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Transport reactions and vaporization studies of some vanadium halides

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STUDIES OF SOME VANADIUM HALIDES.

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TRANSPORT REACTIONS AND VAPORIZATION
STUDIES OF SOME VANADIUM HALIDES

by

James William Roddy

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In Charge of ~~Major Work~~

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Ames, Iowa

1962

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INTRODUCTION

The vaporization characteristics of many of the vanadium halides have been known for several years, but the associated thermodynamic data have not been investigated. The lack of information may be explained by the complicated reactions which are inherently present in these sublimation processes. Such complications can be seen in the elements where, instead of vaporizing as a well-defined form, many have been found to vaporize also as dimers or as higher polymers. Examples can be found in the vaporization of sodium, phosphorus, sulfur and carbon. Some well-known compounds which are known to vaporize as mixtures of monomers and polymers are Al_2Cl_6 , P_4O_{10} and Cu_3Cl_3 . In recent years, a concentrated effort has been undertaken to obtain the value for many of the physical constants which are presently unknown or which have been erroneously reported in the literature. The purpose of this investigation has been to clarify the existing knowledge which is known concerning the properties of some of the vanadium halides.

Preparation and Stability of Vanadium Halides

After the discovery of vanadium in 1831 by Sefström (1), very little work was done with its compounds owing to the extreme difficulty of separating the metal from its ore. In 1865 Sir Henry E. Roscoe (2), who may be considered the father of vanadium chemistry, began a rather extensive study of various vanadium substances, and in 1869, he produced the metal by the hydrogen reduction of vanadium(II) chloride. In the years since Roscoe's preparation, intensive research has been done on vanadium and its chemistry. A brief review of a part of this chemistry, that pertaining to the halides and their stabilities, will now be discussed.

Vanadium(IV) chloride

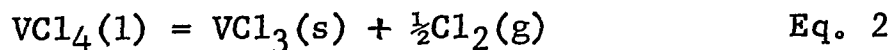
The preparation of this material has been accomplished via several methods (3, 4, 5). However, the best method developed is the direct chlorination of ferrovanadium (6). A low oxygen content alloy must be used to prevent the formation of the oxytrichloride since the separation of this liquid from the tetrachloride is very difficult. Any iron (III) chloride formed is easily removed by distillation.

Vanadium(IV) chloride is a viscous liquid, red brown in color, which fumes in air. The molecule possesses a regular tetrahedral structure with V-Cl distances of $2.03 \pm 0.02 \text{ \AA}$ and Cl-Cl distances of $3332 \pm 0.03 \text{ \AA}$ (7). Simons and Powell (8) have determined the expression for the vapor pressure between 39.5° and 80.2°C to be:

$$\log P_{\text{VCl}_4} = -\frac{1998}{T} + 7.581 \text{ (in mm.)}. \quad \text{Eq. 1}$$

The molar heat of vaporization calculated from this expression is -9.1 kilocalories. The same workers obtained a Trouton constant of 21.3. Ruff and Friederich (3, p. 296) have estimated the heat of formation to be -165 ± 4 kilocalories, while Brewer (9) gives a value of -141 ± 30 kilocalories. The latest Bureau of Standards circular (10) lists a value of -138 kilocalories.

The tetrachloride of vanadium has been shown (11) to decompose slowly at room temperature to yield vanadium(III) chloride and chlorine. This reaction, which is quite rapid at the boiling point of the tetrachloride (154°C), has been studied by Simons and Powell (8, p. 77). These authors obtained a heat of reaction (eq. 2) of 13.8 kilocalories;



it should be stated that their measurements extended over a range of only twenty degrees centigrade (160° to 180°C). This decomposition should be expected from the heats of formation of the tri- and tetrachloride of vanadium, as the conversion of the tetrachloride into the trichloride and free chlorine evolves approximately 22 kilocalories per mole of the tetrachloride. At higher temperatures (above 650°C), the tetrachloride and the dichloride are the stable compounds present. The tetrachloride is readily attacked by water to give hydrochloric acid and vanadium(IV) oxydichloride.

Vanadium(III) chloride

Many procedures have been devised for the preparation of this substance, but the synthesis of this compound in high purity has met with little success.

Initial experiments towards preparation of the solid were performed by Roscoe (2, p. 347) by passing a mixture of the tetrachloride and hydrogen through a hot tube. Gutmann (12) has shown that mixtures of the dichloride and trichloride are formed owing to the difficulty in controlling the reaction temperature.

The method still favored for the preparation of the

trichloride, developed by Meyer and Backa (13), involves the thermal decomposition of the tetrachloride by refluxing in a stream of inert gas. Additional work on this procedure has been conducted by Foley *et al.* (14).

Other methods for the preparation of vanadium(III) chloride include: (1) heating a mixture of disulfur dichloride and vanadium(V) oxide in a sealed tube at 300°C (2, p. 326), (2) the reaction of sulfur with either vanadium(IV) chloride or vanadium(V) oxytrichloride (4, p. 515), (3) the reaction of fine vanadium powder with iodine monochloride (12, p. 1157). The difficulty in completely removing sulfur decreased the efficiency of the first two methods. The third method was inadequate since it yielded only twenty per cent product.

Vanadium(III) chloride is a violet solid of rather low volatility. The structure of the compound is rhombohedral; it may also be described in terms of a hexagonal unit cell containing six molecules. By utilization of x-ray diffraction techniques, the lattice constants were determined to be: $a_0 = 6.012 \text{ \AA}$, $c_0 = 17.34 \text{ \AA}$ (15). Ruff and Friederich (3, p. 302) have estimated the heat of formation of the trichloride to -187 ± 0.8 kilocalories. Brewer (9, p. 108)

predicts a value of -139 ± 30 kilocalories, while the value given in the Bureau of Standards circular (10, p. 52) is -137 kilocalories.

Ruff and Lickfett (4, p. 508) indicate that under heating, the trichloride changes chemically by disproportionation to the dichloride and the tetrachloride. This fact has been substantiated by other workers (16, 17, 3, p. 280). Oranskaya et al. (18) have recently determined the equilibrium for this reaction using the transpiration method. The equation for the disproportionation pressure may be written in the form:

$$\log P_{\text{VCl}_4} = - \frac{0.837 \times 10^4}{T} + 11.58 \text{ (in mm.)} \quad \text{Eq. 3}$$

for the temperature range of 425° to 655°C . The error in the experimental tetrachloride pressure is given as five to six per cent. From the resulting disproportionation equation the heat of reaction is determined as 38 ± 1 kilocalories while the entropy of the reaction is 39.6 ± 0.5 entropy units. These values agree favorably with those calculated from the heats of formation provided by the Bureau of Standards circular (10, p. 52).

Vanadium(III) chloride is quite hygroscopic and easily dissolves in water. It may be recrystallized from water,

yielding the hexahydrate which is analogous to the hexahydrate of chromium(III) chloride.

Vanadium(II) chloride

This material has been prepared by the hydrogen reduction of vanadium(III) chloride (4, p. 518) at 750°C, and by the thermal disproportionation of the trichloride (4, p. 520) at temperatures near 900°C.

The dichloride is an apple-green practically non-volatile substance which is slowly affected in air, taking up water and oxygen to yield a brown solution. The crystal structure is of the cadmium(II) iodide type with lattice constants of: $a_0 = 3.60 \pm 0.01 \text{ \AA}$, $c_0 = 5.83 \pm 0.01 \text{ \AA}$ (19, 20, 21). The dichloride is a very stable material to thermal decomposition; its melting point has been determined to be $1350 \pm 25^\circ\text{C}$ (22). The heat of formation of the solid has been given values of -147 ± 4 (3, p. 300), -110 ± 8 (23), -108 (10, p. 52), -117 ± 20 (9, p. 108) kilocalories per mole.

Oranskaya and Perfilova (24) have determined the vapor pressure of the dichloride using a transpiration method. From the equation relating pressure and temperature (eq. 4),

$$\log P_{\text{VCl}_2} = \frac{-9720.7}{T} + 8.60 \text{ (in mm.)} \quad \text{Eq. 4}$$

a heat of vaporization of 44 ± 1 kilocalories and an entropy of vaporization of 26.1 ± 0.5 entropy units was obtained. The values estimated by Brewer (9, p. 200) are 35 kilocalories and 21 entropy units respectively.

Vanadium(IV) bromide

This material has been reported nonexistent and impossible to prepare by several workers (25, 13, p. 187, 26). Brewer (9, p. 223) has stated that the tetrabromide is quite unstable at room temperature decomposing to the tribromide and bromine, but becomes stable again at temperatures over 500°K . He lists a heat of vaporization of 12 kilocalories and an entropy of vaporization of 23 entropy units. His value for the heat of formation is given as -122 ± 30 kilocalories per mole.

Vanadium(III) bromide

The solid black platelets have been prepared by the direct bromination of the carbide (26, p. 2534), the nitride (25, p. 28), and the metal at temperatures over 450°C (13, p. 187). The tribromide may be prepared by the reaction of the metal with bromine at 40°C (13, p. 187); this is unlike

the trichloride. Its properties are very similar to those of the trichloride in regards to moisture. Both compounds form a hexahydrate and are very soluble in water. The only thermodynamic value given for the solid is -115 ± 30 kilocalories per mole for the heat of formation. Ruff and Lickfett (26, p. 2535) report that the tribromide, unlike the trichloride, may be sublimed without decomposition or disproportionation.

Vanadium(II) bromide

The pale ocher solid has been prepared by the hydrogen reduction of the tribromide at temperatures exceeding 400°C (27). The structure of the dibromide has been determined by Klemm and Grimm (28) to be hexagonal with lattice constants of: $a_0 = 3.768 \text{ \AA}$, $c_0 = 6.180 \text{ \AA}$. Brewer (9, p. 108) estimates the heat of formation to be -100 ± 20 kilocalories per mole.

Transport Processes

The application of this method for the preparation of single crystals and of difficult to prepare solid solutions has been known for several years. " Schafer, who is one of

the better known investigators in this field, has studied many of the transport properties of the transition elements (29, 30, 31). He has given a rather extensive discussion of the transport phenomenon when applied to a substance in a temperature gradient (32).

In a reaction such as that given in equation 5, the



process may be considered to be one of transporting solid A from temperature T_1 to T_2 by forming the intermediate gas C. "Schafer has derived an equation which can be used to calculate the amount of material transported after a certain period of time if the diffusion coefficient, cross sectional area of the diffusion section, and the linear flow velocity are known.

In another paper (33) "Schafer discusses the use of enthalpy and entropy values to determine the feasibility of a transport process of the type of equation 5. His conclusions may be summarized as follows:

1. The transport process will occur if there is no crystal phase present on one side of the equation.
2. When the heat of reaction is zero, no transport will occur.

3. A reaction with an extreme equilibrium value will yield no measurable crystal phase transfer.

4. If the entropy of reaction is small, then a very small amount of material will be transported.

5. There exists, for each value of the entropy of reaction different from zero, a value which will yield the maximum transfer effect. For the transfer to be large, the equilibrium constant must be approximately one. For large values of the entropy, a considerable crystal phase transfer is only possible if the enthalpy and the entropy have the same sign.

6. A reaction exhibiting a sufficiently large positive entropy will only show an appreciable crystal transfer in the direction from higher to lower temperature.

7. The amount of material transported increases with an increase in the numerical value of the entropy when the enthalpy is correspondingly changed.

8. A change in the temperature will usually produce a rather drastic change in the equilibrium constant and hence in the quantity of material transported.

Vaporization Processes

In order to determine the thermodynamic data associated with any vaporization process, the exact nature of the gaseous species must be known. All substances may be considered to vaporize in at least one of the following methods. In many cases several of these processes may occur simultaneously and different ones may occur at different temperatures.

Simple vaporization

The simplest process known is that in which the vapor component is identical to that found in the solid or liquid. Examples of this process can be found in the vaporization of



many of the metals.

Polymer vaporization

In some instances, the vapor does not correspond to the

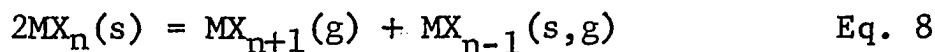


simple monomer but is composed of dimers or higher polymers.

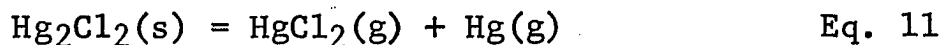
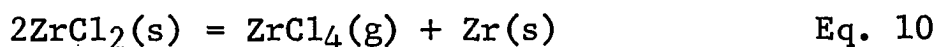
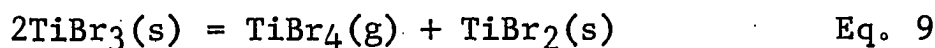
Examples of this process may be seen in the aluminum(III) chloride and iron(III) bromide systems.

Disproportionation vaporization

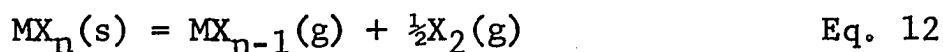
In addition to the methods given previously, the vapor may consist of a volatile higher halide and a volatile or nonvolatile lower halide or, in some cases, even the element.



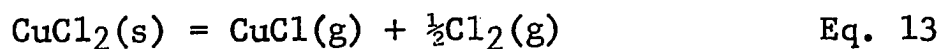
As examples, the following reactions may be noted:

Decomposition vaporization

Vaporization may also occur by a simple process of decomposition, in which case a lower halide or even an element may be formed. This phenomenon may occur during the



heating process when the original compound decomposes to a more volatile compound. The following reactions may be considered as examples in this class:



The four processes have been discussed as if pertaining only to the halides, but these various vaporization methods are quite general and may be extended to all substances.

Methods for the Determination of Vapor Pressures
and Decomposition Pressures

Many methods and countless variations have been utilized for the determination of vapor pressure, each presenting its own specific advantages and disadvantages. Several recent comprehensive reviews of these methods are found in the literature. In the reviews the methods of vapor pressure measurement are critically discussed.

Ditchburn and Gilmour (34) described the methods in use and critically discussed vapor pressure data which had accumulated in the literature from 1925 to 1941. Dushman (35) compiled tables of vapor pressures of metals and discussed the data available in 1949. Speiser and Johnston (36) discussed in some detail the sublimation, evaporation, and effusion techniques in use in 1950. Brewer (9) gives one of the most comprehensive studies of thermodynamic data available to date. In the following discussion is described several of the methods used for the measurements of low vapor pressure.

Bourdon gauge

The use of a glass pressure gauge for the measurement

of pressures of vapors which attack mercury, or for measurements in which the experiment requires the manometer to be at a high temperature, was introduced by Landenburg and Lehman (37). For the statical determination of vapor pressure of many pure substances and dilute solutions, and of chemical equilibria, a Bourdon gauge is almost indispensable. Many changes and various forms have been made to improve the original design; a brief review of the more interesting ones will now be discussed.

Warburg and Leithauser (38) developed a gauge, Figure 1a, consisting of a thin glass membrane to which a mirror has been attached. The change in pressure is noted by the deflection of a beam of light from the mirror.

Smith and Taylor (39) have designed a rather novel gauge, Figure 1b, which can be heard when the equilibrium is upset. As the pressure is altered across the gauge, the membrane is first distorted and then, when it changes position, an audible click is heard. The authors report a sensitivity as low as 0.2 millimeter mercury.

Daniels has reported two gauges which utilize electrical contacts for balancing purposes. In the first cell (40), Figure 1c, a thin glass membrane is coated with platinum and

Figure 1a

- A. Light beam
- B. Membrane
- C. Mirror

Figure 1b

- A. Membrane

Figure 1c

- A. Platinum
- B. Electrical connections
- C. Membrane

Figure 1d

- A. Membrane
- B. Electrical connections

Figure 1e

- A. Spoons
- B. Fulcrum
- C. Pointer

Figure 1f

- A. Spiral
- B. Pointer
- C. Window
- D. Damping liquid

Figure 1. Various Bourdon Gauges

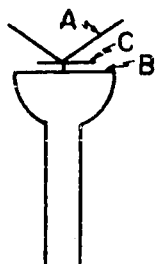


FIGURE 1a

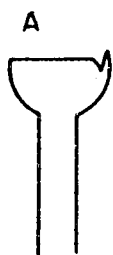


FIGURE 1b

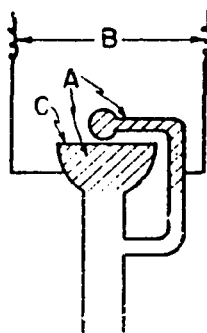


FIGURE 1c

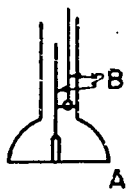


FIGURE 1d

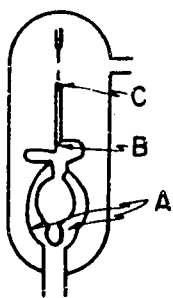


FIGURE 1e

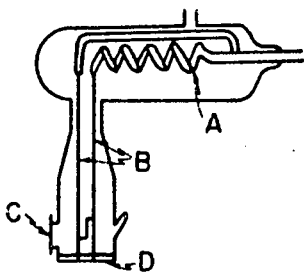


FIGURE 1f

a glass arm, also covered with platinum, is sealed to the side of the gauge. Fluctuations in the pressure are observed by the interruptions in the current flowing through the cell. The diaphragm has a sensitivity of approximately one millimeter mercury. Difficulty in keeping the platinum scrupulously clean and the necessity of preventing sparking are two disadvantages.

The second gauge designed by Daniels (41) is very similar to the one previously discussed but the new innovation is the utilization of platinum wire instead of a platinum coating for the electrical contacts (see Figure 1d). As the glass membrane is deflected by a slight pressure change, the small platinum wire sealed to the side of the cell is pressed against the attached wire extending from the glass rod. Electrical contact is made indicating that equilibrium is no longer maintained in the cell.

Stanwick (42) described a double spoon gauge (see Figure 1e) for detecting pressure differences as low as 10^{-2} millimeters of mercury. The two spoons are connected facing each other by a rigid glass support which in turn is joined to the pointer by a lever type mechanism. For maximum sensitivity, the length of the pointer to the lower end of the

fulcrum is found to be five millimeters. The gauge is stated to be very stable when subjected to vibration, much more so when compared to single spoon gauges of similar sensitivity. The greatest drawback with any spoon gauge is its inability to withstand large pressure differences; one has not yet been constructed that can survive differences in pressure of one atmosphere.

An excellent discussion is given by Vaughan (43) concerning the construction of a Bordenstein quartz spiral manometer (see Figure 1f). Its many advantages include: (1) a very small volume, (2) ability to withstand elevated temperatures, (3) ease of manipulation, and (4) ruggedness. Its greatest shortcomings include the extreme difficulty in fabrication and the problems associated with cleaning of the cell. A well-constructed cell will have a sensitivity of 0.1-0.2 millimeters mercury and can readily withstand one atmosphere pressure difference.

Transpiration method

One of the most commonly used methods for the determination of vapor pressure is one which has been known by several names; viz., gas-saturation, transpiration, and

transportation method. In most cases, a steady stream of inert gas, whose volume is measured, is passed over the material under investigation, whose temperature is carefully controlled. The rate of flow is slow enough so that complete saturation of the inert gas by the vaporizing species is obtained. The vapor from the sample is condensed or collected by absorption or chemical combination at a cooler portion of the apparatus. The measurements are usually obtained over a range of flow rates so that the proper rate for complete saturation may be determined. Figure 2a shows the effect of flow rate on the apparent vapor pressure; high values at low flow rates are due to diffusion effects and low values at high flow rates are due to incomplete saturation of the carrier gas. Merten (44) gives an excellent discussion concerning the problem associated with diffusion effects related to this method. Another excellent but rather mathematical discussion of the entire transpiration method is given by Lepore and Van Wazer (45). In Figure 2b is shown a typical apparatus, of which many variations may be found in the literature (46, 47).

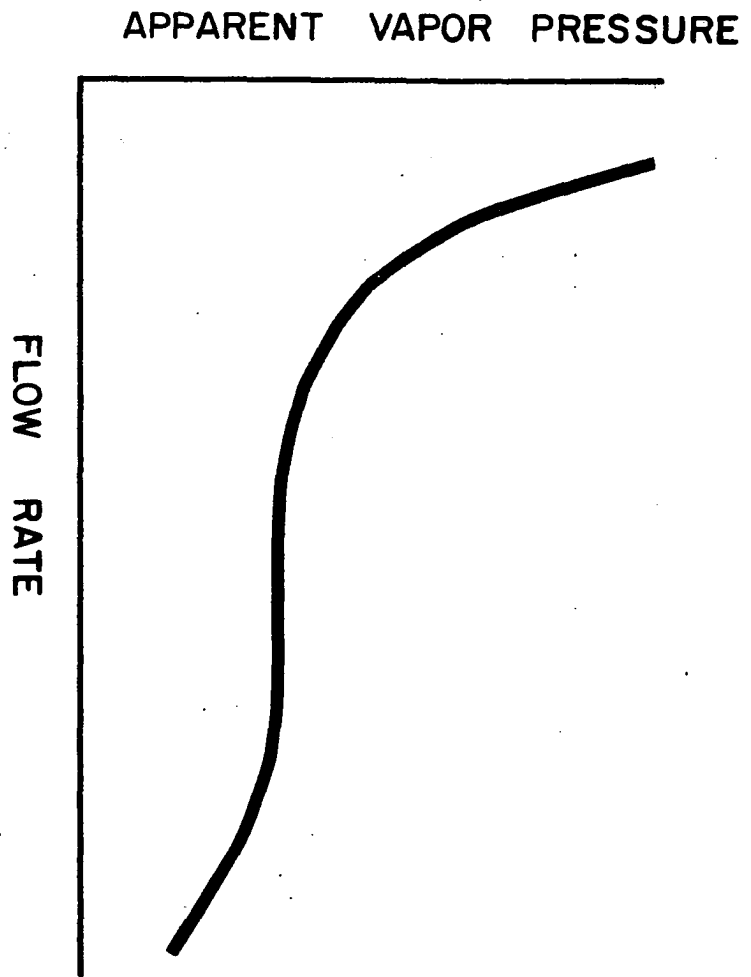
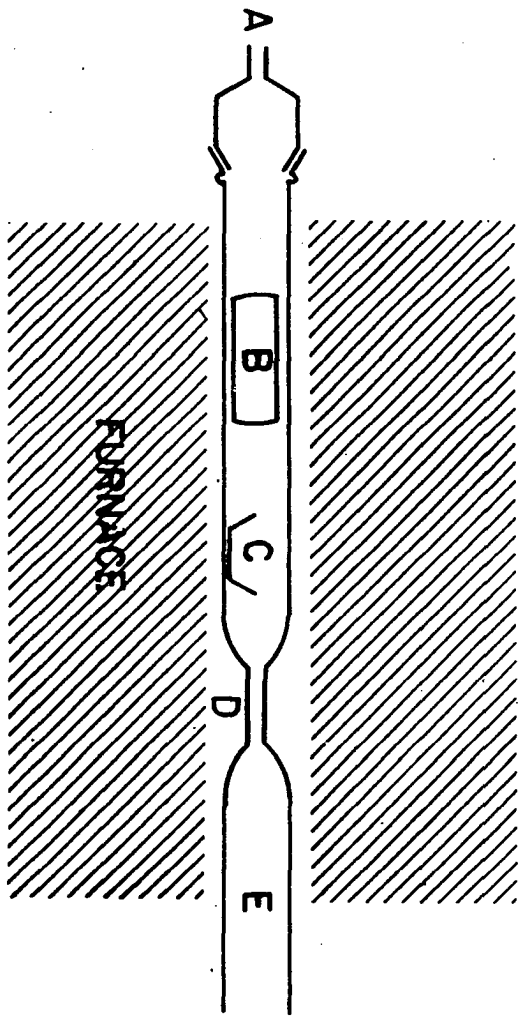
The partial pressure of the vapor species being measured is calculated from the volumes or mole fractions of the trans-

Figure 2a. Effect of Flow Rate on Vapor Pressure

Figure 2b. Typical Transpiration Apparatus

- | | |
|------------------|--------------------|
| A. Gas inlet | D. Capillary |
| B. Gas preheater | E. Condensing tube |
| C. Sample boat | |

Figure 2. Transpiration Effects and Apparatus



ported substance and the transporting gas at standard temperature and pressure, assuming Dalton's law and the ideal gas law are valid. A more rigorous treatment is discussed by Gerry and Gillespie (48).

The lower limits of the method appear to be in the 10^{-3} millimeter range with accuracies of approximately five per cent. One of the major difficulties in operating in this very low pressure region arises from the microscopic quantity of material that is transported during the experiment. The desirability of a fairly extensive investigation into adequate analytical procedures before utilizing this method are relatively apparent. Another important factor which must be considered is the attainment of a properly slow flow rate to secure complete saturation.

Effusion method

The Knudsen method (49) consists essentially of a measurement of the rate at which atoms effuse through an orifice in an enclosed chamber containing the material being studied at its equilibrium vapor pressure. When the gas is in thermal equilibrium with the chamber and one of the condensed phases of the gas, the pressure in the vessel is by

definition the equilibrium (saturated) vapor pressure. By utilization of kinetic theoretical considerations, the rate of mass flow can be related to the equilibrium vapor pressure. In the following discussion the vaporizing species will be considered to be monoatomic and behave as an ideal gas.

The relationship between the pressure and the mass flow of a gas across a plane of unit area of the gas is predicted by kinetic theory to be

$$P = m(2\pi RT/M)^{\frac{1}{2}}, \quad \text{Eq. 15}$$

where m is the mass of gas crossing unit area of the plane per second, P is the pressure of the gas, T is the absolute temperature of the gas, R is the gas constant per mole and M is the molecular weight. The units in this discussion will be of the cgs system unless otherwise indicated. The derivation of equation 15 may be found in Kennard (50).

If the interior of the gas is considered, effusive flow may be defined as being possessed by those molecules which move in one direction across a plane of finite area drawn anywhere in the gas at equilibrium. The gas can be considered to be in complete equilibrium when its temperature is the same as the enclosing vessel. If a very small hole of

area a is opened in the wall of the vessel of such a size that it does not disturb the equilibrium inside the vessel, the flow of gas through the hole will constitute effusive flow. Since effusive flow is unilateral, the gas pressure on the exterior of the vessel has no effect on the mass of gas leaving the hole. For convenience in experimental measurements, the vessel containing the gas is placed in a vacuum where the external pressure is due only to the residual gases. Knudsen (51) has determined the limits which must be placed on the size of the hole for the measurement of pressure by the effusion method. The nature of the flow through the orifice must be entirely molecular, that is, the atoms of the effusing substance must have free paths of at least ten times the diameter of the orifice. If this condition is not met and higher pressures exist, the flow will have streaming characteristics and the kinetic theory will no longer apply. When this condition is satisfied for a small size orifice, equation 15 may be rewritten in the form

$$P = (g/a) (2\pi RT/M)^{\frac{1}{2}} \quad \text{Eq. 16}$$

where a is again the area of the orifice and g is the mass of gas leaving per unit time. The orifice must have a thin edge in order to approximate a geometric plane. An orifice

possessing thick walls would return into the vessel a fraction of the molecules entering it, thereby altering the distribution of the effusing gas molecules with respect to direction of travel. In addition, an orifice whose walls have appreciable thickness may exhibit temperature difference between the wall and the rest of the cell.

The effect of the orifice area and thickness on the equilibrium between the gas and the condensed phase in the Knudsen cell can be computed. Assume the area of the substance effective in the evaporation is S and that the material has an accommodation coefficient α . The accommodation coefficient is defined (50, p. 20) as the ratio of the mass of molecules which actually condense on a surface to the mass which strikes the surface. The mass of molecules which actually condense per unit time is given by αm .

If equilibrium were established at the true vapor pressure P' , then $\alpha m(P')S$ grams of gas would condense per unit time on the effective area S , where $m(P')$ is the mass of molecules striking a unit area of surface per unit time in a gas of pressure P' whose temperature is T . The same mass would also evaporate from the condensed phase. Now when the orifice of area a is opened in the wall of the vessel,

the equilibrium will be disturbed by the escape of molecules from the orifice. A steady state will be established at a lower pressure such that the flow of molecules from the hole is balanced by the net evaporation from the surface S . The rate of effusion is $am(P)$ where $m(P)$ is defined for P in the same manner as $m(P')$ was defined for P' . In this nonequilibrium case the net rate of evaporation is the total rate of evaporation, $\alpha m(P')S$, less the gross rate of condensation, $\alpha m(P)S$. Hence, the following relationship

$$am(P) = \alpha m(P')S - \alpha m(P)S, \quad \text{Eq. 17}$$

or

$$m(P) = m(P') \frac{\alpha}{(a/S) + \alpha}. \quad \text{Eq. 18}$$

If both sides of equation 18 are multiplied by $(M/N)(2\pi RT/M)^{\frac{1}{2}}$, where N is Avogadro's number, the result is

$$P = P' \frac{\alpha}{(a/S) + \alpha}. \quad \text{Eq. 19}$$

The necessary conditions for the pressure calculated from the rate of effusion to be equal to the saturation (equilibrium) pressure can be seen from equation 19. The accommodation coefficient can be neglected if $(a/S) \ll \alpha$, in which case $P = P'$. Thus when the ratio of the area of the orifice to the effective surface area of the sample is much

less than the accommodation coefficient, the loss of molecules has no appreciable effect on the equilibrium in the Knudsen cell. This condition is experimentally determined by obtaining the rate of effusion from Knudsen cells of several a/S values. If the rates are independent of these ratios, then the pressures calculated from equation 16 will be the equilibrium vapor pressure. The pressure determined in this way is independent of the accommodation coefficient.

A rather comprehensive discussion by Whitman (52) treats the effects of the size and shape of the effusion vessel, of the diameter and thickness of the orifice, and of the accommodation coefficient on the measured vapor pressure. Whitman derives an equation giving the relationship between the pressure and the mass flow when the geometrical factors of the vessel's size and shape are considered. The equation is noted below

$$P = \frac{g}{\alpha a K} (2\pi RT)^{\frac{1}{2}} (1-b) , \quad \text{Eq. 20}$$

where

$$b = (1-\alpha) \left[1 - W_a + K \frac{W_a}{W_b} (1-fW_b) \right] , \quad \text{Eq. 21}$$

and where

$$K = \frac{W_a W_b}{1 - (1-fW_b)(1-W_a)} . \quad \text{Eq. 22}$$

W_a is the probability that a molecule evaporating from the condensed substance reaches the orifice. W_b is the probability that a molecule reaching the orifice passes through it. The factor f is the ratio of the diametric cross sectional area of the vessel to the area of the orifice. All other symbols in equation 20 have the meaning previously stated.

Clausing (53) has developed theoretical values for quantities similar to these probabilities for various ratios of orifice radius to length. However, the following four conditions must be satisfied:

1. Only collisions of the molecules with the walls of the tube are allowed.
2. A diffuse reflection of molecules is obtained after collision.
3. The molecules leave the orifice and enter the condensation tube with the usual cosine distribution of directions.
4. The molecules enter uniformly over the face of the condensation tube.

The lower pressure limit of about 10^{-5} millimeter of mercury for the method is determined by the sensitivity of

the weighing or other detecting device. The upper pressure limit of approximately 10^{-2} millimeter of mercury is determined by the requirement that the mean free path of the atoms flowing through the orifice be at least ten times the dimensions of the orifice and by practical difficulties in making and using small orifices. A serious limitation is placed on this method since the molecular weight of the vaporizing species must be known.

Evaporation method

For substances which are quite refractory and hence have very low vapor pressures even at elevated temperatures, an indirect method is used. As in the Knudsen method a quantity which is directly related to the vapor pressure is measured.

When a substance is in equilibrium with its vapor, as many atoms per unit area per unit time condense on its surface as evaporate from it. If no reflections of atoms occur, that is, if all atoms striking the surface are held for a finite length of time and do not rebound, then the number of atoms moving away from the surface in its neighborhood is equal to the number of atoms evaporating. This number is

equal to the rate at which atoms cross any plane in the gas. Thus, the vapor pressure is directly related to the rate of evaporation or sublimation from the surface of the substance, and hence to a decrease in weight.

Langmuir (54) was the first to utilize this method when he determined the vaporization characteristics of tungsten filaments at high temperatures. The equation used for the determination of vapor pressure is obtained by combining the definition of the accommodation coefficient with the equation for effusive flow to give

$$P = (m/\alpha) (2 \pi RT/M)^{\frac{1}{2}} \quad \text{Eq. 23}$$

where the symbols have their usual meaning. The method has been successfully applied to vapor pressures as low as 10^{-8} millimeter of mercury. The disadvantages in the method include uncertainties in the accommodation coefficient, length of time required to complete an experiment, accurate determination of the temperature, and lack of knowledge about the molecular weight of the vaporizing species.

Torsion method

This method, developed by Volmer (55), consists of a Knudsen effusion cell suspended by a thin fiber. The place-

ment of the two effusion holes are rather critical; usually they are placed on opposite sides of the cell in such a manner that the axes of the two holes are parallel and are perpendicular to both the axis of suspension and the long axis of the cell. The two streams of effusing gas tend to twist the cell which rotates until compensated by the opposing torque of the fiber. The pressure of the effusing substance may be determined if the force constant of the fiber and the dimensions of the cell are known.

Customarily, the cell is calibrated with a substance of known vapor pressure, but it is possible to perform the calibration from measurements of the effusion hole areas, the distance between the centers of the holes and the axis of suspension, and the force constant of the fiber.

The major advantage attributed to this method lies in the fact that no assumptions about the molecular weight of the vapor are required. Several investigators (56, 57) in recent years have used this method for the determination of molecular weights at high temperatures, but they have met with only limited success. The values obtained averaged about twenty to thirty per cent low.

However, the torsion method proves to be useful and

convenient for obtaining accurate values of low vapor pressures from 10^{-5} to 10^{-1} millimeter mercury. In addition, the pressure may be determined continuously at several temperatures once the cell is loaded. The method requires a considerable amount of attention and much care as the cell is quite fragile and sensitive to vibration.

Mass spectrometric method

This method is identical to the one developed by Knudsen except in the manner in which the final measurement is made. A small effusion cell in the form of a covered crucible contains the material and its vapor. Atoms of the vapor escape from a hole in the crucible's cover and strike a heated filament. They are immediately evaporated and a fraction of them are evaporated as singly charged positive ions which are analysed by a mass spectrometer. Multiple charges are not produced. The ion beam current is then directly proportional to the vapor pressure.

Several advantages may be attributed to this method. Almost instantaneous results can be obtained which allow observations of melting point and solid to solid phase transitions to be made directly. In some instances the sensitivity of Knudsen's method has been increased by a

factor of a thousand due to the increased sensitivity in the measurement of ion currents. The distinction made by the mass spectrograph between ions of different mass to charge ratios permit the separation of impurity ions from ions of interest. Dimers or higher polymers can easily be detected.

The method does present serious disadvantages. The method is not applicable to all species because many have too low a probability of ionization at the filament. For most species the probability of ionization is only approximately known. To measure vapor pressures directly, the ionization probability and the geometry of the system must be independently known. In most instances the systems are calibrated by using substances of known vapor pressure, while occasionally the calibration is performed during the actual determination of the unknown (58).

Thermodynamic Data from Vapor Pressure Measurements

Various thermodynamic quantities can be related to the temperature dependence of the saturated vapor pressure. The form of the equation that is used is called the Clausius-Clapyron relation. The latent heat of sublimation determined at any temperature may be related to the value at zero degrees

absolute by means of the Kirchhoff relation. When the Clausius-Clapyron and the Kirchhoff equations are combined the result is the equation of the vaporization curve. The vapor pressure is then related to the absolute temperature by means of experimentally determined quantities.

Clausius-Clapyron equation

This relation can be written as

$$\frac{dP}{dT} = \frac{\Delta H_t}{T(V_g - V_c)}, \quad \text{Eq. 24}$$

where P is the equilibrium saturated gas pressure, T the absolute temperature, ΔH_t the latent heat of vaporization per mole, V_g the molar volume of the gas and V_c the molar volume of the condensed phase, either solid or liquid. The derivation of this equation may be found in almost any physical chemistry textbook (59, 60). The Clausius-Clapyron equation is quite general and holds for any equilibrium between two phases of a substance, e.g., solid and liquid, solid and vapor, or two crystalline forms. In any case ΔH_t is the heat absorbed in the transition at temperature T and $V_g - V_c$ is the increase in volume. The heat of vaporization can be determined if the temperature dependence of the

equilibrium vapor pressure is known.

The molar volume of the condensed phase is so much smaller than that of the gas phase that the former can be neglected. The gas, when pressures range from zero to one atmosphere, is considered to be ideal. The ideal gas law for one mole can be written as

$$PV = RT , \quad \text{Eq. 25}$$

where P is the pressure, V the molar volume of the gas, R a constant called the gas constant and T the absolute temperature of the gas. By combining equations 24 and 25 and neglecting V_c the result can be written as

$$\frac{d \ln P}{d(1/T)} = - \frac{\Delta H_t}{R} . \quad \text{Eq. 26}$$

If the equilibrium vapor pressure is known as a function of the absolute temperature, then equation 26 can be utilized to determine the heat of vaporization. The slope of a plot of the logarithm of the pressure as a function of reciprocal temperature will yield the latent heat of vaporization.

Kirchhoff relation

The temperature dependence of the heat of vaporization may be related to the heat of sublimation at zero degrees absolute, the specific heats of the substances, and any

heats of phase change by the Kirchoff equation. A derivation of this relationship may be found in Zemansky (61).

The equation may be expressed in the following form,

$$\Delta H_t = \Delta H_0 + \int_0^T [C_p(g) - C_p(c)] dt - \sum_i \Delta H_i, \quad \text{Eq. 27}$$

where H_t is the heat of sublimation per mole at temperature T ; ΔH_0 the heat of sublimation per mole at zero degrees absolute; $C_p(g)$ is the specific heat of a mole of the gas; $C_p(c)$ is the specific heat of a mole of the condensed substance and ΔH_i is the molar heat of a phase change in the condensed phase. As can be seen from equation 27, the heat of sublimation is a slowly varying function of temperature at elevated temperatures since the specific heats vary slowly with temperature. The specific heat values are determined experimentally by careful calorimetry.

When equation 26 and 27 are combined and integrated, the result can be expressed as

$$\ln P = - \frac{\Delta H_0 - \sum_i \Delta H_i}{RT} - \int_0^T \frac{dt}{RT^2} [C_p(g) - C_p(c)] dt + I \quad \text{Eq. 28}$$

which is commonly called the equation of the vaporization curve. This relation illustrated the dependence of the equilibrium vapor pressure upon the temperature both explicitly and implicitly in the temperature dependence of the

specific heat and heats of phase change. The graph of equation 28 shows very little curvature and for portions corresponding to a temperature range of several hundred degrees is nearly a straight line.

The utilization of equation 28 for determining heats of vaporization has been made extensively by Kelley (62) and Brewer (9). Accurate determination of both the pressure and specific heat is required to obtain a value for ΔH_t by the use of equation 28. The use of the Clausius-Clapyron relation requires only a measurement of pressure and determination of ΔH_t can be more direct and precise. A determination of ΔH_0 is subject to considerable uncertainty because of the difficulties in measuring specific heats over the wide range of temperatures required.

Sigma function

The accepted procedure for the determination of heats of vaporization is to plot the logarithm of the pressure against the reciprocal temperature and from the slope of the curve obtain a value for the heat of vaporization. The entropy of vaporization is determined as the intercept of the line with the axis at a reciprocal temperature value of

zero. Treatments of this type give only an average value for the heat of vaporization over the temperature range and the entropy may be in error by several entropy units.

Brewer and Searcy (63) describe a procedure which uses in addition to the vapor pressure measurements any heat capacity and entropy data available from calorimetric or spectroscopic measurements.

When heat capacity data is available then the normal method of calculating the thermodynamic quantities can be utilized; however, if they are unknown for the molecules being investigated, they should be estimated from data for similar molecules. Even if a constant value is assumed for ΔC_p , much more accurate and useful results will be obtained in the free energy equation.

Assuming a constant value for ΔC_p , Brewer and Searcy obtained the following equations:

$$\Delta C_p = a \quad \text{Eq. 29}$$

$$\Delta H^\circ = \Delta H^\circ_0 + aT \quad \text{Eq. 30}$$

$$\Delta F^\circ = \Delta H^\circ_0 - aT \ln T + IT \quad \text{Eq. 31}$$

$$\Delta S^\circ = a + a \ln T - I \quad \text{Eq. 32}$$

The integration constant I must be determined experimentally if no entropy data is available from calorimetric or spec-

troscopic investigations. By rearranging equation 31 to

$$\Delta F^{\circ}/T + a \ln T = \Delta H_{\circ}/T + I, \quad \text{Eq. 33}$$

the value I may be obtained by plotting $\Delta F^{\circ}/T + a \ln T$ as a function of reciprocal temperature, the slope of the curve will be ΔH_{\circ} , and the intercept at a reciprocal temperature value of zero will be I . The value of $\Delta F^{\circ}/T + a \ln T$ has been defined as σ . This method should yield somewhat more reliable values for the entropy when compared to the more common procedure of utilizing the intercept of the vapor pressure plot. The entropy obtained in the second method is strongly influenced by small errors in the experimental slope.

EXPERIMENTAL

Materials

Vanadium

The vanadium metal used for the preparation of the vanadium halides was obtained through the courtesy of Dr. O. N. Carlson and Mr. C. Owens of this Laboratory (64). The metal was purified by the Van Arkel-de Boer iodide decomposition process starting with crude metal. A representative analysis of the purified metal showed the following elements were present in the amounts indicated.

| | | | |
|-------------|----------|--------------|---------|
| Carbon----- | 100 ppm | Silicon----- | <30 ppm |
| Oxygen----- | 100 ppm | Magnesium-- | <30 ppm |
| Nitrogen--- | <10 ppm | Manganese-- | <30 ppm |
| Hydrogen--- | 10 ppm | Nickel----- | <30 ppm |
| Iron----- | <200 ppm | Aluminum--- | <30 ppm |
| Chromium--- | 200 ppm | Calcium---- | <30 ppm |

Chlorine

The chlorine gas was obtained from lecture size cylinders supplied by The Matheson Co. Purification was obtained by passing the gas through a potassium permanganate solution

to remove hydrogen chloride and then through sulfuric acid and over tetraphosphorus decoxide to remove moisture.

Bromine

The liquid, obtained from J. T. Baker Chemical Co., was of reagent grade purity. Moisture was removed by the vacuum distillation (at 10^{-5} millimeter mercury) of the liquid from tetraphosphorus decoxide. The liquid was stored in an evacuated flask connected to the vacuum system by a stopcock lubricated with fluorocarbon grease.

Iodine

The solid was obtained from J. T. Baker Chemical Co. Though of high purity, the material was further purified by grinding the solid with potassium iodide to remove any free chlorine and bromine. The moisture content was then reduced by the sublimation of the iodine from tetraphosphorus decoxide.

All other reagents used in this investigation were those obtained from the usual commercial sources without further purification unless otherwise noted.

Analytical Procedures

Vanadium

The procedure for the determination of vanadium in the halides was principally the one that is found in Scott's Standard Methods of Chemical Analysis (65). The sample was dissolved in 1:1 nitric acid followed by the addition of sulfuric acid, whereupon the solution was evaporated to fumes of sulfur trioxide. After cooling, water was added until the solution contained about five per cent acid. It was then heated to boiling and the vanadium was oxidized by adding tenth normal potassium permanganate until the solution was a faint permanent pink. The determination was completed by reducing the vanadium to the plus four state with sulfur dioxide gas; the excess gas was removed with a flow of carbon dioxide and the solution was titrated with tenth normal potassium permanganate until the pink color returned. The accuracy of the method was at least 0.15 per cent while a precision of better than 0.2 per cent was obtained.

For vanadium contents in the 0.02 to 5 milligram range a procedure developed by Wright and Mellon (66) was used.

The reaction upon which the method was based was performed by adding sodium tungstate and phosphoric acid to an acid solution containing pentavalent vanadium. An immediate reaction occurred in which a yellow or brownish yellow solution was formed, varying in hue and intensity with the vanadium concentration. The spectrum of this solution did not show a maximum but it did exhibit a ridge at $420\text{ m}\mu$. The concentration of the reagents was not too critical but optimum concentrations were given in the original paper. A blank and a standard solution were run during each series of measurements; the optical density of the solutions was read from a Beckman Model DU spectrophotometer. The calibration curve obeyed Beer's law for values of the optical density near 1.000 corresponding to approximately three milligrams of vanadium. With careful consideration to detail the method will yield an accuracy of about one to two per cent. The precision obtained was usually somewhat better than this, averaging less than one per cent.

Chloride

For the determination of this element in the absence of the other halides, the standard Volhard or Mohr method was

used. In the presence of other halides, the chloride content was obtained by one of the following two methods.

For mixtures of chloride and bromide, the procedure developed by McAlpine (67) gave acceptable results. The method consisted of forming a compound with bromine which was unreactive toward silver nitrate. McAlpine has determined that bromine forms such a compound with acetone. The chloride was then determined using the standard Volhard method. The method gave results which were consistently one per cent high when standard solutions were run. Better accuracy, usually of the order of 0.5 per cent, was obtained when the chloride was determined gravimetrically. The precision was about the same order of magnitude.

The other method used for the separation of all three halides was that developed by DeGreiss et al. (68). The procedure consisted of collecting the mixture of halides on a column containing Dowex 1-X10 ion exchange resin which had been equilibrated with 0.5M sodium nitrate. The first eluent, 0.5M sodium nitrate, removed all chloride after 55 millimeters of eluate had been collected. The concentration of the eluting agent was increased to 2M sodium nitrate which removed all bromide after about 55 millimeters of

eluate had been collected. Iodide was stripped from the column by further addition of sodium nitrate. The chloride and bromide accuracy was ± 0.2 per cent. Since a large volume of eluent was required to remove all of the iodide, the method presented serious disadvantages for the determination of this element. The results were quite acceptable but the procedure was rather tedious and required very careful manipulation to obtain complete separation of the halides.

Bromide

This element was determined by utilization of the Volhard method when no other halides were present.

For the determination of bromide in the presence of chloride, the procedure developed by Kolthoff and Yutzy (69) yielded excellent results. Accuracy and precision of the method were on the order of 0.3 per cent. The method consisted of oxidizing the bromide to bromate by hypochlorite at a pH of 6 to 6.5. The excess hypochlorite was removed by sodium formate and the bromate determined iodometrically.

Low concentrations of bromide ion were determined colorimetrically by utilization of its reaction with one of several alkaloids (70). Among the alkaloids used were

brucine, strychnine, and cinchonidine. Brucine gave the most sensitive color test. If chloride was present, bromide was determined with strychnine. The solutions contained the alkaloid, phosphoric acid and potassium persulfate and were read at a wave length of 540 $m\mu$ using a Beckman Model DU spectrophotometer. The calibration curve obeyed Beer's law up to concentrations near 1.5 milligram bromide per ten millimeter sample. Accuracy of the method varied from one to two per cent.

Iodide

This element was determined in mixed halides by oxidizing the ion to the element with bromine water (71). Excess bromine was then destroyed by the addition of sodium formate. The iodine was then determined in the normal manner.

Preparation of the Halides

Vanadium(IV)-chloride

The synthesis of this material was accomplished by two methods. First, the method of Bodforss et al. (5) was used since a large quantity of high purity vanadium(V) oxide was readily available. The pentoxide was reduced with hydrogen

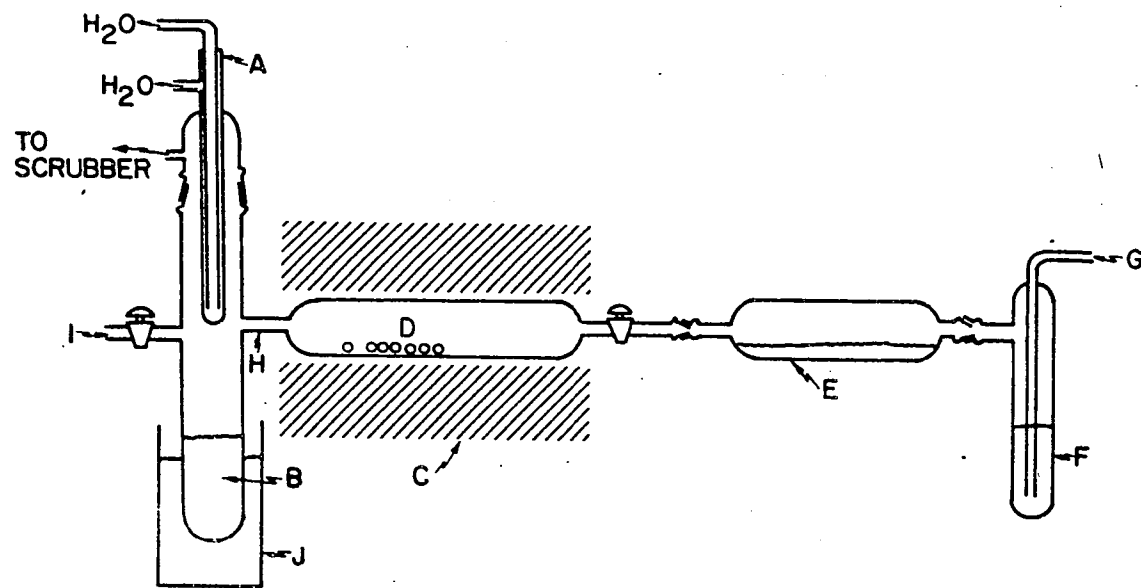
at 525°C to yield the trioxide. When the reduction was completed, the resulting trioxide was reacted with carbon tetrachloride by passing a stream of helium saturated with the tetrachloride vapor over the oxide at 525°C; the product, vanadium(IV) chloride, was condensed using the system shown in Figure 3. In the second method the tetrachloride was prepared by the chlorination of crystal-bar vanadium at a temperature of 400°C; the apparatus is identical to that previously shown. The liquid was not used directly but served only as an intermediate for the preparation of the lower halides of vanadium.

Vanadium(III) chloride

The trichloride was prepared by the method of Meyer and Backa (13) where the tetrachloride is refluxed in a stream of nitrogen. The liquid was refluxed for 48 to 72 hours at 160° to 170°C. The residue was then heated to 200°C and evacuated to 10^{-3} millimeter mercury before taking into the glove box. The solid was ground so as to pass through a 40-mesh screen, transferred to another tube and then outgassed at 200°C under vacuum to remove the last traces of the tetrachloride.

Figure 3. Chlorination Apparatus

- A. Cold finger
- B. Vanadium(IV) chloride
- C. Furnace
- D. Vanadium metal or vanadium(V) oxide
- E. Tetraphosphorus decoxide
- F. Sulfuric acid or carbon tetrachloride
- G. Chlorine, hydrogen or helium
- H. Tube sealed off after chlorination
- I. Inlet for nitrogen
- J. Dibutyl phthalate bath



Vanadium(II) chloride

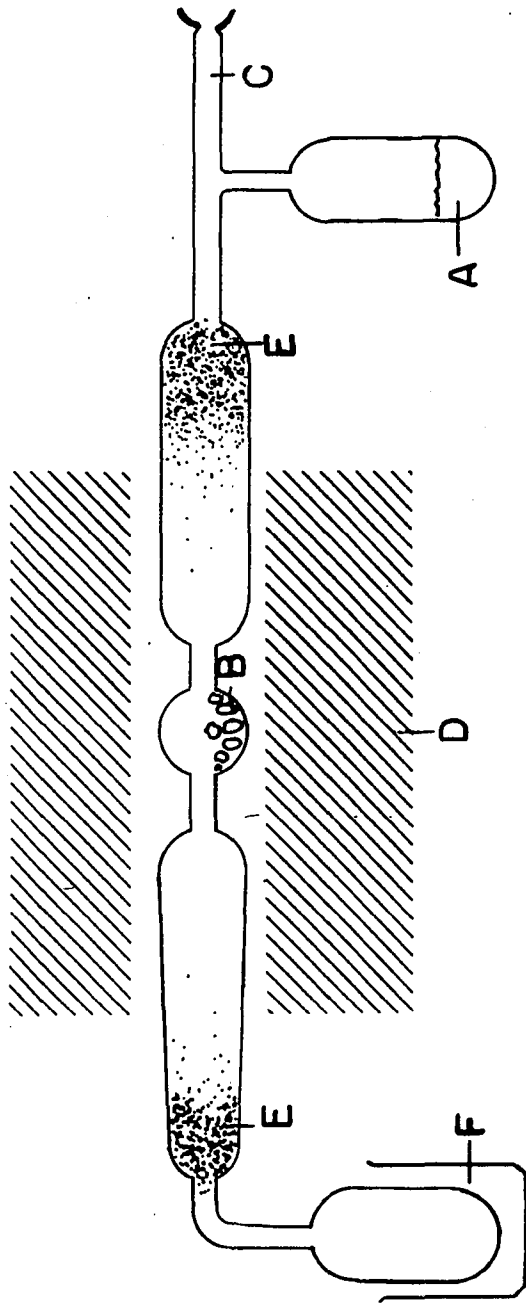
This green solid was prepared by the hydrogen-reduction of the trichloride at 475°C. The resulting dichloride was then heated to 700°C under vacuum to remove any of the unreduced trichloride.

Vanadium(III) bromide

The tribromide was obtained by the direct combination of the elements in a sealed evacuated tube at 400°C. The reaction tube, Figure 4, containing the metal was first outgassed at 400°C at a vacuum of less than 10^{-5} millimeter of mercury. Bromine was distilled into the reaction tube and the system reevacuated to less than 10^{-5} millimeter mercury. The tube was then sealed. During the course of the reaction, bromine was distilled repeatedly over the metal to hasten the rate of the reaction. The tribromide formed as black platelets on the cooler portions of the tube. The material was purified by sublimation in a bromine atmosphere at 350° to 400°C.

Figure 4. Bromination Apparatus

- A. Bromine
- B. Vanadium metal
- C. Tube sealed after evacuation
- D. Furnace
- E. Vanadium(III) bromide
- F. Ice water



Vanadium(II) bromide

The dibromide was prepared by the hydrogen reduction of the tribromide at 450°C. The impure solid was purified by heating to 700°C under vacuum to decompose any tribromide not reduced.

Solid Solution Formation

The formation of solid solutions between two compounds which decompose before melting can present a formidable problem. Four methods were used to prepare solid solutions of vanadium(III) chloride with vanadium(III) bromide.

The weighed samples of the two components were intimately mixed by grinding them together. This powder was then placed in a vycor tube and evacuated to a pressure not exceeding 10^{-4} millimeter mercury. The tube was sealed, then heated to 700°C for at least twelve hours. The tube was rapidly quenched to room temperature by dropping it directly from the furnace into a container of ice water. The sample was annealed at 200°C for 24 hours after which it was slowly cooled to room temperature; the rate did not exceed 20° in a twelve hour period. The material was then removed, ground, and samples taken for analysis and x-ray diffraction analysis.

Weighed samples of vanadium(III) bromide were equilibrated with known amounts of hydrogen chloride gas in an evacuated sealed tube at temperatures near 500°C.

Weighed samples of vanadium(III) bromide were equilibrated with chlorine gas at various partial pressures in a sealed tube at temperatures ranging from 400° to 450°C. Equilibrium periods were on the order of forty hours.

The tribromide and the trichloride of vanadium were intimately mixed and then placed in an evacuated sealed tube containing bromine at a pressure of 220 millimeters mercury. When the mixture was heated to 325°C, a transport reaction occurred yielding the desired solid solution.

Transport Reactions

These reactions were attempted using two slightly different tube designs.

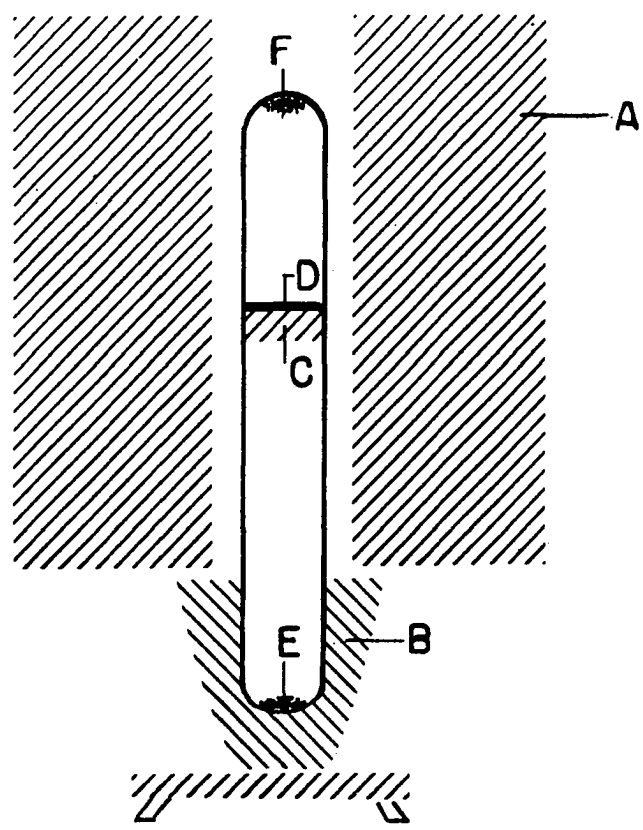
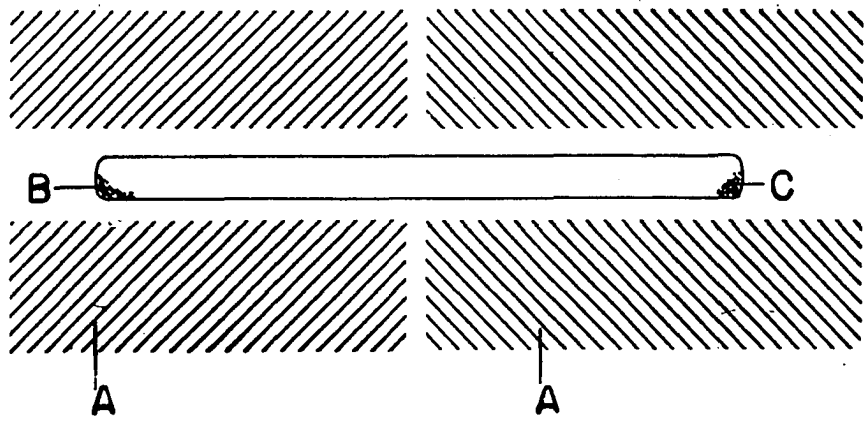
The first series of experiments were performed using the type of apparatus shown in Figure 5a. The method consisted of placing a small amount of the compound to be transported in one end of a straight tube. The tube was then evacuated and sealed, or in some cases, another component was added before the tube was sealed. The tube was

Figure 5a. Transport Apparatus

- A. Two separately controlled furnaces
- B. Sample
- C. Transported material

Figure 5b. Transport Apparatus

- A. Furnace
- B. Molten woods metal
- C. Fritted disk
- D. Sample
- E. Iodine
- F. Transported material



placed into a tubular resistance furnace containing two separate heating elements; the temperature of each element was then regulated by a temperature controller.

A schematic diagram of the apparatus used in the second series of experiments is shown in Figure 5b. This equipment was used mainly for the transport of a substance in the presence of iodine vapor. The sample, whose temperature was regulated from 300° to 450°C , was placed on top of a fritted disk. The iodine was located in the bottom of the tube where its temperature was controlled between 130° and 185°C . The top of the furnace was left open to yield a temperature ranging from 210° to 275°C . The transport of the material occurred from the disk to the top of the tube. The transported material was then heated to 150°C under vacuum to remove any excess iodine.

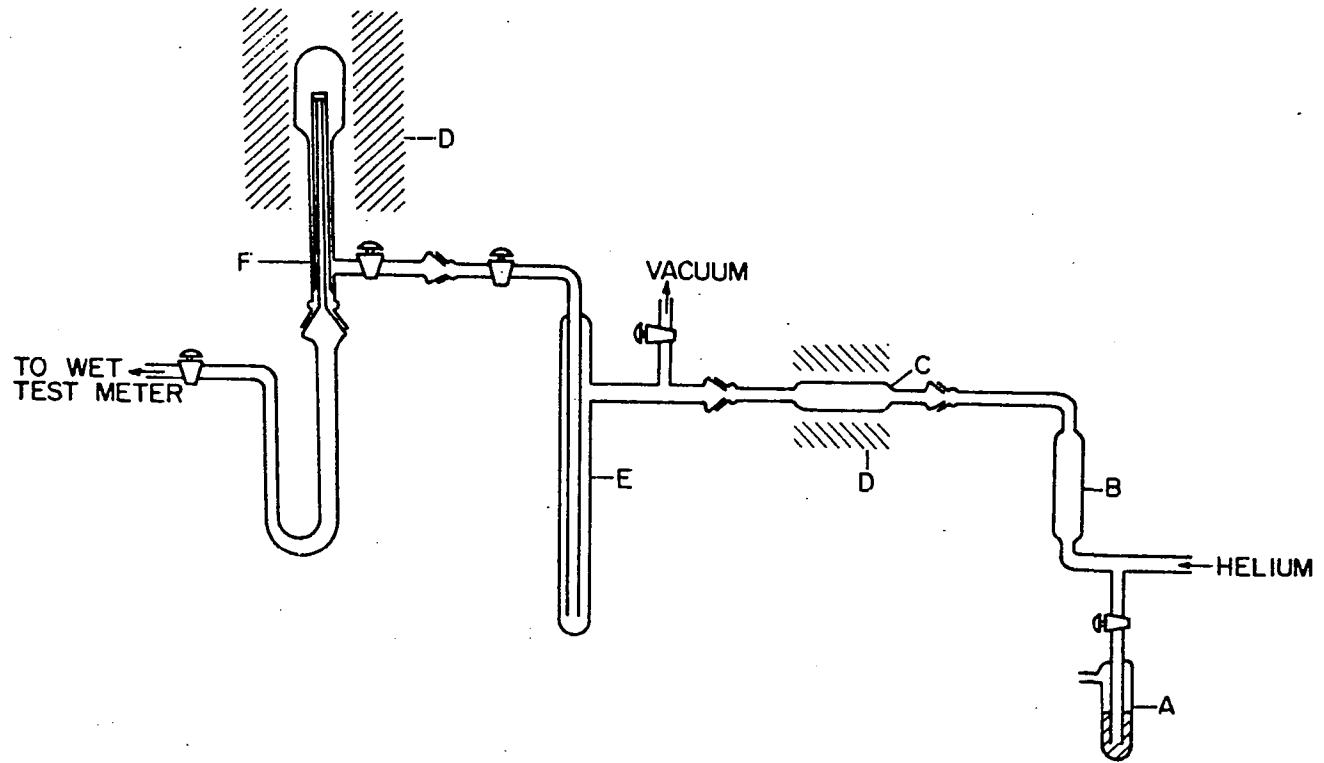
Vapor Pressure Measurements

Transpiration Method

A diagram of the apparatus is shown in Figure 6. Helium was used as a carrier gas. It was purified by flow through a tube of molecular sieves (Linde type 4A) which had been

Figure 6. Transpiration Apparatus

- A. Dibutyl phthalate bubbler
- B. Molecular sieves
- C. Uranium turnings
- D. Furnace
- E. Cold trap with glass beads
- F. Cell



previously outgassed at 200°C until a pressure of 10^{-3} millimeter mercury was obtained. The gas was then passed through uranium turnings at 800°C and finally through a trap at liquid nitrogen temperature. The over-pressure in the system was obtained by a reading of the dibutyl phthalate level in the bubbler located at the front of the gas-purification train.

The cell used was a modification of that of Treadwell and Werner (72). The complete cell is shown in Figure 7a and the condenser for vanadium(III) bromide and the trap for bromine are shown in Figure 7b.

The purified helium entered the cell as indicated in Figure 6 and then the saturated gas passed out through the tribromide condenser into the bromine trap. From the trap, the helium passed through a drying tube (to prevent back-diffusion of water vapor) into a water saturator and finally into a wet test meter for the measurement of the total gas flow.

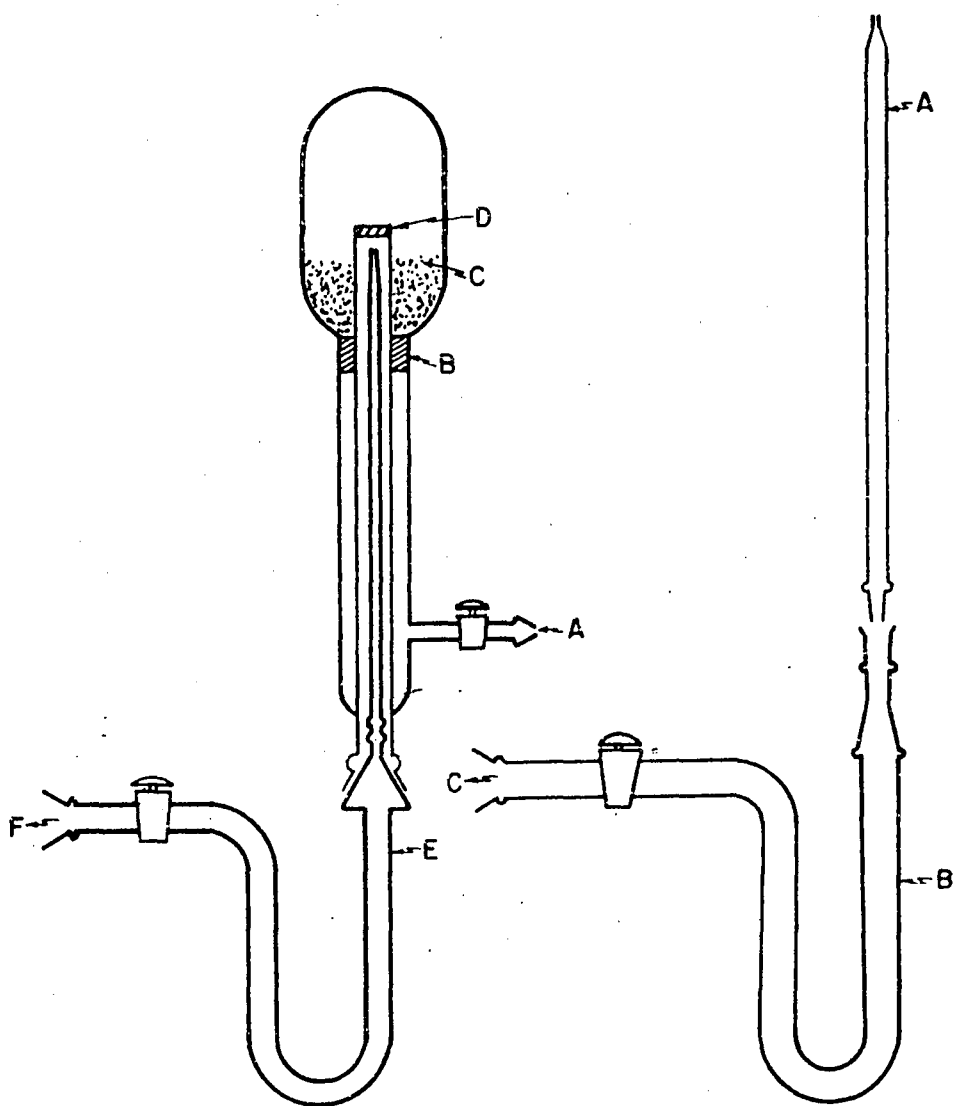
The furnace was of the nichrome resistance type containing double windings at the ends to prevent heat loss and a one-eighth inch thick steel liner to reduce any temperature gradients that were present. The furnace was arranged so

Figure 7a. Cell for Transpiration Experiment

- A. Helium inlet
- B. Pyrex wool
- C. Sample
- D. Coarse fritted disk
- E. Condensing system
- F. Outlet to wet-test meter

Figure 7b. Condensing System for Transpiration Experiment

- A. Vanadium(III) bromide condenser
- B. Bromine and vanadium(IV) halide condenser
- C. Outlet to wet-test meter



that it could be raised and lowered over the cell. This allowed the furnace to be brought to temperature before lowering it into position over the cell. A Honeywell proportional controller maintained the temperature of the sample within $\pm 1^{\circ}$. The cell temperature was measured with a chromel-alumel thermocouple which had been calibrated by use of the boiling point of sulfur and the melting point of lead.

All cells were loaded in an argon filled glove box which had a dew-point averaging no more than -60°C . After filling, the cell was mounted in place and connected to the gas purification train. The system was then evacuated to less than 5×10^{-4} millimeter mercury with the usual vacuum system composed of a mechanical pump and a mercury diffusion pump.

The furnace was brought to temperature in a position above the cell after which it was lowered around the cell. Thermal equilibrium was established before the helium flow was started. The desired flow rate had been previously established by noting the flow rate through the bubbler located at the front of the purification train.

At the end of a run, the furnace was lifted away from the cell. When the cell had cooled, the condenser was re-

moved and the amount of tribromide determined by spectrophotometric analysis. The amount of bromine collected was determined either iodometrically or by spectrophotometric analysis.

Additional transpiration experiments were performed on vanadium(III) bromide using bromine as the carrier gas. The pressure of bromine, which was determined by balancing it against a measured pressure of air in a diaphragm gauge, was controlled by immersing the excess liquid in either a thermostat or one of several slush baths. The baths consisted of a pure liquid in equilibrium with its solid at the melting point.

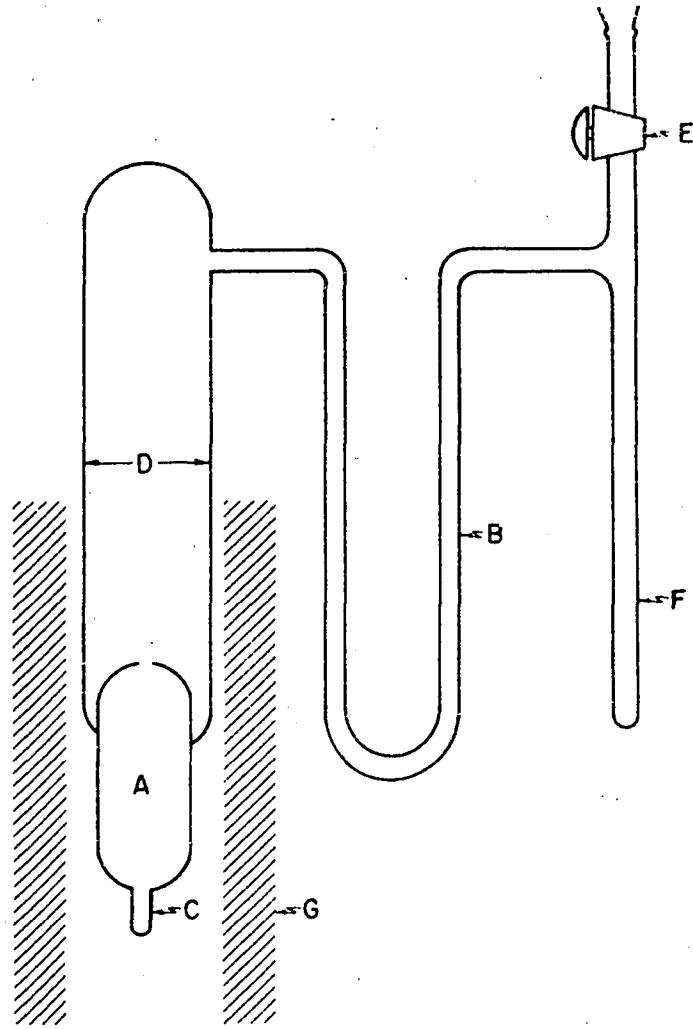
The system was evacuated to approximately 10^{-3} millimeter mercury and allowed to reach thermal equilibrium. Bromine was then passed over the sample and all volatile products were condensed in a trap at liquid nitrogen temperature. The amount of bromine was determined either by weighing or by iodimetric analysis. The vanadium was determined by spectrophotometric analysis.

Effusion

A schematic diagram of the effusion apparatus is shown in Figure 8. Two cells were constructed, one of pyrex and

Figure 8. Effusion Apparatus

- A. Effusion cell
- B. Trap (liquid nitrogen)
- C. Entrance tube
- D. Effused material
- E. Stopcock
- F. Bromine condensing tube
- G. Furnace



the other of vycor. The cell A, twenty millimeters in diameter, was sealed to a twenty-five millimeter tube. The trap B was attached directly to the cell to prevent contamination of the effusing vapors with stopcock lubricant. Fresh samples of the material were inserted into the cell through the small tube C which was then sealed off. Fresh samples were used in each run to ensure that the activity of the material remained near unity. The system was evacuated to less than 5×10^{-6} millimeter mercury and a preheated furnace moved into position around the cell. The furnace had double windings on each end and an eighth-inch steel liner was used to reduce any temperature gradients. The temperature was measured with two thermocouples spaced along the cell. A maximum variation of $\pm 1^{\circ}$ was obtained through the use of a Brown proportioning controller.

The material effusing from the cell condensed in a well-defined ring D at the cool portion of the tube. The sublimate was dissolved in either water or nitric acid. The vanadium was then determined spectrophotometrically.

The tetrabromide of vanadium that had effused into the cold trap was decomposed with stopcock E closed. The resulting bromine was condensed in side arm F, the arm sealed off

and the bromine determined either by weighing directly or by spectrophotometric or iodometric analysis. The remaining tribromide was washed from the trap with dilute nitric acid and determined spectrophotometrically.

Diaphragm gauge measurements

The reactions of bromine with the tribromide and trichloride of vanadium were performed utilizing the all pyrex system shown in Figure 9. The cell, a null type Bourdon gauge, is reproduced in Figure 10. The gauges used in this investigation exhibited sensitivities of 0.2 millimeter for each millimeter pressure change when viewed with a 17X telescope. The cells could be heated to 450°C with no apparent change in the null-point. Pressures from the manometer were measured with a Gaertner precision cathetometer having a sensitivity of 0.05 millimeter mercury.

Initially, each cell was thoroughly dried by outgassing at 450°C for twelve to fifteen hours at 10^{-5} millimeter mercury. The material being studied was transferred to the cell in an argon filled glove box and then the cell was re-evacuated for at least six hours at 150° to 200°C. When the desired amount of bromine had been distilled into the cell,

Figure 9. Pyrex Diaphragm System

A. Cell

B. Ballast volume

C. Manometer

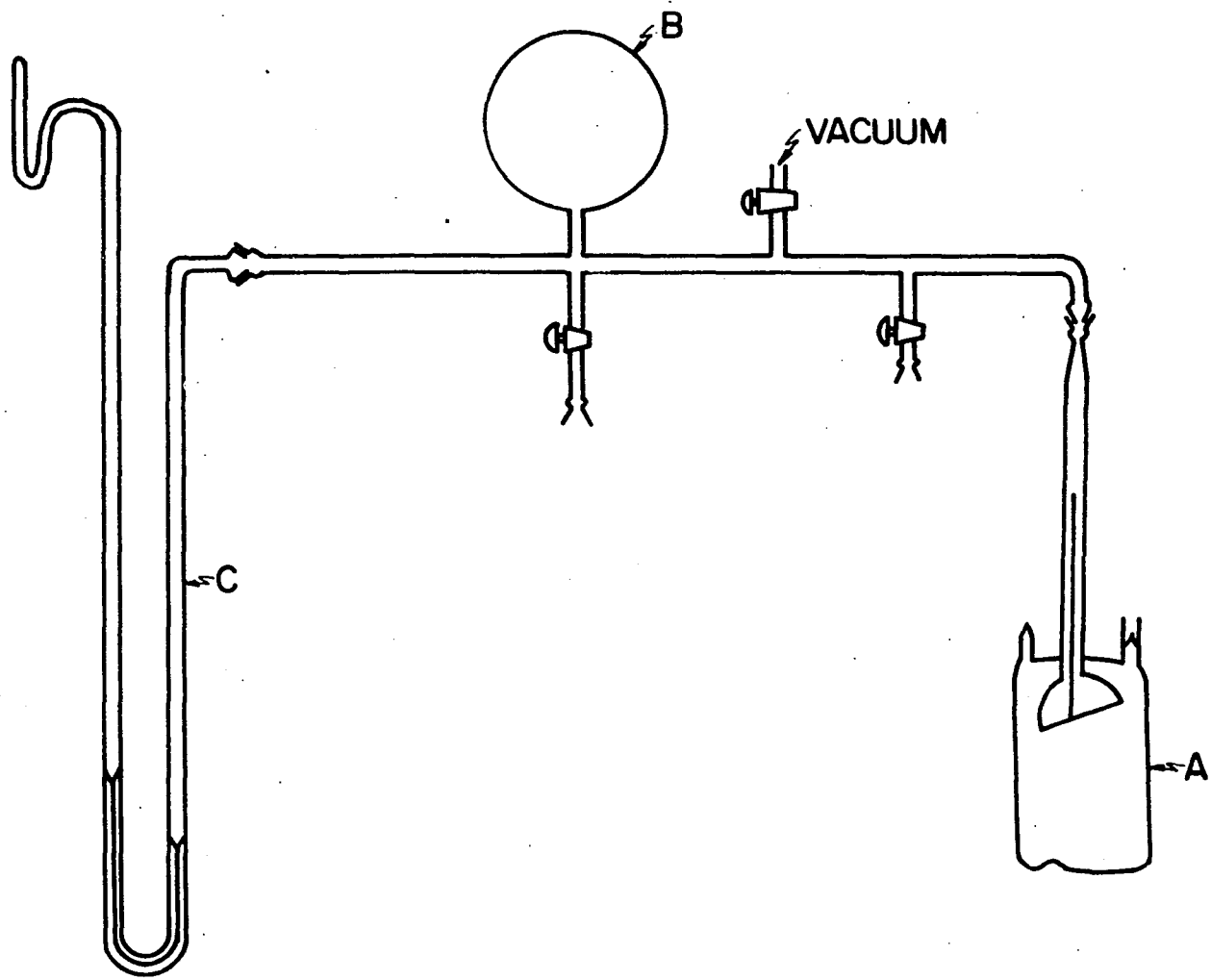
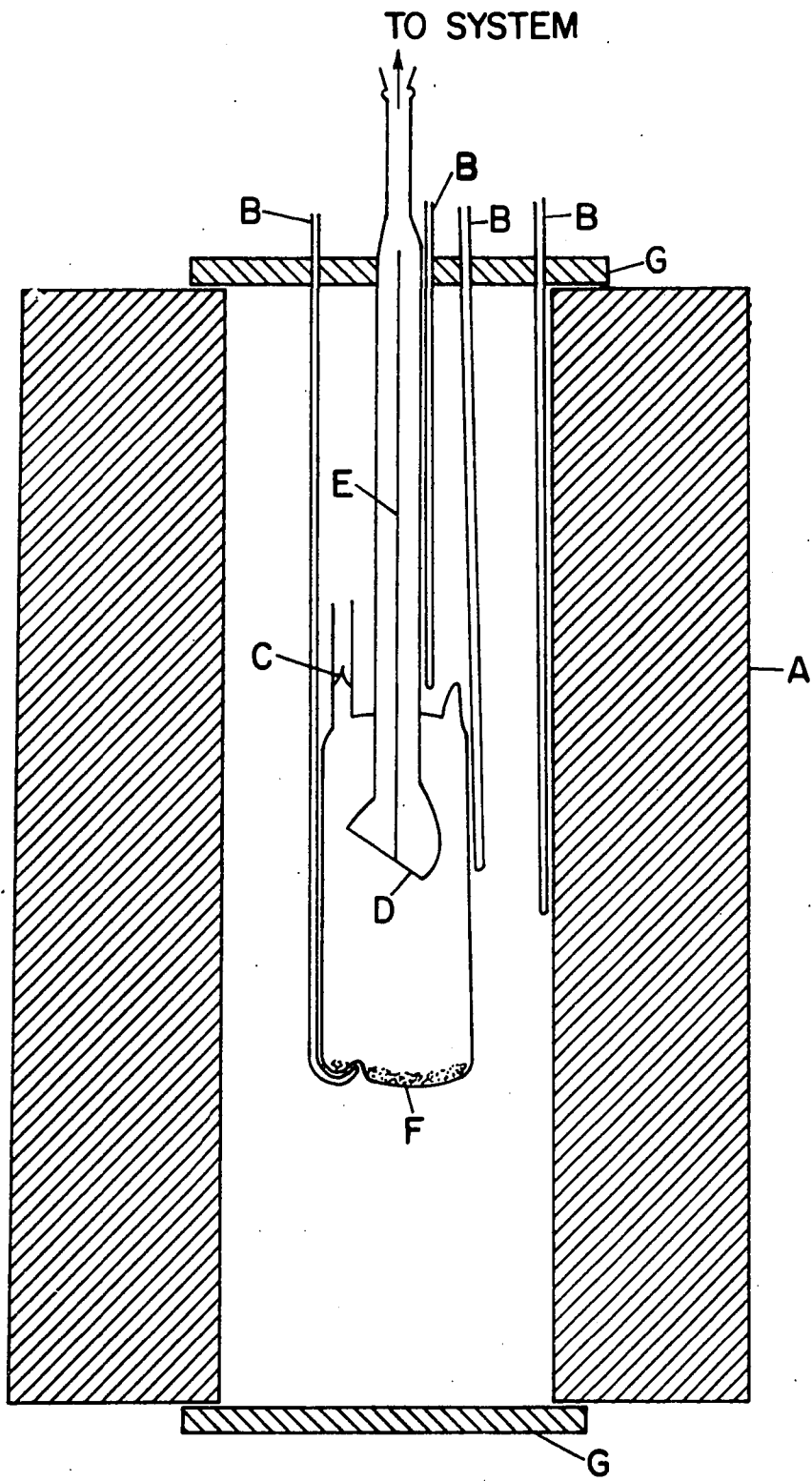


Figure 10. Pyrex Diaphragm Cell

- A. Furnace
- B. Thermocouple
- C. Break seal
- D. Glass membrane
- E. Pointer
- F. Sample
- G. Transite shields



the vapor was condensed with a dry ice acetone bath. The cell was reevacuated and then sealed off.

The cell was centered in a vertical, twelve inch Marshall furnace insulated at each end with a covering of transite and asbestos. Three thermocouples were located on the cell; one recessed in the bottom to measure the sample temperature, another located parallel and in contact with the cell wall approximately equidistant from its top and bottom, and the third located at the top of the cell. These three thermocouples were used to measure the temperature gradient along the cell. To reduce the temperature gradient, each cell was wrapped in aluminum foil. By adjusting shunts on the furnace taps a gradient of 3° to 6° was obtained at 400°C with the top portion of the cell at the highest temperature. A Rubicon potentiometer permitted direct reading of the temperature to 0.2°C . The chromel-alumel thermocouples which were employed in these experiments were calibrated using the boiling point of sulfur (444.6°C) and the melting point of lead (327.3°C) as reference standards.

The furnace temperature was controlled by a Honeywell Electronik circular indicating proportional controller which was used in conjunction with a Raytheon voltage stabilizer.

Pressure readings were taken at 10° to 15° intervals by alternately heating and cooling the cell allowing sufficient time for equilibrium to be established. Checks were made to ensure equilibrium was obtained by holding the sample at temperature for extended periods of time and measuring the pressure until a constant value was reached.

Preparation of Vanadium(IV) Bromide

The synthesis of this compound presented more a problem of stabilization than of preparation. Two different procedures were developed to condense this material from the vapor phase.

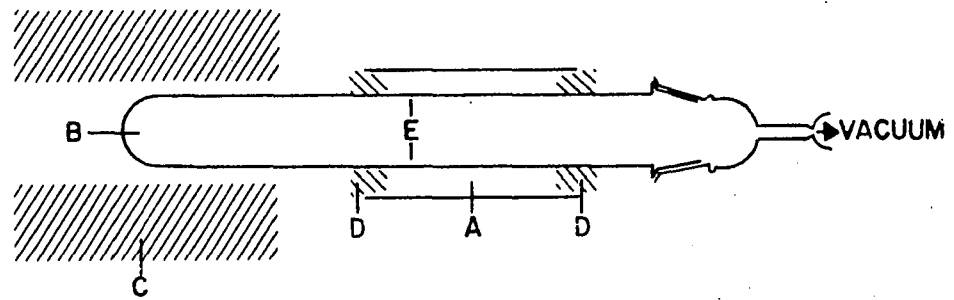
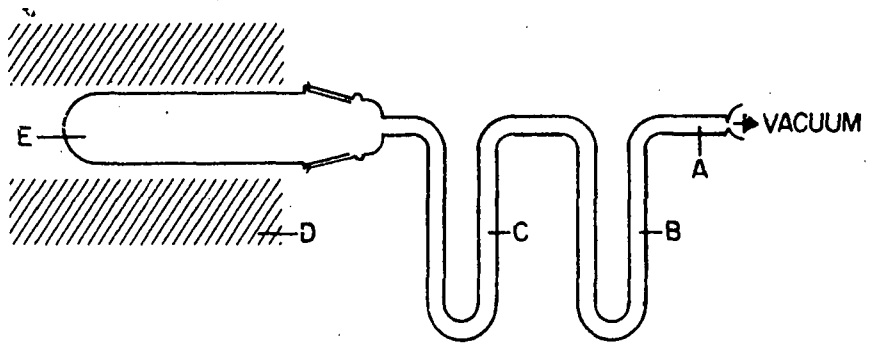
In the first series of experiments vanadium(III) bromide was placed in a tube and connected to the vacuum system by several cold traps (Figure 11a). When the sample was heated to 325°C, any vanadium(IV) bromide formed from the disproportionation was collected in the first trap. Bromine vapors formed from the decomposition passed through the trap since its vapor pressure was relatively high at the temperature of the cold trap. The tube was sealed off at A and the tetrabromide allowed to decompose by warming to room temperature. The bromine resulting from the decomposition was frozen in

Figure 11a. Vanadium(IV) Bromide Apparatus

- A. Seal-off point
- B. Bromine trap
- C. Original vanadium(IV) bromide trap
- D. Furnace
- E. Vanadium(III) bromide

Figure 11b. Vanadium(IV) Bromide Apparatus

- A. Powdered dry ice
- B. Vanadium(III) bromide
- C. Furnace
- D. Corks
- E. Vanadium(IV) bromide



trap B and then sealed off. Analyses were performed for bromine and vanadium in both residues.

The second series of experiments (Figure 11b) were performed in a similar manner except powdered dry ice was placed around the reaction tube so that any tetrabromide vapor leaving the furnace would be condensed immediately. The vapor pressure of bromine was too high to be condensed at this temperature (-78°C) when compared to the pressure in the system (10^{-5} millimeter mercury).

RESULTS AND DISCUSSION

Preparation of Halides

Vanadium chlorides

In initiating research for the preparation of various vanadium chlorides, several methods were investigated which used readily available high purity materials as starting products. Several such methods have been reported in the literature but all seem to possess inherent disadvantages which have been observed by subsequent workers.

Ruff and Lickfett (4, p. 516) have reported the preparation of rather pure vanadium(III) chloride by the reaction of vanadium(V) oxytrichloride with sulfur. However, McCarley and Roddy (73) and Foley et al. (14) have shown that the oxydichloride was formed as a by-product. In addition, the method presented a formidable problem in the separation of the trichloride from any unreacted sulfur.

In this investigation the method of Bodforss et al. (5) consisting of reacting vanadium(III) oxide with carbon tetrachloride to produce vanadium(IV) chloride, was attempted since quantities of the starting materials were available

in high purity. The product produced in each series of reactions was decomposed and an analysis made of the resulting trichloride. The effect of reaction temperature and quantity of carbon tetrachloride on the purity of the final product was studied. The results are given in Table 1.

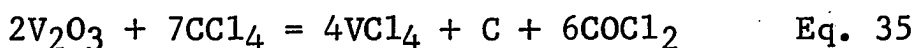
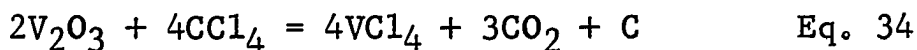
The values given for the amount of carbon tetrachloride are only approximate since the stoichiometry of the reaction was not determined.

Table 1. Experimental Results of the Reaction of Vanadium (III) Oxide with Carbon Tetrachloride

| Temp. of Reaction (°C) | Temp. of CCl ₄ (°C) | Amt. of CCl ₄ used | Analysis of Product | | | |
|------------------------|--------------------------------|-------------------------------|---------------------|------|---------|------|
| | | | % V | % Cl | Total % | Cl/V |
| 520 | 25 | excess | 33.6 | 65.7 | 99.3 | 2.82 |
| 525 | 25 | large excess | 34.6 | 66.0 | 100.6 | 2.75 |
| 525 | 25 | 90% of theoretical | 32.4 | 67.2 | 99.6 | 2.98 |
| 475 | 0 | 30% excess | 32.6 | 67.1 | 99.7 | 2.96 |
| 475 | 0 | 10% excess | 33.0 | 66.9 | 99.9 | 2.91 |

For calculation purposes, equations 34 and 35 were used.

During the thermal decomposition of the tetrachloride and



subsequent outgassing of the trichloride, a white crystalline solid was observed to sublime from the product. A portion of the white material was separated from the trichloride and purified by recrystallization from an alcohol-water mixture. A melting point determination gave a value of 182° to 184°C . From the melting point data and an observation of other physical properties, the substance was identified as hexachloroethane (melting point = 187°C) and higher homologs. Complete removal of this material by sublimation proved to be an extremely slow process. The trichloride obtained by this method would be acceptable for general use but a suitable procedure for the complete removal of the various chlorocarbons that occur as by-products would be required if high purity material were desired. Two attempts to prepare vanadium(II) chloride from the trichloride by the hydrogen reduction method gave chloride to vanadium molar ratios for the products of 1.98 to 1.87.

The method which yielded the highest purity chlorides was the most obvious one, that of the direct combination of the elements. Representative values for the analysis of the trichloride obtained by the chlorination of crystal-bar vanadium followed by decomposition are listed in Table 2.

The only impurity of any consequence found in the final product was carbon which had been carried over during the chlorination. Evidence of its presence was found in the dichloride preparations where black particles were observed in the green solid. In Table 2 is also listed the results of the dichloride preparations by the hydrogen reduction of the trichloride. The low result obtained for sample 6 was caused by a too high a temperature during the hydrogen reduction.

Table 2. Analysis of Vanadium(III) Chloride and Vanadium(II) Chloride Preparations

| Sample number | % V | % Cl | Total % | Molar Ratio Cl/V |
|----------------------|------|------|---------|------------------|
| VC1 ₃ --1 | 32.2 | 67.7 | 99.9 | 3.00 |
| 2 | 32.1 | 67.7 | 99.8 | 3.00 |
| 3 | 32.3 | 67.8 | 100.1 | 2.99 |
| 4 | 32.3 | 67.5 | 99.8 | 2.98 |
| VC1 ₂ --5 | 41.8 | 58.1 | 99.9 | 1.99 |
| 6 | 42.1 | 58.0 | 100.1 | 1.95 |

Vanadium bromides

Since the chlorination of crystal-bar vanadium produced such a high purity product, the tribromide was synthesized in a similar manner using bromine as the brominating reagent.

A representative analysis of the product obtained is given in Table 3.

The dibromide was made in a similar manner to that of the dichloride, a representative analysis is given in Table 3.

Table 3. Analysis of Vanadium(III) Bromide and Vanadium(II) Bromide Preparations

| Sample number | % V | % Br | Total % | Molar Ratio Br/V |
|----------------------|------|------|---------|------------------|
| VBr ₃ --1 | 17.5 | 82.4 | 99.9 | 2.99 |
| 2 | 17.6 | 82.5 | 100.1 | 2.99 |
| 3 | 17.4 | 82.5 | 99.9 | 3.00 |
| VBr ₂ --4 | 24.1 | 75.8 | 99.9 | 2.00 |

Solid Solution Studies

The crystal structures of anhydrous vanadium(III) chloride, vanadium(III) bromide, and of some vanadium(III) mixed halides were investigated by x-ray powder techniques. The diffraction patterns were obtained of samples which had been sealed in capillaries with 0.2 millimeter inside diameter. A Phillips camera, 11.46 centimeters in diameter, was used with nickel-filtered, copper K α radiation.

National Bureau of Standards tables (74) were used to convert θ to distances.

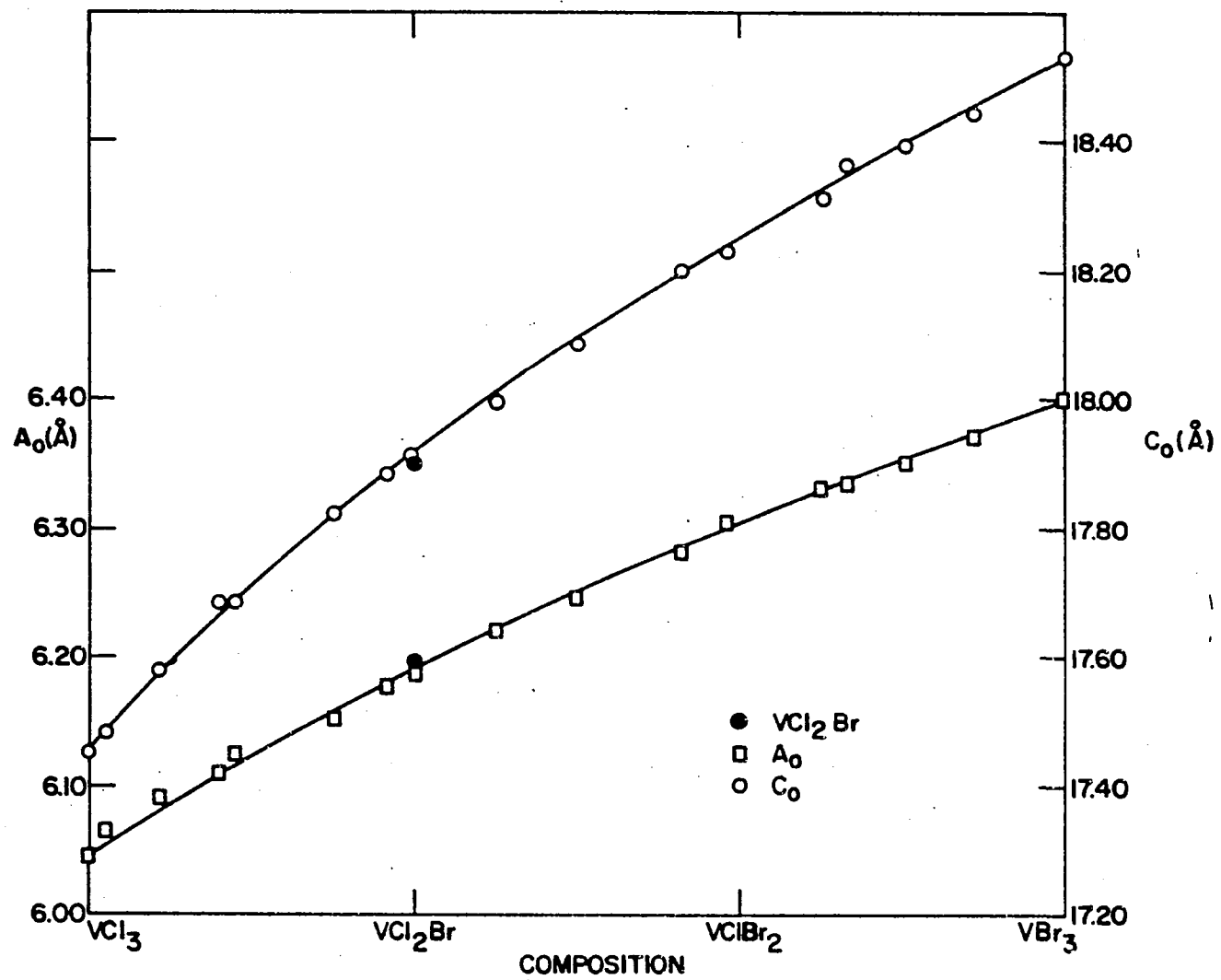
The structures of the vanadium(III) halides were sufficiently similar to permit indexing of powder patterns from the known characteristics of vanadium(III) chloride. Klemm and Krose (15) have made a crystal study of this material and found it to be isostructural with iron(III) chloride. The lattice constants for the vanadium compound were listed as: $a_0 = 6.012 \text{ \AA}$, $c_0 = 17.34 \text{ \AA}$.

The lattice parameters in this investigation were obtained by using the method of Taylor and Sinclair (75), a detailed discussion of which can be found in the Appendix. In addition, all films were corrected for shrinkage effects.

The parameters for all of the solid solutions are given in the Appendix along with the values obtained for the trichloride and tribromide in this Laboratory. The relationship of these data to the corresponding values of the molar ratio of halogen to vanadium is given in Figure 12. In the majority of cases the lattice parameters were known with greater precision than the composition. The method for determining the composition is discussed in the Appendix.

The solutions all possessed the bismuth(III) iodide

Figure 12. Lattice Constants vs. Composition in the System $\text{VCl}_3\text{-VBr}_3$



structure, a structure exhibited by many of the metallic halides with a formula of MX_3 . The structure consists of a double-layer lattice of halogens based on hexagonal closest packing arrangement. In this type of packing arrangement are located holes in a plane midway between those of the close-packed atoms. Some of these holes, called octahedral holes, may be occupied by metal atoms, forming a composite layer X-M-X consisting of two adjacent layers of halogen atoms with a layer of metal atoms between them. Since the primary valencies of the M and X atoms are satisfied within such a layer, there being only van der Waals forces between adjacent layers, it may be regarded as an infinite 2-dimensional molecule. The composition of the layer (i.e. the ratio of M:X atoms) is determined by the proportion of octahedral holes occupied by metal atoms. In the layer structure being considered, the maximum number of octahedral holes that may be occupied is one-half of the total. In the trichloride structure the vanadium atoms occupy two-thirds of the octahedral interstices within the layer containing the metal atoms.

The structures of VCl_2I and VI_3 were impossible to obtain owing to the extreme difficulty in isolating these

compounds.

The " a_0 " lattice constant of the solutions showed a slight positive deviation from ideal behavior. The " c_0 " lattice constant exhibited a similar although somewhat larger positive deviation from ideality. The effect of these variations on the axial ratio c_0/a_0 can be seen in Table 4. The mixed halide, VCl_2Br , was in fairly close accord with that which would be expected from a solid solution of the same composition. The somewhat larger " c_0 " deviation could be explained by the fact that " a_0 " is effectively determined by the V-X distance whereas " c_0 " is also dependent on the closeness of packing of the halogen layers. Since the trichloride has a structure where the metal is located in alternate layers, the introduction of a larger halogen atom will tend to exert its influence to a greater extent in the " c_0 " direction by separating the layers. This influence will result in a somewhat larger increase in the " c_0 " lattice parameter than the " a_0 " parameter.

As expected, VBr_2I exhibited lattice constants somewhat larger than those of the tribromide. Even though the comparison of these parameters with those of the triiodide can not be made, one can probably assume that solid solution

Table 4. Lattice Constants of Vanadium(III) Chloride and Bromide Solid Solutions

| Sample number | Molar ratio (Cl/V) | Lattice Parameters | | |
|------------------|--------------------|--------------------|-----------|-----------|
| | | a_0 (Å) | c_0 (Å) | c_0/a_0 |
| VCl ₃ | 3.00 | 6.045 | 17.45 | 2.886 |
| 19 | 2.95 | 6.063 | 17.48 | 2.883 |
| 9 | 2.78 | 6.090 | 17.58 | 2.886 |
| 39 | 2.71 | 6.106 | 17.66 | 2.892 |
| 10 | 2.60 | 6.108 | 17.69 | 2.896 |
| 41 | 2.55 | 6.124 | 17.74 | 2.896 |
| 38 | 2.24 | 6.149 | 17.82 | 2.898 |
| 12 | 2.25 | 6.146 | 17.81 | 2.897 |
| 6 | 2.08 | 6.164 | 17.86 | 2.897 |
| 34 | 2.01 | 6.166 | 17.91 | 2.904 |
| 11 | 2.00 | 6.180 | 17.91 | 2.898 |
| 42 | 1.99 | 6.184 | 17.92 | 2.897 |
| 13 | 1.75 | 6.213 | 17.99 | 2.895 |
| 43 ^a | 1.50 | 6.240 | 18.08 | 2.897 |
| 14 | 1.45 | 6.249 | 18.11 | 2.898 |
| 21 | 1.18 | 6.278 | 18.17 | 2.894 |
| 17 | 1.12 | 6.285 | 18.20 | 2.895 |
| 25 ^a | 1.19 | 6.293 | 18.20 | 2.892 |
| 22 | 1.04 | 6.304 | 18.23 | 2.891 |
| 15 | 1.08 | 6.293 | 18.21 | 2.893 |
| 44 ^a | 0.94 | 6.311 | 18.23 | 2.888 |
| 3 | 0.67 | 6.338 | 18.36 | 2.896 |
| 20 | 0.63 | 6.346 | 18.37 | 2.894 |
| 18 | 0.42 | 6.366 | 18.41 | 2.891 |
| 16 | 0.26 | 6.380 | 18.45 | 2.891 |
| 47 ^b | 0.07 | 6.394 | 18.47 | 2.888 |
| 48 ^b | 0.16 | 6.383 | 18.46 | 2.892 |
| 49 ^b | 0.13 | 6.390 | 18.46 | 2.888 |
| 50 ^b | 0.04 | 6.396 | 18.48 | 2.889 |
| 51 ^b | 0.28 | 6.371 | 18.42 | 2.891 |
| 52 ^a | 0.49 | 6.350 | 18.39 | 2.896 |
| 53 ^a | 0.74 | 6.328 | 18.31 | 2.893 |
| VBr ₃ | 0.00 | 6.400 | 18.53 | 2.895 |

^aTransport of solid solution with bromine

^bEquilibration of vanadium(III) bromide with chlorine

formation would occur for this system, since they would be expected to behave in a similar manner as the trichloride-tribromide system. The lattice parameters for the stoichiometric compounds are listed in Table 5.

Table 5. Lattice Parameters of the Stoichiometric Compounds of the Vanadium(III) Halides

| Compound | a_0 (Å) | c_0 (Å) | c_0/a_0 |
|---------------------|-----------|-----------|-----------|
| VCl ₃ | 6.045 | 17.45 | 2.892 |
| VBr ₃ | 6.400 | 18.53 | 2.894 |
| VCl ₂ Br | 6.186 | 17.90 | 2.894 |
| VBr ₂ I | 6.589 | 19.30 | 2.933 |

The values listed in the table for VCl₃ are approximately one per cent higher than those reported by Klemm and Krose. Since no analysis was listed for their product, the difference may be due to impurities present in their sample.

Transport Reaction Studies

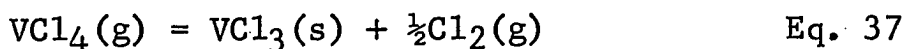
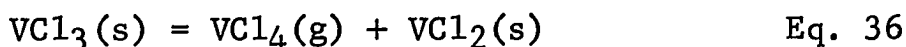
The preparation of relatively large crystals of the di- and trichlorides and of the di- and tribromides of vanadium was attempted via the transport process. The majority of reactions were performed in the presence of either chlorine,

bromine, or iodine to facilitate the formation of a volatile species.

Vanadium(III) chloride

Since the synthesis of this material is almost always performed by the thermal decomposition of the tetrachloride, any large crystals are quite difficult to prepare. Single crystals can not be obtained by a simple vaporization process since the trichloride undergoes disproportionation at elevated temperature to yield the dichloride and the tetrachloride. Knowledge of the occurrence of this reaction was used in the first series of experiments.

As the trichloride was known to exhibit extensive disproportionation at temperatures over 425°C, the sample was heated to 450°C. The opposite end of the evacuated sealed pyrex tube was maintained at 160° to 170°C. The decomposition of the tetrachloride in this temperature range has been shown to be quite rapid. Hence, the disproportionation of VC1₃ occurred at 450°C (equation 36) and the decomposition



of VC1₄ at 160° to 170°C (equation 37) to produce a net

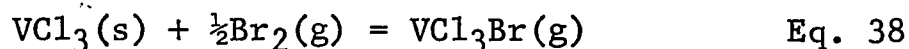
transfer of the trichloride from the hot to the cool end of the tube. After approximately 24 hours, 34 milligrams of material were transported. The shiny almost black platelets located in the cooler portion of the tube analyzed correctly as the trichloride. The addition of chlorine did not materially increase the rate of transfer. This effect may be explained by noting that the addition of chlorine would increase the formation of the tetrachloride but would hinder its decomposition.

The introduction of iodine into the sample produced no net increase in the quantity of material transferred. The anticipated formation of the mixed halide vapor species did not seem to occur.

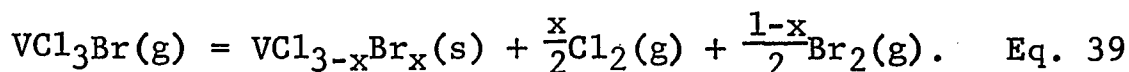
When transport experiments were performed in the presence of bromine, a four to five gram sample could be transported in a 24 hour period. The sample could be at any temperature varying from 325° to over 450°C with the cooled portion of the tube at room temperature. The results of these experiments (Table 6) show that some exchange had occurred between the bromine and chloride in the deposited material. The transport process occurred through the reaction

Table 6. Analysis of Reaction Product of the Transport of Vanadium(III) Chloride with Bromine

| V.P. of Br ₂ (mm. Hg) | Reaction temp. (°C) | % V | % Cl | % Br | Total % | Molar Ratio Cl/V | Ratio X/V | a _o o A | c _o o A |
|--|---------------------------|------|------|------|------------|---------------------|--------------|--------------------------|--------------------------|
| 220 | 400 | 31.8 | 65.5 | 2.5 | 99.8 | 2.96 | 3.01 | 6.06 | 17.46 |
| 67 | 400 | 32.1 | 66.2 | 1.6 | 99.9 | 2.97 | 3.00 | 6.08 | 17.47 |



and the decomposition by the reaction

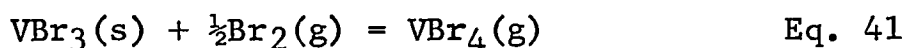
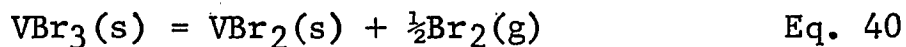


The bromine contaminant would present further problems if high purity trichloride was desired. The preparation of large single crystals by this method could not be obtained since the transfer effect was much too rapid for slow growth.

Vanadium(III) bromide

Relatively large black platelets approximately five millimeters square could be grown when the sample was at 300°C and the cooler portion of the evacuated sealed tube was at room temperature. The tribromide could be sublimed in the absence of bromine under the same conditions but only small crystals were obtained. Since the tribromide had such a low vapor pressure at these temperatures, sublimation could not have produced such a rapid transport (four to five grams in a 24 hour period). From vaporization characteristics of the tribromide, which will be discussed later, the formation of the crystal phase can be explained as a true transport process. Part of the tribromide decomposed

at the hotter portion of the tube to yield bromine (equation 40). This bromine then reacted with excess tribromide to form the more stable (at temperatures over 500°K) and more volatile tetrabromide (equation 41). This volatile



compound diffused to the cooler portion of the tube where it decomposed to yield the tribromide, and the transport process had occurred.

Vanadium(II) chloride

The transport reactions of this solid were investigated with bromine and iodine added to facilitate the formation of a vapor species.

The reaction of the dichloride with excess bromine was performed with the sample at approximately 375°C and the cooler portion of the tube at room temperature. The vapor pressure of bromine was 220 millimeters mercury. Complete transfer was obtained in twelve hours but the material was a black-colored sublimate which analyzed as a compound of the formula VCl_2Br . A discussion of the x-ray diffraction analysis of this material was given in the section on solid

solution studies. Several thermal decompositions were performed on this material under a working vacuum at temperatures ranging from 600° to 750°C. The residues seemed to consist of a solid solution of the dichloride and dibromide of vanadium. From the analysis, the vanadium content remained constant at a value of 36.3 per cent while the chloride and bromide values varied in such a manner that the total halogen to vanadium molar ratio approximated two.

Transport reactions were attempted in a straight evacuated tube with the dichloride at 540° to 570°C while the other end of the tube was at 800°C. Three separate experiments were performed with vapor pressures of bromine ranging from 15 to 210 millimeters mercury. There was evidence of reactions occurring in each case since the light green color of the dichloride had darkened considerably, but no transport was observed.

When iodine was used, the growth rate was slow enough to yield green platelets approximately four millimeters square when the sample temperature varied between 350° C and 400°C and the decomposition temperature was 275°C. X-ray patterns proved this material to be the dichloride. Although the exact nature of the vapor species was not determined,

its composition can be estimated by comparing it with other systems studied in this investigation. The direct vaporization of the dichloride can be eliminated since its vapor pressure at the temperatures in question was negligible. The presence of any vanadium(III) compound in the vapor phase was rather remote since its stability at the temperatures in question was very low. Hence, by a process of elimination, the presence of a vanadium(IV) compound must be assumed, and the most likely one would be that of the mixed halide, VCl_2I_2 .

Vanadium(II) bromide

Using a procedure identical to the one used for the dichloride, the reaction of the dibromide with iodine proceeded to give a mixed halide of the formula, VBr_2I . A discussion of the x-ray analysis of this material was discussed in the section on solid solution studies. The vapor species during the transport probably consisted of the mixed halide, VBr_2I_2 .

Vapor Pressure of Vanadium(II) Chloride and Bromide

The vapor pressure of these two substances was investigated using the method developed by Knudsen. By substituting the various geometric factors of the vycor effusion

cell into the basic equation for the vapor pressure, the following expression results;

$$P_{\text{mm.}} = \frac{(6.01 \times 10^2) (G) (T/M)^{\frac{1}{2}}}{t} \quad \text{Eq. 42}$$

where G is the weight of effused material in grams, T is the absolute temperature, M is the molecular weight of the vaporizing species, and t is the time of effusion in seconds.

The results of a study of the vaporization of these two substances are plotted in Figures 13 and 14. The vapor species were assumed to be monomers since the results obtained by Sime and Gregory (76) indicated that the vapor over chromium(II) bromine was largely monomer. Also, the mass spectrometer has been used to study the iron(II) halides (77) and the results indicated the monomer was the predominant vapor species. The dashed line on the figures represents the pressure if complete dimerization was assumed. The accommodation coefficient was assumed to be approximately one. The pressures measured in the cell were assumed to be equilibrium pressures owing to the consistency of the results and to the good agreement with the transpiration data on vanadium(II) chloride by Oranskaya and Perfilova (24, p. 257). The lines drawn through the experimental points can

Figure 13. Vapor Pressure of Vanadium(II) Chloride

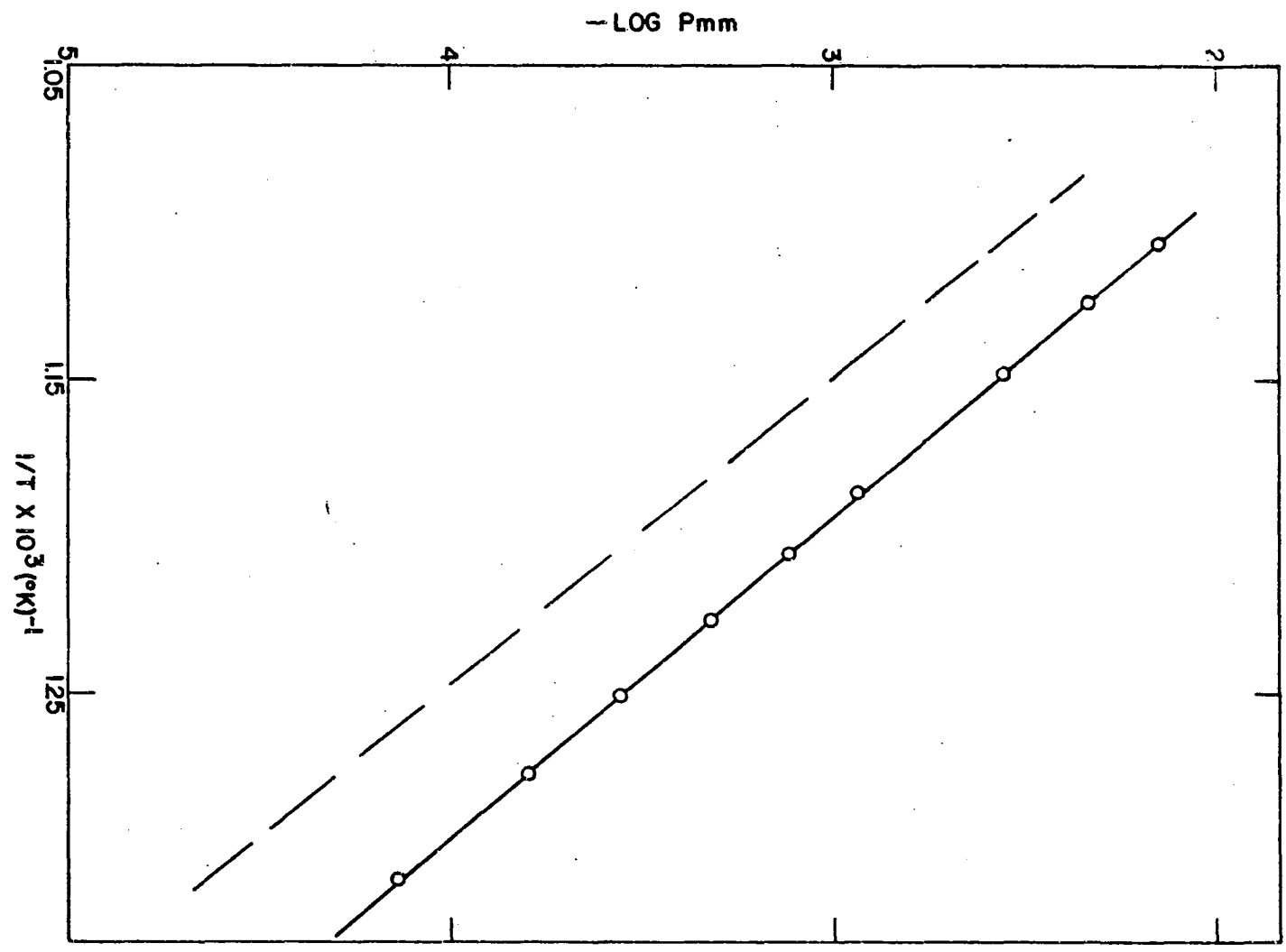
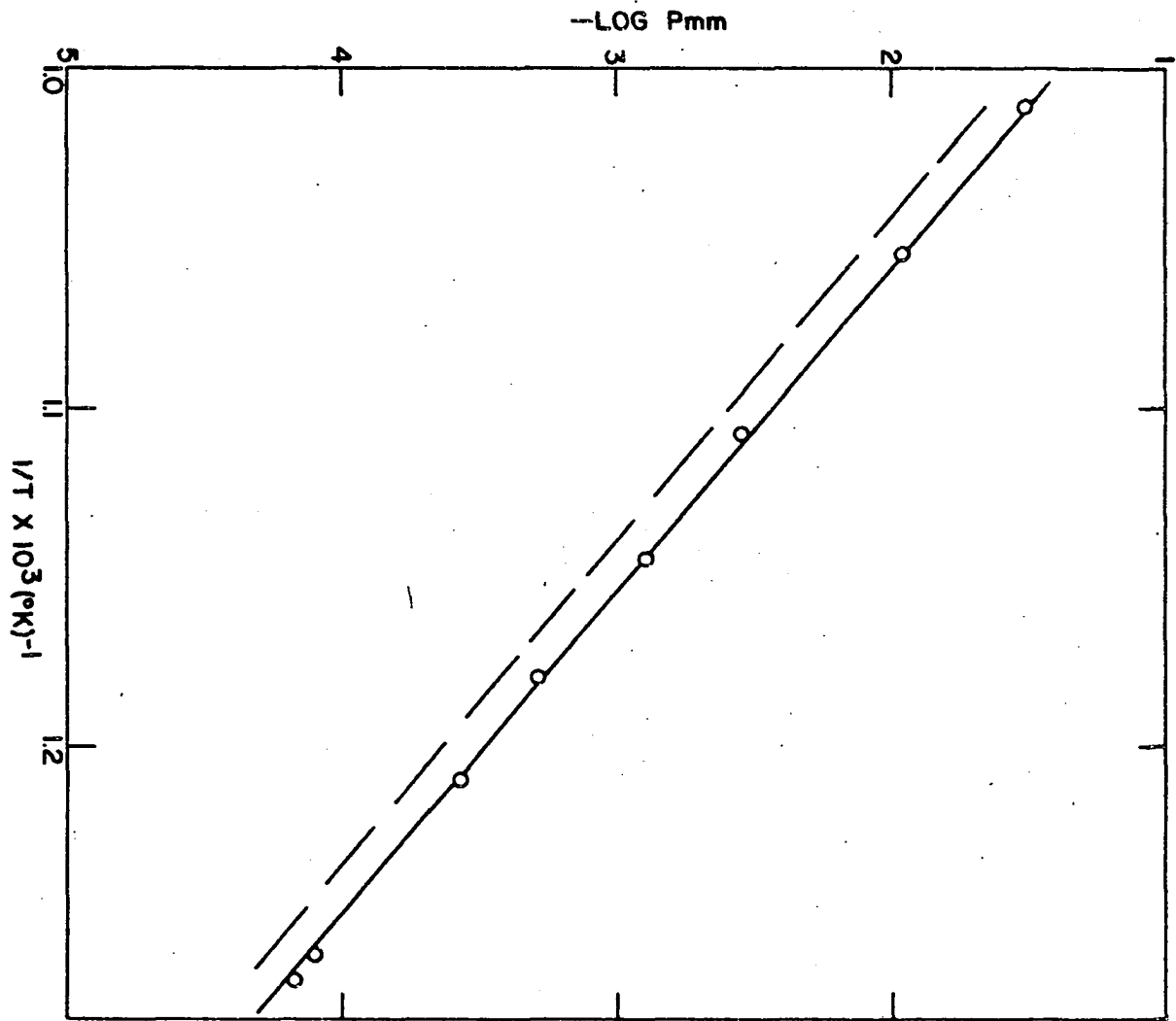


Figure 14. Vapor Pressure of Vanadium(II) Bromide



be represented by an equation of the form:

$$\log P_{\text{mm.}} = -A/T + B \quad \text{Eq. 43}$$

from which the standard enthalpy of vaporization can be obtained. The results, valid in the temperature range of 750° to 950°K, are summarized in Table 7.

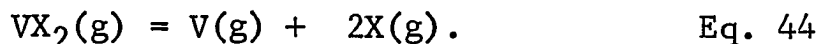
No values have been reported in the literature for any of the vaporization characteristics of the dibromide but just recently Oranskaya and Perfilova (24) have reported data on the vapor pressure and related thermodynamic values for the dichloride. Their values, obtained by transpiration experiments, are also given in Table 7 for comparison.

Table 7. Vaporization Data for Vanadium(II) Chloride and Bromide

| Sample | A | B | ΔH (kcal/mole) | ΔS (eu) |
|------------------------------|------------------|-------------------|---------------------------|--------------------|
| VCl ₂ (This work) | 9,804 \pm 300 | 8.713 \pm 0.200 | 44.8 \pm 1.4 | 26.6 \pm 0.8 |
| VCl ₂ (O&P) | 9,721 \pm 500 | 8.605 \pm 0.300 | 44.2 \pm 2.2 | 27.6 \pm 1.2 |
| VBr ₂ | 10,460 \pm 350 | 9.081 \pm 0.300 | 47.8 \pm 1.6 | 28.3 \pm 0.8 |

The bond energies may be calculated from the vapor pressure studies if several other thermodynamic data are known or can be estimated. The average bond energy may be defined

(78) as the change in enthalpy resulting from the dissociation of the gaseous compounds into atoms at 298°K. For the vanadium(II) halides, the V-X bond energy is equal to one-half the enthalpy change for the reaction



To calculate the enthalpy change for this reaction, the heat of sublimation must be known at 298°K. To estimate this quantity, ΔC_p for sublimation was assumed to be minus eight calories per degree by comparison with similar halides (79). The heat of sublimation at 298°K can be estimated if the sigma function, discussed in the introduction, is used. If a plot of sigma vs. reciprocal temperature is constructed, a straight line is obtained with a slope equal to ΔH_0° and an intercept equal to I. Sigma function plots for the dichloride and the dibromide are given in Figures 15 and 16; the values for ΔH_0° and I are given in Table 8. Equations for ΔH_T° are also given.

Table 8. Sigma Function Values for Vanadium(II) Chloride and Bromide

| Sample | ΔH_0° (cal.) | I | ΔH_{298}° (cal.) | Eq. for ΔH_T° (cal.) |
|------------------|------------------------------|-------|----------------------------------|--------------------------------------|
| VCl ₂ | 50,600 | -80.6 | 48,500 | $H_T^\circ = 50,600 - 8T$ |
| VBr ₂ | 52,800 | -81.4 | 50,700 | $H_T^\circ = 52,800 - 8T$ |

Figure 15. Sigma Function Plot for Vanadium(II) Chloride

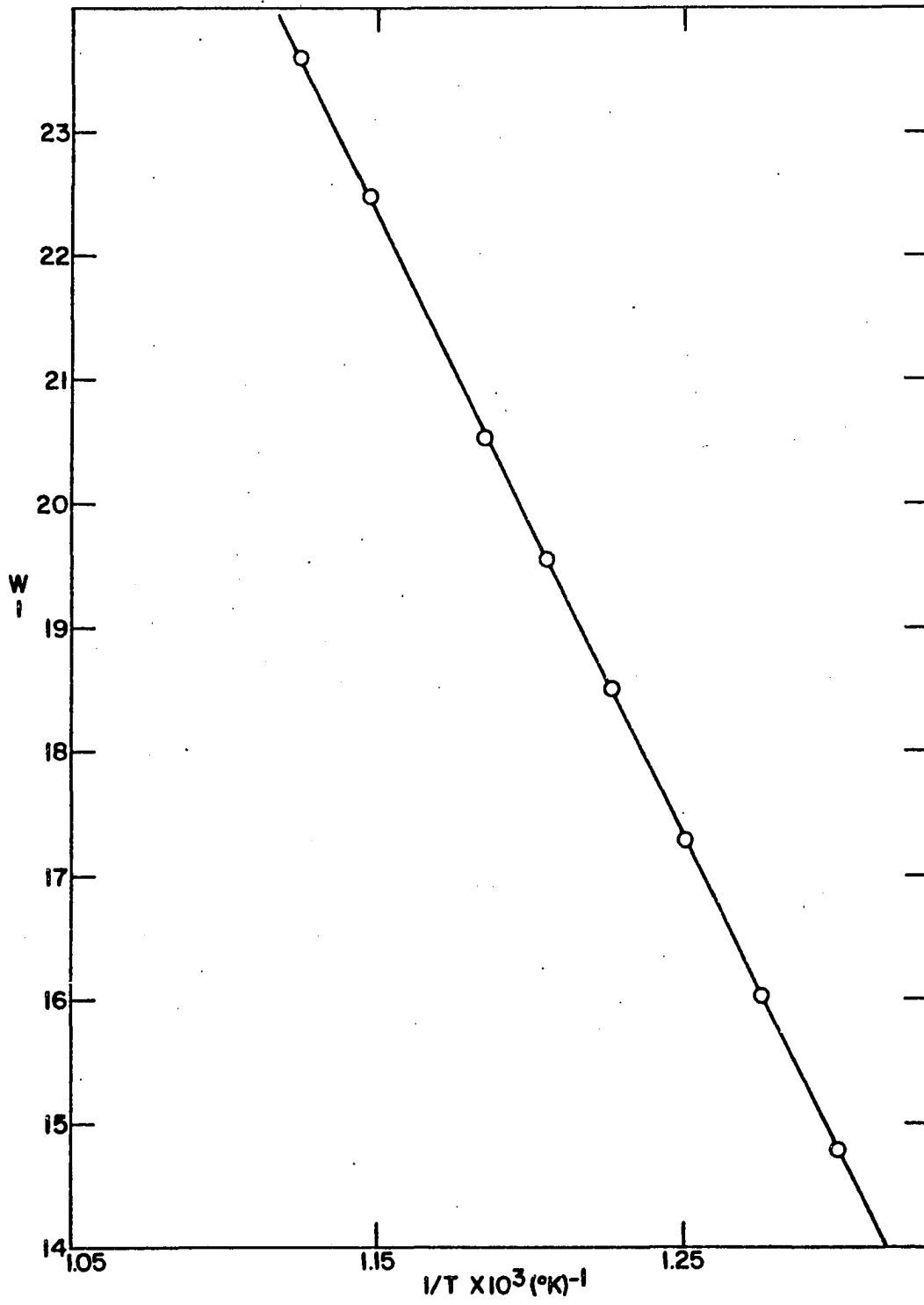
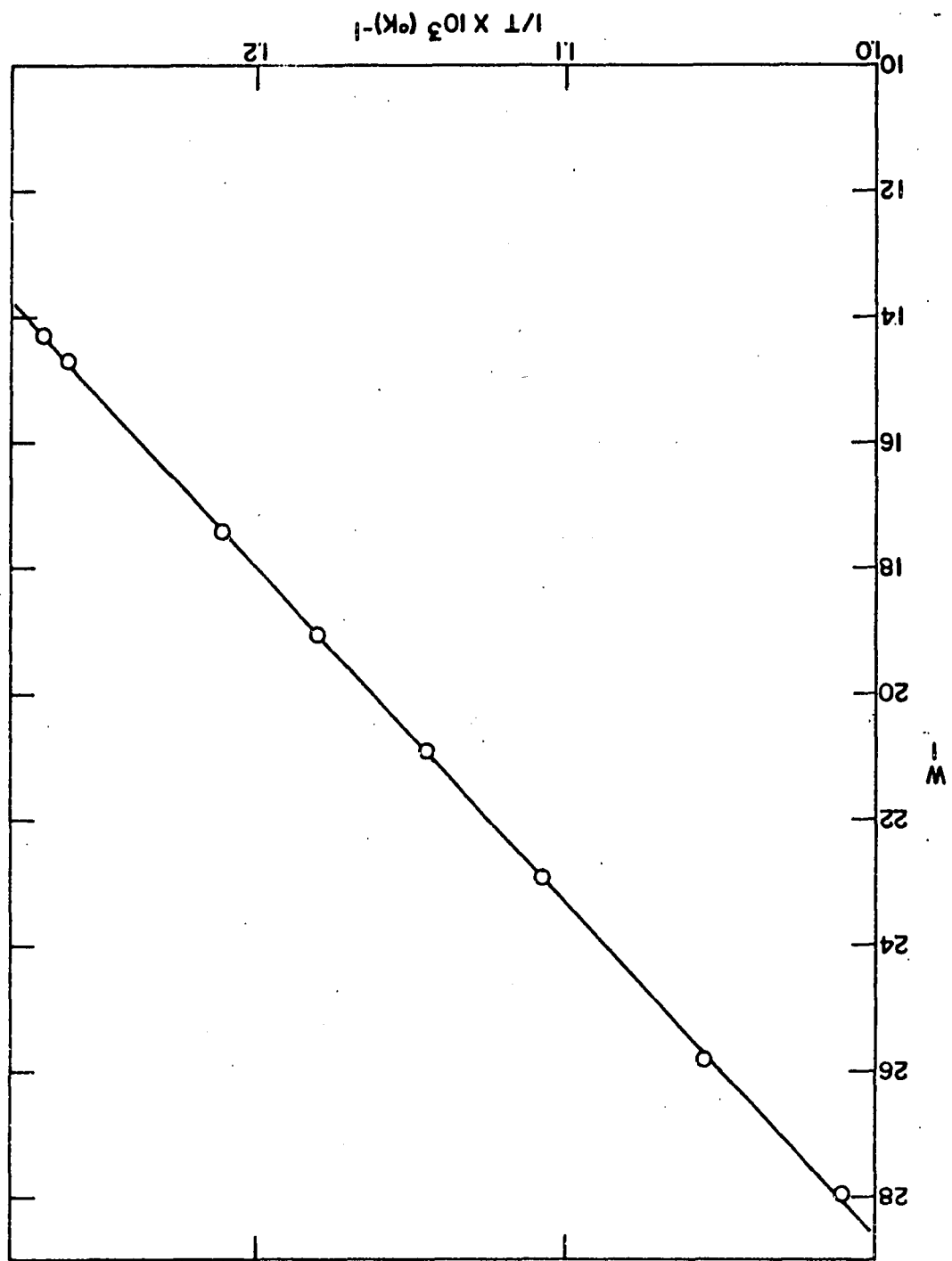


Figure 16. Sigma Function Plot for Vanadium(II) Bromide



The heats of atomization of the dichloride and dibromide are calculated below.

| Reaction | ΔH_{298}° (kcal.) | Reference |
|-----------------------------|----------------------------------|-----------|
| $VCl_2(g) = VCl_2(s)$ | -48.5 | This work |
| $VCl_2(s) = V(s) + Cl_2(g)$ | 108 | (10) |
| $V(s) = V(g)$ | 122 | (80) |
| $Cl_2(g) = 2Cl(g)$ | 58 | (78) |
| <hr/> | | |
| $VCl_2(g) = V(g) + 2Cl(g)$ | 239.5 | Eq. 45 |
| | | |
| $VBr_2(g) = VBr_2(s)$ | -50.7 | This work |
| $VBr_2(s) = V(s) + Br_2(l)$ | 100 | (10) |
| $V(s) = V(g)$ | 122 | (80) |
| $Br_2(l) = 2Br(g)$ | 53.4 | (78) |
| <hr/> | | |
| $VBr_2(g) = V(g) + 2Br(g)$ | 224.7 | Eq. 46 |

A V-Cl bond energy of 120 kilocalories can be calculated from equation 45. A value of 112 kilocalories can be calculated for the V-Br bond energy using equation 46. These two bond energies can be compared with values calculated by means of an equation developed by Pauling (81). In the equation, the dissociation energies and electronegativities

$$D(V-X) = \frac{1}{2} [D(V-V) + D(X-X)] + 23(x_X - x_V)^2 \quad \text{Eq. 47}$$

of the halogens and vanadium were those listed above and in Pauling's book. The metal-metal single bond energy was taken as one-sixth of the heat of atomization of vanadium (82). The values calculated from equation 47, 84 kilocalories for the V-Cl bond and 69 kilocalories for the V-Br bond, are considerably lower than the ones given in the table. Allen (83) gives an excellent discussion of the calculation of transition metal bond energies and states that the bond energy is greater as the valency of the metal decreases. Then to, the values for the heats of formation of the halides were only estimated and may be in error by as much as 15 kilocalories.

Pauling's value for the electronegativity of vanadium, 1.6, was calculated for the tetravalent ion. By substituting the V-Cl bond energy of 120 kilocalories into Pauling's equation, an electronegativity of 1.2 was obtained. This lower value is more consistent when compared to values that have been experimentally determined for other metal halides. For instance, in the iron(II) halide system, Pauling lists a value of 1.7 for the electronegativity of iron but Allen (83, p. 1645) calculated a value of 1.3. Another example

can be found in the chromium(II) halide system where the value obtained by Pauling of 1.6 is 0.4 units higher than that experimentally determined by Sime (76).

Vaporization of Vanadium(III) Chloride

The Knudsen effusion method was used to determine the vapor pressure of this substance. In addition, values were obtained for the disproportionation process during the same set of experiments.

When the various geometric factors of the pyrex cell were substituted in the basic effusion equation for the vapor pressure, the following equation was obtained;

$$P_{\text{mm.}} = \frac{(7.31 \times 10^2)(G)(T/M)^{\frac{1}{2}}}{t} \quad \text{Eq. 48}$$

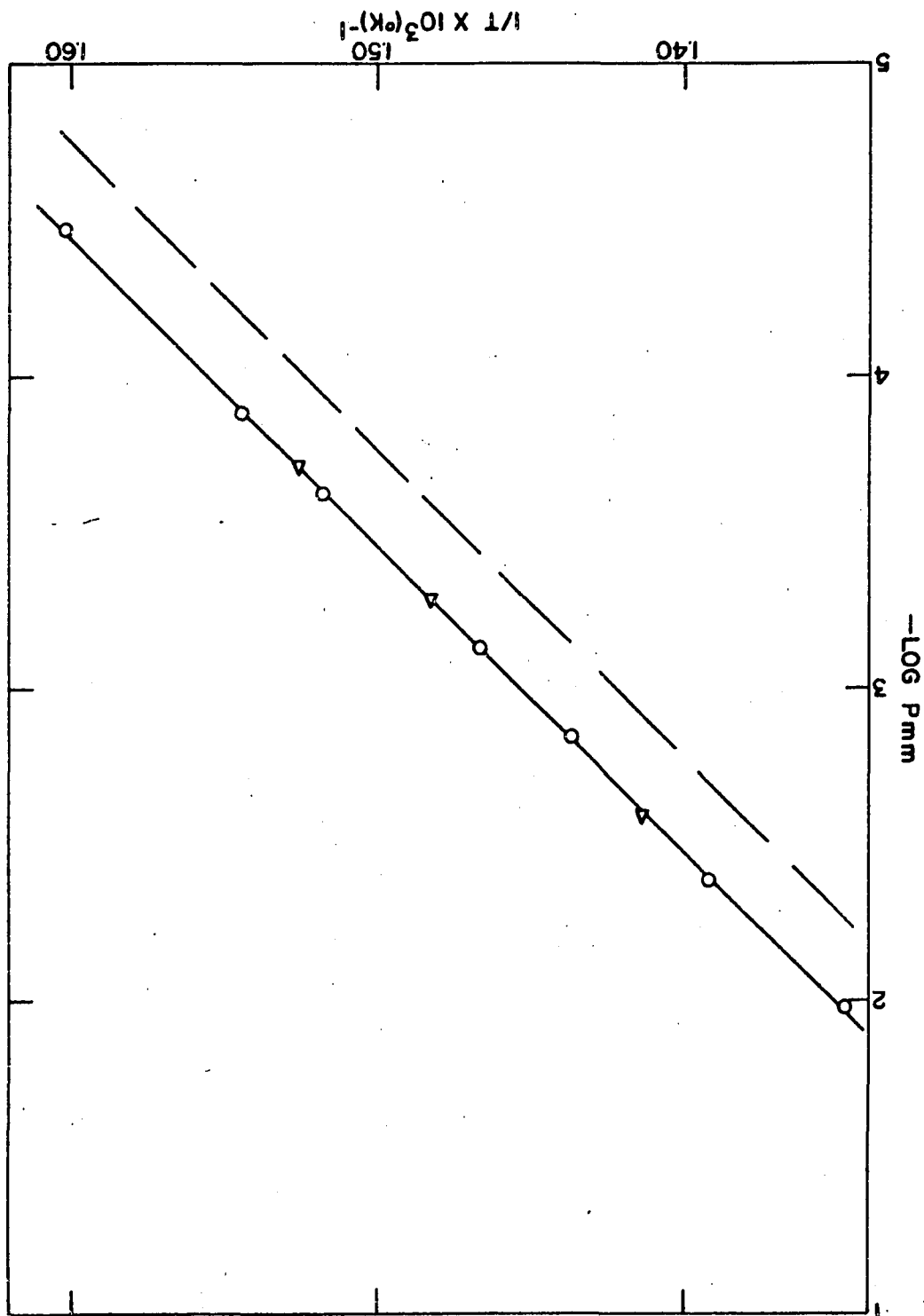
where the terms have the same meaning as previously defined.

The vapor pressure of the trichloride is plotted against reciprocal temperature in Figure 17. The pressures were calculated assuming that the vapor over vanadium(III) chloride consisted of monomer. If complete dimer formation occurred, the slope of the line and hence the heat of vaporization would not be effected but the vapor pressure would differ by a factor of $(2)^{\frac{1}{2}}$. The entropy of vaporization would also show a considerable change. The dashed line

Figure 17. Vapor Pressure of Vanadium(III) Chloride

0 - Pyrex cell

- Vycor cell



represents the vapor pressure if complete dimerization had occurred.

The fact that the measured pressures were independent of effusion hole size showed that the accommodation coefficient for the vaporization process was near unity. Therefore, the steady state pressures were assumed to be true equilibrium pressures.

The equation of the vapor pressure can be expressed in the form:

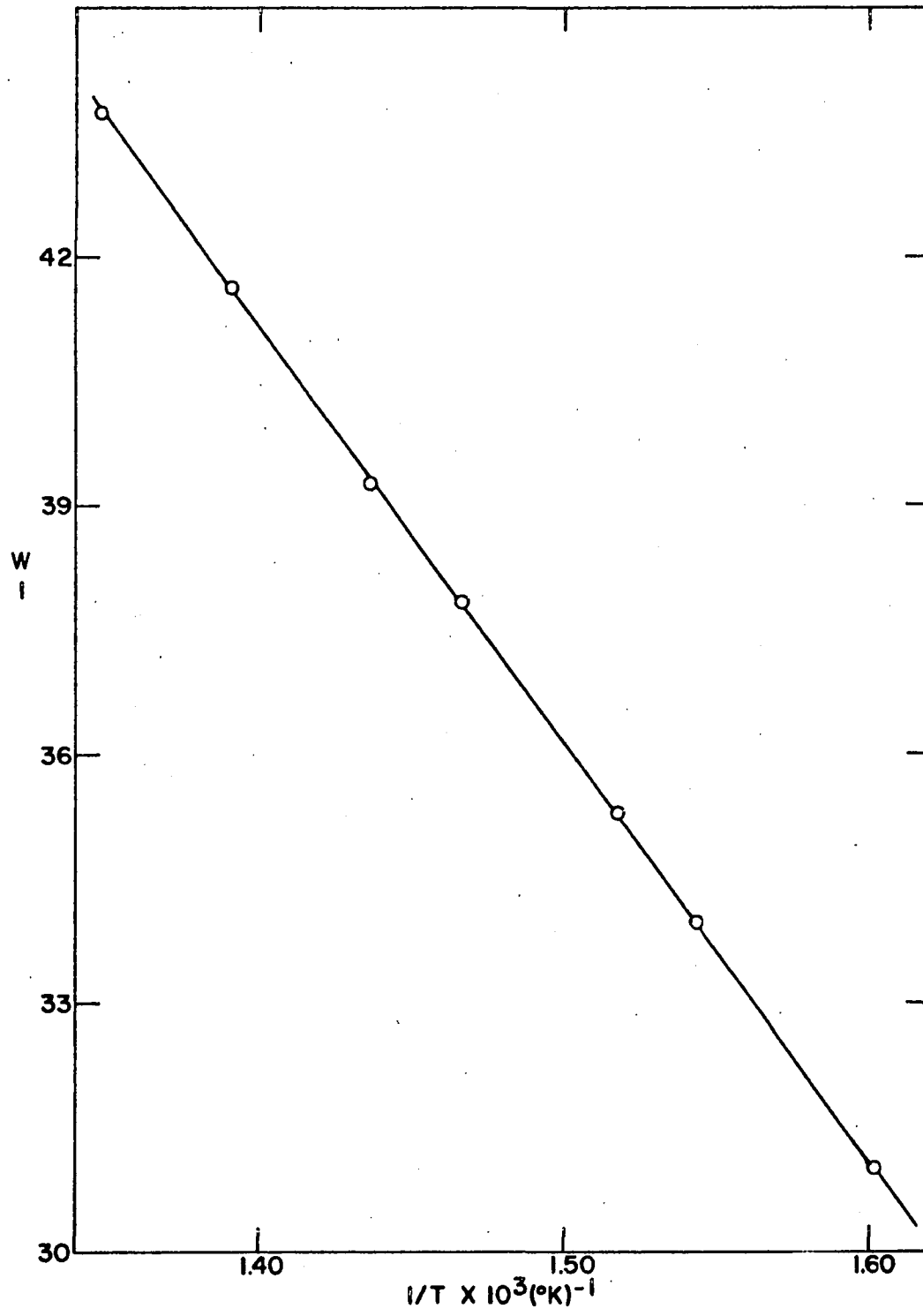
$$\log P_{\text{VCl}_3} = \frac{-9777}{T} + 11.20 \text{ (in mm.)} \quad \text{Eq. 49}$$

which yielded a heat of vaporization of 44.7 ± 1.4 kilocalories and an entropy of 38.0 ± 0.8 entropy units. Equation 49 is valid in the range of 625° to 740°K and has an error of no more than three per cent. The results of a sigma plot are shown in Figure 18. The equation for ΔH_T^0 obtained from the plot can be written as

$$\Delta H_T^0 = 50,000 - 8T, \text{ (in cal.)} \quad \text{Eq. 50}$$

where ΔC_p was assumed to be minus eight calories per mole degree. The value of I was determined to be -108.2. A calculation of the bond energy resulted in a value of 100 kilocalories, somewhat less than that obtained from the vaporization of vanadium(II) chloride. This value seemed

Figure 18. Sigma Plot for Vanadium(III) Chloride



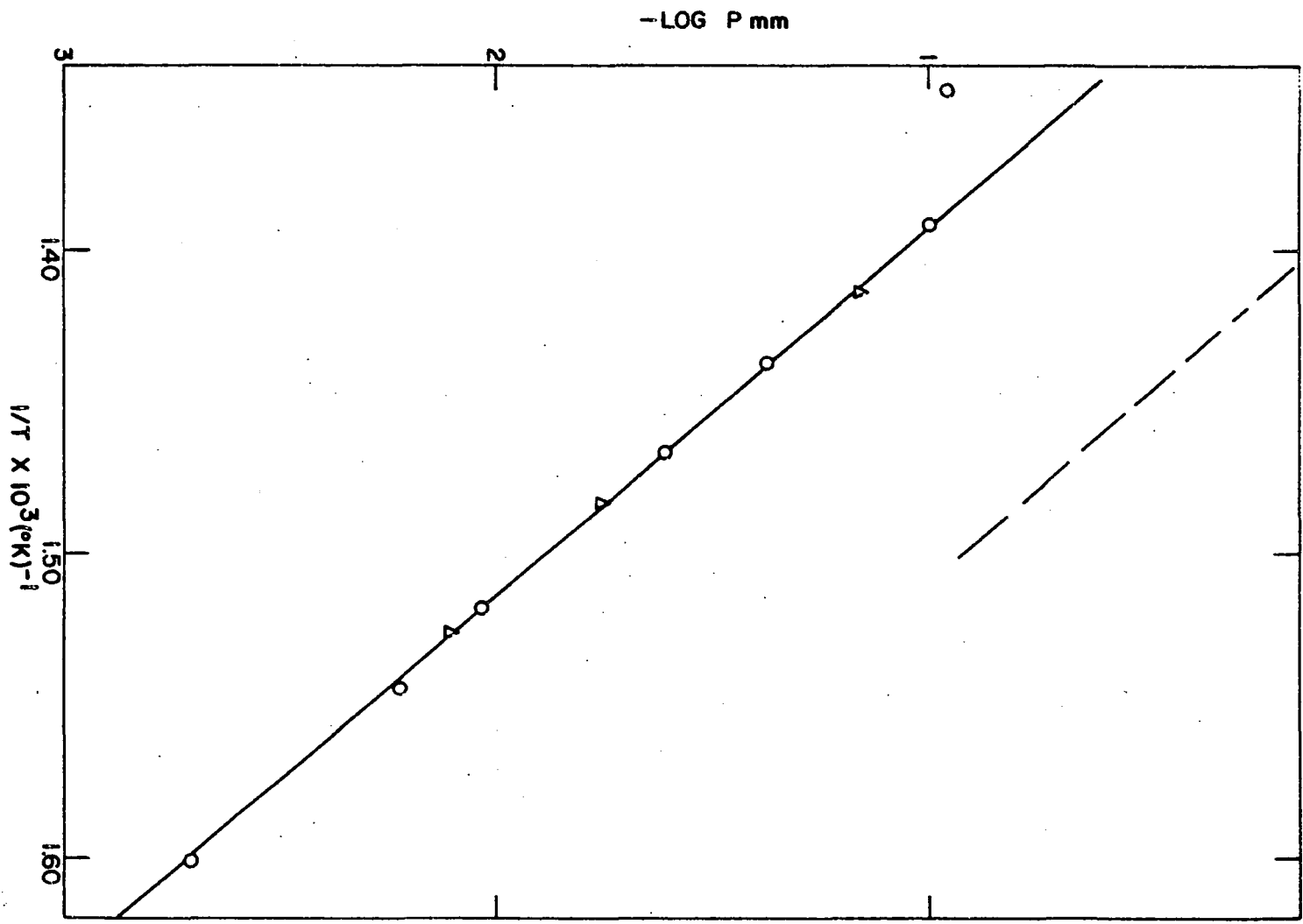
to support Allen's conclusions that the bond energy decreases with an increase in valence.

The vapor pressure for the disproportionation is plotted against reciprocal temperature in Figure 19. The pressures were calculated again assuming that only monomer was present in the vapor phase. At the higher temperatures are plotted (dotted line) the results of the disproportionation pressure of the trichloride as determined by Oranskaya et al. (18). The slope and therefore the heat of vaporization agreed quite favorably but there was a noticeable difference in the entropy of vaporization. The higher results obtained by Oranskaya et al. may be due to contamination of their starting material with a more volatile oxychloride of vanadium. The presence of impurities in the carrier gas would also produce the same results. Then too, the difference may be due to a low accommodation coefficient in the effusion experiments. If this was the case, the apparent vapor pressure would be lower than the true equilibrium pressure. Since the values obtained by the effusion method were considerably lower than the ones obtained by transpiration, the accommodation coefficient for the disproportionation reaction may have been much less than unity. In addition, the temperature

Figure 19. Disproportionation Pressure of Vanadium(III) Chloride

----- Oranskaya et al.

_____ This investigation



ranges studied did not overlap except at relatively high values for disproportionation pressure in the effusion measurements. When measured effusion pressures are relatively high, it has been observed (84) that apparent vapor pressure tends to fall off. In addition, since the pressures were in the lower regions of feasibility for the transpiration method, the relative error of the data obtained by Oranskaya et al. were expected to be quite large.

The equations of the lines plotted in Figure 19 and the heats and entropies of vaporization obtained from this investigation and those obtained by Oranskaya et al. are given in Table 9. The values listed in the table are precise to approximately four per cent.

Table 9. Disproportionation Data for Vanadium(III) Chloride

| Investigator | Equation for $P_{\text{mm.}}$ | Temp. range (°K) | ΔH (kcal.) | ΔS (eu.) |
|--------------|------------------------------------|------------------|--------------------|------------------|
| Oranskaya | $\log P = \frac{-8350}{T} + 11.58$ | 700-900 | 38 ± 1 | 39.6 ± 1 |
| This work | $\log P = \frac{-7801}{T} + 9.84$ | 625-740 | 36 ± 1 | 32 ± 1.2 |

Vaporization of Vanadium(III) Bromide

The vaporization of this material was studied by use of the effusion method and the transpiration method. Values were obtained for the simple vaporization, the decomposition, and the disproportionation of the tribromide during the same series of experiments.

Effusion Studies

Figure 20 is a plot of the vapor pressure of the tribromide vs. reciprocal temperature. In the calculation of the vaporization, the assumption was made that there was no dimer formation present in the vapor phase. If the vapor were entirely dimer, no change would result in the slope of the line and hence in the heat of vaporization, but the actual vapor pressure would differ by a factor of $(2)^{\frac{1}{2}}$.

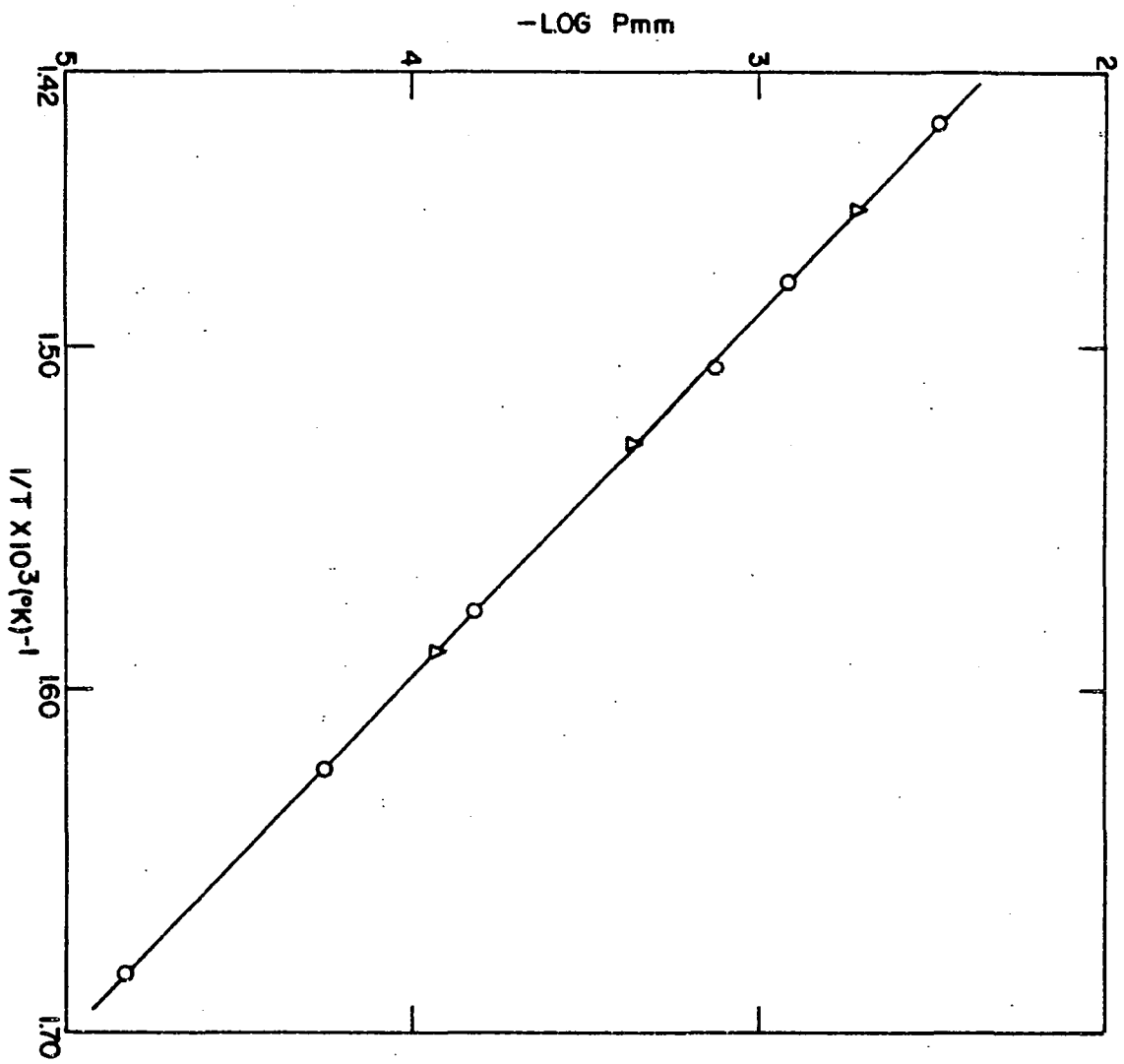
The accommodation coefficient for the vaporization process was near one as the measured pressures were independent of orifice size; hence the steady state pressures were assumed to be equilibrium pressures.

The equation for the vaporization of the tribromide can be expressed in the form:

Figure 20. Vapor Pressure of Vanadium(III) Bromide

0 - Pyrex cell

Δ - Vycor cell



$$\log P_{\text{VBr}_3} = \frac{-9470}{T} + 11.12, \text{ (in mm.)} \quad \text{Eq. 51}$$

from which was calculated a heat of vaporization of 43.3 ± 1.2 kilocalories and an entropy of vaporization of 37.7 ± 1 entropy units. The vapor pressure calculated from the equation has an estimated error of about three per cent. The temperature interval for the equation is 590° to 700°K .

The results of a sigma plot are given in Figure 21. The equation for ΔH_T° obtained from the plot can be written as

$$\Delta H_T^\circ = 52,900 - 8T, \text{ (in cal.)} \quad \text{Eq. 52}$$

where ΔC_p was assumed to be minus eight calories per mole degree. The value of I determined was -117.0 .

The results of the disproportionation, previously unreported in the literature, are plotted in Figure 22. These values may be expressed as the straight line function

$$\log P_{\text{VBr}_4} = \frac{-7460}{T} + 8.65 \text{ (in mm.)} \quad \text{Eq. 53}$$

for the temperature range of 590° to 700°K . The value obtained from this expression for the heat of disproportionation was 34.1 ± 1 kilocalories while the entropy was 26.4 ± 0.7 entropy units. A very slight variation was noted in the vapor pressure when the effusion hole size was changed. The

Figure 21. Sigma Plot for Vanadium(III) Bromide

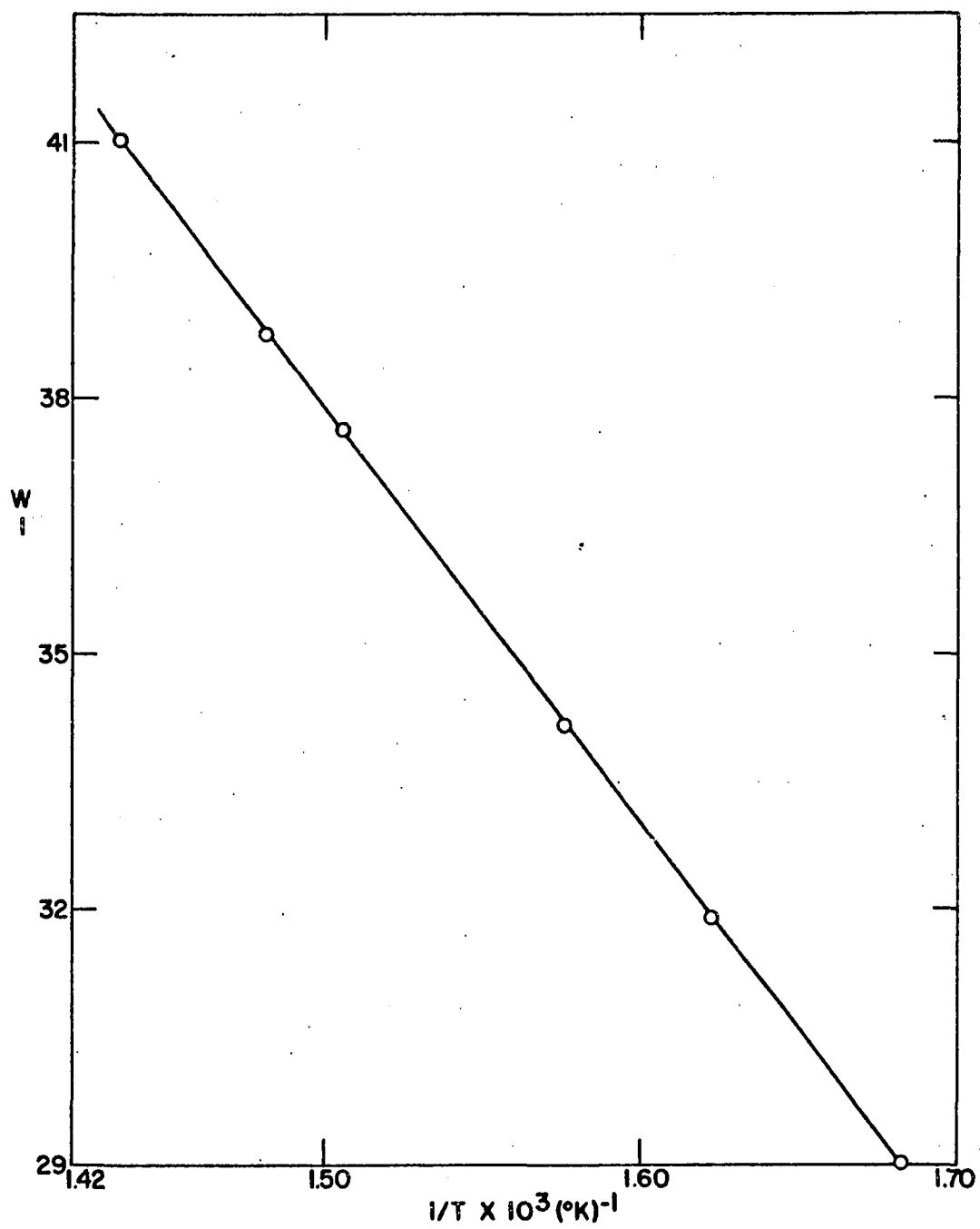
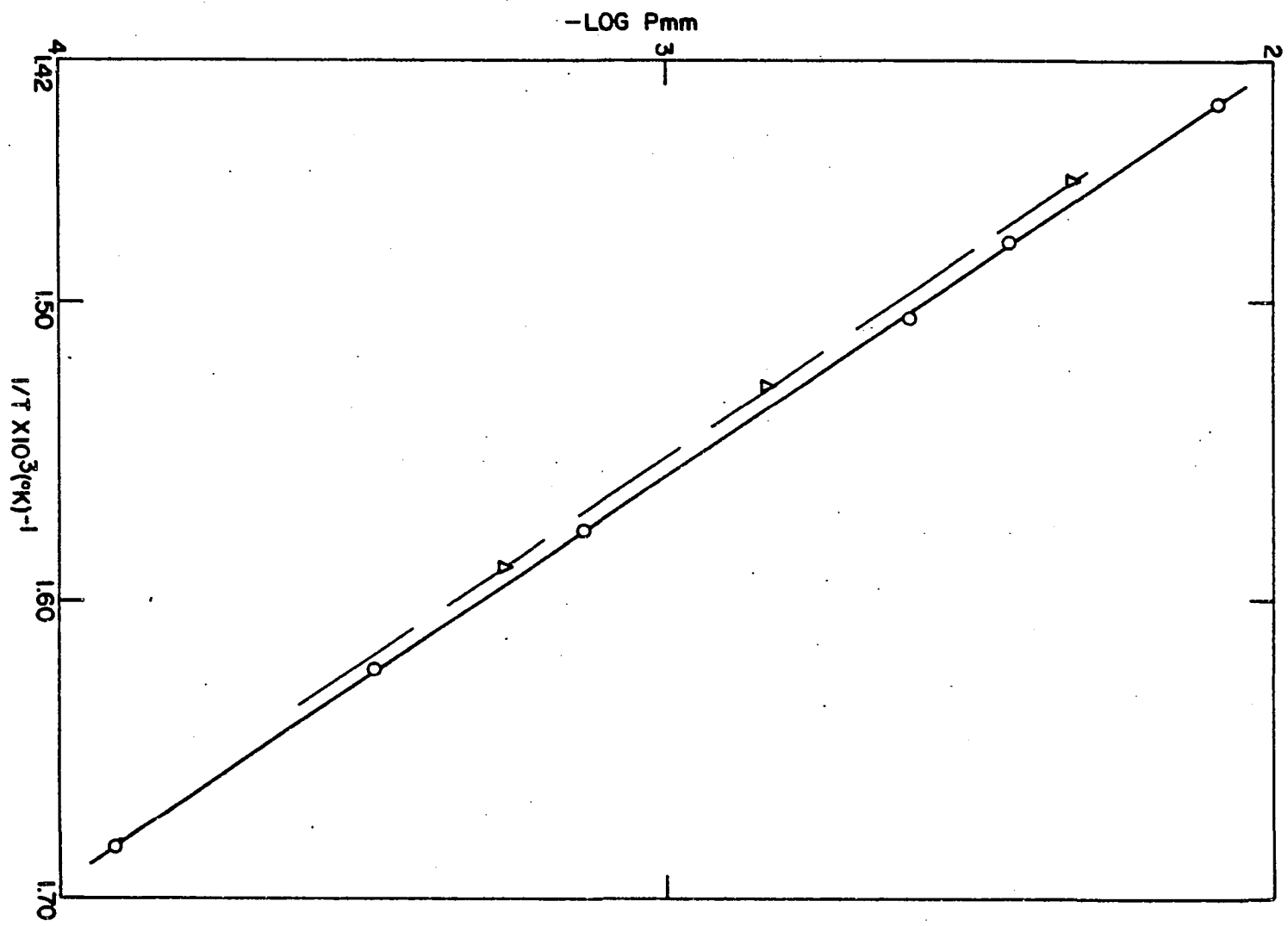


Figure 22. Disproportionation Pressure of Vanadium(III)
Bromide

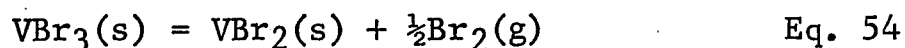
0 - Pyrex cell

Δ - Vycor cell

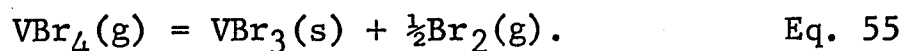


values obtained must not have been equilibrium values owing to a low accommodation coefficient.

During the course of study on the vaporization characteristics of vanadium(III) bromide, it was noted that decomposition was occurring according to the following equation. This phenomenon was not observed in the case of



the trichloride. Analysis was performed for bromine; the amount resulting from the decomposition was obtained by subtracting from the total number of moles of bromine one-half the number of moles of vanadium determined from the disproportionation. This correction was necessary since bromine also resulted from the decomposition of the tetrabromide according to the equation



A plot of the bromine pressures so obtained vs. reciprocal temperature is given in Figure 23. When a least squares analysis of the data was made, the equation representing the straight line through the points was

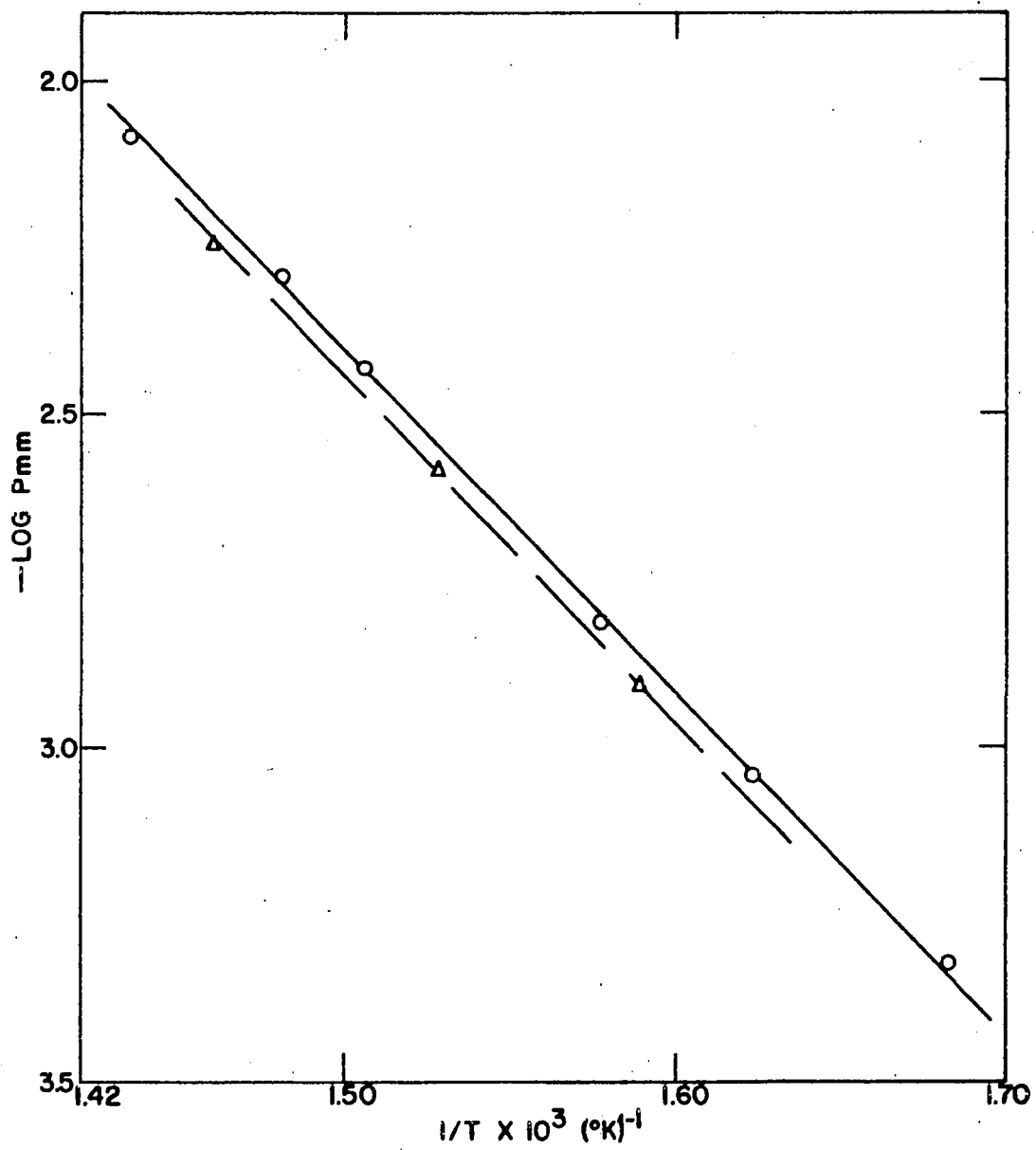
$$\log P_{\text{Br}_2} = \frac{-5090}{T} + 5.23 \text{ (in mm.)}. \quad \text{Eq. 56}$$

The heat and entropy of decomposition as calculated from

Figure 23. Decomposition Pressure of Vanadium(III)
Bromide

0 - Pyrex cell

Δ - Vycor cell



the data were 23.2 ± 1 kilocalories and 10.7 ± 0.5 entropy units respectively. The temperature range of the equation is 590° to 700°C . Somewhat more scatter was observed in these values and there was observed a slight difference in the vapor pressure when a change in orifice size was made. These values indicated that the accommodation coefficient was much less than unity and that equilibrium pressures were not observed for bromine. The scattering of the data may also have been the result of solid solution formation between the remaining tribromide and the dibromide that was formed during the decomposition. If solid solutions were present, a lower activity of the tribromide phase would have resulted and hence a change in the decomposition pressure would have been obtained. X-ray examinations of the residues remaining after effusion measurements indicated that solid solution formation had not occurred. The uncertainties in the accommodation coefficient tend to make the Knudsen method unreliable for these decomposition measurements.

Transpiration measurements

Since the values obtained from the effusion experiments for the decomposition and disproportionation reactions

depended to such a great extent on the accommodation coefficient, a further verification of these values was deemed desirable.

The calculations for the transpiration method were performed using the method given by Thomson (85). Dalton's law and the ideal gas law were assumed to be valid. The vapor pressure of the compound was obtained from the equation

$$P_S = P_s / (K + 1) \quad \text{Eq. 57}$$

where

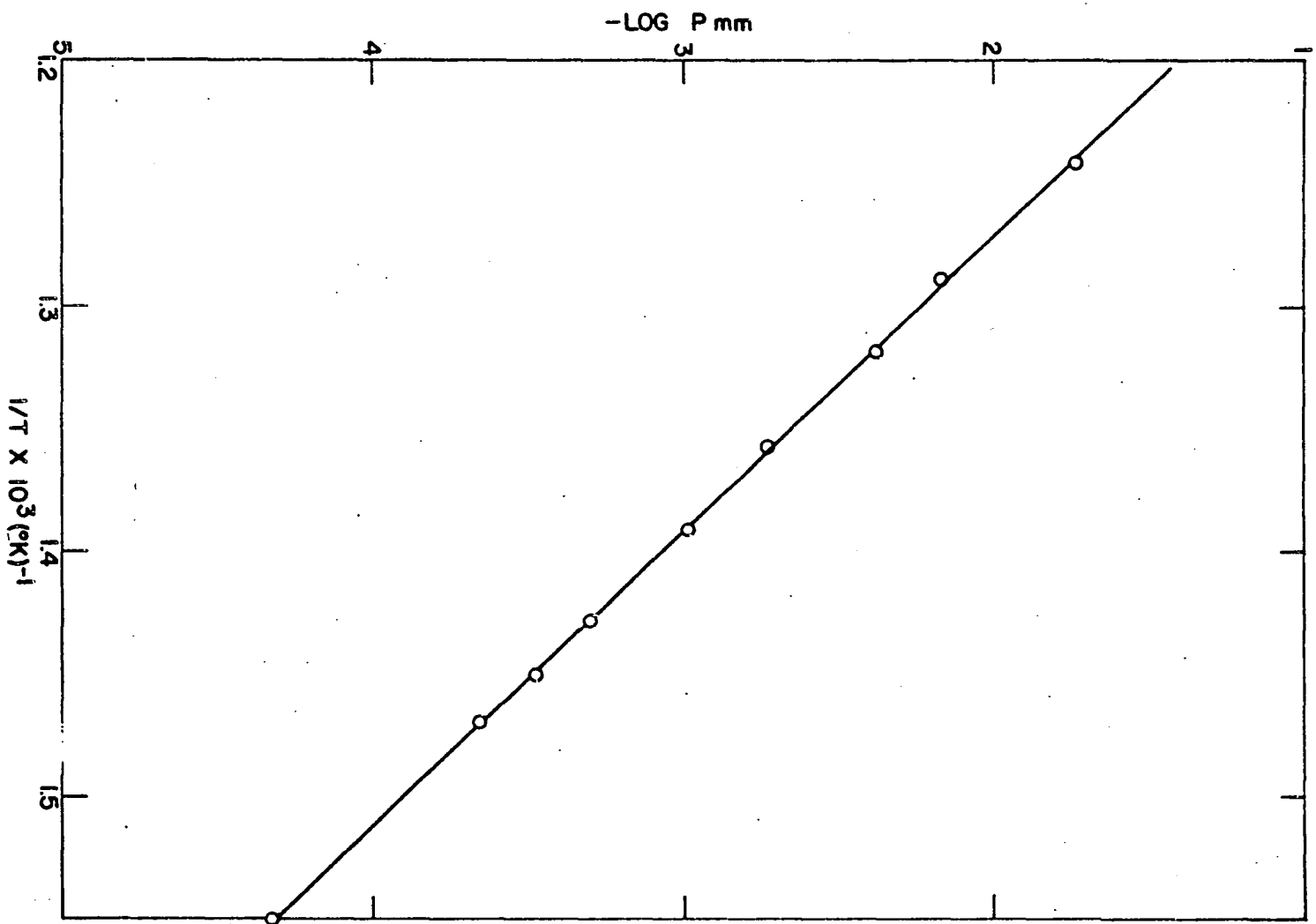
$$K = (MW) (V_m) (P_m - P_w) / gRT_m \quad \text{Eq. 58}$$

and where P_S was the total pressure in the cell, p_s was the vapor pressure of the compound, MW was the molecular weight of the vapor, V_m was the measured volume from the wet test meter, P_m was the total pressure at the meter, p_w was the vapor pressure of water at T_m , g was the grams of material transported, and T_m was the temperature of the meter.

The simple vaporization was not obtained in these experiments as the vapor pressure of the tribromide was too low to be measured.

A plot of the disproportionation pressure vs. reciprocal temperature is given in Figure 24. The equation of the

Figure 24. Disproportionation Pressure of Vanadium(III)
Bromide



straight line drawn through the points can be expressed as

$$\log P_{VBr_4} = \frac{-8240}{T} + 8.47 \text{ (in mm.)} \quad \text{Eq. 59}$$

for the temperature range 590° to 697°K. The maximum error in the equation was approximately four per cent. A heat of reaction of 37.7 ± 1.3 kilocalories and an entropy of reaction of 25.5 ± 0.8 entropy units can be calculated from this expression. These results gave support to the conclusion that the accommodation coefficient was less than unity in the effusion studies. Further support was found in the decomposition vapor pressure plotted in Figure 25. When a least squares analysis of this plot was made, the equation of the line was calculated to be

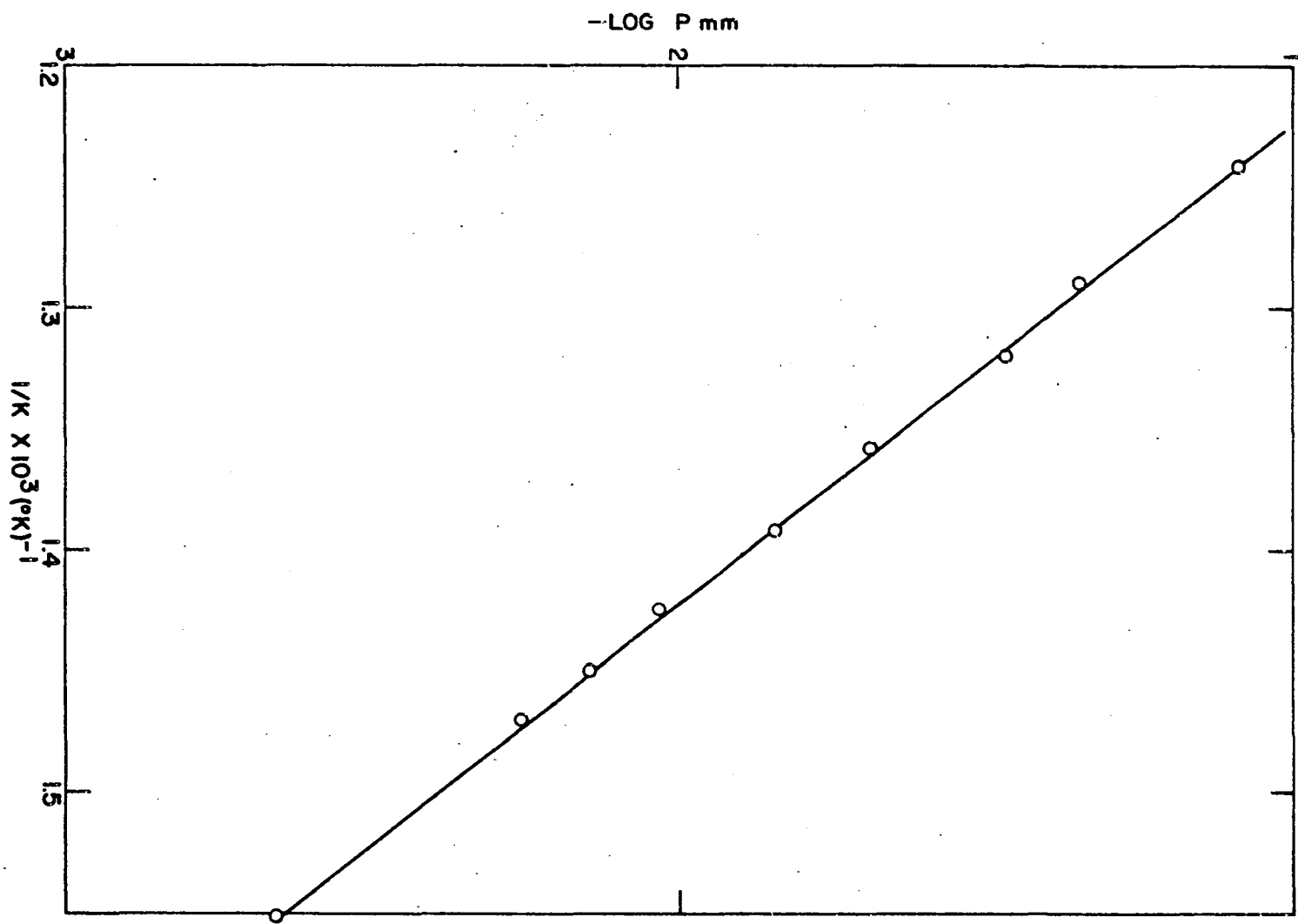
$$\log P_{Br_2} = \frac{-5070}{T} + 5.02 \text{ (in mm.)} \quad \text{Eq. 60}$$

for the temperature range of 590° to 700°K. The heat and entropy of reaction as calculated from this equation were 23.1 ± 0.9 kilocalories and 9.3 ± 0.4 entropy units respectively. Again, the results were somewhat lower than those obtained from effusion experiments.

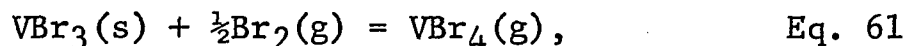
Vanadium(IV) Bromide and Mixed Vanadium Halides

At elevated temperatures, vanadium(III) bromide reacted with bromine to form vanadium(IV) bromide. Evidence of its

Figure 25. Decomposition Pressure of Vanadium(III)
Bromide



formation had been observed in the gas phase. At temperatures at which it was expected to condense, the material was apparently unstable with respect to solid tribromide and bromine. For the reaction



the equilibrium constant may be written as

$$K = \frac{P_{\text{VBr}_4}}{P_{\text{Br}_2}^{1/2}} \quad \text{Eq. 62}$$

where pressures have been substituted for activities and the activity of the solid was taken as one. Evidence that this reaction was of importance in the vaporization of vanadium (III) bromide in bromine was provided by measuring the total pressure above the tribromide at various bromine pressures. The tribromide pressure was found to be proportional to the square root of the bromine pressures. The vapor pressures were measured by the pyrex diaphragm gauge and by the transpiration method using bromine as a carrier gas.

Pyrex diaphragm gauge measurements

Five reactions of the tribromide were performed with bromine using this method. The only reaction that was considered to be occurring in the cell was that of equation 61.

The simple vaporization of the tribromide was neglected since it exhibited a vapor pressure of less than 4×10^{-3} millimeter mercury at 700°K , the maximum temperature to which the cell was heated. The temperatures were low enough so that the dissociation of bromine molecules into atoms ($\log K_p = -6.0$ at 640°C) could be neglected (86). The decomposition of the tribromide was also neglected as it would be suppressed by the bromine present, except at very high temperatures outside the range of these measurements.

The equilibrium constant for the reaction was determined in the following manner. If the original bromine pressure in the cell was P_{Br_2} at T_1 , then after equilibrium had been established in the cell at T_2 , the total pressure will be given by

$$P_t = \left(\frac{T_2}{T_1}\right) P_{\text{Br}_2} + \frac{1}{2}P_{\text{VBr}_4}, \quad \text{Eq. 63}$$

assuming the gases exhibited ideal behavior. The pressure of the tetrabromide was calculated by rearranging equation 63 to

$$P_{\text{VBr}_4} = 2 \left(P_t - \frac{T_2}{T_1} P_{\text{Br}_2} \right). \quad \text{Eq. 64}$$

The actual pressure of bromine was then calculated from the

equation

$$P_{\text{Br}_2} = \left(\frac{T_2}{T_1} \right) P'_{\text{Br}_2} - \frac{1}{2} P_{\text{VBr}_4}. \quad \text{Eq. 65}$$

Difficulty was experienced during the runs as the residual bromine pressure after the reaction was always somewhat greater than that originally introduced into the cell. The increase in pressure was assumed to be the result of hydrogen bromide formed by slight hydrolysis of the sample. All values reported in the Appendix were corrected for this residual pressure. These values were obtained by either condensing the bromine in the cell with dry ice chloroform mixtures and reading the residual pressure directly, since hydrogen bromide does not condense until a temperature of -67°C is attained, or by noting the increase in pressure as the cell was heated to a temperature sufficient to cause hydrolysis but not high enough for the reaction to commence.

In Figures 26, 27, and 28 are plotted $\log K$ vs. reciprocal temperature for the reaction of the tribromide, the trichloride, and the mixed halide of vanadium. In Table 10 are listed the values for the heat of reaction along with the equation for the equilibrium constant as a function of temperature. An average of the values for the tribromide yielded a value of 15.8 ± 1.5 kilocalories for the heat of

Figure 26. Cell Reaction of Vanadium(III) Bromide
with Bromine

0 - Ascending temperature

Δ - Descending temperature

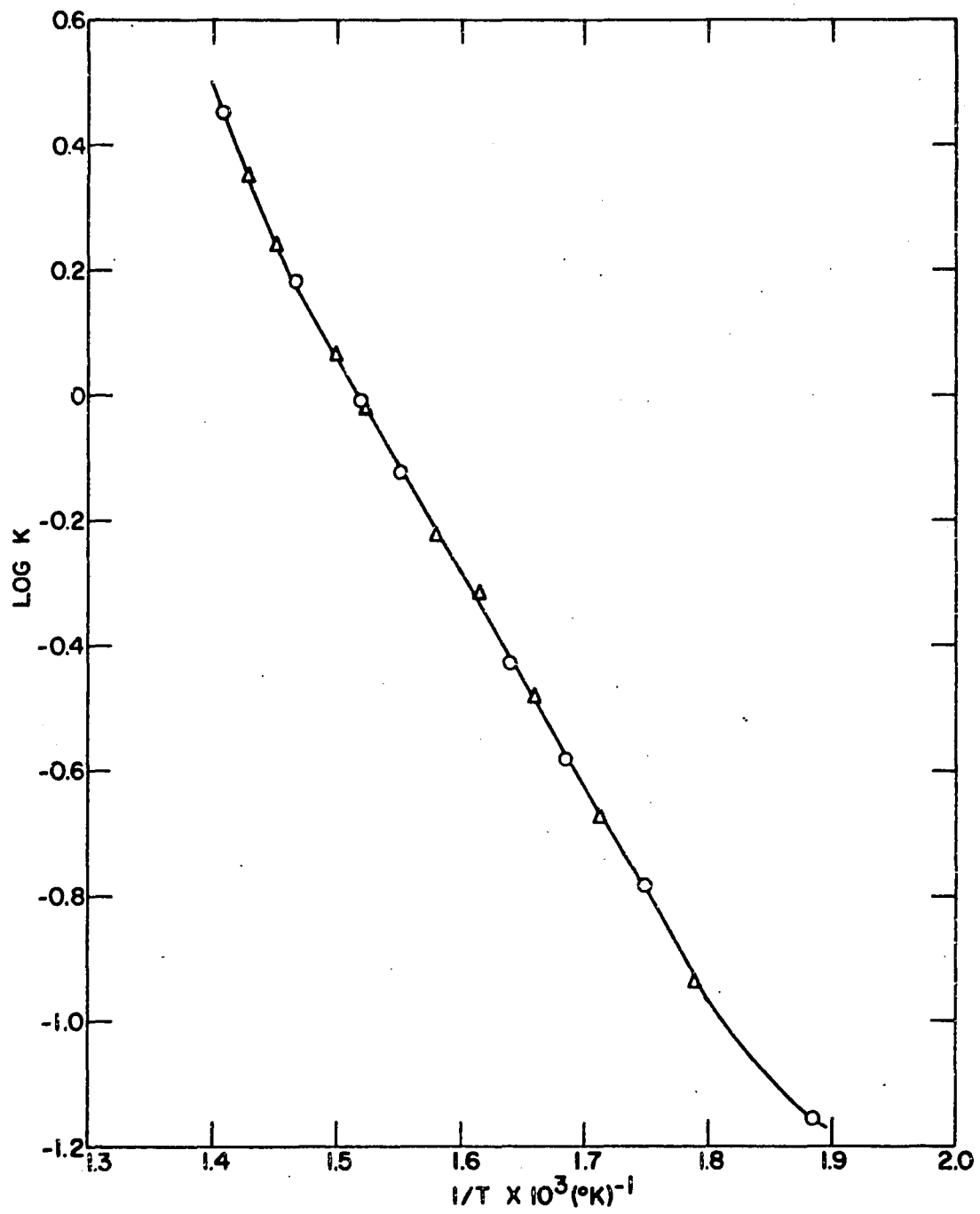


Figure 27. Cell Reaction of Vanadium(III) Chloride
with Bromine

0 - Ascending temperature

Δ - Descending temperature

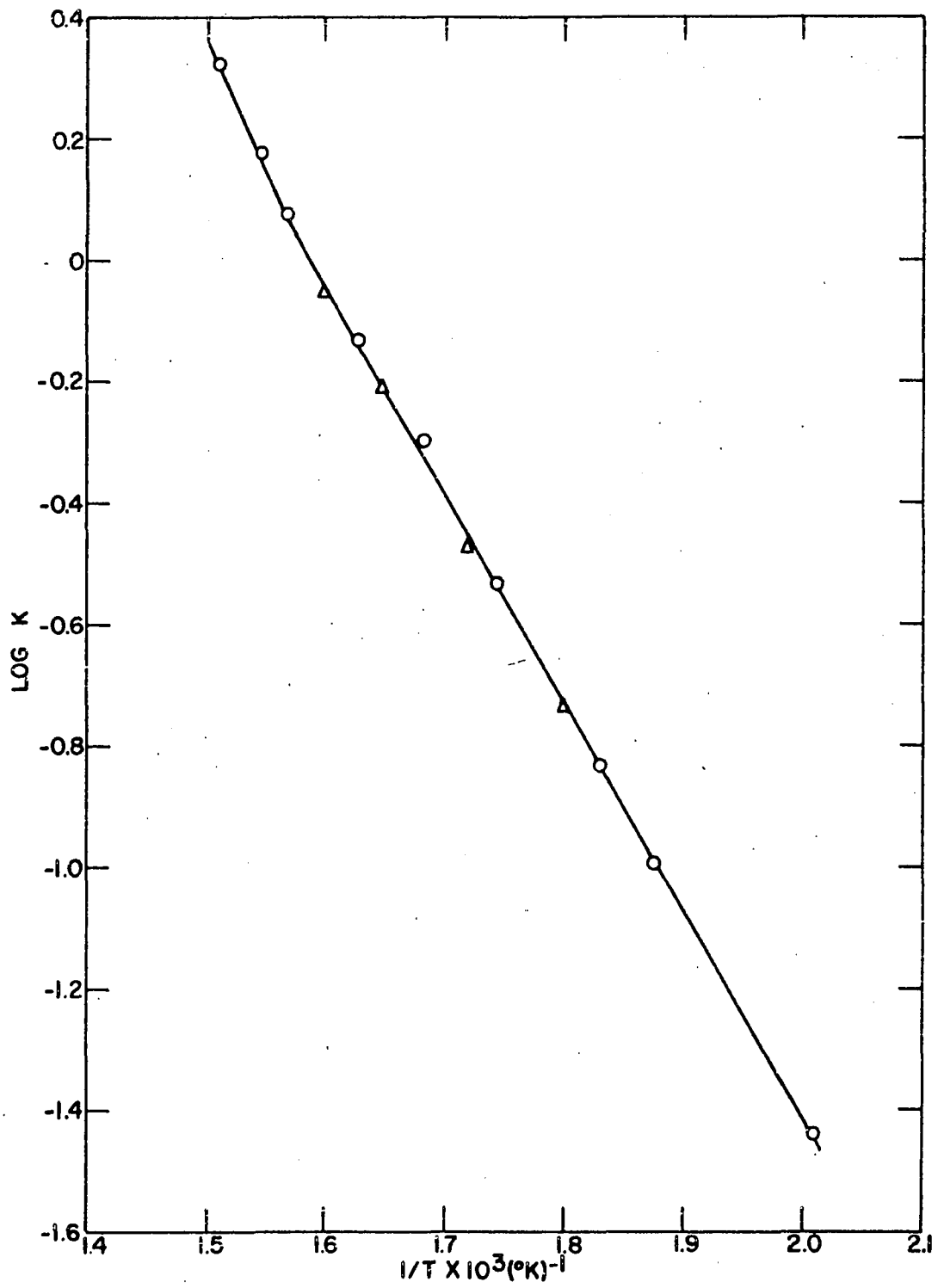


Figure 28. Cell Reaction of the Mixed Halide, VCl_2Br ,
with Bromine

0 - Ascending temperature

Δ - Descending temperature

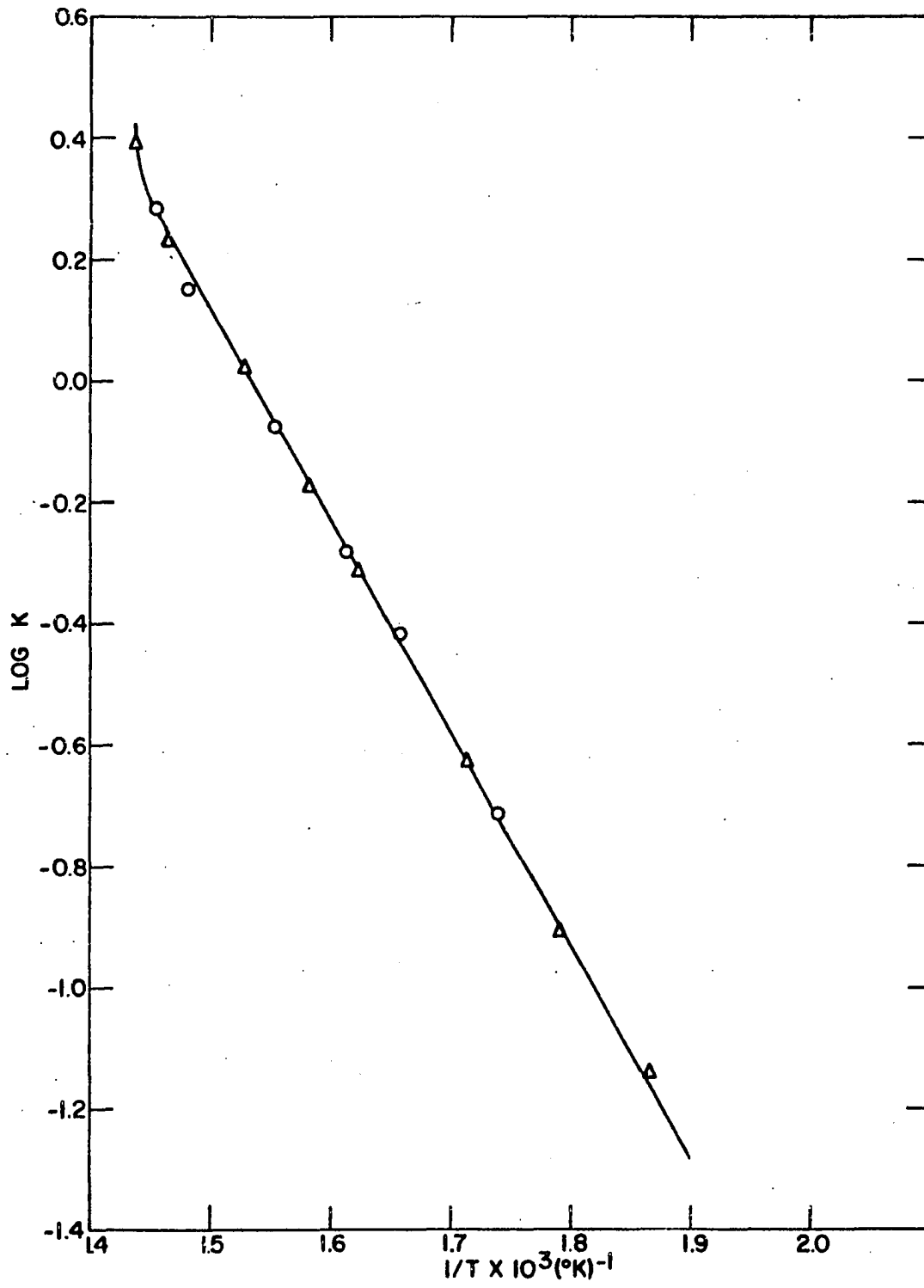


Table 10. Cell Reactions of Vanadium(III) Halides with Bromine

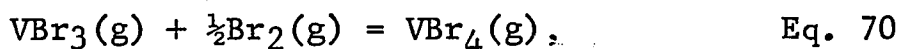
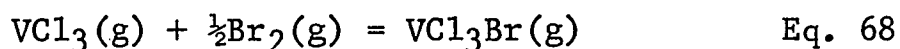
| Sample | Pressure of Br ₂ (mm.) | Equation for K (Least squares) | ΔH (Kcal.) |
|---------------------|-----------------------------------|-----------------------------------|------------|
| VBr ₃ | 43.6 | $\log K = \frac{-3494}{T} + 5.23$ | 16.0 ± 1.5 |
| VBr ₃ | 88.0 | $\log K = \frac{-3463}{T} + 5.22$ | 15.8 ± 1.5 |
| VBr ₃ | 107.0 | $\log K = \frac{-3447}{T} + 5.22$ | 15.8 ± 1.5 |
| VBr ₃ | 124.0 | $\log K = \frac{-3454}{T} + 5.23$ | 15.8 ± 1.5 |
| VBr ₃ | 163.0 | $\log K = \frac{-3470}{T} + 5.27$ | 15.9 ± 1.5 |
| VCl ₃ | 140.6 | $\log K = \frac{-3450}{T} + 5.48$ | 15.8 ± 1.5 |
| VCl ₂ Br | 120.0 | $\log K = \frac{-3460}{T} + 5.30$ | 15.8 ± 1.5 |

reaction and yielded an equation for the equilibrium constant of

$$\log K = \frac{-3465}{T} + 5.23. \quad \text{Eq. 66}$$

The heats of reaction for the three halides are essentially identical. This similarity was rather unexpected since the lattice energy of the trichloride was somewhat larger than

that of the tribromide. If the reactions proceeded in the following manner,



one would expect the heat of vaporization of the trichloride to be larger than that of the tribromide (proven in this investigation) and that the heats of reaction for processes 68 and 70 would be comparable; hence a somewhat larger heat of reaction would result for the trichloride system. Since this was not the case, one must conclude that process 68 exhibited a more negative heat of reaction than did process 70. When heats of reaction were calculated for these two processes, a value of -28.9 kilocalories was obtained for equation 68 and a value of -27.5 kilocalories was obtained for equation 70, supporting the conclusions given.

The values of the equilibrium constant showed a change in slope at the higher temperatures. The data gave conclusive proof that the bromine in the cell had been depleted enough so that the decomposition reaction of the tribromide had become important.

Transpiration experiments

In the transpiration method the total pressure in the system was assumed to be the sum of the three gas pressures as shown in the following equation.

$$P_t = P_{VBr_3} + P_{VBr_4} + P_{Br_2} \quad \text{Eq. 71}$$

The following expression may also be written

$$P_{VBr_3} + P_{VBr_4} = \frac{n_v}{n_v + n_{Br_2}} P_T, \quad \text{Eq. 72}$$

where n_v was the total number of moles of vanadium transported by n_{Br_2} moles of bromine. The value of n_v was determined by the amount of vanadium(III) bromide deposited in the cold trap. The equilibrium constant for reaction 61 may be written in the form

$$P_{VBr_4} = K(P_{Br_2})^{\frac{1}{2}}. \quad \text{Eq. 73}$$

If, in addition, the tribromide was undergoing simple vaporization, the equation may be written as

$$P(VBr_4 + VBr_3) = K(P_{Br_2})^{\frac{1}{2}} + P_{VBr_3} \quad \text{Eq. 74}$$

where $P(VBr_4 + VBr_3)$ was the total quantity of halide vaporized. When a plot of $P(VBr_4 + VBr_3)$ vs. $(P_{Br_2})^{\frac{1}{2}}$ was made at a constant temperature, a straight line resulted, the slope of which was equal to K and the intercept was equal

to P_{Br_3} .

A plot (Figure 29) relating the apparent tetrabromide vapor pressure to the flow rate exhibited the expected behavior of high values at low flow rates and low values at high flow rates. The equilibrium pressures of the tri- and tetrabromide were measured at three temperatures and four different pressures.

For the determination of the equilibrium constant as given in equation 74, the quantity $P(\text{VBr}_4 + \text{VBr}_3)$ was plotted vs. the square root of the bromine pressure, at temperatures of 515° , 551° , and 585°K (Figure 30). The lines in this figure are represented by equation 74. The slope of the line was K and the intercept was the vapor pressure of vanadium(III) bromide. As can be seen in the figure, the vapor pressure of the tribromide can be neglected at these temperatures. Table 11 lists the values obtained for K at the temperatures in question. Figure 31 is a plot of $\log K$ vs. reciprocal temperature. The straight line drawn through the points has the equation

$$\log K = \frac{-3455}{T} + 5.22 . \quad \text{Eq. 75}$$

The free energy, as given by the equation above, can be

Figure 29. Apparent Vanadium(IV) Bromide Vapor Pressure
vs. Flow Rate

- A. 0.217 atm. bromine
- B. 0.111 atm. bromine
- C. 8.9×10^{-1} atm. bromine
- D. 1.58×10^{-2} atm. bromine

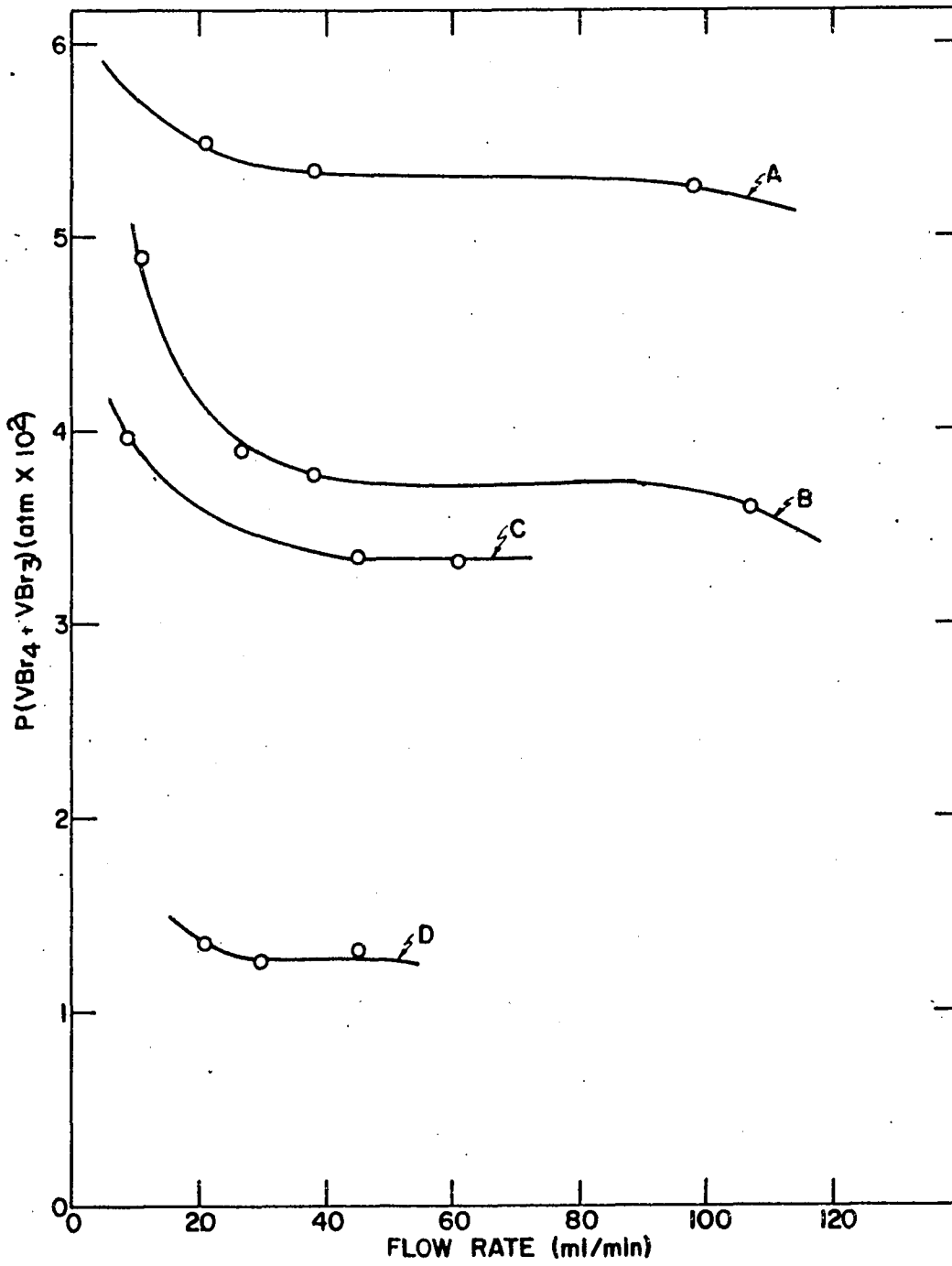


Figure 30. Determination of Equilibrium Constant for the
Reaction of VBr_3 with Bromine

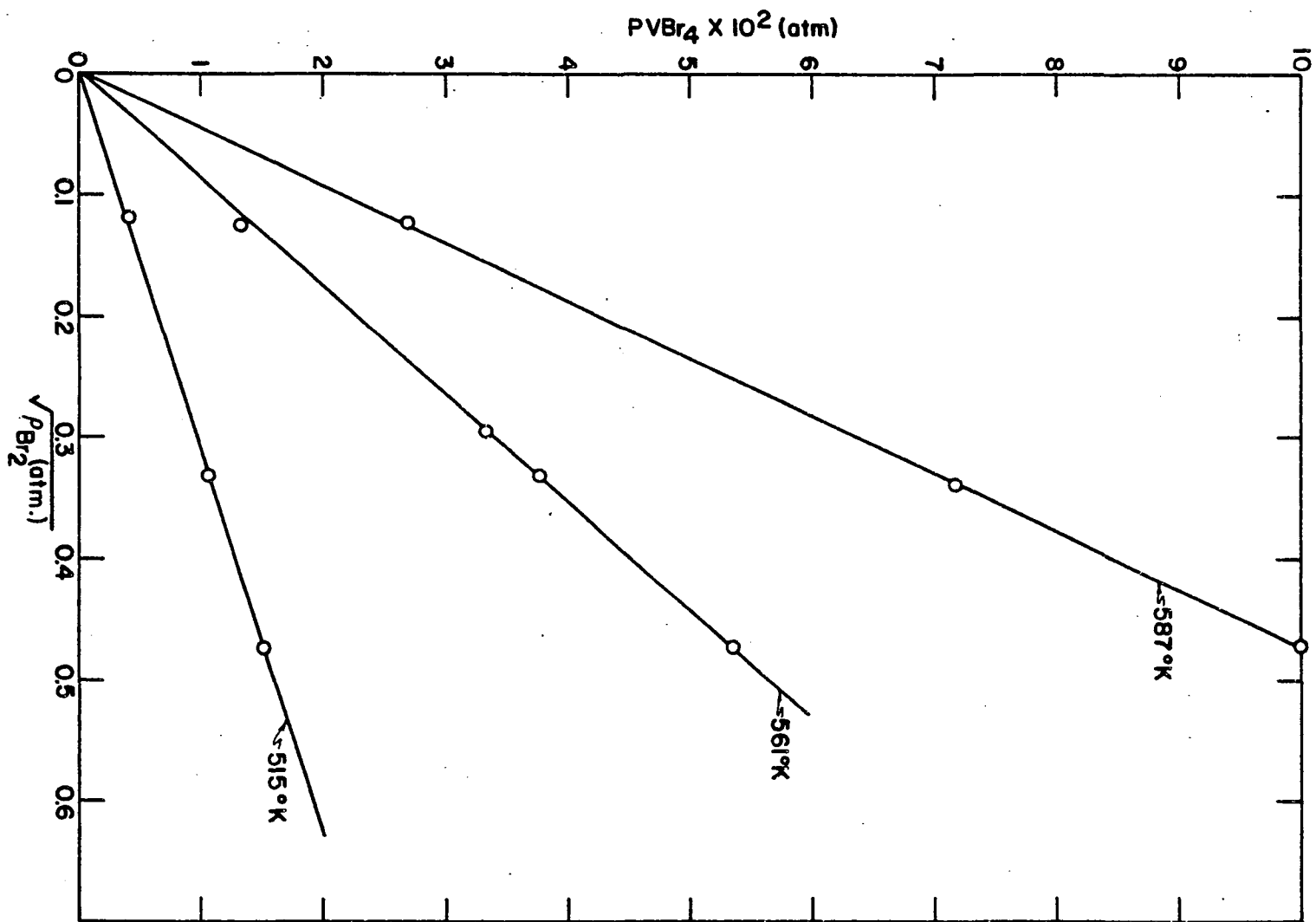


Figure 31. Plot of Equilibrium Constant for the Reaction
of VBr_3 with Bromine

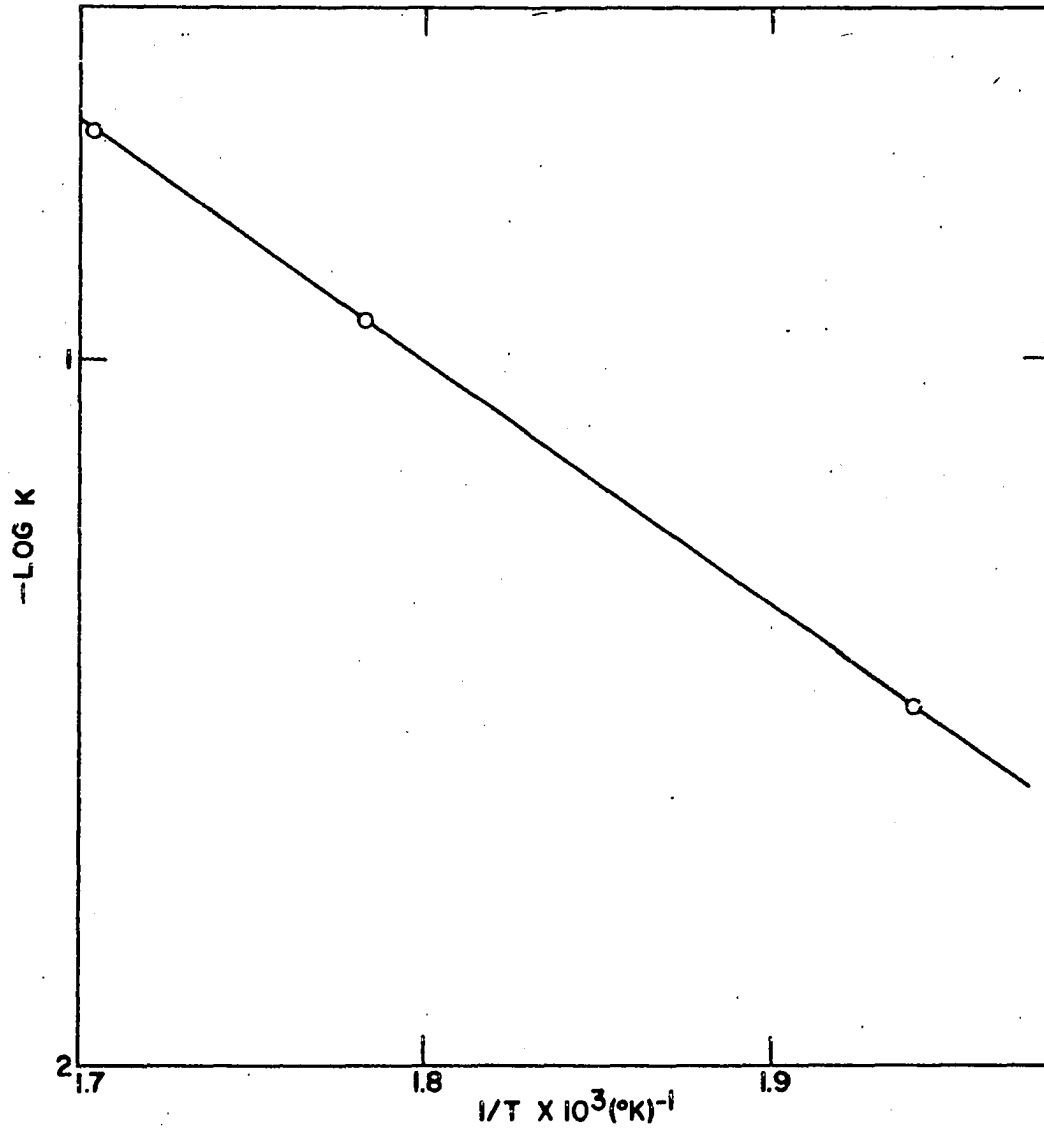


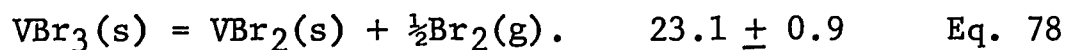
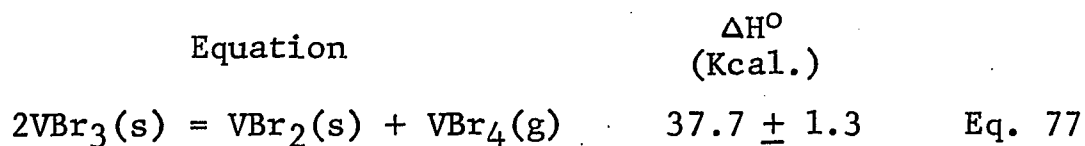
Table 11. Equilibrium Constants for Transpiration Reaction

| Temp. (°K) | $1/T \times 10^3$ (°K) ⁻¹ | K (atm.) ^{1/2} × 10 ² | -log K |
|---------------|---|--|--------|
| 515 | 1.941 | 3.16 | 1.500 |
| 561 | 1.782 | 11.26 | 0.949 |
| 587 | 1.703 | 21.1 | 0.676 |

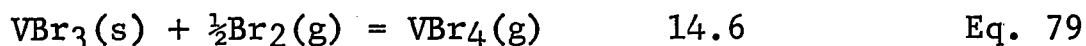
expressed as

$$\Delta F^{\circ} = 15,800 - 23.8T. \quad \text{Eq. 76}$$

Equations 75 and 76 agreed quite favorably with those obtained from the Bourdon gauge measurements. A verification of these results was made by comparing the heats of reaction of the processes that occur during the vaporization of vanadium(III) bromide. From the transport data of the tribromide using helium as the carrier gas, the following equations and their respective heats of reaction can be written:



If equation 78 is subtracted from equation 77, then the equation for the process under investigation results.



The heat of reaction, 14.6 kilocalories, agreed quite well with the experimental value of 15.8 kilocalories obtained in the cell measurements when one considers the uncertainty in the method was approximately two kilocalories.

The value obtained by Simons and Powell for the formation of the tetrachloride from VCl_3 and chlorine was 9.1 kilocalories.

Preparation of Vanadium(IV) Bromide

The desirability of preparing a sample of the tetrabromide to prove conclusively the presence of this substance in the vapor phase led to a series of experiments in which the vapor species over vanadium(III) bromide was condensed at relatively low temperatures.

In the first series of experiments, reliable results could not be obtained owing to premature decomposition of the solid resulting from the fluctuations in the level of the cold trap liquid.

Effective condensation and then decomposition of the solid phase was obtained in the second series of experiments; the results of the three runs are given in Table 12. As can be seen, the total bromide to vanadium molar ratio definitely

confirmed the presence of the tetrabromide. At dry ice temperatures and below, the tetrabromide was a magenta color; it was stable at -45°C but slowly decomposed at -23°C to the tribromide and bromine.

Table 12. Preparation of Vanadium(IV) Bromide

| Sample number | Br ₂ (mg.) | VBr ₃ (mg.) | Br ₂ (mmolesx10 ²) | VBr ₃ (mmolesx10 ²) | Molar Ratio Br/V |
|---------------|-----------------------|------------------------|---|--|------------------|
| 1 | 7.3 | 26.4 | 4.57 | 9.10 | 4.01 |
| 2 | 29.7 | 107 | 18.6 | 37.0 | 4.02 |
| 3 | 57.4 | 210 | 35.9 | 72.2 | 3.98 |

SUMMARY

Transport reactions of the vanadium di- and trichlorides and di- and tribromides were performed in a temperature gradient in an attempt to prepare single crystals of these compounds. Success was obtained for the divalent compounds when iodine was used to facilitate the formation of a volatile vapor species. Both trihalides were transported in the presence of a large excess of bromine vapor.

Solid solution studies were made on the $\text{VCl}_3\text{-VBr}_3$ system using x-ray diffraction techniques. Both lattice parameters of the hexagonal solids exhibited slight positive deviation from ideal behavior, but it was more apparent in the " c_0 " direction. The lattice constants of the mixed halide, VCl_2Br , possessed the values which would be expected for a solid solution of the same composition.

The vapor pressures and related thermodynamic data for the dichloride and dibromide of vanadium were determined using the Knudsen effusion method. In addition, the vaporization characteristics of the trichloride and tribromide were investigated using the methods of Knudsen and of gas saturation.

The existence of vanadium(IV) bromide as the predominant vapor species over VBr_3 at elevated temperatures was conclusively proven by Bourdon gauge and transpiration measurements. The mixed halides, VCl_3Br and VCl_2Br_2 , were demonstrated to be the major vapor phases present in the transport processes of VCl_3 and VCl_2Br in the presence of bromine.

The vaporization or equilibrium data obtained in this investigation may be represented by the equation:

$$\log P_{\text{mm.}} (\text{or } K) = -A/T + B. \quad \text{Eq. 80}$$

In Table 13 are listed the data obtained for the various vanadium halides undergoing the processes of equations 81 through 85.

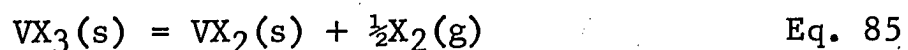
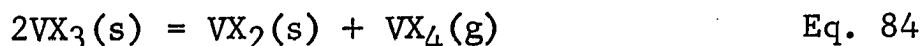
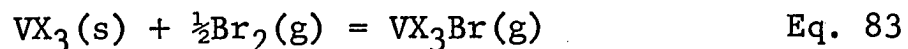


Table 13. Thermodynamic Data of Some Vanadium Halides

| Substance | Process | A | B | Temp. Range (°K) | ΔH (kcal.) | ΔS (eu.) |
|---------------------|---------|-------|-------|---------------------|-----------------------|---------------------|
| VCl ₂ | 81 | 9804 | 8.71 | 750-950 | 44.8 \pm 1.4 | 26.6 \pm 0.8 |
| VBr ₂ | 81 | 10460 | 9.08 | 750-950 | 47.8 \pm 1.6 | 28.3 \pm 0.8 |
| VCl ₃ | 82 | 9777 | 11.20 | 625-740 | 44.7 \pm 1.4 | 38.0 \pm 0.8 |
| VCl ₃ | 83 | 3450 | 5.48 | 525-680 | 15.8 \pm 1.5 | 25.0 \pm 2.5 |
| VCl ₃ | 84 | 7801 | 9.84 | 625-740 | 36.0 \pm 1.0 | 32.0 \pm 1.2 |
| VBr ₃ | 82 | 9470 | 11.12 | 590-700 | 43.3 \pm 1.2 | 37.7 \pm 1.0 |
| VBr ₃ | 83 | 3465 | 5.23 | 540-680 | 15.8 \pm 1.5 | 23.9 \pm 2.4 |
| VBr ₃ | 84 | 8240 | 8.47 | 590-697 | 37.7 \pm 1.3 | 25.5 \pm 0.8 |
| VBr ₃ | 85 | 5070 | 5.02 | 590-700 | 23.1 \pm 0.9 | 9.3 \pm 0.4 |
| VCl ₂ Br | 83 | 3460 | 5.30 | 540-680 | 15.8 \pm 1.5 | 24.2 \pm 2.3 |

SUGGESTIONS FOR FURTHER WORK

The work performed in this thesis represents only a small part of the work which might be done in connection with the study of the properties of the vanadium halides. Very little basic thermodynamic data have been experimentally determined for these compounds. The estimated heats of formation are reported, in many cases, with uncertainties as large as ± 30 kilocalories. From accurate solution calorimetry the uncertainty in these values could be materially reduced.

Since the heat of decomposition of vanadium(IV) chloride was determined over such a narrow temperature range by Simons and Powell (8), other measurements of this reaction should be made, preferably by some other method than that used.

As the stable vapor species over the chlorides and bromides of vanadium(II) and (III) were shown to be the di- and tetravalent halides respectively, a study of the fluoride compounds of vanadium would prove most interesting. The existence of possible mixed halides with chlorine, bromine, and iodine could be determined. Since the tri-fluoride exhibits such a low volatility at temperatures

below ca. 1000°C, difficulty is usually experienced in growing large crystals of this material. A higher vaporization rate may be possible in the presence of one of the other halogens. Such investigations could be performed with the use of a Bourdon gauge with little difficulty.

A study of the vanadium iodide compounds should be undertaken to characterize the vapor species present in this system. Preliminary experiments on the transport of the diiodide in excess iodine indicated the presence of the vanadium(IV) iodide as the volatile species. Such a study would help in understanding the processes occurring in the vanadium crystal-bar process.

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APPENDIX

Solid Solution Determination

Lattice constant refinement

A valuable contribution to extrapolation techniques for the Debye-Scherrer camera was made independently by Taylor and Sinclair (75) and Nelson and Riley (87). Attacking the problem from different angles, these investigators showed that errors in the lattice parameters caused by absorption can be materially reduced providing the source has an exponential intensity profile.

The method, which utilizes all the data, was one of successive approximations. The first step was to calculate approximate values, a_1 and c_1 , of the lattice parameters from the positions of the two highest angle lines. The approximate axial ratio c_1/a_1 was then calculated and used in equation 86 to determine an "a" value for each line on the pattern. These values of "a"

$$a = \frac{\lambda}{2\sin\theta} \left[\frac{4}{3}(h^2+hk+k^2) + \frac{l^2}{(c/a)^2} \right]^{1/2} \quad \text{Eq. 86}$$

were then extrapolated against the function

$$\frac{1}{2} \left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta} \right) \quad \text{Eq. 87}$$

to find a more accurate value of "a", namely "a₂". The value of c₂ was found in a similar manner by use of the relation

$$c = \frac{\lambda}{2\sin\theta} \left[\frac{4}{3} \left(\frac{c}{a} \right)^2 (h^2 + hk + k^2) + \lambda^2 \right]^{\frac{1}{2}} \quad \text{Eq. 88}$$

and another extrapolation against the function in equation 87. The process was repeated using a least squares analysis to determine the intercept in each case. All angles were employed in making the extrapolations. The values obtained for the lattice constants of VCl₃ and VBr₃ for each line are included in this section to demonstrate the accuracy of the method.

Composition determination

The compositions of the solid solutions were determined in a number of ways, in many cases depending upon the method by which the solution was prepared. The table listing the solid solution data has four columns for the composition. The one actually used for the composition was determined in the following manner.

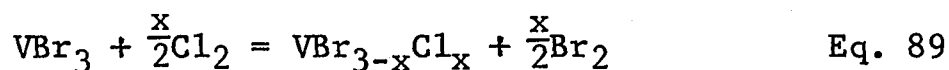
The first value given in the table was calculated from the as weighed components before mixing. Since losses may

possibly occur during transfer, this value was only an approximation.

The second column was obtained from a determination of the percentage vanadium for each solution; the composition was then ascertained from a graph plotting per cent vanadium vs. composition.

The third column was obtained from the determination of the percentage vanadium, percentage bromide, and percentage chloride. In most cases, this value was used for the composition.

In the equilibration experiments with chlorine, the composition was determined by calculating the number of moles present from the ideal gas law and then assuming that the reaction



proceeded to completion.

Discussion of Errors

Effusion

Area of orifice The preparation of a circular knife-edge orifice in vycor or pyrex tubing proved to be one of the most frustrating problems in this investigation.

The absolute error in the area was most difficult to estimate but the deviation from the mean of the values obtained from several measurements was assumed to be of the same order of magnitude of the error and was found to be approximately two per cent.

Temperature Thermocouples were calibrated at the melting point of lead and the boiling point of sulfur. Since the thermocouples were located closer to the furnace walls, the values obtained were somewhat higher than the true sample temperature. Differences of no more than $\pm 1.5^{\circ}$ were obtained. This error was approximately what was seen in the controller temperature fluctuations.

Timer Time was measured with a Precision Time-It meter which could be read to 0.1 second. The error was considered negligible. Difficulty was experienced in the time required for the sample to reach thermal equilibrium. Corrections were applied to reduce this effect in the shorter times by using a weighted average value for the temperature.

Clousing factor The value of this factor was experimentally determined and showed an error of less than 0.5 per cent.

Analysis Vanadium contents could be determined to within one per cent in most experiments. Occasionally, in the very low concentrations, the error increased to near three per cent. The same accuracy was obtained in the bromine determinations.

The maximum total estimated error would be obtained by summation:

| | |
|-----------------|-------------|
| area | 2.0% |
| temperature | 0.5% |
| time | 2.0% |
| clausing factor | 0.5% |
| <u>analysis</u> | <u>1.0%</u> |
| | 6.0% |

The errors listed for the values, which were obtained by calculating the standard deviation of the data, are somewhat less than the estimated total above. This is to be expected, since the errors are random and may tend to cancel.

Transpiration

Flow rate The measurement of carrier gas volume which passed through the system was experimentally verified for accuracy by first determining the vapor pressure of water. Consistent results were obtained with accuracies of about one to two per cent.

Other errors Unmeasurable sources of error include the contamination of the saturating gas during a determination by water, oxygen and any other contaminating material. Several sources of error listed under the effusion method also apply to this method as well as to the cell measurements.

Table 14. The Lattice Parameters of Vanadium(III) Chloride

| hkl | a_0 | c_0 |
|--------|-------|-------|
| 006 | 6.049 | 17.44 |
| 113 | 6.049 | 17.44 |
| 116 | 6.048 | 17.44 |
| 030 | 6.046 | 17.43 |
| 033 | 6.050 | 17.44 |
| 119 | 6.057 | 17.46 |
| 226 | 6.052 | 17.45 |
| 229 | 6.069 | 17.49 |
| 143 | 6.046 | 17.43 |
| 146 | 6.050 | 17.44 |
| 330 | 6.054 | 17.45 |
| 149 | 6.056 | 17.46 |
| 03(15) | 6.062 | 17.48 |

Table 15. The Lattice Parameters of Vanadium(III) Bromide

| hkl | a_0 | c_0 |
|-----|-------|-------|
| 113 | 6.386 | 18.48 |
| 116 | 6.388 | 18.50 |
| 300 | 6.397 | 18.52 |
| 033 | 6.403 | 18.54 |
| 119 | 6.398 | 18.51 |
| 306 | 6.399 | 18.53 |
| 223 | 6.392 | 18.51 |
| 226 | 6.400 | 18.52 |
| 229 | 6.405 | 18.54 |
| 143 | 6.399 | 18.53 |
| 146 | 6.384 | 18.48 |
| 149 | 6.401 | 18.53 |

Table 16. Lattice Constants of Vanadium(III) Bromide and Chloride

| Sample number | Composition (Cl/V) | | | | Lattice parameters | |
|------------------|--------------------|---------|---------------|------------|--------------------|-------------------|
| | As mixed | From %V | From Analysis | Value used | $a(\text{\AA})$ | $c_o(\text{\AA})$ |
| VC1 ₃ | 3.00 | 2.99 | 2.98 | 3.00 | 6.046 | 17.45 |
| 19 | 2.95 | 2.98 | 2.95 | 2.95 | 6.063 | 17.48 |
| 9 | 2.78 | 2.78 | 2.78 | 2.78 | 6.090 | 17.58 |
| 39 | 2.71 | 2.68 | 2.74 | 2.68 | 6.106 | 17.66 |
| 10 | 2.60 | 2.61 | 2.66 | 2.61 | 6.108 | 17.69 |
| 41 | 2.55 | 2.58 | 2.52 | 2.52 | 6.124 | 17.74 |
| 38 | 2.24 | 2.33 | 2.35 | 2.33 | 6.149 | 17.82 |
| 12 | 2.25 | 2.26 | 2.25 | 2.25 | 6.146 | 17.81 |
| 6 | 2.08 | 2.09 | 2.10 | 2.09 | 6.164 | 17.86 |
| 34 | 2.01 | 2.06 | 2.06 | 2.06 | 6.166 | 17.91 |
| 11 | 2.00 | 2.06 | 1.98 | 1.98 | 6.180 | 17.91 |
| 42 | 1.99 | 1.98 | 1.97 | 1.97 | 6.184 | 17.92 |
| 13 | 1.75 | 1.78 | 1.73 | 1.73 | 6.213 | 17.99 |
| 43 | 1.50 | 1.50 | 1.55 | 1.50 | 6.240 | 18.08 |
| 14 | 1.45 | 1.48 | 1.55 | 1.48 | 6.249 | 18.11 |
| 21 | 1.18 | 1.30 | 1.25 | 1.25 | 6.278 | 18.17 |
| 17 | 1.12 | 1.14 | 1.05 | 1.05 | 6.285 | 18.20 |
| 25 | 1.19 | 1.10 | 1.15 | 1.10 | 6.293 | 18.20 |
| 22 | 1.04 | 1.15 | 1.11 | 1.11 | 6.304 | 18.23 |
| 15 | 1.08 | 1.03 | 1.01 | 1.01 | 6.293 | 18.21 |
| 44 | 0.94 | 0.90 | 0.88 | 0.88 | 6.311 | 18.23 |
| 3 | 0.67 | 0.68 | 0.63 | 0.63 | 6.338 | 18.36 |
| 20 | 0.63 | 0.60 | 0.54 | 0.54 | 6.346 | 18.37 |
| 45 | 0.52 | 0.52 | 0.57 | 0.52 | 6.406 | 18.48 |
| 18 | 0.42 | 0.34 | 0.41 | 0.34 | 6.366 | 18.41 |
| 35 | 0.27 | 0.30 | 0.30 | 0.30 | 6.406 | 18.48 |
| 16 | 0.26 | 0.20 | 0.24 | 0.20 | 6.380 | 18.45 |

Table 16. (Continued)

| Sample number | Composition (Cl/V) | | | | Lattice parameters | |
|------------------|--------------------|-------------------|---------------|------------|--------------------|--------------------|
| | As mixed | From %V | From Analysis | Value used | a(Å) | c _o (Å) |
| 47 ^a | 0.07 ^b | 0.10 ^b | -- | 0.07 | 6.394 | 18.47 |
| 48 ^a | 0.16 ^b | 0.20 ^b | -- | 0.16 | 6.383 | 18.46 |
| 49 ^a | 0.13 ^b | 0.14 ^b | -- | 0.13 | 6.390 | 18.46 |
| 50 ^a | 0.04 ^b | 0.00 ^b | -- | 0.04 | 6.396 | 18.48 |
| 51 ^c | 0.29 | 0.28 | 0.28 | 0.28 | 6.371 | 18.42 |
| 52 ^c | 0.50 | 0.49 | 0.49 | 0.49 | 6.350 | 18.39 |
| 53 ^c | 0.73 | 0.74 | 0.74 | 0.74 | 6.328 | 18.31 |
| VBr ₃ | 3.00 | 2.97 | 2.98 | 3.00 | 6.402 | 18.49 |

^aEquilibration of VBr₃ with chlorine

^bFrom gas law calculations

^cTransport of solid solutions with bromine

Table 17. Determination of Clausing Factor for Vycor Cell^a

| Sample number | Temp. (°C) | P _{Hg} actual (mm.) | P _{Hg} obtained (mm.) | Clausing factor |
|---------------|------------|------------------------------|--------------------------------|-----------------|
| 1 | 48.2 | 0.01115 | 0.0100 | 0.897 |
| 2 | 55.0 | 0.01801 | 0.0162 | 0.902 |
| 3 | 60.6 | 0.02631 | 0.0236 | 0.897 |

^aArea of orifice = $3.17 \times 10^{-2} \text{ cm}^2$

Table 18. Determination of Clausing Factor for Pyrex Cell^a

| Experiment number | Temp. (°C) | Theoretical vapor pressure of Hg (mm.) | Found vapor pressure of Hg (mm.) | Clausing factor |
|-------------------|------------|--|----------------------------------|-----------------|
| 1 | 40.2 | 0.00627 | 0.00534 | 0.852 |
| 2 | 52 | 0.0146 | 0.0124 | 0.850 |
| 3 ^b | 56 | 0.0192 | 0.0130 | 0.680 |
| 4 | 62 | 0.0288 | 0.0244 | 0.847 |

^aArea of orifice = $2.76 \times 10^{-2} \text{ cm}^2$

^bDiscarded

Table 19. Vapor Pressure of Vanadium(II) Chloride by Effusion

| Sample number | VCl ₂ effused (mg.) | Temp. (°K) | Time of run (sec.) | Final pressure (microns) | 1/Tx10 ³ (°K) ⁻¹ | P _{VCl₂} (mm.x10 ⁴) | -Σ | -log P _{VCl₂} |
|---------------|--------------------------------|------------|--------------------|--------------------------|--|---|--------|-----------------------------------|
| 252 | 0.86 | 763 | 18000 | 0.006 | 1.310 | 0.72 | 14.793 | 4.143 |
| 253 | 1.66 | 784 | 15000 | 0.007 | 1.276 | 1.59 | 16.026 | 3.799 |
| 254 | 2.15 | 799 | 12000 | 0.011 | 1.251 | 2.75 | 17.269 | 3.561 |
| 255 | 3.72 | 815 | 12000 | 0.009 | 1.227 | 4.80 | 18.496 | 3.319 |
| 256 | 4.85 | 829 | 10000 | 0.010 | 1.206 | 7.60 | 19.540 | 3.119 |
| 257 | 6.65 | 843 | 9000 | 0.012 | 1.186 | 11.7 | 20.522 | 2.932 |
| 258 | 12.4 | 871 | 7200 | 0.015 | 1.148 | 27.6 | 22.441 | 2.559 |
| 259 | 16.9 | 888 | 6000 | 0.009 | 1.126 | 45.7 | 23.592 | 2.340 |
| 260 | 15.9 | 904 | 3600 | 0.014 | 1.107 | 72.0 | 24.620 | 2.143 |

Table 20. Vapor Pressure of Vanadium(II) Bromide by Effusion

| Sample number | VBr ₂ effused (mg.) | Temp. (°K) | Time of Run (sec.) | Final pressure (microns) | 1/Tx10 ³ (°K) ⁻¹ | P _{VBr₂} (mm.x10 ⁴) | -Σ | -log P _{VBr₂} |
|---------------|--------------------------------|------------|--------------------|--------------------------|--|---|--------|-----------------------------------|
| 201 | 1.00 | 793 | 15000 | 0.0074 | 1.261 | 0.78 | 14.704 | 4.108 |
| 202 | 1.99 | 826 | 9000 | 0.0097 | 1.210 | 2.63 | 17.403 | 3.580 |
| 203 | 4.11 | 847 | 9000 | 0.010 | 1.180 | 5.49 | 19.028 | 3.260 |
| 204 | 6.18 | 873 | 6000 | 0.011 | 1.145 | 12.6 | 20.901 | 2.900 |
| 205 | 12.4 | 902 | 5000 | 0.0097 | 1.108 | 30.9 | 22.911 | 2.510 |
| 206 | 43.2 | 947 | 5000 | 0.012 | 1.055 | 110 | 25.766 | 1.958 |
| 207 | 44.3 | 989 | 2000 | 0.011 | 1.011 | 288 | 27.994 | 1.541 |
| 208 | 0.98 | 787 | 15000 | 0.0092 | 1.269 | 0.70 | 14.294 | 4.155 |

Table 21. Vaporization of Vanadium(III) Chloride by Effusion Using Pyrex Cell

| Sample number | VCl ₄ effused (mg.) | Temp. (°K) | Time of run (sec.) | Final pressure (microns) | 1/Tx10 ³ (°K) ⁻¹ | P _{VCl₄} (mm.x10 ³) | VCl ₃ effused (mg.) | P _{VCl₃} (mm.x10 ⁴) |
|---------------|--------------------------------|------------|--------------------|--------------------------|--|---|--------------------------------|---|
| 101 | 21.3 | 624 | 14,000 | 0.0081 | 1.602 | 2.00 | 0.33 | 0.34 |
| 102 | 44.2 | 648 | 10,000 | 0.010 | 1.544 | 5.92 | 0.88 | 1.31 |
| 103 | 54.7 | 659 | 8,200 | 0.0096 | 1.518 | 9.00 | 1.27 | 2.32 |
| 105 | 127 | 682 | 7,200 | 0.012 | 1.467 | 24.2 | 3.50 | 7.40 |
| 106 | 147 | 696 | 5,000 | 0.011 | 1.437 | 41.0 | 4.55 | 14.0 |
| 107 | 212 | 719 | 3,000 | 0.017 | 1.392 | 100 | 7.78 | 40.7 |
| 108 | 301 | 742 | 2,000 | 0.014 | 1.348 | 218 | 12.9 | 103 |

Table 22. Vaporization of Vanadium(III) Chloride by Effusion Using Vycor Cell

| Sample number | VCl ₄ effused (mg.) | Temp. (°K) | Time of run (sec.) | Final pressure (microns) | 1/Tx10 ³ (°K) ⁻¹ | P _{VCl₄} (mm.x10 ³) | VCl ₃ effused (mg.) | P _{VCl₃} (mm.x10 ⁴) |
|---------------|--------------------------------|------------|--------------------|--------------------------|--|---|--------------------------------|---|
| 51 | 50 | 655 | 7,200 | 0.0091 | 1.526 | 7.7 | 1.14 | 1.95 |
| 52 | 80 | 674 | 5,000 | 0.0097 | 1.482 | 18.0 | 2.01 | 5.02 |
| 53 | 150 | 707 | 2,500 | 0.010 | 1.413 | 69.6 | 4.92 | 25.1 |

Table 23. Vaporization of Vanadium(III) Bromide by Effusion Using Pyrex Cell

| Sample number | VBr ₃ effused (mg.) | Bromine effused (mg.) | Temp. (°K) | Time of run (sec.) | Final Pressure (microns) |
|---------------|--------------------------------|-----------------------|------------|--------------------|--------------------------|
| 7 | 0.19 | 4.4 | 594 | 13,100 | 0.0080 |
| 8 | 0.84 | 6.3 | 634 | 6,000 | 0.0097 |
| 9 | 1.42 | 5.2 | 664 | 2,100 | 0.010 |
| 12 | 0.40 | 4.7 | 616 | 7,500 | 0.0093 |
| 14 | 2.18 | 6.8 | 675 | 2,000 | 0.010 |
| 15 | 5.40 | 9.7 | 697 | 1,800 | 0.014 |

Table 23. (Continued)

| Sample number | $1/T \times 10^3$ (°K) ⁻¹ | P_{VBr_3} (mm. $\times 10^5$) | P_{Br_2} (mm. $\times 10^4$) | VBr ₄ effused | P_{VBr_4} (mm. $\times 10^3$) |
|---------------|--------------------------------------|----------------------------------|---------------------------------|--------------------------|----------------------------------|
| 7 | 1.683 | 1.51 | 4.73 | 1.74 | 0.123 |
| 8 | 1.577 | 15.3 | 15.3 | 4.61 | 0.733 |
| 9 | 1.506 | 74.6 | 36.9 | 6.60 | 3.06 |
| 12 | 1.623 | 5.68 | 9.0 | 2.63 | 0.330 |
| 14 | 1.481 | 121 | 51.0 | 7.47 | 3.68 |
| 15 | 1.435 | 340 | 82.2 | 14.8 | 8.22 |

Table 24. Vaporization of Vanadium(III) Bromide by Effusion Using Vycor Cell

| Sample number | VBr ₃ effused (mg.) | Bromine effused (mg.) | Temp. (°K) | Time of Run (sec.) | Final pressure (microns) |
|---------------|--------------------------------|-----------------------|------------|--------------------|--------------------------|
| 16 | 1.04 | 8.25 | 629 | 8,000 | 0.0086 |
| 17 | 2.38 | 10.7 | 655 | 5,000 | 0.0094 |
| 19 | 6.17 | 13.6 | 685 | 3,000 | 0.010 |

Table 24. (Continued)

| Sample number | 1/Tx10 ³ (°K) ⁻¹ | P _{VBr₃} (mm.x10 ⁵) | P _{Br₂} (mm.x10 ⁴) | VBr ₄ effused (mg.) | P _{VBr₄} (mm.x10 ³) |
|---------------|--|---|--|--------------------------------|---|
| 16 | 1.589 | 11.5 | 12.3 | 5.48 | 0.537 |
| 17 | 1.528 | 42.7 | 26.0 | 9.12 | 1.46 |
| 19 | 1.460 | 190 | 56.5 | 17.1 | 4.64 |

Table 25. Transpiration of Vanadium(III) Bromide

| Sample number | P_s (mm.) | V_m (l.) | P_{M-k_w} (mm.) | T_M (°K) | G_{VBr_4} (mg.) | K (10^3) | Time of run (sec.) |
|---------------|----------------|---------------|----------------------|---------------|----------------------|-------------------|--------------------|
| 1 | 742.2 | 3.04 | 720.4 | 294.4 | 101 | 0.437 | 6,105 |
| 2 | 748.7 | 2.01 | 726.0 | 295.1 | 26.1 | 1.125 | 4,120 |
| 3 | 748.5 | 3.02 | 726.3 | 294.7 | 23.9 | 1.846 | 5,870 |
| 4 | 740.8 | 3.01 | 717.6 | 295.7 | 10.8 | 4.05 | 6,220 |
| 5 | 742 | 3.07 | 719.2 | 295.2 | 6.1 | 7.34 | 6,080 |
| 6 | 743.2 | 6.01 | 718.8 | 295.5 | 5.8 | 15.0 | 11,250 |
| 7 | 740.7 | 9.00 | 718.1 | 295.2 | 5.8 | 22.6 | 18,100 |
| 8 | 739.1 | 10.00 | 720.6 | 294.2 | 4.3 | 33.7 | 19,800 |
| 9 | 736.0 | 15.00 | 714.0 | 294.5 | 1.4 | 156 | 27,900 |

Table 25. (Continued)

| Sample number | T_s (°K) | $1/T_s \times 10^3$ (°K) ⁻¹ | P_{VBr_4} (mm. $\times 10^4$) | Total Br_2 (mg.) | Br_2 from VBr_4 (mg.) | G_{Br_2} net (mg.) | K (10^4) | P_{Br_2} (mm. $\times 10^2$) |
|---------------|---------------|---|-------------------------------------|-----------------------|------------------------------|----------------------------|-------------------|------------------------------------|
| 1 | 805 | 1.242 | 170 | 23.8 | 21.7 | 2.10 | 0.910 | 8.16 |
| 2 | 775 | 1.290 | 66.5 | 6.40 | 5.63 | 0.77 | 1.65 | 4.54 |
| 3 | 758 | 1.319 | 40.5 | 6.02 | 5.15 | 0.87 | 2.18 | 3.43 |
| 4 | 736 | 1.358 | 18.3 | 2.84 | 2.32 | 0.52 | 3.63 | 2.04 |
| 5 | 718 | 1.392 | 10.1 | 1.68 | 1.31 | 0.37 | 5.21 | 1.42 |
| 6 | 700 | 1.428 | 4.96 | 1.72 | 1.25 | 0.47 | 8.04 | 0.92 |
| 7 | 689 | 1.451 | 3.28 | 1.79 | 1.25 | 0.54 | 10.5 | 0.71 |
| 8 | 680 | 1.470 | 2.19 | 1.39 | 0.92 | 0.47 | 13.4 | 0.55 |
| 9 | 644 | 1.552 | 0.47 | 0.48 | 0.30 | 0.18 | 33.0 | 0.22 |

Table 26. Cell Reaction of Vanadium(III) Bromide with Bromine

| Measurement number | Sample temp. ($^{\circ}$ K) | Average temp. of cell ($^{\circ}$ K) | Gas Law P_{Br_2} (mm.) | Actual P_{Br_2} (mm.) | P_{VBr_4} (mm.) |
|--------------------|------------------------------|---------------------------------------|---------------------------------|--------------------------------|--------------------------|
| 1 | 354.0 | 356.7 | 52.97 | 52.94 | 0.06 |
| 2 | 474.2 | 499.8 | 73.98 | 72.06 | 3.84 |
| 3 | 555.8 | 560.8 | 83.01 | 70.72 | 24.58 |
| 4 | 577.4 | 590.4 | 87.41 | 66.72 | 41.38 |
| 5 | 586.8 | 602.9 | 89.24 | 63.23 | 52.02 |
| 6 | 607.6 | 611.0 | 90.44 | 52.73 | 75.42 |
| 7 | 618.2 | 620.8 | 91.89 | 46.08 | 91.62 |
| 8 | 629.4 | 633.3 | 93.74 | 40.68 | 106.12 |
| 9 | 635.8 | 640.6 | 94.82 | 36.89 | 115.86 |
| 10 | 653.0 | 655.8 | 97.07 | 26.99 | 140.16 |
| 11 | 665.4 | 668.3 | 98.92 | 21.14 | 155.56 |
| 12 | 678.2 | 680.6 | 100.75 | 15.45 | 170.60 |
| 13 | 687.2 | 689.1 | 102.00 | 9.50 | 185.00 |
| 14 | 699.2 | 701.0 | 103.76 | 2.92 | 201.68 |
| 15 | 711.0 | 712.0 | 105.39 | 0.68 | 209.42 |
| 16 | 683.0 | 686.8 | 101.66 | 10.47 | 182.38 |
| 17 | 659.4 | 663.7 | 98.24 | 20.23 | 156.02 |
| 18 | 645.0 | 649.6 | 96.15 | 27.50 | 137.30 |
| 19 | 624.7 | 627.9 | 92.94 | 37.88 | 110.12 |
| 20 | 608.0 | 609.0 | 90.14 | 47.48 | 85.32 |
| 21 | 587.4 | 591.6 | 87.57 | 53.89 | 67.36 |
| 22 | 554.0 | 559.5 | 82.82 | 61.29 | 43.06 |
| 23 | 504.2 | 506.9 | 75.03 | 62.11 | 25.84 |
| 24 | 427.7 | 429.9 | 63.63 | 53.01 | 21.24 |

Table 26. (Continued)

| Measure- ment number | Pressure in cell (mm.) | $(P_{\text{Br}_2})^{\frac{1}{2}}$ (mm.) $^{\frac{1}{2}}$ | K in (mm.) $^{\frac{1}{2}}$ | K in (atm.) $^{\frac{1}{2}}$ | $1/T \times 10^3$ (°K) $^{-1}$ |
|----------------------------|------------------------------|---|--------------------------------|---------------------------------|-----------------------------------|
| 1 | 53.00 | 7.274 | -- | -- | 2.824 |
| 2 | 75.90 | 8.489 | 0.452 | 0.0164 | 2.108 |
| 3 | 95.30 | 8.410 | 2.922 | 0.1060 | 1.800 |
| 4 | 108.10 | 8.168 | 5.066 | 0.1838 | 1.730 |
| 5 | 115.25 | 7.952 | 6.541 | 0.2372 | 1.702 |
| 6 | 128.15 | 7.262 | 10.385 | 0.3766 | 1.645 |
| 7 | 137.70 | 6.788 | 13.497 | 0.4890 | 1.617 |
| 8 | 146.80 | 6.378 | 16.638 | 0.6034 | 1.588 |
| 9 | 152.75 | 6.074 | 19.074 | 0.6918 | 1.572 |
| 10 | 167.15 | 5.195 | 26.979 | 0.9785 | 1.532 |
| 11 | 176.70 | 4.597 | 33.839 | 1.227 | 1.502 |
| 12 | 186.05 | 3.933 | 43.376 | 1.573 | 1.474 |
| 13 | 194.50 | 3.064 | 60.378 | 2.190 | 1.455 |
| 14 | 204.60 | 1.709 | 118.01 | 4.280 | 1.430 |
| 15 | 210.10 | 0.825 | 253.84 | 9.207 | 1.406 |
| 16 | 192.85 | 3.235 | 56.377 | 2.045 | 1.464 |
| 17 | 176.25 | 4.497 | 34.694 | 1.258 | 1.516 |
| 18 | 164.80 | 5.244 | 26.182 | 0.9496 | 1.550 |
| 19 | 148.00 | 6.155 | 17.891 | 0.6479 | 1.600 |
| 20 | 132.80 | 6.890 | 12.383 | 0.4491 | 1.643 |
| 21 | 121.25 | 7.341 | 9.176 | 0.3328 | 1.702 |
| 22 | 104.35 | 7.832 | 5.573 | 0.2023 | 1.805 |
| 23 | 87.95 | 7.881 | 3.278 | 0.1189 | 1.983 |
| 24 | 74.25 | 7.281 | 2.917 | 0.1058 | 2.338 |

Initial Br₂ pressure in cell = 43.55 mm. Hg at 21°C

Final Br₂ pressure in cell = 49.40 mm. Hg at 22°C

Table 27. Cell Reaction of Vanadium(III) Bromide with Bromine

| Measure- ment number | Sample temp. (°K) | Average temp. of cell (°K) | Gas Law P_{Br_2} (mm.) | Actual P_{Br_2} (mm.) | P_{VBr_4} (mm.) |
|----------------------------|-------------------------|-------------------------------------|---------------------------------------|--------------------------------------|-----------------------------|
| 1 | 531.4 | 533.3 | 160.33 | 148.51 | 23.64 |
| 2 | 563.8 | 559.8 | 168.09 | 145.73 | 44.72 |
| 3 | 585.8 | 586.0 | 176.18 | 138.46 | 75.44 |
| 4 | 577.2 | 577.5 | 173.53 | 142.26 | 62.54 |
| 5 | 606.6 | 606.9 | 182.31 | 124.62 | 115.38 |
| 6 | 596.2 | 598.5 | 179.93 | 129.91 | 100.04 |
| 7 | 632.0 | 634.6 | 189.43 | 102.31 | 174.24 |
| 8 | 621.0 | 621.7 | 186.91 | 112.77 | 148.28 |
| 9 | 647.0 | 646.1 | 194.24 | 89.68 | 209.12 |
| 10 | 619.8 | 629.2 | 189.16 | 116.92 | 144.48 |
| 11 | 657.6 | 658.4 | 197.94 | 77.63 | 240.62 |
| 12 | 678.2 | 678.9 | 204.10 | 57.15 | 293.90 |
| 13 | 667.5 | 669.2 | 201.19 | 65.88 | 270.62 |
| 14 | 690.0 | 695.8 | 209.19 | 29.98 | 358.42 |
| 15 | 695.7 | 706.6 | 212.43 | 23.96 | 376.94 |
| 16 | 630.7 | 638.3 | 191.90 | 92.50 | 198.80 |
| 17 | 573.4 | 576.4 | 173.29 | 133.63 | 79.32 |
| 18 | 525.2 | 533.4 | 160.36 | 137.17 | 46.38 |

Table 27. (Continued)

| Measure- ment number | Pressure in cell (mm.) | $(P_{\text{Br}_2})^{\frac{1}{2}}$ (mm.) $^{\frac{1}{2}}$ | K in (mm.) $^{\frac{1}{2}}$ | K in (atm.) $^{\frac{1}{2}}$ | $1/T \times 10^3$ ($^{\circ}\text{K}$) $^{-1}$ |
|----------------------------|------------------------------|---|--------------------------------|---------------------------------|---|
| 1 | 172.15 | 12.186 | 1.940 | 0.0704 | 1.883 |
| 2 | 190.45 | 12.071 | 3.705 | 0.1344 | 1.773 |
| 3 | 213.90 | 11.762 | 6.422 | 0.2329 | 1.706 |
| 4 | 204.80 | 11.927 | 5.244 | 0.1902 | 1.733 |
| 5 | 240.00 | 11.163 | 10.335 | 0.3748 | 1.647 |
| 6 | 229.95 | 11.397 | 8.777 | 0.3184 | 1.678 |
| 7 | 276.55 | 10.114 | 17.227 | 0.6248 | 1.582 |
| 8 | 261.05 | 10.619 | 13.963 | 0.5064 | 1.610 |
| 9 | 298.80 | 9.453 | 22.14 | 0.8027 | 1.546 |
| 10 | 261.40 | 10.813 | 13.361 | 0.4846 | 1.613 |
| 11 | 318.25 | 8.811 | 27.30 | 0.9902 | 1.520 |
| 12 | 351.05 | 7.560 | 38.87 | 1.4098 | 1.475 |
| 13 | 336.50 | 8.117 | 33.33 | 1.2089 | 1.499 |
| 14 | 388.40 | 5.475 | 65.46 | 2.374 | 1.449 |
| 15 | 400.90 | 4.894 | 77.02 | 2.794 | 1.437 |
| 16 | 291.30 | 9.618 | 20.66 | 0.7493 | 1.585 |
| 17 | 212.95 | 11.559 | 6.862 | 0.2489 | 1.745 |
| 18 | 183.55 | 11.712 | 3.960 | 0.1436 | 1.905 |

Initial Br₂ pressure in cell = 88.00 mm. Hg at 19.5°C

Final Br₂ pressure in cell = 93.85 mm. Hg at 20°C

Table 28. Cell Reaction of Vanadium(III) Bromide with Bromine

| Measurement number | Sample temp. ($^{\circ}\text{K}$) | Average temp. of cell ($^{\circ}\text{K}$) | Gas Law P_{Br_2} (mm.) | Actual P_{Br_2} (mm.) | P_{VBr_4} (mm.) |
|--------------------|-------------------------------------|--|---------------------------------|--------------------------------|--------------------------|
| 1 | 378.6 | 384.2 | 148.02 | 148.02 | -- |
| 2 | 413.4 | 420.0 | 161.87 | 161.90 | -- |
| 3 | 478.2 | 479.9 | 184.89 | 183.15 | 3.50 |
| 4 | 563.6 | 566.0 | 217.94 | 195.63 | 44.62 |
| 5 | 591.4 | 594.3 | 228.79 | 185.92 | 85.78 |
| 6 | 585.0 | 592.4 | 228.03 | 190.74 | 74.51 |
| 7 | 618.1 | 623.1 | 240.04 | 167.33 | 145.77 |
| 8 | 601.2 | 607.5 | 234.10 | 181.82 | 105.63 |
| 9 | 635.7 | 641.0 | 246.43 | 147.13 | 195.97 |
| 10 | 620.3 | 625.7 | 240.92 | 165.12 | 151.83 |
| 11 | 652.4 | 658.2 | 253.64 | 127.62 | 252.08 |
| 12 | 641.1 | 644.7 | 248.16 | 141.61 | 213.64 |
| 13 | 663.5 | 667.9 | 257.31 | 111.04 | 290.96 |
| 14 | 681.8 | 687.2 | 264.49 | 87.63 | 355.57 |
| 15 | 673.4 | 678.5 | 261.24 | 98.78 | 325.92 |
| 16 | 704.0 | 709.2 | 273.02 | 55.66 | 431.74 |
| 17 | 690.0 | 693.0 | 267.14 | 77.10 | 384.05 |
| 18 | 714.3 | 718.5 | 276.36 | 46.24 | 448.81 |

Table 28. (Continued)

| Measure- ment number | Pressure in cell (mm.) | $(P_{\text{Br}_2})^{\frac{1}{2}}$ (mm.) $^{\frac{1}{2}}$ | K in (mm.) $^{\frac{1}{2}}$ | K in (atm.) $^{\frac{1}{2}}$ | $1/T \times 10^3$ ($^{\circ}\text{K}$) $^{-1}$ |
|----------------------------|------------------------------|---|--------------------------------|---------------------------------|---|
| 1 | 148.00 | | -- | -- | 2.641 |
| 2 | 161.90 | | -- | -- | 2.419 |
| 3 | 186.65 | 13.532 | 0.259 | 0.0094 | 2.091 |
| 4 | 240.25 | 13.986 | 3.205 | 0.1162 | 1.774 |
| 5 | 271.70 | 13.637 | 6.267 | 0.2274 | 1.691 |
| 6 | 265.25 | 13.802 | 5.400 | 0.1961 | 1.704 |
| 7 | 313.10 | 12.931 | 11.265 | 0.4093 | 1.618 |
| 8 | 287.45 | 13.459 | 7.848 | 0.2847 | 1.663 |
| 9 | 343.10 | 12.129 | 16.153 | 0.5872 | 1.573 |
| 10 | 316.95 | 12.851 | 11.805 | 0.4288 | 1.612 |
| 11 | 379.70 | 11.283 | 22.344 | 0.8116 | 1.533 |
| 12 | 355.25 | 11.882 | 17.982 | 0.6539 | 1.560 |
| 13 | 402.00 | 10.537 | 27.598 | 1.002 | 1.507 |
| 14 | 443.20 | 9.360 | 38.02 | 1.380 | 1.467 |
| 15 | 424.70 | 9.935 | 32.84 | 1.192 | 1.485 |
| 16 | 487.40 | 7.458 | 57.87 | 2.104 | 1.420 |
| 17 | 461.15 | 8.781 | 43.78 | 1.590 | 1.449 |
| 18 | 495.05 | 6.798 | 66.15 | 2.403 | 1.400 |

Initial Br₂ pressure in cell = 107.00 mm. Hg at 20.2 $^{\circ}\text{C}$

Final Br₂ pressure in cell = 113.05 mm. Hg at 20.0 $^{\circ}\text{C}$

Table 29. Cell Reaction of VBr_3 with Bromine

| Measure- ment number | Sample temp. (°K) | Average temp. of cell (°K) | Gas Law P_{Br_2} (mm.) | Actual P_{Br_2} (mm.) | P_{VBr_4} (mm.) |
|----------------------------|-------------------------|-------------------------------------|--------------------------------|-------------------------------|----------------------|
| 1 | 347.2 | 343.4 | 144.24 | -- | -- |
| 2 | 482.4 | 480.0 | 201.62 | 199.62 | 2.00 |
| 3 | 492.7 | 500.5 | 210.24 | 204.53 | 11.42 |
| 4 | 531.2 | 540.2 | 226.91 | 212.82 | 28.18 |
| 5 | 558.8 | 563.3 | 236.61 | 213.42 | 46.38 |
| 6 | 584.0 | 591.2 | 248.33 | 206.71 | 83.24 |
| 7 | 572.4 | 581.4 | 244.22 | 211.24 | 65.96 |
| 8 | 602.4 | 612.6 | 257.32 | 193.84 | 126.96 |
| 9 | 593.2 | 598.9 | 251.57 | 200.64 | 101.86 |
| 10 | 620.0 | 628.2 | 263.88 | 175.61 | 176.54 |
| 11 | 609.2 | 615.4 | 258.50 | 188.30 | 140.40 |
| 12 | 631.6 | 638.2 | 268.08 | 162.76 | 210.64 |
| 13 | 656.3 | 658.0 | 276.39 | 128.03 | 296.72 |
| 14 | 645.0 | 644.8 | 270.76 | 145.62 | 250.28 |
| 15 | 666.4 | 669.3 | 281.14 | 111.63 | 339.02 |
| 16 | 657.2 | 660.6 | 277.49 | 125.28 | 304.42 |
| 17 | 684.8 | 690.8 | 290.17 | 76.99 | 426.36 |
| 18 | 681.6 | 681.7 | 286.35 | 89.40 | 393.90 |
| 19 | 710.0 | 712.2 | 299.16 | 50.82 | 496.68 |
| 20 | 700.5 | 698.9 | 293.24 | 61.38 | 463.72 |
| 21 | 720.6 | 721.7 | 303.15 | 36.30 | 533.70 |

Table 29. (Continued)

| Measure- ment number | Pressure in cell (mm.) | $(P_{\text{Br}_2})^{\frac{1}{2}}$ (mm.) $^{\frac{1}{2}}$ | K in (mm.) $^{\frac{1}{2}}$ | K in (atm.) $^{\frac{1}{2}}$ | $1/T \times 10^3$ ($^{\circ}\text{K}$) $^{-1}$ |
|----------------------------|------------------------------|---|--------------------------------|---------------------------------|---|
| 1 | 144.00 | -- | -- | -- | -- |
| 2 | 202.62 | 14.041 | 0.1424 | 0.0052 | 2.075 |
| 3 | 215.95 | 14.301 | 0.7986 | 0.0290 | 2.029 |
| 4 | 241.00 | 14.588 | 1.9317 | 0.0700 | 1.883 |
| 5 | 259.80 | 14.609 | 3.175 | 0.1151 | 1.789 |
| 6 | 289.95 | 14.378 | 5.789 | 0.2099 | 1.712 |
| 7 | 277.20 | 14.534 | 4.538 | 0.1645 | 1.748 |
| 8 | 320.80 | 13.923 | 9.118 | 0.3307 | 1.661 |
| 9 | 302.50 | 14.165 | 7.190 | 0.2607 | 1.686 |
| 10 | 352.15 | 13.252 | 13.321 | 0.4831 | 1.613 |
| 11 | 328.70 | 13.722 | 10.231 | 0.3710 | 1.642 |
| 12 | 373.40 | 12.758 | 16.510 | 0.5988 | 1.582 |
| 13 | 424.75 | 11.315 | 26.223 | 0.9511 | 1.524 |
| 14 | 395.90 | 12.067 | 20.740 | 0.7522 | 1.550 |
| 15 | 450.65 | 10.566 | 32.085 | 1.164 | 1.502 |
| 16 | 429.70 | 11.193 | 27.197 | 0.9864 | 1.522 |
| 17 | 503.35 | 8.774 | 48.59 | 1.762 | 1.460 |
| 18 | 483.30 | 9.455 | 41.66 | 1.511 | 1.466 |
| 19 | 547.50 | 7.129 | 69.67 | 2.527 | 1.408 |
| 20 | 525.10 | 7.835 | 59.18 | 2.146 | 1.429 |
| 21 | 570.00 | 6.025 | 88.58 | 3.213 | 1.387 |

Initial Br₂ pressure in cell = 124.00 mm. Hg at 22^oC

Final Br₂ pressure in cell = 129.80 mm. Hg at 22.4^oC

Table 30. Cell Reaction of Vanadium(III) Bromide with Bromine

| Measure- ment number | Sample temp. (°K) | Average temp. of cell (°K) | Gas Law P_{Br_2} (mm.) | Actual P_{Br_2} (mm.) | P_{VBr_4} (mm.) |
|----------------------------|-------------------------|-------------------------------------|---------------------------------------|--------------------------------------|-----------------------------|
| 1 | 457.7 | 462.2 | 256.52 | 255.84 | 1.36 |
| 2 | 476.4 | 486.1 | 269.78 | 267.96 | 3.64 |
| 3 | 520.7 | 532.3 | 295.42 | 281.04 | 28.76 |
| 4 | 562.4 | 568.8 | 315.68 | 284.86 | 61.64 |
| 5 | 591.2 | 594.1 | 329.72 | 269.09 | 121.26 |
| 6 | 575.2 | 583.3 | 323.73 | 281.16 | 85.14 |
| 7 | 599.8 | 612.3 | 339.82 | 269.39 | 140.86 |
| 8 | 614.6 | 625.8 | 347.31 | 254.42 | 185.78 |
| 9 | 625.0 | 635.6 | 352.75 | 244.65 | 216.20 |
| 10 | 644.2 | 655.6 | 363.85 | 211.50 | 304.70 |
| 11 | 637.0 | 645.4 | 358.19 | 226.48 | 263.42 |
| 12 | 666.2 | 675.1 | 374.67 | 171.99 | 405.36 |
| 13 | 658.4 | 664.0 | 368.51 | 189.92 | 357.18 |
| 14 | 680.0 | 693.6 | 384.94 | 129.63 | 510.62 |
| 15 | 670.7 | 681.1 | 378.00 | 149.35 | 457.30 |
| 16 | 685.7 | 700.2 | 388.60 | 110.90 | 555.40 |
| 17 | 717.7 | 731.4 | 405.92 | 67.74 | 676.36 |
| 18 | 701.2 | 720.3 | 399.76 | 96.97 | 605.58 |

Table 30. (Continued)

| Measure- ment number | Pressure in cell (mm.) | $(P_{\text{Br}_2})^{\frac{1}{2}}$ (mm.) ^{1/2} | K in (mm.) ^{1/2} | K in (atm.) ^{1/2} | $1/T \times 10^3$ (°K) ⁻¹ |
|----------------------------|------------------------------|---|------------------------------|-------------------------------|---|
| 1 | 257.20 | 15.988 | 0.085 | 0.0031 | 2.183 |
| 2 | 271.60 | 16.364 | 0.222 | 0.0081 | 2.101 |
| 3 | 309.80 | 16.774 | 1.715 | 0.0623 | 1.919 |
| 4 | 346.50 | 16.878 | 3.652 | 0.1324 | 1.779 |
| 5 | 390.35 | 16.404 | 7.392 | 0.2681 | 1.692 |
| 6 | 366.30 | 16.768 | 5.078 | 0.1841 | 1.739 |
| 7 | 410.25 | 16.413 | 8.582 | 0.3112 | 1.667 |
| 8 | 440.20 | 15.950 | 11.647 | 0.4224 | 1.626 |
| 9 | 460.85 | 15.641 | 13.822 | 0.5013 | 1.600 |
| 10 | 516.20 | 14.543 | 20.951 | 0.7599 | 1.553 |
| 11 | 489.90 | 15.049 | 17.504 | 0.6348 | 1.570 |
| 12 | 577.35 | 13.114 | 30.910 | 1.1211 | 1.502 |
| 13 | 547.10 | 13.718 | 26.037 | 0.9443 | 1.520 |
| 14 | 640.25 | 11.386 | 44.846 | 1.6266 | 1.471 |
| 15 | 606.65 | 12.221 | 37.419 | 1.3572 | 1.490 |
| 16 | 666.30 | 10.531 | 52.739 | 1.9129 | 1.458 |
| 17 | 744.10 | 8.230 | 82.18 | 2.9807 | 1.393 |
| 18 | 702.55 | 9.847 | 61.49 | 2.2303 | 1.426 |

Initial Br₂ pressure in cell = 163.00 mm. Hg at 20.5°C

Final Br₂ pressure in cell = 169.05 mm. Hg at 21.2°C

Table 31. Cell Reaction of Vanadium(III) Chloride with Bromine

| Measurement number | Sample temp. ($^{\circ}\text{K}$) | Average temp. of cell ($^{\circ}\text{K}$) | Gas Law P_{Br_2} (mm.) | Actual P_{Br_2} (mm.) | $\text{P}_{\text{VCl}_3\text{Br}}$ (mm.) |
|--------------------|-------------------------------------|--|--|---------------------------------------|--|
| 1 | 373.2 | 373.9 | 179.85 | 179.75 | -- |
| 2 | 405.2 | 407.2 | 195.87 | 195.82 | -- |
| 3 | 391.4 | 392.4 | 188.75 | 188.70 | -- |
| 4 | 416.4 | 418.5 | 201.31 | 201.25 | -- |
| 5 | 471.4 | 475.1 | 228.53 | 225.52 | 6.01 |
| 6 | 497.4 | 502.8 | 241.86 | 234.21 | 15.30 |
| 7 | 523.0 | 529.4 | 254.65 | 232.67 | 44.16 |
| 8 | 513.4 | 518.8 | 249.55 | 229.04 | 41.02 |
| 9 | 545.7 | 552.7 | 265.86 | 234.94 | 61.84 |
| 10 | 554.7 | 563.4 | 271.01 | 232.23 | 77.56 |
| 11 | 582.8 | 591.1 | 284.33 | 219.40 | 129.86 |
| 12 | 573.0 | 580.3 | 279.14 | 219.68 | 118.92 |
| 13 | 605.7 | 614.1 | 295.39 | 181.56 | 227.66 |
| 14 | 592.4 | 600.9 | 289.04 | 192.12 | 193.84 |
| 15 | 623.6 | 632.6 | 304.29 | 152.92 | 302.74 |
| 16 | 612.2 | 620.6 | 298.52 | 164.39 | 268.26 |
| 17 | 647.4 | 657.4 | 316.22 | 105.09 | 422.26 |
| 18 | 637.7 | 646.8 | 311.12 | 126.76 | 368.72 |
| 19 | 676.6 | 687.1 | 330.51 | 63.58 | 533.86 |
| 20 | 669.7 | 679.9 | 327.05 | 80.52 | 493.06 |

Table 31. (Continued)

| Measure- ment number | Pressure in cell (mm.) | $(P_{\text{Br}_2})^{\frac{1}{2}}$ (mm.) $^{\frac{1}{2}}$ | K in (mm.) $^{\frac{1}{2}}$ | K in (atm.) $^{\frac{1}{2}}$ | $1/T \times 10^3$ ($^{\circ}\text{K}$) $^{-1}$ |
|----------------------------|------------------------------|---|--------------------------------|---------------------------------|---|
| 1 | 195.05 | -- | -- | -- | -- |
| 2 | 212.45 | -- | -- | -- | -- |
| 3 | 204.70 | -- | -- | -- | -- |
| 4 | 218.35 | - | -- | -- | -- |
| 5 | 250.93 | 15.076 | 0.401 | 0.0146 | 2.121 |
| 6 | 270.05 | 15.293 | 1.000 | 0.0363 | 2.010 |
| 7 | 298.35 | 15.254 | 2.985 | 0.1050 | 1.912 |
| 8 | 291.25 | 15.134 | 2.710 | 0.0982 | 1.947 |
| 9 | 319.35 | 15.328 | 4.034 | 0.1463 | 1.832 |
| 10 | 332.80 | 15.239 | 5.090 | 0.1846 | 1.802 |
| 11 | 373.40 | 14.812 | 8.767 | 0.3179 | 1.715 |
| 12 | 362.30 | 14.822 | 8.023 | 0.2910 | 1.745 |
| 13 | 434.30 | 13.474 | 16.900 | 0.6129 | 1.650 |
| 14 | 410.50 | 13.861 | 13.984 | 0.5072 | 1.688 |
| 15 | 481.50 | 12.366 | 24.482 | 0.8879 | 1.603 |
| 16 | 458.00 | 12.822 | 20.922 | 0.7588 | 1.633 |
| 17 | 554.20 | 10.251 | 41.192 | 1.494 | 1.544 |
| 18 | 521.90 | 11.259 | 32.749 | 1.188 | 1.568 |
| 19 | 625.50 | 7.974 | 66.950 | 2.428 | 1.477 |
| 20 | 601.35 | 8.973 | 56.074 | 2.034 | 1.493 |

Initial Br₂ pressure in cell = 141.60 mm. Hg at 21.3 $^{\circ}\text{C}$

Final Br₂ pressure in cell = 147.95 mm. Hg at 21.0 $^{\circ}\text{C}$

Table 32. Cell Reaction of VCl_2Br with Bromine

| Measurement number | Sample temp. ($^{\circ}K$) | Average temp. of cell ($^{\circ}K$) | Gas Law P_{Br_2} (mm.) | Actual P_{Br_2} (mm.) | $P_{VCl_2Br_2}$ |
|--------------------|------------------------------|---------------------------------------|--------------------------|-------------------------|-----------------|
| 1 | 376.42 | 380.3 | 154.32 | 154.20 | -- |
| 2 | 402.86 | 405.92 | 164.64 | 164.60 | -- |
| 3 | 536.4 | 541.6 | 208.97 | 194.84 | 28.26 |
| 4 | 557.2 | 560.4 | 217.23 | 193.71 | 47.04 |
| 5 | 583.1 | 586.4 | 228.12 | 184.24 | 87.76 |
| 6 | 574.8 | 578.3 | 233.94 | 196.43 | 75.02 |
| 7 | 616.4 | 619.1 | 250.53 | 165.31 | 170.44 |
| 8 | 603.2 | 605.2 | 244.87 | 175.24 | 139.26 |
| 9 | 631.6 | 634.1 | 259.19 | 147.28 | 223.82 |
| 10 | 619.5 | 623.7 | 251.88 | 160.56 | 182.64 |
| 11 | 654.7 | 657.5 | 266.39 | 113.18 | 306.42 |
| 12 | 643.5 | 649.3 | 263.48 | 130.06 | 266.84 |
| 13 | 680.2 | 685.1 | 277.71 | 75.02 | 405.38 |
| 14 | 671.4 | 680.9 | 275.86 | 90.72 | 370.28 |
| 15 | 692.8 | 694.7 | 281.63 | 55.36 | 452.54 |
| 16 | 684.1 | 687.8 | 279.04 | 72.78 | 412.52 |
| 17 | 701.0 | 704.2 | 285.37 | 47.84 | 475.06 |
| 18 | 663.3 | 667.1 | 270.42 | 100.18 | 340.52 |
| 19 | 710.4 | 711.1 | 288.10 | 37.42 | 501.38 |

Table 32. (Continued)

| Measure- ment number | Pressure in cell (mm.) | $(P_{\text{Br}_2})^{\frac{1}{2}}$ (mm.) ^{1/2} | K in (mm.) ^{1/2} | K in (atm.) ^{1/2} | $1/T \times 10^3$ (°K) ⁻¹ |
|----------------------------|------------------------------|---|------------------------------|-------------------------------|---|
| 1 | 161.85 | -- | -- | -- | -- |
| 2 | 172.80 | -- | -- | -- | -- |
| 3 | 224.10 | 13.953 | 2.023 | 0.0732 | 1.867 |
| 4 | 240.75 | 13.912 | 3.390 | 0.1230 | 1.793 |
| 5 | 272.00 | 13.582 | 6.469 | 0.2347 | 1.716 |
| 6 | 271.45 | 14.102 | 5.324 | 0.1932 | 1.740 |
| 7 | 335.75 | 12.871 | 13.264 | 0.4806 | 1.623 |
| 8 | 314.50 | 13.231 | 10.528 | 0.3819 | 1.658 |
| 9 | 371.10 | 12.137 | 18.432 | 0.6680 | 1.583 |
| 10 | 343.20 | 12.659 | 14.437 | 0.5212 | 1.613 |
| 11 | 419.60 | 10.640 | 28.802 | 1.044 | 1.529 |
| 12 | 396.90 | 11.402 | 23.216 | 0.8423 | 1.553 |
| 13 | 480.40 | 8.661 | 46.75 | 1.696 | 1.470 |
| 14 | 461.00 | 9.524 | 38.91 | 1.410 | 1.481 |
| 15 | 507.90 | 7.443 | 60.80 | 2.204 | 1.443 |
| 16 | 485.30 | 8.531 | 48.26 | 1.751 | 1.462 |
| 17 | 522.90 | 6.915 | 68.71 | 2.491 | 1.427 |
| 18 | 440.70 | 10.004 | 34.05 | 1.235 | 1.508 |
| 19 | 538.80 | 6.115 | 81.98 | 2.974 | 1.408 |

Initial Br₂ pressure in cell = 120.00 mm. Hg at 22.6°C

Final Br₂ pressure in cell = 126.35 mm. Hg at 23.2°C

Table 33. Transport of Vanadium(III) Bromide by Bromine

| Sample number | Mmoles Br ₂ | P _{Br₂} (atm. x 10 ³) | Vol. of Br ₂ (l.) | Flow rate of Br ₂ (ml./min.) | Temp. (°K) | Mmoles V | P _{VBr₄} (atm. x 10 ²) |
|---------------|------------------------|---|--------------------------------|---|------------|----------|--|
| 3 | 0.79 | 1.58 | 2.30 | 30 | 561 | 0.625 | 1.25 |
| 4 | 0.46 | 1.58 | 1.34 | 45 | 561 | 0.381 | 1.31 |
| 5 | 0.36 | 1.58 | 1.14 | 21 | 561 | 0.335 | 1.35 |
| 7 | 2.53 | 88 | 1.32 | 45 | 561 | 0.957 | 3.34 |
| 8 | 1.98 | 89 | 1.03 | 62 | 561 | 0.742 | 3.31 |
| 9 | 4.23 | 88 | 2.21 | 9 | 561 | 1.91 | 3.97 |
| 10 | 3.18 | 88 | 1.66 | 33 | 561 | 1.22 | 3.38 |
| 11 | 3.02 | 111 | 1.26 | 27 | 561 | 1.04 | 3.80 |
| 12 | 4.66 | 111 | 1.94 | 38 | 561 | 1.59 | 3.77 |
| 13 | 8.31 | 112 | 3.47 | 107 | 561 | 2.72 | 3.61 |
| 14 | 5.14 | 111 | 2.14 | 11 | 561 | 1.81 | 3.90 |
| 15 | 7.38 | 217 | 1.57 | 22 | 561 | 1.86 | 5.45 |
| 16 | 9.52 | 216 | 2.03 | 67 | 561 | 2.34 | 5.30 |
| 17 | 11.37 | 217 | 2.43 | 98 | 561 | 2.78 | 5.26 |
| 18 | 10.51 | 217 | 2.23 | 38 | 561 | 2.60 | 5.35 |
| 20 | 1.03 | 1.58 | 3.18 | 52 | 587 | 1.77 | 2.72 |
| 22 | 3.71 | 111 | 1.64 | 47 | 587 | 2.41 | 7.17 |
| 23 | 12.79 | 219 | 2.80 | 30 | 587 | 5.86 | 10.2 |
| 25 | 0.43 | 1.58 | 1.15 | 46 | 515 | 0.112 | 0.41 |
| 26 | 2.78 | 111 | 1.06 | 35 | 515 | 0.272 | 1.08 |
| 27 | 9.93 | 220 | 1.88 | 28 | 514 | 0.673 | 1.51 |