VAPOR PRESSURES OF HAFNIUM (IV) IODIDE, TUNGSTEN (VI) CHLORIDE AND ARSENIC (III) OXIDE BY A METAL DIAPHRAGM TECHNIQUE

by

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VAPOR PRESSURES OF HAFNIUM (IV) IODIDE, TUNGSTEN (VI) CHLORIDE AND ARSENIC (III) OXIDE BY A METAL DIAPHRAGM TECHNIQUE

INTRODUCTION

The increased application of chemical processing to the extraction of metals from their ores has served to motivate basic investigations into the thermodynamic properties of metal halides which are commonly used for extraction processes. The vapor pressures of these compounds have been of interest thermodynamically as a source of latent heats of vaporization and fusion and have provided the basis for obtaining highpurity metals by the unit processes of distillation and fractional sublimation. Though extensive work has been done in the field of vapor pressure measurement (over 300 publications (30) covering approximately 250 metal halides and oxyhalides), there is still little or no data available on many of the halides of the less-common metals which are now needed for their special metallurgical and nuclear properties.

In this work, a metal diaphragm vapor pressure apparatus was constructed and the vapor pressures of tungsten (VI) chloride and hafnium (IV) iodide measured. Tungsten (VI) chloride was chosen because of its importance as an intermediate compound in the preparation of high purity tungsten from scheelite and other tungsten bearing ores. Because of tungsten's high melting point (about 3370° C.) it is currently valued in the missile and satellite programs. Hafnium metal which is principally used in control rods for nuclear reactors (thermal neutron cross section of 120 barns) is prepared in its highest purity by the van Arkle (hot wire) process in which hafnium (IV) iodide acts as an intermediate.

Due to the purity requirements of substances for vapor pressure determination, a significant part of this work was devoted to the preparation of the tungsten (VI) chloride and hafnium (IV) iodide. As both of these materials are hygroscopic, particular care was taken to preclude the contamination with moisture which in the case of tungsten (VI) chloride, formed the more volatile tungsten (VI) oxychloride (WOCl₄). Both halides were prepared by direct combination of the elements.

The vapor pressure of arsenic (III) oxide was also determined to establish the reliability of the apparatus for such measurements and was selected because it is readily available in high purity. It is also stable in air and has a vapor pressure of the same order of magnitude as the halides studied.

To complement the vapor pressure measurements, an apparatus was designed and constructed for determining the freezing and

transition points by thermal analysis. A variable speed, variable range recording potentiometer facilitated the measurements which were generally complicated by low heats of transition and poor thermal conductivities.

A program for the IBM 1620 computor was prepared for processing the results of the vapor pressure measurements and was used to establish the least squares fit of the log P vs 1/T plot of the data. Standard deviations of the constants in the vapor pressure equation (log P = A - B/T) and other statistical values were also calculated.

THEORETICAL BACKGROUND

A. Vaporization Processes

Vaporization of a substance from the solid or liquid phase is often complicated by the occurrence of one or more processes, such as vapor phase polymerization, disproportionation, and/or decomposition (2, p. 193-195). The vaporization of a substance to a gaseous monomer is the simplest form of vaporization and can be represented by

(1)
$$MX_n$$
 (solid or liquid) = MX_n (gas)

where M is the metal ion and X the halogen. The subscript n denotes the valence of the cation. In similar fashion, vaporization which results in polymerization of the vapor may be represented by

(2)
$$aMX_n$$
 (s) = M_aX_{an} (g).

These two methods of vaporization present little problem in conventional vapor pressure studies, although special measurements of density or molecular mass are necessary to determine the molecularity of the gaseous phase. Dissociation of polymers at higher temperatures, however, complicate the interpretation of such vaporization reactions.

Disproportionation of the substance being investigated to related compounds of greater or lesser volatility or even to the metal are not uncommon and may be represented by

(3a)
$$2MX_n$$
 (s) = $MX_n + 1$ (g) + $MX_n - 1$ (s or g)

or

(3b)
$$2MX_n (s) = MX_{n+2} (g) + MX_{n-2} (s)$$

Examples of the above are vanadium (III) chloride which disproportionates on heating according to equation (3a)

$$2 \text{ VCl}_3$$
 (s) = VCl_4 (g) + VCl_2 (s),

while zirconium (II) chloride disproportionates to zirconium metal and the tetravalent halide according to equation (3b)

$$2 \operatorname{ZrCl}_2(s) = \operatorname{ZrCl}_4(g) + \operatorname{Zr}(s)$$
.

Decomposition in the vaporization process also occurs frequently with metal halides, in which case the halide undergoes reduction and gives off free halogen.

(4)
$$MX_n$$
 (s) = MX_{n-1} (g) + $1/2$ X₂ (g)

As Brewer points out, several of these processes may occur simultaneously with one or another predominating at different temperatures. It is apparent that the presence of free halogen or a more volatile disproportionation product would result in high vapor pressure values.

The scope of this project was limited to vapor pressure measurements of substances which vaporize according to the first two of the above processes. One oxyhalide system, which appeared to vaporize by decomposition, was investigated, but no vapor pressure data were

obtained or calculated for the decomposition product.

B. Thermodynamic Considerations

Vapor pressure data are commonly reported in terms of the integrated Clausius-Clapeyron equation, i.e.,

$$\log P = A - B/T$$

where

A = Constant of integration B = $\Delta H_L / 2.303R$ ΔH_L = Latent heat of sublimation or vaporization at T R = Gas constant P = Vapor pressure T = Absolute temperature

or the more general expression,

(6) $\log P = a - b/T + c \log T + d T + . .$

where a, b, c, and d are constants. Both are derived thermodynamic-

ally from free energy relationships.

Consider the vaporization of a substance according to equation (1).

By definition, the free energy is:

$$(7) F = H - TS$$

where

- F = Free energy
- H = Enthalpy
- S = Entropy
- T = Absolute temperature

Differentiation gives

dF = dH - d(TS)

Since dH = dE + d(PV) and dE = TdS - PdV, substitution gives

dF = VdP - SdT

where V is the molar volume.

In a one component system, as described by equation (1), the free energies and changes of free energy at equilibrium are equal for each phase, i.e.,

- (10a) $F(\alpha) = F(\beta)$
- (10b) $dF(\alpha) = dF(\beta)$

where \propto and β are phase designations. From equation (9) it is apparent that

(11)
$$V^{\alpha} dP - S^{\alpha} dT = V^{\beta} dP - S^{\beta} dT$$

or

(12)
$$\frac{\mathrm{dP}}{\mathrm{dT}} = \frac{\mathbf{S}^{\alpha} - \mathbf{S}^{\beta}}{\mathbf{V}^{\alpha} - \mathbf{V}^{\beta}} = \frac{\Delta \mathbf{S}}{\Delta \mathbf{V}}$$

Now, for the vaporization process under consideration, $\Delta S = \Delta H_L$ by definition and $\Delta V = V_g - V_s$. This gives

(13)
$$\frac{dP}{dT} = \frac{\Delta H_{L}}{T(V_{g} - V_{s})}$$

which is an exact thermodynamic relationship known as the Clapeyron equation. Assuming that (1) $V_g > V_s$ and (2) that $V_g = \frac{RT}{D}$, the

Clausius-Clapeyron equation for an ideal gas is obtained; viz.,

(14)
$$\frac{d \ln P}{dT} = \frac{\Delta H_L}{RT^2}$$

or

(15)
$$\frac{d \ln P}{d (1/T)} = \frac{-\Delta H_L}{R}$$

Integration gives

(16)
$$\log P = A - \frac{\Delta H_L}{2.303 \text{ RT}}$$

which is of the same form as equation (5). This relationship holds satisfactorily for most halides at low pressures where the vapors tend to behave as an ideal gas. The integration of equation (15) tacitly assumes that the latent heat, ΔH_L , is constant over the temperature interval under consideration.

The expression for vapor pressure in equation (6) can be derived from the free energy relationship of equation (9) for a constant temperature process, such that

$$dF = V dP.$$

If the more general property of fugacity is used instead of pressure (19, p. 138-140), the free energy is given by

$$dF = \mathbf{RT} \, d\ln f$$

Integration gives

(18)
$$F - F^{\circ} = RT \ln f/f^{\circ}$$

where

 F° = standard state free energy

 f° = standard state fugacity

or in terms of activity, a,

(19)
$$F - F^{\circ} = RT \ln a$$

The free energy change for any reaction can then be expressed as the sum of the free energies of the products minus the sum of the free energies of the reactants. This leads to the expression of the equilibrium constant, where

(20)
$$\Delta F - \Delta F^{\circ} = RT \ln K$$

and

$$K = a (gas) / a (solid)$$

for the reaction of equation (1).

It is now convenient to choose the standard state as a pure solid at one atmosphere pressure. Since the fugacity of the solid varies so slightly with pressure the activity may be considered to be unity. Similar reasoning applies to liquids. Then, if the gaseous phase is assumed to behave ideally over the pressure range under consideration, and if a standard state of one atmosphere pressure is taken for the gas, the equilibrium constant is simplified to

$$K = a (gas) = P$$

where P is the vapor pressure of the substance considered. It should be noted that K = P for the reaction of equation (2) as well as equation (1). Since the free energy change at equilibrium is zero, equation (20) becomes

$$\Delta F^{\circ} = -RT \ln P$$

or

(22)
$$\ln P = \frac{-\Delta F^{\circ}}{RT} = \frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$

From the definition of entropy,

$$dS^{\circ} = \frac{C_{p}^{\circ} dT}{T}$$

We get on integration

$$S^{\circ}$$
 (gas) = $\int \frac{C_{p}^{\circ} dT}{T} + I$

$$S^{\circ}$$
 (solid) = $\int \frac{C_{p}^{\circ} dT}{T} + I'$,

Then

(23)
$$\Delta S^{\circ} = S^{\circ} (gas) - S^{\circ} (solid) = \int \frac{\Delta C_{p}^{\circ} dT}{T} + i.$$

This then gives

(24)
$$\ln P = \frac{\Delta H^{\circ}}{-RT} + \frac{1}{R} \int \frac{\Delta C_{p} dT}{T} + i.$$

If the heat of vaporization is related to its hypothetical value at absolute zero, i. e.,

(25)
$$\Delta H^{\circ} = \Delta H_{T=0}^{\circ} + \int_{0}^{T} \Delta C_{p}^{\circ} dT$$
,

substitution into equation (24) gives

(26)
$$\ln P = -\frac{\Delta H_0^{\circ}}{RT} - \frac{1}{RT} \int_{0}^{T} \Delta C_{p}^{\circ} dT + \frac{1}{R} \int \frac{\Delta C_{p}^{\circ}}{T} dT + i$$

Upon integrating by parts it can be shown that

(27)
$$-\frac{1}{RT}\int \Delta C_{p}^{\circ} dT + \frac{1}{R}\int \frac{\Delta C_{p}^{\circ}}{T} dT = \frac{1}{R}\int \left(\int_{0}^{T} \Delta C_{p}^{\circ} dT\right) dT + r$$

which gives

(28)
$$\ln P = -\frac{\Delta H_0^{\circ}}{RT} + \frac{1}{R} \left(\int_{0}^{T} \frac{\Delta C_p^{\circ} dT}{T^2} dT + (r+i) \right)$$

,

Then if

$$\Delta C_p^{\circ} = a_0 + a_1 T + a_2 T^2 + \dots$$

integration gives

(29)
$$\log P = -\frac{\Delta H_0^2}{2.303 \text{ RT}} + \frac{1}{2.303 \text{ R}} \left(a_0 \ln T + \frac{a_1}{2} + T + \frac{a_2}{6} + T^2 + \dots \right) + j$$

where j is (r + i)/2.303, and the coefficient of T^{-1} , i. e.

 ΔH_0° is independent of temperature. The heat of vaporization at 2.303 R absolute zero can then be obtained by correlating log P with temperature variables of equation (29).

Vapor pressure data are usually sufficiently linear on a log P vs 1/Tplot that the integrated Clausius-Clapeyron equation is adequate for calculating the latent heat of vaporization. However, some cases arise in which the data are best represented by equation (6).

The heats of vaporization or sublimation, depending on the state of the condensed phase, which are calculated from equations (5) and (6) differ in that ΔH_L of equation (5) is the value of the latent heat at the temperature and pressure of the system while ΔH_0° is the latent heat at absolute zero and one atmosphere pressure. The pressure dependency of the latent heat is usually insignificant.

Heats of fusion and transition of the solid, from one phase to another are obtained by subtracting the respective heats of sublimation (6, p. 147).

The entropy of fusion and transition may be estimated by dividing the respective latent heats by the fusion or transition temperature; i.e.,

(30)
$$\Delta S_{f} = \frac{\Delta H_{f}}{T_{f}}$$
; $\Delta S_{t} = \frac{\Delta H_{t}}{T_{t}}$

where the subscript f refers to fusion and t to transition.

Similarly, the entropy of vaporization can be calculated by dividing the heat of vaporization, or heat of sublimation for substances which sublime, by the normal boiling point, or that temperature at which the vapor pressure is 760 mm Hg.

C. Methods of Vapor Pressure Measurement

High temperature vapor pressures have been measured by several different techniques which are applicable to the systems studied in this project and are characterized by certain advantages and disadvantages. Of these techniques, the transpiration or vapor saturation method, the Maier method, and various static methods (diaphragm, sickle gauge, etc.) have been successfully utilized to measure vapor pressures ranging from a few millimeters of mercury up to several atmospheres. Radioactive tracer techniques have also been used to a limited extent. The various effusion methods (Knudsen and torsion effusion) are generally used to measure vapor pressures of relatively nonvolatile materials in the $10^{-7} - 10^{-4}$ atmosphere pressure range, and are not considered in detail here.

Transpiration Method

The transpiration method, is based on evaporation of the sample, whose vapor pressure is to be determined, into a stream of inert gas; the amount of substance vaporized depending on the gas flow rate and temperature of the system. In principle, the gas stream becomes saturated at the lower flow rates such that the vapor pressure may be calculated from

$$P_i = \frac{N_i}{N_i + N_g} \mathcal{T}$$

where

 P_i = vapor pressure of substance i

 π = total pressure of the system

 N_i , N_g = number of mols of substance i vaporized and carrier gas g, respectively.

Essential measurements in such vapor pressure determinations include the gas flow rate, the amount of sample vaporized over the time interval of the measurement (either as weight loss of sample or recovered sublimate) and the temperature and pressure of the system.

The requirement that equilibrium be established between the condensed phase and the flowing gas stream is sometimes difficult to verify. However, saturation can often be assumed by repeating the measurements at successively lower flow rates until the results become independent of the gas rate. Practical limitations to lower flow rates are diffusion and build up of system pressure. Precautions are necessary to prevent premature condensation of the sublimate from the gas stream. In view of these limitations, it seems questionable that this method would give satisfactory results for substances which approach equilibrium very slowly, such as arsenic (III) oxide. Vapor pressure measurements by this method range from less than one up to several hundred millimeters mercury; the upper limit of measurement being dependent on the large sample requirements for higher vaporization rates. End effects (i.e. initiation and termination of the measurement) also become important at higher vapor pressures.

Maier Method

The Maier method, developed by C. G. Maier (17) of the Federal Bureau of Mines in 1925, is based on the principle of direct measurement of the vapor pressure in which the pressure sensing device (at ambient temperature) is connected to the sample chamber (in the hot zone) by a capillary tube. Pressures are measured by balancing a mercury filled U-tube against the sample pressure. In this respect, the Maier method resembles the isoteniscope method, though applicable at higher temperatures. Such an apparatus is applicable for vapor pressure measurements from a few millimeters mercury to an atmosphere or more pressure. In addition to vapor pressure determinations, modifications of the system have been used to study decomposition reactions.

The vapor pressure samples are conveniently charged to the sample chamber by vacuum sublimation after which the system is sealed off.

The principal disadvantage of this system is the tendency for the capillary to become plugged by condensation of vapors transported from the

higher temperature sample zone to the lower temperature regions along the capillary. Some of the advantages which are common to other static methods, include: (1) utility over wide pressure range, (2) small sample requirements which serves for the whole series of measurements, (3) applicability for determining the molecularity of the vapor, and (4) suitability for following the rate of approach to equilibrium.

Radioactive Tracer Method

Radioactive tracers have found application in various types of vapor pressure apparatuses in which the radioactive tracer merely facilitates analytical detection of small samples. A static method, however, has been used to measure the activity of a fixed volume of gas which is in equilibrium with the condensed phase. Calibration is achieved by comparison with a labelled substance of known vapor pressure. The advantages are similar to other static systems in which measurements can be made at different temperatures without dismantling the apparatus and the rate of approach to equilibrium can be strictly followed.

The method is relatively insensitive due to absorption of the emitted radiation in the walls of the gas chamber, coupled with low geometric efficiency. Adsorption of active molecules on the walls could, in certain instances, lead to serious errors.

Diaphragm Methods

Vapor pressure measurements have been successfully made from pyrex and quartz diaphragms (including bourdon and sickle type gauges) in addition to the metal diaphragm which is described in detail later. The design of glass diaphragm type gauges vary widely, but in principle, each depends upon the movement of a long pointer which magnifies the distortion of the pressure sensitive part of the apparatus to which the pointer is attached. The pressure sensitive part, for example, may be a spoon shaped bourdon tube or merely a flat surface with the pointer attached at an oblique angle to the plane of the surface. The pointer is restored to its null position by an applied balance pressure which then becomes a measure of the vapor pressure. Such diaphragms can be used over a wide range of temperatures and pressures as long as the softening point of the glass is not exceeded. Since the pressure sensitive membrane must often be made quite thin in order to give suitable sensitivity, problems are sometimes encountered with diffusion of the balance pressure gas into the sample chamber. Such problems may be minimized, however, by using gases of larger molecular size.

Glass systems generally have the advantage of good corrosion resistance except in special cases in which the sample reacts with the sample chamber. Metal fluorides often react with glass to give SiF_4 (e. g. CaF_2 , WF_6). This can be a serious handicap in halide systems as the silicon halides are quite volatile. The advantages of the direct measurement techniques listed above are evident with these systems to a greater or lesser degree. Glass systems offer the flexibility of possible sample purification by resublimation within the apparatus, both before and after a series of measurements by utilizing glass break-off tips to reopen the system. The system is easily closed again, after evacuation, by sealing off the glass connection.

The method of vapor pressure measurement used in this study is based on the use of an inert gas to balance a nickel diaphragm which becomes distorted as the vapor pressure increases. The sample is enclosed within a cylindrical chamber bounded by the diaphragm on one end and a high temperature platinum tipped valve on the other. Vapor pressures can be measured up to 700-800° C. and pressures ranging from a few millimeters mercury to 2-3 atmospheres.

One advantage that seems to be unique with this static method is that momentary degassing of the vapor phase from the condensed phase at 200-300 millimeters mercury is possible. This facilitates effective separation of otherwise difficult to remove volatile components at the expense of losing a portion of the desired substance. Other advantages,

include, small sample requirements, large number of data points per run, ability to measure equilibrium vapor pressures, and others mentioned above which are typical of most static vapor pressure techniques.

Corrosion products are common causes of errors in closed systems; however, the nickel halides, which constitute the principal impurity in such corrosions, is essentially nonvolatile below 700° C. A small sample chamber was used to ensure an isothermal environment for the sample. It is apparent that as the sample volume is reduced, the sample purity becomes more important, since volatile impurities have a more pronounced effect. The design and construction details of the nickel diaphragm apparatus are described in considerable detail in the following section.

DESCRIPTION OF EQUIPMENT

A. Metal Diaphragm Apparatus

١

Metal diaphragms have been used as effective pressure relays as early as 1944 by Cromer (4). Minor changes were made in Cromer's apparatus by K. O. Johnsson (12) and later by N. W. Gregory (8) in adapting the principle to vapor pressure measurements at high temperatures. The apparatus described in this work is closely patterned after Gregory's apparatus with a few basic modifications. As this work was done on a cooperative agreement with the Bureau of Mines (Albany, Oregon), a description of the apparatus is given in a Report of Investigation along with data on the arsenic (III) oxide system (31).

The metal diaphragm transmits pressure changes in the closed sample chamber by actuating an electrical indicator circuit. As the system temperature increases, the sample vapor pressure distorts the diaphragm and closes the electrical circuit. Similarly, as temperatures are lowered, contact is broken by the decreasing vapor pressures. In either case, a manually controlled balance pressure, applied to the other side of the diaphragm restores it to its "null" position. This balance pressure, after appropriate corrections, is then a measure of the vapor pressure.

Figure 1 gives a schematic picture of the overall apparatus with the important features labeled. A detail of the diaphragm pressure relay is shown in figure 2.



- 1. Metal diaphragm vapor pressure assembly
- 2. Tube furnace
- 3. Thermocouple vacuum gauge
- 4. Liquid nitrogen cold trap

- 5. Vacuum manifold
- 6. Surge reservoir
- 7. Solenoid valve
- 8. Mercury manometer
- 9. Vacuum valve

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FIGURE I-Vapor Pressure System.



FIGURE 2-Metal Diaphragm and Sample Chamber

Diaphragm Pressure Relay

The diaphragm, which is the sensitive component of the apparatus, was made from 0.0035-inch thick annealed nickel sheet. Corrugated diaphragms were used for the vapor pressure determinations of tungsten (VI) chloride and one run of the arsenic (III) oxide. The corrugations were made by pressing the nickel sheet in a die assembly of aluminum and hard rubber at about 1300-1400 lbs/in². The die assembly used is shown in figure 3. Uncorrugated diaphragms were used for the other two arsenic (III) oxide runs and the vapor pressure determination of hafnium (IV) iodide. Both types of diaphragms worked satisfactorily, although the uncorrugated diaphragms were somewhat more sensitive. A small nickel disc was spot welded to the center of the diaphragm to provide reinforcement at the contact point. Photographs of the sample block, before and after welding uncorrugated diaphragm, are shown in the appendix.

The diaphragm and sample chamber were sized to fit conveniently within a 3-inch Hevi-Duty tube furnace (Model M-3024); the effective diaphragm size was, therefore, limited to two inches in diameter. After 2-3 runs, the diaphragms became somewhat insensitive and were replaced by machining off the weld, resurfacing the adjacent faces and welding in a new diaphragm. The sample block to which the diaphragm was originally welded measured 3 inches outside diameter, 3 inches long



I. Aluminum die3. Hard rubber (50 Durometer)2. Nickel sheet4. Steel base

FIGURE 3.- Die Assembly for Corrugating Diaphragm. $\mathbf{24}$

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and 3/4-inch wall thickness.

Inconel was chosen as a construction material for the sample chamber because of its excellent corrosion resistance and creep strength. A nickel apparatus would likely be more suitable at higher temperatures because of the absence of alloying materials whose corrosion products (viz. halides) are more volatile than the nickel halides.

The sample chamber is separated from the diaphragm with a 1/4inch thick back-up plate which has four 1/4-inch diameter access holes. The back-up plate was undercut 0.005 to 0.020 inches on each side of the diaphragm to permit free movement. This back-up plate also serves as a plane of reference for calibrating the diaphragm.

An integral part of the pressure relay is the electrical contact rod which senses the movement of the diaphragm. This rod is positioned at a specified distance from the back-up plate by first screwing the rod snugly against the back-up plate and then backing off the desired distance which is defined as the "set point". Since this dimension, or set point, is very critical, a micrometer-like handle with very fine threads is used to facilitate reproducible settings. During the course of measuring the vapor pressures, this set point must be frequently re-established because of the non-uniform thermal expansion of the contact rod with respect to the housing. A thin chromium film was electroplated on the tip of the contact rod to reduce friction when screwing against the back-up plate.

The contact rod is radially positioned near the diaphragm with a ceramic insulator of hydrous aluminum silicate (LAVA) which can withstand temperatures on the order of 1000° C. without failure. Externally, the contact rod is made vacuum tight by the use of conventional Wilson Quad seals and O-rings. A special assembly, shown in figure 4 A is used to keep the rod electrically insulated from the housing which serves as the electrical ground to the diaphragm.

The sensitivity and calibration of the diaphragms were determined after degassing the sample chamber at elevated temperatures. The diaphragm sensitivity is merely a measure of the change in balance pressure required to just make or break the electrical circuit between the diaphragm and contact rod. Its value depends on the "set point" of the contact rod (i.e. position of maximum diaphragm sensitivity) at usual operating set points, the electrical circuit is opened and closed with pressure changes which are normally undetectable and rarely exceed one millimeter of mercury. Calibration of the diaphragm was necessary since the set point of the diaphragm was not always at the "null' position (i.e. the position where the pressure on each side of the diaphragm is equal). The calibration was obtained by merely measuring and plotting the difference in chamber pressure and balance pressure for different distances of the



FIGURE 4.-Vacuum Seal Assembly.
contact rod from the back-up plate (i.e. different set points). Figure 5 shows a typical calibration curve for a new uncorrugated diaphragm which was used for the hafnium (IV) iodide determinations. A calibration curve for a corrugated diaphragm is shown in figure 6. The set point is generally selected where the pressure difference is smallest for a unit change of contact rod position. Since this pressure difference serves as a correction to the measured balance pressure, such calibrations were made before each vapor pressure determination and also afterwards when possible.

Balance Pressure System

The balance pressure, or pressure which maintains the diaphragm at its specified set point, is read from a 50-inch mercury manometer. This pressure may be manually or automatically controlled by means of a solenoid valve and electrical relay system. The electrical circuitry is shown in figure 7.

For manual operation, the solenoid is maintained open and the balance pressure is then regulated by needle valves. Automatic control is achieved for increasing or decreasing pressures by maintaining the solenoid "normally closed" or "normally open", respectively. In the case of an increasing vapor pressure, the solenoid is closed until the diaphragm makes contact and closes the circuit. This then opens the solenoid until







FIGURE 7-Electrical Wiring Diagram for Pressure Relay.

enough argon has entered the balance system to force the diaphragm off the contact. The reverse applies for the automatic balancing of decreasing vapor pressures. The solenoid is closed as long as contact is made with the diaphragm. When the vapor pressure has decreased enough for the diaphragm to break contact, the solenoid opens to the vacuum system and correspondingly lowers the balance pressure until contact is again made with the diaphragm. When vapor pressure data are being recorded, the diaphragm is balanced manually to give more accurate results.

High Temperature Vacuum Valve

One of the main problems of making accurate vapor pressure determinations was that of adequately sealing the investigated substance within the sample chamber. This was accomplished by sealing a flush fitting, platinum tipped valve head against an inconel seat. The valve head was connected to the valve stem in such a way that no rotation of the head occurred as the valve was tightened. This precluded galling of the platinum surface while sealing the valve. Platinum was chosen because of its softness compared to inconel at the anticipated operating temperatures and also because of its chemical inertness. The valve stem is made vacuum tight by the use of a conventional vacuum seal assembly shown in figure 4 B. The vacuum seals for both the valve stem and the contact rod are protected by cooling coils. After each run, the valve head and

seat were resurfaced by machining off a thin platinum layer from the valve head and surface grinding the valve seat with a 4 A grinding compound.

On heating the apparatus in the tube furnace, the valve stem (about 18-inches long) heats more slowly than the casing. If the valve is sealed tightly during this heat-up period, the compression resulting from the delayed thermal expansion of the valve shaft seals the relatively soft platinum tip against the hard valve seat. Small temperature increases, subsequent to the initial heat-up, do not appear to affect the valve seal. Temperature Measurement and Control

Accurate temperature measurement of the sample was achieved with a platinum vs. platinum-10 percent rhodium thermocouple which was calibrated against a National Bureau of Standards certified thermocouple by methods outlined by Roeser and Lonberger (21, p. 9-16). Thermocouple calibration data are given in the appendix. The couple was inserted in a hole drilled axially into the 3/4-inch thick wall of the sample block; the leads extended out of the furnace through a monel protection tube. The thermocouple was connected to copper lead wires with a mercury junction at zero degrees centigrate and the emf measured with a portable potentiometer to $\frac{1}{2}$ 1 microvolt.

The 3-inch long sample chamber was positioned within a 4-inch zone in the middle of the tube furnace where the temperature varied less

than 1° C. The furnace temperature was accurately controlled with a Wheelco precision control unit which consisted of a vane-type proportional controller (Wheelco Capacitrol, Model 407), a magnetic amplifier (Model 610) to amplify the direct current from the controller, and a saturable core reactor (Style 11790). The amplified direct current served to saturate the core of the reactor, and thus impede the current to the furnace element in proportion to the difference between the actual furnace temperature and the set control value. Fluctuations of furnace temperatures at equilibrium were very small and in no case varied more than 1° C. Due to the relatively high heat capacity of the sample block, the fluctuation of the sample temperature was negligible.

B. Thermal Analysis Apparatus

To complement the vapor pressure studies, an apparatus was designed and built to facilitate thermal and differential thermal analysis by which melting and transitions temperatures of the substance under investigation could be independently checked.

Sharply defined melting and transition temperatures of materials with low heats of transformation and low thermal conductivities, such as arsenic (III) oxide, are difficult to obtain by the usual thermal analysis methods (5, p. 202-204). Carefully controlled cooling and heating rates and high speed variable range, recording potentiometers

facilitated detection of the temperature halts. In this work, two different systems were used for these measurements: the first apparatus was based on measurements in an inert gas system at one atmosphere pressure while the second was based on the sample being sealed within a glass tube under vacuum, such that the transformation point was measured at the vapor pressure of the sample (viz. triple point). Since the pressure dependency of the melting and transition points is usually small, both measurements are approximately equivalent.

The first apparatus shown in figure 8A, consisted of a small diameter (1/4-inch) glass sample tube, open at one end, which was inserted in a metal block to give thermal uniformity. (Small diameter tubes were used to reduce the obliquity of the temperature halts). The sample temperature was measured with a 28 gauge chromel-alumel thermocouple which was calibrated against the same National Bureau of Standards certified couple mentioned earlier. Temperature measure ments were facilitated by inserting the couple in an inconel protection tube which was immersed in the sample to a depth of about 4 inches. A Brown recorder, Model No. SY153X(6B)-(V12AH)-II-III-(106)-N4, of 0.5 second response time was used to trace the sample temperature. The instrument was equipped with an adjustable chart speed between 7 1/2 and 240 inches per hour and a variable emf range between 0-1

and 0-21 millivolts.

Thermal analyses of hygroscopic materials (viz. tungsten (VI) chloride) were made by enclosing the sample block and capsule in an outer air-tight tube. In this case a nickel block was used to preclude corrosion problems. Such samples were loaded into the apparatus under the inert atmosphere of a "dry" box to prevent the deleterious action of moisture on the sample.

The primary difference between system one and system two, in addition to the pressure consideration, was that a glass thermocouple well was used in the latter. Though the sensitivity was reduced significantly, the special precautions of avoiding atmospheric contaminants of the sample were avoided. The sample capsule of this second apparatus was of approximately the same dimensions as the first and was maintained at a uniform temperature by placing it in an 8-inch long copper block which was itself placed in a ceramic reaction tube and 2-inch tube furnace as shown in figure 8 B. Measurements were conducted in an isolated laboratory of near uniform temperature to minimize irregularities in the rate of heating and cooling.

In the thermal analysis of arsenic (III) oxide and hafnium (IV) iodide, differential thermal analyses were simultaneously made with the heating and cooling curves to define more accurately the often difficult to observe transitions. Differential thermal analyses were accomplished by bucking one thermocouple placed inside the sample tube against one place outside of the copper block. The melting or transition temperature was defined when the differential thermal analysis and a plateau or discontinuity in the time-temperature curve coincided. A good example of this is the thermal analysis of As_2O_3 , shown in figure 13 B.



ARSENIC (III) OXIDE VAPOR PRESSURE

Literature Survey

Vapor pressure data of arsenic (III) oxide have been reported by a number of different authors; however, only those data of Smits and Beljaars (28) and Rushton and Daniels (23) have been reported for the liquid phase which is the primary concern of this work. Kelley (13) and Stull (32), in their compilations, have based their values for the liquid primarily on the work of the former.

Rushton and Daniels, in 1925, measured vapor pressures between 225° and 520°C. with a glass diaphragm apparatus. The heat of vaporization and normal boiling point, calculated from their data above the melting point are 12.5 Kcal/gm mol As₄O₆ and 477°C., respectively. Vapor pressure data of the solid octahedral modification were also given, from which the heat of sublimation was calculated to be about 30.6 Kcal/gm mol and the heat of fusion 18 Kcal/gm mol. The solidus line intersects the liquidus line at 275°C, the melting point of the octahedral As₂O₃.

By a similar method, Smits and Beljaars, in 1931, measured the vapor pressure of arsenic (III) oxide between 240° and 368°C. and obtained a heat of vaporization of 14.7 Kcal/gm mol as As_4O_6 . Their data for the octahedral (β) form gave 29.8 Kcal/gm mol for the heat of sublimation. This corresponds to a heat of fusion of 15.1 Kcal/gm mol. Intersection of the

solidus and liquidus lines gives the melting point of the octahedral As_2O_3 at about 272° C.

Schulman and Schumb (24) have, in recent years, reported vapor pressures of both the monoclinic and octahedral forms of arsenic (III) oxide within the temperature ranges of 199-297°C. and 171-275°C., respectively, by the transpiration method. The heat of sublimation of the octahedral form was reported to be 27.1 Kcal/gm mol.

Stelzner (29), Niederschulte (20), Smellie (27) Johnsson (12) and Welch and Duschak (34) have also measured vapor pressures of solid As_2O_3 with varying degress of success, the latter determining the melting point of the monoclinic As_2O_3 to be 313°C. Pertinent thermodynamic values are compared with the results of this work in table 4.

It is apparent from previous work (23, p. 387-388; 34, p. 14-15) that measurements of solid phase vapor pressures of arsenic (III) oxide are complicated by the existence of the two allotropic forms with relatively slow rates of transformation from the octahedral to the more stable monoclinic form, which often results in misleading vapor pressure data (24, p. 881). Since the main objective for measuring the vapor pressure of As_2O_3 was to determine the reliability of the newly constructed diaphragm apparatus, emphasis was placed on measuring the vapor pressures above $313^{\circ}C_{\cdot}$, the fusion temperature of the monoclinic As_2O_3 , where the complication was avoided.

Sample Preparation and Operating Procedure

Samples of pure arsenic (III) oxide (99.9%) were obtained from the National Bureau of Standards (Standard Sample 83b) and the Johnson, Matthey and Company, Limited of London, England (Catalogue No. J. M. 642, Laboratory 16715). Three separate vapor pressure determinations were made (one with the National Bureau of Standards sample and two with the Johnson, Matthey and Company sample) in which sample preparation and mode of operation were varied.

Run 1 was made with the National Bureau of Standards sample without any special processing except for the usual sample degassing within the apparatus prior to sealing off the sample chamber. Approximately 1/2gram was loaded into the sample chamber with a long handled spoon which fit through the valve port into the sample block. No special handling procedures were necessary due to the stability of As_2O_3 in air. A plain, uncorrugated diaphragm was used for this determination and particular care was taken to insure that at least five "equilibrium" vapor pressure points were obtained above the fusion temperature. "Equilibrium" points are those data points for which both temperature and pressure had become essentially constant with time. Other, nonequilibrium points were also obtained for comparison.



FIGURE 9-Sublimation Tube.

Run 2 was made with the Johnson, Matthey and Company arsenic (III) oxide, also without any extra preparation. In this case a corrugated diaphragm was used. Since the nonequilibrium points of Run 1 appeared to be consistent with the "equilibrium" points, this run was made by measuring the vapor pressure as the temperature was progressively increased without completely establishing equilibrium.

The sample for Run 3 was specially prepared by vacuum sublimation of a portion of the Johnson, Matthey arsenic (III) oxide into a glass capsule. This was accomplished by placing 8 - 10 grams of As_2O_3 in zone 1 of the sublimation tube shown in figure 9. The tube was sealed off at $X_1 - X_1$ after having been evacuated over the week end at less than 0.1 micron pressure. The As_2O_3 was then sublimed from zone 1 to zone 2A and then to zone 2B. Before sublimation into the sample capsule (zone 3), some of the As_2O_3 in zone 2B was back sublimed to remove any trace quantities of more volatile components after which the two end capsules were sealed off at $X_2 - X_2$. Finally, a few grams were sublimed into the sample capsule which was then sealed off at $X_3 - X_3$. The sample capsule was made slightly longer than the sample chamber, such that closing the valve would break the capsule and expose the sample.

Prior to loading the arsenic (III) oxide samples into the vapor pressure apparatus, the sample chamber was cleaned thoroughly by pickling (18, p. 243 - 244) the inconel with a 1:8:16 hydrochloric acid-nitric acid-water

solution (70°C.) and the nickel diaphragm with a 1:2 hydrochloric acid – water solution (80°C.) followed by a hot water rinse and a 1:4:8 water-nitric acid-sulfuric acid solution with a few drops of HCl (room temperature). Pickling was followed by a thorough water rinse and than an acetone rinse to facilitate rapid drying.

The apparatus was assembled after the above cleaning, evacuated to 5 - 10 microns pressure, and degassed by heating in excess of 500° C. for about 6 hours to remove traces of volatile material. The degassing tem perature was well above the maximum anticipated operating temperature for the vapor pressure determination. Then, prior to loading the sample, the diaphragm was calibrated to determine the vapor pressure correction at the chosen set point. The sample was then loaded, the valve assembly replaced, and the apparatus evacuated to less than 5 microns pressure. The sample was heated to 100° C. at this pressure for 1 - 2 hours to degas newly adsorbed gases after which the entire apparatus was cooled to facilitate sealing the platinum tipped valve by thermal expansion as discussed previously. <u>Results</u>

The vapor pressure data of Run 1 were measured for the liquid arsenic (III) oxide over the temperature range 317-453°C. with five "equilibrium" data points (viz., 318, 350, 400, 425, and 453°C.). No irregularities in the data were observed above 317°C., although the characteristic irregularities of the vapor pressure curve below the

monoclinic melting point were apparent. That is, on rapid heating through the octahedral melting point, the pressure tends to follow a continuation of the solid vapor pressure curve. The data of Stelzner (29) particularly show this effect. As no "equilibrium" points were taken at the lower temperatures, these results were considered only transitory.

The heat of vaporization was calculated from the integrated Clausius-Clapeyron equation to be 14.03 \pm 0.05 Kcal/gm. mol by least squares analysis of the data. The vapor pressure data of this run are represented by

Log $P_{mm} = 7.059 \pm 0.018 - (3,066 \pm 12)/T$

from which the normal boiling point was calculated to be 460.6° C. These data give an entropy of vaporization at the boiling point (Troutan's constant) of 19.1 e.u. The vapor pressure data for this run are listed in table 1 and plotted in figure 10.

Since the nonequilibrium data of Run 1 appeared to fall on the straight line, it was decided to measure the vapor pressures of Run 2 without waiting the extra two or three hours for each "equilibrium" point, However, the results of Run 2, as is apparent from figure 11, shows that the pressure response lagged behind the increases in temperature, giving a nonlinear curve with low values (50-100 mm Hg) at the higher temperatures compared to Runs 1 and 3. This points out the importance of obtaining equilibrium vapor pressure data. A few of the lower temperature data, in which equilibrium

TABLE 1. - Vapor pressure of arsenic (III) oxide, Run 1

	<u>T (°C.</u>)	1000/T(°K)	P (mm Hg)	Log Pmm
1	317.2	1.693	71.9	1.856
2	317.8	1.692	77.7	1,890
3	317.8	1.692	74.3	1.871
4	317.8*	1.692	74.4	1.871
5	343.2	1.622	120.8	2.082
6	348.2	1.609	133.5	2.125
7	350.2	1.604	139.9	2.145
8	350.5*	1.603	140.1	2.146
9	393.5	1.500	287.1	2.458
10	396.6	1.493	305.6	2.485
11	399.5	1.486	315.0	2.498
12	400.0	1.485	320.0	2.505
13	400.0	1.485	320.9	2.506
14	400.0	1.485	323.9	2.510
15	400.0 *	1.485	319.9	2.505
16	423.5	1.435	447.1	2.650
17	424.6	1.433	451.4	2.654
18	424.6	1.433	457.4	2.660
19	424.6	1.433	463.6	2.666
20	424.6	1.433	464.0	2.666
21	424.6	1.433	468.0	2.670
22	424.6*	1.433	465.2	2.667
23	451.5	1.380	655.8	2.816
24	453.0	1.377	694.0	2.841
25	453.0	1.377	697.5	2.843
26	453.0	1.377	696.8	2.843
27	453.0	1.377	698.1	2.843
28	453.0	1.377	700.3	2.845
29	453.0*	1.377	697.2	2.843

*"equilibrium data points"

TABLE 2 Vapor p	ressure of arsen	c (III) oxide	, Run S
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	T (°C)	1000/T (°K)	_P (mm Hg)	Log Pmm
Octahedra	al As $_2O_3$			
1	253.3	1,899	14.1	1.149
2	254.6	1.894	15.2	1.182
3	257.1	1.885	17.2	1.235
4	257.9	1.883	16.5	1.217
5	258.6	1.880	16.9	1.228
6	258.6 *	1.880	17.0	1.230
7	260.7	1.873	18.7	1.272
8	261.5	1.870	18.8	1.274
9	263.9	1.862	20.8	1.318
10	266.0	1.854	22.7	1.356
11	269.9	1.841	28.1	1.448
12	273.3	1.829	31.0	1.491
Liquid A	s_2O_3			
13	282.5	1.799	38.8	1.589
14	289.2*	1.778	47.6	1.677
15	299.4	1.746	56.9	1.755
16	311.4	1.710	69.4	1.841
17	321.6	1.681	84.4	1.926
18	325.1	1.671	91.1	1.959
19	327.0	1.666	96.2	1.983
20	327.5*	1.664	97.9	1.990
21	337.5	1.637	117.2	2.069
22	353.9	1.594	155.0	2.190
23	366.3	1.563	190.2	2.279
24	370.5	1.553	207.0	2.316
25	371.7*	1.550	213.7	2.329
26	381.5	1.527	247.1	2,392
27	397.0	1.492	309.1	2.490
28	410.8	1.462	376.3	2,575
29	413.5	1.456	394.8	2,596
30	413.8	1,455	405.8	2,608
31	414.0	1.455	409.1	2.611
32	414.0*	1.455	411.8	2.614
33	423.8	1.435	467.3	2.669
34	433.3	1.415	525.1	2.720
35	439.2	1.404	569.3	2 755

	<u>T (°C)</u>	1000/T (°K)	P (mm Hg)	Log Pmm
36	452.9	1,377	673.0	2.828
37	454.2	1.375	696.3	2,842
38	454.2	1.375	709.4	2.850
39	454.2 *	1.375	711.4	2.852
40	462.4	1.359	776.7	2.890
41	472.7	1.340	868.9	2.938
42	480.4	1.327	958.7	2.981
43	480.5	1.327	977.1	2.989
44	480.6 *	1.326	983.8	2.992

TABLE 2	Vapor pressure	of arsenic (III	() oxide	Run 3	(cont.)
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*"equilibrium" data points



National Action of



was more closely approached, are plotted in figure 10 for comparison with the data of the other runs. No meaningful thermodynamic values could be calculated from these data.

The vapor pressure data of Run 3, which covered the temperature range $253 - 481^{\circ}$ C. with six "equilibrium" points (viz. 289, 328, 372, 414, 454, and 481, C.) are given in table 2 and plotted in figure 10 with data of the previous runs. The data below 273° C. represent the vapor pressure of the octahedral modification while those data points above 282° C. represent the fused arsenic (III) oxide. Vapor pressure of the liquid As_2O_3 , between 275° and 481° C., may be represented by

 $\log P_{mm} = 6.875 \pm 0.029 - (2929 \pm 19) / T$

Intersection of the solid and liquid vapor pressure curves fix the melting point of the octahedral oxide in the vicinity of 278° C., which agrees reasonably well with the value of 275° C. reported by Rushton and Daniels (19). From the limited number of data points for the octahedral As₂O₃, the heats of sublimation and fusion were estimated to be 22 and 9 Kcal/gm mol, respectively.

The heat of vaporization of the liquid arsenic (III) oxide was calculated (using the "equilibrium" points only) to be 13.40 ± 0.09 Kcal/gm.mol of As₄O₆. The value for all points tabulated for the liquid was calculated at 13.58 Kcal/gm mol which indicates that the intermediate data points are in satisfactory agreement with the "equilibrium" points and that the main errors of nonequilibrium data appear to be the result of accumulation. The normal boiling point for this run, 460.9°C., is the same as Run 1 (460.6°C) within experimental accuracy, giving a value of 18.2 e.u. for the entropy of vaporization.

The results of this work are compared with literature values in figure 12 and table 3.

By thermal analysis, the average values of the melting points of the monoclinic and octahedral As₂O₃ were 314.4+1.3° and 278 + 5°C., respectively. It was interesting that these thermal analyses showed that it is possible to obtain the melting point of the monoclinic As2O3 by cooling the liquid slowly through the region 320° to 310°C. Four separate determinations showed breaks in the cooling curve within that region. A particularly well defined temperature halt, occurring at 312, 4°C, (1 atmosphere pressure) in which the liquid became slightly supercooled before solidification, is represented in figure 13A. The monoclinic melting point was also determined by slowly heating a sample which had been conditioned for three days at about 295°C. in order to convert all octahedral to monoclinic form. A well marked plateau in the time-temperature curve occurred at about 315°C. which lasted nearly 45 minutes. This curve is represented in figure 13B. The results of the thermal analysis are listed in table 4. These results are consistent with the melting point of 313°C, which was reported by Welch and Duschak (34) for the monoclinic arsenic (III) oxide.

Attempts to sharply define the melting point of the octahedral arsenic (III) oxide were less successful. The time – ΔT curve for the differential analysis indicated the fusion began at 273–275°C.; however, the first noticeable break in the time-temperature curve was at about 278°C., lasting until about 283°C. Both are in agreement with the determination from vapor pressure data within experimental accuracy and are also consistent with the reported value of 275°C. by Rushton and Daniels (23).



	Liquid BP	∆H _{vap} Kcal/	ΔS_{vap}	<u>Qct</u> MP	<u>ahedra</u> l ΔH _{subl}	∆H _{fusion} Kcal/	Monoclinic MP	
	°C.	gm mol	e.u.	° <u>C</u>	Kcal/gm mol	gm mol	<u>°C</u>	ΔH_{subl}
Stelzner					25.8			
Welch and Duschak				251	26.5		313	-
Rushton and Daniels	477	12.5	16.6	275	30.6	18.1		(28, 2)
Smits and Beljaars		14.7		272	29.8	15.1	312.3	23.7
Schulman and Schumb					27.1			27.1
This work (Run 3)	461	13.4	18.2	278	(22.)	(9.)	314.4	

TABLE 3. - Thermodynamic properties of arsenic (III) oxide

Values in parenthesis are only approximations



Apparatus	Method of analysis	Rate of temperature change, °C/min.	Melting point, °C octahedral	Monoclinic
А	Cooling curve	0,21		312.4
А	Cooling curve			314.6
в	Heating curve	0.12		315.5
			Mean	$=$ 314.4 \pm 1.4
В	Heating curve	0.36	273–283° C	

TABLE 4. - Melting points of As_2O_3 by thermal analysis *

*Temperatures taken from upper side of temperature halt.

TUNGSTEN (VI) CHLORIDE VAPOR PRESSURE

Literature Survey

The first attempt to measure the vapor pressure of WCl_6 was made by Vernon (33) in 1937, in which he obtained four somewhat scattered data points between 25° and 150° C. by the vapor saturation method.

Subsequent measurements by Ketelaar, Oosterhout and Braun (14) in 1943 were obtained over the interval 152° to 362° C. by a static method using a quartz spring manometer. The data of Vernon, in comparison, is much higher and gives the appearance of being contaminated with the more volatile WOCl₄. Ketelaar and co-workers reported solid-solid transitions at 167.9-169.5° C. and 226.93° C. in addition to the fusion temperature (triple point) at 284.0° C. as determined by thermal analysis. The he at of vaporization was reported to be 15.24 Kcal/gm. mol and the heats of sublimation of the β -solid and α -solid were, respectively, given as 17.54 and 20.94 Kcal/gm. mol. At the normal boiling point, 336.5° C., as determined from their data, the entropy of vaporization was calculated to be 24.9 e.u. which is a reasonable value of the Trouton constant. The heats of fusion and transition $(\alpha - \beta)$ were calculated from the latent heats of sublimation and vaporization to be 2.3 and 3.4 Kcal/gm. mol, respectively. Ketelaar, et al., noted that on cooling from above the fusion temperature,

the vapor pressure followed a continuation of the liquidus line down to about the ($\alpha - \beta$) transition.

In 1953, Novikov and Shchukarev (21), unaware of Ketelaar's work, reported vapor pressure data on the tungsten (VI) chloride system between 156° and 383° C. using a static gravimetric method. They reported a heat of vaporization of 13.7 Kcal/gm. mol from their data. No transition points were reported and are evidently absent as can be seen from a plot of their data (figure 16).

Again, in 1956, Shchukarev and Novikov (25) reported vapor pressure data of tungsten (VI) chloride over the interval 215 - 341° C. which were in this case obtained by a glass-membrane apparatus. They reported the heat of vaporization for these data to be 14.6 Kcal/gm. mol. As in the previous case, no transition points were observed.

It is evident from a comparison of their data (figure 16), that the data of these latter two investigations differ, particularly at temperatures above the melting point, the first of the two being from 25 - 75 mm Hg higher than the second. The data of Novikov and Shchukarev (21) compare closely with the data of Ketelaar in that region; however, both (21 and 25) are much higher at temperatures below the melting point. At the lower temperatures Novikov and Shchukarev reported their data to be a good continuation of Vernon's data. A marked irregularity in the vapor pressure curve at the melting point is evident from the plot of Shchukarev and Novikov's data, and, in addition, their first reported values (21) appear to have a greater slope for the vapor-liquid curve than for the vapor-solid curve. A least squares analysis of their data confirmed that the difference in slopes is significantly greater than the standard deviation of their measurements. This analysis is summarized in table 5 in which the heats of vaporization and sublimation are compared.

From this analysis, it is evident that the heat of vaporization is greater than the heat of sublimation (i.e., slope of liquidus line greater than solidus line) and would consequently suggest that the fusion reaction is exothermic, which is contrary to normal experience. No explanation of this anomolous condition was given by the authors.

It is noteworthy that the reported ΔH_{vap} values do not compare with the calculated values but are approximately the same as the calculated heats of sublimation. It is, therefore, apparent that the heat of vaporization values reported should not be compared with other literature values for the heat of vaporization.

	∆H _{vap} reported Kcal/gm.mol	ΔH _{vap} calculated* <u>Kcal/gm.mol</u>	^{∆H} subl.** calculated* <u>Kcal/gm.mol</u>
Novikov and Shchukarev (21)	13.7	14.9 ⁺ 0.15	13.8-0.1
Shchukarev and Novikov (25)	14.6	13.9 [±] 0.8	14.7+0.7

 TABLE 5. - Comparison of selected literature values of the thermodynamic properties of tungsten (VI) chloride

* Calculated by least squares analysis by an IBM 1620 computor.

** No heat of sublimation value was reported by investigators.

Sample Preparation

The tungsten (VI) chloride used in this study was prepared by direct combination of the elements at 800-850° C. and one atmosphere pressure (32) $W + 3 Cl_2 ---->WCl_6$

in a glass apparatus shown in figure 14. Due to the influence of small quantities of volatile oxychloride on vapor pressure measurements, special precautions were taken to prevent their formation by side reactions of the WCl₆ with moisture; viz.,

(33)
$$WCl_6 + H_2O ----> WOCl_4 + 2HCl_4$$

(34)
$$WOCl_4 + H_2O ----> WO_2Cl_2 + 2HCl$$

To prevent such reactions, the apparatus was evacuated and degassed at $450-500^{\circ}$ C. for an extended period of time to remove adsorbed moisture from the glassware. After degassing, the system was backfilled with chlorine which was dried by bubbling through concentrated sulfuric acid, passing it through a double bulb of anhydrone desiccant and a double bulb of crude tungsten (VI) chloride which also served as a moisture getter. At a furnace temperature of $650-700^{\circ}$ C. the first traces of WCl₆ began to appear in the condensation zone, and at $800-850^{\circ}$ C. the reaction proceeded very rapidly.

The reaction was terminated by cooling when a sufficient quantity of WCl_6 was formed. It was apparent that in spite of the precautions, small traces of WOCl4 (reddish color) had been formed and had condensed in the



FIGURE 14.- Apparatus for Tungsten (VI) Chloride Preparation.
colder zone. The WCl_6 was transferred to the sample capsules, which had been maintained at 300-350° C. during the course of the chlorination, by melting the WCl_6 with a hand burner and allowing it to flow through the constrictions. Care was taken not to overfill the capsules since WCl_6 expands as it solidifies and could, therefore, fracture the glassware.

To remove the trace quantities of oxychloride, the system was evacuated and heated to $100-150^{\circ}$ C. for several hours at which temperatures noticeable amounts of WOCl₄ were condensed in a cooler portion of the tube. As a final step before sealing off the sample capsule at $X_1 - X_1$, the WCl₆ was repeatedly heated and allowed to cool through the transition temperature at 225-230° C. As the sample cooled through the transition, the densely packed mass vigorously broke into finely divided particles, releasing, in theory, intersticially trapped oxychloride molec ules. About half the sample was vaporized from the sample capsule during the course of this purification procedure. The sample at this point had the appearance of being nearly blue-black in color compared to the reddish cast of the WCl₆ in the earlier stages of its preparation. The vapor pressure sample was sealed off first, followed by the second capsule after purification in the same manner.

The second sample was used for analytical determinations of metallic impurities and the ratio of chlorine to tungsten. Spectrographic analysis identified only a few metals in the parts per million range: viz., Al = 50, B = 10, Ba = 10, Cu = 50, Mg = 200, Ni = 20 and Si = 500. All others were not detected at the level of the test. The chloride and tungsten analyses were 53.4 and 47.1 weight percent respectively, which gives a 5.88 mol ratio. This compares to theoretical values of 53.6 and 46.4 weight percent for the chlorine and tungsten, and, of course, a 6.0 mol ratio. The result of these calculations, based on a single observation, gives a general indication of the sample composition. The low mol ratio could mean the presence of lower chlorides; however, the above variation is believed to be within the limits of accuracy for the single determination.

The remaining WCl_6 , after similar purification, was used for determining melting and transition points by thermal analysis.

Experimental Procedure

The vapor pressure apparatus with a corrugated nickel diaphragm was prepared and the sample loaded in essentially the same manner as for the As_2O_3 determination; i.e., degassing at 500-550° C., calibration of diaphragm, loading sample capsule and subsequent degassing of the sample chamber. A corrugated diaphragm was used. The evacuated system was then cooled, sample capsule broken by closing the valve and the valve

sealed by rapid heating to about 200° C.

Several preliminary vapor pressure runs were made with the sample being degassed after each run at increasingly higher temperatures to verify the absence of volatile impurities, specifically WOCl₄. After two interim degassings at 100-105° C. and 123° C., it was apparent that removal of the volatile contaminant from the tungsten (VI) chloride by this technique was not sufficiently effective.

Consequently a higher temperature degassing procedure was decided upon, in which the sample was heated above its melting point. At 280° C., the vapor pressure of WCl_6 is in the vicinity of 200 mm Hg, while the vapor pressure of the $WOCl_4$ is about 4000 mm Hg. It seemed reasonable to suppose that the vapor phase would be significantly enriched with the $WOCl_4$ at that temperature and that momentary evacuation of the vapor phase from the sample would result in an effective purification at the expense of losing a portion of the WCl_6 . Therefore, after the temperature had become constant at about 280° C., the platinum tipped valve was carefully opened momentarily, allowing the vapor phase to escape into the evacuated manifold. This was repeated three times, after which the system was allowed to stabilize. The resulting pressure drop after stabilization was about 100 mm Hg. The system was then heated to about 285° C. to assure complete melting and again degassed. This time, however, the pressure dropped from about 230 mm Hg to about 75-80 mm Hg. It was apparent on cooling the system down, that all but a small portion of the sample had been removed from the sample chamber during the course of the evacuations. Vapor pressure data were obtained, however, from about 240° to 187° C. where it was evident that a two phase system again existed. No detectable residual pressure remained after the system had been cooled down.

A second tungsten (VI) chloride sample was prepared to complete the vapor pressure determination at the higher temperatures (Run 2). Since an effective purification technique had been found, viz., degassing at the melting point, a starting material with an oxychloride contaminant was tolerated. Therefore, WCl_6 , which had a slight $WOCl_4$ contamination, was transferred within a dry box into a sublimation tube similar to the one pictured in figure 9. This then was purified as much as possible by the technique described for the first sample, sealed off, and loaded into the vapor pressure apparatus which had, in the meantime, been reprepared as previously described.

This sample was degassed within the apparatus three times above the melting point in the before mentioned manner over a 20 hour interval before taking vapor pressure measurements. As a result of these degassings, the sample size was reduced such that it became completely

vaporized at about 325° C., and the highest vapor pressure value obtained was about 575 mm Hg.

Results

From the two runs previously described, the vapor pressure of tungsten (VI) chloride was determined between 187° and 325° C. The data of Run 1, which consists mainly of low temperature data, are listed in table 6. The data listed as Run 1 A are those data for decreasing temperatures which were obtained after degassing of the sample at the melting point. The Run 1 B data are those vapor pressure data obtained the following day on a check run while heating the system back up to 240° C. and then back down again. The data obtained from the second sample, after the high temperature degassing, are listed in table 7.

As some measurements of Runs 1 and 2 were closer to equilibrium condition than others, two figures were prepared, viz., figures 15 A and 15 B; the more significant data are plotted in figure 15 A. Figure 15 B contains, in addition, to the data points of figure 15 A, the rest of the data listed in tables 6 and 7. It is apparent from the data plots that the data on heating are in reasonably good agreement with the data obtained on cooling.

The heat of vaporization, calculated by the method of least squares on the interval of 281.5 to 325° C. was determined to be 14.9 ± 0.3

	<u>T, °C</u> .	<u>1000/°K</u>	P, mm Hg	Log Pmm
Run 1A	Descending			
1	278.1 *	1.814	188.7	2.275
2	283.3 *	1.797	218.5	2.339
3	285.0	1.791	231.1	2.363
4	239.5 *	1.950	61.6	1.790
5	235.0	1.967	54.2	1.734
6	227.9	1.995	41.5	1.618
7	220.8 *	2.024	34.0	1.531
8	206.2	2.086	18.9	1.276
9	202.0	2.104	15.8	1.198
10	197.9	2,122	15.5	1,190
Run 1B	Ascending			
11	193.1	2,144	9,9	, 995
12	207.0	2,082	20.6	1.314
13	210.5	2,067	21.2	1.326
14	220.0	2.027	32.3	1,509
15	224.1	2.010	38.6	1.586
16	226.5	2,001	43.1	1.634
17	228.9 *	1,991	44.6	1.649
18	239.1 *	1,952	63.7	1.804
19	234.2	1.970	54.1	1,733
20	231.8	1,980	50.0	1,699
21	230.1	1,986	45.3	1,656
22	225.4 *	2,005	39,9	1,607
23	218.8	2.032	29.7	1,472
24	214.1	2,052	25.8	1,411
25	210.8	2,066	22.3	1,348
26	208.1 *	2.077	21.4	1,330
27	202.9	2,100	18,9	1,276
28	201.3	2.107	17.5	1,243
29	199.3 *	2.116	15.0	1,176
30	192.8	2.145	12.2	1.086
31 32	190.6 189.4	2.156 2.161	9. 5 8.5	.978 .929

TABLE 6. - Tungsten (VI) chloride vapor pressure data, Run 1

* Data points at or near equilibrium used in figure 15A

	T, °C.	<u>1000/°K</u>	P, mm Hg	Log Pmm
Ascending				
1	281.7 *	1.802	219.5	2,341
2	282,8 *	1.798	223.3	2.348
3	188.7	2,165	9.1	. 959
4	194.1	2,139	10,9	1,037
5	198.4	2,120	12,2	1.086
6	205.3	2,089	15,8	1,198
7	207.3	2,081	17.7	1,248
8	213.0	2.056	21.3	1,328
9	217.1	2,039	26.5	1,423
10	220.6	2.025	32.1	1.506
11	223.9	2.011	37.4	1,573
12	231.1	1.983	48.7	1.687
13	239.7	1.949	62.5	1,796
14	246.9	1.922	76.5	1.883
15	255.4	1.891	97.1	1.987
16	261.5	1.870	117.9	2,071
17	266.5	1,853	135.9	2.133
18	270.6	1.839	156.2	2.193
19	274.0	1.827	171.0	2,233
20	280.0	1.807	197.3	2,295
21	283.4	1.796	221.3	2.345
22	285.9	1.788	235.8	2,372
23	290.4 *	1.774	264.6	2.422
24	294.7	1.761	294.3	2,468
25	299.3	1.746	327.3	2.514
26	304.8	1.730	370.5	2.568
27	309.5 *	1.716	409.2	2.611
28	315.4	1.699	462.2	2.664
29	318.7	1.689	496.9	2.696
30	321.3 *	1.682	531.2	2.725
31	325.1	1.671	574.6	2.759
32	194.8 *	2.136	11.8	1.072
33	196.0 *	2.131	12.1	1.083
34	208.8	2.074	19.7	1.294
35	210.1	2.069	21.1	1.324
36	211.5	2.063	22.1	1.344
37	213.0	2.056	23.3	1,367

TABLE 7. - Tungsten (VI) chloride vapor pressure data, Run 2

*Data points at or near equilibrium used in figure 15A





Kcal/gm. mol. The heats of sublimation of the β and α phases were calculated to be 16.4 ± 0.3 and 18.3 ± 0.4 Kcal/gm. mol, respectively. Estimates of the heat of fusion and the (α - β) transition from these values are 1.5 ± 0.4 and 1.9 ± 0.5 Kcal/gm. mol, respectively. From the intersection of the vapor pressure curves on the log P vs 1/T plot, the melting and transition points were found to be approximately 285° and 230° C., respectively, which are in satisfactory agreement with the results of the thermal analysis which will be discussed later. A normal boiling point of 339° C. was obtained by extrapolation of the liquidus vapor pressure curve to 760 mm Hg. These data give a normal Trouton constant (entropy of vaporization) of 24.3 e.u.

These data are summarized in table 8 and the smoothed data compared with literature values in figure 16. Thermodynamic values are compared with literature values in table 9.

The results of the thermal analysis of WCl₆ are shown in table 10. The melting points and the $(\alpha - \beta)$ transition gave sharp breaks in the cooling curves as shown in figures 17 A and C. The lower temperature transition, $(\alpha_I - \alpha_{II})$, according to the designations of Ketelaar, showed, however, only slight breaks in the time-temperature curves (figure 17 B) which were not always reproducible. The observed breaks, however, were confirmed by differential thermal analysis. The mean values were $281.5 \stackrel{+}{-} 0.1$, $230.0 \stackrel{+}{-} 0.5$ and $185 \stackrel{+}{-} 2^{\circ}$ C. for the melting point, ($\propto_{II} - \beta$), and ($\propto_{I} - \alpha_{II}$) transitions, respectively. No other breaks were observed between 160° and 180° C. The sample used for the lower temperature transition was known to have some WOCl₄ contamination and, though the effects of WOCl₄ contamination on the thermal analyses were not studied, its presence in small quantities is not believed to seriously affect the results. The vapor pressure data in that vicinity were not accurate enough to give any reliable indication of the temperature of the ($\propto_{I} - \propto_{II}$) transition.

The peculiar double halt in the $(\not - \beta)$ transition was very reproducible with the second halt being 4-5° C. below the first. (i.e. about 226° C.). This effect, though conceivably due to contamination, seemed characteristic of the system. This second transition could very likely account for the difference between the value reported by Ketelaar (i.e. 226.9° C.) and the 230.0° C. value reported for this study.

TABLE 8. - Vapor pressure equations and thermodynamic properties of tungsten (VI) chloride *

Temperature interval °C	<u>A** + OA</u>	$\frac{B^{**} + O_A}{A}$	ΔH _{vap} Kcal/gm mol	ΔH _{subl} K <u>cal/gm</u> mol	ΔS _{vap.} Kcal/gm mol, °K
281.5 - 325	8.194 + 0.107	3253 ± 61	14.9 ± 0.3	Kana Apare	24.3
230.0 - 281.5	8.794 ± 0.132	3588 + 69	NUM MER	16.4 ± 0.3	
185.0- 230.0	9.615 ± 0.197	3996 + 95	8185	$18,3^{\pm}0.4$	Ella sue

 $\Delta H_{transition} = 1.9 \pm 0.5$ Kcal/gm. mol

 $\Delta H_{fusion} = 1.5 \pm 0.4$ Kcal/gm. mol

Transition temperature and melting point from intersection of the vapor pressure curves are 230° and 285°C, respectively.

* Values calculated from data shown in figure 15A **Constants A and B are same as in equation 5,

viz., $Log P_{mm} = A - B/T$

and σ_i represents the standard deviations of i.



	BP °C	MP °C	TP(∝ _{II} -β) _°C	^{TP(∞} I - ∝I	
Ketelaar, et al.(14) Novikov and Shchukarev (21)	336.5 335 *	284.0	226.93	167.9-169.	5 2 4.9 24.5 *
Shchukarev and Novikov (25)	345 *				22.5 *
Ints work	339 ± 1	281.5 ± 0.1	230.0 ± 0.5	$5 185 \pm 2$	24.3
	ΔH _{vap}	ΔH_{subl} (/3)	ΔH_{subl} (%)	ΔH_{fusion}	$\frac{\Delta H_{\text{transition}}(\sim -\beta)}{2}$
Ketelaar, et al.(14)	15.24	17.54	20.94	2.3	3.4
Novikov and Shchukareve (21)	14 . 9 <u>+</u> 0.2	*			
This work	$13.9 \pm 0.$	8	-		
THE WOLK	14.9 + 0.	3 16.4+0.3	18.3 + 0.4	1.5 + 0.4	1.9+0.5

TABLE 9. - Comparison of thermodynamic properties of tungsten (VI) chloride with literature values

*Values recalculated by least squares analysis of data Note: ΔH values in Kcal/gm mol

Apparatus Molting poir	Method of analysis	Rate of temperature change, °C/min.	Temperature, °C.
Meiting poin			
А	Cooling curve	1.2	281.4
А	Cooling curve	3.1	281.6
Α	Cooling curve	0.8	281.6
А	Cooling curve	1.1	281.4
А	Cooling curve	0.9	281.4
Transition p	oint (\propto_{II} - β)		
А	Cooling curve	0.9	230.0
А	Cooling curve	1,4	230.5
А	Cooling curve	0.9	229.4
Transition p	oint ($\propto_{\rm I}$ - $\propto_{\rm II}$)	*	
в	Cooling curve	0.4	186.7
в	Cooling curve	0.7	183.2
В	Heating curve	0.25	185.2

TABLE 10. - Melting and transition temperatures of tungsten (VI) chloride by thermal analysis

* Thermal analyses confirmed by differential thermal analyses





HAFNIUM (IV) IODIDE VAPOR PRESSURE

Literature Survey

Up to the present time, little information was available in the literature on the hafnium (IV) iodide system, and no information on its vapor pressure. The heat and entropy of vaporization, however, were estimated by Brewer (2, p. 200) to be on the order of 28 Kcal/gm. mol, and 40 e.u., respectively, based on analogy with related halide systems.

Krause, et al., (15) isolated a small quantity of hafnium (IV) iodide in capillaries for X-ray studies from which they reported data on the X-ray diffraction pattern. The description of the preparation is scanty, merely stating that preparation was by direct combination of the elements and that its color is yellow-orange.

Hampel (10, p. 204) gives a brief description in the Rare Metals Handbook of the preparation of pure hafnium by the iodide process. The only information regarding the preparation of the HfI_4 , however, is that in the van Arkle process, the hafnium metal is maintained at about 600° C. In principle, then, the iodine reacts with the metal to form HfI_4 which diffuses to the hot wire filament (1600° C.) where it decomposes to pure hafnium and free iodine. The iodine then recycles and perpetuates the process.

Sample Preparation

The hafnium (IV) iodide for the vapor pressure study was prepared by direct combination of the elements within an evacuated reaction tube at $400 - 450^{\circ}$ C. High purity iodine was supplied to the reaction by decomposition of previously prepared chromium (III) iodide according to the following reaction:

(35)
$$2 \operatorname{CrI}_3 \longrightarrow 2 \operatorname{CrI}_2 + \operatorname{I}_2$$

$$Hf + 2I_2 \implies HfI_4$$

The CrI_3 , being a hygroscopic compound, served as a getter of any moisture which may have been a potential source of contamination to the HfI₄. The apparatus used for the CrI_3 preparation and subsequent HfI₄ preparation is shown in figure 18 A.

The chromium (III) iodide was prepared by the method outlined by Gregory and Handy (9, p. 128-130) by placing 100-120 grams of reagent grade iodine crystals and 7-10 grams of high purity electrolytic (-100 mesh) chromium in zones 3 and 5 of the apparatus, respectively, as indicated in figure 18A. The three zones 3, 4 and 5, were isolated from the rest of the system with a fragile break-off tip. The part of the system under consideration was then evacuated to less than 10^{-5} mm Hg (<0.01 μ) for 15-20 hours. Between the vacuum system (mechanical and oil diffusion pumps) and the reaction tubes were placed a titanium chip



- I. Tube furnace
- 2. Titanium gettering chips
- 3. Iodine crystals
- 4. Zone for sublimed iodine
- 5. Electrolytic chromium
- 6. Glass break-off tip
- 7. Liquid nitrogen cold trap
- 8. Glass rams filled with iron filings
- 9. Hafnium metal
- 10. Hfl4 condensation zone
- 11, 12, 14. Hfl₄ sample capsule
- I3. Hfl₄ vapor pressure sample capsule
- 15. Hfl4 sample capsule for thermal analysis
- 16. Thermocouple well
- X-X Seal-off locations

62-77X

FIGURE 18-Apparatus for Hafnium (IV) lodide Preparation.

gettering furnace and a liquid nitrogen cold trap to facilitate the trapping out of moisture from the system. After flaming off 10-20 grams of iodine, the vacuum was sealed off at $X_1 - X_1$. The iodine was then slowly sublimed to zone 4 by heating the first tube to about 100° C. When the transfer of the iodine from the first to the second tube was complete, 10-15 grams of iodine were back sublimed to zone 3 after which it was sealed off.

The chromium (III) iodide was formed by heating the chromium zone to 475° C. and the iodine zone to 225° C. (pressure about 3 atmospheres) for about 48 hours to assure completion of the reaction. The excess iodine was sublimed from the CrI₃ at 200° C. for an extended period of time, after which the iodine tube was sealed off. The CrI₃ obtained in this manner was nearly black in color.

The rest of the system was then evacuated to 10^{-5} mm Hg or less for 8-10 hours during which time the system was heated to 400-450° C. to degas any adsorbed moisture. After sealing off the vacuum at $X_4 - X_4$, the seal between the CrI₃ tube and the hafnium reaction zone was broken by magnetically ramming the break-off tip with the capsule filled with iron filings. The hafnium (IV) iodide reaction was then initiated by heating the hafnium button to about 425-450° C. and the CrI₃ to 250° C. It was found by trial in an open system that the rate of reaction was negligible below 400° and above 500° C. Condensation of the HfI_4 in the connecting tube and end sample capsules was prevented by heating these areas to $350-400^{\circ}$ C. The region between the reaction zone and the sample capsules was maintained at about 150° C. to allow condensation of the HfI_4 without condensing any iodine.

The characteristic orange condensate appeared in only trace amounts until the CrI₃ temperature was increased to $450-500^{\circ}$ C. The relatively slow iodation reaction was allowed to proceed for several days at these conditions. After an estimated 10-15 grams of HfI₄ had been formed, the temperature profile of the system was changed to sublime the HfI₄ into zone 12. The amount formed was directly dependent on the amount of CrI₃ available for decomposition. After the sublimation, the system was re-evacuated for 4 - 5 hours by breaking the seal between the reaction zone and the vacuum system. After back subliming a portion of the HfI₄ to the first sample tube, zones 12 and 13 were sealed off at $X_6 - X_6$, followed by sealing off the HfI₄ at $X_7 - X_7$.

The final step of the preparation of the HfI_4 sample for the vapor pressure determination was subliming 4 - 5 grams of the HfI_4 into the end capsule and sealing it off at $X_8 - X_8$ such that the capsule length was 2.50 inches. The HfI_4 , sealed off for the vapor pressure measurement, had a very pure orange color, while the substance remaining behind had a stratified appearance of yellow-orange, orange and red. The other sample tube, containing the back sublimed HfI_4 , was then sealed off and analysed for impurities and the hafnium and iodine composition.

Though the hafnium metal used in the preparation was of very high purity (viz., Al = 60, B = 0.3, Cd = <0.5, Cr = 10, Cu = 15, Fe = 10-50, Mg = 5-80, and Mo = 10 ppm, by spectrographic analysis), it did contain 3.8 percent of the very difficult to separate, zirconium. This, as expected, iodated along with the hafnium such that the ratio Zr/(Zr+Hf)for the iodide was the same as for the metal (i.e., 3.8 percent). The reported iodine and hafnium values were 74.3 and 25.7 weight percent, respectively. These compare with the theoretical values of 74.8 and 25.5 percent for a sample with an equivalent ZrI_4 content. Metal impurities in the HfI_4 sample were in the ppm range and not considered as significant contaminants.

Operating Procedure

A new, uncorrugated nickel diaphragm was welded into the apparatus prior to the hafnium (IV) iodide vapor pressure determination. After degassing the system at 500° C. and less than one micron pressure for 6-7 hours, the diaphragm was calibrated and found to be very sensitive; at a set point of 10.0, the pressure correction was essentially zero. The calibration curve for this diaphragm is shown in figure 5. The hafnium (IV) iodide capsule was carefully cleaned and dried with acetone and then loaded into the apparatus. The system was evacuated to less than one micron pressure and degassed at 100 - 125° C. for 3-4 hours, after which the apparatus was cooled to ambient temperature over the weekend to facilitate sealing the newly-surfaced platinum tipped vacuum valve. The liquid nitrogen cold trap was filled well in advance of breaking the sample capsule to insure the absence of moisture in the system. The valve was closed, breaking the sample capsule, and sealed by rapid heating to about 200° C., similar to the other runs.

The null position of the diaphragm was measured intermittently to detect when the vapor pressure became measurable. After the first vapor pressure measurements were made, at 263° C., the temperature was increased in jumps of 10 - 15° C. at 2-3 hour intervals. This was done to observe any tendency for the pressure response to lag the temperature increase which proved particularly troublesome for the As_2O_3 system.

An irregularity in the vapor pressure curve in the vicinity of 300° C. indicated partial transformation to a more stable modification. After completing Run 1, this peculiarity was checked out by heating the sample as before to the 300° C. temperature and observing the change of pressure as the temperature became constant. As this resulted in the

transformation to a low pressure HfI_4 modification, the vapor pressure measurements were repeated, as before. Data points for both increasing and decreasing temperatures were obtained. As the temperature was decreased to about 353° C. (206 mmHg) the vapor phase was degassed from the sample as was done with tungsten (VI) chloride to verify the absence of volatile impurities. Subsequent degassing, after two data points had been obtained, resulted in the loss of the sample from the system which terminated the run (Run 2).

A third vapor pressure measurement was made using a second sample, prepared similarly to the first. This capsule contained only a very small amount of sample which was expected to vaporize completely during the course of the vapor pressure determination and thereby make possible an evaluation of the molecularity of the gaseous specie. The molecular weight of the gas molecule can be determined from equation (37) provided the sample weight and the temperature and pressure at which the sample becomes completely vaporized are established.

$$M = \frac{mRT}{PV}$$

where

M = molecular weight
m = mass of sample

Results

The vapor pressure of hafnium (IV) iodide was determined for the metastable form between 263° and 401° C., with 12 "equilibrium" points being determined at various intervals throughout the temperature range. The data for this run (Run 1) are listed in table 11 and plotted in figure 20. The heat of sublimation, calculated by least squares analysis of the data, is 28.37 $\frac{+}{-}$ 0.04 Kcal/gm.mol; the entropy of sublimation was calculated to be 42.7 e.u. at the atmospheric sublimation point, 392° C. The equation of the vapor pressure-temperature relationship (equation 5) is

$$\log P_{mm} = 12.210 - 6201/T$$

for the temperature interval studied.

From both figures 19 (time vs temperature and pressure plot) and figure 20 (log P vs 1/T plot) a partial transformation is noted at about 295° C., at which point the pressure did not increase significantly for corresponding temperature increases. However, after increasing the temperature to the next "equilibrium" value, the vapor pressure returned to the curve of the lower temperature data and remained on that same straight line for the remainder of the measurements, even though ample opportunity was given at subsequent "equilibrium" points for the pressure to show the same anomolous effect. Vapor pressures obtained while

	T, (°C.)	1000/T(°K)	P (mm Hg)	$\log P_{mm}$
Increa	sing temperatu	re		
1	263.2	1.864	4.4	.643
2	264.5	1.859	4.7	.672
3	268.1	1.847	5.6	.748
4	271.6	1.835	6.7	. 826
5	272.1*	1.834	7.0	. 845
6	274.8	1.824	7.7	. 886
7	276.5	1.819	8.7	.939
8	278.9	1.811	9.8	.991
9	280.9*	1.804	10.8	1.033
10	286.7	1.786	13.7	1.137
11	289.4	1.777	16.3	1.212
12	290.1	1.775	16.5	1.207
13	292.1	1.769	18.5	1.267
14	304.1	1.732	28.7	1.458
15	307.2	1.723	32.4	1.510
16	309.2	1.717	35.5	1.550
17	310.5	1.713	38.1	1.581
18	311.0*	1.711	38.9	1.590
19	317.8	1.692	50.9	1.706
20	321.8	1.680	60.2	1.779
21	326.9	1.666	74.7	1,873
22	329.2	1.660	82.8	1.918
23	331.2	1.654	89.1	1.950
24	331.9	1.652	90.5	1.956
25	332.0	1.652	91.2	1,960
26	332.0*	1.652	91.1	1.959
27	334.8	1.644	102.2	2.009
28	336.7	1.639	110.9	2.045
29	339.5	1.632	122.4	2.087
30	340.9	1.628	130.7	2.116
31	341.2*	1.627	131.3	2.118
32	344.7	1.618	148.4	2.171
33	346.2	1.614	159.2	2.202
34	348.0	1.610	170.6	2.232
35	350.4	1.603	187.0	2.271
36	351.3*	1.601	193.5	2.286
37	357.8	1,585	243.5	2.386
38	360.7	1.577	274.0	2.437

TABLE 11 - Hafnium (IV) iodide vapor pressure data, Run 1

	<u>T, (°C.)</u>	1000/T(°K)	P (mm Hg)	Log Pmm
0.0	0.00 4	1 1		9 409
39	363.4	1.571	303.6	2.482
40	365.2	1.566	322.9	2.509
41	366.0*	1.564	332.6	2.521
42	372.0	1.550	402.9	2.605
43	373.8	1,545	428.7	2.632
44	375.1*	1.542	452.4	2.655
45	380.4	1.530	529.0	2.723
46	382.4	1.525	562.4	2.750
47	384.1	1.521	601.3	2.779
48	385.1*	1.519	623.0	2.794
49	391.2	1.505	748.3	2.874
50	392.0	1.503	774.1	2.888
51	393.5	1.500	810.8	2.908
52	394.7	1.497	840.6	2.924
53	395.4	1.495	861.2	2.935
54	395.4*	1.495	863.6	2.936
55	398.0	1.490	925. 9	2.966
56	399.1	1.487	958.3	2,981
57	400.2	1.485	990.9	2.995
58	400.7*	1.484	1006.0	3.002
Decrea	asing temperat	ure		
59	395 8	1 495	907 6	2 957
60	390.9	1 506	768.8	2,885
61	390.3	1 507	750.3	2.875
62	381 3	1 528	567 3	2.753
63	376.7	1.538	493.7	2.693
64	375 8	1 541	473 4	2.675
65	374 9	1 543	453 4	2,656
66	374 8	1.543	449.9	2,653
67	365.0	1.567	319.5	2.504
68	362.3	1.573	293 5	2.467
69	346 2	1.614	164 4	2,216
70	334 3	1 646	102.9	2.012
10	001.0	1.040	104.0	2. U12

 TABLE 11 - Hafnium (IV) iodide vapor pressure data, Run 1 (cont.)

	<u>T, (°C.)</u>	<u>1000/T(°K)</u>	P (mm Hg)	Log Pmm
71	331.3	1.654	90.5	1,956
72	319.3	1.687	55.1	1.741
73	310.5	1.713	39.0	1,591
74	300.9	1.742	27.0	1.431
75	298.5	1.749	24.8	1.394
76	297.6	1.752	23.6	1.373
77	296.6	1.755	22.4	1,350
78	295.0	1.760	20.2	1.305
79	292.1	1.769	18.1	1.257
80	292.1	1.769	17.0	1,230

TABLE 11 - Hafnium (IV) iodide vapor pressure data, Run 1 (cont.)

Data indicating transformation not included.

* 'Equilibrium'' data points





decreasing the temperature were the same, within experimental accuracy, as for the increasing temperatures.

Upon completion of Run 1, the second run was commenced by heating the sample back to the temperature of the noted anomoly. As the temperature became constant with time (see figure 21) the pressure dropped from about 25 to 9 mmHg over an 18 to 20 hour period.

The results of the subsequent vapor pressure measurements are listed in table 12 and represented in figure 22. Data were obtained up to 406° C. (about 1070 mm Hg) before decreasing the temperature. Two transitions appeared in the vicinities of 324° and 372° C., thus defining three stable phases, the α , β and λ . The heats of sublimation calculated from the vapor pressure equations listed in table 13, are 48.9, 33.7 and 28.2 Kcal/gm. mol for the α , β and γ forms, respectively. From these values, the heats of transition are estimated to be 15.2 and 5.5 Kcal/gm. mol for the (α - β) and (β - λ) transitions, respectively. The entropy of sublimation of the λ form at the atmospheric sublimation point, 394° C., was 42.3 e.u.

The data on decreasing temperatures notably followed the original vapor pressure curve for the metastable hafnium (IV) iodide. When it was apparent that these data were going to continue along the original curve, it was decided to degas the vapor phase from the sample chamber



FIGURE 21-Time vs. Temperature and Pressure, Hfl₄, Run 2, Transformation from Metastable to Stable Form.

	<u>T, °C.</u>	1000/°K	P, mm Hg	Log Pmm
Increa	sing temperatu	re		
1	293.1	1.766	18.5	1.267
2	296.7	1.754	24.0	1.380
3	297.6	1.752	23.3	1.367
4	299.6	1.746	24.9	1.396
5	301.4	1.740	26.1	1.416
6	303.6	1.733	28.3	1.452
7	302.2	1.738	8.6	. 934
8	302.2*	1.738	9.5	.978
9	305.8	1.727	13.0	1.114
10	306.1	1.726	13.1	1.117
11	309.6	1.716	15.9	1.201
12	311.3	1.711	17.9	1.253
13	314.0	1.703	21.4	1.330
14	316.1	1.697	26.2	1,418
15	316.4	1.696	28.2	1.450
16	320.5	1.684	35.5	1.550
17	321.8	1.680	37.7	1.576
18	324.7	1.672	46.6	1.668
19	325.5	1.670	49.2	1.692
20	328.5	1.662	53.7	1.730
21	329.8	1.658	56.5	1.752
22	331.2	1,654	61.9	1.791
23	337.7	1.637	81.9	1,913
24	340.4	1,629	99.8	1,999
25	340.8	1.628	94.7	1.976
26	349.8	1.605	151.6	2.180
27	351.9	1.599	163.7	2.214
28	358.2	1.584	195.2	2.290
29	360.9	1.577	211.3	2.324
30	361.2	1.576	233.4	2.368
31	361.2	1.576	233.9	2.369
32	361.9*	1.574	236.8	2.374
33	368.4	1.558	301.4	2.479

TABLE 12. - Hafnium (IV) iodide vapor pressure data, Run 2

	<u>Т, °</u> С.	1000/°K	P, mm Hg	Log Pmm
34	369.9	1.555	318.0	2.502
35	371.3	1.551	344.4	2.537
36	367.9	1.560	336.1	2.526
37	367.9	1.560	329.6	2.518
38	367.7*	1.560	324.9	2.511
39	377.1	1.538	436.9	2.640
40	377.1	1.538	436.9	2.640
41	379.1	1.533	457.7	2.660
42	379.2	1.533	470.6	2.672
43	385.1	1.519	549.4	2.739
44	388.9	1.510	634.6	2.802
45	389.7	1.508	658.7	2.818
46	393.5	1.500	740.7	2.869
47	394.8	1.497	772.8	2.888
48	394.6*	1.497	783.4	2.893
49	397.8	1.490	871.1	2.940
50	399.0	1.487	888.9	2.948
51	403.1	1.478	991.3	2.996
52	405.0	1.474	1057.0	3.023
53	405.2*	1.474	1069.0	3.028
decrea	sing temperate	ure		
54	401.2	1.483	999.5	2.999
55	400.5	1.484	978.3	2.990
56	395.6	1.495	853.1	2.930
57	395.4	1.495	838.3	2.923
58	394.7	1.497	823.3	2.915
59	390.5	1.506	728.3	2.862
60	389.5	1.509	711.4	2.852
61	384.8	1,520	619.4	2.791
62	381.4	1.527	555.3	2.744
63	373.9	1.545	435.9	2.639
64	372.7	1.548	419.8	2.623
65	371.8	1.550	397.4	2.599
66	365.4	1.566	321.6	2.507

TABLE 12. - Hafnium (IV) iodide vapor pressure data, Run 2 (cont.)

	<u>T, °C.</u>	<u>1000/°K</u>	P, mm Hg	Log Pmm
67	363.5	1.570	306.2	2.486
68	354.9	1.592	216.9	2.336
69	353.2	1.596	212.8	2.328
70	351.8*	1.600	206.5	2.314
71	350.9	1.602	185.0	2.267
72	350.4*	1.603	178.9	2.252

TABLE 12. - Hafnium (IV) iodide vapor pressure data, Run 2 (cont.)

* "Equilibrium" data points


	Temperature range	A $\pm \sigma_A$	в ± б в	ΔH_{subl} Kcal/gm,mol	∆S _{subl} e. u.
Metastabl	e Form (Atm (263-401°C)	ospheric sublin 12.210-0.013	nation point =392 6201 ⁺ - 8	°C.) 28.37 [±] 0.04	42.7
∽- F 0rm	(302-324°C)	19.56-0. 48	$10,700^{\pm}280$	48.9-1.3	
/3 - Forr	m (325-372°C)	13.97 - 0.20	7,360 + 130	33.7-0.6	
δ-Form	n (atmosphe (375-405°C)	eric sublimation 12.13 ± 0.16	n point = 394°C) 6, 173 [±] 110	28.2 [±] 0.5	42.3

 TABLE 13. - Thermodynamic properties and vapor pressure equations of hafnium (IV) iodide.

 $\begin{array}{l} \Delta \, \mathrm{H}_{\mathrm{transition}} \left(\boldsymbol{\backsim} - \boldsymbol{\beta} \right) &= 15.2^{\pm} 1.4 \\ \Delta \mathrm{H}_{\mathrm{transition}} \left(\boldsymbol{\beta} - \boldsymbol{\curlyvee} \right) &= 5.5^{\pm} 0.8 \end{array}$

Transition temperatures from intersection of the vapor pressure curves are 324° and 372° C. for the (\propto - β) and (β - \varkappa) transitions, respectively.

to verify the absence of volatile impurities. This was done with no significant deviation of the subsequent data points from the metastable curve. As mentioned previously, the second degas resulted in the loss of the sample from the sample chamber. The heat of sublimation, calculated from the data points on decreasing temperatures was 28.95 Kcal/gm.mol compared to 28.44 Kcal/gm.mol determined for the metastable form of Run 1 over the same temperature interval.

After completion of these vapor pressure measurements, one of the remaining samples of HfI_4 was heated in a tube furnace to $300-310^{\circ}$ C. for an extended period of time and visually in spected for change of appearance. The color of the HfI_4 changed from an orange color to a red-orange and seemed to have more crystalline appearance than the apparently amorphous iodide before the heat treatment. Upon heating to higher temperatures, viz., 325° to 400° C., the color became significantly darker red (almost purple). It was noted, however, that when the sample was removed from the hot zone, an orange film condensed out on the sides of the capsule and had much the same appearance as the original sample (i.e., amorphous).

A sample of hafnium (IV) iodide was prepared for thermal analysis in the apparatus shown in figure 18 B by direct iodation of the hafnium with twice resublimed iodine. The results of the thermal analysis, though giving distinct indication of the transition region, were not as conclusive

as those for the tungsten (VI) chloride. Positive results were obtained only for heating curves after heat treating the sample at about 300° C. for extended periods to convert all of the metastable to the stable form.

Two heating curves are represented in figures 23 A and B for the $(\beta - \delta)$ and $(\prec -\beta)$ transitions, respectively. The results of the thermal analyses are listed in table 14.

Run 3, as expected, resulted in the small HfI_4 sample becoming completely vaporized within the sample chamber; however complete vaporization occurred at a lower pressure region than hoped for. The log P vs 1/T curve broke sharply at 288.3° C., and at an abnormally high system pressure of 21.8 mm Hg. By carefully weighing the sample capsule before the run and the broken fragments after, the sample weight was estimated to be 0.0238 gms. Since the volume of the sample chamber is about 38.4 cc., the molecular weight of the gas was calculated from equation (37) to be about 1000. If, however, the vapor pressure of the metastable form were used in the calculation at the temperature indicated, a molecular weight of 1530 is calculated. Both are greater than the 686 value for monomeric HfI_4 ; the molecular weight of the dimer being 1372.



Apparatus	Method of analysis	Rate of temperature change °C/min	Transition temperature °C.
Tra	nsition		
	heating curve	0.97	327-332 *
	heating curve	0.46	327-332
	heating curve	0.12	327.5
Tran	sition		
	heating curve	0.15	375.4
	heating curve	0.77	372-377

TABLE 14. Thermal analysis of hafnium (IV) iodide

* Differential thermal analysis

CONCLUSIONS AND RECOMMENDATIONS

Arsenic (III) Oxide

From the result of the arsenic (III) oxide vapor pressure determinations, it may be concluded that the metal diaphragm apparatus gives a reliable measure of vapor pressures to at least 500° C. and is particularly useful for verifying equilibrium results where rates of pressure response to temperature changes are slow. Arsenic (III) oxide is a typical system of slow response to temperature change. It was apparent from the results of the As₂O₃ determination (Run 2) that equilibrium data points should be interspersed throughout the temperature range, particularly at higher temperatures, in order to establish the vapor pressure with certainty.

Since the plot of log P vs 1/T is essentially linear, it is reasonable to conclude that the heat of vaporization of arsenic (III) oxide is relatively independent of temperature within the temperature range studied (282-481° C.). Though the difference between the heat of vaporization obtained from Runs 1 and 3 is less than 5 percent, it is greater than the 1 percent experimental accuracy of the measurements. No good explanation of this is apparent. Since the data of Run 2 tend to confirm those of Run 3 (i.e. Run 2 data are higher than Run 1 and lower than Run 3 by virtue of non-equilibrium conditions), it seems improbable that either the type of diaphragm (i.e. corrugated vs uncorrugated) or special sample preparation accounts for the difference. Besides the fact that Run 1 was the first vapor pressure measurement made with the apparatus, the prime difference between Runs 1 and 3 is the sample used (i.e. National Bureau of Standards vs Johnson-Matthey). Further work would be necessary to establish possible differences between the two samples to substantiate any conclusion. The results of Run 3 are, however, preferred since they verify the position of the octahedral melting point.

The results of both runs give significantly higher vapor pressure data than those reported by Rushton and Daniels at the higher temperatures, with a resulting higher heat of vaporization (about 7 percent). Since their measurements were made with a glass diaphragm apparatus, having many similar advantages and disadvantages as the apparatus used in this work, it may be possible that equilibrium conditions were not sufficiently attained, though they reported that temperatures were increased slowly $(5 - 10^{\circ} C. per hour)$ to avoid thermal lag. Continuous temperature change without intermittent equilibrium points could cause low vapor pressure results due to accumulation effects as was the case with Run 2 of this work. From figure 12, it is apparent that fair agreement is obtained with the results of Smits and Beljaars who determined vapor pressures also with a glass diaphragm apparatus at lower temperatures.

The melting point of the octahedral arsenic (III) oxide, determined from the vapor pressure measurements (278°C.), agreed reasonably well with the value determined by thermal analysis (273 - 283°C.) and values published by Rushton and Daniels (275°C.) and Smits and Beljaars (272°C.).

At the upper temperature limits of this investigation there was a slight indication that the As_4O_6 was undergoing decomposition. This was not expected as Blitz had reported that the stable from was As_4O_6 up to 700°C. Though the observation is inconclusive, this may be worth a closer check in future work.

Tungsten (VI) Chloride

Reasonably consistent vapor pressure data for the tungsten (VI) chloride system were obtained with the corrugated diaphragm between 187° and 325°C., as is evident from figures 15 A and B. Comparison of the WCl₆ vapor pressure data with other literature values (figure 16) shows good agreement with the results obtained by Ketelaar below the melting point, but the vapor pressure data are significantly lower at higher temperatures. The heats of vaporization, calculated from the slopes, however, are in good agreement (about 15 Kcal/gm. mol) and both give reasonable entropies of vaporization (24 - 25 e. u.). There is

little difference between these values and the calculated values (distinguished from reported values) of Novikov and Shchukarev (14.9 Kcal/gm.mol) and later by Shchukarev and Novikov (13.9 Kcal/gm.mol). However, because of the inconsistencies of their data, particularly in the vicinity of the melting point and below, there is some hesitancy to place much emphasis on their values.

The results of the thermal analysis agreed well with values of the melting and transition points determined from intersection of vapor pressure curves. The low temperature (< I - < II) transition reported by Ketelaar at 168 - 169° C. was observed at a higher temperature, viz. 185° C., by thermal analysis. Due to the null position of the diaphragm, accurate vapor pressure data were not obtained below 185° C.; consequent-ly an independent measurement of the lower temperature transition was not obtained.

This study of the vapor pressure of tungsten (VI) chloride pointed out the importance of sample purity on vapor pressure results. Even trace amounts of volatile oxychlorides which formed along with the WCl_6 were troublesome, in spite of the careful preparation techniques employed. However, the method of degassing the sample at the higher temperature proved to be a useful technique for removing last traces of the volatile impurity. The molecularity of the tungsten (VI) chloride vapor has been assumed to be unity, i.e. monomolecular, in this and other investigations. Since the apparatus described in this work is suited for such measurements further work could be done to establish experimentally the molecular weight of the gas.

Decomposition of WCl_6 to lower chlorides has been ignored in this study, though the possibility definitely exists that partial decomposition to WCl_5 occurs, in which case the pressure values obtained would be representative of an equilibrium mixture instead of the assumed pure substance. Further work is necessary to determine the significance of this possible effect.

Hafnium (IV) Iodide

The vapor pressure determination of hafnium (IV) iodide has presented an interesting assortment of facts for consideration. As no previous HfI_4 vapor pressure data have been reported, no comparison can be made to explain the peculiarities of this system. In view of the extreme care taken to insure high sample purity and the high-sensitivity of the diaphragm apparatus during the course of the measurements (particularly during Run 1) the data obtained are believed to be without serious errors with respect to either the sample or the apparatus.

The results of the vapor pressure measurements show that a metastable HfI_4 phase exists up to at least 400° C., and that this phase transforms to the stable modification at temperatures near 300° C. It is possible that the transformation also takes place at higher temperatures, though no evidence was found in this investigation. It may at least be stated that the rate of transformation appears to be greater at the 300° C. temperature region. This can be seen from figures 19, 20 and 21.

Once transformed to the stable low temperature form (\propto modification), a new vapor pressure curve results with solid-solid transitions appearing at 327 - 332° C. and 372 - 377° C. with the formation of the β and δ modifications, respectively. Upon cooling the system down, however, the vapor pressure of the metastable HfI₄ is obtained. This effect resembles closely the phosphorus system in which the white phosphorus transforms monotropically (i.e. irreversibly) to the violet form and is converted back only by condensation from the vapor phase (19, p. 109-110). To this extent the HfI₄ system behaves monotropically. The apparent reversal of the transformation of the metastable to the stable form at the 300° C. temperature region, as observed during Run 1, does not seem consistant with expected results. No explanation for this behavior is apparent.

The heats of sublimation of the metastable (28.37 Kcal/gm.mol) and

 χ modification (28.2 Kcal/gm. mol) are the same within experimental error and both are in good agreement with the estimates of Brewer (28 Kcal/gm.mol). The slight curvature of the log P vs 1/T plot of the metastable HfI₄ vapor pressure data is probably due to the effect of heat capacity on the heat of vaporization. This effect is, however, small (less than a Kcal/gm. mol). The respective entropies of sublimation (42.7 and 42.3 e.u.) also agree reasonably well with the value of 40 e.u. estimated by Brewer.

Both transitions, $(< -\beta)$ and $(\beta - \delta)$, were detected by thermal analysis of a sample which had been heat treated at 300 - 310° C. for an extended period of time. The reversibility of the $(< -\beta)$ and $(\beta - \delta)$ transitions is speculative since no temperature halts were observed when cooling, only on heating through the transition. This however, is not conclusive evidence in view of the relatively poor results obtained by the thermal analysis.

The small amount of zirconium (IV) iodide which was unavoidably present with the high purity hafnium metal during preparation behaves so similarly to HfI_4 that its presence is not believed to significantly affect the results.

The results of the hafnium (IV) iodide molecularity test, Run 3, seem to indicate that the gaseous molecule is the dimer. However, the

experimental uncertainty of this measurement is large, particularly because of the small sample size which results, of course, in a low and relatively uncertain vapor pressure at complete vaporization. Further work is necessary to establish conclusively the extent of polymerization in the gaseous phase.

In view of the fact that this is the first vapor pressure study on the hafnium (IV) iodide system, it is reasonable to recommend that the vapor pressure results be confirmed by subsequent measurements, particularly of the stable modifications. The effects of the \mathbf{ZrI}_4 content on the vapor pressure and transition temperatures may well be incorporated in such a study.

To complete the thermodynamic investigation of this compound, heat capacities should be determined, such that free energies may be calculated. The drop-calorimeter appears to have limitations in determining the enthalpy of the different crystal forms as a result of the condensation of the metastable form from the vapor phase on cooling. Other techniques, however, are available for such studies.

Recommendations for further work also lean towards gaining a better understanding of the transformation from the metastable HfI₄ to the stable modifications and the temperature dependency of the transformation. Since the transformation of the metastable HfI₄ to the stable form was observed rather fortuitously, it seems probable that similar unnoticed transformations take place in other systems. The data of Ketelaar show one such case in which he obtained vapor pressure data which followed a continuation of the liquidus line. The anomolous partial transformation at 300° C. is of particular interest and deserves a more fundamental approach than was possible in this work. High temperature X-ray diffraction studies would undoubtedly provide a better insight into the phase phenomenon of this system.

BIBLIOGRAPHY

- Biltz, H. Ueber die Bestimmung der Molekulargrösse einiger anorganischer Substanzen. Zeitschrift fur physikalische Chemie 19:385-430. 1896.
- Brewer, Leo. The fusion and vaporization data of the halides. Paper 7 In: The chemistry and metallurgy of miscellaneous materials, by Laurence L. Quill. New York, McGraw-Hill, 1950. p. 193-275.
- Christiansen, J. A. Manual of physico-chemical symbols and terminology. Journal, American Chemical Society 82:5517-5584. 1960.
- Cromer, S. Pressure transmitter and relay. N. p., 1944, 19 numb. leaves. (U. S. Atomic Energy Commission. A-1286)
- Foote, Paul D., C. O. Fairchild and T. R. Harrison. Pyrometric practice. Washington, D. C., 1921. 326 p. (National Bureau of Standards. Technologic Paper No. 170)
- 6. Gambill, Wallace R. Find heat of fusion and sublimation. Chemical Engineering 65:147-150. 1958.
- 7. Gore, W. L. Statistical methods for chemical experimentation. New York, Interscience, 1952. 210 p.
- Gregory, N. W. Application of a diaphram guage for the investigation of vapor pressures and chemical equilibria at high temperatures.
 N. p., 1946. 23 numb. leaves. (U. S. Atomic Energy Commission. BC-16)
- Gregory, N. W. and Lyman L. Handy. Chromium (III) iodide. In: Therald Moeller's Inorganic syntheses, vol. V. New York, McGraw-Hill, 1957. p. 128-130.
- Hampel, Clifford A. Rare metals handbook. 2d. ed. London, Reinhold, 1961. 715 p.

- International Union of Pure and Applied Chemistry. Nomenclature of inorganic chemistry. Journal, American Chemical Society 82:5523-5544. 1960.
- Johnsson, K. O. The vapor pressure of uranium tetrafluoride. Oak Ridge, Tenn., 1947. 19 numb. leaves. (U. S. Atomic Energy Commission. Y-42)
- Kelley, K. K. Contributions to the data on theoretical metallurgy. III. The free energies of vaporization and vapor pressures of inorganic substances. Washington, D. C., 1935. 132 p. (U. S. Bureau of Mines. Bulletin 383)
- Ketelaar, J. A. A., G. W. van Oosterhout and P. B. Braun. Investigation of tungsten halides. II. Vapor pressure of tungsten hexachloride. Recueil des travaux chimiques Pays-Bas 62:597-605. 1943.
- 15. Krause, Brigitte, et al. X-ray powder diffraction studies of hafnium tetraiodide. Analytical Chemistry 32:1210-1211. 1960.
- 16. Kubaschewski, O. and E. Ll. Evans. Metallurgical thermochemistry. New York, Pergamon, 1958. 426 p.
- Maier, C. G. Vapor pressure of the common metallic chlorides and static method at high temperatures. Washington, D. C., 1925.
 54 p. (U. S. Bureau of Mines. Technical Paper 360)
- Metals and Plastics Publications, Inc. Metal finishing guidebookdirectory. 1961. 754 p.
- 19. Moore, Walter J. Physical Chemistry. New York, Prentice-Hall, 1950, 592 p.
- Nierderschulte, Gustav. Vapor pressure of solid substances. Doctor's thesis. Erlangen, Germany, Friedrich-Alexanders-Universität, 1903. 26 p.

- Novikov, G. I. and S. A. Shchukarev. Gravimetric method for measuring the pressure of a saturated vapor. Uchenye Zapiski, Leningradskogo Gosudarstvennogo Ordena Lenina Universiteta imeni A. A. Zhdanova, No. 163, Seriya Khimicheskikh Nauk. No. 12: 37-40. 1953.
- Roeser, Wm. F. and S. T. Lonberger. Methods of testing thermocouples and thermocouple materials. Washington, D. C., 1958.
 21 p. (National Bureau of Standards. Circular 590)
- Rushton, E. R. and Farrington Daniels. The vapor pressure of arsenic trioxide. Journal, American Chemical Society. 48:384-389. 1926.
- Schulman, James H. and Walter C. Schumb. The polymorphism of arsenious oxide. Journal, American Chemical Society 65:878-883. 1943.
- Shchukarev, S. A. and G. I. Novikov. Thermodynamic study of some chlorine derivatives of tungsten. I. Saturated vapor pressure of the hexa-, penta-, and oxytetrachlorides of tungsten. Zhurnal Neorganicheskoi Khimii 1:356-357. 1956.
- 26. Shenker, Henry, et al. Reference tables for thermocouples. Washington, D. C., 1955. 84 p. (National Bureau of Standards. Circular 561)
- 27. Smellie, P. The vapour pressure of arsenious oxide. Journal of the Society of Chemical Industry 42:466-468. 1923.
- Smits, A. and E. Beljaars. The complexity of arsenic trioxide. Proceedings of the Royal Academy of Sciences of Amsterdam 34:1141-1155, 1318-1326. 1931.
- Stelzner, Karl. Vapor pressure of solid substances. Doctor's thesis. Erlangen, Germany, Friedrich-Alexanders-Universität, 1901. 25 p.
- Stevenson, F. D. and S. D. Hill. Tabulation of metal halide vapor pressure references and bibliography. Washington, D. C., 1962.
 53 numb. leaves. (U. S. Bureau of Mines. Information Circular. In press)

- Stevenson, F. D. and C. E. Wicks. A metal diaphragm vapor pressure apparatus. Vapor pressure of arsenic (III) oxide.
 Washington, D. C., 1962. 26 numb. leaves. (U. S. Bureau of Mines. Report of Investigation. In press)
- Stull, Daniel R. Vapor pressure of pure substances. Inorganic compounds. Industrial and Engineering Chemistry 39:540-550. 1947.
- Vernon, Arthur A. The vapor pressure and dissociation of tungsten hexachloride in the gas phase. Journal, American Chemical Society 59:1832-1834. 1937.
- Welch, H. V. and L. H. Duschak. The vapor pressure of arsenic trioxide. Washington, D. C., 1915. 21 p. (U. S. Bureau of Mines. Technical Paper 81)

APPENDIX

I. TABULATION OF METAL HALIDE VAPOR PRESSURE REFERENCES WITH BIBLIOGRAPHY

Due to importance of metal halide vapor pressures in the application of chemical processing in the metals field, a major literature survey was made to locate references which contain actual experimental vapor pressure data.

The results of this literature search are reported in two main sections; (1) a tabulation of vapor pressure references for each of the metal halides and oxyhalides (listed by metal) and (2) a bibliography of the citations. In the tabulation, both bibliographic reference number and the year of publication are given: eg., the vapor pressure references for ZrF_4 are listed as: (231, 1953) (233, 1954) (234, 1958). The chemical name based on the Stock system (3, p. 5528-5529) follows the chemical formula in the tabulation: e. g. the name of ZrF_4 is given as zirconium (IV) fluoride.

References were primarily obtained from a comprehensive search of the Chemical Abstracts between January 1907 and January 1961; chiefly under the indexed headings of "Vapor Pressure". The Nuclear Science Abstracts were also consulted between January 1951 and June 1959. Vapor pressure compilations and other works not containing original vapor pressure data are not included in the bibliography. However, compilations by Kelley (13), Stull (32), Brewer (2), and Kubaschewski and Evans (16) served as a valuable source of cross references. References containing boiling point data only were generally omitted as were those on decomposition and disproportionation reactions; although, some of both were included in special cases.

Formula	Chemical Name	Reference Number
Aluminum		
AlF ₃	Aluminum (III) fluoride	(151, 1939)(200, 1934)(292, 1959)
A1F	Aluminum (I) fluoride	(11, 1957)
A1Cl ₃ (Al ₂ Cl ₆)	Aluminum (III) chloride	(55, 1958)(77, 1932)(81, 1888) (138, 1925)(152, 1939)(191, 1914) (256, 1938)(257, 1932)(264, 1954) (270, 1932)
AlBr3 (Al ₂ Br ₆)	Aluminum (III) bromide	(8, 1895)(55, 1958)(77, 1932) (191, 1914)(301, 1937)
AlBr	Aluminum (I) bromide	(229, 1957)
AlBrCl ₂ (Al ₂ Br ₂ Cl ₄)	Aluminum (III) bromide dichloride	(55, 1958)
All3 (Al2I ₆)	Aluminum (III) iodide	(77, 1932)(148, 1936)(191, 1914)
Americium		
AmF3	Americium (III) fluoride	(38, 1955)(294, 1958)
Antimony		
\mathbf{SbF}_{5}	Antimony (V) fluoride	(99, 1957)(236, 1951)
SbF3	Antimony (III) fluoride	(194, 1936)
SbCl ₅	Antimony (V) chloride	(7, 1886)(8, 1895)(30, 1926)
SbCl3	Antimony (III) chloride	(7, 1886)(8, 1895)(30, 1926) (105, 1916)(138, 1925)(191, 1914) (300, 1939)

A. TABULATION OF METAL HALIDE VAPOR PRESSURE REFERENCES

$SbBr_3$	Antimony (III) bromide	(8, 1895)(23, 1932)(191, 1914)
SbI3	Antimony (III) iodide	(8, 1895)(191, 1914)
Arsenic		
AsF5	Arsenic (V) fluoride	(196, 1932)
AsF_3	Arsenic (III) fluoride	(208, 1941)
$AsOF_3$	Arsenic (V) oxide fluoride	(146, 1958)
AsCl ₃	Arsenic (III) chloride	(8, 1895)(16, 1920)(105, 1916) (143, 1950) (138, 1925)
AsBr ₃	Arsenic (III) bromide	(8, 1895)(23, 1932)(105, 1916) (279, 1902)
AsI3	Arsenic (III) iodide	(71, 1933)(101, 1927)
Barium		
BaF ₂	Barium (II) fluoride	(200, 1934)
$BaCl_2$	Barium (II) chloride	(138, 1925)
Beryllium		
BeF2	Beryllium (II) fluoride	(124, 1959)(165, 1958)(232, 1954)
BeCl ₂	Beryllium (II) chloride	(84, 1960) (181, 1933)
BeBr_2	Beryllium (II) bromide	(181, 1933)
BeI2	Beryllium (II) iodide	(181, 1933)
Bismuth		
BiF ₅	Bismuth (V) fluoride	(78, 1959)
BiCl ₃	Bismuth (III) chloride	(45,1958)(47, 1959)(61,1929) (121,1960) (138, 1925)

BiBr3	Bismuth (III) bromide	(43, 1958) (61, 1929)
Bil3	Bismuth (III) iodide	(44, 1959)
Boron		
BF3	Boron (III) fluoride	(28, 1932)(65, 1845)(176, 1932) (196, 1932)
BF ₂ (B ₂ F ₄)	Boron (II) fluoride	(69, 1958)
BCl ₃	Boron (III) chloride	(182, 1862)(235, 1957)(262, 1914)
BCl (B ₄ Cl ₄)	Boron (I) chloride	(275, 1952)
BI3	Boron (III) iodide	(6, 1953)
BBr ₃	Boron (III) bromide	(261, 1914)
Cadmium		
CdF_2	Cadmium (II) fluoride	(200, 1934)
$CdCl_2$	Cadmium (II) chloride	(25, 1958)(88, 1933)(138, 1925) (162, 1940)(266, 1935)(267, 1937)
$CdBr_2$	Cadmium (II) bromide	(88, 1933)(162, 1940)(226, 1923) (269, 1960)
CdI ₂	Cadmium (II) iodide	(162, 1940)(226, 1923)(269, 1960)
Calcium		
CaF_2	Calcium (II) fluoride	(200, 1934)
Cesium		
CsF	Cesium (I) fluoride	(205, 1922) (282, 1921)
CsC1	Cesium (I) chloride	(42, 1948)(70, 1926)(158, 1960) (161, 1938)(203, 1921)(271, 1953) (282, 1921)

$CsBr_3$	Cesium (III) bromide	(60, 1917)
CsBr	Cesium (I) bromide	(42, 1948)(161, 1938)(203, 1921) (282, 1921)
CsI3	Cesium (III) iodide	(60, 1917)
CsI	Cesium (I) iodide	(42, 1948)(48, 1936)(203, 1921) (282, 1921)
Chromium		
CrCl3	Chromium (III) chloride	(52, 1937)(60, 1917)(108, 1929) (278, 1943)
CrCl2	Chromium (II) chloride	(52, 1937) (278, 1943)
CrO_2Cl_2	Chromium (VI) dioxide chloride (Chromyl (VI) chloride)	(145, 1959) (147, 1912)
CrBr ₃	Chromium (III) bromide	(246, 1959)(248, 1960)(278, 1943)
CrBr_2	Chromium (II) bromide	(246, 1959)(249, 1960)(278, 1943)
CrI ₂	Chromium (II) iodide	(4, 1956)(95, 1931)
Cobalt		
CoCl ₂	Cobalt (II) chloride	(1, 1956)(138, 1925)(220, 1952)
Copper		
CuCl ₂	Copper (II) chloride	(20, 1927)(60, 1917)(137, 1956) (138, 1925)
CuCl (Cu ₂ Cl ₂)	Copper (I) chloride	(20, 1927)(138, 1925)(266, 1935)
CuBr (Cu2Br2)	Copper (I) bromide	(109, 1929)(281, 1922)
CuI	Copper (I) iodide	(88, 1933)(109, 1929)(281, 1922)

Gallium

$GaCl_3$ (Ga_2Cl_6)	Gallium (III) chloride	(75, 1936) (131, 1940)
GaBr ₃	Gallium (III) bromide	(75, 1936)
GaI3	Gallium (III) iodide	(75, 1936) (255, 1958)
Germanium		
GeCl ₄	Germanium (IV) chloride	(132, 1926)(160, 1887)
GeBr4	Germanium (IV) bromide	(32, 1927)
GeI4	Germanium (IV) iodide	(114, 1952)
Gold		
AuCl ₃ (Au ₂ Cl ₆)	Gold (III) chloride	(21, 1928) (72, 1928)(173,1925) (190, 1895)
AuC1	Gold (I) chloride	(72, 1928)
AuBr ₃	Gold (III) bromide	(241, 1959)
AuBr	Gold (I) bromide	(72, 1928) (241, 1959)
Hafnium		
HfCl ₄	Hafnium (IV) chloride	(40,1959)(74, 1939)(130,1949) (171, 1958)(188, 1949)
HfBr ₄	Hafnium (IV) bromide	(74, 1939)
Indium		
InCl ₃	Indium (III) chloride	(186, 1936)(255, 1958)
InCl ₂	Indium (II) chloride	(186, 1936)(187, 1935)
InC1	Indium (I) chloride	(186, 1936)(187, 1935)

InBr ₃	Indium (III) bromide	(186, 1936)(255, 1958)
InBr ₂	Indium (II) bromide	(186, 1936)(187, 1935)
InBr	Indium (I) bromide	(13, 1955)(14, 1955)(186, 1936) (187, 1935)
InI ₃	Indium (III) iodide	(255, 1958)
InI	Indium (I) iodide	(13, 1955)(14, 1955)(186, 1936) (187, 1935)
Iridium		
IrF ₆	Iridium (VI) fluoride	(35, 1961)
Iron		
FeCl ₃ (Fe ₂ Cl ₆)	Iron (III) chloride	(108, 1929)(119, 1950)(138, 1925) (211, 1938)(213, 1950)(222, 1953) (260, 1925)
FeCl ₂	Iron (II) chloride	(138, 1925)(221, 1952)(246, 1959) (247, 1960)
$FeBr_3(Fe_2Br_6)$	Iron (III) bromide	(87, 1955)
FeBr ₂	Iron (II) bromide	(136, 1955)(246, 1959)(247, 1960)
FeI2	Iron (II) iodide	(217, 1956)(246, 1959)(247, 1960)
Lanthanum		
LaCl ₃	Lanthanum (III) chloride	(156, 1959)
Lead		
PbF2	Lead (II) fluoride	(154, 1959)(281, 1922)
PbCl ₂	Lead (II) chloride	(56, 1919)(88, 1933)(107, 1930) (138, 1925)(162, 1940)(266, 1935) (267, 1937)(277, 1929)(281, 1922)

		126
PbBr ₂	Lead (II) bromide	(88, 1933)(102, 1951)(107, 1930) (162, 1940)(277, 1929)(281, 1922)
PbI2	Lead (II) iodide	(88, 1933)(109, 1929)(162, 1940)
Lithium		
LiF	Lithium (I) fluoride	(62, 1959)(205, 1922)(234, 1958) (282, 1921)
LICI	Lithium (I) chloride	(138, 1925)(157, 1959)(161, 1938) (203, 1921)(282, 1921)
LiBr	Lithium (I) bromide	(203, 1921)(282, 1921)
LiI	Lithium (I) iodide	(203, 1921)
Magnesium		
MgF_2	Magnesium (II) fluoride	(200, 1934)
MgCl2	Magnesium (II) chloride	(138, 1925)
Manganese		
MnCl ₂	Manganese (II) chloride	(59, 1929)(138, 1925)(215, 1955)
Mercury		
HgCl2	Mercury (II) chloride	(72, 1928)(111,1911)(178, 1910) (184, 1886)(192, 1914)(193, 1954) (226, 1923)(245, 1936)(263, 1929) (290, 1905)
HgC1	Mercury (I) chloride	(254, 1911)
HgBr ₂	Mercury (II) bromide	(111, 1911)(178, 1910)(192, 1914) (245, 1936)(290, 1905)
HgBr (Hg ₂ Br ₂)	Mercury (I) bromide	(115, 1930)

HgI2	Mercury (II) iodide	(51, 1903)(111, 1911)(137, 1956) (178, 1910)(185, 1928)(192, 1914) (245, 1936)(263, 1929)(290, 1905)
Molybdenum		
Mof ₆	Molybdenum (VI) fluoride	(35, 1961)(195, 1931)
MoF ₅	Molybdenum (V) fluoride	(36, 1961)
MoOF ₄	Molybdenum (VI) oxide fluoride	(36, 1961)
MoCl5	Molybdenum (V) chloride	(39, 1951)(244, 1956)
MoO_2Cl_2	Molybdenum (VI) dioxide chloride	(15, 1957)
Neptunium		
NpF ₆	Neptunium (VI) fluoride	(139, 1958)(286, 1958)(287, 1959)
<u>Nickel</u>		
NiF2 NiCl2 NiBr2	Nickel (II) fluoride Nickel (II) chloride Nickel (II) bromide	(68, 1958) (138, 1925)(215, 1955) (218, 1956)
Niobium (Columbiur	<u>n)</u>	
NbF5	Niobium (V) fluoride	(64, 1951)(117, 1952)(204, 1911)
NbC15	Niobium (V) chloride	(2, 1949)(167, 1937)(216,1952) (265, 1940)
NbCl4	Niobium (IV) chloride	(214, 1954)(216, 1952)
NbOC13	Niobium (V) oxide chloride	(63, 1959)(149,1955)(219,1960) (224, 1960)
$NbBr_5$	Niobium (V) bromide	(2, 1949)
NbI5	Niobium (V) iodide	(3, 1949)

Osmium

OsF_8	Osmium (VIII) fluoride	(206, 1913)(286, 1958)
OsF ₆	Osmium (VI) fluoride	(35, 1961)(206, 1913)
OsF_5	Osmium (V) fluoride	(36, 1961)
OsF_4	Osmium (IV) fluoride	(206, 1913)
Palladium		
$PdCl_2$	Palladium (II) chloride	(18, 1961)(169, 1960)
Phosphorus		
PF_5	Phosphorus (V) fluoride	(134, 1937)(227, 1959)
PF4	Phosphorus (IV) fluoride	(141, 1961)
PF_3	Phosphorus (III) fluoride	(27, 1939)(227, 1959)(268, 1941)
POF_3	Phosphorus (V) oxide fluoride (Phosphoryl (V) fluoride)	(227, 1959)(268, 1941)
PCl ₅	Phosphorus (V) chloride	(76, 1938)(253, 1914)
PCl ₃	Phosphorus (III) chloride	(54, 1941)(105, 1916)(182, 1862) (258, 1952)(268, 1941)
PCl ₂ F ₃	Phosphorus (V) dichloride fluoride	(122, 1959)
PCl_2F	Pho sphorus (III) dichloride fluoride	(27, 1939)(227, 1959)(122, 1959)
PClF ₂	Phosphorus (III) monochloride fluoride	(27, 1939)(227, 1959)
POC13	Phosphorus (V) oxide chloride (Phosphoryl (V) chloride)	(9, 1929)(258, 1952)(268, 1941)

POCl2F	Phosphorus (V) oxide dichlorid fluoride (Phosphoryl (V) dichloride fluoride)	e (227, 1959) (268, 1941)
POCIF ₂	Phosphorus (V) oxide mono- chloride fluoride (Phosphoryl (V) monochloride fluoride)	(227, 1959) (268, 1941)
PBr_5	Phosphorus (V) bromide	(53, 1941) (94, 1958)
PBr ₃	Phosphorus (III) bromide	(105, 1916)
Platinum		
PtF6	Platinum (VI) fluoride	(284, 1957) (286, 1958)
Plutonium		
PuF6	Plutonium (VI) fluoride	(140, 1956)(274, 1961)(286, 1958) (287, 1959)
PuF3	Plutonium (III) fluoride	(31, 1949)(38, 1955)(174, 1949)
PuCl3	Plutonium (III) chloride	(31, 1949)(85, 1959)(174, 1949)
PuBr3	Plutonium (III) bromide	(31, 1949)(106, 1958)(174, 1949)
PuI3	Plutonium (III) iodide	(31, 1949)
Potassium		
KF	Potassium (I) fluoride	(151, 1939)(161, 1938)(180,1958) (205,1922)(282, 1921)
KC1	Potassium (I) chloride	<pre>(29, 1953)(48, 1936)(70, 1926) (88, 1933)(90, 1926)(98, 1936) (100, 1928)(104, 1921)(129, 1929) (144, 1938)(151,1939)(155, 1957) (159, 1958)(161, 1938)(180, 1958) (203, 1921)(271, 1953)(280, 1921)</pre>

(302, 1944)

(302, 1944)

KI Potassium (I) iodide (33, 1958)(42, 1948)(70, 1926) (88, 1933)(161, 1938)(203, 1921) (280, 1921)(302, 1944)

Rhenium

KBr

ReF ₆	Rhenium (VI) fluoride	(35, 1961)(198, 1934)(199, 1932)
ReF ₅	Rhenium (V) fluoride	(36, 1961)
ReF4	Rhenium (IV) fluoride	(198, 1934)
ReOF_5	Rhenium (VII) oxide fluoride	(36, 1961)
ReOF ₄	Rhenium (VI) oxide fluoride	(36, 1961)(198, 1934)
ReO ₂ F ₃	Rhenium (VII) dioxide fluoride	(36, 1961)
ReO_2F_2	Rhenium (VI) dioxide fluoride	(198, 1934)
ReO ₂ Cl ₂	Rhenium (VI) dioxide chloride	(15, 1957)
ReO ₃ Cl	Rhenium (VII) trioxide chloride	(293, 1957)
Rubidium		
RbF	Rubidium (I) fluoride	(205, 1922)(234, 1958)(282, 1921)
RbCl	Rubidium (I) chloride	(144, 1938)(161, 1938)(203, 1921) (271, 1953)(282, 1921)
RbBr	Rubidium (I) bromide	(144, 1938)(203, 1921)(282, 1921)
RbI	Rubidium (I) iodide	(33, 1958)(161, 1938)(203, 1921) (282, 1921)
Ruthenium		
RuF ₅	Ruthenium (V) fluoride	(19, 1948)(207, 1925)

Ruff3Ruthenium (V) fluoride(19, 1948)(207, 1925)RuCl3Ruthenium (III) chloride(17, 1961)(237, 1958)

ScCl3	Scandium (III) chloride	(74, 1939)
ScBr3	Scandium (III) bromide	(74, 1939)
ScI3	Scandium (III) iodide	(74, 1939)
Selenium		
SeF ₆	Selenium (VI) fluoride	(126, 1932)(295, 1933)
SeF4	Selenium (IV) fluoride	(172, 1953)
$\mathrm{SeO}_2\mathrm{F}_2$	Selenium (VI) dioxide fluoride (Selenonyl (VI) fluoride)	(58, 1957)(110, 1957)
SeCl ₄	Selenium (IV) chloride	(296, 1930)
SeOCl ₂	Selenium (IV) oxide chloride (Seleninyl (IV) chloride)	(133, 1922)
Silver		
AgC1	Silver (I) chloride	(138, 1925)(266, 1935)(281, 1922)
AgBr	Silver (I) bromide	(109, 1929)
AgI	Silver (I) iodide	(109, 1929)
Sodium		
NaF	Sodium (I) fluoride	(151, 1939)(161, 1938)(165, 1958) (180, 1958)(203, 1921)(205, 1922) (230, 1957)(282, 1921)
NaCl	Sodium (I) chloride	<pre>(70, 1926)(88, 1933)(90, 1926) (98, 1936)(100, 1928)(129, 1929) (138, 1925)(144, 1938)(151, 1939) (159, 1958)(161, 1938)(203, 1921) (280, 1921)(302, 1944)</pre>

Sodium

NaBr	Sodium (I) bromide	(42, 1948)(98, 1936)(144, 1938) (161, 1938)(203, 1921)(229, 1957) (280, 1921)
NaI	Sodium (I) iodide	(42, 1948)(88, 1933)(280, 1921) (282, 1921)
Strontium		
SrF_2	Strontium (II) fluoride	(200, 1934)
Tantalum		
TaF ₅	Tantalum (V) fluoride	(64, 1951)(204, 1911)
TaCl5	Tantalum (V) chloride	(2, 1949)(167, 1937)(265, 1940)
TaOCl ₃	Tantalum (V) oxide chloride	(224, 1960)
TaBr5	Tantalum (V) bromide	(2, 1949)(291, 1949)
TaI ₅	Tantalum (V) iodide	(3, 1949)
Tellurium		
TeF ₆	Tellurium (VI)fluoride	(126, 1932)(295, 1933)(297, 1944)
TeF ₅ (Te ₂ F ₁₀)	Tellurium (V) fluoride	(297, 1944)
TeF4	Tellurium (IV)fluoride	(116, 1952)
TeCl4	Tellurium (IV) chloride	(37, 1879)(250, 1930)(288, 1941)
TeCl ₂	Tellurium (II) chloride	(37, 1879)(288, 1941)
TeBr ₄	Tellurium (IV) bromide	(37, 1879)
TeBr ₂	Tellurium (II) bromide	(37, 1879)

TIF	Thallium (I) fluoride	(13, 1955)
T1C1	Thallium (I) chloride	(13, 1955)(26, 1958)(162, 1940) (277, 1929)(281, 1922)
TlBr	Thallium (I) bromide	(13, 1955)(162, 1940)(277, 1929) (281, 1922)
TII	Thallium (I) iodide	(13, 1955)(162, 1940)(277, 1929) (281, 1922)
Thorium	5	
ThF	Thorium (IV) fluoride	(46, 1958)
ThCl ₄	Thorium (IV) chloride	(74, 1939)
ThBr4	Thorium (IV) bromide	(74, 1939)
ThI4	Thorium (IV) iodide	(74, 1939)
Tin		
SnCl4	Tin (IV) chloride	(80, 1948)(97, 1940)(118, 1951) (150, 1913)(289, 1919)(299, 1891)
SnCl ₂	Tin (II) chloride	(37, 1879)(73, 1939)(80, 1948) (138, 1925)
nBr4	Tin (IV) bromide	(118, 1951)(228, 1941)
SnBr_2	Tin (II) bromide	(37, 1879)(73, 1939)
SnI_4	Tin (IV) iodide	(118, 1951)(153, 1936)(228, 1941)
SnI_2	Tin (II) iodide	(73, 1939)
Titanium		
TiF ₄	Titanium (IV) fluoride	(93, 1958)
TiCl ₄	Titanium (IV) chloride	(10, 1929)(34, 1956)(82, 1954) (209, 1957)(225, 1953)(283, 1958) (175, 1959)
<u>T itanium</u>

Grant George Conception of Con		
TiCl3	Titanium (III) chloride	(66, 1955)(210, 1955)(223, 1957) (252, 1955)
TiCl ₂	Titanium (II) chloride	(67, 1956)(82, 1954)(83, 1956) (89, 1957)
TiBr4	Titanium (IV) bromide	(22, 1925)(92, 1958)(120, 1955) (228, 1941)
TiBr ₂	Titanium (II) bromide	(91, 1959)
TiI4	Titanium (IV) iodide	(24, 1947)
TiI2	Titanium (II) iodide	(96, 1956)
Tungsten		
WF ₆	Tungsten (VI) fluoride	(12, 1956)(35, 1961)(195, 1931)
WOF ₄	Tungsten (VI) oxide fluoride	(36, 1961)
WC16	Tungsten (VI) chloride	(123, 1943)(164, 1953)(238, 1956) (276, 1937)
wCl ₅	Tungsten (V) chloride	(238, 1956)(239, 1958)
WOCl4	Tungsten (VI) oxide chloride	(127, 1940)(183, 1931)(238, 1956)
WO ₂ Cl ₂	Tungsten (VI) dioxide chloride	(127, 1940)
WBr ₅	Tungsten (V) bromide	(240, 1959)
Uranium		
UF ₆	Uranium (VI) fluoride	(5, 1948)(125, 1951)(135, 1953) (142, 1949)(166, 1953)(179, 1958) (197, 1911)(285, 1948)
UF ₅	Uranium (V) fluoride	(179, 1958)
UF4	Uranium (IV) fluoride	(112, 1947)(177, 1959)

UC16	Uranium (VI) chloride	(86,1946) (113,1958)
UCl ₄	Uranium (IV) chloride	(113, 1958)(243, 1956)(298, 1958)
UOCl ₂	Uranium (IV) oxide chloride (Uranyl (IV) chloride)	(243, 1956)
UBr ₄	Uranium (IV) bromide	(106, 1958)(163, 1952)(259, 1958)
UBr ₃	Uranium (III) bromide	(57, 1958)
Vanadium		
VF ₅	Vanadium (V) fluoride	(41,1957)(273,1957)
VOF3	Vanadium (V) oxide fluoride (Vanadyl (V) fluoride)	(201,1911)(272,1958)
VCl4	Vanadium (IV) chloride	(22, 1925)(168,1961)(189,1870) (202,1911)(242,1956)(251,1945)
VCl ₂	Vanadium (II) chloride	(170, 1961)
VOCI3	Vanadium (V) oxide chloride (Vanadyl (V) chloride)	(79,1937)(128,1952)
Yttrium		
YBr3	Yttrium (III) bromide	(106, 1958)
YI ₃	Yttrium (III) iodide	(49, 1959)
Zinc		
$2nF_2$	Zinc (II) fluoride	(200, 1934)
ZnCl ₂	Zinc (II) chloride	(25,1958)(108,1929)(138,1925) (162,1940)(266,1935)(267,1937)
ZnBr ₂	Zinc (II) bromide	(50, 1933)(103, 1930)(162, 1940)
ZnI2	Zinc (II) iodide	(162, 1940)

Zirconium

ZrF_4	Zirconium (IV) fluoride	(231,	1953)(233,	1954)(234,	1958)
ZrCl_4	Zirconium (IV) chloride	(130, (188,	1949)(171, 1949)(212,	1958)(181, 1950)	1933)
ZrBr ₄	Zirconium (IV) bromide	(181,	1933)		
ZrI4	Zirconium (IV) iodide	(181,	1933)		

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B. BIBLIOGRAPHY OF METAL HALIDE VAPOR PRESSURES

- 1. ALEXANDER, C. A., AND SMITH, T. S. Vapor Pressure of Cobaltous Chloride. Bull. Am. Phys. Soc., vol. 2, 1, 1956, p. 270.
- ALEXANDER, K. M., AND FAIRBROTHER, F. Halides of Columbium and Tantalum. I. The Vapor Pressures of Columbium and Tantalum Pentachlorides and Pentabromides. Jour. Chem. Soc., 1949, pp. S223-S227.
- 3. ______. Halides of Columbium and Tantalum. II. The Vapor Pressure of Tantalum Pentaiodide. Jour. Chem. Soc., 1949, pp. 2472-2476.
- ALLEN, T. L. Vapor Pressure and Heat of Sublimation of Chromous Iodide. The Chromium-Iodine Bond Energy in Chromous Iodide. Jour. Am. Chem. Soc., vol. 78, 1956, pp. 5476-5478.
- 5. AMPHLETT, C. B., MULLINGER, L. W., AND THOMAS, L. F. Physical Properties of Uranium Hexafluoride. Trans. Faraday Soc., vol. 44, 1948, pp. 927-938.
- ANDERSEN, H. C., AND BELZ, L. H. Vapor Pressures of Boron Triiodide and Silicon Tetraiodide. Jour. Am. Chem. Soc., vol. 75, 1953, p. 4828.
- ANSCHUTZ, R., AND EVANS, P. N. (Contribution to the Knowledge of the Chlorine Compounds of Antimony). Ber. deut. chem. Gesell., vol. 19, 1886, pp. 1994-1995.
- 8. ANSCHUTZ, R., AND REITTER, H. (Distillation Under a Reduced Pressure in the Laboratory). 2nd Ed. Cohen, Bonn, 1895.
- 9. ARII, K. Vapor Pressure of Phosphorus Oxychloride. Bull. Inst. Phys. Chem. Res. (Tokyo), vol. 8, 1929, pp. 545-551.
- 10. _____. Vapor Pressure of Titanium Tetrachloride. Bull. Inst. Phys. Chem. Res. (Tokyo), vol. 8, 1929, pp. 714-718.
- BAIMAKOV, A. Yu. (Vapor Tension and Composition of Aluminum Fluoride of Lower Valency). Trudy Leningrad. Politekh. Inst. im. M.I. Kalinina, Elektromet. Tsvetnykh Metal., No. 188, 1957, pp. 156-161.

Titles enclosed in parentheses are translations from the language in which the item was published.

- 12. BARBER, E. J., AND CADY, G. H. Physical Properties of Tungsten Hexafluoride. Jour. Phys. Chem., vol. 60, 1956, pp. 505-506.
- BARROW, R. F., JEFFRIES, E. A. N. S., AND SWINSTEAD, J. M. Heats of Sublimation of Inorganic Substances. III. Thallous Halides. Trans. Faraday Soc., vol. 51, 1955, pp. 1650-1656.
- BARROW, R.F., PUGH, A. C. P., AND SMITH, F. J. Heats of Sublimation of Inorganic Substances. IV. Indium Monobromide and Monoiodide. Trans. Faraday Soc., vol. 51, 1955, pp. 1657-1660.
- BASITOVA, S. M., DAVYDOVSKAYA, R. M., AND BEKHTLE, G. A. Determination of the Vapor Pressure of Molybdenum and Rhenium Oxychlorides). Izvest. Otdel. Estestven. Nawk Akad. Nauk Tadzhik (S. S. R.), No. 23, 1957, pp. 35-39.
- BAXTER, G. P., BEZZENBERGER, K. F., AND WILSON, C. H. Vapor Pressures of Certain Substances: Chloropicrin, Cyanogen Bromide, Methyl-Dichloro-Arsine, Phenyl-Dichloro-Arsene, Diphenyl-Chloro-Arsene, and Arsenic Trichloride. Jour. Am. Chem. Soc., vol. 42, 1920, p. 1386.
- BELL, W. E., GARRISON, M. C., AND MERTEN, U. Thermodynamic Properties of Gaseous Ruthenium Chlorides at High Temperature. Jour. Phys. Chem., vol. 65, 1961, pp. 517-522.
- BELL, W. E., MERTEN, U., AND TAGAMI, M. Palladium-Chlorine System at High Temperature. Jour. Phys. Chem., vol. 65, 1961, pp. 510-517.
- BERNHARDT, H. A., FARRAR, JR., R. L., GUSTISON, R. A., AND KIRSLIS, S. S. Preparation of Rutenium Pentafluoride and the Determination of Its Melting Point and Vapor Pressure. AECD-2390 (K-294), November 1, 1948. (Decl. December 3, 1948) 17 pp.
- BILTZ, W., AND FISCHER, W. (Systematic Affinity Principle. XLIII. The System: Cuprous Chloride - Cupric Chloride). Ztschr. anorg. u. allgem. Chem., vol. 166, 1927, pp. 290-298.
- BILTZ, W., FISCHER, W., AND JUZA, R. (Systematic Affinity Principle. L. Pneumatolytic Transfer of Gold by Means of Chlorine). Ztschr. anorg. u. allgem. Chem., vol. 176, 1928, pp. 121-142.
- BILTZ, W., AND KUENECKE, E. (Systematic Affinity Principle. XXXI. Thiohydrates). Ztschr. anorg. u. allgem. Chem., vol. 147, 1925, pp. 171-187.

- BILTZ, W., SAPPER, A., AND WUNNENBERG, E. (Molecular and Atomic Volumes. XXXIV. Low-Temperature Density of Several Halides of Elements of the Fourth to Sixth Groups). Ztschr. anorg. u. allgem. Chem., vol. 203, 1932, p. 277.
- BLOCHER, JR., J.M., AND CAMPBELL, I. E. Vapor Pressure of Liquid Titanium Tetraiodide. Jour. Am. Chem. Soc., vol. 69, 1947, pp. 2100-2101.
- 25. BLOOM, H., AND WELCH, B. J. Vapor Pressure of Cadmium and Zinc Chlorides. Jour. Phys. Chem., vol. 62, 1958, pp. 1594-1595.
- BOL'SHAKOV, K. A., FEDOROV, P. I., AND SHAKHOVA, M. N. (Pressures of the Saturated Vapor of Thallium Chloride). Nauch Doklady, Vysshei Shkoly, (S.S.S.R.) Khim. i. Khim. Tekhnal, No. 3, 1958, pp. 408-412.
- 27. BOOTH, H. S., AND BOZARTH, A. R. Fluorination of Phosphorus Trichloride. Jour. Am. Chem. Soc., vol. 61, 1939, p. 2927.
- BOOTH, H. S., AND CARTER, J. M. Critical Constants and Vapor Pressure of Boron Trifluoride. Jour. Phys. Chem., vol. 36, 1932, pp. 1359-1363.
- BRADLEY, R. S., AND VOLANS, P. Rates of Evaporation. VI. The Vapor Pressure and Rate of Evaporation of Potassium Chloride. Proc. Roy. Soc. (London) A 217, 1953, pp. 508-523.
- BRAUNE, H., AND TIEDJE, W. (Dissociation of Antimony Pentachloride). Ztschr. anorg. u. allgem. Chem., vol. 152, 1926, pp. 39-51.
- 31. BREWER, L., BROMLEY, L., GILLES, P. W., AND LOFGREN, N.L. Thermodynamic Properties and Equilibria at High Temperatures of the Compounds of Plutonium. Paper 6.40 in National Nuclear Energy Series, Div. IV, vol. 14B, Transuranium Elements: Research Papers, Pt. II, by G. T. Seaborg, J. J. Katz, and W. M. Manning. McGraw-Hill Book Co., Inc., New York, N. Y., 1949, pp. 861-886.
- 32. BREWER, F. M., AND DENNIS, L. M. Germanium. XIX. The Vapor Pressure of Germanium Tetrabromide. Jour. Phys. Chem., vol. 31, 1927, pp. 1101-1105.
- BRIDGES, H. E. Vapor Pressures of Alkali by the Method of Surface Ionization. Univ. Microfilms. (Ann Arbor, Mich.) L. C. Card No. Mic. 58-675, 82 pp., Dissertation Abstr. 18, 1958, pp. 822-825.

- BUTTA, H. Liquid-Vapor Equilibriums. XVIII. The System Titanium (IV) Chloride - 1, 1, 2, 2, Tetrachloroethane. Chem. Listy, vol. 50, 1956, pp. 1646-1648.
- CADY, G. H., AND HARGREAVES, G. B. Vapor Pressures of Some Heavy Transition-Metal Hexafluorides. Jour. Chem. Soc., 1961, pp. 1563-1568.
- 36. Vapor Pressures of Some Fluorides and Oxyfluorides of Molybdenum, Tungsten, Rhenium, and Osmium. Jour. Chem. Soc., 1961, pp. 1568-1573.
- 37. CARNELLEY, T., AND WILLIAMS, W. C. Melting and Boiling Points of Certain Inorganic Substances. Jour. Chem. Soc., vol. 35, 1879, pp. 563-567. (see also vol. 37, 1880, pp. 125-127).
- CARNIGLIA, S. C., AND CUNNINGHAM, B. B. Vapor Pressures of Americium Trifluoride and Plutonium Trifluoride, Heats and Free Energies of Sublimation. Jour. Am. Chem. Soc., vol. 77, 1955, pp. 1451-1453.
- CHILDS, W. J., CLINE, J. E., KISNER, W. M., AND WULFF, J. Molybdenum Plating by Reduction of the Pentachloride Vapor. Trans. Amer. Soc. Metals, vol. 43, 1951, p. 105.
- 40. CHU, S. Y., AND MOROZOV, I. S. (Vapor Pressure of Hafnium Tetrachloride). Zhur. Neorg. Khim., vol. 4, 1959, p. 492.
- CLARK, H. C., AND EMELEUS, H. J. Physical and Chemical Properties of Vanadium Pentafluoride. Jour. Chem. Soc., 1957, pp. 2119-2122.
- 42. COGIN, G. E., AND KIMBALL, G. E. Vapor Pressure of Some Alkali Halides. Jour. Chem. Phys., vol. 16, 1948, pp. 1035-1048.
- CUBICCIOTTI, D. D., AND KENESHEA, JR., F. J. Vapor Pressure of BiBr₃ over Liquid Bi-BiBr₃ Solutions. Jour. Phys. Chem., vol. 62, 1958, pp. 999-1002.
- 44. _____ Vapor Pressure of BiI₃ over Liquid Bi-BiI₃ Solutions. Jour. Phys. Chem., vol. 63, 1959, pp. 295-297.

- 45. CUBICCIOTTI, JR., D.D., KENESHEA, JR., F. J., AND KELLEY,
 C. M. Vapor Pressures of BiCl₃ over Bi-BiCl₃ Solutions. Jour.
 Phys. Chem., vol. 62, 1958, pp. 463-467.
- DARNELL, A. J., AND KENESHEA, JR., F. J. Vapor Pressure of Thorium Fluoride. U. S. Atomic Energy Comm. NAA-SR-2710, 1958, 14 pp. Jour. Phys. Chem., vol. 62, 1958, pp. 1143-1145.
- DARNELL, A. J., AND YOSIM, S. J. Thermodynamic Properties of Solid Bismuth Chlorides. U. S. Atomic Energy Comm. NAA-SR-3827, 1959, 11 pp.
- 48. DEITZ, V. Vapor Pressures of Potassium Chloride and Cesium Iodide Crystals. Jour. Chem. Phys., vol. 4, 1936, pp. 575-580.
- DENNISON, D. H., SPEDDING, F. H., AND DAANE, A.H. Determination of the Melting Point, the Vapor Pressure, and the Decomposition Temperature of Yttrium Tri-iodide. U. S. Atomic Energy Comm., IS-57, Nov. 1959, 16 pp.
- DESAI, M. S., (Determination of the Vapor Pressure of Zinc Bromide). Bull. Acad. Sci. United Provinces Agra and Oudh, India, vol. 2, 1933. pp. 119-128. (Correction reported: ibid., vol. 3, 1933, pp. 31-32).
- 51. DITTE, A. (Action of Mercuric Iodide on Sulfuric Acid and on the Sulfates of Mercury). Compt. rend., vol. 140, 1903, p. 1162.
- 52. DOERNER, H. A. Chemistry of the Anhydrous Chlorides of Chromium. Bureau of Mines Tech. Paper 577, 1937, 51 pp.
- DRIEL, M. van, AND GERDING, H. (Vapor Pressure Measurements on Phosphorus Pentabromide). Rec. trav. chim., vol. 60, 1941, pp. 869-876.
- 55. DUNNE, T.G., AND GREGORY, N. W. Vapor Pressures of Aluminum Chloride and Aluminum Bromide and the Mixed Halide Al₂Br₂Cl₄. Jour. Am. Chem. Soc., vol. 80, 1958, 1526-1530.
- 56. EASTMAN, E. D., AND DUSCHAK, L. H. Vapor Pressure of Lead Chloride. Bureau of Mines Tech. Paper 225, 1919, 16 pp.

- 57. EASTMAN, E. D., AND STRICKLAND, A. E. Equilibrium Pressures in the System Uranium-Uranium Bromide. U. S. Atomic Energy Comm. TID-5290, Book 1, 1958, pp. 215-217.
- ENGELBRECHT, A., AND STOLL, B. (Preparation and Properties of Selenium Dioxydifluoride). Ztschr. anorg. u. allgem. Chem., vol. 292, 1957, pp. 20-24.
- ENGSTROM, R. (Vapor Tension and Dissociation Pressure Over Magnesium Chloride). Kgl. Norske Videnskab. Selskabs Forh. I, pp. 1926-1928 Medd. No. 45, 1929, pp. 131-134.
- EPHRAIM, F. Nature of Subsidiary Valencies. XV. Polyhalides. Ber. deut. chem. Gesell., 1917, pp. 1069-1088. Jour. Chem. Soc., vol. 112, II, 1917, pp. 531-532.
- EVNEVICH, E. V., AND SUKHODSKII, V.A. (Vapor Tension of Bismuth Chloride and Bismuth Bromide). Jour. Russ. Phys. Chem. Soc., vol. 61, 1929, pp. 1503-1512.
- EVSEEV, A. M., POZHARSKAYA, G. V., NESMEYANOV, A. N., AND GERASIMOV, Ya. I. (Vapor Pressure of Lithium Fluoride). Zhur. Neorg. Khim., vol. 4, 1959, pp. 2189-2191.
- FAIRBROTHER, F., COWLEY, A. H., AND SCOTT, N. Oxytrichlorides and Oxytribromides of Niobium (Columbium) (V) and Tantalum (V). Jour. Less-Common Metals, vol. 1, 1959, pp. 206-216.
- FAIRBROTHER, F., AND FRITH, W. C. Halides of Niobium (Columbium) and Tantalum. III. The Vapor Pressure of Niobium and Tantalum Pentafluorides. Jour. Chem. Soc., 1951, pp. 3051-3056.
- 65. FARADAY, MICHAEL. On the Liquefaction and Solidification of Bodies Generally Existing as Gases. Phil. Trans., 135 A, 1845, pp. 155-177.
- 66. FARBER, M., AND DARNELL, A. J. Disproportionation and Vapor Pressure of TiCl₃. Jour, Phys. Chem., vol. 59, 1955, pp. 156-159.
- 67. _____ Disproportionation and Vapor Pressure of Titanium (II) Chloride. Jour. Chem. Phys., vol. 25, 1956, pp. 526-530.
- FARBER, M., MEYER, R. T., AND MARGRAVE, J. L. Vapor Pressure of Nickel Fluoride. Jour. Phys. Chem., vol. 62, 1958, pp. 883-884.

- FINCH, A., AND SCHLESINGER, H. I. Diboron Tetrafluoride. Jour. Am. Chem. Soc., vol. 80, 1958, pp. 3573-3574.
- FIOCK, E. F., AND RODEBUSH, W. H. Vapor Pressures and Thermal Properties of Potassium and Some Alkali Halides. Jour. Am. Chem. Soc., vol. 48, 1926, pp. 2522-2528.
- FISCHER, W. (Thermal Properties of Halides. V. Influence of Constitution on Melting Points, Boiling Points, Heats of Vaporization and Volumes of Halides). Ztschr. anorg. u. Chem., vol. 211, 1933, pp. 321-348.
- 72. FISCHER, W., AND BLITZ, W. (Systematic Affinity Principle. XLIX. The Relation of Chlorine and Other Halogens to Gold). Ztschr. anorg. u. allgem. Chem., vol. 176, 1928, pp. 81-111.
- FISCHER, W., AND GEWEHR, R. (Thermal Properties of the Halides. XIII. Saturation Pressures of the Stannous Halides). Ztschr. anorg. u. allgem. Chem., vol. 242, 1939, pp. 188-192.
- 74. FISCHER, W., GEWEHR, R., AND WINGCHEN, H. (Thermal Properties of the Halides. XII. A New Arrangement for Vapor Pressure Measurement, and the Melting Points and Saturated Vapor Pressures of the Halides of Scandium, Thorium, and Hafnium). Ztschr. anorg. u. allgem. Chem., vol. 242, 1939, pp. 161-187.
- FISCHER, W., AND JUBERMANN, O. (Thermal Properties of the Halides. X. Vapor Pressure and Vapor Density of Gallium (III) Halides). Ztschr. anorg. u. allgem. Chem., vol. 227, 1936, pp. 227-236.
- 76. ______. (Thermal Properties of the Halides. XI. Phosphorus Pentachloride and Aluminum Phosphorus Chloride, AIP Cl8). Ztschr. anorg. u. allgem. Chem., vol. 235, 1938, pp. 337-351.
- 77. FISCHER, W., RAHLFS, O., AND BENZE, B. (Molecular-Weight Determinations by Horstmann's Combination of Vapor Pressure Measure-Ments. II. Vapor Pressures and Vapor Densities of Aluminum Halides). Ztschr. anorg. u. allgem. Chem., vol. 205, 1932, pp. 1-41.
- 78. FISHER, J., AND RUDZITIS, E. Preparation and Properties of Bismuth Pentafluoride. Jour. Am. Chem. Soc., vol. 81, 1959, pp. 6375-6377.

- FLOOD, H., GORRISSEN, J., AND VEIMO, R. Fusion Point, Vapor Pressure and Heat of Evaporation of Vanadium Oxytrichloride. Jour. Am. Chem. Soc., vol. 59, 1937, pp. 2494-2495.
- FRENTS, G. S. (Interaction of Metal Oxides and Sulfides with Metal Chlorides). Izvest. Akad. Nauk (S.S.S.R.) Otdel. Tekh. Nauk., 1948, pp. 235-238.
- FRIEDEL, C., AND CRAFTS, J. M. (On the Vapor Density of Aluminum Chloride Vapor and Its Molecular Weight). Compt. rend., vol. 106, 1888, p. 1767.
- FUNAKI, K., AND UCHIMURA, K. System Titanium-Titanium Tetrachloride. Jour. Chem. Soc. (Japan) Ind. Chem. Sect., vol. 57, 1954, pp. 538-540.
- 83. ______. Reaction Between TiCl2 and TiCl4. Jour. Chem. Soc. (Japan), Ind. Chem. Sect., vol. 59, 1956, pp. 14-17.
- FURBY, E., AND WILKINSON, K. L. Melting and Boiling Points of Beryllium Chloride and An Investigation of the NaCl-BeCl₂ System. Jour. Inorg. and Nuclear Chem., vol. 14, 1960, pp. 123-126.
- GARNER, C. S. Forming Plutonium Salts from Plutonium Oxalates.
 U. S. Atomic Energy Comm. U.S. Patent 2, 875, 025, 1959.
- 86. GREGORY, N. W. Application of a diaphram gage for the Investigation of Vapor Pressures and Chemical Equilibria at High Temperatures.
 U. S. Atomic Energy Comm., BC-16, 1946, 23 pp.
- GREGORY, N. W., AND MacLAREN, R.O. Vaporization Reactions. The Iron-Bromine System. Jour. Phys. Chem., vol. 59, 1955, pp. 110-113.
- GREINER, B., AND JELLINEK, K. (Vapors of the Reciprocal Salt Pair NaCl-KI and the Binary Mixtures PbCl₂-PbBr₂, PbCl₂ - PbI₂, PbI₂ -Cul and CdCl₂ - CdBr₂). Ztschr. physik. Chem. A 165, 1933, pp. 97-120.
- GROSS, P., AND LEVI, D. L. (High-Temperature Equilibriums Involving the Lower Titanium Chlorides). Congr. intern. chim. pure et appl., 16^e Paris 1957, Mem. Sect. Chim. Minerale, 1958, pp. 627-636.
- HACKSPILL, L., AND GRANDADAM, R. (Contribution to the Study of Some Salts of Potassium and Sodium). Ann. chim., vol. 5, 1926, pp. 218-250.

- HALL, E. H., AND BLOCHER, J. M. Thermodynamics of the Disproportionation of Titanium Tribromide. Jour. Phys. Chem., vol. 63, 1959, p. 1526.
- 92. HALL, E. H., BLOCHER, JR., J. M., AND CAMPBELL, I. E. Vapor Pressure of Titanium Tetrabromide. Jour. Electrochem. Soc., vol. 105, 1958, pp. 271-275.
- 93. _____. Vapor Pressure of Titanium Tetrafluoride. Jour. Electrochem. Soc., vol. 105, 1958, pp. 275-278.
- HARRIS, G. S., AND PAYNE, D. S. Vapor Density and Dissociation Pressure of Phosphorus Pentabromide. Jour. Chem. Soc., 1958, pp. 3732-3733.
- 95. HEIN, F., AND WINTNER-HOLDER, I. (Studies of Chromium Halides. II. Investigation of the System Chromium-Iodine. 1. Preparation of Chromous Iodide, and its Behavior Toward Hydrogen). Ztschr. anorg. u. allgem. Chem., vol. 202, 1931, pp. 81-98.
- HERCZOG, A., AND PIDGEON, L. M. Measurements of Pressures in the Titanium-Iodine System by the Effusion Method. Can. Jour. Chem., vol. 34, 1956, pp. 1687-1692.
- 97. HIEBER, W., AND REINDL, E. (Heats of Formation and the Constitution of the Molecular Compounds of Tin Tetrachloride). Ztschr. Elektrochem., vol. 46, 1940, pp. 559-570.
- HINTZ, H., AND JELLINEK, K. (Vaporization Equilibria of the Binary Salt Mixture HgCl₂ - HgBr₂, as Well as of the Reciprocal Salt Pairs (Na, K) (Cl, Br). Ztschr. Elektrochem., vol. 42, 1936, pp. 187-200.
- HOFFMAN, C. J., AND JOLLY, W. L. Antimony Pentafluoride; Density, Melting Point, and Vapor Pressure. Jour. Phys. Chem., vol. 61, 1957, pp. 1574-1575.
- 100. HORIBA, S., AND BABA, H. Determination of the Vapor Pressures of Sodium and Potassium Chlorides. Bull. Chem. Soc. (Japan), vol. 3, 1928, pp. 11-17.
- HORIBA, S., AND INOUYE, R. (Determination of the Vapor Pressure of Arsenic Triiodide). Sexgint, Y. Osaka. Chem. Inst. Dept. Science Kyoto Imp. Univ., 1927, pp. 279-287.

- 102. HYDE, J. L. Melting Point, Oxidation, and Vapor Pressure of Lead Bromide. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 1860-1861.
- ISHIKAWA, F., AND YOSHIDA, T. Thermodynamic Study of Zinc Bromide, Bull. Inst. Phys. Chem. Research (Tokyo)., vol. 9, 1930, pp. 87-93.
- 104. JACKSON, D. D., AND MORGAN, J. J. Measurement of Vapor Pressures of Certain Potassium Compounds. Jour. Ind. Eng. Chem., vol. 13, 1921, pp. 110-118.
- 105. JAEGER, F. M., AND KAHN, J. (Investigations on the Temperature Coefficient of the Free Molecular Surface Energy of Liquids Between-80° and 1650°. XVI. The Surface Tension of Some Halides of Sulfur, Phosphorus, Arsenic, Antimony and Bismuth). Proc. Acad. Sci. (Amsterdam), vol. 19, 1916, pp. 397-404.
- JAFFEY, A. H., AND SEABORG, G. T. Separating Plutonium, Uranium, and Fission Products by Bromination and Distillation.
 U. S. Atomic Energy Comm. U. S. Patent 2, 865, 704. 1958.
- JELLINEK, K., AND GOLUBOWSKI, A. (Vapor Tensions of Molten Mixtures of Lead Chloride and Lead Bromide at High Temperatures). Ztschr. physik. Chem., vol. A147, 1930, pp. 461-469.
- JELLINEK, K., AND KOOP, R. (Heterogeneous Equilibrium of Metallic Halides with Hydrogen Chloride). Ztschr. physik. Chem., vol. A145, 1929, pp. 305-329.
- 109. JELLINEK, K., AND RUDAT, A. (Vapor Pressures of Lead Iodide, Cuprous Iodide, Cuprous Bromide, Silver Iodide, and Silver Bromide by a Modified Streaming Method). Ztschr. physik. Chem., vol. A143, 1929, pp. 55-61.
- 110. JERSCHKEWITZ, H. G. (Selenium Dioxydifluoride) Angew. Chem., vol. 69, 1957, p. 562.
- 111. JOHNSON, F. M. G. Vapor Pressure of Mercuric Chloride, Bromide, and Iodide. Jour. Am. Chem. Soc., vol. 33, 1911, pp. 777-781.
- 112. JOHNSON, K. O. Vapor Pressure Of Uranium Tetrafluoride. U. S. Atomic Energy Comm. Y-42, 1947, 19 pp.

- 113. JOHNSON, O., BUTLER, T., AND NEWTON, A. S. Preparation, Purification, and Properties of Anhydrous Uranium Chloride.
 U. S. Atomic Energy Comm. TID-5290, Book 1, 1958, pp. 1-28.
- 114. JOLLY, W. L., AND LATIMER, W. M. Vapor Pressure of Germanic Iodide. The Entropies of Germanic Halides. The Disproportionation of Germanous Iodide. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 5754-5757.
- 115. JUNG, G., AND ZIEGLER, W. (Vapor Pressure and Constitution of the Vapor of Mercurous Bromide). Ztschr. physik. Chem., vol. A150, 1930, pp. 139-144.
- 116. JUNKINS, J. H., BERNHARDT, H. A., AND BARBER, E. J. Preparation and Properties of Tellurium Tetrafluoride, Jour. Am. Chem. Soc., vol. 74, 1952, pp. 5749-5751.
- 117. JUNKINS, J. H., FARRAR, JR., R. L., BARBER, E. J., AND BERNHARDT, H. A. Preparation and Physical Properties of Niobium Pentafluoride. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 3464-3466.
- KABESH, A., AND NYHOLM, R. S. Coordination Chemistry. X. The Vapor Pressure and Heats of Vaporization of the Stannic Halides. Jour. Chem. Soc., 1951, pp. 3245-3252.
- KANGRO, W., AND BERNSTORFF, H. (Decomposition of Dimeric Iron (III) Chloride Vapor into the Monomer). Ztschr. anorg. u. allgem. Chem., vol. 263, 1950, pp. 316-323.
- KATO, H., AND ABE, M. (Vapor Pressure of Liquid Titanium Tetrabromide). Nippon Kagaku Zasshi, vol. 76, 1955, pp. 1182-1183.
- 121. KENESHEA, F. S., WILSON, W., AND CUBICCIATTI, D. D. Vapor Pressures of Liquid Bi - BiCl₃ Solutions. Jour. Phys. Chem., vol. 64, 1960, pp. 827-829.
- 122. KENNEDY, T., AND PAYNE, D. S. Mixed Halides of Phosphorus. Jour. Chem. Soc., 1959, p. 1228.
- 123. KETELAAR, J. A. A., van OOSTERHOUT, G. W., AND BRAUN, P. B. (Investigation of Tungsten Halides. II. Vapor Pressure of Tungsten Hexachloride). Rec. trav. chim., vol. 62, 1943, pp. 597-605.

- 124. KHANDAMIROVA, N. E., EVSEEV, A. M., AND POZHARSKAYA,
 G. V. (Vapor Pressure of Beryllium Fluoride). Zhur. Neorg. Khim., vol. 4, 1959, pp. 2192-2195.
- 125. KIGOSHI, K. Synthesis of Uranium Hexafluoride and Measurement of its Vapor Pressure. Jour. Chem. Soc. (Japan), Pure Chem. Sect., vol. 72, 1951, pp. 57-59.
- 126. KLEMM, W., AND HENKEL, P. (Some Physical Properties of SF₆, SeF₆, TeF₆, CF₄.) Ztschr. anorg. u. allgem. Chem., vol. 207, 1932, pp. 73-86.
- 127. KOMANDIN, A. V., AND TARASENKOV, D. N. (Physicochemical Investigation of Tungsten Oxychlorides.) Jour. Gen. Chem. (U.S.S.R.) vol. 10, 1940, pp. 1333-1342.
- 128. KOMANDIN, A. V., AND VLODAVETS, M. L. (Vapor Pressure of Vanadium Oxytrichloride.) Zhur. Fiz. Khim., vol. 26, 1952, pp. 1291-1297.
- 129. KORDES, E., AND RAAZ, F. (Boiling-Point Diagrams for Binary High Boiling Point Liquid Mixtures.) Ztschr. anorg. u. allgem. Chem., vol. 181, 1929, pp. 225-236.
- KUHN, D. W., RYON, A. D., AND PALKO, A. A. Vapor Pressures of Zirconium Tetrachloride and Hafnium Tetrachloride. U. S. Atomic Energy Comm. AECD-2768, 1949, 2 p.
- 131. LAUBENGAYER, A. W., AND SCHIRMER, F. B. Chlorides of Gallium. Jour. Am. Chem. Soc., vol. 62, 1940, pp. 1578-1583.
- LUABENGAYER, A. W., AND TABERN, D. L. Germanium.
 XIV. Germanium Tetrachloride. Jour. Phys. Chem., vol. 30, 1926, pp. 1047-1048.
- LENHER, V., SMITH, G. B. L., AND TOWN, G. G. Vapor Pressure of Selenium Oxychloride. Jour. Phys. Chem., vol. 26, 1922, pp. 156-160.
- LINKE, R., AND ROHRMANN, W. (Determination of the Dipole Moments of Phosphorus Pentafluoride and Boron Trifluoride and the Vapor Pressure Curve of Phosphorus Pentafluoride). Ztschr. physik. Chem., B35, 1937, pp. 256-260.

- 135. LLEWELLYN, D. R. Physical Properties of Uranium Hexafluoride. Jour. Chem. Soc., 1953, pp. 28-36.
- MacLAREN, R. O., AND GREGORY, N. W. Vapor Pressure of Iron (II) Bromide. Jour. Phys. Chem., vol. 59, 1955, pp. 184-186.
- 137. MAGEE, D. W. Determination of the Vapor Pressures of Sulfur, Mercuric Iodide, and Cuprous Chloride by the Torsion-Effusion Method. Univ. Microfilms (Ann Arbor, Mich.) Publ. No. 14474, 77 p., Dissertation Abstr. 16, vol. 35, 1956.
- MAIER, C. G. Vapor Pressure of the Common Metallic Chlorides and a Static Method at High Temperatures. Bureau of Mines Tech. Paper 360, 1925, 54 p.
- MALM, J. G., WEINSTOCK, B., AND WEAVER, E. Preparation and Properties of NpF₆; a Comparison with PuF₆. Jour. Phys. Chem., vol. 62, 1958, pp. 1506-1508.
- 140. MANDLEBERG, C. J., ET. AL. Plutonium Hexafluoride. Jour. Inorg. Nuclear Chem., vol. 2, 1956, pp. 358-367.
- 141. MANDLEBERG, C. J., AND DAVIES, D. Vapor Pressure of Plutonium Tetrafluoride. Jour. Chem. Soc., 1961, pp. 2031-2036.
- 142. MASI, J. F. Heats of Vaporization of Uranium Hexafluoride. Jour. Chem. Phys., vol. 17, 1949, pp. 755-758.
- 143. MATTHEWS, J. B., SUMNER, J. F., AND MOELWYN-HUGHES, E. A. Vapor Pressures of Certain Liquids. Trans. Faraday Soc., vol. 46, 1950, pp. 797-803.
- 144. MAYER, J. E., AND WINTNER, I. H. Measurements of Low Vapor Pressures of Alkali Halides. Jour. Chem. Phys., vol. 6, 1938, pp. 301-306.
- 145. MILLER, F. A., CARLSON, G. L., AND WHITE, W. B. Infrared and Raman Spectra of Chromyl Chloride. Spectrochim. Acta, 1959, pp. 709-716.
- 146. MITRA, G. Arsenyl Fluoride. Jour. Am. Chem. Soc., vol. 80, 1958, pp. 5639-5640.
- 147. MOLES, E., AND GOMEZ, L. (Chromyl Chloride.) Ztschr. physik. Chem., vol. 80, 1912, pp. 513-530.

- 148. MOLES, E., AND VIAN, A. (Vapor Pressure of Aluminum Iodide). Annales soc. espan. fis. quim., vol. 34, 1936, pp. 782-786.
- 149. MOROZOV, I. S., AND KORSHUNOV, B. G. (Chlorination of Niobium Pentoxode and Zirconium Dioxide). Khim. Redkikh Elementov, Akad. Nauk (S. S. S. R.) Inst. Obschei i Neorg. Khim., vol. 2, 1955, pp. 102-114.
- MUNDEL, C. F. (Experimental Determination and Theoretical Calculation of Small Vapor Pressure at Low Temperatures). Ztschr. physik. Chem., vol. 85, 1913, pp. 435-465.
- 151. NARYSHKIN, I. I. (Vapor Pressures of Some Salts at High Temperatures). Jour. Phys. Chem. (U.S.S.R.), vol. 13, 1939, pp. 528-533.
- 152. . (Determination of the Vapor Pressure of Aluminum Chloride and its Melts with Sodium Chloride at High Temperatures.) Jour. Phys. Chem. (U.S.S.R.), vol. 13, 1939, pp. 690-692.
- 153. NEGISHI, G. R. Heat of Fusion and Vapor Pressure of Stannic Iodide. Jour. Am. Chem. Soc., vol. 58, 1936, pp. 2293-2296.
- 154. NESMEYANOV, A. N., AND IOFA, B. Z. (Vapor Pressure of Solid Lead Fluoride). Zhur. Neorg. Khim., vol. 4, 1959, pp. 486-488.
- 155. NESMEYANOV, A. N., AND SAZONOV, L. A. (Measurement of the Vapor Pressure of Potassium Chloride and of the Partial Pressures of the Components of the KCl-RbCl System by Using Radioactive Indicators). Zhur. Neorg. Khim., vol. 2, 1957, pp. 1183-1189.
- 156. (Measurement of the Vapor Pressure of Anhydrous Lanthanum Chloride by Method of Radioactive Tracer). Zhur. Neorg. Khim., vol. 4, 1959, pp. 230-231.
- 157. _____. (Measurement of Vapor Pressure of Lithium Chloride). Zhur. Neorg. Khim., vol. 4, 1959, pp. 231-233.
- 158. ______. (Measurement of Saturated Vapor Pressure of Cesium Chloride by Use of Radioactive Tracer Cs¹³⁷). Zhur. Neorg. Khim., vol. 5, 1960, pp. 519-521.

- 159. NEUHAUS, A., AND RETTING, W. (Condensation and Evaporation of Zinc Sulfide and Cadmium Sulfide in a High Vacuum). Ztschr. Elektrochem., vol. 62, 1958, pp. 33-40.
- 160. NILSON, L. F., AND PETTERSSON, O. (Concerning Some Physical Constants of Germanium and Titanium). Ztschr. physik. Chem., vol. 1, 1887, pp. 27-38.
- 161. NIWA, K. Determination of the Vapor Pressures of Solid Salts. II. Vapor Pressures of Alkali Halides and Their Thermodynamic Calculation. Jour. Chem. Soc. (Japan), vol. 59, 1938, pp. 637-649.
- 162. NIWA, K., SATO, M., AND YOSIYAMA, M. Determination of the Vapor Pressure of Solid Salts. III. Vapor Pressure of TlCl, TlBr, Tl I, PbCl₂,PbBr₂, PbI₂, ZnCl₂, ZnBr₂, ZnI₂, CdCl₂, CdBr₂, and Cd I₂ and Calculation of their Thermodynamic Values. Jour. Fac. Sci., Hokkaido Imp. Univ., Ser. III 3, No. 1, 1940, pp. 17-33.
- 163. NOTTORF, R. W. Some Problems in Chemistry of Uranium and Thorium of Interest to the Development of Atomic Power. Iowa State Coll. Jour. Sci., vol. 26, 1952, pp. 255-257.
- 164. NOVIKOV, G. I., AND SHCHUKAREV, S. A. (Gravimetric Method for Measuring the Pressure of a Saturated Vapor). Uchenye Zapiski, Leningrad, Gosudarst Univ. im A. A. Zhdanova, No. 163. Ser. Khim. Nauk., No. 12, 1953, pp. 37-40.
- 165. NOVOSELOVA, A. V., MURATOV, F. Sh., RESHETNIKOVA, L. P., AND GORDEEV, I. V. (Dissociation Pressure of Sodium Fluoroberyllate of the Composition Na₂ BeF₄). Vestnik Moskov. Univ., Ser. Mat., Mekhan., Astrom., Fiz. i Khim., vol. 13, No. 6, 1958, pp. 181-190.
- 166. OLIVER, G. D., MILTON, H. T., AND GRISARD, J. W. Vapor Pressure and Critical Constants of Uranium Hexafluoride. Jour. Am. Chem. Soc., vol. 75, 1953, pp. 2827-2829.
- 167. OPYKHTINA, M. A., AND FLEISHER, N. A. (Vapor Pressure of Tantalum and Columbium Chlorides). Jour. Gen. Chem. (U.S.S.R.), vol. 7, 1937, pp. 2016-2021.
- 168. ORANSKAYA, M. A., LEBEDEV, U. S., AND PERFILOVA, I. L. (Disporportionation of Vanadium Trichloride). Zhur. Neorg. Khim., vol. 6, 1961, pp. 259-260.

- 169. ORANSKAYA, M. A., AND MIKHAILOVA, N. A. (Dissociation Pressure and Vapor Pressure of Palladium Chloride). Zhur. Neorg. Khim., vol. 5, 1960, p. 12.
- ORANSKAYA, M. A., AND PERFILOVA, I. L. (Saturated Vapor Pressure of Vanadium Dichloride). Zhur. Neorg. Khim., vol. 6, 1961, pp. 257-258.
- 171. PALKO, A. A., RYON, A. D., AND KUHN, D. W. Vapor Pressure of Zirconium Tetrachloride and Hafnium Tetrachloride. Jour. Phys. Chem., vol. 62, 1958, pp. 319-322.
- 172. PEACOCK, R. D. Properties of Selenium Tetrafluoride. Jour. Chem. Soc., 1953, pp. 3617-3619.
- 173. PETIT, M. Dissociation of Auric Chloride. Bul. soc. chim., vol. 37, 1925, pp. 615-623.
- PHIPPS, T. E., SEARS, C. W., SEIFERT, R. L., AND SIMPSON, O. C. Vapor Pressure of Plutonium Halides, Paper 6.1a in National Nuclear Energy Series, Div. IV, vol. 14B, Transuranium Elements: Research Papers, Pt. I, by G. T. Seaborg, J. J. Katz, and W. M. Manning. McGraw-Hill Book Co., Inc., New York, N. Y., 1949, pp. 682-703.
- 175. PIKE, F. P., AND FOSTER, C. T. Vapor Pressure and Boiling Point of Titanium Tetrachloride. Jour. Chem. Engr. Data, vol. 4, 1959, pp. 305-306.
- POHLAND, E., AND HARLOS, W. (Non-metallic Halogen Compounds. III. Saturation Pressures of Boron Trifluoride). Ztschr. anorg. u. allgem. Chem., vol. 207, 1932, pp. 242-245.
- 177. POPOV, M. M., KOSTYLEV, F. A., AND ZUBOVA, N. V. (Vapor Pressure of Uranium Tetrachloride). Zhur. Neorg. Khim., vol. 4, 1959, p. 1708.
- 178. PRIDEAUX, E. B. R. Vapor Pressures and Molecular Volumes of the Mercuric Halides and the Relations Between Atomic Volumes of Elements Before and After Combination. Jour. Chem. Soc., vol. 97, 1910, pp. 2032-2044.

- 179. PRIEST, H. F. The Vapor Pressure of Uranium Hexafluoride in Equilibrium with Uranium Pentafluoride. U. S. Atomic Energy Comm. TID-5290, Bk. 2., Paper 74, 1943, pp. 738-741.
- 180. PUGH, A. C. P., AND BARROW, R. F. Heats of Sublimation of Inorganic Substances. V. Alkali Metal Fluorides. Trans. Faraday Soc., vol. 54, 1958, pp. 671-678.
- 181. RAHLFS, O., AND FISCHER, W. (Thermal Properties of Halides. VI. Vapor Pressures and Vapor Densities of Beryllium and Zirconium Halides). Ztschr. anorg. u. allgem. Chem., vol. 211, 1933, pp. 349-367.
- 182. REGNAULT, H. V. (Saturation Vapor Pressures in the Vacuum). Mem. de Paris., vol. 26, 1862, p. 339.
- 183. REINDERS, W., AND van LIEMPT. J. A. M. (Tungsten Oxytetrachloride). Rec. trav. Chim., vol. 50, 1931, p. 1002.
- RICHTER, V. (Concerning the Socalled Critical Pressure of Solid Substances). Ber. deut. chem. Gesell., vol. 19, 1886, p. 1057.
- RINSE, J. (Vapor Pressure and Dissociation of Mercuric Iodide). Rec. trav. Chim., vol. 47, 1928, pp. 33-36.
- 186. ROBERT, C. (Vapor Pressure Measurements of Indium Halides). Helv. Phys. Acta, vol. 9, 1936, pp. 405-436.
- 187. ROBERT, C., AND WEHRLI, M. (Vapor Pressure Measurements on Indium Halides). Helv. Phys. Acta., vol. 8, 1935, pp. 322-324.
- ROGERS, B. A., ET. AL. A Progress Report in Metallurgy. III. The Production of Zirconium. U. S. Atomic Energy Comm. ISC-45. 1949.
- 189. ROSCOE, H. E. (Researches on Vanadium). Annal. Chem. Pharm. (Suppl. Bd.), VII, 1870, pp. 70-87.
- 190. ROSE, T. K. Dissociation of Chloride of Gold. Jour. Chem. Soc., vol. 67, 1895, p. 881.
- ROTINYANZ, L., AND SUCHODSKII, V. (Determination of the Critical Temperature of the Aluminum and Antimony Halides). Ztschr. physik. Chem., vol. 87, 1914, pp. 635-637.

- ROTINYANZ, L., AND SUCHODSKII, V. (Determination of the Critical Temperature of Some Mercury-Halides). Ztschr. physik. Chem., vol. 87, 1914, pp. 253-256.
- 193. RUF, R., AND TREADWELL, W. D. (Vapor Pressure of Mercuric Chloride). Helv. Chim. Acta, vol. 37, 1954, pp. 1941-1948.
- 194. RUFF, O. (Fluorine and its Compounds). Ber. deut. chem. Gesell., 69A, 1936, pp. 181-194.
- 195. RUFF, O., AND ASCHER, E. (Some Physical Constants of SiF₄, WF₆, and MoF₆). Ztschr. anorg. u. allgem. Chem., vol. 196, 1931, pp. 413-420.
- 196. RUFF, O., BRAIDA, A., BRETSCHNEIDER, O., MENZEL, W., AND PLAUT, H. (Preparation, Vapor Pressure and Density of BF₃, AsF₅, and BrF₃). Ztschr. anorg. u. allgem. Chem., vol. 206, 1932, pp. 59-64.
- 197. RUFF, O., AND HEINZELMANN, A. (Uranium Hexafluoride). Ztschr. anorg. u. allgem. Chem., vol. 72, 1911, pp. 63-84.
- 198. RUFF, O., AND KWASNIK, W. (Rhenium Fluorides (Especially ReF6, ReOF4, ReO₂F₂, ReF4, and K₂ReF6). Ztschr. anorg. u. allgem. Chem., vol. 219, 1934, pp. 65-81.
- 199. RUFF, O., KWASNIK, W., AND ASCHER, E. (Fluorination of Rhenium). Ztschr. anorg. u. allgem. Chem., vol. 209, 1932, pp. 113-122.
- 200. RUFF, O., AND LEBOUCHER, L. (Vapor Pressures of Zinc, Cadmium, Magnesium, Calcium, Strontium, Barium and Aluminum Fluorides). Ztschr. anorg. u. allgem. Chem., vol. 219, 1934, pp. 376-381.
- 201. RUFF, O., AND LICKFETT, H. (Vanadium Fluorides). Ber. deut. chem. Gesell., vol. 44, 1911, pp. 2539-2549.
- 202. _____. (Vanadium Chlorides). Ber. deut. chem. Gesell., vol. 44, 1911, pp. 506-521.
- 203. RUFF, O., AND MUGDAN, S. (High Temperature Studies. XIII. The Measurement of Vapor Pressures at High Temperatures and the Vapor Pressures of Alkali Halides). Ztschr. anorg. u. allgem. Chem., vol. 117, 1921, pp. 147-171.
- 204. RUFF, O., AND SCHILLER, E. (Tantalum and Columbium Pentafluorides, and the Preparation of Pure Tantalic and Columbic Acids). Ztschr. anorg. u. allgem. Chem., vol. 72, 1911, pp. 329-358.

- 205. RUFF, O., SCHMIDT, G., AND MUGDAN, S. (Studies at High Temperatures. XV. The Vapor Pressures of the Alkali Fluorides). Ztschr. anorg. u. allgem. Chem., vol. 123, 1922, pp. 83-88.
- 206. RUFF, O., AND TSCHIRCH, F. W. (Fluorides of Osmium). Ber. deut. chem. Gesell., vol. 46, 1913, pp. 929-949.
- 207. RUFF, O., AND VIDIC, E. (Ruthenium Pentafluoride and a Method for the Separation of Platinum and Ruthenium). Ztschr. anorg. u. allgem. Chem., vol. 143, 1925, pp. 163-182.
- 208. RUSSELL, JR., H., RUNDTE, R.E. AND YOST, D. M. Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure and Entropy of Arsenic Trifluoride. Jour. Am. Chem. Soc., vol. 63, 1941, pp. 2825-2828.
- SAHEKI, Y., AND FUNAKI, K. (Purification and Thermodynamic Properties of Titanium Tetrachloride). Nippon Kagaku Zasshi, vol. 78, 1957, pp. 754-759.
- SANDERSON, B. S. Disproportionation and Vapor Pressures of Titanium Trichloride. Univ. Microfilms, Publ. No. 12,187, 79 pp. Dissertation abstr. 15, 1955, pp. 992-993.
- 211. SANO, K. Thermodynamic Studies of Metallic Chlorides. VII. The Vapor Pressure of Ferric Chloride. Jour. Chem. Soc. (Japan), vol. 59, 1938, pp. 1073-1074.
- SCARBOROUGH, J. M., AND PLUCKNETT, W. K. Vapor Pressure of Zirconium Tetrachloride by Molecular Effusion. U. S. Atomic Energy Comm. ISC-92, 1950, 31 p.
- 213. SCHAFER, H. (System $Fe_2O_3 FeCl_3 H_2O HCl$. VI. The System $Fe_2O_3 - FeOCl - FeCl_3 - H_2O - HCl$ between 100 and 1000°). Ztschr. anorg. Chem., vol. 261, 1950, pp. 142-152.
- 214. SCHAFER, H., AND BAYER, L. (Niobium and Tantalum. XIII. Saturation Pressure over Solid Niobium (IV) Chloride). Ztschr. anorg. u. allgem. Chem., vol. 277, 1954, pp. 140-145.
- SCHAFER, H., BAYER, L., BREIL, G., ETZEL, K., AND KREHL, K. (Saturation Pressures of Manganese Chloride, Ferrous Chloride, Cobaltous Chloride, and Nickel Chloride). Ztschr. anorg. u. allgem. Chem., vol. 278, 1955, pp. 300-309.

- 216. SCHAFER, H., BAYER, L., AND LEHMANN, H. (Chemistry of the Elements Niobium and Tantalum. IX. Equilibrium Pressure of the Decomposition of Niobium Tetrachloride). Ztschr. anorg. u. allgem. Chem., vol. 268, 1952, pp. 268-278.
- 217. SCHAFER, H., AND HONES, W. J. (Gaseous Ferric Iodide and the Iron-Iodine Equilibrium). Ztschr. anorg. u. allgem. Chem., vol. 288, 1956, pp. 62-80.
- SCHAFER, H., AND JACOB, H. (Saturation Pressures over Nickel Bromide). Ztschr. anorg. u. allgem. Chem., vol. 286, 1956, pp. 56-57.
- 219. SCHAFER, H., AND KAHLENBERG, F. (Chemistry of Niobium and Tantalum. XXIII. The Thermochemistry of the Niobium Chlorides). Ztschr. anorg. u. allgem. Chem., vol. 305, 1960, pp. 291-326.
- 220. SCHAFER, H., AND KREHL, K. (Gaseous Cobalt (III) Chloride and its Thermochemical Properties). Ztschr. anorg. u. allgem. Chem., vol. 268, 1952, pp. 25-34.
- 221. (System Iron-Chlorine. II. The Reaction Equilibrium $FeCl_2(g) + H_2 = Fe + 2HCl$). Ztschr. anorg. u. allgem. Chem., vol. 268, 1952, pp. 35-46.
- 222. SCHAFER, H., AND OEHLER, E. (System Iron-Chlorine. III. Chlorine Pressure Over the Crystal Phases Iron (III) Chloride and Iron (II) Chloride). Ztschr. anorg. u. allgem. Chem., vol. 271, 1953, pp. 206-210.
- 223. SCHAFER, H., AND SIBBING, E. (Saturation Pressure of Titanium (III) Chloride and its Association in the Gas Phase). Angew. Chem., vol. 69, 1957, p. 479.
- 224. SCHAFER, H., SIBBING, E., AND GERKEN, R. (Chemistry of Niobium and Tantalum Oxychloride). Ztschr. anorg. u. allgem. Chem., vol. 307, 1960, pp. 163-173.
- 225. SCHAFER, H., AND ZEPPERNICK, F. (Saturation Pressure over Liquid Titanium Tetrachloride). Ztschr. anorg. u. allgem. Chem., vol. 272, 1953, pp. 274-278.
- 226. SCHMIDT, G. C., AND WALTER, R. (Electrical Conductivity of Salt Vapors. IV.) Ann. Physik, vol. 72, 1923, pp. 565-594.

- 227. SEEL, F., AND BALLREICH, K. (Preparation of Inorganic Fluorine Compounds with Benzoyl Fluoride and Benzensulfonyl Fluoride). Chem. Ber., vol. 92, 1959, pp. 2117-2122.
- 228. SEKI, S. Vapor Pressure of Molecular Crystals. II. The Vapor Pressure of CBr4, TiBr4, SnBr4 and SnI4. Jour. Chem. Soc. (Japan), 1941, pp. 789-795.
- 229. SEMENKOVICH. S. A. (Aluminum Monobromide). Zhur. Priklad. Khim., vol. 30, 1957, pp. 933-936.
- 230. SENSE, K. A., ALEXANDER, C. A., BOWMAN, R. E., STONE, R. W., AND FILBERT, JR., R. B. Vapor Pressure of Sodium Fluoride. Jour. Phys. Chem., vol. 61, 1957, p. 384.
- 231. SENSE, K. A., SNYDER, M. J., AND CLEGG, J. W. Vapor Pressures of Beryllium Fluoride and Zirconium Fluoride. U. S. Atomic Energy Comm. AECD-3708, 1953, 18 pp.
- 232. _____. Vapor Pressure of Beryllium Fluoride. Jour. Phys. Chem., vol. 58, 1954, pp. 223-224.
- 233. SENSE, K. A., SNYDER, M. J., AND FILBERT, JR., R. B. Vapor Pressure of Zirconium Fluoride. Jour. Phys. Chem., vol. 58, 1954, pp. 995-996.
- 234. SENSE, K. A., AND STONE, R. W. Vapor Pressures and Molecular Composition of Vapors of RbF - ZrF₄ and LiF - ZrF₄ Systems. Jour. Phys. Chem., vol. 62, 1958, pp. 1411-1418.
- SEVRYUGOVA, N. N., UVAROV, O. V., AND ZHAVORONKOV, N. M. Separation Coefficient of Boron Isotopes During Equilibrium Evaporation of Boron Chloride. Jour. Nuclear Energy, vol. 4, 1957, pp. 483-489.
- 236. SHAIR, R. C., AND SCHURIG, W. F. Vapor-Liquid Equilibrium of Antimony Pentafluoride-Hydrogen Fluoride. Ind. Eng. Chem., vol. 43, 1951, pp. 1624-1627.
- 237. SHCHUKAREV, S. A., KOLBIN, N. I., AND RYABOV, A. N. Dissociation and Sublimation Pressure of Ruthenium Trichloride). Zhur. Neorg. Khim., vol. 3, 1958, pp. 1721-1726.

- SH CHUKAREV, S. A., AND NOVIKOV, G. I. (Thermodynamic Study of Some Chlorine Derivatives of Tungsten. I. Saturated Vapor Pressure of the Hexa-, Penta-, and Oxytetrachlorides of Tungsten). Zhur. Neorg. Khim., vol. 1, No. 3, 1956, pp. 357-366.
- 239. SHCHUKAREV, S. A., NOVIKOV, G. I., AND ANDREEVA, N. V. (Thermodynamic Study of Lower Tungsten Chlorides). Zhur. Obshchei Khim., vol. 28, 1958, pp. 1998-1999.
- 240. SHCHUKAREV, S. A., NOVIKOV, G. I., AND KOKOVIN, G. A. (Determination of the Vapor Pressure and the Molecular Weight of Tungsten Pentabromide). Zhur. Neorg. Khim., vol. 4, 1959, pp. 2184-2188.
- 241. SHCHUKAREV, S. A., AND ORANSKAYA, M. A. (Thermal Dissociation of Gold Bromide). Zhur. Neorg. Khim., vol. 3, 1959, pp. 1478-1482.
- 242. SHCHUKAREV, S. A., ORANSKAYA, M. A., TOLMACHEVA, T. A., AND YAKHKIND, A. K. (Pressure of Saturated Vapor of Vanadium Tetrachloride). Zhur. Neorg. Khim., vol. 1, No. 1, 1956, pp. 30-35.
- 243. SHCHUKAREV, S. A., VASIL'KOVA, I. V., EFIMOV, A. I., AND KIRDYASHEV, V. P. (Determination of the Vapor Pressure of UCl₄ and of the Disproportionation Pressure of UOCl₂.) Zhur. Neorg. Khim., vol. 1, 1956, pp. 2272-2277.
- 244. SHCHUKAREV, S. A., VASIL'KOVA, I. V., AND SHARUPIN, B. N. (Molybdenum Halides. I. The Evaporation and Dissociation Pressures of Molybdenum Pentachloride). Zhur. Obschei Khim., vol. 26, 1956, pp. 2093-2097.
- 245. SHIBATA, Z., AND NIWA, K. Vapor Pressure Determination of Solid Mercuric Halides. Jour. Chem. Soc. (Japan), vol. 57, 1936, pp. 1309-1319.
- 246. SIME, R. J. Vaporization Characteristics of Some Iron and Chromium Halides. Univ. Microfilm. (Ann Arbor, Mich.) L.C. Card No. Mic. 59-3346, 103 pp.Dissertation Abstr. 20, 1959, p. 903.
- 247. SIME, R. J., AND GREGORY, N. W. Vapor Pressure of FeCl₂, FeBr₂ and Fel₂ by the Torsion Effusion Method. Jour. Phys. Chem., vol. 64, 1960, pp. 86-89.
- 248. _____. Vaporization of Chromium (III) Bromide. Jour. Am. Chem. Soc., vol. 82, 1960, pp. 93-96.

- 249. SIME, R. J., AND GREGORY, N. W. Vapor Pressure of Chromium (II) Bromide. Jour. Am. Chem. Soc., vol. 82, 1960, pp. 800-801.
- 250. SIMONS, J. H. Properties of Tellurium Tetrachloride. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 3488-3493.
- 251. SIMONS, J. H., AND POWELL, M. G. Properties of VCl₄. Jour. Am. Chem. Soc., vol. 67, 1945, pp. 75-77.
- 252. SKINNER, G. B., AND RUEHRWEIN, R. A. Thermodynamic Properties of the Titanium Chlorides. Jour. Phys. Chem., vol. 59, 1955, pp. 113-117.
- 253. SMITH, A., AND CALVERT, R. P. Dissociation Pressures of Ammonium-and Tetramethyl Ammonium Halides and of Phosphonium Iodide and Phosphorus Pentachloride. Jour. Am. Chem. Soc., vol. 36, 1914, pp. 1363-1382.
- 254. SMITH, A., AND MENZIES, A. W. C. (Vapor Pressure Studies. VII. The Vapor Pressure of Dried Calomel). Ztschr. physik. Chem., vol. 76, 1911, pp. 713-720.
- 255. SMITH, F. J., AND BARROW, R. F. Heats of Sublimation of Inorganic/Substances. VI. Some Halides of Gallium and Indium. Trans. Faraday Soc., vol. 54, 1958, pp. 826-829.
- 256. SMITS, A., AND MEIJERING, J. L. (Complexity of Aluminum Chloride). Ztschr. physik. Chem. B41, 1938, pp. 98-111.
- 257. SMITS, A., MEYERING, J. L., AND KAMERMANS, M. A. (Complexity of Aluminum Chloride. II). Proc. Acad. Sci. (Amsterdam) vol. 35, 1932, pp. 193-196.
- SOKOLOVA, T. I., ILLARIONOV, V. V., AND VOL'FKOVICH, S. I. (Separation of Mixtures of POCl₃ and PCl₃). Jour. Appl. Chem. (U.S.S.R.), vol. 25, 1952, pp. 727-731.
- 259. SPEDDING, F. H., ET. AL. Preparation and Some Properties of UBr4, UBr3, UOBr2 and UO2Br2. U. S. Atomic Energy Comm. TID-5290, Book 1, 1958, pp. 91-119.
- STIRNEMANN, E. (System Iron Chloride-Water at High Temperatures). Neues Jahrb. Mineral. Geol. Beil. - Bd. 52A, 1925, pp. 334-377.

- 261. STOCK, A., AND KUSS, E. (Boron Tribromide). Ber. deut. chem. Gesell. vol. 47, 1914, pp. 3113-3115.
- 262. STOCK, A., AND PRIESS, O. (Boron Trichloride. A Greaseless Glass Valve). Ber. deut. chem. Gesell., vol. 47, 1914, pp. 3109-3113.
- 263. STOCK, A., AND ZIMMERMANN, W. (Vapor Pressures of Mercury and Some Mercury Compounds at Low Temperatures). Monatsh., vol. 53-54, 1929, pp. 786-790.
- 264. TAKAHASHI, T. Sublimation of Anhydrous Aluminum Chloride. Jour. Chem. Soc. (Japan). Ind. Chem. Sect., vol. 57, 1954, pp. 337-339.
- 265. TARASENKOV, D. N., AND KOMANDIN, A. V. (Vapor Pressure of Tantalum and Columbium Pentachlorides and its Mixtures with Titanium Tetrachloride). Jour. Gen. Chem. (U.S.S.R.), vol. 10, 1940, pp. 1319-1327.
- 266. TARASENKOV, D. N., AND KOZHMYAKOV, P. A. (Vapor Pressure of Zinc Chloride, Lead Chloride, Cadmium Chloride, Cuprous Chloride, and Silver Chloride). Jour. Gen. Chem. (U.S.S.R.), vol. 5, 1935, pp. 830-835.
- 267. TARASENKOV, D. N., AND SKULKOVA, G. V. (Vapor Pressures of Zinc Chloride, Lead Chloride, and Cadmium Chloride in Atmospheres of Chlorine and Nitrogen). Jour. Gen. Chem. (U.S.S.R.), vol. 7, 1937, pp. 1721-1728.
- 268. TARBUTTON, G., EGAN, JR., E. P., AND FRARY, S. G. Phosphorus-Halogen Compounds from Phosphorus Pentoxide and Halides. Properties of Phosphorus Trifluoride and Phosphorus Oxyfluoride. Jour. Am. Chem. Soc., vol. 63, 1941, pp. 1782-1789.
- 269. TOLMACHEVA, T. A., AND ANDRINOVSKAYA, T. L. (Vapor Pressures of Cadmium Iodide and Bromide). Vestnik Leningrad, Univ., vol. 15, No. 10, Ser. Fiz, i Khim. No. 2., 1960, pp. 131-136.
- TREADWELL, W. D., AND TEREBESI, L. (Chlorination of Aluminum Oxide with Chlorine and Charcoal). Helv. Chim. Acta, vol. 15, 1932, pp. 1053-1066.

- 271. TREADWELL, W. D., AND WERNER, W. (Vapor Pressure of Solid Cesium, Rubidium, and Potassium Chlorides by the Transport Method in a Stream of Nitrogen). Helv. Chim. Acta, vol. 36, 1953, pp. 1436-1444.
- 272. TREVORROW, L. E. Vapor Pressure of Vanadium Oxytrifluoride. Jour. Phys. Chem., vol. 62, 1958, p. 362.
- 273. TREVORROW, L. E., FISCHER, J., AND STEUNENBERG, R. K. Preparation and Properties of Vanadium Pentafluoride. Jour. Am. Chem. Soc., vol. 79, 1957, pp. 5167-5168.
- 274. TREVORROW, L. E., SHINN, W. A., AND STEUNENBERG, R. K. Thermal Decomposition of Plutonium Hexafluoride. Jour. Phys. Chem., vol. 65, 1961, pp. 398-403.
- 275. URRY, G., WARTIK, T., AND SCHLESINGER, H. I. New Subchloride of Boron, B₄Cl₄. Jour. Am. Chem. Soc., vol. 74, 1952, p. 5809.
- 276. VERNON, A.A.Vapor Pressure and Dissociation of Tungsten Hexachloride in the Gas Phase. Jour. Am. Chem. Soc., vol. 59, 1937, pp. 1832-1833.
- 277. VOLMER, F. (Vapor Pressure of Thallium and Lead Halides). Physik. Ztschr., vol. 30, 1929, pp. 590-596.
- 278. WAGNER, C., AND STEIN, V. (Volatility of Cr Halides and the Equilibriums Involved in Chromizing Fe.). Ztschr. physik. Chem., vol. 192, 1943, pp. 129-156.
- 279. WALDEN, P. (Inorganic Solvents and Ionization Agents). Ztschr. anorg. u. allgem. Chem., vol. 29, 1902, p. 371.
- 280. WARTENBERG, H. van, AND ALBRECHT, P. (Vapor Pressures of Some Salts). Ztschr. Elektrochem., vol. 27, 1921, pp. 162-167.
- 281. WARTENBERG, H. yan, AND BOSSE, O. (Vapor Pressure of Some Salts. III.). Ztschr. Elektrochem., vol. 28, 1922, pp. 384-387.
- 282. WARTENBERG, H. yan, AND SCHULZE, H. (Vapor Pressure of Some Salts. II.). Ztschr. Elektrochem., vol. 27, 1921, pp. 568-573.

- 283. WEED, JR., H. C. Vapor Pressure of Titanium Tetrachloride. Univ. Microfilms (Ann Arbor, Mich.) L. C. Card No. Mic. 58-581, 147 pp. Dissertation Abstr., vol. 18, 1958, pp. 843-844.
- 284. WEINSTOCK, B., CLAASSEN, H. H., AND MALM, J. G. Platinum Hexafluoride. Jour. Am. Chem. Soc., vol. 79, 1957, p. 5832.
- 285. WEINSTOCK, B., AND CRIST, R. H. Vapor Pressure of Uranium Hexafluoride. Jour. Chem. Phys., vol. 16, 1948, pp. 436-441.
- 286. WEINSTOCK, B., AND MALM, J. G. Recent Studies with Hexafluorides. Paper P/942 in Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, vol. 28, Basic Chemistry in Nuclear Energy. United Nations Publication, New York, N. Y., 1958, pp. 125-129.
- 287. WEINSTOCK, B., WEAVER, E. E., AND MALM. J. G. Vapor Pressures of Neptunium Hexafluoride and Plutonium Hexafluoride; Thermodynamic Calculations with Uranium Hexafluoride, Neptunium Hexafluoride and Plutonium Hexafluoride. Jour. Inorg. and Nuclear Chem., vol 11, 1959, pp. 104-114.
- WEHRLI, M., AND GUTZWILLER, N. (Vapor Pressure and Band Spectrum of Tellurium Dichloride). Helv. Phys. Acta, vol. 14, 1941, pp. 307-309.
- 289. WERTHEIMER, E. (Shape and Regularities of Vapor-Pressure Curves). Ber. deut. physi. Ges., vol. 21, 1919, pp. 692-708.
- WIEDEMANN, E. (Concerning the Vapor Pressure, Especially for Solid Substances, According to Investigations by K. Stelzner and G. Niederschulte). Ber. deut. physik. Ges., vol. 3, 1905, pp. 159.
- 291. WISEMAN, E. L., AND GREGORY, N. W. Vapor Pressure of Tantalum Pentabromide. Jour. Am. Chem. Soc., vol. 71, 1949, pp. 2344-2346.
- 292. WITT, W. P., AND BARROW, R. F. Heats of Sublimation of Aluminum Trifluoride and Heats of Formation of Aluminum Monofluoride. Trans. Faraday Soc., vol 55, 1959, pp. 730-735.
- 293. WOLF, C. J., CLIFFORD, A. F., AND JOHNSTON, W. H. Preparation and Properties of Rhenium Oxychloride. Jour. Am. Chem. Soc., vol. 79, 1957, pp. 4257-4258.

- 294. YAKOVLEV, G. N., AND KOSYAKOV, V. N. Investigation of the Chemistry of Americium. Paper P/2127 in Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, vol. 28, Basic Chemistry in Nuclear Energy. United Nations Publication, New York, N. Y., 1958, pp. 373-384.
- 295. YOST, D. M., AND CLAUSEN, W. H. Thermochemical Constants of the Hexafluorides of Sulfur, Selenium and Tellurium. Jour. Am. Chem. Soc., vol. 55, 1933, pp. 885-891.
- 296. YOST, D. M., AND KIRCHER, C. E. Vapor Pressures of Selenium Tetrachloride. The Existence of Selenium Dichloride. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 4680-4685.
- 297. YOST, D. M., AND RUSSEL, JR., H. Systematic Inorganic Chemistry. Prentice-Hall, New York, N. Y., 1944, 423 pp.
- 298. YOUNG, H. S., AND GRADY, H. F. Physical Constants of Uranium Tetrachloride. U. S. Atomic Energy Comm. TID-5290, 1958, pp. 749-756.
- 299. YOUNG, S. Vapor Pressures, Specific Volumes, Heats of Vaporization, and Critical Constants of Thirty Pure Substances. Sci. Proc. Roy. Dublin Soc., vol. 12, 1891, pp. 374-443.
- 300. ZHURAVLEV, D. I. (Some Thermodynamic Parameters of Antimony Trichloride). Jour. Tech. Phys. (U.S.S.R.), vol. 9, 1939, pp. 1331-1332.
- 301. ZHURAVLEV, D. I., AND KOSTROVA, N. A. (Table of the Thermodynamic Parameter of Aluminum Bromide at the Saturation Line). Jour. Tech. Phys. (U.S.S.R.), vol. 7, 1937, pp. 1626-1629. Chem. Zntr. II., 1938, pp. 665-666.
- 302. ZIMM, B. H., AND MAYER, J. E. Vapor Pressures, Heats of Vaporization and Entropies of Some Alkali Halides. Jour. Chem. Phys., vol. 12, 1944, pp. 362-369.

II. STATISTICAL ANALYSIS OF DATA AND AN IBM 1620 COMPUTOR PROGRAM

The vapor pressure equations and thermodynamic properties of the systems studied in this work were evaluated by the method of least squares as outlined by W. L. Gore (7 p. 127-131). The temperature and pressure data obtained from the measurements were correlated on the basis of the vapor pressure equation, viz.,

$$(5) \quad \log P = A - B/T$$

By letting X = 1/T and $Y = \log P$, the problem is reduced to the analysis of a linear equation in X and Y. The equations used for evaluating the constants of equation (5) and their respective standard deviations are given below.

If N is the number of temperature and pressure observations, the values of A and B are merely

$$(38) \qquad A = \overline{Y} - B\overline{X}$$

(39)
$$B = \underbrace{\sum XY - \sum X \sum Y/N}_{\sum X^2 - (\sum X)^2/N}$$

where X and Y, the mean values of X and Y, are

(40)
$$\overline{X} = \sum X/N; \quad Y = \sum \overline{Y}/N$$

The standard deviations of A and B, however, are obtained by first calculating the regression coefficient, r; viz.,

(41)
$$\mathbf{r} = \frac{\Sigma X \mathbf{Y} - \Sigma X \Sigma \mathbf{Y}/N}{\left[(\Sigma X^2 - (\Sigma X)^2/N) \quad (\Sigma \mathbf{Y}^2 - (\Sigma \mathbf{Y})^2/N) \right]^{1/2}}$$

Then from the standard deviation of Y, viz.,

(42)
$$S_y = \left[\sum (Y - Y)^2 / (N - 1)\right]^{1/2}$$

the estimate of the standard deviation of other calculated values of Y is given by

(43)
$$S_y \text{ (est)} = S_y \left[(1 - r^2) (N-1) / (N-2) \right]^{1/2}$$

It is possible to then calculate the variance of reliability of B from

(44)
$$S_B = S_y \text{ (est)} / [\Sigma X^2 - (\Sigma X)^2 / N]^{1/2}$$

such that the slope of the log P vs 1/T plot is $B \pm S_B$. The reliability of A is then given by

(45)
$$S_A = \left[S_y^2 \text{ (est) / } N + S_B^2 \bar{X}^2\right]^{1/2}$$

such that the intercept of the log P vs 1/T plot is A \pm $S_{\rm A}.$

The above least squares analysis of the vapor pressure data was facilitated by means of a Fortran program for the IBM 1620 computor. This program was designed to calculate and tabulate T (°C), T (°K), 1000/T (°K), P(mmHg), and Log P(mmHg) from an input of temperature (°C or mv) and pressure (mmHg) data. Then, by the method of least squares, a correlation is made between log P and 1/T. The constants of the vapor pressure equation (Log P = A-B/T) are calculated and tabulated along with other statistical values including the standard deviations of A and B and the correlation coefficient. Secondary statistical data are tabulated optionally which includes the sums of the independent and dependent variables (SX and SY), the sum of the product of X and Y (SXY), the sum of squares of X and Y (SX2 and SY2) the standard deviation of Y (SBY) and the standard deviation of the estimate of Y (SBYE) when calculated from Y = A - B/T

Data are prepared for the computor on regular IBM data cards as follows:

- I Vapor pressure processing
 - 1. Punch all data in decimal form. (Decimal must be punched)
 - Temperature data (either °C or mv) are punched first followed by a space and then the pressure data (mmHg). (Example: 100.0 760.) Note space between numbers.
 - 3. Punch only one set of data per card.
 - 4. Each series of N data cards must be followed by a dummy card with
 - (i) 1.0 $0.0 \neq$ for °C input, or (ii) 100.0 $0.0 \neq$ for my input
- II Least squares correlation of two variables
 - For least squares correlation ONLY a card with the number of data points (S, N) must be on top of the other data cards (Note that S and N are numerically the same value with S value with S being a decimal number and N a nondecimal number.) (Example: 5.05≠)
 - 2. The dummy card at the end is unnecessary for the correlation.

The operating procedure for the IBM 1620, equipped with tape feed,

is as follows:

- I Clear machine
 - 1. Press INSERT
 - 2. Type 310000300002.

- Press RELEASE, then START. (Allow the machine to run a few seconds).
- 4. Press INSTANT STOP, then RESET
- II. Load the program tape.
 - Ready the program tape on the reader. (Be sure the switch is set on REEL)
 - 2. Press REEL power button on the tape reader.
 - 3. Press INSERT (on console).
 - 4. Type 36000000300.
 - 5. Press RELEASE, then START.
 - 6. While program is loading, set the console margins at 15 and 95 with tab sets at 30, 45, 60, and 75.
- III. Execute the program
 - When program has been loaded, press START. (Machine will type out instructions for setting sense switches and will pause until switches are set).
 - 2. Set sense switches.
 - No. 1 ON for centrigrade temperature input. (OFF for millivolt temperature input)
 - No. 2 ON for temperature and pressure print out.
 - No. 3 ON for punch out of 1/T and Log P data for least squares analysis.
 - No. 4 ON for bypass to least squares analysis (normally off).

- 3. Press START to continue.
- 4. Load DATA TAPE and
 - (i) for °C input press "shift" and type the number of data points (S, N) to be processed, followed by a record mark ([‡]). (Note: if the number of data points is five, type 5. 5≠) or
 - (ii) for mv input, type in the values of A, B, C, D, E*, where each are decimal numbers (positive or negative) with spaces between them and a record mark, ≠, at the end. Negative sign must be typed in (positive not necessary).
- 5. Press RELEASE and then START. For mv input the number of data points (S, N) are to be typed in here.
- 6. After data have been processed, check sense switch 3 and press START.
 Sense switch 3:
 ON for least squares correlation of punched data.
 OFF for return to accept new data.
- 7. Load punched data tape and turn sense switch 2 ON for print out of secondary statistical data.
- 8. After correlation of data, press START to process more data.

* The generalized emf-temperature equation is

$$\mathbf{E} = \mathbf{A} + \mathbf{BT} + \mathbf{CT}^2$$

where E is in millivolts and T in °C (22, p. 13). The constants A, B, and C depend on the type of thermcouple used and its calibration. The constants D and E are used to obtain the first estimate of T from the linear approximation equation:

$$E = D + ET$$

By fitting a second order polynominal to the data from the standard thermocouple tables, the constants A, B, and C were obtained for a platinum vs platinum -10% rhodium thermocouple. These values, along with the approximation constants D and E are as follows:

1. Temperatures between $650 - 1050^{\circ}$ C. (accuracy about $\pm 0.1^{\circ}$ C)

A = -	.259	D =8	29
B =	.00811	E = .0	0102
C =	.00000172		

2. Temperatures between 200 - 1100°C. (accuracy about + 1.0°C.)

A = -	.245	D =	.829
B =	.00805	$\mathbf{E} =$.0102
C =	.00000176		

Occasionally difficulties are encountered, and it is desired to start

again at the beginning. In this case,

- 1. Press INSTANT STOP, then RESET and INSERT, in that order.
- 2. Type in $4907500 \ddagger$, and press RELEASE followed by START. The computor then returns to the first instruction as described in III-1.

This situation arises when an incorrect number has been typed, a

card with incorrect data is processed, a machine error occurs, or several other possible reasons.


FIGURE 24-Computor Flow Diagram of Vapor Pressure Processor.

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III. STANDARD THERMOCOUPLE CALIBRATION DATA

As indicated previously, the thermocouples used in the vapor pressure and thermal analysis studies were calibrated by comparison with a National Bureau of Standards certified platinum vs platinum - 10 percent rhodium thermocouple. The apparatus used for the thermocouple calibration is shown in figure 25.

Certification was obtained for a thermocouple which was prepared by usual procedures from platinum and platinum -10 percent rhodium thermocouple wire supplied by Bishop and Company, premium grade. The calibration data for this standard thermocouple are given below in table 15. Also, comparison of the emf is made with standard table values.

Temperature,	Emf, Absolute Millivolts	
°C.(Int. 1948)	Standard Thermocouple*	Standard Tables (26)
0	0.0	0.0
100	0.0	0.0
100	0.647	0.643
200	1.441	1.436
300	2,323	2.316
400	3,259	3.251
500	4,231	4.221
600	5,235	5.224
700	6.271	6.260
800	7.341	7.329
900	8.443	8.432
1000	9.579	9.570
1100	10.747	10.741
1200	11.94	11,935
1300	13.14	13,138
1400	14.33	14.337
* NBS Test N	lo. G-29859	

TABLE 15. - Standard Thermocouple Calibration



FIGURE 25-Thermocouple Calibration Apparatus.

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FIGURE 26A - Diaphragm and Sample Chamber, Before Welding



FIGURE 26B - Diaphragm and Sample Chamber After Welding