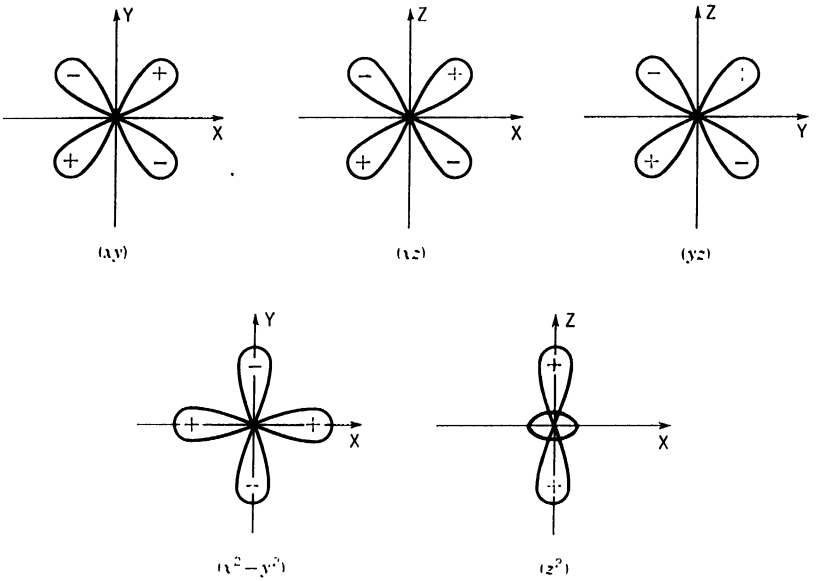

Fig. 3. The five d-orbitals.

d-orbitals will no longer have the same energy; the five-fold degeneracy has been at least partially lifted.

Let us now rotate our molecule about one of the three-fold axes (Fig. 2). This means that ligand 1 will go into ligand 2, 2 into 3, 3 into 1, 5 into 4, and so forth. However, the "new" molecule is identical with the "old" molecule; indeed, if we had not known that it had been rotated, we would have no way of knowing that anything had happened at all. During this rotation $x \rightarrow y$, $y \rightarrow z$, and $z \rightarrow x$, so that $(xz) \rightarrow (xy)$, $(xy) \rightarrow (yz)$, and $(yz) \rightarrow (xz)$. However, as the only "difference" before and after the rotation is the numbering of the ligands, and as the energy must be independent of such a labeling, we observe that the energies of the orbitals (xz), (yz), and (xy) must be the same. This is, of course, evident too from Figure 3. By means of similar arguments one finds that $E(x^2 - y^2) = E(z^2)$.

The three-fold degenerate level is called a t_{2g} level, the two-fold degenerate level an e_g level. It is easy to see, if we remember the physical consequences of the electronic distribution, that

$$E(t_{2g}) < E(e_g)$$

In view of this we would expect $Ti(H_2O)_6^{3+}$ to have one absorption band (of the first class) corresponding to the transition $t_{2g} \rightarrow e_g$, and such a band is indeed found at about 20,000 cm.$^{-1}$.

Let us try to calculate the intensity of this band. To do so, we need to evaluate the integrals $\int t_{2g}\vec{r}e_g d\tau$. We start with

$$\int (xz)\vec{r}(x^2 - y^2)d\tau = \int (xz)(\boldsymbol{i}x + \boldsymbol{j}y + \boldsymbol{k}z)(x^2 - y^2)d\tau$$

Performing what is known as an inversion i– namely, a reflection through the center of the coordinate system––we see that the octahedron will go "into itself." As the system thus remains the same, this operation cannot change any of its physical properties. Under the inversion $x \rightarrow -x$, $y \rightarrow -y$, and $z \rightarrow -z$, we obtain

$$\int (xz)\vec{r}(x^2 - y^2)d\tau \rightarrow -\int (xz)\vec{r}(x^2 - y^2)d\tau$$

However, this integral represents a physical quantity which must remain unaltered under a symmetry operation. It follows that the integral is zero, and the same holds true for all the other five integrals. Consequently, the band should not be observed at all. This result is generally known by the name of "Laporte's rule," which states that no transitions can take place between states of the same parity. (By parity is understood the behavior of orbitals under inversion. All d-wave functions are "even" (g), since they do not change sign under an inversion; p-orbitals, on the other hand, are "odd" (u), since they do change sign under this operation.)

Consider now a transition from a d-orbital to one of the p-orbitals p_x, p_y, or p_z. As $\int (xz)\vec{r}(x)d\tau$, for example, remains unchanged during an inversion, we know that at least it need not be zero so far as this symmetry operation is concerned. Let us next consider the effect of a reflection in the XY plane. The molecule goes into itself, and $x \rightarrow x$, $y \rightarrow y$, and $z \rightarrow -z$. We get here

$$\begin{aligned}\int (xz)(\boldsymbol{i}x + \boldsymbol{j}y + \boldsymbol{k}z)(x)d\tau &= \int (xz)(\boldsymbol{i}x)(x)d\tau + \int (xz)(\boldsymbol{j}y)(x)d\tau \\ &\quad + \int (xz)(\boldsymbol{k}z)(x)d\tau \\ &\rightarrow \int -(xz)(\boldsymbol{i}x + \boldsymbol{j}y - \boldsymbol{k}z)(x)d\tau \\ &= -\int (xz)(\boldsymbol{i}x)(x)d\tau - \int (xz)(\boldsymbol{j}y)(x)d\tau + \int (xz)(\boldsymbol{k}z)(x)d\tau\end{aligned}$$

It is thus only the z component of the integral which can make any contribution, and this holds true under all symmetry operations of the group. We say that the transition is polarized along the Z axis.

Obviously, we could then get some intensity into our $d \rightarrow d$ absorption bands if the wave functions were not pure d-orbitals, but had

some admixture of p character. Perturbation theory tells us that the extent of such a mixing is determined by the formula

$$\Psi = \psi(d) - \{\int \psi(d)\mathfrak{H}\psi(p)d\tau/[E_p - E_d]\}\psi(p)$$

where $\mathfrak{H}$ is the Hamiltonian of the system—that is, the operator which describes the total energy of the system. In order to calculate the mixing of d- and p-orbitals, we must evaluate $\int \psi(d)\mathfrak{H}\psi(p)d\tau$, a pure number.

Now $\mathfrak{H}$, the energy of the system, *must* remain the same under all symmetry operations. It *cannot* change in sign or magnitude so long as the system remains the same apart from the physically unimportant numbering of the ligands. Let us therefore perform the inversion $x \rightarrow -x$, $y \rightarrow -y$, and $z \rightarrow -z$. Then

$$\int \psi(d)\mathfrak{H}\psi(p)d\tau \rightarrow -\int \psi(d)\mathfrak{H}\psi(p)d\tau$$

that is, the integral is zero. It follows that we cannot mix d- and p-orbitals in a regular octahedral complex and that the bands still remain without intensities.

The foregoing conclusions are all rigorously true so long as the molecule has an inversion center—that is, so long as all six bond distances are equal. Let us therefore consider the expansion of the Hamiltonian, $\mathfrak{H}$, with respect to small variations of these bond distances. This corresponds physically either to considering the *vibrations* of the ligands about their sites or to accounting for a *static dissymmetry* in the arrangement of the ligands around the metal ion. By expansion,

$$\mathfrak{H} = \mathfrak{H}_0 + Qd\mathfrak{H}_0/dQ$$

where $\mathfrak{H}_0$ is the energy of the "regular" octahedron and $Qd\mathfrak{H}_0/dQ$ is the variation of the energy with respect to small bond-distance variations. Again $Qd\mathfrak{H}_0/dQ$ must remain unaltered by all symmetry operations. But Q is a normal *vibration of the ligands*, that is, a quantity related solely to the ligands, and $d\mathfrak{H}_0/dQ$ is the variation of the *electronic energy of the system* due to these variations. Consider now the mixing of d- and p-orbitals:

$$\begin{aligned}\Psi &= \psi(d) - \{\int \psi(d)[\mathfrak{H}_0 + Qd\mathfrak{H}_0/dQ]\psi(p)d\tau/[E_p - E_d]\}\psi(p) \\ &= \psi(d) - \{Q\int \psi(d)[d\mathfrak{H}_0/dQ]\psi(p)d\tau/[E_p - E_d]\}\psi(p)\end{aligned}$$

Remembering that it is only the *product* $Qd\mathfrak{H}_0/dQ$ which has to remain unaltered under all symmetry operations, we notice that if we have an

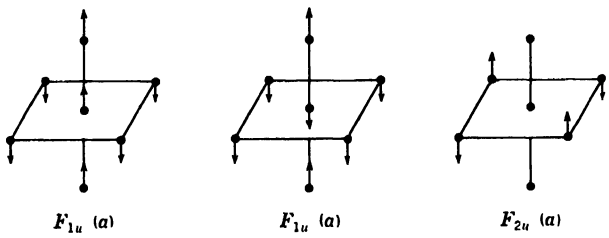

Fig. 4. Odd vibrations of the ligands in an octahedral molecule.

"odd" vibration Q, that is, a vibration which changes sign under inversion, $d\mathfrak{H}_0/dQ$ must change sign, too, under this operation.

In order to treat the intensities of the electronic bands we are thus forced to look into the properties of the vibrational infrared absorption lines of octahedral molecules. Fortunately, these features are well known (see, e.g., Herzberg (23)), and we give in Figure 4 a component of each of the three odd, three-fold degenerate, normal modes found in an octahedral molecule. We notice that by reflection of the arrows (which indicate the displacement of the atoms) through the center of the molecule we get a "negative" displacement as compared with the initial situation.

As $d\mathfrak{H}_0/dQ$ and p thus both change sign under inversion, we obtain a nonzero value for the "mixing integral" if we couple the electronic wave functions with vibrations of the ligands. Such couplings are called "vibronic" interactions. We find

$$\Psi_{\text{electronic}} = \psi(d) + cQ\psi(p)$$

and the total wave function is a product of the electronic wave function, Ψ_{el}, with a vibrational wave function, φ_{vib}. For the ground state we have

$$\Theta = \psi(d)\varphi_{\text{vib}}^{(1)} + c_1 Q\psi(p)\varphi_{\text{vib}}^{(1)}$$

with a similar expression for the excited state. The transition moment, P, is then

$$P = \int \Theta_{\text{ground}}\, \vec{r}\, \Theta_{\text{excited}}\, d\tau_{\text{el}} d\tau_{\text{vib}}$$

containing integrals of the form

$$c \int \psi(d)\vec{r}\psi(p) d\tau_{\text{el}} \cdot \int \varphi_{\text{vib}}^{(1)} Q \varphi_{\text{vib}}^{(2)} d\tau_{\text{vib}}$$

Assuming a harmonic potential and that the geometry of the molecule is the same in the initial and final states, we find that $\int \varphi^{(1)}\, Q\varphi^{(2)} d\tau$ differs from zero only if the vibrational quantum numbers of the two states differ by one (1). Thus we do not see the $0 \rightarrow 0$ band, but the first band will correspond to the $0 \rightarrow 1$ transition.

Actual calculations (3-8,26,27) have shown that this is indeed the most important mechanism by which the octahedral complexes acquire intensity, and the calculated f numbers ($10^{-3} \rightarrow 10^{-5}$) are in excellent agreement with the measured ones.

As already mentioned, intensity can also be obtained by means of any "natural" dissymmetry inherent in the molecule (19). It appears, e.g., that in the absorption spectra of ruby (Cr_2O_3 dissolved in Al_2O_3) nearly all of the band intensity is due to a coupling of odd and even states via an inherent trigonal field. This result (19), however, does not agree too well with the results of Moffitt (20) obtained by a study of the rotatory dispersion curves of certain Cr^{3+} and Co^{3+} complexes.

For complexes not imbedded in a strong crystal lattice an inherent dissymmetry is at any rate less important as an intensity-giving source than the one just treated. It is true that, e.g., *cis*-$Co(NH_3)_4Cl_2^+$ has somewhat greater band intensities than *trans*-$Co(NH_3)_4Cl_2^+$, presumably because of the lack of an inversion center in the former (9). Nevertheless, the major source of intensity in both cases is definitely a "vibronic" coupling. Indeed, interpretation of dichroism studies (10) directly proves the validity of the arguments outlined above.

IV. Spin-Forbidden Bands

Careful measurements of the spectra of the transition metal complexes often reveal a number of bands with a very small molar extinction coefficient. In contrast to the "spin-allowed" bands discussed above, all such "small bands" arise from transitions between states which do not have the same number of unpaired electrons. It is therefore natural to call them "spin-forbidden bands." For instance, the ground state of $Mn(H_2O)_6^{2+}$ has five unpaired spins, but all the excited states have only three or one unpaired spins. Because of spin orthogonality one would then expect transitions between these states to be strictly forbidden (1). Furthermore, we still have the parity restriction.

While the latter must be treated as before, we have now in addition to consider the spin-orbit coupling in order to break down the selection rules (1) imposed upon us by the spin quantum number, S. The spin-orbit coupling allows states with different values of S to mix together, the amount of mixing being determined by the value of the spin-orbit coupling parameter, ξ, and how close the states in question approach each other. As the spin-orbit coupling can only couple states together which differ by $\Delta S = 1$, in $Mn(H_2O)_6^{2+}$, for example, we will see only transitions from the ground state ($S = {}^5/_2$) to the excited states with $S = {}^3/_2$. Exact calculations of the intensities of spin-forbidden bands have been carried out by Koide and Pryce (11) on the system $Mn(H_2O)_6^{2+}$.

There is experimental evidence that the value of the spin-orbit coupling parameter, ξ, is closely related to the strength of the crystalline field (12). This fact seems to account for the curious phenomena of the existence of the "double peak" (at ~14,000 cm.$^{-1}$) in $Ni(H_2O)_6^{2+}$, compared to the single peak found in $Ni(NH_3)_6^{2+}$. The level in question is split via a spin-orbit coupling (13), but as ξ is smaller for the latter compound than for $Ni(H_2O)_6^{2+}$, no splitting of the band is observed for $Ni(NH_3)_6^{2+}$ in contrast to $Ni(H_3O)_6^{2+}$. Thus the appearance of the "double peak" is not connected with the accidental occurrence of a nearby "spin-forbidden" state as has been maintained (6,13,14).

V. Charge Transfer Bands

So far we have only considered absorption bands arising from transitions within the d-shells and with a molar extinction coefficient less than about ~200. It is, however, well known that many complexes have very high and steeply rising absorption bands in the near ultraviolet. The intensity of these bands is so high that we must assume that they are due to "allowed" (even → odd) transitions. Fortunately, it is at least qualitatively easy to understand such a feature, as there exist certain linear combinations of ligand orbitals which can be combined with the odd $4p$-orbitals to form an odd high-lying state.

In the molecular orbital scheme (15–17) we can write down an expression showing how the total wave function, Ψ, is made up by a linear combination of metal and ligand wave functions. In this way for the "d- and p-orbitals":

$$\Psi = \alpha\psi_d + (1 - \alpha^2)^{1/2}\sum_j \psi_{1ig}$$

and

$$\Phi = \beta\psi_p + (1 - \beta^2)^{1/2}\sum_i \varphi_{1ig}$$

where α and β measure "the degrees of covalency" and $\sum_j \psi_{1ig}$ and $\sum_i \varphi_{1ig}$ are normalized linear combinations of the ligand orbitals.

In order to make up such a combination we must remember that the linear combination of ligand orbitals should behave exactly as does the metal orbital to which it is linked under all symmetry operations of the molecule. If, say, rotation about a two-fold axis changes the sign of the metal orbital, the linear combination of the ligand orbitals must also change sign.

The transition moment, P, does then contain integrals of the form

$$\alpha(1 - \beta^2)^{1/2}\int \psi_d \vec{r}\sum_i \varphi_{1ig} d\tau + \beta(1 - \alpha^2)^{1/2}\int \psi_p \vec{r}\sum_j \psi_{1ig} d\tau$$
$$+ \alpha\beta\int \psi_d \vec{r}\psi_p d\tau + (1 - \alpha^2)^{1/2}(1 - \beta^2)^{1/2}\int \sum_j \psi_{1ig}\vec{r}\sum_i \varphi_{1ig} d\tau$$

usually different from zero.

It is important to realize that while the integral $\int \psi_d \vec{r}\varphi_i d\tau$ never is equal to zero (it is a two-center integral), the integral

$$\int \psi_d \vec{r}\sum_i \varphi_{1ig} d\tau$$

can be zero. This feature arises from the fact that the signs of the individual φ_i's may cause the various contributions to cancel. (This was the reason that we did not consider such mechanisms in the $d \rightarrow d$ transitions. As the linear combination of ligand wave functions must follow the d-orbital under inversion, that is, cannot change sign, all such transition integrals are here zero.)

Actual calculations of P reveal that it is the first and second integrals in the expression which contribute the major part to the band intensity. Further, as these two integrals are of the same order of magnitude, we see that it is rather pointless to ask if the electron jumps from the ligands to the metal ion or vice versa. Such a question would have meaning only if one of the integrals were the dominating contributor. All we can say is that the allowed transitions from the ground state to these higher states involve the formal transfer of

electrons "across the complex," and we speak of "charge transfer" to indicate the nature of the transition (24,25).

However, so far no accurate measurements have been made of these transitions, and without good experimental data to guide us, it is impossible to test the theory critically.

VI. Tetrahedral Coordinated Ions

Experiments show that the bands of tetrahedrally coordinated ions such as $CoCl_4^{2-}$ or $CuCl_4^{2-}$ have oscillator strengths of about 10^{-2}. Such large oscillator strengths cannot be accounted for by means of vibronic couplings, and, as we shall see, we need not consider this effect for tetrahedrally coordinated metal ions. It is, of course, still necessary to "mix" some "odd" wave functions into the "even" d-orbitals, but here this can be done directly via the Hamiltonian, $\mathcal{H}$, of the molecule, as the tetrahedron does *not* possess a center of inversion. We have

$$\Psi = \psi(d) - c\psi(p)$$

with $c = \int \psi(d)\mathcal{H}\psi(p)d\tau/(E_p - E_d)$.

Explicit calculations (15) show that it is not sufficient to look only at the atomic d- and p-orbitals for the metal ion, but that we need to augment our wave functions in such a way as to consider the role played by the ligand wave functions. This follows from the fact that a mixing of d- and p-orbitals merely as above yields intensities which are still from ten to one hundred times too small. We are thus forced to conclude that, at least for $CoCl_4^{2-}$ and $CuCl_4^{2-}$, the predominant contribution to the observed intensities is neither vibronic couplings nor crystal field couplings of the $3d$ and $4p$ levels. This circumstance implies that these complexes have some covalent character, and consequently we shall treat them by means of the molecular orbital scheme (15–17), exactly as we treated the "charge transfer" spectra.

As in that case, we have for our wave functions

$$\Psi = \alpha\psi_d + (1 - \alpha^2)^{1/2} \sum_i \psi_{1i_E}$$

where α measures " the degree of covalency" in the complex and $\sum\psi_{1i_E}$ is a normalized linear combination of the ligand orbitals. The

tetrahedron does not possess an inversion center, so the linear combination of ligand wave functions does not have such a feature either. With a ground state $\Psi = \psi_d$ and an excited state

$$\Phi = \alpha\theta_d + (1 - \alpha^2)^{1/2} \sum_i \varphi_{1ig}$$

we get a transition moment, P

$$P = (1 - \alpha^2)^{1/2} \int \psi_d \vec{r} \sum_i \varphi_{1ig} \, d\tau$$

usually different from zero.

In order to account for the observed intensities we must assume a value of $\alpha \simeq 1/2$. This is a rather interesting result, for it shows that as far as energy calculations are concerned, the crystal field approximation is not very good. It must be remarked that the above considerations hold true for "labile" complex ions as $CoCl_4^{2-}$ and $CuCl_4^{2-}$, where we can assume that the ligands are bonded to the metal ion via σ-bonds (1,15). If we try to account for the absorption band intensities of such stable complexes as MnO_4^- and CrO_4^{2-}, we find that it is necessary to take π-bonding between the metal ion and the ligands into account (15 17). This is, of course, eminently reasonable from a chemical point of view, as these latter compounds surely must be more tightly bonded than the former complexes.

VII. Conclusion

The oscillator strength, f, is, of course, only a measure of the product of the two observable quantities, the maximum extinction coefficient, ϵ_{max}, and the half width, $\nu_{1/2}$. It is, however, of some interest that a qualitative estimate of $\nu_{1/2}$ can be rather easily obtained. The idea is as follows: consider the bands as originating between the split atomic levels. This splitting varies with the crystalline field strength; it is intuitively clear that the greater the difference in slopes of the initial and final states, the broader the band (and the more it is displaced by a substitution). It can therefore be shown (18) that the half-width of the band is related to the expression

$$dE/dDq = -4nt_{2g} + 6ne_g$$

where nt_{2g} and ne_g are the numbers of t_{2g} and e_g electrons in the system.

A further point of interest is that as all our wave functions are made up of one-electron determinantal wave functions, we will only see transitions corresponding to a one-electron excitation. At least partially, every observed state *must* be made up by determinantal wave functions differing only in one orbital from the ground state.

This may not always be apparent. Indeed, sometimes a state is observed which seemingly disobeys this rule. However, it has to be borne in mind that the electronic configurations are determined by the steric configuration of the molecule as a whole. In some cases it is found that a lower symmetry crystalline field (e.g., a slight distortion from a regular octahedron) can introduce intensity into a transition which otherwise could not be observed (8).

It must, of course, be realized that the theories outlined here apply to complexes of all the transition elements, and it is for concreteness that we have chosen all our examples from the first series. However, the absorption spectra of the rare earth compounds present some rather special features in addition. As these are dealt with by Satten (21,22), we shall not pursue this subject further here.

All in all, we must conclude that an understanding of the various intensity-giving mechanisms has been reached. Even if there are still some points which need careful measurements and calculations, we may rest assured that the ligand field theory, so powerful in predicting the absorption bands, can also deal with the intensities of these bands.

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Unusual Oxidation States of Some Actinide and Lanthanide Elements

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I. Introduction

Investigations into the chemistry of the actinide* and lanthanide* elements have become increasingly numerous in the past twenty years. The research connected with atomic fission increased interest in lanthanide as well as actinide chemistry, but was hampered by

* The term actinides refers to elements of atomic numbers 89–103, and the term lanthanides to numbers 57–71. Although other names and groupings of these elements have been proposed, the terminology adopted here is both convenient and common.

lack of pure materials. The availability of cheap, pure lanthanide elements in the past few years has encouraged new investigations in this field as has the synthesis of larger amounts of more suitable isotopes in the field of actinide chemistry.

The selection of the subject matter for this chapter has been guided not only by the authors' interests but also by the view that in a review of this nature comprehensive treatment of a few topics is better than a limited treatment of many. The oxidation states of the various elements chosen for discussion are "unusual" in the sense of being either limited to a very few compounds or else "difficultly obtainable." The term "oxidation state" as used in this chapter cannot be defined precisely in certain compounds (such as sub-oxides, nitrides, hydrides, etc.) where metallic bonding is of primary importance. These compounds therefore are excluded from consideration. The convention of using Roman numerals in parentheses, e.g., La(III) for trivalent lanthanum, to denote the oxidation state is adopted throughout. An effort has been made to discuss the various studies of each state critically and to present the sum of chemical knowledge concerning each subject.

Among the lanthanide elements, the only valence states known other than the (III) state are: cerium(IV), praseodymium(IV), neodymium(IV), samarium(II), europium(II), terbium(IV), dysprosium-(IV), thulium(II), and ytterbium(II).* Many claims have been made for valence states other than those listed, but, in the opinion of the authors, none are supported by convincing evidence. Among the actinide elements, oxidation states greater than three are known for all elements from thorium through berkelium. The oxidation states of the lanthanide and actinide elements to be discussed here have been chosen somewhat arbitrarily, as explained previously. Among the lanthanides, Ce(IV) has been omitted, while Pr(IV), Nd(IV), Sm(II), Eu(II), Tb(IV), Dy(IV), Tm(II), and Yb(II) have been included. From the actinides, we have chosen Pa(IV), U(V), Pu(V), Am(IV), Cm(IV), Bk(IV), and Cf(V) as "unusual" states. Critical discussions of the evidence for lower valence states of thorium and americium are presented also. A brief discussion of the newer elements E (99), Fm (100), and Mv (101) is incorporated.

Each section includes a discussion of the character of the oxidation

* A preparation of ND(II) has recently been reported by L. F. Druding and J. D. Corbett, [*J. Am. Chem. Soc.*, *81*, 5512 (1959)]. Because of time limitations their work is not discussed in this chapter.

state, the ions and compounds in which it occurs, methods of preparation, measurements employed in characterizing the state, and other data such as absorption spectrum, nuclear magnetic resonance, magnetic susceptibility, crystal structures, etc., which may have been obtained. The section concludes with a discussion of the properties of this state, including thermodynamic values wherever possible.

II. The Lanthanides

A. PRASEODYMIUM(IV)

A higher oxide of praseodymium has been known for three-quarters of a century. It is formed by the ignition of most praseodymium salts in air, or by alkaline fusion. As so prepared, the composition is commonly referred to as "Pr_6O_{11}." It has been found, however, that the praseodymium-oxygen system is highly complex (1,7). The crystal structure and composition are dependent on the temperature and pressure of oxygen in contact with the solid phase (cf. Tb, Section II-E).

An oxide of the stoichiometric composition PrO_2 may be prepared by heating finely divided Pr_2O_3 with oxygen of 100 atmospheres pressure at 500°C. for 8–12 hours (6). The dioxide has the cubic calcium fluoride lattice type with $a = 5.395 \pm 0.005$ Å. Diffraction studies (8) on quenched samples of PrO_x prepared at high temperatures indicate that as the oxygen content is gradually varied from $PrO_{1.83}$ to $PrO_{1.5}$ the structure of the oxide changes from f.c.c. to rhombohedral to b.c.c. to hexagonal.

None of the recent work on praseodymium oxides suggests oxidation beyond the (IV) state, even by ozone (11).

Although higher binary oxides of praseodymium are readily obtained, attempts (2,5) to prepare higher binary fluorides have not been successful.

Fluorination to a higher state does occur in mixed crystals, however. An interesting situation is observed in the reaction of gaseous fluorine with solid solutions of PrF_3 in CeF_3 (4). Fluorination of CeF_3 to CeF_4 is complete at all mole fractions of cerium, but fluorination of PrF_3 becomes complete only when the mole fraction of Pr is about 0.9. The fluorination then drops with further increase in praseodymium content, becoming zero for pure PrF_3.

A higher fluoride of praseodymium may be obtained as a double salt

with alkali fluorides (3,9,10). Mixtures of alkali fluorides in various stoichiometric ratios are mixed with a salt of praseodymium and the mixture treated with fluorine gas at 300–500°C. The compounds $NaPrF_5$, Na_2PrF_6, K_2PrF_6, Rb_2PrF_6, and Cs_2PrF_6 have been prepared and identified. The tetravalency of the praseodymium in these compounds has been established by magnetic susceptibility (9), by analysis (3,9), by absorption spectrophotometry (3), and by X-ray powder methods (3,9).

The tetrapositive ion of praseodymium is a very powerful oxidizing agent. Measurements of the heat of solution of PrO_2 give a calculated value of -2.9 v. (6) for the couple:

$$Pr^{3+} = Pr^{4+} + e^-$$

The potential is such that the tetrapositive ion would be rapidly reduced by water in aqueous solution. Stabilization of the ion in aqueous solution might possibly be achieved by appropriate complexing, but to date this has not been accomplished.

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B. NEODYMIUM(IV) AND DYSPROSIUM(IV)

References to neodymium(IV) or -(V) in oxides (3,8,13,21,23), and in organic complex compounds (15–17) have appeared in the literature. Nearly all of this work was repeated recently, and the conclusion was reached that no firm evidence has been reported for an oxidation state of neodymium greater than (III) (14,18,19,22). The

use of impure materials or mistaken identification of the products presumably explains the reports of oxidation. Attempted oxidation of Nd_2O_3 by atomic oxygen under conditions where TbO_2 was prepared give no hint of any oxidation (7).

The work of Klemm and associates on stabilization of a number of higher valence states of the transition elements by forming double salts with the alkali metals (11) led to an attempt to oxidize certain lanthanides above the (III) state by the action of fluorine gas on an alkali metal–trivalent lanthanide double salt. Double fluorides with Na, K, Rb, and Cs containing tetravalent praseodymium were found (1,9), although pure PrF_4 has not been successfully prepared (4,12,20). Neodymium tetrafluoride could not be prepared by means of chlorine trifluoride or bromine trifluoride (20).

Observed trends in oxidation-reduction behavior of the lanthanide elements suggest that neodymium(III) and dysprosium(III) would be most readily susceptible to further oxidation, outside the elements already known to exhibit the (IV) state. Accordingly, alkali metal chlorides were mixed in varying stoichiometric ratios with neodymium or dysprosium trichlorides, dissolved in water, and evaporated. The dried compounds were ground and placed in optical quality calcium fluoride containers. The absorption spectrum of the compound was then recorded on a Cary Model 14 recording spectrophotometer. The fluorite disks were placed in a fluorinator and treated with fluorine gas at 1–3 atmospheres and temperatures up to 400°C. for various periods of time. Upon removal from the fluorinator, Fluorlube oil (completely fluorinated oil made by the Hooker Electrochemical Co.) was used to cover the compounds to protect the salts from atmospheric contamination.

In the case of the two elements neodymium and dysprosium, when admixed with either cesium or rubidium in the ratio of 1 mole of lanthanide to 2 or more moles of alkali metal, the product of the fluorination was a bright orange-yellow salt (1,10). In similar experiments with lanthanum or holmium there was no evidence of reaction nor did a reaction occur with potassium dysprosium salts (1).

Since Cs_3PrF_6 and Rb_3PrF_6 are known compounds (5), most work was carried out with a 3:1 mole ratio of alkali metal to lanthanide. Absorption lines due to the (III) state, which were prominent before the fluorination, were reduced in intensity by a factor of ten or more in the Cs_3NdF_x and Cs_3DyF_x compounds (1). Exposing these com-

pounds to a moist atmosphere resulted in reappearance of these lines. Below 6500 A. extremely strong absorption was present in both compounds but with no sharp absorption lines in the spectrum of either. A number of discrete absorption peaks in the region of 7,000–25,000 A. were found for both the neodymium and dysprosium salts. These peaks, as well as the intense absorption in the visible and ultraviolet, disappear upon reduction by hydrogen or water vapor or upon thermal decomposition in high vacuum at >300°C.

X-ray powder data reveal (1) what apparently is a face-centered cubic structure for the oxidized compounds and also for the colorless reduction products. It is doubtful whether significantly different diffraction patterns would be obtained for compounds such as Cs_3NdF_6 and Cs_3NdF_7 which differ by only one fluoride.

Analytical data obtained by dissolving the products in potassium iodide solution and titrating the iodine liberated indicate (1) that the compounds containing 3Cs:1Nd or 3Cs:1Dy readily oxidize iodide ion. However, the amount of iodide oxidized is only 10–20% of that calculated on the assumptions that all of the lanthanide is initially quadrivalent and that the only reaction occurring is the oxidation of iodide with the concurrent reduction of the lanthanide(IV) ion to the trivalent state. These low results may result from partial reduction by water as has been observed (2) with other compounds. Treatment of these fluorinated compounds by water followed by collection of the evolved gas gives a volume about one-third of that expected for a tetravalent ion oxidizing water to oxygen (1). Other reactions yielding gases such as F_2O may occur.

Preliminary susceptibility data in the case of Cs_3DyF_7 indicate that about one-half of the Dy is in the tetravalent state (10).

Before the tetrapositive states of neodymium and dysprosium can be accepted as firmly established, further analytical and physical measurements must be made. Certainly, both Nd(IV) and Dy(IV) will be extremely strong oxidizing agents, more so even than Pr(IV) which has an estimated $E°$ value of -2.9 v. for the (III)–(IV) couple (6).

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C. SAMARIUM(II)

The first compound of divalent samarium, $SmCl_2$, was prepared by Matignon and Cazes in 1906 (19). The blood red Sm(II) ion is a very powerful reducing agent; it is unstable in aqueous solution owing to the reduction of water. The divalent ion of samarium is less stable toward oxidation than either Eu(II) or Yb(II). A number of compounds containing divalent samarium have been prepared; among them are the halides, sulfate, chromate, phosphate, hydroxide, and carbonate.

Samarium(II) has been prepared from aqueous solutions of Sm(III) by reduction with alkali metal amalgams (8,9,18), by electrolytic reduction at a mercury cathode (1,20), and by the action of magnesium metal on samarium chloride solutions in alcoholic hydrochloric acid (3). The divalent halides may be prepared by the reduction of the anhydrous trihalides by hydrogen or ammonia at elevated tempera-

tures (11,12,14,15,21). Thermal decomposition of the triiodide has been used to prepare SmI_2 (13). Other compounds may be prepared from the divalent halides by metathetical reactions in aqueous solution. All of the compounds containing Sm(II) are thermodynamically unstable with respect to oxidation of the Sm(II) by oxygen or water, but may be kept indefinitely in an inert environment.

The absorption and fluorescence spectra of Sm(II) have been measured in aqueous solution and in various matrices such as NaCl and $SrCl_2$ (2). Sm(II) spectra have been observed where the samarium occurred as a natural impurity in fluorite (10,22,23). In aqueous solution, Sm(II) shows heavy diffuse bands which were assigned to $4f \rightarrow 5d$ or $4f \rightarrow 6s$ transitions (2). This divalent ion also shows narrow, weak bands correlated with those of isoelectronic Eu(III). Sm(II) dissolved in $SrCl_2$ fluoresces a brilliant red with a single broad maximum at about 6760 A.

Magnetic susceptibility measurements have been made for the isoelectronic pair Sm(II) and Eu(III) (24,25). Over the temperature range studied, from about 80 to 360° K., correspondence of the moments of Sm(II) and Eu(III) was very close, indicating that both ions have the electronic configuration $5f^6$.

The crystal structures of a number of Sm(II) compounds have been investigated; among them are the halides, sulfate, and carbonate. The difluoride of samarium, CaF_2 structure, prepared by metathetical reaction with $SmSO_4$ (1), exhibited a variable lattice constant among different preparations, as did the fluorite type compounds obtained by hydrogen reduction of the molten trifluoride in graphite crucibles. In the latter case the compositions were found by analysis to lie in the range $SmF_{2.2}$–$SmF_{2.5}$. The products are a single phase solid solution of SmF_3 in SmF_2, analogous to the CaF_2–YF_3 system, which also is cubic (27). The same phenomenon occurs with EuF_2 and YbF_2.

The chloride, $SmCl_2$, is orthorhombic with a = 8.973 A., b = 7.532 A., and c = 4.497 A. (4). This compound, like most other divalent compounds of samarium that have been investigated, is isostructural with the corresponding barium or strontium compounds. Powder patterns of $SmBr_2$ show this compound to be isostructural with $SrBr_2$, but no lattice constants are available (4). SmI_2 is not isostructural with SrI_2; it has the EuI_2 structure, which has not been determined (4). Orange samarium(II) sulfate is orthorhombic with

$a = 8.15 \pm 0.02$ A., $b = 5.38 \pm 0.02$ A., and $c = 6.91 \pm 0.02$ A. (1). Green $SmCO_3$ is orthorhombic with $a = 5.09 \pm 0.02$ A., $b = 8.58 \pm 0.02$ A., and $c = 5.97 \pm 0.02$ A. (1). Although pure preparations of the samarium(II) carbonate decompose fairly rapidly, the X-ray measurements were of sufficiently good quality to show that it is isostructural with $BaCO_3$. A number of samarium(II) compounds have been prepared for which no measurements have been made and for which few data are reported other than color.

The monoxide of samarium, SmO, has been studied rather extensively (5). It has the NaCl structure with a lattice constant of $a = 4.9883 \pm 0.0003$ A. Compounds having a NaCl structure previously ascribed to SmO gave values of the lattice parameters from 5.015 to 5.050 A. (7); this variation is apparently due to partial nitride formation, giving mixed monophasic nitride oxides (5,6). A phase containing less oxygen than SmO has a zinc blende structure with a lattice constant varying from about 5.37 to 5.38 A. for the range $SmO_{0.4}$–$SmO_{0.6}$. Some evidence for a phase $SmO_{\sim 0.1}$ exists. The nature of the bonding in SmO is uncertain, although it may be an ionic compound of Sm(II).

The heat of formation of $SmCl_2$ has been measured as -195.6 ± 1.0 kcal. at 298.16°K. (17). The best $E°$ value for the half reaction Sm(II) = Sm(III) + e appears to be 1.55 v. (26) from polarographic measurements, although earlier estimates gave values that were much less positive (16).

The ionic radius of Sm(II) is given by Zachariasen (28) as 1.11 A.

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D. EUROPIUM(II)

Divalent europium was not discovered until 1911 when the compound $EuCl_2$ was prepared (48). Eu(II) is colorless in aqueous solutions and is quite stable in weakly acidic solutions in the absence of atmospheric oxygen or other oxidizing agents; it is the most stable of the divalent lanthanides. The oxidation of Eu(II) has been studied in various concentrations of HCl and at differing pressures of hydrogen, oxygen, and air; the rate of oxidation shows extreme sensitivity to the concentration of oxygen (46). Photochemical oxidation of Eu(II) by water has been observed (10). The rate of reduction of Eu(III) has been investigated by measurement of the magnetic susceptibility and by the technique of nuclear induction (14). Kinetic studies have been made of the reduction of Eu(III) by Yb(II); of the oxidation of Eu(II) by V(III), Cr(III), Ti(III), and Ce(IV) in $HClO_4$; and of the Eu(II)–Eu(III) exchange (21). Studies of the Eu(II)–Eu(III) exchange reaction in HCl have shown that the reaction is rapid, first order in Eu(II), first order in Eu(III), and first order in chloride ion. It is essentially independent of the hydrogen

ion concentration in the range 0.3–1.0 f. (34). A large number of compounds containing Eu(II) have been prepared; among them are the halides, the sulfate, the phosphate, the perchlorate, the hydroxide, the sulfide, the selenide, the telluride, the carbonate, and the monoxide, if indeed the monoxide is a compound of divalent europium.

Europium(II) has been prepared from aqueous solutions of the trichloride reduction with magnesium, aluminum, iron, or zinc (28,40). Electrolytic reduction at a mercury cathode has been extensively used, primarily for separation and purification (27,29,37,38,49). Marsh has used alkali metal amalgams extensively for separation of samarium-europium mixtures and their subsequent purification (31,32). The solid divalent halides are usually made by reduction of the anhydrous trihalides by hydrogen or ammonia or by their thermal decomposition (8,15,17–20,48). Europium(II) sulfide has been prepared by hydrogen reduction of $Eu_2(SO_4)_3$ (3). Other compounds have been made from the halides by metathetical reactions in aqueous solution.

The absorption and fluorescence spectra of Eu(II) have been measured both in aqueous solution and in various salts such as NaCl, $SrCl_2$, and CaF_2 as matrices (7,13,41,42). In aqueous solution, Eu(II) shows intense diffuse bands which have been assigned to $4f \rightarrow 5d$ or $4f \rightarrow 6s$ transitions (7). Narrow weak bands of Eu(II) may be correlated with those of isoelectronic Gd(III). In $SrCl_2$, Eu(II) fluoresces violet with a band at 4090 A. (41). A study of the color centers and luminescence of Eu(II) in $LaCl_3$ after irradiation with ultraviolet light or gamma radiation has been made (12). Natural fluorite with Eu(II) as an impurity has been studied (42). Pure $EuCl_2$ is reported to exhibit a bright purple fluorescence with red bands at 6300 and 6900 A. (13).

Very thorough magnetic measurements on the isoelectronic pair Eu(II) and Gd(III) have been made (10,16,22,44,45). The molar susceptibility, χ_m, for Eu(II) in $EuSO_4$ has been found to be $25{,}800 \times 10^{-8}$ c.g.s. units at 25°C., which is to be compared with $25{,}700 \times 10^{-8}$ for Gd(III). Further, Eu(II) follows the Curie-Weiss law

$$\chi = C/t + \Delta$$

where $\Delta = 4$. This is very convincing proof that the Eu(II) electronic structure is identical with that of Gd(III), namely, . . . $4f^7 5s^2 5p^6$. Measured susceptibilities of the dichloride, the dibromide, and the diiodide all give an effective Bohr magneton number of 7.9 for Eu(II),

the same as that for Gd(III) (22). The difluoride gives an apparently low value of 7.4, which is discussed below in Section II-D on the structure of Eu(II) compounds. Magnetic measurements have been made on the sulfide, selenide, and telluride of Eu(II), and fair agreement with the other Eu(II) compounds is found.

A number of measurements of the paramagnetic resonance spectrum of Eu(II) have been made (1,25,26,30,33,43). Eu(II) and Gd(III) occurring naturally in calcium fluoride give splittings appropriate to a cubic crystalline field (25); the cubic field splitting pattern has been calculated (24). Nuclear spins of Eu^{151} and Eu^{153} have been determined by observations of the hyperfine structure of the spectrum of Eu(II) in SrS (4,26).

Crystal structure data exist for EuF_2 (2,3,9), $EuCl_2$ (9), $EuBr_2$ (9), EuI_2 (9), $EuSO_4$ (2,39), EuS (23,36), EuSe (23), EuTe (23), $Eu(CO_3$ (2), and EuO (11). As is the case with Sm(II) compounds, Eu(II) compounds are isostructural with the analogous barium or strontium salts for the most part. The difluoride has been shown to have a fluorite structure, but there is uncertainty about the lattice constant, values of 5.796 ± 0.006 (36) and 5.82_3 (23) A. having been reported. Magnetic measurements have shown that the compound with a constant of 5.82_3 gives a low value for the magnetic moment and thus presumably has some Eu(III) in it. More recent work (2) shows that a large range of values from 5.75 to 5.842 A. are obtained, depending on the method of preparation. Solid solutions of YF_3 in CaF_2 containing up to 30 mole % yttrium have been reported (47) which have the fluorite structure. Analytical results on EuF_2, SmF_2, and YbF_2 indicate that a solid solution of the trifluoride in the difluoride is the cause of the variation in lattice constants for each of the lanthanide difluorides. The value of 5.84_2 A. was observed for the product resulting from treatment of molten EuF_3 with hydrogen and, since this was the most drastic reduction treatment given any of the preparations, should be the lattice constant for the compound nearest to EuF_2 (2).

Europium dichloride has been shown to be orthorhombic with a = 8.914 A., b = 7.499 A., and c = 4.493 A. and to have the lead chloride structure (9). $EuBr_2$ and $SmBr_2$ are isostructural with orthorhombic $SrBr_2$ with nearly the same cell constants, but the data necessary to calculate the lattice constants have not been reported (9). Europium diiodide is not isostructural with SrI_2, and the structure has not been

interpreted, although powder pattern data have been reported (9); it is isostructural with SmI_2.

Europium(II) sulfate has been studied by Pauling (39) and more recently by Asprey *et al.* (2). It has the orthorhombic $BaSO_4$ structure with $a = 8.32 \pm 0.02$ A., $b = 5.34 \pm 0.02$ A., and $c = 6.82 \pm 0.02$ A. Although α and β forms with different physical properties have been reported (50), only the one orthorhombic structure could be confirmed (2). The newly measured lattice constants are slightly different from those reported by Pauling, and the variations of the several measurements may be due to incorporation of some Eu(III) in the crystal. However, there is no doubt that the salt is isostructural with $BaSO_4$.

The sulfide, EuS, has the sodium chloride structure with $a = 5.956 \pm 0.001$ A. (23,36), as do the selenide, EuSe, with $a = 6.173 \pm 0.001$ A. (23) and the telluride, EuTe, with $a = 6.572 \pm 0.001$ A. (23). The carbonate, $EuCO_3$, has the orthorhombic $BaCO_3$ structure with $a = 5.10 \pm 0.02$ A., $b = 8.45 \pm 0.02$ A., and $c = 6.05 \pm 0.02$ A. (2).

A number of studies of the monoxide, EuO, have been made, both in combination with SrO (5,6) and as the pure compound (11). The compound has the NaCl type structure with $a = 5.1439 \pm 0.0005$ A. When admixed with SrO, it is reported to be rose-red in color and to oxidize in air at room temperature.

If considered to be an ionically bonded compound, the calculated radius of Eu in the monoxide is 1.11 A. The value obtained from the difluoride and dichloride is 1.09 A. (51).

The potential of the (II)–(III) couple is far more accurately known for europium than for any other lanthanide. For the half-reaction $Eu(II) = Eu(III) + e^-$, $E^\circ = 0.43$ v., measured both potentiometrically (29) and polarographically (35). This value fits well with observations of the chemical behavior of Eu(II) in solution.

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E. TERBIUM(IV)

A higher oxide of terbium has been known almost since the discovery of the element by Mosander in 1843. The composition is commonly, but not accurately, given as Tb_4O_7. An oxide of the stoichiometric composition TbO_2 was first reported by Gruen, Koehler, and Katz (4). The only other known binary compound of tetravalent terbium is the tetrafluoride, first prepared in 1954 (3). The tetrapositive ion is a very powerful oxidizing agent, since dissolution of the higher oxide in acid yields only Tb(III). Considerable gas evolution accompanies the dissolution, owing presumably to the oxidation of water to oxygen.

The terbium-oxygen system has recently been investigated with some care (5). Equilibrium compositions depend upon the temperature and partial pressure of oxygen above the solid phase. X-ray diffraction studies on quenched samples have shown that there are three stable oxides in the composition range $TbO_{1.5}$–$TbO_{1.81}$ having the stoichiometric compositions $TbO_{1.5}$, $TbO_{1.71}$, and $TbO_{1.81}$. Body-centered cubic $TbO_{1.5}$ takes up oxygen to about $TbO_{1.60}$. The oxide $TbO_{1.71}$ has a rhombohedral structure, and $TbO_{1.81}$ a cubic calcium fluoride structure with $a = 5.286 \pm 0.003$ Å.

A composition in the range between $TbO_{1.71}$ and $TbO_{1.81}$ is ordinarily obtained by the ignition of nitrate, oxalate, etc., in air, followed by cooling. The exact composition probably depends somewhat on the ignition temperature and rate of cooling.

The oxide TbO_2, referred to previously, was obtained by oxidation of Tb_2O_3 with atomic oxygen at 450°C. The dioxide has the fluorite structure with $a = 5.213 \pm 0.002$ A.

Colorless TbF_4 is obtained by reacting gaseous fluorine with TbF_3 at about 300–500°C. The tetrafluoride is monoclinic and isostructural with CeF_4 and ThF_4. The fluorination of TbF_3 to form TbF_4 is

quite sensitive to the presence of impurities. It has been found (2), for example, that in mixed crystals of TbF_3 and YbF_3, almost no TbF_4 is formed unless the mole fraction of TbF_3 exceeds 0.93 (compare with PrF_4). Solid terbium tetrafluoride does not react rapidly with either cold or hot water and dissolves only slowly in 1*M* HCl or HNO_3. If iodide ion is present, the dissolution is accompanied by the formation of some iodine. Compounds of the type M_xTbF_{x+4}, where M is K, Rb, or Cs and $x \geqq 2$, have been prepared (1).

No exact estimate is possible for the Tb(III)-Tb(IV) couple, but Tb(IV) is undoubtedly a very strong oxidizing agent with a potential as or more negative than that for the Pr(III)-Pr(IV) couple.

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F. THULIUM(II)

The electronic configurations of the tripositive ions of thulium and samarium are analogous in the sense that each occurs two positions ahead of an especially stable electronic configuration—$4f^{14}$ and $4f^7$, respectively. It may be argued that each element should show a similar tendency to approach the stable configuration by acquiring an additional electron to form the dipositive state. Although the argument is of doubtful merit, there is substantial evidence for the existence of stable Tm(II). Some inconclusive evidence for the possible divalency of thulium has been reported in work on the amount of free metal obtained by hydrogen reduction of anhydrous thulium trichloride (4,8). Fluorescence measurements on traces of thulium in various calcium salts also indicate the possibility of a stable Tm(II) (5,6). Treatment of molten TmF_3 by hydrogen results in the formation of a small proportion of reddish inclusions reminiscent of partially reduced SmF_3 (1).

The recent synthesis of thulium diiodide has demonstrated conclusively the existence of divalent thulium in a solid compound (2).

In solution, the ion is so powerful a reducing agent that it reacts violently with water. A fleeting violet-red color, presumably due to Tm(II), has been observed. Tm(II) appears to be even less stable than Sm(II) in aqueous solution.

Attempts to prepare $TmCl_2$ and TmI_2 by hydrogen reduction of the trihalides failed (3). The only successful method of preparation reported is the reduction of anhydrous thulium triiodide by thulium metal at 500–600°C. (2). The very dark-colored or black material obtained was shown by X-ray powder diffraction methods to have an hexagonal cell, isostructural with YbI_2. The lattice constants for TmI_2 are $a = 4.520 \pm 0.003$ A. and $c = 6.967 \pm 0.006$ A., which may be compared to $a = 4.503 \pm 0.003$ A. and $c = 6.972 \pm 0.004$ A. for YbI_2. The ionic radius of Tm(II) is 0.94 A., very near the 0.93 A. radius (9) of Yb(II).

Evidence for the existence of Tm(II) in aqueous solution has recently been obtained (7). The magnetic susceptibility of a solution prepared by strontium amalgam treatment of a thulium(III) sulfate solution increased with time until a constant value was reached. Such a solution also reduced permanganate ion. When a similar treatment was given to a yttrium solution, no such effects were found.

No quantitative estimate may be made for the stability of divalent thulium at the present. Reduction of thulium trichloride by hydrogen does not appear to proceed under conditions which yield $SmCl_2$. (3). Qualitative observations of the reaction of thulium diiodide with water suggest that the Tm(II) ion is considerably less stable than is Sm(II). On this basis, $E°$ for the reaction Tm(II) = Tm(III) + e would be more positive than $\sim$1.5 v.

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G. YTTERBIUM(II)

Although Sm(II) and Eu(II) were discovered in 1906 and 1911, respectively, it was not until 1929 that Klemm and Schuth (10) first prepared Yb(II) as the dichloride. The green Yb(II) ion is a powerful reducing agent and is oxidized by water quite rapidly in aqueous solution. It is more stable than Sm(II) but considerably less so than Eu(II). A number of compounds of divalent ytterbium have been prepared; among them are the sulfate, the carbonate, the halides, the sulfide, the selenide, the telluride, and possibly the monoxide.

Ytterbium(II) has been prepared from aqueous solutions of Yb(III) by electrolytic reduction at a mercury cathode (2–3,4,17,25) and at an amalgamated lead cathode (13), and by electrolysis with a lithium amalgam (16). A study of the variables involved in preparing ytterbium amalgams has recently been made (20). The dihalides of ytterbium may be prepared by hydrogen reduction of the anhydrous trihalides (10), or, in the case of YbI_2, by thermal decomposition (8,9). Other compounds may be prepared by metathesis of the halides or the sulfate in aqueous solution. The Yb(II) salts are stable in the absence of water or oxidizing agents.

Measurements of the absorption and fluorescence spectrum of Yb(II) in aqueous solution and in $BaCl_2$ and $SrCl_2$ have been made (5). The Yb(II) ion shows heavy diffuse absorption bands attributed to $4f \rightarrow 5d$ or $4f \rightarrow 6s$ transitions. The ion shows weak fluorescence in the violet centered at about 4020 A. Yellow fluorescence of Yb(II) in CaF_2 has been reported (18,19).

Magnetic measurements have been reported for the compounds $YbCl_2$ and $YbSO_4$ (7,10,21). Since Lu(III) is diamagnetic, Yb(II) was expected to be so. However, it was found to be very slightly paramagnetic. There is some question as to whether the paramagnetism arises from some Yb(III) remaining in the salt or is due to a small temperature-independent paramagnetism as in the case of Ce(IV) (21). It seems probable that the electronic configuration of Yb(II) is the same as that of Lu(III). The selenide and telluride have been studied (22,23), and a sharp drop in the paramagnetism was noted during the reduction from Yb(III) to Yb(II).

The crystal structures of the halides, the selenide, the telluride, the

sulfate, the carbonate, and the monoxide of divalent ytterbium have been determined. The difluoride, YbF_2, has been prepared and studied by X-ray powder methods (2,6). As with SmF_2 and EuF_2, a fluorite type of structure is obtained with a lattice constant which depends on the method of preparation. Analysis indicates that the nearest approach to YbF_2 of any of the preparations was $YBF_{2.24}$ where $a = 5.571$ A. The variation observed is probably due to the solubility of YbF_3 in YbF_2 as is discussed more fully in Section II-D on Eu(II). The dichloride has been shown to have an orthorhombic structure with $a = 6.53$ A., $b = 6.68$ A., and $c = 6.91$ A., which is not isostructural with $EuCl_2$ (6). It is described as a distorted fluorite structure. X-ray measurements on powdered $YbBr_2$ have been made, but the structure is unknown and is not the same as $SrBr_2$. The diiodide has the hexagonal cadmium iodide structure (6) with constants $a = 4.503 \pm 0.003$ A. and $b = 6.972 \pm 0.004$ A. It is isostructural with TmI_2 (cf. Tb, Section II-F). The selenide and telluride both have the NaCl structure with $a = 5.867 \pm 0.002$ A. and $a = 6.340 \pm 0.002$ A., respectively (23). The sulfate, $YbSO_4$, is not isostructural with $SmSO_4$ or $EuSO_4$, but has the hexagonal $CePO_4$ structure described by Mooney (14), with $a = 7.025 \pm 0.003$ A. and $c = 6.428 \pm 0.003$ A. (2). The carbonate, $YbCO_3$, is orthorhombic, isostructural with $BaCl_2$, with cell constants $a = 4.98 \pm 0.03$ A., $b = 8.13 \pm 0.04$ A., and $c = 5.87 \pm 0.03$ A. (2). The poor precision of the measurements is due to the chemical instability of the compound. The monoxide, YbO, has the NaCl structure with $a = 4.86 \pm 0.02$ A. (1). The ionic radius is calculated to be 0.93 A. (26).

The $E°$ value for the Yb(II)-Yb(III) couple is somewhat uncertain. Laitinen (11) has pointed out that zinc, with a potential of 0.763 v. (12), does not reduce Yb(III) to Yb(II), although this would be expected from the potentiometric value of 0.578 v. for the Yb(II)–Yb(III) couple (24). He suggests that the platinum electrode used in the potentiometric measurement may have been functioning partly as a hydrogen electrode. His polarographic measurements give 1.15 v. for $E°$ in agreement with earlier polarographic work (15). This value is also consistent with other known aspects of the chemistry of Yb(II).

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III. The Actinides

A. THORIUM(II) AND THORIUM(III)

Reduction of Th(IV) halides to lower valent compounds has been reported by a number of investigators (1,2,4,8). In most cases the reductions have been carried out on the solid halides with finely divided metals, such as thorium or aluminum, at temperatures of a few hundred degrees. There is no doubt that in this work reduction to lower oxidation states occurred.

On the other hand, a recent report (6) of the reduction of $ThBr_4$ to $ThBr_3$ by hydrogen at about 400°C. is undoubtedly erroneous. Attempts to repeat this work have been entirely unsuccessful (3).

Even in the case of successful reductions, however, the characteriza-

tion of the reduction products is unsatisfactory. In general, X-ray diffraction patterns of these substances have not been interpretable. An early report (1) on the crystal structure of ThI_2 has not been verified. It is not certain at present that a pure compound of either Th(III) or Th(II) has ever been prepared.

The compounds ThS and Th_2S_3 are well characterized crystallographically (9), but they have a semimetallic appearance and low specific resistance. Both are diamagnetic. They are not here considered as compounds of Th(II) or Th(III).

If thorium metal is dissolved in 1–2*M* hydrochloric acid in the absence of air, the solution takes on a distinct yellow appearance and some black insoluble residue remains. The solution exhibits very strong absorption in the blue and ultraviolet region of the spectrum, and the absorption is diminished if air is now admitted (7). It has not been shown that the absorption behavior mentioned above is related to the presence of a lower oxidation state of thorium in solution. The solid residue has been reported to be ThO (5).

It appears that lower valence states of thorium have been prepared, but probably not in pure form, and certainly only inadequately characterized.

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B. PROTOACTINIUM(IV)

Evidence for the existence of a lower oxidation state of protoactinium was provided in 1947 by Boussières and Haissinsky (2), whose

studies of the coprecipitation behavior of trace concentrations of protoactinium in the presence of reducing agents led them to the conclusion that the lower state probably was Pa(IV). Pure compounds of Pa(IV) were first prepared in 1950. Microgram amounts of these materials were identified by X-ray diffraction (5).

Polarographic studies (6) of Pa(V) in oxalate solution have shown that reduction at a dropping mercury cathode proceeds in two distinct one-electron steps, neither of which is reversible. The second polarographic wave is the only evidence to date for Pa(III). In an investigation of the hydrogen ion concentration dependence of the protoactinium half-wave potentials in this system, the potential of the first wave was found to be hydrogen ion independent, and the second to be hydrogen ion dependent. This feature of the polarographic behavior of protoactinium has not been interpreted.

The absorption spectrum of Pa(IV) has been measured in different acids (4,6–8). The absorption spectrum (7) of Pa(IV) in 1*M* HCl exhibits maxima at 276, 255, and 224 mμ. The spectrum is similar to that of Ce(III), except that the Ce(III) absorption occurs at somewhat shorter wavelengths. The solutions of Pa(IV) in 1*M* HCl used in the optical work were found to be quite stable in the absence of air.

Recent paramagnetic resonance studies (1) on Pa(IV) in a single-crystal matrix of Cs_2ZrCl_6 have shown that the resonance exhibits four hyperfine lines due to the nuclear spin of the isotope Pa^{231} and has an isotropic g value equal to 1.148 $\pm$ 0.002. The paramagnetic resonance studies strongly indicate that the electronic configuration of Pa(IV) is $5f^1$.

Compounds (9) of Pa(IV) of known structure include $PaCl_4$, PaF_4, PaO_2, and PaOS. The tetrachloride is tetragonal, isostructural with UCl_4, with $a_1 = 8.377 \pm 0.004$ A. and $a_3 = 7.482 \pm 0.004$ A. PaF_4 is a reddish brown solid of the ZrF_4 structure type, isostructural with UF_4, NpF_4, etc. (10). PaO_2 is cubic, of the calcium fluoride structure type, with $a = 5.505 \pm 0.001$ A. PaOS is tetragonal, of the PbFCl structure type, with $a_1 = 3.832 \pm 0.001$ A. and $a_3 = 6.704 \pm 0.004$ A.

Protoactinium dioxide may be prepared (9) by reduction of the pentoxide with hydrogen at 1550°C. Treatment of the dioxide with CCl_4 vapor at 500°C. yields a sublimate of the greenish yellow tetrachloride (9). Alternatively, the pentachloride, produced from the pentoxide and CCl_4 vapor at 300°C., may be reduced (9) to the tetrachloride with hydrogen at 800°C. In this latter process the pentachloride

is forced to pass as a vapor through a hot zone containing hydrogen.

Reddish brown PaF_4 is made (9) by reacting PaO_2 at a temperature near 600°C. with a mixture of hydrogen and hydrogen fluoride gases at a volume ratio of 5:1.

Protoactinium oxysulfide, of composition approximately $Pa_{0.95}OS$, has been prepared by treating the pentoxide at 1200°C. with H_2S gas at one atmosphere pressure saturated with CS_2 at −50°, and also by the action of the same mixture of gases on $PaCl_5$, presumably in the presence of some water or oxygen (9). The latter reaction is carried out at gradually increasing temperatures from room temperature to 900°C.

In solution, Pa(V) in 6–9*M* HCl is readily reduced to the (IV) state by chromous ion (3), thus suggesting that Pa(III) is not an extremely strong reducing agent. Fried and Hindman (7) estimate the E° value of the Pa(IV)-Pa(V) couple to be +0.1 v.

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C. URANIUM(V)

The possible existence of an oxidation state of uranium intermediate between (IV) and (V) is suggested by the composition of the oxide, U_3O_8, which has been known for more than a century. Since the stoichiometry of the compound may be satisfied by an appropriate mixture of either U(IV) or U(V) with U(VI), the evidence is only

presumptive, however. Magnetic susceptibility studies made in 1940 (2) support the view that the oxide contains U(V) and U(VI) in the mole ratio 2:1.

Purely chemical evidence for the existence of a stable compound of U(V) was supplied at a much earlier date, however, by the discovery of UCl_5 (13) and, later, of UF_5 (14). Of course, on the basis of composition alone, it could still be argued that these compounds contain equimolar mixtures of U(IV) and U(VI), but the fact that UF_5, at least, is colorless indicates that it is not a mixed oxidation state compound. The question has been decided conclusively by X-ray diffraction evidence (16), which shows that all fluorine atoms are equivalent, and the uranium-fluorine distance is reasonable for a U^{5+} F^- ionic bond.

The existence of U(V) in aqueous solution was first suggested by Herasymenko (6) on the basis of his investigation of the polarographic behavior of uranyl solutions. Nearly twenty years elapsed before Herasymenko's observations were confirmed (3,4).

Pentapositive uranium, whether in the form of solid compounds or as the aqueous ion, UO_2^+, is relatively labile. The pentahalides are subject both to thermal decomposition and disproportionation, and the UO_2^+ ion is appreciably stable only in a pH range of about 2–4.

That the principal species of U(V) in acidic aqueous solution is indeed UO_2^+ has been shown by the reversibility of the U(V)-U(VI) couple (3,4) and the magnitude of the hydrolysis constant (10). The pentapositive ion of uranium in strongly acidic aqueous solution is highly unstable with respect to the reaction

$$2UO_2^+ + 4H^+ = U^{4+} + UO_2^{2+} + 2H_2O$$

for which K is about 10^9 (cf. PuO_2^+). At pH 2.5–3, however, UO_2^+ may be prepared in 70% yield or better by controlled potential electrolysis of oxygen-free solutions of UO_2^{2+} at a platinum cathode (10). Although the $\sim 10^{-3}M$ uranium(V) solutions obtained in this way are unstable with respect to disproportionation, the rate of disproportionation may remain very slow for long periods of time until there is a sudden onset of polymerization of the U(IV) species.

The UO_2^+ ion shows no strong absorption in the region from 3600 to 10,000 A., but begins to absorb strongly below 3500 A.

Solid compounds containing only U(V) include UF_5, α form, tetragonal, $a_1 = 6.512 \pm 0.001$ A., $a_3 = 4.463 \pm 0.001$ A., which trans-

forms below 125° to the β form, tetragonal, $a_1 = 11.450 \pm 0.002$ A., $a_3 = 5.198 \pm 0.001$ A. (16). The pentachloride (13), UCl_5, is reddish brown or black, and the structure is unknown. The complex compounds $UCl_5 \cdot SOCl_2$ (5), $UOCl_3 \cdot C_2H_5OH$ (1), and $(C_5H_6N)_2UOCl_5$ (1), as well as the uranium pentaalkoxides (1, 15), are known.

Uranium pentafluoride may be prepared by treating solid UF_4 with gaseous UF_6 at a pressure of 120–140 mm. of Hg. At 100°C. β-UF_5 is obtained, at 200°C. the product is the α form. Fluorides of intermediate composition U_2F_9, U_4F_{17} are obtained at higher temperatures. Alternatively, α-UF_5 of high purity can be obtained by treating the tetrafluoride with fluorine gas at 150–250°C.

As mentioned previously, UF_5 is unstable with respect to disproportionation, the reaction proceeding to give gaseous UF_6 and intermediate solid fluorides. At 200°C., for example, the equilibrium pressure of UF_6 in the reaction

$$3UF_5(\alpha) = U_2F_9 + UF_6(g)$$

is about 26 mm. (7). Uranium pentachloride similarly has been observed to disproportionate into $UCl_4(g)$ and $UCl_6(g)$ in high vacuum at 100–175°C. (8).

The limited stability of UCl_5 makes its preparation somewhat difficult, but the compound may be obtained by reacting U_3O_8 or UO_3 with CCl_4 in a sealed tube at 250°C. (12) or by prolonged boiling at atmospheric pressure of UO_3 with a large excess of CCl_4 saturated with Cl_2 (9). The second method is not self-sufficient, since it is necessary to add considerable amounts of UCl_5 to catalyze the formation of additional pentahalide. UCl_5 may also be made by treatment of UCl_4 with chlorine gas (9).

The $E°$ value of the U(IV)-U(V) couple is -0.62 v. and that of the U(V)-U(VI) couple is -0.05 v. (11).

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D. PLUTONIUM(V)

The pentapositive oxidation state of plutonium was first identified in 1944 (1), well after the (III), (IV), and (VI) states had been recognized. Belated recognition of plutonium(V) can be attributed in part to its instability in acidic aqueous solution, and in part to its failure to form characteristic compounds readily.

Pu(V) was first noted as a state of transitory existence in the reduction of Pu(VI) by SO_2 or hydroxylamine in aqueous solution. Its absorption of light in the visible region of the spectrum is much less than that of Pu(III), -(IV), or -(VI), so that in the reductions mentioned above, the temporary fading of the solution provided the first clue to the existence of Pu(V). The equilibrium constant for the reaction

$$2PuO_2^+ + 4H^+ = Pu^{4+} + PuO_2^{2+} + 2H_2O$$

is about 2×10^4, so that in $0.5M$ H^+ the concentration of Pu(V) in equilibrium with an equimolar mixture of Pu(IV) and Pu(VI) is about 2%. Stabilization of Pu(V) would be expected to increase with further decrease in hydrogen ion concentration, but the situation is complicated by the hydrolysis and polymerization of Pu(IV) at lower acidities, and the further reaction

$$Pu^{4+} + PuO_2^+ = Pu^{3+} + PuO_2^{2+}$$

for which K is about 9.

Optimum stability of Pu(V) occurs in the pH region 1.4 to about 5 (5).

The most prominent absorption bands of PuO_2^+ occur at 5690 and 7750 A. These bands may be used for analytical purposes, but neither is free from interference in the same region by Pu(III), -(V), and -(VI). Binary compounds of Pu(V) are not known, but several salts of PuO_2^+ have been reported (2). Early claims of the preparation of compounds such as Co(II)Pu(V) carbonate and Hg(I)Pu(V) carbonate may be correct, but have not been substantiated.

On the other hand, the compound $KPuO_2CO_3$ is well established. It is prepared by reduction of Pu(VI) to Pu(V) in dilute nitric acid with the stoichiometric amount of KI, extracting the iodine, and adding potassium carbonate to pH $\cong$ 7. The potassium plutonium(V) carbonate has a hexagonal structure, with lattice constants $a = 5.09 \pm 0.01$ A. and $c = 9.83 \pm 0.02$ A. Plutonium in this structure is in the form of colinear O—Pu O radicals (3,7). The analogous compound $NH_4PuO_2CO_3$ has the same structure with $a = 5.09 \pm 0.01$ A. and $c = 10.39 \pm 0.02$ A. (3). An orthorhombic form of $KPuO_2CO_3$ and a monoclinic form of $NaPuO_2CO_3$ have not been completely characterized (7).

A pentafluoride, PuF_5, is of doubtful existence. Although thought at one time to be formed by the disproportionation reaction

$$2PuF_4(s) = PuF_3(s) + PuF_5(g)$$

recent studies (4) have cast doubt on this view, and certainly no pure phase of PuF_5 has ever been identified.

The $E°$ value of the Pu(IV)-Pu(V) couple is -1.15 v. and that of the Pu(V)-Pu(VI) couple is -0.93 v. (6).

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E. AMERICIUM(II)

Since americium in the actinide series holds a position analogous to that of europium in the lanthanide series, the dispositive state was originally expected to be readily attainable because of the known special stability of a half-filled "*f*" subshell (9). Europium(II) is quite easily prepared, and the reasonable assumption was made that it would be correspondingly easy to reduce americium to the (II) state. A considerable effort was made to reduce americium(III) to americium(II) in solution and in solid compounds. Since that time, it has been recognized that 5*f* electrons in the actinides are more readily ionized than are 4*f* electrons in the lanthanides. Americium-(II) would therefore be a stronger reducing agent, and hence more difficult to prepare, than europium(II). Thus, in retrospect, it does not seem particularly surprising that americium(II) has not yet been shown to exist.

The only evidence for americium(II) comes from some tracer studies using both americium and curium (11). The general method employed was that developed by J. K. Marsh (7) for separations of samarium, europium, and ytterbium in which sodium amalgam is used as the reducing agent. Tracer quantities of americium and curium were used along with macro concentrations of lanthanum(III), samarium(III), and europium(III) in sulfuric acid solution. After shaking the solution with sodium amalgam, the resulting precipitate of $SmSO_4$ and $EuSO_4$ was separated and leached rapidly with cold dilute nitric acid to dissolve the $SmSO_4$ and leave the $EuSO_4$ undissolved. The results of this treatment were that about 40% of the americium and only 20% of the curium were in the nitric acid fraction, suggesting that the increase in the Am/Cm ratio was due to partial reduction of the americium(III) to americium(II). Since tracer-scale experiments are frequently misleading because of differences in carrying, occlusion, etc., a great deal more work has been carried out using macro amounts of americium (1).

The reduction of anhydrous samarium trichloride by hydrogen or ammonia at elevated temperatures has been used to prepare $SmCl_2$ (3–6, 8). The use of similar techniques with $AmCl_3$ gave no evidence of the reduction of americium(III) over a wide range of temperatures

and pressures. The possibility of reduction was checked by chemical behavior and by X-ray powder procedures.

When a sulfate–acetate solution of samarium(III) is electrolyzed with a mercury cathode in a cell with a separated anode compartment, $SmSO_4$ is produced as a solid compound (2). Similar electrolysis of an americium(III) solution gave only an americium amalgam with no precipitate and no color change. Treatment of this amalgam with aqueous ammonium sulfate or sulfuric acid gave pure americium(III) solutions with no evidence for americium(II) (1). By analogy with samarium, which has approximately the same ionic radius as americium (10), the $E°$ value for the reaction Am(II)-Am(III) couple must be more positive than the value of 1.55 v. accepted for the Sm(II)-Sm(III) couple. This value does not exclude the possibility of preparing a compound of americium(II). The recent preparation of TmI_2 reported in this chapter suggests that there is the possibility of preparing AmI_2 by reacting AmI_3 with americium metal.

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F. AMERICIUM(IV)

The preparation and partial characterization of the solid compound AmO_2 occurred very soon after the isolation of the element in microgram quantities (7,17). The compound of the stoichiometry approximating AmO_2 can be obtained by ignition of americium salts in air or oxygen at temperatures where reaction rates are appreciable.

Two other compounds have been prepared (1) containing Am(IV), the tetrafluoride and potassium americium(IV) fluoride.

In aqueous solution, Am(IV) is unstable with respect both to disproportionation and to reduction by water. As a consequence, no absorption spectrum of aqueous Am(IV) exists. The work of Yakovlev and Kosyakov (15) has shown that when AmO_2 is dissolved in sulfuric acid, the following reactions may be inferred:

$$2Am(IV) = Am(III) + Am(V)$$

$$Am(IV) + Am(V) = Am(VI) + Am(III)$$

with some reduction of Am(IV) by water. Penneman (12) has shown that 1*M* perchloric acid dissolves AmO_2 to give only Am(III) and Am(V), with a considerable part of the Am(IV) reduced by water. Interpretation of the Am(V) disproportionation reaction data also necessitates the assumption that Am(IV) is present as an intermediate (6,9,11,13). Tetravalent americium has been shown to exist in the black hydroxide prepared by treatment of $Am(OH)_3$ with peroxydisulfate ion (6).

The absorption spectrum of Am(IV) in the solid compound AmF_4 has been measured (4) and 10 peaks are reported in the region 3,500–10,000 A. No interpretation of these data has been made as yet.

Structural measurements using X-ray powder pattern techniques have been reported for the compounds AmO_2 (3,14), AmF_4 (1), and $KAmF_5$ (1). The dioxide has the fluorite type of structure, with a lattice constant in the range of 5.388–5.376 A. (3,14), the value of 5.376 ± 0.001 A. having been obtained from a sample prepared from extremely pure americium by ignition in an ozone-oxygen stream. The uncertainty in the lattice constant may arise from variations in the composition of the oxide due to its method of preparation. A direct measurement of the amount of oxygen uptake by Am_2O_3 to give the higher oxide indicated the composition to be $AmO_{1.98\pm0.02}$ (2). A recent measurement of the specific activity of Am^{241}, however, seems to indicate that the O/Am ratio is appreciably greater than 2 (10). The difficulty has not yet been resolved. The tetrafluoride, AmF_4, has been prepared by fluorination of both the oxide and the trifluoride; it is monoclinic, isostructural with UF_4, NpF_4, and PuF_4 (16), with $a = 12.49$ A., $b = 10.47$ A., $c = 8.20$ A., and $\beta = 126 \pm 1$ degrees (1). The compound $KAmF_5$ is rhombohedral, isostructural with $KPuF_5$ (16), with $a = 9.29$ A., $\alpha = 107°35'$ (1).

Two crystalline compounds containing americium, fluoride, and either rubidium or ammonium have been prepared (5) by treatment of Am(V) solutions with the alkali fluoride. Preliminary data based on chemical analysis, X-ray powder patterns, and absorption spectrophotometry indicate that the compounds contain Am(IV) and that the compositions approximate Rb_2AmF_6 and $(NH_4)_2AmF_6$.

The vapor pressure of AmF_4 has been investigated using the Knudsen effusion technique with a nickel chamber, and radiometric alpha analysis to determine the sublimed americium (15). The pressure is believed to be known to $\pm 6\%$ in the range 385–640°C., and the heat of sublimation derived from these data is 49.8 ± 0.3 kcal./mole. Above 640°C. the vapor pressure falls sharply, probably because of decomposition of the tetrafluoride.

An $E°$ value of -2.44 ± 0.2 v. for the Am(III)-Am(IV) couple has been estimated (8). A measurement of the heat of reaction of AmO_2 in 6*M* nitric acid gave $\Delta H = -30.4 \pm 0.4$ kcal./mole which was combined with other data and estimated values to give this $E°$ value. The assumption was made that all of the Am(IV) reacted with water to give Am(III). The recent work (12,15) discussed above on the dissolution of AmO_2 in acid throws some doubt on this value of ΔH. If some Am(V) or Am(VI) actually resulted from the dissolution of AmO_2 in 6*M* nitric acid, the estimated $E°$ value is too positive. Further experimental work should show whether any serious error is present. Certainly, all chemical evidence points to the fact that Am(IV) is a very strong oxidizing agent.

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G. CURIUM(IV)

The investigation of the chemistry of curium has been seriously hampered by lack of availability of a suitably long-lived isotope. The short-lived Cm^{242} with a half-life of 162.5 days (11), although available, emits so much gamma radiation that sample sizes below 1 μg. are necessary in X-ray work to prevent excessive film blackening. The intense alpha radiation produces rapid destruction of crystal lattices. Solution chemistry is made difficult because of rapid buildup of hydrogen peroxide in aqueous solution. The increasing availability of Cm^{244} with a half-life of 17.9 years (11) has made possible both better solution studies and the preparation and identification of a number of solid compounds.

Although attempts have been made (6,8–10) to oxidize Cm(III) in aqueous solution, none have been successful.

In the solid state, Cm(IV) has been shown to exist in the compounds CmO_2 (3) and CmF_4 (4). The black oxide prepared by oxygen or ozone treatment of Cm_2O_3 has the fluorite structure, isostructural with UO_2 (7), NpO_2, PuO_2, and AmO_2, with $a = 5.372 \pm 0.003$ A. Extrapolation of the lattice constants of the uranium, neptunium, plutonium, and americium dioxides indicates that CmO_2 should have a constant of about 5.37 A. Since in addition the white or pale tan sesquioxide, Cm_2O_3, has a constant of 5.50 ± 0.01 A. for the pseudo cube, there is little doubt that this black oxide has an O/Cm ratio near 2; the results of magnetic susceptibility measurements agree with this conclusion (12). Further evidence for the existence of Cm(IV) has been provided by the preparation and identification of the tetrafluoride, CmF_4 (4). The compound is monoclinic, isostructural with UF_4 (13), NpF_4 (13), PuF_4 (13), and AmF_4 (1), with $a = 12.45 \pm 0.06$ A., $b = 10.45 \pm 0.05$ A., $c = 8.16 \pm 0.05$ A., and $\beta =$

126° ± 30′. It may be prepared by fluorination of the trifluoride with fluorine gas at 400°C. From X-ray diffraction data, the ionic radius of Cm(IV) is calculated to be 0.88 A.

The absorption spectrum of Cm(IV) has been measured in the solid compound CmF_4 (5). Thirteen lines were found in the region 3,500–20,000 A; no interpretation of this spectrum has been made.

The $E°$ value for the Cm(III)-Cm(IV) couple has not been measured. Since Am(III) can be oxidized to Am(V) or Am(VI) in aqueous solution and curium apparently cannot be oxidized at all under such conditions, the speculation may be made that the different oxidation behavior of the two elements is due to the more negative $E°$ of the curium(III)-(IV) couple. That curium(IV) is less stable in comparable solid compounds than Am(IV) may be inferred from the fact that CmO_2 readily loses oxygen and reduces to Cm_2O_3 at 600° in vacuum, while AmO_2 does not lose oxygen appreciably at this temperature (2). Therefore, the conclusion is reached that Cm(IV) is less stable to reduction than is Am(IV). No evidence has been found for oxidation states of curium higher than Cm(IV) either in solutions or in solid compounds.

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H. BERKELIUM(IV)

Evidence for the existence of Bk(IV) was first published in 1950 (2). Tracer studies showed that berkelium(III) in aqueous solution could be oxidized by strong oxidizing agents such as Ce(IV) or BrO_3^- to an oxidation state in which the berkelium could be carried by $Zr_3(PO_4)_4$ or $Ce(IO_3)_4$. This oxidation state of Bk is certainly (IV). From experiments in which the redox potential of the solution was adjusted by varying the ratio of Ce(IV) to Ce(III) it was concluded that the potential of the Bk(III)-Bk(IV) couple in nitric acid does not differ from that of the corresponding Ce(III)-Ce(IV) couple of −1.61 v. (1) by more than 60 mv.

Limitations on the availability of berkelium have thus far precluded a more extensive investigation of the oxidation states of this element, but it is to be anticipated from the magnitude of the aqueous potential of the Bk(III)-Bk(IV) couple that both BkO_2 and BkF_4 will be stable compounds.

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I. CALIFORNIUM(IV) AND CALIFORNIUM(V)

Attempts to oxidize trace amounts of californium with bismuthate or peroxydisulfate in acidic aqueous solution to a state higher than (III) have been unsuccessful (1–3). From trends in the values of the (III)-(IV) oxidation potentials of the actinide elements, it appears that the (III)-(IV) potential of californium is too negative to permit significant oxidation to the (IV) state in aqueous solution. On the other hand, oxidation to the (V) state may be possible. Failure to oxidize trace concentrations may be due to kinetic rather than thermodynamic factors. Conclusions concerning the stability of Cf(V) in aqueous solutions cannot safely be drawn until the oxidation behavior of macro concentrations of Cf(III) has been investigated.

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J. EINSTEINIUM HIGHER STATES

The oxidation behavior of einsteinium(III) has been investigated only at trace concentrations in acidic aqueous solution. No evidence exists for oxidation states higher than (III), even in the presence of strong oxidizing agents such as peroxydisulfate or bismuthate (1,2).

Einsteinium(VI) would have the specially stable $5f^7$ configuration and may possibly exhibit some stability in solution.

The question of an oxidation state higher than (III) cannot be decided until macro concentrations of einsteinium are available for study.

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K. FERMIUM HIGHER STATES

To date, only trace amounts of fermium have been available for study. No evidence exists for an oxidation state higher than (III), although attempts have been made to oxidize the tripositive aqueous ion with powerful oxidizing agents (1,2).

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L. MENDELEVIUM HIGHER OR LOWER STATES

Mendelevium, actinide homolog of thulium in the lanthanide series, may possibly possess a dipositive oxidation state of some stability in aqueous solution, but no evidence now exists for such a lower state (1,2).

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Metal Alkoxides

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I. Introduction

Although metal alkoxides have been known for many years and used in a number of organic reactions, it is surprising how little systematic work has been carried out on these compounds. The metal alkoxide $M(OR)_x$, where M is a metal of valency x and R is an alkyl group, may be considered as derived from the progenitive alcohol ROH by replacement of the hydroxylic hydrogen by the metal. Accordingly, the chemistry of the metal alkoxides involves the study

of the metal-oxygen-carbon bond system and is thus an intriguing borderline field. For example, the inorganic chemist is primarily interested in the way in which the valency, coordination number, and stereochemistry of the metal determine the properties of the alkoxide, while the organic chemist is more concerned with the catalytic behavior of metal alkoxides in certain organic reactions. The important steric and electronic effects on the alkyl groups on the properties of the alkoxides provide an interest for the physical chemist, from the viewpoint of the effect of molecular structure of intermolecular forces. During the past ten years there has been a noticeable increase in the industrial applications of metal alkoxides, and these developments have emphasized the inadequacy of our present fundamental knowledge of these compounds. Consequently, this review will be notable more for the questions which are raised in it than for the number which are answered.

II. Preparation of Metal Alkoxides

As would be expected, the methods of preparing metal alkoxides are mainly determined by the properties of the metal or its oxide, hydroxide, or halide. Thus the electropositive metals react spontaneously with alcohols forming metal alkoxide and hydrogen, while the alkoxides of metals with valencies of four or higher are usually obtained from reactions involving the chloride.

A. ACTION OF METALS ON ALCOHOLS

The following is the simplest method of preparing metal alkoxides:

$$M + xROH \longrightarrow M(OR)_x + x/2H_2 \qquad (1)$$

However, this method appears to be confined to the more electropositive metals such as the alkali metals, beryllium, magnesium, and aluminum. The nature of the alcohol is also an important factor in these reactions. For example, while sodium reacts vigorously with methanol and ethanol, its rate of reaction with isopropanol is considerably slower, and with tertiary butanol the reaction is extremely slow. The mechanisms of these reactions have not been elucidated, but the rate of reaction appears to depend on the acidity of the hydroxylic hydrogen atom. Beryllium (46), magnesium, and aluminum require catalysts to cause them to react with alcohols, and this is believed to be due to the need to disperse the insoluble oxide film which renders

the metal inactive. Perhaps the most interesting example of the formation of a metal alkoxide from the metal and alcohol involves thallium. Thus it was found by Lamy (1) that thallium suspended in boiling ethanol was unreactive, yet the same metal held in the air above the surface of the alcohol was readily converted to thallous ethoxide. It appears that oxidation to the metal oxide is a prerequisite to the formation of thallous ethoxide as follows:

$$2Tl + {}^1/_2O_2 \longrightarrow Tl_2O \tag{2}$$

$$Tl_2O + EtOH \longrightarrow TlOEt + TlOH \tag{3}$$

$$TlOH + EtOH \rightleftharpoons TlOEt + H_2O \tag{4}$$

It was pointed out by Menzies (2) that the conversion of the thallous hydroxide to the ethoxide was practically complete because the latter is immiscible with ethanol and separates out, thus disturbing the equilibrium of equation 4.

B. ACTION OF METAL HYDROXIDES ON ALCOHOLS

The alkali metal alkoxides may also be prepared by dissolving the metal hydroxide in the alcohol:

$$NaOH + EtOH \rightleftharpoons NaOEt + H_2O \tag{5}$$

For example, sodium ethoxide solution may be produced from sodium hydroxide and ethanol by removing the equilibrium water of equation 5 by azeotropic distillation with benzene. Since sodium ethoxide ionizes in dilute ethanolic solution (3) and sodium hydroxide is ionic, it is more realistic to replace equation 5 by the ionic equilibrium:

$$OH^- + EtOH \rightleftharpoons H_2O + EtO^- \tag{6}$$

Our knowledge of this important equilibrium has been extended by the valuable quantitative work of Caldin and Long (4) who showed by a spectrophotometric method that in ethanolic solutions containing small percentages of water, the equilibrium strongly favors the formation of the ethoxide ion.

In a decimolar solution of sodium "hydroxide" in 99% ethanol they found that 96% of the base was present as ethoxide ions. The reversibility of equation 6 imposes limitations on the ultimate drying of ethanol by metallic sodium. On the other hand, the iodine-catalyzed reaction of magnesium with ethanol was found by Lund and Bjerrum (5) to provide an excellent means of drying alcohol initially containing less than 1% of water.

$$Mg + 2EtOH \xrightarrow{I_2} Mg(OEt)_2 + H_2 \quad (7)$$

$$Mg(OEt)_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2EtOH \quad (8)$$

Evidently the effectiveness of this method depends on the very low solubility of magnesium hydroxide and the consequent absence of hydroxyl ions.

There are few other examples of the formation of alkoxides by interaction of metal hydroxides and alcohol, but Prandtl and Hess (6) showed that freshly precipitated hydrated vanadium pentoxide would slowly form the vanadyl alkoxide, $VO(OR)_3$, in boiling alcoholic solution.

C. METHODS INVOLVING USE OF METAL CHLORIDES

For the polyvalent metals the foregoing methods are inapplicable and the alkoxides are usually obtained via the anhydrous metal chlorides. In general, metal chlorides undergo solvation and/or partial solvolysis with the lower straight chain aliphatic alcohols, but in no case is replacement of the chloride complete. Formation of the metal alkoxide is then achieved by the addition of a base. An early example of this method was the attempt by Demarçay (7) to prepare titanium tetraethoxide by the reaction involving titanium tetrachloride and ethanolic sodium ethoxide. Unfortunately his product was impure because of hydrolysis, and it remained for Bischoff and Adkins (8) to achieve the preparation of pure titanium tetraethoxide by this method.

$$TiCl_4 + 4NaOEt \longrightarrow Ti(OEt)_4 + 4NaCl\downarrow \quad (9)$$

By allowing the titanium tetrachloride to react with the ethanol first it was possible to economize on the sodium ethoxide by taking advantage of the volatility of hydrogen chloride:

$$TiCl_4 + 3EtOH \longrightarrow TiCl_2(OEt)_2 \cdot EtOH + 2HCl\uparrow \quad (10)$$

The generality of equation 10 for lower aliphatic alcohols was first established by Jennings *et al.* (9), who also corrected the erroneous deduction by Demarçay (7) that $TiCl(OEt)_3 \cdot HCl$ was produced in this reaction. The formation of a metal alkoxide is not always realized by the method illustrated for titanium ethoxide in equation 9. For example, Meerwein and Bersin (10) could not obtain zirconium tetraalkoxides directly from reactions involving zirconium tetrachloride and alcoholic sodium alkoxides. Instead, they isolated

double alkoxides of sodium and zirconium due to the fact that zirconium tetramethoxide and tetraethoxide are strong Lewis acids and immediately combine with sodium alkoxides. However, Nelles (11) later found that in the preparation of titanium alkoxides the sodium alkoxide could be replaced by anhydrous ammonia.

$$TiCl_4 + 4ROH + 4NH_3 \longrightarrow Ti(OR)_4 + 4NH_4Cl\downarrow \quad (11)$$

Applying the same method to zirconium tetrachloride, Bradley and Wardlaw (12) succeeded in preparing zirconium tetraalkoxides directly. These authors and their co-workers have since shown that the same method is suitable for the preparation of the alkoxides of hafnium (13), cerium (14), niobium (15), tantalum (16), iron (17), uranium (18), and plutonium (19). For cerium (IV) and plutonium (IV), which do not form stable tetrachlorides, the double chlorides $(C_5H_6N)_2MCl_6$, where C_5H_6N is pyridinium, were used instead.

$$(C_5H_6N)_2MCl_6 + 6NH_3 + 4ROH \longrightarrow M(OR)_4 + 6NH_4Cl + 2C_5H_5N \quad (12)$$

An interesting variant of the "ammonia" method is due to Herman (20) who allowed titanium tetrachloride, alcohol, and ammonia to react in the presence of an amide or nitrile. In this method the titanium tetraalkoxide separates out as the upper layer, while the ammonium chloride dissolves in the amide or nitrile in the lower layer, and the need for filtration is eliminated.

The ammonia method is not always applicable. For example, Bradley *et al.* (21) were unable to prepare a pure stannic alkoxide directly from the reaction involving stannic chloride, alcohol, and ammonia; the product contained tin, alkoxide, chloride and amide (or ammonia). Moreover, attempts to prepare thorium alkoxides by a similar method were also unsuccessful because the replacement of chloride was incomplete (22). However, the same authors succeeded in preparing thorium tetraisopropoxide by the sodium alkoxide method and observed that the thorium alkoxide gave an alkaline reaction in alcoholic solution. Hence the thorium alkoxide is a stronger base than ammonia in alcoholic solution, and the following equilibrium favors the thorium ion:

$$Th(OR)_4 + NH_4^+ \rightleftharpoons Th(OR)_3\cdot(solv.)^+ + NH_3 + ROH \quad (13)$$

This equilibrium, coupled with the significant solubility of ammonium chloride in ammoniacal alcohol, prevents the complete precipitation of chloride from $ThCl(OR)_3$. In the presence of the sodium alkoxide

the removal of chloride from the thorium is achieved because of the very low solubility of sodium chloride in alcoholic solution.

One other important feature of alkoxide preparations involving metal chlorides demands attention, and that is the effect of the nature of the alkyl group. Whereas the lower straight chain aliphatic alcohols (e.g., methanol and ethanol) undergo a relatively straightforward reaction with the metal chloride and base, this is not the case when alcohols containing strongly electron-releasing alkyl groups are employed. Instead the yield of metal alkoxide is very low, and it is clear that side reactions have assumed a dominant role. There is no doubt that in the case of tertiary alcohols this is partly due to side reactions involving the hydrogen chloride produced in the initial between metal chloride and alcohol, viz.:

$$MCl_x + y\text{ROH} \longrightarrow MCl_{x-y}(OR)_y + y\text{HCl} \quad (14)$$

$$\text{HCl} + \text{ROH} \longrightarrow \text{RCl} + H_2O \quad (15)$$

$$\text{HCl} + \text{ROH} \longrightarrow \text{Olefin} + \text{HCl} + H_2O \quad (16)$$

It is noteworthy that in either the esterification (eq. 15) or the elimination reaction (eq. 16) water is produced, and this causes hydrolysis and a consequent reduction in yield of the metal alkoxide.

In the cases of titanium and zirconium methods have been devised to obviate these side reactions. Cullinane *et al.* (23) obtained a high yield of titanium tetra-*tert*-butoxide by allowing the titanium tetrachloride and *tert*-butanol to react in the presence of sufficient pyridine to combine with the hydrogen chloride formed in reaction 14. In this case the concentration of hydrogen chloride was always kept low and reactions 15 and 16 were thus minimized. An alternative approach was adopted by Bradley *et al.* (24) in the preparation of zirconium alkoxides. They used dipyridinium hexachlorozirconate, $(C_5H_6N)_2ZrCl_6$, which is inert to alcohols, in place of the highly reactive zirconium tetrachloride and thus eliminated the possibility of forming hydrogen chloride (cf. eq. 14). In the presence of ammonia the complex chloride reacts with certain alcohols to form the alkoxide as shown in equation 12. However, it was still not possible to prepare zirconium tetra-*tert*-butoxide directly even by this method. Although the hydrolytic side reactions were eliminated by using the complex chloride, the reaction with *tert*-butanol and ammonia in pyridine did not displace all of the chlorine, and the product was

zirconium monochloride tri-*tert*-butoxide with addended pyridine, viz.:

$$(C_5H_6N)_2ZrCl_6 + 3Bu^tOH + 5NH_3 \longrightarrow ZrCl(OBu^t)_3 \cdot 2C_5H_5N + 5NH_4Cl \quad (17)$$

The complex chloride of cerium(IV) behaved similarly and gave $CeCl(OBu^t)_3 \cdot C_5H_5N$ (25). It is tempting to explain this behavior in terms of steric effects which prevent the displacement of all of the chloride by *tert*-butoxide groups. This would be consistent with the fact that the monochloride was found to react with ethanol and ammonia, with the formation of the mixed alkoxide $Zr(OEt)(OBu^t)_3$. On the other hand, from purely stereochemical arguments it would then be expected that less substitution of chloride by *tert*-butoxide would occur in the case of titanium, and this is contrary to the facts. Recent work by Bradley *et al.* (26) showed that the complex chlorides of zirconium or cerium(IV) were converted to the tetraalkoxides when combined with "chlorbutol" (1-methyl-1-trichloromethyl-ethanol) in the presence of ammonia. Since the steric effect of "chlorbutol" is much greater than that of *tert*-butanol, it is clear that the failure of reaction 17 to proceed beyond the zirconium monochloride stage cannot be due to a simple steric effect.

Before leaving the question of the preparation of alkoxide from metal chlorides mention must be made of the preparation of uranium(IV) tetramethoxide by Gilman *et al.* (27). These authors overcame the problem of the insoluble nonvolatile nature of the product by using lithium methoxide as the base.

$$UCl_4 + 4LiOMe \longrightarrow U(OMe)_4\downarrow + LiCl \quad (18)$$

Lithium chloride is soluble in methanol and was thus extracted away from uranium methoxide. Bradley and co-workers have demonstrated the scope of this method by similarly preparing uranyl methoxide (28) and lanthanum trimethoxide (29), both of which are insoluble.

D. MISCELLANEOUS METHODS

Gilman and co-workers developed some novel methods in the preparation of uranium alkoxides. For example, they utilized the readiness with which uranium tetraethoxide is oxidized to prepare uranium pentaethoxide (30,31). They found that with molecular

oxygen as the oxidant the yield of pentaethoxide was 80% based on equation 19.

$$5U(OEt)_4 + O_2 \longrightarrow 4U(OEt)_5 + UO_2 \quad (19)$$

However, they did not verify the formation of uranium dioxide, and inspection of their results reveals that the conversion of tetraethoxide to pentaethoxide is also 80% according to equation 20, which involves the formation of the more stable U_3O_8.

$$15U(OEt)_4 + 4O_2 \longrightarrow 12U(OEt)_5 + U_3O_8 \quad (20)$$

The same authors found that the highest conversion (90–95%) was obtained using bromine as oxidant followed by treatment of the uranium(V) monobromide tetraethoxide with sodium ethoxide, viz.:

$$U(OEt)_4 + {}^1/_2Br_2 \longrightarrow UBr(OEt)_4 \quad (21)$$

$$UBr(OEt)_4 + NaOEt \longrightarrow U(OEt)_5 + NaBr \quad (22)$$

Further investigations showed that the oxidation of uranium (V) ethoxide to uranium(VI) ethoxide was more difficult to achieve, and the best results were obtained by the following sequence of reactions (31):

$$U(OEt)_5 + NaOEt \longrightarrow NaU(OEt)_6 \quad (23)$$

$$2NaU(OEt)_6 + (C_6H_5CO)_2O_2 \longrightarrow 2U(OEt)_6 + 2C_6H_5CO_2Na \quad (24)$$

Yields of the order of 40–60% were obtained with benzoyl peroxide as the oxidant, whereas with lead tetraacetate only about 20% conversion was effected. A number of other oxidants were also tried, but they were much less effective.

In attempting to prepare uranyl alkoxides by the alcoholysis of uranyl methoxide, $UO_2(OMe)_2{\cdot}MeOH$, Bradley *et al.* (28,32) discovered a novel method of obtaining certain uranium(VI) hexaalkoxides. The reactions with isopropanol, *sec*-butanol, or *tert*-butanol were characterized by a remarkable disproportionation into an insoluble substance more "hydrolyzed" than $UO_2(OR)_2$ and a soluble substance less "hydrolyzed" than $UO_2(OR)_2$ which underwent further disproportionation when heated. For example, with isopropanol the compositions of the products were nearly in accordance with the requirements of the following equations:

$$3UO_2(OPr^i)_2{\cdot}Pr^iOH \longrightarrow U_2O_5(OPr^i)_2{\cdot}2Pr^iOH\downarrow + UO(OPr^i)_4{\cdot}Pr^iOH \quad (25)$$

$$5UO(OPr^i)_4{\cdot}Pr^iOH \longrightarrow 3U(OPr^i)_6\uparrow + U_2O_5(OPr^i)_2{\cdot}2Pr^iOH + 3Pr^iOH\uparrow \quad (26)$$

The disproportionation of the uranyl group under mild conditions in nonaqueous media is quite without precedent and merits further examination.

In their investigations on quadrivalent uranium, Gilman *et al.* (33) showed that tetrakis(diethylamido)uranium(IV) could be converted to the alkoxides by treatment with the appropriate alcohol.

$$U(NEt_2)_4 + 4ROH \longrightarrow U(OR)_4 + 4Et_2NH \quad (27)$$

Since the diethylamido derivative is prepared from the metal chloride, then, indirectly, the alkoxide preparation is from the metal chloride too. However, this indirect method appears to offer advantages over the direct methods described in Section II-C. This has already proved to be the base in connection with vanadium. Earlier work by Bradley *et al.* (34) showed that the reactions involving vanadium tetrachloride and certain alcohols gave rise to vanadium dichloride dialkoxide alcoholates, $VCl_2(OR)_2 \cdot ROH$, but attempts to convert these to $V(OR)_4$ were unsuccessful. However, Thomas (35) has recently shown that the vanadium tetraalkoxides may be obtained as follows:

$$VCl_4 + 4LiNMe_2 \longrightarrow V(NMe_2)_4 + 4LiCl \quad (28)$$

$$V(NMe_2)_4 + 4ROH \longrightarrow V(OR)_4 + 4Me_2NH \quad (29)$$

A characteristic property of metal alkoxides is their ability to exchange alkoxide groups with alcohols, and this has been extensively utilized as a means of preparing new alkoxides of aluminium, germanium, tin(IV), titanium, zirconium, hafnium, niobium, tantalum, iron(III), lanthanum, thorium, uranium, and plutonium.

$$M(OR)_x + xR'OH \rightleftharpoons M(OR')_x + xROH \quad (30)$$

If the alcohol R'OH has a higher boiling point than ROH, then the equilibrium in equation 30 is easily disturbed by removing ROH by fractional distillation. When necessary, the reaction may be effected with just the theoretical quantity of the alcohol R'OH using benzene or some other inert compound as the solvent. In fact, the use of benzene as solvent has other advantages besides economy in the use of the alcohol. One advantage lies in the ease of drying of the mixture of R'OH and benzene by azeotropic distillation compared with the drying of a large quantity of the alcohol. In addition, there are cases where a more favorable separation factor exists between the binary azeotropes of the alcohols with benzene than between the

alcohols alone (e.g., Pr^iOH and Bu^tOH). One of the limitations of the alcohol-interchange method is manifested in some reactions involving branched chain alcohols where there may be steric factors which oppose the complete replacement of OR groups by OR′. This gives rise to mixed alkoxides, $M(OR)_{x-y}(OR')_y$, which are considered more fully in Section II-E. The importance of the alcohol-interchange method was demonstrated in the work on zirconium alkoxides. These compounds cannot be obtained in a high state of purity by the direct reactions involving the tetrachloride. Nevertheless, it was found that the impure zirconium isopropoxide could be readily purified by crystallization of the alcoholate, $Zr(OPr^i)_4 \cdot Pr^iOH$, from isopropanol. The solvate was then used as a pure starting material for preparing other alkoxides by alcohol interchange.

Another valuable method for converting one alkoxide to another is the transesterification employed by Mehrotra (36):

$$M(OR)_x + xCH_3CO_2R' \rightleftharpoons M(OR')_x + xCH_3CO_2R \qquad (31)$$

In certain cases the separation of the alkyl acetates (e.g., isopropyl and *tert*-butyl) is more readily achieved than the separation of the alcohols. Moreover, this method appears to be less prone to steric limitations than the alcohol-interchange in the cases of aluminium, zirconium, or hafnium alkoxides.

Meerwein and co-workers (37,38) showed that a number of metal alkoxides were catalysts in the Meerwein-Ponndorf-Verley redox system, and this property is discussed later (Section III). The Meerwein-Ponndorf-Verley reaction clearly has potentialities as an alternative method for the preparation of metal alkoxides. Recent work (26) has fulfilled these expectations by showing that the tetrakis-(2,2,2-trichloroethoxy) derivatives of titanium and zirconium may be prepared by the action of chloral on the metal isopropoxide.

$$Ti(OPr^i)_4 + 4CCl_3CHO \longrightarrow Ti(OCH_2CCl_3)_4 + 4Me_2CO \qquad (32)$$

In the case of zirconium it was interesting to find that a stable co-ordination compound with two molecules of acetone was produced.

$$Zr(OPr^i)_4 + 4CCl_3CHO \longrightarrow Zr(OCH_2CCl_3)_4 \cdot 2Me_2CO + 2Me_2CO \qquad (33)$$

This method may well be important for the preparation of alkoxides containing substituents in the alkyl group and where the appropriate alcohol is not available.

E. PREPARATION OF MIXED ALKOXIDES

In attempting to prepare zirconium tetra-*tert*-butoxide by alcohol interchange involving, the tetramethoxide, a crystalline compound approximating in formula to $Zr(OMe)(OBu^t)_3$, was obtained after the apparent completion of the reaction in the presence of excess *tert*-butanol (112). The mixed alkoxide disproportionated when heated under reduced pressure essentially in accordance with the requirements of the following equation:

$$3Zr(OMe)(OBu^t)_3 \longrightarrow 2Zr(OBu^t)_4\uparrow + Zr(OMe)_3(OBu^t) \qquad (34)$$

Likewise the product from the interchange of zirconium tetraethoxide and *tert*-butanol was also a mixed alkoxide which was disproportionated by heating under low pressure. However, the disproportionation was not as extensive as for the zirconium methoxide tri-*tert*-butoxide and, after the removal of the volatile tetra-*tert*-butoxide, a mixed alkoxide approximating to $Zr(OEt)_2(OBu^t)_2$ distilled over (b.p. 190°/1.5 mm.). The latter was the first recorded example of a metal mixed alkoxide which could be distilled unchanged. This work was extended by Mehrotra (39) who prepared $Zr(OMe)(OAm^t)_3$ from the reaction involving zirconium tetramethoxide and tertiary amyl alcohol and showed that the mixed alkoxide was dimeric. Disproportionation of this compound followed the same pattern as in equation 34. In addition, some zirconium methoxide *tert*-butoxide and ethoxide *tert*-butoxides were prepared by the exothermic reactions of either methanol or ethanol with zirconium tetra-*tert*-butoxide.

$$Zr(OBu^t)_4 + ROH \longrightarrow Zr(OR)(OBu^t)_3 + Bu^tOH \qquad (35)$$

$$Zr(OBu^t)_4 + 2ROH \longrightarrow Zr(OR)_2(OBu^t)_2 + 2Bu^tOH \qquad (36)$$

Another interesting discovery was that the mixed alkoxide $Zr(OMe)(OBu^t)_3$ may be formed by a reproportionation reaction:

$$Zr(OMe)_2(OBu^t)_2 + Zr(OBu^t)_4 \longrightarrow 2Zr(OMe)(OBu^t)_3 \qquad (37)$$

Mehrotra (36,40,80) also showed that mixed alkoxides of aluminum may be obtained by alcohol interchange involving aluminum isopropoxide and either *tert*-butanol or *tert*-amyl alcohol.

$$Al(OPr^i)_3 + 2\ tert\text{-}ROH \longrightarrow Al(OPr^i)(OR\text{-}tert)_2 + 2Pr^iOH \qquad (38)$$

It appears that replacement of the isopropoxide in $Al(OPr^i)$-$(OR\text{-}tert)_2$ by a tertiary alcohol is very slow, although recent work by Bains (41) has proved that both the tri-*tert*-butoxide and tri-*tert*-

amyloxide may be obtained by alcohol interchange. In 1954, Nesmeyanov and Nogina (42) reported the preparation of mixed alkoxides of titanium by the following method:

$$TiCl(OR)_3 + R'OH + R''_3N \longrightarrow Ti(OR')(OR)_3 + R''_3N \cdot HCl \quad (39)$$

Later some interesting results were published by Ghosh *et al.* (43) who claimed to have isolated mixed alkoxides of titanium containing up to three different alkoxide groups using the following routes:

$$TiCl_2(OR)_2, R'OH + C_5H_5N \longrightarrow TiCl(OR')(OR)_2 + C_5H_5N \cdot HCl \quad (40)$$

$$TiCl(OR')(OR)_2 + NaOR'' \longrightarrow Ti(OR'')(OR')(OR)_2 + NaCl \quad (41)$$

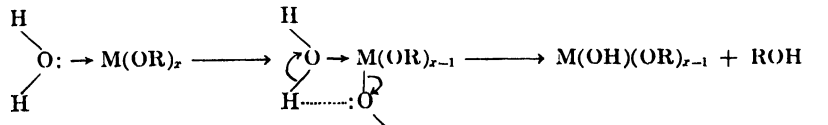
These mixed alkoxides were distilled under reduced pressure, e.g., $Ti(OMe)(OPr^i)(OBu)_2$, b.p. 160°/2.5 mm. Recent work by Bradley *et al.* (44) has also revealed that mixed alkoxides of tantalum may be obtained by the action of secondary or tertiary alcohols on penta-primary-alkoxides of tantalum. These compounds have the formula $Ta(OR)(OR')_4$, where R = primary and R′ = *sec-* or *tert*-alkyl, and volatilize unchanged *in vacuo*. When niobium ethoxide was treated with isopropanol, a mixed ethoxide isopropoxide was similarly obtained; but when tertiary alcohols were employed, the products were niobium oxide *tert*-alkoxides. There is little doubt that more work on the preparation of mixed alkoxides would be justified especially where the method of alcohol interchange is concerned. Thus, in addition to the conflicting results obtained by Mehrotra and Bains with aluminium alkoxides, Holloway (45) in our laboratories was unable to repeat our earlier work (44) on niobium and tantalum alkoxides. He found, for example, that *sec*-butanol readily replaced all of the methoxide from niobium pentamethoxide.

III. Chemical Properties of Metal Alkoxides

A. HYDROLYSIS

All metal alkoxides so far investigated have been characterized by the ease with which they are hydrolyzed. In many cases the alkoxides are so sensitive even to traces of water that very special precautions have to be adopted in order to study their properties. When an excess of water is present, the ultimate product is the metal hydroxide or more commonly the hydrated metal oxide. Recent work has shown that under carefully controlled conditions intermedi-

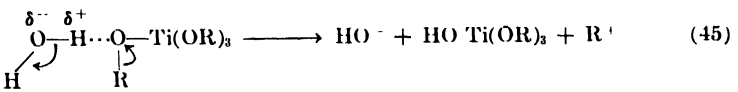
ate products called metal oxide alkoxides, $MO_x(OR)_y$, may be isolated, and these compounds, which are polymeric, are extremely interesting from the structural point of view (see Section IV). Nevertheless, the fact remains that little is known concerning the mechanism of the hydrolysis of metal alkoxides. It seems reasonable to suppose that the initial step involves the coordination of a water molecule through its oxygen to the metal in a facile nucleophilic



$$M(OH)(OR)_{x-1} + M(OR)_x \longrightarrow (RO)_{x-1}MOM(OR)_{x-1} + ROH \quad (43)$$

$$2M(OH)(OR)_{x-1} \longrightarrow (RO)_{x-1}MOM(OR)_{x-1} + H_2O \quad (44)$$

process. One of the protons on the water molecule interacts with the oxygen of an alkoxide group through hydrogen bonding and, following an electronic rearrangement, a molecule of alcohol is expelled (eq. 42). The hydroxy-metal alkoxide formed in equation 42 may react further to form the oxide alkoxide by either of reactions 43 or 44. Bearing in mind that most metal alkoxides containing lower aliphatic alkyl groups are actually coordination polymers, it is clear that the above schemes are probably a gross oversimplification. Apart from product analysis the only experimental evidence in support of the above mechanism is the work of D'Adamo and Kienle (47). These authors showed that the hydrolysis of titanium tetraneopentyloxide afforded neopentyl alcohol, thus eliminating the possibility that a carbonium ion was formed, i.e.:



The neopentyl carbonium ion rearranges rapidly, and tertiary amyl alcohol would be formed as a consequence of the mechanism illustrated in equation 45. Hence it is clear that in the hydrolysis of titanium neopentyloxide metal-oxygen bond fission occurs, and this is consistent with equation 42. A number of investigators have studied the hydrolysis of titanium alkoxides in recent years (48–55), and there is an

accumulation of evidence which suggests that as the extent of hydrolysis increases the ease of hydrolysis of the remaining alkoxide groups decreases. In particular, the butoxide group in $(\equiv TiO)_3TiOBu$ appears to be significantly stable (49,54,55,130), and it is possible that the following equilibrium occurs:

$$(\equiv TiO)_3TiOBu + H_2O \rightleftharpoons (\equiv TiO)_3TiOH + BuOH \qquad (46)$$

It seems to be established that in general the ease of hydrolysis of metal alkoxides decreases as the chain length of the *n*-alkyl groups is increased. Also, the more water-repellent the alcohol, the less readily does its alkoxide hydrolyze. The most remarkable case of resistance to hydrolysis by an alkoxide yet found concerns uranium(VI) hexa-*tert*-butoxide (32). This compound appeared unaffected by contact with water, and its solution in benzene survived vigorous shaking with water. However, in homogeneous aqueous solution (acetone) the compound was slowly hydrolyzed. It is probable that this compound owes its stability to the powerful steric effect of the six *tert*-butoxide groups around the uranium, which should thus be protected from nucleophilic attack by water molecules.

B. ALCOHOL INTERCHANGE (ALCOHOLYSIS)

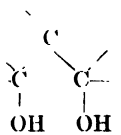
Although alcohol-interchange has been much used as a preparative method, the mechanism of the reaction is unknown. It is probably analogous to the first stage of the hydrolysis reaction, viz.:

$$R'OH + M(OR)_x \longrightarrow \begin{matrix} & R' & \\ & \diagdown & \\ & O: & \\ & \diagup\ \diagdown & \\ H & \cdots\cdots : O & R \end{matrix} \rightarrow M(OR)_{x-1} \longrightarrow$$

$$(R'O)M(OR)_{x-1} + ROH \qquad (47)$$

There is no doubt that alcoholysis must involve metal-oxygen bond fission as in equation 47 because carbon-oxygen fission in the MOR system would give rise to a hydrolysis product, an ether, and sometimes (e.g., tertiary alkoxides) some olefin. In fact, the reaction is characterized by its speed, reversibility, and absence of side reactions. Moreover, the neopentyl oxides of a large number of metals have been prepared quantitatively by this method. With the lower straight chain alcohols the interchange is so rapid that a special technique for fast reactions will be needed to study the kinetics. However, as stated in Section II-D there are some examples involving

highly branched alcohols where the final stages of alcohol interchange are quite slow and mixed alkoxides may be isolated. Some preliminary work by Bains (41) has shown that the interchange of aluminium isopropoxide with *tert*-butanol is relatively slow in benzene at 28°C. Experiments with C^{14}-labeled aluminum isopropoxide and unlabeled isopropanol in benzene at 20°C. show that exchange is fast but should be amenable to kinetic study. This work is still in progress. Little work has been published on metal alkoxides derived from polyhydric alcohols. Mehrotra (56) investigated the reactions of ω,ω'-polymethylene glycols, $HO(CH_2)_nOH$ (n = 2–10), with titanium and zirconium alkoxides. The products were always diglycollates, $M[O_2(CH_2)_n]_2$, whose insoluble and nonvolatile nature suggests that they were polymers. Reeves and Mazzeno (61) studied the interaction of some glycols with titanium tetra-*tert*-butoxide by means of cryoscopy in *tert*-butanol. They concluded that simple monomeric compounds were not formed, but instead species with two or three titanium atoms per molecule were suggested, e.g., $Ti_3(OBu^t)_2(glycollate)_6$. Some diols such as hexylene glycol (2-methylpentane-2,4-diol) and octylene glycol (2-ethylhexane-1,3-diol) form soluble compounds which are relatively stable toward hydrolysis (57). It is noteworthy that both of these diols have the hydroxyl groups on carbon atoms which are in turn separated by one carbon atom



and it seems likely that the other alkyl groups in these diols help to force the molecules into conformations which are favorable for chelation.

C. REACTIONS WITH OTHER HYDROXYLIC COMPOUNDS

Water and alcohols are just two examples of hydroxylic compounds which react with metal alkoxides, and it appears that the alkoxides react with any molecule containing a hydroxyl group. For example, carboxylic acids combine with alkoxides to produce metal soaps. Mehrotra and co-workers (58–60) have shown, however, that some of these reactions are more complex than might have been expected.

The work with aluminum isopropoxide (58) was of special significance because it established beyond doubt the existence of aluminum tri-soaps.

$$Al(OPr^i)_3 + 3RCO_2H \longrightarrow Al(O_2CR)_3 + 3Pr^iOH \quad (48)$$

The reaction depicted in equation 48 was used to prepare the tripalmitate and the tristearate. Nevertheless, in attempting to prepare titanium tetra-soaps by an analogous method, Pande and Mehrotra (59) discovered that the fourth alkoxide group per titanium atom was resistant to replacement even in the presence of excess acid, i.e.:

$$Ti(OR)_4 + 3RCO_2H \longrightarrow Ti(OR)(O_2CR)_3 + 3ROH \quad (49)$$

The results were the same using either titanium tetraethoxide or tetraisopropoxide with acetic, propionic, *n*-butyric, *n*-valeric, lauric, myristic, palmitic, and stearic acids. Moreover, in attempting to prepare tetra-soaps of zirconium by employing the reaction between zirconium isopropoxide and stearic, palmitic, lauric, or caproic acid, Kapoor and Mehrotra (60) obtained the zirconium oxide carboxylates, $Zr_2O(O_2CR)_6$, which could be recrystallized unchanged from dioxane. Detailed investigation of the stepwise replacement of isopropoxide groups by palmitic or stearic acids revealed that the first two are replaced rapidly and quantitatively, and the triisopropoxy monocarboxylates and diisopropoxy dicarboxylates were isolated according to equations 50 and 51.

$$Zr(OPr^i)_4 \cdot Pr^iOH + RCO_2H \longrightarrow Zr(OPr^i)_3(O_2CR) + 2Pr^iOH \quad (50)$$

$$Zr(OPr^i)_4 \cdot Pr^iOH + 2RCO_2H \longrightarrow Zr(OPr^i)_2(O_2CR)_2 + 3Pr^iOH \quad (51)$$

Addition of the third molecule of carboxylic acid also displaced isopropanol practically quantitatively.

$$Zr(OPr^i)_4 \cdot Pr^iOH + 3RCO_2H \longrightarrow Zr(OPr^i)(O_2CR)_3 + 4Pr^iOH \quad (52)$$

However, special precautions were required to obtain the zirconium monoisopropoxide tricarboxylate in a pure state because at temperatures above 30°C. it underwent the following reaction:

$$Zr(OPr^i)(O_2CR)_3 \longrightarrow ZrO(O_2CR)_2 + RCO_2Pr^i \quad (53)$$

Moreover, the isopropyl ester of the organic acid was also isolated from the reaction involving the zirconium monoisopropoxide tricarboxylate and zirconium tetracarboxylate.

$$Zr(OPr^i)(O_2CR)_3 + Zr(O_2CR)_4 \longrightarrow Zr_2O(O_2CR)_6 + RCO_2Pr^i \quad (54)$$

The failure to obtain the zirconium tetra-soaps from the original reaction of the zirconium isopropoxide with excess carboxylic acid can thus be traced to the side reactions shown in equations 53 and 54. This view was further substantiated by the preparation of the tetra-soaps by means of direct reaction of the carboxylic acids with zirconium tetrachloride.

$$ZrCl_4 + 4RCO_2H \longrightarrow Zr(O_2CR)_4 + 4HCl \qquad (55)$$

The side reactions discussed above are extremely interesting and obviously merit further investigation.

Certain molecules will enolize, and it is found that the enol form will interact with metal alkoxides. The β-diketones or keto esters are especially interesting because their enols give rise to chelate derivatives. We found an interesting contrast in the behavior of titanium (62) and zirconium (63) alkoxides with acetylacetone. In the case of titanium a rapid disubstitution occurs, but further replacement of alkoxide appears to be resisted.

$$Ti(OR)_4 + 2\ acacH \longrightarrow Ti(acac)_2(OR)_2 + 2ROH \qquad (56)$$

This is consistent with the formation of a 6-coordinated titanium complex wherein the titanium has reached its coordination maximum. Schmidt (64) has also studied the action of acetylacetone or ethyl acetoacetate on titanium alkoxides and claims that two types of compound are formed, $Ti(OR)_4acacH$ (I) and $Ti(OR)_2(acac)_2$ (II), both involving 6-coordinated titanium. However, more recently Yamamato and Kambara (65) have made a detailed study of reactions involving $Ti(OR)_4$, where R = Et, Pr^n, or Bu^n, and acetylacetone or ethyl acetoacetate, and they claim that Schmidt's compound (I) is really a 5-coordinated titanium complex, $Ti(acac)(OR)_3$.

$$Ti(OR)_4 + acacH \longrightarrow Ti(acac)(OR)_3 + ROH \qquad (57)$$

Their conclusions were based on the analyses of isolated products, molecular weight determinations, and infrared absorption measurements. Their work also verified the disubstitution reaction depicted in equation 56. Nevertheless, their main evidence for the 5-coordination of the titanium in the monochelated compounds, $Ti(acac)(OR)_3$, involves cryoscopic molecular weight measurements in benzene. These results do not look decisive. The observed molecular weights are

higher than calculated, and $Ti(acac)(OEt)_3$ shows a concentration dependence of molecular weight which points to the formation of a dimer in which the titanium would be 6-coordinated. On the other hand, the observed molecular weights for the bischelated derivatives, $Ti(acac)_2(OR)_2$, are lower than calculated. It is interesting to note that Reeves and Mazzeno (61) also concluded that a bischelate compound was formed from titanium tetra-*tert*-butoxide and ethyl acetoacetate. By and large most authors in the field seemed agreed about the formation of compounds such as $Ti(OR)_2(chelate)_2$ which could in principle exist in *cis* and *trans* forms. With zirconium alkoxides the enols reacted vigorously through to the tetrakischelates (63) wherein the zirconium exhibits the coordination number 8.

$$Zr(OR)_4 + 4acacH \longrightarrow Zr(acac)_4 + 4ROH \quad (58)$$

By varying the conditions of the reaction other compounds such as $Zr(acac)_2(OR)_2$ were obtained (63).

Some preliminary work with tantalum alkoxides suggested that trisubstitution occurred with benzoylacetone (66).

$$Ta(OEt)_5 + 3(bzac)H \longrightarrow Ta(OEt)_2(bzac)_3 + 3EtOH \quad (59)$$

The tris(benzoylacetonato)tantalum diethoxide would probably involve the tantalum in a coordination number of 8, but the oily product was intractable and this precluded a molecular weight determination.

A novel example of exchange involving an enol and a titanium alkoxide is that reported by Haslam (67) who obtained titanium divinyloxide diisopropoxide as follows:

$$Ti(OPr^i)_4 + 2CH_3CHO \longrightarrow Ti(OCH{=}CH_2)_2(OPr^i)_2 + 2Pr^iOH \quad (60)$$

It seems clear that the reaction must involve the enol form of acetaldehyde, and it is interesting that this reaction takes precedence over the alternative involving a Meerwein-Ponndorf-Verley oxidation-reduction:

$$Ti(OPr^i)_4 + 2CH_3CHO \longrightarrow Ti(OEt)_2(OPr^i)_2 + 2Me_2CO \quad (61)$$

The aldehydes $C_6H_5CH_2CHO$ and $C_6H_{13}CHO$ similarly gave derivatives of the appropriate unsaturated alcohols. On the other hand, titanium isopropoxide caused an aldol-type condensation of acetone, since triacetone dialcohol was formed in 20% yield (68).

D. REACTIONS WITH CARBONYL COMPOUNDS

Reactions involving metal alkoxides and carbonyl compounds have been known for many years and have held a place of importance in organic chemistry. The basic alkoxides (alkali metal derivatives) tend to cause either enolization or condensation (e.g., aldolization of aldehydes). It was Tishchenko (69) who in 1906 found that aluminum alkoxides effected the conversion of aldehydes into carboxylic esters.

$$2RCHO \longrightarrow RCO_2CH_2R \tag{62}$$

More recently Villani and Nord (70) carried out an interesting study which revealed how the aldehyde reaction was affected by the "acidity" of the metal alkoxides. For example, aluminum ethoxide, which is a Lewis acid, produced simple esters by the straightforward Tishchenko reaction. However, the mildly basic double alkoxides such as $Mg[Al(OEt)_4]_2$, $Ca[Al(OEt)_4]_2$, $Na[Mg(OEt)_4]$, $Mg(OEt)_2$, or $Ca(OEt)_2$ caused the formation of trimeric glycol esters.

$$3RCH_2CHO \longrightarrow RCH_2\underset{\displaystyle OH}{\underset{|}{C}}HCHRO_2CH_2R \tag{63}$$

The strongly basic sodium ethoxide caused only the aldol condensation. Our knowledge of the Tishchenko reaction was advanced by the investigations of Lin and Day (71) who studied reactions involving two different aldehydes in the presence of a catalytic amount of aluminum isopropoxide. In principle the two aldehydes can give four different esters including two "mixed esters." Lin and Day found that the predominating mixed ester was the one whose carboxyl group was derived from the aldehyde which by itself underwent the Tishchenko reaction more readily.

An extremely well-known reaction involving carbonyl compounds and metal alkoxides is the Meerwein-Ponndorf-Verley reaction

$$R_2CO + R'_2CHOH \rightleftharpoons R_2CHOH + R'_2CO \tag{64}$$

The system depicted by equation 64 involves ketones and secondary alcohols, but aldehydes and primary alcohols also take part.

A detailed consideration of this redox system would be out of place in this article, but there are a few features of special relevance. For example, it is of interest to know something about the role of the metal alkoxide in the reversible reaction 64. Meerwein and co-

workers (38) showed that alkoxides of aluminum, zirconium, tin(IV), titanium, antimony, and iron were effective in addition to those of sodium or magnesium. However, it is most usual to employ the readily available aluminum alkoxides, since they tend to give the minimum degree of side reactions. Although the redox reaction (eq. 64) does not perceptibly occur in the absence of the metal alkoxide, it has been argued that the latter is not a true catalyst. The presence of the alcohol is not essential because reaction will take place between the metal alkoxide and the carbonyl compound alone:

$$R_2CO + {}^1/_3Al(OCHR'_2)_3 \longrightarrow R'_2CO + {}^1/_3Al(OCHR_2)_3 \qquad (65)$$

Nevertheless, it is easy to imagine a system containing a large amount of the alcohol and a small concentration of aluminum alkoxide in which the behavior of the latter is essentially catalytic.

It was Meerwein (72) who originally suggested that the mechanism of the reaction must involve the coordination of the carbonyl oxygen to the aluminum, viz.:

$$R'_2CO + Al(OCHR_2)_3 \rightleftharpoons \begin{matrix} R' \\ \diagdown \\ C{-}O{\rightarrow}Al(OCHR_2)_3 \\ \diagup \\ R' \end{matrix} \rightleftharpoons$$

$$(R'_2CHO)(R_2CHO)_2Al{\rightarrow}O{-}\begin{matrix} R \\ \diagdown \\ C \\ \diagup \\ R \end{matrix} \rightleftharpoons (R'_2CHO)(R_2CHO)_2Al + R_2CO \qquad (66)$$

As a consequence of recent studies by Woodward *et al.* (73), Jackman *et al.* (74), McGowan (75), Rekasheva and Miklykhin (76), Williams *et al.* (77), and Doering *et al.* (78), it seems reasonably well established that the mechanism of the reaction involves a cyclic transition state in which there is transfer of an incipient hydride ion from an alkoxide to the ketone, both of the latter being attached to the aluminum.

$$R'_2CO{\rightarrow}Al(OCHR_2)_3 \rightleftharpoons \begin{matrix} R' & H & R \\ \diagdown & \curvearrowleft & \diagup \\ R'{-}C & & C{-}R \\ \| & & \| \\ O & & O: \\ \diagdown & & \diagup \\ & Al & \\ \diagup & & \diagdown \\ R_2CH & & OCHR_2 \end{matrix} \rightleftharpoons R_2CO{\rightarrow}Al(OCHR'_2)(OCHR_2)_2 \qquad (67)$$

The postulated mechanism has obvious stereochemical consequences, and this aspect has been verified by Jackman *et al.* (74) and Doering *et al.* (78). Moreover, it is clear that the partial positive charge induced on the carbonyl carbon by virtue of the coordination of the carbonyl oxygen must be a driving force for the subsequent electronic rearrangement. This aspect of the mechanism was confirmed by the important work of McGowan (75) who varied the electronic density on the carbonyl carbon by means of substituents X in the para-substituted acetophenones $XC_6H_4COCH_3$. Jackman and Macbeth (74) studied the kinetics of reaction of aluminum *sec*-butoxide and of aluminum 1-methylheptyloxide with the corresponding ketones. They employed the elegant technique of following the rate of racemization of the optically active alkoxide, thus simplifying the system to one ketone and ensuring that each experiment followed first-order kinetics. The over-all reaction was in fact first order with respect to ketone but zero order with respect to aluminum alkoxide. Now if the slow rate-determining step is the transfer of hydrogen in the ketone–aluminum alkoxide complex, then the reaction rate will be proportional to the concentration of this complex. If the aluminum alkoxide were monomeric the concentration of the complex would simply be proportional to the product of the concentration of ketone and alkoxide, and hence the reaction rate would be first order in ketone and first order in alkoxide. However, it is well known that the alkoxides are polymeric, and this should tend to reduce the order of reaction with respect to alkoxide. Jackman and Macbeth therefore interpreted the zero order of reaction with respect to alkoxide as a consequence of the polymeric nature of the aluminum alkoxide. As the concentration of alkoxide is increased, the tendency for it to combine with the ketone is compensated by the tendency for polymerization to occur and the net effect is that the rate of formation of the complex is not affected by the change in concentration of alkoxide.

Nevertheless, it is clear that the situation is more complicated than this. Thus, to give a quantitative explanation of the zero-order kinetics (toward alkoxide) it is necessary to postulate a very high degree of polymerization of the aluminum alkoxide, whereas molecular weight measurements (79–81) make it unlikely that the average degree of polymerization is greater than six. In addition, it was observed by Mehrotra (80) that aluminum isopropoxide exhibits an "aging" effect in its molecular weight which increases slowly with

time. Therefore it cannot be assumed with confidence that the hydrogen transfer is a slower process than the polymerization-depolymerization phenomenon. It is most interesting to note that Jackman and Macbeth observed in fact that the kinetics in their experiments were erratic in the initial stages and required a considerable time to settle down to the first-order conditions.

In an attempt to simplify the system still further and to eliminate uncertainties, we have in progress some research on the kinetics of the reaction of acetone with aluminum monoisopropoxide di-*tert*-butoxide (41). The extent of the reaction is followed by using C^{14}-labeled isopropoxide and measuring the rate of loss of radioactivity.

$$Me_2CO + Al(O\overset{*}{P}r^i)(OBu^t)_2 \rightleftharpoons \overset{*}{Me}_2CO + Al(OPr^i)(OBu^t)_2 \qquad (68)$$

This system has the advantage that only one group per aluminum is involved in the Meerwein-Ponndorf reaction, and it is known that this mixed alkoxide is dimeric (80). Furthermore, the tracer method ensures that each experimental run will conform to first-order kinetics, thus simplifying the determination of the order of reaction with respect to ketone and aluminum alkoxide. Preliminary results show that the system is far from simple, and instead of finding the reaction first order with respect to ketone and one-half order with respect to the aluminum mixed alkoxide as expected, it appears that the order of reaction depends on the temperature. It is quite clear that much more research will be required to clarify the detailed mechanism of the Meerwein-Ponndorf-Verley reaction.

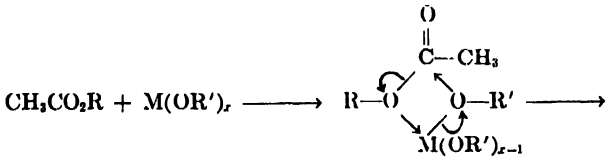
E. REACTIONS WITH ESTERS AND ANHYDRIDES

It has already been mentioned (Section II-D) that metal alkoxides undergo transesterification with carboxylic esters and that this afforded a method of conversion from one alkoxide of a metal to another. Recently, Bradley and Thomas (82) showed that an analogous reaction occurs when a trialkylsilyl acetate was used in place of an alkyl acetate.

$$M(OR')_x + xCH_3CO_2SiR_3 \longrightarrow M(OSiR_3)_x + xCH_3CO_2R' \qquad (69)$$

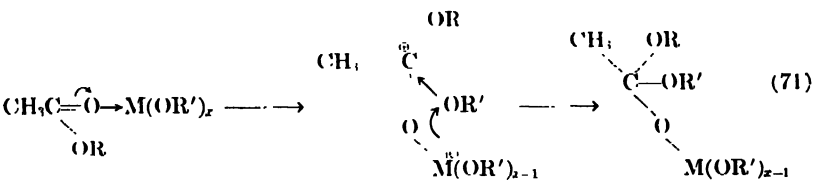
In contrast to the transesterification involving alkyl acetates it appears that reaction 69 is irreversible. Moreover, there is a tendency for metal acetate to be formed in the presence of excess trialkylsilyl acetate.

In considering a plausible mechanism for the transesterification reaction it must be remembered that either the alkoxide oxygen or the carbonyl oxygen of the ester could initiate the reaction by coordination to the metal.



$$CH_3CO_2R + M(OR')_x \longrightarrow CH_3CO_2R' + M(OR)(OR')_{x-1} \quad (70)$$

In either case the initial coordination of oxygen would induce a partial positive charge on the carbonyl carbon which would then be more vulnerable to attack by an alkoxide group from the metal. In the case where alkoxide oxygen initiates the reaction a simple cyclic transition state could be visualized, as in equation 70, although an ionic mechanism cannot be ruled out. On the other hand, coordination through the carbonyl oxygen might draw the π-electrons onto the oxygen, leaving the carbon with a vacant orbital which would receive the electron pair from an alkoxide oxygen, as in equation 71.



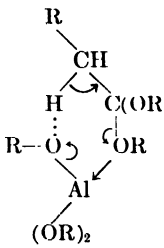
(71)

Either of the alkoxy groups in the orthoester–metal alkoxide complex could reverse the process depicted in equation 71. However, it does not follow that the mechanism is as simple as this, and it is possible that two molecules of metal alkoxide may be required to effect the transesterification with one molecule of alkyl acetate. In addition, there is a further complication that many metal alkoxides are polymeric, and it is possible that the alkyl acetate may interact with the polymeric alkoxide. Lappert (83) has recently deduced from infrared absorption measurements that in the complexes formed by alkyl acetates and boron trihalides the ester is definitely coordinated through the carbonyl oxygen, and this evidence seems to favor the initiating step indicated in equation 71. We hope that tracer kinetic

studies in these laboratories on the transesterification system will shed further light on the mechanism of the reaction.

It is interesting to note that McElvain and co-workers (84) discovered a different course of reaction when carboxylic orthoesters were heated with aluminum alkoxide. In this case dealcoholation of the orthoester takes place with the formation of ketenacetal and alcohol:

$$RCH_2C(OR)_3 + Al(OR)_3 \longrightarrow$$



$$\longrightarrow RCH{=}C(OR)_2 + Al(OR)_3 + ROH \quad (72)$$

These authors suggested that the reaction takes the course indicated by equation 72 involving a cyclic transition state. They noted that the less polymerized aluminum alkoxides (e.g., *tert*-butoxide or isopropoxide) were most effective and suggested that this was due to a greater ease of coordination of these derivatives with the orthoester.

Metal alkoxides react with carboxylic acid anhydrides to form the metal carboxylate and alkyl acetate:

$$M(OR)_x + x(R'CO)_2O \longrightarrow M(O_2CR')_x + xR'CO_2R \quad (73)$$

Mehrotra and Pande (85) have reported that reactions involving the alkoxides of aluminum or titanium with anhydrides show features which call to mind the behavior of the same alkoxides with carboxylic acids (Section III-D). For example, with aluminum alkoxides the replacement of two alkoxide groups per aluminum was rapid and exothermic and afforded the aluminum monoalkoxide dicarboxylates.

$$Al(OR)_3 + 2(R'CO)_2O \longrightarrow Al(OR)(O_2CR')_2 + 2R'CO_2R \quad (74)$$

In the presence of excess anhydride the remaining alkoxide was replaced with the formation of the aluminum tri-soaps. In the case of titanium alkoxides reaction with an excess of acetic anhydride resulted in the formation of the titanium oxide acetate, $Ti_2O(OAc)_6$. More detailed investigation involving the stepwise molar addition of

acetic anhydride to titanium tetraisopropoxide showed that the first two stages of the replacement occur rapidly and exothermically, viz.:

$$Ti(OPr^i)_4 + (CH_3CO)_2O \longrightarrow Ti(OPr^i)_3(O_2CCH_3) + CH_3CO_2Pr^i \quad (75)$$

$$Ti(OPr^i)_4 + 2(CH_3CO)_2O \longrightarrow Ti(OPr^i)_2(O_2CCH_3)_2 + 2CH_3CO_2Pr^i \quad (76)$$

Thereafter complication occurred because the addition of anhydride to isopropoxide in the molar ratio of 3:1 resulted in the formation of a titanium oxide isopropoxide acetate, $Ti_2O(OPr^i)_2(OAc)_4$. It appears that the third stage of replacement is slow:

$$Ti(OPr^i)_2(O_2CCH_3)_2 + (CH_3CO)_2O \xrightarrow{\text{slow}} Ti(OPr^i)(O_2CCH_3)_3 + CH_3CO_2Pr^i \quad (77)$$

The slowly formed titanium monoisopropoxide triacetate combines with the diisopropoxide diacetate as follows:

$$Ti(OPr^i)_2(O_2CCH_3)_2 + Ti(OPr^i)(O_2CCH_3)_3 \longrightarrow Ti_2O(OPr^i)_2(O_2CCH_3)_4 + CH_3CO_2Pr^i \quad (78)$$

Moreover, the titanium product of reaction 78 was shown to combine with excess acetic anhydride with the formation of $Ti_2O(O_2CCH_3)_6$.

F. REACTIONS WITH HALOGENS AND HALIDES

Nesmeyanov and co-workers (86) have studied the action of chlorine and of bromine on the tetraethoxide, tetra-*n*-propoxide, and tetra-*n*-butoxide of titanium. In each case the titanium dihalide dialkoxide alcoholate, $TiX_2(OR)_2 \cdot ROH$, was isolated. Moreover, they isolated *n*-butyl propionate from the reaction involving titanium butoxide and chlorine in carbon tetrachloride solution and thereby deduced that in the halogenation of the titanium alkoxide alkoxy radicals take part as follows:

$$Ti(OCH_2R)_4 + X_2 \xrightarrow{X = Cl \text{ or } Br} TiX_2(OCH_2R)_4 + 2RCH_2O \quad (79)$$

$$2RCH_2O \longrightarrow RCH_2OH + RCHO \quad (80)$$

$$TiX_2(OCH_2R)_2 + RCH_2OH \longrightarrow TiX_2(OCH_2R)_2 \cdot RCH_2OH \quad (81)$$

$$2RCHO \longrightarrow RCO_2CH_2R \quad (82)$$

This interesting reaction is clearly worthy of further detailed investigation, especially in view of the fact that uranium tetraethoxide is practically quantitatively oxidized to the monobromo tetraethoxide by bromine (30).

Metal alkoxides combine readily with hydrogen halides, and alkoxide groups are thereby replaced by halides.

$$M(OR)_x + yHX \longrightarrow MX_y(OR)_{x-y} + yROH \quad (83)$$

In the case of titanium or zirconium alkoxides, Mehrotra (87) has shown that the action of excess hydrogen halide results in the formation of substantially the same product as is obtained by the reaction involving the metal chloride and alcohol, viz.:

$$Ti(OR)_4 + 2HX \xrightarrow{X = Cl \text{ or } Br} TiX_2(OR)_2 \cdot ROH + ROH \quad (84)$$

$$TiX_4 + 3ROH \xrightarrow{R = Et \text{ or } Pr^i} TiX_2(OR)_2 \cdot ROH + 2HCl \quad (85)$$

The following products were obtained by the action of hydrogen chloride or bromide on the appropriate zirconium alkoxide: $ZrCl_3(OEt) \cdot 2EtOH$, $ZrCl_3(OPr^i) \cdot Pr^iOH$, $Zr_2Cl_5(OPr^n)_3 \cdot 3Pr^nOH$, and $Zr_3Br_8(OPr^i)_4 \cdot Pr^iOH$.

Gilman and co-workers (88) have shown that uranium pentaethoxide reacts with hydrogen chloride in ethereal solution and the following compounds were isolated from reactions involving the appropriate molar ratios of reactants: $UCl(OEt)_4$, $UCl_2(OEt)_3$, and $UCl_3(OEt)_2$. There seems to be no reason to doubt that all metal alkoxides will react to some extent with the hydrogen halides.

Another method which allows the replacement of alkoxide groups by halogens is the reaction involving metal alkoxides and acetyl chloride. For example, Wardlaw and co-workers (9) first prepared titanium monochloride triethoxide as follows:

$$Ti(OEt)_4 + CH_3COCl \longrightarrow TiCl(OEt)_3 + CH_3CO_2Et \quad (86)$$

Cullinane and co-workers (89) also used this method for preparing titanium chloride alkoxides in some later work. However, in attempting to prepare titanium trichloride monoethoxide by the reaction involving titanium chloride and acetyl chloride, in appropriate molar proportions, Bradley *et al.* (90) isolated a stable addition compound, $TiCl_3(OEt) \cdot CH_3CO_2Et$, i.e.:

$$Ti(OEt)_4 + 3CH_3COCl \longrightarrow TiCl_3(OEt) \cdot CH_3CO_2Et + 2CH_3CO_2Et \quad (87)$$

The molecule of ethyl acetate is evidently very strongly coordinated to the titanium because the complex survives distillation at 90°C. under 0.5 mm. pressure. When excess of acetyl chloride was em-

ployed, all of the ethoxide groups in titanium tetraethoxide were replaced by chlorine and another complex was isolated.

$$Ti(OEt)_4 + 4CH_3COCl \longrightarrow TiCl_4 \cdot CH_3CO_2Et + 3CH_3CO_2Et \quad (88)$$

The titanium tetrachloride–ethyl acetate complex was distilled unchanged at ca. 85°/2 mm. On the other hand, it appears that titanium tetra-*tert*-amyloxide is resistant to attack by acetyl chloride. Thus the addition of acetyl chloride to the titanium compound in the molar ratio of 3:1 gave instead of $TiCl_3(OAm^t)$ a mixture of $TiCl(OAm^t)_3$ and $Ti(OAm^t)_4$. The action of acetyl chloride on zirconium alkoxides was first studied by Bradley, Halim, and Wardlaw (91), who carried out the following reactions:

$$Zr(OEt)_4 + CH_3COCl \longrightarrow ZrCl(OEt)_3 + CH_3CO_2Et \quad (89)$$

$$Zr(OEt)_4 + 2CH_3COCl \longrightarrow ZrCl_2(OEt)_2 \cdot CH_3CO_2Et + CH_3CO_2Et \quad (90)$$

$$ZrCl_3(OEt) \cdot EtOH + ZrCl_2(OEt)_2 + 2CH_3COCl \longrightarrow 2ZrCl_3(OEt) \cdot CH_3CO_2Et + HCl \quad (91)$$

$$ZrCl_2(OEt)_2 + 2CH_3COCl \longrightarrow ZrCl_4 \cdot CH_3CO_2Et + CH_3CO_2Et \quad (92)$$

$$ZrCl_3(OEt) \cdot EtOH + 2CH_3COCl \longrightarrow ZrCl_4 \cdot CH_3CO_2Et + HCl + CH_3CO_2Et \quad (93)$$

Two important features were noticed: (*1*) that the product of the reaction of excess acetyl chloride and zirconium ethoxide or any zirconium chloride ethoxide was the tetrachloride with ethyl acetate of addition and (*2*) that only one molecule of ethyl acetate was coordinated and the stability of the complex decreased as chloride was replaced by ethoxide in the series: $ZrCl_4$, $CH_3CO_2Et > ZrCl_3(OEt)$, $CH_3CO_2Et \gg ZrCl_2(OEt)_2$, $CH_3CO_2Et \gg$ [$ZrCl(OEt)_3 \cdot CH_3CO_2Et$ (not isolated)]. In a later paper Bradley *et al.* (92) explored the reactions of other zirconium alkoxides with acetyl chloride. Excess of acetyl chloride and zirconium isopropoxide isopropanolate, $Zr(OPr^i)_4 \cdot Pr^iOH$, gave the coordination complex $ZrCl_4 \cdot 2CH_3CO_2Pr^i$. With zirconium tetra-*n*-propoxide reaction with excess acetyl chloride yielded $ZrCl_4 \cdot CH_3CO_2Pr^n$. Similarly, with zirconium tetra-*n*-octyloxide it was deduced that a tetrachloride complex was formed, although the complex was not isolated. On the other hand, with zirconium tetra-1-ethylpropoxide chlorination with acetyl chloride did not proceed beyond the zirconium trichloride monoalkoxide stage, while with zirconium *tert*-amyloxide the extent of reaction was considerably less. In the latter system a fairly detailed study shows that the introduction of the first chloride was much more facile than

the introduction of the second and the addition of a large excess of acetyl chloride failed to produce the zirconium dichloride di-*tert*-amyloxide. This is a very interesting situation and would be worthy of further investigation. It is clear that the limited degree of substitution of *tert*-amyloxide groups by chloride is not the result of a simple steric phenomenon because this would make the first substitution more difficult than the second. Further work on the acetyl chloride–zirconium isopropoxide solvate revealed the following reactions:

$$Zr(OPr^i)_4 \cdot Pr^iOH + CH_3COCl \longrightarrow ZrCl(OPr^i)_3 \cdot Pr^iOH + CH_3CO_2Pr^i \quad (94)$$

$$Zr(OPr^i)_4 \cdot Pr^iOH + 2CH_3COCl \longrightarrow ZrCl_2(OPr^i)_2 \cdot Pr^iOH + 2CH_3CO_2Pr^i \quad (95)$$

These reactions were conducted in benzene solution and were characterized by their rapidity and the lack of evolution of hydrogen chloride. It is possible that the acetyl chloride reacts more rapidly with the $Zr(OPr^i)$ groups than with the coordinated isopropanol. Also it is clear that the zirconium chloride isopropoxides coordinate preferentially with the isopropanol rather than with isopropyl acetate. The work described above has involved only acetyl chloride and some alkoxides of titanium and of zirconium. However, there is no reason to doubt that other metal alkoxides would be reactive with acetyl chloride and other acid chlorides.

It is noteworthy that in several of the above reactions involving acetyl chloride the resultant metal chloride alkoxide was obtained as stable complex with alkyl acetate. In certain cases e.g., $TiCl_3(OEt) \cdot CH_3CO_2Et$—the complex was so stable as to preclude the isolation of the metal chloride alkoxide. However, it was also found (90) that titanium alkoxides reacted with titanium tetrachloride to form the required titanium chloride alkoxide. In particular, the hitherto unknown titanium trichloride monoalkoxides were readily obtained when an excess of titanium tetrachloride was employed.

$$Ti(OR)_4 + 3TiCl_4 \longrightarrow 4TiCl_3(OR) \quad (96)$$

Nesmeyanov *et al.* (93) have also prepared titanium chloride alkoxides by this method. The titanium chloride alkoxides are reasonably volatile, and this facilitated the isolation of products from the reactions involving titanium alkoxides and titanium tetrachloride. In the case of zirconium, the chloride alkoxides are usually solids which decompose when attempts are made to sublime them. On the other hand, some of them form crystalline complexes with donor

molecules and this enabled certain reactions to be established (92), e.g.:

$$Zr(OPr^i)_4 \cdot Pr^iOH + ZrCl_4 \cdot 2CH_3CO_2Pr^i \longrightarrow ZrCl_2(OPr^i)_2 \cdot Pr^iOH + ZrCl_2(OPr^i)_2 \cdot CH_3CO_2Pr^i \quad (97)$$

$$Zr(OPr^i)_4 \cdot Pr^iOH + ZrCl_2(OPr^i)_2 \cdot Pr^iOH \longrightarrow 2ZrCl(OPr^i)_3 \cdot Pr^iOH \quad (98)$$

For example, in reaction 97 the zirconium dichloride diisopropoxide isopropanolate, $ZrCl_2(OPr^i)_2 \cdot Pr^iOH$, was isolated by crystallization from carbon tetrachloride. These three reactions are all characterized by their rapidity, and it seems likely that this is a common feature of the interaction of metal alkoxides and metal chlorides generally.

G. DOUBLE ALKOXIDES

Meerwein and Bersin (10) observed that alcoholic solutions of the alkoxides of aluminum, iron(III), titanium, tin(IV), and zirconium were acidic and could be titrated to a sharp end point with an alkali metal alkoxide using thymolphthalein as indicator, i.e.:

$$NaOEt + Al(OEt)_3 \longrightarrow Na[Al(OEt)_4] \quad (99)$$

The products were considered as alkoxy salts derived by neutralization of the alkoxy acid by the base. Moreover, they showed that these "alkoxy salts" could be formed from many pairs of metal alkoxides, including pairs of alkali metal alkoxides. In general, they suggested that the more "basic" alkoxide (i.e., the one derived from the more electropositive metal) transferred its alkoxide groups to the more "acidic" alkoxide which became the complex ion involving a metal in its higher coordination number. The following compounds illustrate the point: $K[Li(OPr^i)_2]$, $K_2[Be(OEt)_4]$, $Na_2[Mg(OPr^n)_4]$, $K[Zn(OMe)_3]$, $Na[Fe(OEt)_4]$, $K[Fe(OEt)_4]$, $Li[Al(OMe)_4]$, $Ca[Al(OEt)_4]_2$, $Ni[Al(OEt)_4]_2$, $NaH_3[Sn(IV)(OEt)_6]_2$, $K_2Sn(II)[Sn(IV)(OEt)_6]_2$, $KH_3[Ti(OBu)_6]_2$, $NaH[Zr(OEt)_6]$. Alkoxides of nonmetallic elements and metalloids also formed these "alkoxy salts," e.g., in $Li[B(OMe)_4]$, $Na(Sb(III)(OEt)_4]$, $NaH[Se(IV)(OEt)_6]$, $NaH[Te(IV)(OEt)_6]$ and $Na[Sb(OEt)_6]$.

Meerwein and Bersin noted that the stability of the "alkoxy salt" depended on the difference in "electrochemical character" of the metals in the component alkoxides. The most stable compounds resulted when one metal was strongly electropositive and the other weakly electropositive and preferably amphoteric viz.: $Na[Al(OR)_4]$,

$NaH_3[Ti(OR)_6]_2$, and $NaH[Zr(OR)_6]$. In the case of calcium or magnesium aluminum alkoxides—i.e., $Ca[Al(OR)_4]_2$ or $Mg[Al(OR)_4]_2$—the "alkoxy salt" could be distilled under reduced pressure in contrast to the nonvolatile parent alkoxides of calcium or magnesium. On the other hand, compounds such as $K[Li(OPr^i)_2]$, $K_2[Be(OEt)_4]$, $Na_2[Mg(OPr)_4]$, or $K_2[Ca(OCH_2C_6H_5)_4]$, were relatively unstable and dissociated into the component alkoxides in alcoholic solution. Also there was no evidence for the combination between "acidic" alkoxides such as $B(OR)_3$, $Al(OR)_3$, $Ti(OR)_4$, or $Sb(OR)_5$. However, in the case of zinc aluminum alkoxides two types of double alkoxide were formed, $Zn[Al(OR)_4]_2$ and $Al[Zn(OR)_3]_3$, and this does not seem to support the formulation of these compounds as salts. In fact, there is very little physical evidence for regarding the "alkoxy salts" as salts at all. While it is quite possible that the compounds such as $K[Al(OMe)_4]$, which are formed in neutralization reactions, may be salts, yet it is not known whether they are electrolytes. On the other hand, such physical properties (e.g., solubility in organic solvents and volatility) as are available on most of the other "alkoxy salts" suggest that these compounds are covalent rather than ionic and are best termed double alkoxides.

Later work has raised doubts concerning the formulation of some of Meerwein and Bersin's double alkoxides. In particular, these authors claimed that the titration of zirconium methoxide or ethoxide with the appropriate sodium alkoxide was in accordance with the requirements of the following equation:

$$Zr(OEt)_4 + NaOEt + EtOH \longrightarrow NaH[Zr(OEt)_6] \qquad (100)$$

The sodium hydrogen zirconium ethoxide was also obtained as a crystalline compound, sparingly soluble in ethanol but soluble in hot xylene, from the reaction involving zirconium tetrachloride and ethanolic sodium ethoxide.

$$ZrCl_4 + 5NaOEt + EtOH \longrightarrow NaH[Zr(OEt)_6] + 4NaCl \qquad (101)$$

In attempting to repeat this work Bradley and Wardlaw (12) obtained a crystalline compound from the reaction involving zirconium tetrachloride and sodium ethoxide having the same physical properties as the alleged $NaH[Zr(OEt)_6]$ but with an analysis corresponding to $Na_4Zr_6(OEt)_{21}(OH)_7$. Moreover, they were unable to confirm the reaction depicted by equation 100, although a sharp end point was

observed after the addition of only 0.5 gram equivalent of NaOEt per gram mole of $Zr(OEt)_4$. Later work by Bartley and Wardlaw (94) not only confirmed the results of Bradley and Wardlaw but showed that the reaction between alkali metal alkoxides and zirconium alkoxides is in accordance with the following equation:

$$MOR + 2Zr(OR)_4 \longrightarrow MZr_2(OR)_9 \qquad (102)$$

Most of these alkali metal zirconium alkoxides were monomeric in benzene and could be distilled under reduced pressure. The volatility and solubility in organic solvents of these compounds suggest strongly that they are covalent compounds rather than salts. They are of special interest in view of the rarity of volatile covalent compounds of the alkali metals. Bartley (94) also obtained double alkoxides of the type $MZr(OBu^t)_5$, where M = alkali metal, and also $M_2Zr(OBu^t)_6$ and $LiZr_2(OPr^i)_9Pr^iOH$, but under no conditions did he obtain compounds with the formula $NaH[Zr(OR)_6]$ reported by Meerwein and Bersin. An interesting double alkoxide of quadrivalent uranium and aluminum was obtained by Albers *et al.* (95) from the reaction involving uranium tetrachloride and sodium aluminum isopropoxide.

$$UCl_4 + 4NaAl(OPr^i)_4 \longrightarrow UAl_4(OPr^i)_{16} + 4NaCl \qquad (103)$$

The uranium aluminum alkoxide could be distilled under reduced pressure. Recently, Gilman *et al.* (88) reported that uranium pentaethoxide could be titrated with sodium ethoxide in accordance with the following equation:

$$NaOEt + U(OEt)_5 \longrightarrow NaU(OEt)_6 \qquad (104)$$

This shows that uranium pentaethoxide is a "Lewis acid," and it is interesting to find that it combines with another "Lewis acid"—namely, aluminum ethoxide—forming the volatile double alkoxide $U_3Al(OEt)_{18}$. This behavior does not accord with Meerwein and Bersin's alkoxy salt theory. Gilman *et al.* also found that uranium pentaethoxide combined with calcium ethoxide to give the double alkoxide $U_2Ca(OEt)_{12}$, which could be sublimed under reduced pressure. An interesting feature of these three double alkoxides of quinquevalent uranium is that they are green in contrast to uranium pentaethoxide which is brown.

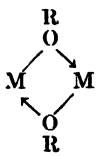
Recently Carter (96) has studied the formation of double alkoxides containing titanium. He found that titanium ethoxide or *n*-butoxide

could be titrated to a well-defined end point with the corresponding sodium alkoxide. However, the composition of the products was $MTi_2(OR)_9$ in contrast to the formula $KH_3[Ti(OBu)_6]$, proposed by Meerwein and Bersin. Carter also found that titanium alkoxides were rather weaker "Lewis acids" than zirconium alkoxides as judged by their tendency to form stable double alkoxides. It is noteworthy that titanium isopropoxide, which is monomeric, did not give a 9 alkoxide, $MTi_2(OPr^i)_9$, but formed instead $MTi(OPr^i)_5$. This behavior is analogous to that of zirconium *tert*-butoxide, which is also monomeric and forms $MZr(OBu^t)_5$.

While the majority of the excellent work by Meerwein and Bersin appears to be correct, it is clear that some of their results are open to doubt. Also their simple classification of the double alkoxides as alkoxy salts has obvious limitations and could be misleading, although in many cases it gives a logical interpretation of the facts. It appears that more research into the nature of the double alkoxides would be justified.

H. COORDINATION COMPLEXES OF METAL ALKOXIDES

A remarkable feature of the metal alkoxides is that they form very few coordination compounds with donor molecules. However, a large number of metal alkoxides are polymeric, and it is believed that this is a consequence of covalency expansion of the metal involving coordination of oxygen from neighboring alkoxide groups. Why the metal alkoxides should prefer to form "auto complexes" than to add on a donor molecule is still an intriguing problem. It is possible that there is some special stability in the four-membered ring



formed by the alkoxide bridges in the coordination polymers. Also the charge separation in the $\overset{\delta+}{M}—\overset{\delta-}{O}R$ group would probably confer greater donor power to the alkoxide oxygen compared to the oxygen in an organic donor molecule, e.g., R_2O. It is quite clear that the tendency of the metal to add on a donor molecule is increased by the attachment of electron-attracting groups to the metal. This is well

illustrated by the metal chloride alkoxides which form stable addition compounds with alcohols and organic esters (see Section III-F). Even more striking is the effect produced by the halo-alkoxide groups. For example, Gilman *et al.* (88) found that uranium penta-2,2,2-trifluoroethoxide formed addition compounds of moderate stability with ammonia or aliphatic amines. Furthermore, Bradley *et al.* (26) found that zirconium tetra-2,2,2-trichloroethoxide formed a stable addition compound containing two molecules of acetone, while the tetrakis[1-methyl-1-(trichloromethyl)ethoxy] derivatives of cerium and thorium gave addition compounds with pyridine. There are a few examples of addition compounds formed by the metal compounds of the lower aliphatic alcohols, viz.: $Ti(OBu^i)_4 \cdot Bu^iOH$, $Zr(OPr^i)_4 \cdot Pr^iOH$, $Zr(OPr^i)_4 \cdot C_5H_5N$, $Ce(OPr^i)_4 \cdot Pr^iOH$, and $Ce(OPr^i)_4 \cdot C_5H_5N$. However, it is probable that in these cases the steric effect of the alkyl groups in the alkoxide $M(OR)_4$ opposes the formation of the alkoxide bridges required to give a polymer, but does not prevent the coordination of a donor molecule.

I. THERMAL STABILITY OF METAL ALKOXIDES

Little systematic work has been carried out on the thermal stability of metal alkoxides. In 1900, Tishchenko (107) reported his studies on the pyrolysis of various aluminum alkoxides. The products included alcohols, ethers, and olefins. Meerwein and Geschke (106) studied the pyrolysis of the ethoxides of tin, iron, cobalt, nickel, and copper. The ethoxides of tin(IV) and iron(III) produced acetaldehyde, ethanol, and the ethoxide of the metal in its lower valency.

$$Sn(OEt)_4 \longrightarrow Sn(OEt)_2 + CH_3CHO + C_2H_5OH \qquad (105)$$

The lower valency metal alkoxides were shown to be considerably more stable. The double ethoxides of cobalt(II), nickel(II), or copper(II), respectively, with aluminum ethoxide were also readily pyrolyzed under conditions in which aluminum ethoxide alone was stable. Bradley and Faktor (97) have recently reported the results of kinetic studies on zirconium alkoxides. It was clear that stabilities were in the order $Zr(OEt)_4 \gg Zr(OPr^i)_4 > Zr(OBu^t)_4 \cdot Zr(OAm^t)_4$. Moreover, these results encouraged the view that metal methoxides should exhibit high thermal stability, and this has been confirmed (98). Thus the methoxides of lithium, magnesium, and lanthanum remained unchanged by the action of heat at 360°C.

over a period of 18 hours. The methoxides of aluminum and zirconium, previously regarded as nonvolatile, were sublimed readily at 240 and 280°C., respectively, *in vacuo*. Detailed studies on the tertiary alkoxides of zirconium revealed that the low thermal stability of these compounds is fundamentally related to the ease of dehydration of the tertiary alcohol which forms water and olefin. The water molecule formed in this reaction hydrolyzes the metal alkoxide, thereby producing two molecules of *tert*-alcohol in place of the one consumed. Inevitably a chain reaction sets in because it is impossible in practice to obtain the metal alkoxide completely free from minute traces of water or tertiary alcohol. Hence, at any temperature at which the dehydration of the tertiary alcohol is reasonably fast, the metal alkoxide cannot be indefinitely stable. Bradley and Faktor showed that the characteristically sigmoid pressure-time curves for the thermal decomposition were in accordance with the above mechanism. Furthermore, they proved that the tetrakis-(trialkylsilyl)oxy derivative of the metal is inherently more stable than the corresponding *tert*-alkoxide because the mode of dehydration of the trialkylsilanol does not allow the development of the chain reaction. It is desirable that further work be carried out on the decomposition of the more stable primary alkoxides of the metals because it is possible that alkoxy radicals could be involved.

IV. Physical Properties of Metal Alkoxides

A. GENERAL

The physical properties of the metal alkoxides depend in a striking manner on the size and shape of the alkyl group and on the valency, atomic radius, stereochemistry, and coordination number of the metal. There is a gradual change from the insoluble nonvolatile ionic alkoxides of some of the alkali metals to the volatile covalent alkoxides of the metals of valency three, four, five, or six. The fact that an alkoxide is insoluble in hydrocarbon solvents and is nonvolatile does not necessarily prove that it is ionic because it could alternatively be a giant covalent polymer. Neither does the electrical conductivity of dilute solutions of sodium alkoxides in alcohols (3) prove that the solid sodium alkoxides or their alcoholates are ionic. It seems important to emphasize this point because there is a tendency for alkali metal compounds in general to be labeled automatically as ionic. The co-

valent properties of the sodium zirconium alkoxides (94) demand that a careful examination of the alkali metal alkoxides be made before accepting that the latter are ionic. On the other hand, Masdupuy and Gallais (99) reported that molten aluminum ethoxide exhibited a negligible electrical conductivity over a wide temperature range, and this clearly proves that aluminum ethoxide is essentially covalent in character. It seems highly probable that the alkoxides of all the metals of valency four or higher are covalent with the possible exception of thorium. The physical properties of these covalent metal alkoxides are determined by the resultant of two opposing tendencies. One tendency is that of the metal to expand its coordination number by intermolecular bonding with oxygen; this causes the formation of relatively nonvolatile compounds which may also be sparingly soluble in typical organic solvents. The opposite tendency is the screening or steric effect of the alkyl groups which interfere with the coordination process to a degree which depends on their size and shape. In the limit, the steric effect of the alkyl groups can completely prevent intermolecular bonding, and a volatile monomeric alkoxide results. It is in these monomeric derivatives that the covalent character of metal alkoxides is most highly developed.

B. MOLECULAR WEIGHT STUDIES

Direct evidence for the polymeric nature of certain metal alkoxides resulted from the determination of molecular weights in organic solvents. For example, in 1930, Sidgwick and Sutton (100) discovered that thallous alkoxides were tetramers. Shortly afterward Ulich and Nespital (81) and Robinson and Peak (79) showed that a number of aluminum alkoxides were polymeric. In recent years Bradley and Wardlaw and their co-workers (13–18,21,22,25,26,32,34, 44,101–103,105,109–113,115) have made systematic studies on the molecular weights of a large number of alkoxides of titanium, zirconium, cerium, thorium, niobium, tantalum, and uranium alkoxides. Mehrotra (36,39,80) has made a similar study on the aluminum alkoxides. The measurements by Bradley, Wardlaw, and Mehrotra *et al.* were made ebullioscopically in benzene under carefully standardized conditions and are thus of special value for a detailed comparative study. It is not proposed to give an exhaustive account of these results because the essential features can be reasonably well illustrated by Table I, which contains data on the isomeric amyloxides.

TABLE I
Degrees of Polymerization of Metal Amyloxides

R in $M(OR)_x$	Metal							
	Al (40)	Fe (105)	Ti (101)	Zr (101)	Ce (14,25,102)	Th (14,25,102)	Nb (15)	Ta (103)
$CH_3(CH_2)_4$	4.0	3 0	1 4	3 2	4.20	6.20	2.00	2.01
$(CH_3)_2CH(CH_2)_2$	4 0	3 0	1 2	3 3	—	—	1.81	1 98
$(CH_3)(C_2H_5)CHCH_2$	4 1	3 0	1 1	3.7	—	—	1.81	1 97
$(CH_3)_3CCH_2$	2.07	2.0	1 3	2.4	2.53	4.0	1.52	1 35
$(C_2H_5)_2OH$	2 08	2 0	1 0	2 0	2.90	—	1 16	1 02
$(CH_3)(n\text{-}C_3H_7)CH$	2.06	1 9	1 0	2.0	3.11	—	1.03	0.99
$(CH_3)(\text{iso-}C_3H_7)CH$	1 98	1 9	1 0	2.0	3.00	—	1.05	1.02
$(CH_3)_2(C_2H_5)C$	—	1 5	1 0	1 0	2 4	2.8	—	1 00

The amyl group was chosen because it exists in eight isomeric forms and provides four primary, three secondary, and one tertiary alkoxide groups having the same number of carbon atoms. This factor was even more important from the viewpoint of comparing volatilities. One clear feature emerging from the data in Table I is the decrease in degree of polymerization caused by progressive branching of the amyl group from primary to secondary to tertiary isomers. The one exception is the value for titanium neopentyloxide, which appears anomalously high, particularly in view of the high volatility of this alkoxide. Nevertheless, in the cases of aluminum, iron(III), zirconium, niobium, and tantalum, the neopentyloxide has a considerably lower degree of polymerization than the other primary amyl oxides and the more limited data on cerium and thorium appear to conform to the same pattern (see ref. 102 for discussion on neopentyloxides). Accepting the hypothesis that the metal alkoxides are polymeric by virtue of the intermolecular bonding between metal and oxygen caused by the metal expanding its covalency, there are two alternative explanations of the change in degree of polymerization caused by branching of the alkyl group. One explanation is that the phenomenon is due to the electron-releasing property of the alkyl group. This would tend to stabilize covalency expansion of the metal by intramolecular coordination with oxygen, viz., $\overset{-}{\text{M}}=\overset{+}{\text{O}}—\text{R}$. Clearly, electron release by the group R will help to stabilize the metal-oxygen double bond by reducing the formal positive charge on the oxygen. Formation of the double bond by overlap of a vacant p_π or d_π orbital of the metal with a filled p_π orbital of the oxygen allows the metal to achieve its covalency expansion without recourse to polymerization of the metal alkoxide. Since the order of electron release by the amyl groups is tertiary > secondary > primary, then the electronic effect of the amyloxide groups should result in the observed decrease in polymerization of the metal amyloxide with increase in branching of the amyl group. A necessary consequence of this phenomenon would be a high degree of double bonding in the monomeric metal alkoxides and an appropriate shortening of the metal-oxygen bond length. It would be difficult to predict the extent to which the metal-oxygen double bonding would vary from one metal to another because the metals under discussion are characterized by a tendency not to form π-bonds with oxygen. The alternative explana-

tion of the chain-branching phenomenon involves the steric effect of the alkoxide groups. It is self-evident that the metal-oxygen intermolecular bond must be sensitive to the steric effect of the alkoxide groups in the sense that branching of the alkyl group will oppose the close approach of neighboring molecules. In the limit, steric interaction of the alkyl groups will prevent molecules from getting close enough to form the intermolecular bond and a monomeric alkoxide will result. Thus the experimental results would be explained on either steric or electronic grounds, and it is notoriously difficult to isolate these two effects from one another. However, the behavior of the neopentyloxide group was considered by Bradley, Mehrotra, and Wardlaw (101) to lend strong support to the view that the chain-branching phenomenon resulted predominantly from the steric effect. Although the neopentyloxide group has a considerable steric or "screening" effect on the metal, it is clear that its electron-releasing effect must be considerably less than that of a tertiary alkoxide group. Therefore the fact that the neopentyloxide has a considerably lower degree of polymerization than the other primary amyloxides was taken as evidence that powerful steric effects were operative. Another feature of metal alkoxides is the way in which the degree of polymerization for a given alkoxide depends on the metal. According to the stereochemical approach the size of the metal will be extremely important. Obviously, the alkoxide of a large metal will be much less affected by the steric interaction of the alkoxide group than will the same alkoxide of a smaller metal. Or, looking at the problem from another angle, a large metal will require a much larger and more highly branched alkoxide group to screen it completely than will a smaller metal. These consequences of the stereochemical hypothesis are abundantly confirmed by the behavior of the tetraalkoxides of titanium, zirconium, hafnium, cerium(IV), and thorium. The fact that some nonintegral degrees of polymerization are listed in Table I shows that more than one polymeric species must often be present. Moreover, if there is an equilibrium between the various polymeric species, then a concentration dependence of the number average molecular weight would be expected. It is a remarkable feature of the ebullioscopic measurements that in no case was concentration dependence observed, although in some cases a wide concentration range was studied. However, cryoscopic molecular weight determinations on titanium alkoxides in benzene by Cullinane *et al.*

(50) revealed that the average degree of polymerization increased with increase in concentration. The same effect was independently reported by Caughlan *et al.* (108) who discovered that the degree of polymerization of titanium tetraethoxide, tetra-*n*-propoxide, and tetra-*n*-butoxide reached a limiting value of three at higher concentrations and concluded that the trimer was of structural significance (see Section IV-F). The cryoscopic method has also proved invaluable where the metal alkoxide has an appreciable volatility at the boiling point of benzene. For example, tantalum penta-*tert*-butoxide had an apparent degree of polymerization of 1.46 in boiling benzene, although from its volatility it was expected to be monomeric. In fact, cryoscopic measurements proved that it was monomeric and the results in boiling benzene were invalid owing to the presence of tantalum compound in the vapor (103). Similar behavior was noted with tantalum pentaisopropoxide (44). There is little doubt that the apparent degree of polymerization of 1.4 for titanium tetraisopropoxide found by Bradley *et al.* (109) by the ebullioscopic method is also invalid because of the volatility of the solute. Recent work by Cook (104) disclosed that this compound is monomeric in benzene at the freezing point, while Hillyer in our laboratories has confirmed that titanium isopropoxide is volatile in boiling benzene. The effect of the nature of the solvent on the polymerization of tantalum *n*-alkoxides was determined by Bradley, Wardlaw, and Whitley (110). It was considered that three factors would be important—namely, the boiling point, dielectric constant, and donor power of the solvent. Clearly a rise in temperature would tend to dissociate the polymers, thus lowering the average degree of polymerization. A solvent consisting of donor molecules could produce a monomeric alkoxide by a coordination mechanism. The effect of dielectric constant would depend on the nature of the intermolecular forces holding the polymer together. Thus the effect of the dielectric constant would be small if covalent intermolecular bonds were involved but very marked if the polymer units were bound by electrostatic (dipole-dipole) forces.

In any one solvent it would be impossible to determine the relative importance of these three factors, but with a variety such as benzene, toluene, acetonitrile, pyridine, and diisopropyl ether it was possible to make reasonable deductions. The data are presented in Table II. The effect of temperature is clearly revealed by the data for benzene and toluene, which are similar in dielectric constant or donor power,

but have a 30° difference in boiling points. Now, comparison of benzene with acetonitrile reveals the effect of the greater donor power and very much higher dielectric constant of acetonitrile. On the other hand, comparison of toluene with pyridine should reveal the effect of the much higher donor power and higher dielectric constant of pyridine. It is noteworthy that the change in degree of polymerization when benzene is replaced by acetonitrile is considerably less than the change caused by replacing toluene by pyridine. Hence it was concluded that donor power was much more important in lowering the degree of polymerization than dielectric constant. Consequently, it is believed that the intermolecular bonding in the tantalum alkoxide

TABLE II
Degrees of Polymerization of Tantalum *n*-Alkoxides in Various Solvents (at the b.p.)

	Solvent				
R in $Ta(OR)_5$	Benzene (b.p. 80°; D 2.28)	Toluene (b.p. 110°; D 2.38)	Aceto-nitrile (b.p. 82°; D 38.8)	Pyridine (b.p. 114°; D 12.5)	Diisopropyl ether (b.p. 68°; D ~3)
Me	1.98	1.83	1.50	1.01	1.75
Et	1.98	1.83	1.50	0.99	1.84
Pr^n	1.95	1.83	1.50	0.99	1.84
Bu^n	2.02	1.83	1.48	0.99	1.84

polymers is covalent rather than electrostatic in nature. It is also interesting to find that all of the tantalum *n*-alkoxides were monomeric in pyridine which suggests the existence of complexes such as $Ta(OR)_5 \cdot C_5H_5N$ with nitrogen coordinated to tantalum. Nevertheless, evaporation of the solvent left the alkoxide free of addendum so that the complexes are relatively unstable. The importance of donor power is also revealed in the comparison between benzene and diisopropyl ether, where the greater donor power of the latter is opposed by the difference in boiling points. The lower degree of polymerization of tantalum methoxide in the ether compared with the other alkoxides strongly suggests that steric factors are involved. The approach of the highly branched ether molecule will obviously be less opposed by the methoxide than by the higher *n*-alkoxides.

TABLE III
Volatilities of Metal Amyloxides
(In °C./mm. Hg)

R in $M(OR)_x$	Metal					
	Al (40)	Fe (105)	Ti (101)	Zr (101)	Nb (15)	Ta (103)
$CH_3(CH_2)_4$	255/1.0	178/0.1	175/0.8	256/0.01	228/0.1	233/0.1
$(CH_3)_2CH(CH_2)_2$	195/0.1	(200/0.1)[a]	148/0.1	247/0.1	199/0.1	210/0.1
$(CH_3)(C_2H_5)CHCH_2$	200/0.6	178/0.1	154/0.5	238/0.1	183/0.1	204/0.1
$(CH_3)_3CCH_2$	180/0.8	159/0 1	105/0.05	188/0.2	126/0.1	130/0.1
$(C_2H_5)_2CH$	165/1.0	163/0 1	112/0.05	178/0.05	138/0.1	153/0.1
$(CH_3)(n\text{-}C_3H_7)CH$	162/0.5	165/0.1	135/1 0	175/0.05	137/0.1	148/0.1
$(CH_3)(\text{iso-}C_3H_7)CH$	162/0 6	162/0.1	131/0 5	156/0.01	139/0.1	137/0.1
$(CH_3)_2(C_2H_5)C$	—	131/0 1	98/0.1	95/0.1	—	139/0.1

[a] Value doubtful because of decomposition.

C. VOLATILITY STUDIES

The striking effect of the alkyl group on the volatility of a zirconium alkoxide was first pointed out by Bradley and Wardlaw (12). Thus, notwithstanding the increase in formula weight from $Zr(OEt)_4$ to $Zr(OPr^i)_4$ to $Zr(OBu^t)_4$, the boiling points decreased dramatically from 180°/10^{-4} mm. to 160°/0.1 mm. to 52°/0.1 mm., respectively. The zirconium tetra-*tert*-butoxide "fumes" in the air because of its appreciable vapor pressure at room temperature. The molecular weight studies showed that the ethoxide and isopropoxide were less volatile than the *tert*-butoxide because they were polymeric whereas the latter was monomeric. Evidently the steric effect of the alkoxide groups controls the intermolecular bonding and hence the volatility.

Bradley, Mehrotra, Wardlaw, and their co-workers have determined the boiling points under reduced pressure for the isomeric amyloxides of a number of metals, and the data are collected together in Table III. The measurements were all made under similar experimental conditions and are therefore especially suitable for comparative purposes. By using an isomeric series it was possible to eliminate any effects due to molecular mass of the monomer unit. Accordingly the data for a given metal reflect differences in intermolecular forces. From Table III it is apparent in all cases that branching of the amyl group leads to an increase in volatility and that the neopentyloxides are conspicuously more volatile than the other primary amyloxides. When the data on degrees of polymerization (Table I) are compared with the data in Table III, the direct correlation between decrease in degree of polymerization and decrease in boiling points is outstanding. This suggested that vaporization of the polymeric alkoxides involved a considerable degree of depolymerization which would cause higher latent heats and entropies of vaporization than for the monomeric alkoxide. Some preliminary vapor pressure measurements on titanium and zirconium alkoxides have amply confirmed this. The data are presented in Table IV in the form of the boiling point under 5.0 mm. pressure, the latent heat of vaporization (ΔH_v, kcal./gram mole), the entropy of vaporization at 5.0 mm. pressure ($\Delta S_{5.0}$, cal./°C./gram mole), and the degree of polymerization in boiling benzene. Some idea of the uncertainty in these data may be gauged from the comparison of measurements on zirconium isopropoxide determined independently. It is clear that the entropies are subject to a large probable error, but fortunately the changes in-

TABLE IV

Compound	B.p.$_{5.0}$, °C.	ΔH_v, kcal./gram mole	$\Delta S_{5.0}$, cal./°C./ gram mole	n[a]	Ref.
$Ti(OEt)_4$	138.3	21.6	52.5	2.4	113
$Ti(OPr^i)_4$	91.3	14.7	40.5	(1.4)	111
$Ti(OBu^t)_4$	93.8	14.5	39.5	1.0	112
$Zr(OEt)_4$	234.8	30.2	59.4	3.6	113
$Zr(OPr^i)_4$	203.8	31.5	66.1	3.0	111
$Zr(OPr^i)_4$	202	33.8	71.2	—	94
$Zr(OBu^t)_4$	89.1	15.2	42 0	1.0	112

[a] n = degree of polymerization.

volved from one alkoxide to another are quite large. The data show that the monomeric compounds $Ti(OPr^i)_4$, $Ti(OBu^t)_4$, and $Zr(OBu^t)_4$ have entropies of vaporization of the order of 40 units, whereas the polymeric species have much higher values corresponding to the breakdown of considerable structure in the liquid prior to vaporization. This is also reflected in the higher latent heats of the polymeric alkoxides. Vapor density measurements on zirconium ethoxide and zirconium isopropoxide at approximately 10 mm. pressure showed that these compounds were essentially monomeric in the vapor phase, although the experimental technique was not very refined (113). Some data obtained by Bartley and Wardlaw (94) on the alkali metal zirconium alkoxides are shown in Table V. It is interesting to observe that $LiZr_2(OPr^i)_9$ and $NaZr_2(OPr^i)_9$, which are both monomeric, have entropies of vaporization similar to those of the monomeric titanium and zirconium alkoxides. Mehrotra (36) determined the

TABLE V

Compound	B.p.$_{5.0}$, °C.	ΔH_v, kcal./gram mole	$\Delta S_{5.0}$, cal./°C./ gram mole	n[a]
$LiZr_2(OPr^n)_9$	249	34.3	65.7	1.7
$LiZr_2(OBu^n)_9$	278	32.0	58.1	1.6
$LiZr_2(OBu^s)_9$	238	31.6	61.8	1.0
$LiZr_2(OPr^i)_9$	220	19.0	38.5	1.0
$NaZr_2(OPr^i)_9$	222	21.0	42.4	1.0
$NaZr_2(OBu^n)_9$	269	31.2	57.6	1.0

[a] n = degree of polymerization.

TABLE VI[a]

Compound	B.p.$_{5.0}$, °C.	ΔH_v, kcal./gram mole	$\Delta S_{5.0}$, cal./°C./gram mole	n[b]
$Al(OEt)_3$	184.5(189.0)	23.9(20.2)	52.2(43.7)	4.1
$Al(OPr^n)_3$	232.5(222.7)	27.5(22.3)	54 5(45.0)	4.0
$Al(OBu^n)_3$	270.0(259.6)	29.9(24.9)	55.0(46.7)	3.9
$Al(OPr^i)_3$	124.0(139.1)	19.4(21.1)	48.9(51.2)	3.0
$Al(OBu^s)_3$	172.0(167.3)	21.6(19.5)	48.5(44 3)	2.4

[a] Values in parentheses obtained by Wilhoit (114), others by Mehrotra (36).
[b] n = degree of polymerization.

vapor pressures of a number of aluminum alkoxides, and his results are shown in Table VI together with the results of some more recent work by Wilhoit (114). The discrepancies between the two sets of results are considerable and, as pointed out by Wilhoit, are beyond the expected errors in measuring temperatures and pressures. Moreover, using the isotenoscope technique Wilhoit discovered that certain of the alkoxides of aluminum (e.g., isopropoxide) required a considerable time (1–4 hours) to establish an apparent equilibrium vapor pressure whether approached from a higher or lower temperature. On the other hand, Mehrotra used a dynamic method, and it seems likely that his results do not correspond to true equilibrium between liquid and vapor. Accepting Wilhoit's results as the more reliable it is evident that, with the exception of the isopropoxide, the aluminum alkoxides have entropies of vaporization of the order of 45 cal./°C./gram mole, which is only a few units higher than the value for *monomeric* titanium and zirconium alkoxides. Since Mehrotra (36) has shown these aluminum alkoxides to be polymeric, it follows that there cannot be a great decrease in degree of polymerization in passing from the liquid to the vapor. Mehrotra (40) has in fact determined the vapor density of the isopropoxide and found it dimeric in the vapor compared with trimeric (freshly distilled) in solution in boiling benzene. The change from a trimeric liquid to a dimeric vapor is consistent with the high entropy of vaporization deduced by Wilhoit. Moreover, it was shown by Mehrotra (40) that aluminum isopropoxide exhibits an "aging" effect during which the degree of polymerization increases over a period of months to the value of four. This behavior is believed to have structural significance and is discussed later (Section IV-6).

The volatilities of monomeric metal alkoxides are worthy of some comments. According to the stereochemical theory these compounds are monomeric because the central metal atom is screened by the alkoxide groups and intermolecular bonding is thereby prevented. On this basis the intermolecular forces of the molecule will then be determined mainly by the peripheral organic groups and the metal atom should make only a minor contribution. This is indeed the case. For example, triethylcarbinol forms monomeric alkoxides with titanium, zirconium, cerium(IV), and thorium, and the boiling points of these compounds are quite close: 166, 166, 160, and 154°/1.0 mm., respectively (115). In addition it was found that tantalum penta-*tert*-butoxide, $TaO_5C_{20}H_{45}$ (b.p. 149.5°/5.5 mm.), was very close in volatility to titanium tetra-*tert*-amyloxide, $TiO_4C_{20}H_{44}$ (b.p. 143°/5.0 mm.), which has practically the same number of carbon and hydrogen atoms. This effect is not confined to tertiary alkoxides and the following list of monomeric compounds containing approximately the same number of carbon and hydrogen atoms per molecule includes both secondary and tertiary groups: $Ti(OCMeEt_2)_4$, b.p. 128°/0.1 mm.; $Zr(OCMeEt_2)_4$, 130°/0.1 mm; $Ti(OCHEtPr^n)_4$, 134°/0.1; $Ti(OCHMeBu^n)_4$, 126°/0.1; $Ti(OCHMeBu^t)_4$, 127°/0.1; $Zr(OCHMeBu^t)_4$, 128°/0.1; $Ta(OCHMePr^i)_5$, 137°/0.1; and $Ta(OCMe_2Et)_5$, 139°/0.1. Preliminary vapor pressure measurements on zirconium and hafnium monomeric alkoxides suggested that the hafnium compound was the more volatile in spite of its greater molecular mass (13). This was contrary to expectations based on the empirical rule that an increase in molecular weight causes an increase in boiling point. Bradley and Swanwick (116) have determined the vapor pressures of some monomeric alkoxides of titanium, zirconium, and hafnium with considerable accuracy using static and dynamic methods. The results were fitted to a "three-constant" equation

$$\log P = a + b/T + c \log T$$

The latent heats of vaporization and the relative volatilities, P_{Zr}/P_{Ti} and P_{Hf}/P_{Zr}, were deduced at various temperatures, and some data are presented in Tables VII and VIII on the *tert*-butoxides and *tert*-amyloxides, respectively.

For both series of alkoxides the order of volatilities over the whole temperature range studied is $P_{Hf} > P_{Zr} > P_{Ti}$. A perusal of the data on ΔH_v shows that this interesting situation, in which the heavier

TABLE VII
Vapor Pressures of Titanium, Zirconium, and Hafnium *tert*-Butoxides

Temp.,	$Ti(OBu^t)_4$		$Zr(OBu^t)_4$		$Hf(OBu^t)_4$		$P_{Zr}/$	$P_{Hf}/$
°K.	P	ΔH_v	P	ΔH_v	P	ΔH_v	P_{Ti}	P_{Zr}
300	0.049	15.8	0.066	15.9	0.069	16.3	1.34	1.05
320	0.25	15.2	0.34	15.3	0.36	15.5	1.34	1.08
340	1.00	14.7	1.35	14.8	1.48	14.7	1.35	1.09
360	3.26	14.1	4.42	14.2	4.80	13.9	1.36	1.09
380	9.04	13.5	12.30	13.7	13.05	13.2	1.36	1.06
400	21.41	13.0	29.77	13.1	30.49	12.4	1.39	1.02

TABLE VIII
Vapor Pressures of Titanium, Zirconium, and Hafnium *tert*-Amyloxides

Temp.,	$Ti(OAm^t)_4$		$Zr(OAm^t)_4$		$Hf(OAm^t)_4$		$P_{Zr}/$	$P_{Hf}/$
°K.	P	ΔH_v	P	ΔH_v	P	ΔH_v	P_{Ti}	P_{Zr}
350	0.117	17.3	0.126	18.7	0.134	18.5	1.08	1.06
370	0.44	16.8	0.52	17.8	0.55	17.7	1.19	1.04
390	1.41	16.4	1.77	16.9	1.84	17.0	1.24	1.04
410	3.89	15.9	4.98	16.0	5.24	16.2	1.28	1.05
430	9.55	15.5	12.13	15.1	12.98	15.5	1.27	1.07
450	21.14	15.0	26.01	14.2	28.53	14.7	1.23	1.10

molecule is more volatile, cannot be explained in terms of intermolecular forces because in most cases the latent heats are practically the same. The theoretical consequences of this phenomenon have been discussed by Bradley (117) in terms of the fundamental effect of mass on volatility. It was deduced that in cases where the intermolecular forces for two molecular species are the same, the effect of the molecular mass on the entropy of vaporization may cause the heavier species to be the more volatile. This frequently occurs in the case of isotopically distinguished molecules. Another interesting feature of the data in Tables VII and VIII is the pronounced temperature dependence of the latent heat of vaporization for all six compounds. This might well be due to a small residual amount of intermolecular association, which is not powerful enough to cause polymerization of these compounds in dilute benzene solution, but nevertheless shows up in the thermodynamic properties of the pure liquid.

D. DENSITIES, VISCOSITIES, SURFACE TENSIONS, AND PARACHORS

Owing to the ease with which the metal alkoxides are hydrolyzed, the measurement of physical properties is beset with difficulties, and the literature is rather sparse on the subject of densities, viscosities, and surface tensions. Cullinane *et al.* (50) carried out some measurements on a number of titanium alkoxides, and their results are given in Table IX. The densities of the titanium normal alkoxides from

TABLE IX
Densities and Viscosities of Titanium Alkoxides at 25°C.

R in $Ti(OR)_4$	Viscosity, poises	d_4^{25}, g./ml.
Ethyl	0.4445	1.1044
n-Propyl	1.6135	1.0329
n-Butyl	0.6174	0.9932
n-Amyl	0.7924	0.9735
n-Hexyl	0.6490	0.9499
Allyl	0.6225	1.1138
Isobutyl	0.9740[a]	0.9601[a]
tert-Butyl	0.0355	0.8834

[a] Measured at 50°C.

ethyl to *n*-hexyl showed the expected decrease with increase on organic content of the compound. The *tert*-butoxide had a lower density and hence higher molar volume than the *n*-butoxide. The viscosities of the normal alkoxides showed a peculiar alternating variation with increase in the number of carbon atoms in the alkyl chain. The *tert*-butoxide was noteworthy for its extremely low viscosity. Recently Bradley and co-workers (118) have published results on a number of alkoxides of titanium, zirconium, tin(IV), cerium(IV), and thorium. Measurements of densities, surface tensions, and viscosities were made over the temperature range 25–40°C., and some typical results are given in Table X. It would be inappropriate to make a detailed discussion of these data in this article, but some interesting points demand comment. For example, an analysis of the parachors of the normal alkoxides of titanium showed that the observed values were of the order of 100 units less than calculated. This behavior is consistent with the polymeric nature of these alkoxides. That the tertiary alkoxides of titanium and zir-

TABLE X
Densities, Surface Tensions, and Viscosities of Metal Alkoxides at 25°C.

Compound	Density, g./ml.	Mol. vol., cm.^{3}	Surface tension, dynes/cm.	Parachor	Viscosity, poises
$Ti(OEt)_4$	1.1066	206.2	23.1	454	0.4469
$Ti(OPr^n)_4$	1.0351	274.6	25.4	616	1.7490
$Ti(OBu^n)_4$	0.9958	341.6	25.5	769	0.6920
$Ti(OBu^t)_4$	0.8836	385.0	22.9	844.5	0.0352
$Ti(OAm^t)_4$	0.9049	438.1	25.8	989	0.0808
$Ti(OCMe_2Pr^n)_4$	0.8898	508.5	26.2	1154.5	0.0479
$Ti(OCMeEt_2)_4$	0.9265	488.5	27.6	1220.5	0.3453
$Zr(OBu^t)_4$	0.9570	400.8	20.3	851.5	0.0317
$Zr(OAm^t)_4$	0.9728	452.1	22.9	992	0.0759
$Zr(OCMe_2Pr^n)_4$	0.9514	521.2	23.9	1154.5	0.0464
$Zr(OCMeEt_2)_4$	0.9890	501.5	24.7	1121	0.2810
$Sn(OAm^t)_4$	1.0984	425.4	21.7	919.5	0.1664
$Sn(OCMe_2Pr^n)_4$	1 0499	498.3	22.5	1088	0.0986
$Sn(OCMeEt_2)_4$	1.1136	488.5	—	—	0.4127
$Ce(OCMe_2Pr^n)_4$	1.1768	462.2	—	—	8.1343
$Ce(OCMeEt_2)_4$	1.0774	505.6	24.3	1130.5	0.2161
$Ce(OCEt_3)_4$	1.0684	562.5	25.5	1269	0.5258
$Th(OCEt_3)_4$	1.2230	566.4	22.0	1231.5	0.4920

conium had very similar values of surface tension, parachor, and viscosity emphasizes once again how effectively the metal atoms are screened by the tertiary alkoxide groups. Also the monomeric tertiary alkoxides of titanium and zirconium had considerably lower viscosities than the normal alkoxides, indicating a difference in mechanism of viscous flow. The tertiary alkoxides of tin(IV) were outstanding in having lower parachors and higher viscosities than the corresponding alkoxides of titanium and zirconium. The cerium(IV) derivative of *n*-propyldimethylcarbinol had an extraordinarily high viscosity, while the derivative of ethyldimethylcarbinol had, as expected, a slightly higher parachor than the titanium and zirconium derivatives. Only one liquid alkoxide of thorium was available, and this had a lower parachor and viscosity than the corresponding cerium(IV) derivative. The surface tensions are all within the range 20–28 dynes/cm., irrespective of the metal or the nature of the alkoxide groups.

E. DIPOLE MOMENTS AND REFRACTIVITIES

The ease of hydrolysis of metal alkoxides makes the accurate measurement of refractive indices a matter of great difficulty. However, some measurements have been made on titanium alkoxides, and these data are collected together by Takatani (120). Applying Denbigh's method (121) Takatani calculated the Ti—O bond refraction for several titanium alkoxides from previously reported refractivity data. The mean value of 4.08 cm.^{3}/mole was obtained, and this was used to calculate the molar refractivity of several more

TABLE XI
Densities, Refractive Indices, and Molecular Refractivities of Titanium Alkoxides at Various Temperatures

Compound	Temp., °C.	d_4^t, g./ml.	n_D^t	Molecular refractivity	
				Obs.	Calc.
$Ti(OPr^n)_4$	35	1.0358	1.4907	79.41	79.68
$Ti(OPr^i)_4$	20	0.9711	1.4678	81.34	79.68
$Ti(OBu^s)_4$	35	0.9463	1.4587	98.27	98.20
$Ti(OBu^t)_4$	20	0.8917	1.4368	99.96	98.20
$Ti(OAm^n)_4$	35	0.9703	1.4813	116.34	116.56
$Ti(OAm^t)_4$	20	0.9118	1.4543	117.82	116.56
$Ti(OC_6H_{11})_4$	35	1.0589	1.5155	126.69	126.72
$Ti(OC_7H_{16}^n)_4$	20	0.9430	1.4830	154.05	153.76

titanium alkoxides. Takatani then prepared these alkoxides and measured their refractive indices. The data in Table XI show the comparison between the measured and calculated molar refractivities. The agreement is definitely poorer for the isopropoxide, *tert*-butoxide, and *tert*-amyloxide than for the other compounds.

Arbusov and Shavsa (119) were the first to report measurements of the dipole (electric) moments of titanium alkoxides. The following results were obtained from measurements in benzene solution at 20°C.: $Ti(OBu^n)_4$, 1.68; $Ti(OC_6H_{13})_4$, 1.62; $Ti(OC_7H_{15})_4$, 1.60; $Ti(OC_8H_{17})_4$, 1.67; and $Ti(OC_9H_{19})_4$, 1.68 Debye units. These values are a little lower than the theoretical 1.70 Debye units calculated by Zahn's method (124) for tetrahedral molecules with freely rotating alkoxide groups. Arbusov and Shavsa (119) calculated a dipole moment of 1.63 Debye units for a conformation containing two alkoxide chains lying in one plane and the other two chains lying in a perpendicular plane. At about the same time Crowe and Caughlan (122) determined the dipole moments of $Ti(OEt)_4$, $TiCl(OEt)_3$, and $TiCl_3(OC_6H_5)$ in benzene solution and obtained values of 1.41, 2.87, and 2.97 Debye units. However, they used Eyring's method (125) and calculated a dipole moment of 2.11 Debye units for a freely rotating tetrahedral titanium tetraalkoxide. Later, Caughlan *et al.* (123) determined the dipole moments of $Ti(OEt)_4$, $Ti(OPr^n)_4$, $Ti(OBu^n)_4$, and $TiCl(OEt)_3$ in *n*-hexane solution and obtained the values 1.50, 1.20, 1.15, and 2.51 Debye units, respectively. These workers pointed out that the decrease in moment in ascending the homologous series from $Ti(OEt)_4$ to $Ti(OBu^n)_4$ could be due to greater restriction of rotation of the alkoxide groups with increase in size of the alkyl group. They also observed that the calculated dipole moment ($\mu^2 = 4m^2 \sin^2 \phi$, where m is the OR bond moment and ϕ the oxygen valence angle) would be sensitive to the oxygen valence angle which might be considerably affected by the ionic character of the Ti—O bond. By and large the situation regarding dipole moments is far from satisfactory because the results of Arbusov and Shavsa for $Ti(OBu^n)_4$ (1.68) were not confirmed by Caughlan *et al.* (1.15). Furthermore, the calculated values for freely rotating tetrahedral alkoxides (i.e., 1.70 or 2.11) are not in agreement. Interpretation of the results is rendered difficult by our lack of knowledge of the bond angles in the metal alkoxides.

F. STRUCTURAL ASPECTS OF METAL ALKOXIDES

A major problem concerning the structural chemistry of the metal alkoxides is the lack of direct structure determinations. There are indications that this unsatisfactory state of affairs is being remedied. Wheatley (126) has disclosed some results on the X-ray powder diffraction patterns of the alkali metal alkoxides and alcoholates. For example, lithium methoxide has a two-dimensional layer structure analogous to that of lithium hydroxide. The $LiOCH_3$ bond angle is 114.5 degrees, the Li—O distance 1.95 A., and the O—CH_3 distance 1.42 A. Each oxygen is bonded to four lithiums and a methyl group in the form of a square pyramid with oxygen at the center and methyl at the apex. Each lithium is surrounded by four oxygens in this form of a squashed tetrahedron. The OLiO angles are 131.1 and 101.7 degrees, while the LiOLi angle is 80.3 degrees. In view of the environment of the oxygens it is simplest to consider the structure as ionic, although a giant covalent polymer cannot be entirely ruled out. Some single crystal work has been carried out by Imam (127) who found that $Zr(OPr^i)_4 \cdot Pr^iOH$ was triclinic, with eight molecules in the unit cell, $Ta(OEt)(OBu^i)_4$ orthorhombic with four molecules in the unit cell, and $Ti(OBu^i)_4 \cdot Bu^iOH$ monoclinic with two molecules in the unit cell. The complexity of these molecules makes a complete structural determination a major task. Caughlan (128) has reported a similar state of affairs with the X-ray diffraction of $Ti(OEt)_4$, which appears to have a large unit cell containing many molecules. This is particularly unfortunate because the structure of titanium tetraethoxide is the crucial factor in a structural theory for metal alkoxides.

Attempts have been made to deduce structures of metal alkoxides on the basis of their degree of polymerization. An early example was the suggestion by Sidgwick and Sutton (100) that the tetrameric thallous alkoxides had a cubic structure containing four thallium atoms and four oxygen atoms at the corners of a cube. Each oxygen was bonded to three thallium atoms and an alkyl group in a compact structure. Robinson and Peak (79) proposed a ring structure for the tetrameric aluminum alkoxides in which each aluminum was tetrahedrally coordinated to oxygen. Caughlan and co-workers (108) found that titanium *n*-alkoxides approached a limiting trimeric state in concentrated solutions and concluded that the trimer was a unit of structural significance. Bearing in mind the 6-coordina-

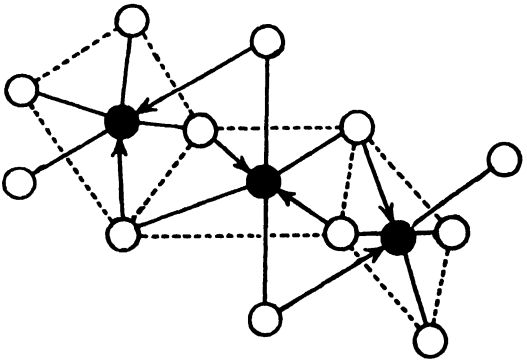


Fig. 1. Structure of $Ti_3(OEt)_{12}$. ● = Ti; O = O in OEt.

tion of titanium by oxygen in rutile (TiO_2), they proposed two alternative structures for $Ti_3(OR)_{12}$ based on octahedrally coordinated titanium. One of these structures, with the ethyl groups omitted, is shown in Figure 1. The structure is based on a group of three octahedra which share faces and form a compact unit. Bradley *et al.* (113) proposed the structure shown in Figure 2 for the dimeric solvated zirconium isopropoxide $Zr_2(OPr^i)_8 \cdot 2Pr^iOH$. This is based on octahedrally coordinated zirconium with two octahedra sharing an edge. A similar structure was proposed by Bradley *et al.* (16) for the dimeric tantalum pentaalkoxides, $Ta_2(OR)_{10}$, with 6-coordinated tantalum. The two coordinated alcohol molecules in Figure 2 are replaced by alkoxide groups in the structure for $Ta_2(OR)_{10}$.

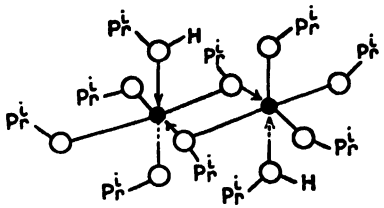


Fig. 2. Structure of $Zr_2(OPr^i)_8 \cdot 2Pr^iOH$. ● = Zr; O = oxygen.

In the case of thorium alkoxides it was suggested by Bradley *et al.* (14) that octameric structures might be present containing 8-coordinated thorium as in $Th_8(OR)_{32}$. A possible structure for the octamer is shown in Figure 3 with a cubic coordination of the thorium.

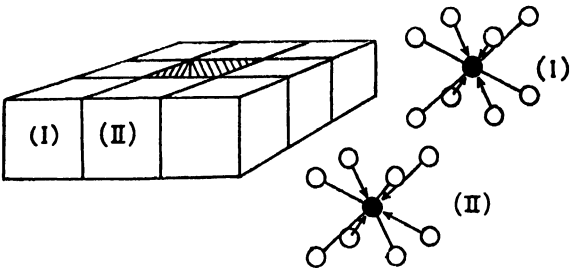


Fig. 3. Structure of $M_8(OR)_{32}$. ● = M; O = O in OR.

There are two types of cube, a corner cube (I) and a side cube (II), which differ only in the distribution of primary covalent and coordinated OR groups around each thorium. A common feature of these structures postulated for polymeric metal alkoxides has been the covalency expansion of the metal. However, it has been necessary arbitrarily to assign a structure for each particular metal alkoxide polymer. Recently a theory was proposed by Bradley (130) which not only correlates the previously proposed structures but also forms a basis for predicting degrees of polymerization and structures in terms of the valency, coordination number, and stereochemistry of the metal. The theory took account of the fact that only low degrees of polymerization were exhibited by metal alkoxides, although on the basis of the suggested coordination numbers of the metal infinite polymers were quite feasible. This peculiarity of forming very low polymers was especially prevalent in the titanium oxide alkoxides $[TiO_x(OR)_{4-2x}]_n$ formed by the hydrolysis of titanium alkoxides. In the case of titanium oxide ethoxides Bradley, Gaze, and Wardlaw (129) obtained remarkable agreement between observed degrees of polymerization and those calculated from the relationship $n = 12/(4-3h)$, where n = degree of polymerization and h = degree of hydrolysis (i.e., ratio of gram moles of water added per gram mole of $Ti(OEt)_4$). This relationship was derived from a consideration of the structures of the titanium oxide ethoxides in terms of 6-coordinated titanium. Thus it was postulated that the trimer units of Figure 1 were brought together in the process of hydrolysis which involved the replacement of TiOEt groups from adjacent units by Ti—O—Ti bridges. Logically the first hydrolytic polymer would contain six titanium atoms from two trimer units in the new molecule,

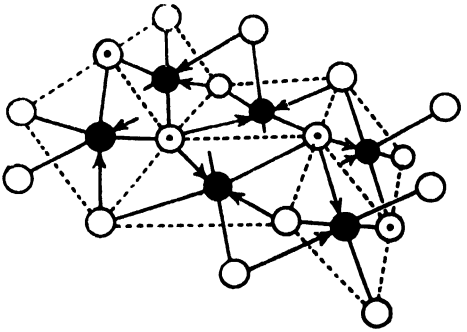


Fig. 4. Structure of $Ti_6O_4(OEt)_{16}$. ● = Ti; O = O in OEt; ⊙ = O in Ti·O·Ti

$Ti_6O_4(OEt)_{16}$. The structure for this hexamer is shown in Figure 4, and it is noteworthy that each titanium is octahedrally coordinated with oxygen. This formula explained very well the analytical data on a crystalline product formed very readily in the early stages of the hydrolysis of titanium ethoxide. It was shown that a series of polymers of the general formula $Ti_{3(x+1)}O_{4x}(OEt)_{4(x+3)}$ (where $x = 0, 1, 2, \ldots \infty$) would be predicted on the basis of the trimerwise mode of hydrolytic polymerization, and this enabled the authors to explain a number of hitherto perplexing features in the hydrolysis of titanium alkoxides. A common feature of these structures was that each one represented the smallest polymer possible for such a derivative of the metal in its higher coordination number. This led Bradley (130) to propose that the metal alkoxides also adopt the smallest possible polymer consistent with all of the metal atoms attaining a higher coordination number. In other words an octahedrally coordinated metal prefers to form alkoxide bridges by involving the three oxygens at the face of an octahedron rather than the two oxygens at an edge or the one at an apex. With this principle in mind and an assumption concerning the stereochemistry of the metal it is possible to work out a feasible structure for any metal alkoxide polymer. A particularly interesting case arises whenever the metal can adopt more than one higher covalency than its characteristic group valency. A case in point is aluminum, which is known to exhibit higher coordination numbers of 4 (tetrahedral) or 6 (octahedral). For the former the structural theory (130) predicts a dimer and for the latter an octamer. There are two other possible structures involving a tetramer and a hexamer containing both 4- and 6-co-

ordinated aluminum. Bradley has suggested that the interesting "aging" effects exhibited by certain aluminum alkoxides might be caused by slow structural rearrangements resulting from the aluminum changing from one higher coordination number to another. If this interpretation is correct, it would not be surprising to find "aging" effects among the alkoxides of zirconium, thorium, and uranium(V) because these metals also have a choice of higher coordination numbers. In addition to explaining the structural aspects of titanium oxide alkoxides (55,129), the theory has also been used in interpreting the nature of the polymers formed by the hydrolysis of the alkoxides of zirconium (96) and of niobium, tantalum, uranium, cerium(IV), tin(IV), and aluminum (45). These theoretical developments serve to emphasize the need for direct structure determination on the metal alkoxides.

Acknowledgments

The author is most indebted to the many collaborators with whom it has been a privilege to work in this field. He thanks Professor C. N. Caughlan, Professor R. C. Mehrotra, and Dr. P. J. Wheatley for releasing advance information on their research work and the Chemical Society for permission to reproduce Figures 1–4.

Thanks are also due to the National Research Council of Canada whose assistance has facilitated the preparation of this article.

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