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THE HIGH-TEMPERATURE CHEMISTRY OF FISSION-PRODUCT ELEMENTS

Summary Report, August 1, 1960 Through July 31, 1961

By
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August 29, 1961

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CHEMISTRY

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FISSION-PRODUCT ELEMENTS

SUMMARY REPORT

August 1, 1960, through July 31, 1961

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I. INTRODUCTION

Since our last summary report⁽¹⁾ was submitted, a study of the rhodium-chlorine system has been completed and work has progressed on the osmium-chlorine system. An extended discussion of the transpiration method,⁽²⁾ based on a paper presented at a Gordon Conference,⁽³⁾ has been written. Papers on the ruthenium-chlorine⁽⁴⁾ and palladium-chlorine⁽⁵⁾ systems have been published. A study has been undertaken to correlate data obtained in this laboratory on the transition metal chlorides with other available data on the transition elements. A paper on the chlorides of the palladium-group metals is to be presented at the International Congress of Pure and Applied Chemistry, August 6-12, 1961.⁽⁶⁾

This report summarizes these accomplishments.

II. THE RHODIUM-CHLORINE SYSTEM

Work on the high-temperature chemistry of the rhodium-chlorine system has been completed, and an account of the work is to be submitted to the Journal of Physical Chemistry.⁽⁷⁾ This work was unique in that a radioactive tracer was used in the vapor-pressure measurements.

The findings of this work may be summarized as follows: Under the conditions studied, RhCl_3 is the only stable condensed chloride. The dissociation pressure of the chloride reaches 1 atm at 970°C . Chlorine pressure-dependence data indicate that RhCl_2 and RhCl_3 are the important gaseous species. At 1504°C and 1 atm chlorine pressure, the partial pressure of RhCl_2 is 6.5×10^{-3} atm and the partial pressure of RhCl_3 is 15×10^{-3} atm. Below 970°C , where RhCl_3 is the condensed phase, the vapor pressures fall off rapidly with decreasing temperature; and at 802°C , the partial pressures of RhCl_2 and RhCl_3 are 4×10^{-7} and 1.7×10^{-5} atm, respectively.

III. THE OSMIUM-CHLORINE SYSTEM

Studies are in progress on the high-temperature chemistry of the osmium-chlorine system. Appendix A is an account of the results obtained thus far; these results are summarized in this section.

Under the conditions studied, OsCl_3 is apparently the stable condensed phase. The dissociation pressure of the chloride reaches 1 atm at $600 \pm 10^\circ\text{C}$. The important vapor species appear to be OsCl_4 , OsCl_3 , and OsCl_2 . Above 600°C , where the metal becomes the stable condensed phase, the partial pressure of OsCl_4 decreases with increasing temperature and OsCl_3 and OsCl_2 become the important gaseous species.

We have found osmium to be a much more intractable element than the others in the platinum metal group that have been studied so far. Complete chlorination of the metal by direct reaction has not been possible. We have produced the chloride in quantity only as vapor which may then be condensed to yield the solid chloride. In the temperature range of 600° to 1100°C , we have not yet been able to obtain equilibrium vapor pressures in measurements by the transpiration method.

IV. THE RUTHENIUM-CHLORINE SYSTEM

A paper on the gaseous chlorides of ruthenium at high temperature has been published in the Journal of Physical Chemistry.⁽⁴⁾

The following is an abstract of the results: Under the conditions studied, RuCl_3 is the only stable condensed chloride of ruthenium. Over $\text{RuCl}_3(\text{s})$, $\text{RuCl}_4(\text{g})$ is the important gaseous species. Above 853°C , the temperature at which $\text{RuCl}_3(\text{s})$ decomposes under 1 atm chlorine pressure, the partial pressure of $\text{RuCl}_4(\text{g})$ decreases with increasing temperature and $\text{RuCl}_3(\text{g})$ becomes the important gaseous species. Thermodynamic quantities were calculated for the various reactions involved.

V. THE PALLADIUM-CHLORINE SYSTEM

An account of our work on the high-temperature chemistry of the palladium-chlorine system has been published in the Journal of Physical Chemistry.⁽⁵⁾

Briefly, the findings of this work are as follows: The only stable solid chloride of palladium is PdCl_2 . It melts at 680°C . The solubility of palladium in liquid PdCl_2 is small near the melting point of the compound but increases with temperature. Over the condensed chloride, a gaseous polymer, $\text{Pd}_5\text{Cl}_{10}$, is the principal gaseous species. Above 980°C , the temperature at which Pd(s) becomes the condensed phase at 1 atm chlorine pressure, the partial pressure of $\text{Pd}_5\text{Cl}_{10}(\text{g})$ decreases rapidly with temperature, and $\text{PdCl}_2(\text{g})$ becomes the main gaseous species.

VI. PRESENTATION AT INTERNATIONAL CONGRESS OF PURE AND APPLIED CHEMISTRY

A paper will be presented⁽⁶⁾ at the International Congress of Pure and Applied Chemistry, Montreal, Canada, August 6-12, 1961, in which the high-temperature chemistry of the chlorides of the palladium-group metals is to be discussed.

VII. DIFFUSION AND KINETIC EFFECTS IN THE TRANSPIRATION METHOD

The kinetic problems encountered in the transpiration method of vapor-pressure measurement are of two principal kinds. At low flow rates vapor diffusion contributes significantly to the quantity of vapor transported, and at high flow rates kinetic limitations prevent saturation of the carrier gas. These aspects of the transpiration method were discussed in an invited paper presented at the Gordon Conference on High Temperature Chemistry held at Meriden, New Hampshire, August 29-September 2, 1960. The text of this paper has since been published in the form of a General Atomic report.⁽³⁾

Diffusion effects in the transpiration method have been studied in conjunction with vapor-pressure and dissociation-pressure measurements in the palladium-chlorine system. The main purpose of this study was to compare experimental behavior with the behavior predicted by a theoretical treatment which has been developed. ⁽⁸⁾⁽⁹⁾ We determined experimentally the effect of flow rate on the quantity of vapor transported at 1400°C; although the data are somewhat scattered, we found reasonable agreement with the predicted behavior. In the diffusion studies, we also looked at the possibility of using interdiffusion coefficients as a means of characterizing diffusing species. This approach does not look promising, however, because too few data are available from other sources to make reliable estimation possible. The results of these diffusion studies are presented in the General Atomic report mentioned above. ⁽³⁾

VIII. THE TRANSPIRATION METHOD

An extensive review covering various aspects of the transpiration method has been issued as a topical report under this contract. ⁽²⁾ Eventually, this information may also be included in a book being compiled and edited by Professor John R. Margrave, University of Wisconsin.

In the report, aspects of experimental techniques that may be helpful to the investigator in designing apparatus and conducting experiments are reviewed. Diffusion and kinetic effects of the transpiration method are discussed to show how they limit the usefulness of the method, particularly in high-temperature chemistry. Techniques for applying the method in order to establish the identity of vapor species are described.

IX. IDENTIFICATION OF VAPOR SPECIES BY VARIATION IN METAL ACTIVITY

At the close of the last reporting period, we had outlined a plan to determine the number of metal atoms in gaseous metal chlorides. The

approach involved a study of the effect of metal activity on vapor pressure. We felt that this was a novel approach, and we planned to use it in the palladium-chlorine system. However, it has since come to our attention that Alcock and Hooper⁽¹⁰⁾ have used the method in studies of the gaseous oxides of the platinum group; therefore, we have not used the method.

X. THE CHEMISTRY OF TRANSITION METAL CHLORIDES

We have undertaken a study of experimental data on chlorides of the transition metal elements to find out how the chemistry of these elements varies across and down the periodic table. The main purpose of this study is to make correlations that will aid in predicting the behavior of elements for which data are not available. The correlations will also be of value as a guide for selecting elements for future studies.

The transition metal elements are peculiar in that they have the ability to form compounds in which the outermost set of five stable electron orbitals is only partially filled. The presence of incomplete electron shells causes deviations in the relative stabilities of the transition metal compounds. For example, the lattice energies of the divalent halides of the metals of the first transition series do not vary steadily through the series; instead, they show a distinct minimum at divalent manganese. This behavior has been adequately explained by the so-called ligand-field theory. The ligand-field theory takes into account the splitting in energies of the d orbitals of the central metal ion produced by the electrostatic field of attached ligands (atoms or groups which are directly attached to a metal ion).

Owing to a lack of experimental data, very little has been done in applying the ligand-field theory to the second and third transition series. It is hoped that enough data can be accumulated to show whether or not the theory applies in these series.

Appendix B describes in detail progress which we have made so far in finding thermodynamic data for the chlorides of the transition elements. Included in the Appendix is a brief discussion of the ligand-field theory.

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Appendix A

THE OSMIUM-CHLORINE SYSTEM AT HIGH TEMPERATURE

by

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INTRODUCTION

This Appendix discusses results which have been obtained thus far in a study of the high-temperature chemistry of the osmium-chlorine system. This work was undertaken to identify condensed phases and vapor species, to measure dissociation and vapor pressures, and to calculate thermodynamic quantities for the various reactions and species involved.

A paper by Ruff and Bornemann⁽¹⁾ appears to be the only literature reference of note on the high-temperature chemistry of the osmium-chlorine system. They reported the preparation of the solid chlorides OsCl_4 , OsCl_3 , and OsCl_2 , and described the properties of these compounds.

EXPERIMENTAL

Dissociation Pressures

Dissociation pressures have not yet been measured quantitatively. Measurements will be attempted by both the static and transpiration methods as described in an earlier report.⁽²⁾

Vapor-pressure Measurements

Vapor pressures are being measured by the transpiration method essentially as described in a previous report.⁽³⁾ Quartz reaction tubes are used up to 1000°C , and mullite tubes are used above that temperature. Chlorine serves as the carrier gas. To determine the quantity of osmium condensed, the condensing region is broken up and placed in nitric acid

solution. The osmium is separated as the volatile oxide and determined colorimetrically using the thiourea method.

Flow-rate Studies

The effect of flow rate and identity of the solid reactant on vapor saturation of the carrier gas has been studied under various conditions of temperature and chlorine pressure. Typical results are shown in Table 1.

It is apparent from these results that saturation vapor pressures are not easily attained under some temperature and chlorine-pressure conditions. This is particularly true at temperatures below 1100°C under chlorine-pressure conditions where Os(s) is the stable condensed phase. There also appears to be some difficulty at higher temperatures when working at low chlorine pressures. There appears to be little difficulty where the stable condensed phase is osmium chloride, that is, at temperatures below 600°C.

The results of the flow-rate studies show that saturation of the carrier gas is greatly aided by (1) using low flow rates, (2) increasing the amount of condensed phase exposed to the carrier gas, and (3) pretreating the metal with hydrogen gas at high temperature prior to an experiment.

A further check on saturation effects can be obtained by using a treatment outlined by Merten and Bell (page 22 of Ref. 4). This treatment considers the effect of evaporation rate on saturation of the carrier gas. Gas mixing is assumed good across the diameter of the reaction tube. To apply this treatment, a value for the evaporation coefficient, α , is needed. This we can obtain by using the Langmuir equation,

$$\alpha = \frac{E(2\pi RTM)^{1/2}}{(p_o - p_a)}, \quad (1)$$

where E is the net evaporation rate (moles/cm²/sec), and p_o and p_a are the saturation vapor pressure and actual vapor pressure, respectively.

The other symbols are defined as usual.

In order to calculate α , we apply Eq. (1) to experiments in which we

Table 1

EFFECT OF FLOW RATE AND IDENTITY OF SOLID REACTANT
ON MOLE RATIO(Moles of Os condensed/mole of Cl_2 passed)

System Pressure (atm)	Cl_2 + Os Flow Rate (millimoles per min)	Weight of Condensed Reactant (g)	Solid Reactant Used*	Mole Ratio $\text{Os}/\text{Cl}_2 \times 10^3$
Temperature, 498°C				
0.99	0.013	1.0	chloride	20.5
0.99	0.020	1.4	reduced	16.9
0.99	0.027	1.1	chloride	16.4
0.99	0.032	1.0	chloride	16.2
0.99	0.047	1.1	chloride	19.6
Temperature, 898°C				
1.0	0.0073	1.9	used	2.6
0.99	0.012	0.4	new	2.9
0.99	0.023	1.9	used	3.0
0.99	0.027	1.0	reduced	18.3
0.99	0.041	1.9	used & reduced	3.6
Temperature, 1204°C				
0.99	0.0085	0.5	used	69
0.99	0.010	2.2	used	73
0.99	0.029	0.4	used	57
0.99	0.037	2.4	new	73
0.99	0.069	2.3	used	26
0.99	0.088	0.4	new & used	26
0.99	0.149	0.4	used	15
Temperature, 1304°C				
0.25	0.007	2.0	used	70.6
0.25	0.022	2.0	used	65.1

*

The solid reactants used were as follows:

Chloride: solid osmium chloride made in a previous experiment.Reduced: osmium metal which had been reduced with hydrogen at high temperature.Used: osmium metal which remained in tube from previous experiment.New: osmium metal sponge as received from Johnson-Matthey Co.

have prepared osmium chloride by heating the underside of a 1-cm-inside-diameter reaction tube containing osmium metal in a chlorine atmosphere, as described below. In a typical experiment, about 1.5 g of osmium chloride condenses on the inside upper surface of the tube in a 24-hr period. We assume the metal sample to have a surface area of 100 cm^2 . In the following discussion, it will be seen that the vapor is OsCl_4 ; therefore, M is 332 g/mole. From these data, we calculate E to be 5.2×10^{-10} mole/ cm^2 /sec. The saturation vapor pressure, p_o , is $\sim 10^{-2}$ atm, T is $\sim 700^\circ\text{K}$, and p_a is assumed to be negligible. Substituting these values into Eq. (1), we calculate α to be 6×10^{-7} . Using this value in the relationship $v \ll 5.1 \times 10^4 \alpha$ (cm^3 /sec) given by Merten and Bell, we find saturation problems will exist unless flow rates are less than $3.0 \times 10^{-2} \text{ cm}^3$ /sec. This value is equivalent to 0.08 millimole/min at room temperature and 1 atm chlorine pressure. Our experimental flow rates are of this order; therefore, it is not surprising that saturation difficulties are being experienced.

General

Osmium sponge (Johnson Matthey, 99.995% purity) ammonium chloroosmate (Engelhard), and $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ (Engelhard) are being employed. The other materials being used are essentially as described previously.⁽³⁾

RESULTS

Condensed Phases

Considerable effort has been devoted to attempts to make pure osmium chloride for use in dissociation-pressure measurements. Direct chlorination of osmium metal powder proceeds very slowly. This is shown by the results of an experiment in which osmium metal and chlorine gas at 1 atm pressure were allowed to react for 18 hr at 500°C . The product contained only enough chlorine to be $\text{OsCl}_{0.4}$. (Analyses of the chlorides were performed gravimetrically by hydrogen reduction.) Dehydration of commercial

$\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ in a chlorine stream at 400°C gave material which was contaminated with oxides.

Several attempts were made to produce the chloride from commercial ammonium chloroosmate, $(\text{NH}_4)_2\text{OsCl}_6$. Samples of the chloroosmate were heated in a chlorine stream at temperatures ranging from 350° to 550°C for as long as 15 hr; however, none of the products were entirely free of ammonia.

Osmium chloride free of contamination can be made by condensing the vapor which results from passing chlorine over the metal at temperatures above 500°C ; however, this is a slow process. Material made in this manner consistently showed a chlorine content close to that of OsCl_4 .

We find that osmium chloride can be made conveniently by heating the underside of a 1-cm-inside-diameter reaction tube containing osmium metal in a chlorine atmosphere. The chloride forms on the hot surface of the metal, vaporizes, and condenses on the inside upper surface of the reaction tube. Since the path from vaporization to condensation is only a few millimeters, the chloride forms rapidly, and a gram or so can be made overnight. Chemical analyses consistently showed material made in this manner to have a chlorine content close to $\text{OsCl}_{3.9}$. The material condenses in the form of a grayish-black crust which does not appear to be hygroscopic. A powder X-ray pattern of the material showed no metal lines and appeared to be similar to patterns obtained for the isomorphous compounds CrCl_3 , RuCl_3 , and RhCl_3 .

Attempts were made to prepare pure $\text{OsCl}_3(\text{s})$ from samples of the chloride made in the manner just mentioned. Samples of the chloride were held at high temperature and at 1 atm chlorine pressure for many hours, and the remaining material was analyzed. A sample held at 590°C for 4 hr yielded $\text{OsCl}_{3.21}$, a second sample at 590°C for 26 hr yielded $\text{OsCl}_{3.27}$, and a third sample at 575°C for 45 hr yielded $\text{OsCl}_{2.90}$. These results suggest that $\text{OsCl}_4(\text{s})$ is unstable under the temperature and chlorine-pressure conditions studied and that $\text{OsCl}_3(\text{s})$ is the stable condensed chloride. The conversion occurs slowly, however.

A sample of $\text{OsCl}_{3.9}$ decomposed completely to metal at 610°C and 1 atm chlorine pressure. This result suggests that lower chlorides, such as $\text{OsCl}_2(\text{s})$ and $\text{OsCl}(\text{s})$, do not exist. Also, this result coupled with above-mentioned results indicates that the dissociation pressure of the chloride reaches 1 atm in the temperature range of 590° to 610°C .

Ruff and Bornemann⁽¹⁾ reported the preparation of $\text{OsCl}_4(\text{s})$ by slow cooling of vapor produced by passing chlorine gas over osmium metal at 650° to 700°C . This compound was produced in the form of a black, brittle crust. On rapid cooling of the vapor, they found that $\text{OsCl}_3(\text{s})$ formed. These investigators attempted to make $\text{OsCl}_3(\text{s})$ by decomposition of ammonium chlorooxamate in a chlorine stream at high temperature; however, they found that the product consistently contained 6% to 7% of ammonium chloride. $\text{OsCl}_3(\text{s})$ was found to be a dark brown, porous, hygroscopic powder. These authors also reported the preparation of $\text{OsCl}_2(\text{s})$ by heating $\text{OsCl}_3(\text{s})$ at about 500°C and at 350 mm chlorine pressure or in vacuum; they found the dichloride to be a dark brown, water-insoluble powder.

On the basis of our results and those of Ruff and Bornemann, we strongly suspect that $\text{OsCl}_4(\text{s})$ is metastable and that $\text{OsCl}_3(\text{s})$ is the stable condensed phase under our temperature and chlorine-pressure conditions. We doubt that $\text{OsCl}_2(\text{s})$ exists as a stable phase.

Dissociation Pressures

The results just discussed indicate that $\text{OsCl}_3(\text{s})$ is the stable condensed phase and that the dissociation pressure of the compound reaches 1 atm at $600 \pm 10^\circ\text{C}$. This knowledge can be used to estimate ΔH_{873}° for the formation reaction,

We estimate $\Delta S_{873}^\circ = -52 \pm 3$ e. u. for this reaction on the basis of ΔS_T° values for analogous reactions in the ruthenium-chlorine and rhodium-chlorine systems.⁽²⁾⁽⁵⁾ From the relationship $\Delta F_T^\circ = 0 = \Delta H_T^\circ - T\Delta S_T^\circ$, we

calculate $\Delta H_{873}^{\circ} = -45 \pm 4$ kcal/mole for reaction (2).

From a rough rule given by Kubaschewski and Evans, ⁽⁶⁾ we estimate ΔC_p for the reaction to be 4.5 cal/mole/ $^{\circ}$ K; assuming it constant over the range 298 $^{\circ}$ to 873 $^{\circ}$ K, we calculate $\Delta H_{298}^{\circ} = -48 \pm 5$ kcal/mole. This is in agreement with Brewer's estimate of -45 ± 5 kcal/mole. ⁽⁷⁾

Identification of Vapor Species

Since the stable condensed phases appear to be Os(s) and OsCl₃(s), the solid-vapor equilibria to be considered are

From the equilibrium constant for reaction (3), we obtain

$$\log p_{\text{Os}_x\text{Cl}_y} = \frac{y}{2} \log p_{\text{Cl}_2} + \log K$$

A similar expression is obtained for reaction (4), and we evaluate $y/2$ and $(y-3x)/2$ by studying the effect of chlorine pressure on vapor pressure. Where both equilibria can be studied at the same temperature, both x and y can be evaluated. This has not yet been done in our studies; therefore, in the following discussion, we assume x to be one.

Chlorine pressure-dependence curves measured at 1104 $^{\circ}$, 1304 $^{\circ}$, and 1506 $^{\circ}$ C are shown in Fig. 1a. The data were plotted assuming one gaseous molecule per osmium atom condensed. Reaction (3) is the vaporization reaction, since Os(s) is the condensed phase under the chlorine pressures used. The observed slopes are 1.4, 1.3, and 1.2 at 1104 $^{\circ}$, 1304 $^{\circ}$, and 1506 $^{\circ}$ C, respectively; thus $y = 2.6$. The fact that this is not a whole number is interpreted to mean that the vapor is composed of both OsCl₂(g) and OsCl₃(g). For this combination of species, one would expect the observed pressure-dependence curves to show more upward concavity than they do.

(a)

(b)

Fig. 1--Effect of chlorine pressure on vapor pressure, assuming one gaseous molecule per osmium atom condensed: (a) at 1104°, 1304°, and 1506°C; (b) at 498°C

In explanation of this, it is presumed that saturation vapor pressures were not attained at the lower chlorine pressures.

A small amount of pressure-dependence data have been obtained in the temperature and chlorine-pressure range where $\text{OsCl}_3(\text{s})$ is the stable condensed phase. These data are shown in Fig. 1b. In this case, reaction (4) is the vaporization reaction. The slope of the line is 0.6; thus, we presume $(y - 3x)/3$ is 0.5. This indicates the important vapor species over the solid chloride to be $\text{OsCl}_4(\text{g})$.

Temperature Dependence of Vapor Pressure

From the results so far mentioned, we surmise that

is the important reaction when $\text{OsCl}_3(\text{s})$ is the stable condensed phase, and that

are the important reactions when $\text{Os}(\text{s})$ is the condensed phase. Reaction (8) apparently becomes less important and reactions (6) and (7) become more important as the temperature increases.

Figure 2 shows the temperature dependence of observed vapor pressures in equilibrium with the stable condensed phase, $\text{Os}(\text{s})$ or $\text{OsCl}_3(\text{s})$, at 1 atm chlorine pressure. The points represent total vapor pressures and were plotted assuming one gaseous molecule per osmium atom condensed. Part of the values were taken from the pressure-dependence curves (Figs. 1a and 1b) and part were calculated from the data in Table 1; the remaining values came from additional experiments. In most cases,

Fig. 2--Temperature dependence of vapor pressure, assuming one gaseous molecule per osmium atom condensed

more than one experimental pressure value was determined at a particular temperature and 1 atm chlorine pressure. Where the values were close together, they were averaged. Where they were not close together, the highest value was selected in the belief that the highest value should be closer to the saturation vapor pressure.

Let us first consider the data in the region $10^3/^{\circ}\text{K} = 1.48$ to $10^3/^{\circ}\text{K} = 1.145$ (400° to 600°C). The vapor-pressure values in this region fall on a straight line. This suggests that near-saturation vapor pressures were attained (this is also suggested by the results of flow-rate studies) and, consequently, that the data are good. In this region, $\text{OsCl}_3(\text{s})$ appears to be the stable solid phase and the important vaporization reaction is (5). From the slope of the line we obtain $\Delta H_{750}^{\circ} = +23 \pm 2$ kcal/mole and from this $\Delta S_{750}^{\circ} = +22 \pm 3$ e. u. for reaction (5). From ΔC_p values for similar chlorides we estimate ΔC_p for the reaction to be about -7 cal/mole/ $^{\circ}\text{K}$, and assuming it to be constant with temperature, we calculate $\Delta S_{298}^{\circ} = +28 \pm 4$ e. u. This value may be compared with $\Delta S_{298}^{\circ} = +32 \pm 3.0$ e. u., which we obtained for the analogous reaction in the ruthenium-chlorine system. (8)

The temperature-dependence curve breaks at $10^3/^{\circ}\text{K} = 1.145$ (600°C), the temperature at which $\text{OsCl}_3(\text{s})$ decomposes at 1 atm chlorine pressure and $\text{Os}(\text{s})$ becomes the stable condensed phase. The slope changes at this point by -45 kcal/mole, the heat of reaction (2).

We next consider the temperature region between $10^3/^{\circ}\text{K} = 1.145$ and $10^3/^{\circ}\text{K} = 0.728$ (600° to 1100°C). It can be seen that the vapor-pressure points are very erratic in this region and do not follow a general trend. This behavior suggests that saturation vapor pressures were not attained. This is not unexpected, since the results of flow-rate studies showed that saturation difficulties existed in this temperature region. Since the data are not reliable, we have drawn the temperature-dependence curve to blend in with the other data (dashed curve in Fig. 2). The curve is concave upward because three reactions, (6), (7), and (8), contribute. Reaction (8) becomes

less important and reactions (6) and (7) become more important as the temperature increases. This behavior is analogous to the behavior of the ruthenium-chlorine system. (8)

In the temperature region above $10^3/^{\circ}\text{K} = 0.728$, the vapor-pressure values fall on a smooth curve. This suggests that saturation vapor pressures were attained. In this region, reactions (6) and (7) appear to be important. We cannot say anything quantitative about this region until sufficient pressure-dependence data are obtained to determine the relative vapor pressures of the two gaseous species, $\text{OsCl}_2(\text{g})$ and $\text{OsCl}_3(\text{g})$.

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Appendix B

THE CHEMISTRY OF TRANSITION METAL CHLORIDES

by

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INTRODUCTION

A study has been undertaken for the purpose of correlating experimental data obtained at General Atomic on the chemistry of chlorides of the transition elements with other available data on the transition elements. Information derived from the study will aid in determining how the chemical properties of the transition elements vary across and down the periodic table and in predicting the properties of elements for which data are not available. The information will also be of value as a guide in selecting elements for future studies.

The first transition series is well understood. Many experimental data are available; numerous correlations have been made of the thermodynamic properties of compounds containing first transition elements, and recently the relative stabilities of compounds in the series have been adequately explained by the ligand-field theory. On the other hand, the second and third transition series are far from being understood. Data are badly needed not only for making correlations but also for determining whether or not the ligand-field theory applies in these series.

This Appendix details the progress made in finding thermodynamic data for the chlorides of the transition elements and shows how the data can be used. The Appendix starts with a brief discussion of the ligand-field theory, since it is so essential in explaining the behavior of the transition metal elements.

THE LIGAND-FIELD THEORY

The transition metal elements differ from other elements in the periodic table in that they have the ability to form compounds in which the outermost set of stable d (or f) electrons is only partially filled. The presence of incomplete electron shells causes deviations in the relative stabilities of transition metal compounds. The theoretical basis for these deviations is known as the ligand-field theory. ⁽¹⁻⁴⁾

An understanding of the ligand-field theory entails some knowledge of d electron orbitals. The five d electron orbitals are designated $d_{x^2-y^2}$, d_{z^2} , d_{xy} , d_{xz} , and d_{yz} . The $d_{x^2-y^2}$ and d_{z^2} orbitals may be pictured as being aligned on the three axes of a rectangular coordinate system. The d_{xy} , d_{xz} , and d_{yz} orbitals are aligned between the axes. In the gaseous metal ions, the d orbitals are equal in energy; however, when anion neighbors (ligands) become coordinated with the cation, the resulting electrostatic field causes the d orbitals to split into groups of orbitals having different energies. The energy difference between the orbitals is called the splitting energy. When electrons go into orbitals of lower energy (compared with the average) in preference to orbitals of higher energy, a relative stabilization, which is called the ligand-field stabilization energy, results.

The exact nature of the ligand-field splitting can be shown by considering, as a specific example, the d electrons of the first transition metal dichlorides. In the solid state, six chloride ions lie along the axes and form an octahedral configuration around the metal ion. In octahedral environment, the d electron orbitals split into two groups. One is labeled the e group and comprises the $d_{x^2-y^2}$ and d_{z^2} orbitals; the other is labeled the t group and comprises the d_{xy} , d_{xz} , and d_{yz} orbitals. Since the e electrons are concentrated along the axes and are directed toward the chloride ions, there exists a mutual repulsion which causes the e orbitals to be of higher energy than the t orbitals. If the average energy of a d

electron is taken as zero and the difference between the t and e groups (the splitting energy) is assigned the value of $10 Dq$ energy units, then a stabilization of $4 Dq$ energy units is gained when an electron is placed in a t orbital; whereas, $6 Dq$ energy units are lost when an electron is placed in an e orbital. This type of ligand-field splitting is shown graphically in Fig. 1.

Fig. 1--Ligand-field splitting in a regular octahedral field

It has been assumed so far that the ligands around the transition metal ion are in the form of a regular octahedron. Because of the Jahn-Teller effect,⁽¹⁾ this is not the case for certain d electron configurations. Ions having d^4 or d^9 configurations (e.g., Cr^{2+} and Cu^{2+}) are distorted by the ligand field. These ions therefore have higher stabilization energies than the simple ligand-field theory would predict.

In the first transition series, the energy difference between the t and e orbitals is small enough that Hund's rule is followed: the first three d electrons fall in t orbitals, and the next two in e orbitals. This results in relative stabilization energies of $4 Dq$, $8 Dq$, $12 Dq$, $6 Dq$, and zero energy

units for the first five metal dichlorides, respectively. The last five metal dichlorides will show the same trend, since each of the last five d electrons pairs with an electron from the first set of five electrons. It can be seen, then, that as the d electron orbitals are filled, the ligand-field stabilization energy will vary across the first transition series in the form of a two-humped curve having a minimum at d^5 , where the ligand-field stabilization energy is zero. Ideally, this behavior would be reflected in the lattice energies of the first transition dichlorides, as shown in Fig. 2. The dashed line is the behavior which would be expected on the basis of a simple ionic model.

The above example illustrates the ligand-field splitting and stabilization occurring in the octahedral field in the solid state of the first transition metal dichlorides. Many different ligand-field splittings and stabilizations may occur, depending on the nature and intensity of the ligand field. The nature of the field splitting will depend on the geometry of the anions surrounding metal ions and will vary with crystal lattice structure as well as physical state.

Fig. 2--Effect of ligand-field stabilization on lattice energy in the ideal case

It should be mentioned that the splitting energy can be calculated from visible absorption spectra. For a good discussion of this important aspect of the ligand-field theory, we refer to Orgel.⁽¹⁾ If the splitting energy becomes greater than the energy required to pair electrons, it will be energetically more profitable to pair electrons in the orbitals of lower energy rather than to place them unpaired into orbitals of higher energy. When this occurs, the resulting configuration is termed a low-spin state. Since the energy required to pair electrons decreases and the splitting energy increases with each successive transition series, it would not be surprising to find low-spin states in compounds of the second and third transition series.

FIRST TRANSITION SERIES

Many thermodynamic data are available for compounds of the first transition metals. Figure 3 shows ΔH values for various reactions plotted against atomic numbers. The data were obtained as follows: heats of formation from George and McClure,⁽⁴⁾ ionization potentials from Moore,⁽⁵⁾ heats of sublimation from Stull and Sinke,⁽⁶⁾ and electron affinity and heat of dissociation for chlorine from Brewer.⁽⁷⁾ Data are included for the elements calcium, which in the divalent state has no d electrons, through zinc, which in the divalent state has the d^{10} configuration.

It will be noted that the lattice energies (curve A in Fig. 3) for the dichlorides follow a double-humped curve which is similar to the ideal curve (see Fig. 2) derived from the ligand-field theory. Differences between the ideal and observed curves may be explained by the observation that the splitting energy varies somewhat with the metal ion. This is a result of the Jahn-Teller effect as well as other variables.⁽¹⁾ Similar-shaped curves have been obtained for the trichlorides, oxides, solution complexes, and other compounds of the first transition metals for which data are available.⁽⁴⁾

Fig. 3-- Variations in thermodynamic properties of first transition metal dichlorides, where

- A = Neg. lattice energy, $-\Delta H$ for $M^{++}(g) + 2Cl^{-}(g) = MCl_2(s)$
- B = Ionization potential, ΔH for $M(g) = M^{++}(g) + 2e$
- C = Heat of dissociation, ΔH for $MCl_2(s) = M(g) + Cl_2(g)$
- D = Neg. heat of formation, $-\Delta H$ for $M(s) + Cl_2(g) = MCl_2(s)$
- E = Heat of sublimation, ΔH for $M(s) = M(g)$

Many interesting trends may be observed in the correlations shown in Fig. 3. It can be seen, for example, that the ionization potential follows rather closely the trend in the negative of the lattice energy. This seems reasonable, since in both cases negative charges are being removed from the metal ion. If the electron affinity and the heat of dissociation for chlorine and the ionization potential of the metal are subtracted from the lattice energy, the resulting curve (curve C in Fig. 3) is that of the heat of formation of the solid chloride from the gaseous metal and gaseous chlorine. For the first transition metal dichlorides, this curve inherits the two-humped form of the lattice-energy curve, although the slope of the base line is quite different. Since this heat of formation is the sum of the heat of sublimation of the metal and the heat of formation of the solid compound from the solid metal and gaseous chlorine, it can be seen why these component heats follow an inverse relationship with drops at Cr^{++} and Cu^{++} .

Correlations like those in Fig. 3 are very useful for predicting thermodynamic data. This may be demonstrated by considering two specific examples. From the trend in the data for curve C, we predict $\Delta H_{298}^{\circ} = -233 \pm 2$ kcal/mole for the reaction $\text{Sc(g)} + \text{Cl}_2(\text{g}) = \text{ScCl}_2(\text{s})$. Combining this with 92 ± 7 kcal/mole for the heat of sublimation for Sc(s) , we obtain -141 ± 9 kcal/mole for the heat of formation of $\text{ScCl}_2(\text{s})$.

We now use this value to predict whether or not $\text{ScCl}_2(\text{s})$ is stable relative to $\text{ScCl}_3(\text{s})$. Combining $\Delta H_{298}^{\circ} = -141 \pm 9$ kcal/mole, the heat of formation for $\text{ScCl}_2(\text{s})$, with $\Delta H_{298}^{\circ} = -221 \pm 1$ kcal/mole for the formation of $\text{ScCl}_3(\text{s})$ (value obtained from Brewer⁽⁷⁾) we obtain $\Delta H_{298}^{\circ} = -19 \pm 29$ kcal/mole for the disproportionation reaction $3\text{ScCl}_2(\text{s}) = \text{Sc(s)} + 2\text{ScCl}_3(\text{s})$. The entropy change for this reaction between solids will be small; therefore, we can say $\Delta F_{298}^{\circ} \cong -20$ kcal/mole. The result suggests that $\text{ScCl}_2(\text{s})$ is not a stable compound, and indeed the preparation of this compound has not been reported.

As a second example, we consider the heat of formation for $\text{VCl}_2(\text{s})$. From the trend in the data of curves A and C of Fig. 3, we conclude that

Brewer's estimate, -117 ± 20 kcal/mole, which was used in plotting the curve, is good, although a lower uncertainty might be assigned. A better predicted value might be -114 ± 5 kcal/mole.

SECOND TRANSITION SERIES

Variations in the thermodynamic properties for the dichlorides of the second and third transition metals have been described by George and McClure.⁽⁴⁾ Figure 4 shows ΔH values which have been reported for the trichlorides of the second transition series. The ionization potentials were obtained from Moore,⁽⁵⁾ heats of sublimation from Stull and Sinke,⁽⁶⁾ and the values used for the electron affinity and heat of dissociation for chlorine from Brewer.⁽⁷⁾

Heats of formation for YCl_3 and $InCl_3$ were calculated from heat-of-solution data and were given in Kubaschewski and Evans.⁽⁸⁾ The values for $ZrCl_3$ and $MoCl_3$ were estimated by Brewer.⁽⁷⁾ The value for $NbCl_3$ was given by Schaffer and Kahlenberg⁽⁹⁾ and was based on a linear extrapolation of heat-of-formation data for $NbCl_{3.13}$ and $NbCl_{2.67}$. The values for $RuCl_3$ and $RhCl_3$ were measured at this Laboratory by dissociation-pressure measurements conducted at high temperatures.⁽¹⁰⁾⁽¹¹⁾

The bottom point of the cusp of the lattice-energy curve shown in Fig. 4 lies considerably above the base line (broad-dashed curve). Similar behavior is exhibited by the small amount of data which are available for the monoxides of the second transition metals (see Fig. 6, Ref. 4). This behavior, which is contrary to the behavior of lattice-energy curves for compounds of the first transition metals, suggests that the second transition metal ions are in low-spin states. This is not surprising, since the ligand-field splitting energy is about 50% greater in the second series than in the first (see Table 11.3, Ref. 2). As mentioned above, increasing the splitting energy increases the likelihood of electron spin-pairing.

Fig. 4--Variations in thermodynamic properties of second transition metal trichlorides, where

- A = Neg. lattice energy, $-\Delta H$ for $M^{+++}(g) + 3Cl^{-}(g) = MCl_3(s)$
- B = Ionization potential, ΔH for $M(g) = M^{+++}(g) + 3e$
- C = Heat of dissociation, ΔH for $MCl_3(s) = M(g) + 3/2 Cl_2(g)$
- D = Neg. heat of formation, $-\Delta H$ for $M(s) + 3/2 Cl_2(g) = MCl_3(s)$
- E = Heat of sublimation, ΔH for $M(s) = M(g)$

THIRD TRANSITION SERIES

Figure 5 shows ΔH values which have been reported for the trichlorides of the third transition series. It is obvious that, outside of heats of sublimation, ΔH data for this series are scarce.

Values for ionization potentials were obtained from Moore⁽⁵⁾ and Brewer.⁽⁷⁾ Heats of sublimations, electron affinity, and heat of dissociation for chlorine were obtained from sources mentioned previously. The heat of formation for LaCl_3 was obtained from Kubaschewski and Evans⁽⁸⁾ and was based on heat-of-solution work which was reported by several experimenters. The value for TaCl_3 was calculated from values for TaCl_5 and TaCl_4 which were obtained from heat-of-solution data by Schaffer and Kahlenberg.⁽¹²⁾ The value for OsCl_3 is based on high-temperature measurements performed at this Laboratory (see Appendix A.) The values for IrCl_3 and AuCl_3 were given by Kubaschewski and Evans⁽⁸⁾ and are based on dissociation-pressure measurements. The value for PtCl_3 was determined by Shchukarev, et al.⁽¹³⁾ The value for TlCl_3 was taken from Kubaschewski and Evans and is based on heat-of-solution data.

As mentioned above, indications are that spin-pairing occurs in the d^5 configuration (Ru^{3+}) of the trichlorides of the second transition series. Other data indicate that the ligand-field splitting energy for the third transition series is about 25% greater than for the second transition series. It would seem, therefore, that if spin-pairing occurs in the trivalent ruthenium ion, it should also occur in the trivalent osmium ion. It is surprising, then, that the bottom of the cusp for the lattice-energy curve lies very close to the base line (broad-dashed curve). An understanding of this anomaly must await more data.

It should be mentioned that the lanthanide series occurs within the third transition series. This fact undoubtedly has some bearing on the relative behavior of compounds of the third transition elements.

Fig. 5--Variations in thermodynamic properties of third transition metal trichlorides, where

- A = Neg. lattice energy, $-\Delta H$ for $M^{+++}(g) + 3Cl^{-}(g) = MCl_3(s)$
 B = Ionization potential, ΔH for $M(g) = M^{+++}(g) + 3e$
 C = Heat of dissociation, ΔH for $MCl_3(s) = M(g) + 3/2 Cl_2(g)$
 D = Neg. heat of formation, $-\Delta H$ for $M(s) + 3/2 Cl_2(g) = MCl_3(s)$
 E = Heat of sublimation, ΔH for $M(s) = M(g)$

THE LIGAND-FIELD THEORY APPLIED TO GASEOUS MOLECULES

Of particular interest in high-temperature chemistry are the thermodynamic properties of gaseous compounds. It is here that the ligand-field theory could be of great benefit, inasmuch as its most ideal form applies to the reactions in which a gaseous molecule forms from gaseous ions.

The character of the ligand-field splitting that exists in the gas phase may be determined from the geometry of the molecule. For example, in a diatomic linear gaseous molecule, the ligands can be pictured as lying along an axis, which we shall assume to be the z-axis. The d_{z^2} orbital will be influenced strongly by the ligands and will therefore occupy the highest energy level. The $d_{x^2-y^2}$ and d_{xy} orbitals will occupy the lowest energy level, since they will be least influenced by the ligands. The d_{xz} and d_{yz} orbitals will lie in between. Berg⁽¹⁴⁾ showed that this splitting arrangement gives a dissociation-energy versus atomic-number curve that agrees with observed data for gaseous oxides of the first transition series.

In Fig. 6, observed data for the dichlorides of the first transition metals manganese to zinc are compared with the ideal dissociation-energy curve (dotted line) as predicted by the above-mentioned splitting arrangement for diatomic molecules. In drawing the ideal curve, we used 900 cm^{-1} (2.57 kcal/mole) for the splitting energy of Cu^{++} as given by Hougen, et al.,⁽¹⁵⁾ and assumed this constant throughout the series. The values for the heats of sublimation used in calculating the observed values from lattice-energy data were obtained from Kubaschewski and Evans⁽⁸⁾ and Brewer.⁽⁷⁾ Two different values for the heat of sublimation of $\text{CoCl}_2(\text{s})$, 61.7 $\pm$ 4 and 46 kcal/mole, were given in these references.

It is obvious that the observed data do not agree with the ideal curve in Fig. 6. This disagreement can be explained by taking into account variations in splitting energies for $\text{FeCl}_2(\text{g})$, $\text{CoCl}_2(\text{g})$, and $\text{NiCl}_2(\text{g})$. The solid curve was drawn assuming that the splitting energies for the gaseous

Fig. 6--Comparison of theoretical and experimental ΔH 's for the reaction $M^{++}(g) + 2Cl^{-}(g) = MCl_2(g)$

chlorides vary as they do for the solid chlorides.* It can be seen that the observed values agree much better with the solid curve and, if we assume this curve to be correct, we can predict a value of 593 kcal/mole for the dissociation energy of $\text{CoCl}_2(\text{g})$. From this, we calculate 58 kcal/mole for the heat of sublimation of the compound. This may be a better value than either of the two literature values.

CONCLUSIONS

Comparison of the data given in Figs. 4 and 5 shows that, in general, heat-of-formation data are relatively more scarce and less reliable than the other thermodynamic data used in calculating lattice energies of the chlorides of the second and third transition elements. Our studies of the chlorides of the transition elements will help to alleviate this situation. From the results of high-temperature measurements already completed at this Laboratory, we have obtained heats for the trichlorides of the second transition metals, ruthenium and rhodium. From work now in progress, we should obtain a value for the trichloride of the third transition metal osmium. The heats for $\text{RuCl}_3(\text{s})$ and $\text{OsCl}_3(\text{s})$ are especially important because they are used in determining the location of the bottom of the cusp of the lattice-energy curves.

It is clear that because of lack of experimental data very little has been done in correlating the chemical properties of gaseous chlorides of the transition metals. Such correlations could be of great help in predicting the stability of gaseous molecules.

*In arriving at the solid curve of Fig. 6, the dissociation energies of the gaseous chlorides were assumed to vary with respect to the ideal curve (dotted curve) in the same manner that the lattice energies of the solid chlorides (Fig. 3) vary with respect to the ideal lattice-energy curve (Fig. 2).

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