

1966

Condensed phase and vaporization equilibria in vanadium(II) halide-iodine systems

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**BERRY, Keith Oran, 1938-
CONDENSED PHASE AND VAPORIZATION
EQUILIBRIA IN VANADIUM(II) HALIDE-
IODINE SYSTEMS.**

**Iowa State University of Science and Technology,
Ph.D., 1966
Chemistry, inorganic**

University Microfilms, Inc., Ann Arbor, Michigan

CONDENSED PHASE AND VAPORIZATION EQUILIBRIA
IN VANADIUM(II) HALIDE-IODINE SYSTEMS

by

Keith Oran Berry

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Inorganic Chemistry

Approved:

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In Charge of Major Work

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Iowa State University
Of Science and Technology
Ames, Iowa

1966

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INTRODUCTION

In recent years a great deal of interest has been shown in the vaporization characteristics of transition metal halide systems (1-6). Although these systems have been known for many years, experimental difficulties probably have caused many investigators to shy away from problems associated with a study of sublimation and vaporization processes.

Transition metals in groups IV, V and VI have halide systems which pose particularly difficult problems. There are several significant factors which contribute to these problems. First, these metals tend to show multiple oxidation states; vanadium, in particular, exhibits oxidation states of 2, 3, 4 and 5 in its binary halides (7). Multiple coordination numbers and varying molecular geometries are observed. Second, many of the metal halides have been difficult to obtain in a sufficiently pure state to insure reliable data. This is especially true with the heavy metals of the same families which have nearly identical atomic radii, such as zirconium-hafnium or niobium-tantalum (8,9). Third, the halides generally are quite reactive in the presence of water vapor, oxygen, or both. Thus they are difficult to prepare and maintain in a pure state. Vacuum and glove box techniques

must be used for the preparation and handling of the samples.

Perhaps the most important factor encountered in the determination of vaporization equilibria is that many systems may have several processes which operate simultaneously. Among these processes the following may be noted: simple (monomeric) vaporization, polymeric vaporization, disproportionation and dissociation into a lower halide and elemental halogen. Vaporization, then, assumes a more general meaning than boiling or sublimation only.

With the advent of the "iodide" process for the purification of transition metals it has become important to know the mechanism by which it operates. The purpose of this investigation has been to clarify and more fully understand the various vaporization processes of the vanadium(II) halides and particularly those of VI_2 .

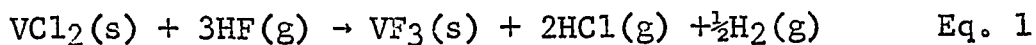
Preparation of Vanadium Halides

Binary halides were, along with the oxides, among the first compounds of vanadium to be prepared (10). Although many reports have been published describing the preparations of these compounds, preparations for the vanadium iodides are scarce. A review of the methods available for the preparation of the vanadium(II) halides will be presented. Roddy

(11) has previously reviewed the preparations and stabilities of the higher halides of vanadium, with the exception of the fluorides, and these will not be repeated. In most cases, however, the most convenient route to a pure lower halide is via reduction, decomposition, or disproportionation of a higher-valent halide.

Vanadium(II) fluoride

Unlike the other divalent halides of vanadium, VF_2 has not been reported. Several methods have been used in an effort to produce this unstable halide including the obvious metathetical reaction between VCl_2 and gaseous hydrogen fluoride (12). Unfortunately the major product was VF_3 as shown in Equation 1.



Mutterties (13) also suggests that the reaction between vanadium metal and liquid hydrogen fluoride produces VF_3 , although the reaction is extremely slow. Manchot (14) has, however, suggested that a solution obtained from the reaction between $\text{V}_8\text{Al}_2\text{Si}_{13}$ and aqueous hydrogen fluoride in the absence of air contained VF_2 ; no product was isolated, nor were any analytical data obtained.

Vanadium(II) chloride

Vanadium(II) chloride is a light green solid which reacts slowly with oxygen and water to produce a brown solution. The color slowly changes to green, the characteristic color of hydrated vanadium(III) ion, upon standing in a closed container. The lattice constants of its cadmium iodide-type lattice are: $a_0 = 3.60 \pm 0.01\overset{\circ}{\text{A}}$, $c_0 = 5.82 \pm 0.01\overset{\circ}{\text{A}}$ (15,16, 17).

This substance has been prepared by hydrogen reduction of VCl_3 at 750°C . (18), and at less than 675°C . (19). It has also been prepared by thermal disproportionation of VCl_3 at temperatures near 800°C . (20,21). Vanadium metal when oxidized with hydrogen chloride gas at 950°C . gives VCl_2 , though the reaction is quite slow (17, p. 2146).

Vanadium(II) bromide

The hexagonal lattice in which this pale pink substance crystallizes has the following constants: $a_0 = 3.768\overset{\circ}{\text{A}}$, $c_0 = 6.180\overset{\circ}{\text{A}}$ (22). Again, as with VCl_2 , a brown solution which changes slowly to green is obtained by dissolving VBr_2 in water.

Hydrogen reduces VBr_3 to VBr_2 above 400°C . (23) and this has become the usual method of preparation.

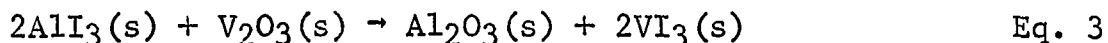
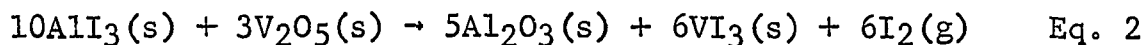
Vanadium(II) iodide

Klemm prepared VI_2 by the reaction between vanadium metal and iodine vapor at temperatures near 400°C . (22, p. 200). The thermal decomposition of VI_3 above 270°C . has been reported (24,25).

The black, micaceous crystals have a hexagonal structure of the cadmium iodide-type with the following reported constants: $a_0 = 4.00\text{\AA}$, $c_0 = 6.67\text{\AA}$ (22, p. 202). Although the solid does react with water and oxygen to produce a brown solution, it is not nearly as susceptible to attack as either VCl_2 or VBr_2 .

Vanadium(III) iodide

Hydrated vanadium(III) iodide, having the formula $\text{VI}_3 \cdot 6\text{H}_2\text{O}$, has been formed by the electrolytic reduction of an aqueous hydriodic acid solution of V_2O_5 (26). Morette (24, p. 220) has suggested that the anhydrous compound may be prepared by reacting powdered vanadium with iodine vapor in a sealed tube between 150 and 280°C . He also states that iodine vapor will react with VI_2 in a reversible equilibrium reaction to give VI_3 . Chaigneau reports the preparation of VI_3 from AlI_3 and V_2O_5 or V_2O_3 at 280°C . according to Equations 2 and 3 (25, p. 888).



Tolmacheva and co-workers (27) indicate the preparation of VI_3 by reacting vanadium foil and liquid iodine at 300°C , the product being deposited on the surface of the metal.

Vanadium(III) iodide is extremely reactive in the presence of oxygen and water vapor; it dissolves easily and care must be taken to prevent hydrolysis.

As well as the iodides previously mentioned, there is a report of V_2I_3 and VI_5 (28). It is likely that the former was a mixture of metal halide and metal or an oxyiodide. The VI_5 was observed in the vapor phase only. It was never isolated and the composition was purely speculation.

Vaporization Processes

One of several general types of processes must be observed in any vaporization operation. Before any of these processes will be considered a few reservations must be pointed out, then specific chemical systems can be considered. Many systems are known for which more than one process occurs simultaneously. An example is the vaporization of VBr_3 (1, p. 55). This substance, under the proper conditions, will vaporize as a monomer, decompose and disproportionate simultane-

ously. Secondly, different processes may occur at different temperatures within the same system.

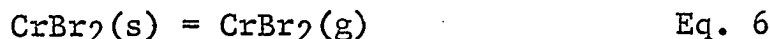
Examples for the following discussion will be taken from metal halide systems, but the processes are equally as applicable to all other systems. All systems will vaporize according to one of the following processes.

Simple vaporization

The simplest and most obvious vaporization process is that in which either a solid or liquid substance becomes a vapor with no change other than its physical state. The general equation for this process is shown in Equation 4.

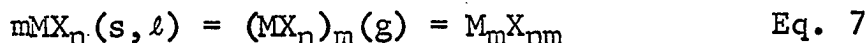


Typical examples of this type of vaporization are the FeCl_2 (29) and CrBr_2 (30) systems, Equations 5 and 6 respectively.

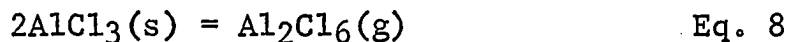


Polymer vaporization

Only slightly more complex is polymeric vaporization. In this case the vapor species is a dimer or higher polymer of the original material. Equation 7 illustrates this process.

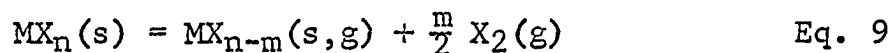


One may cite the vaporization of AlCl_3 (31), as shown in Equation 8, as an example.

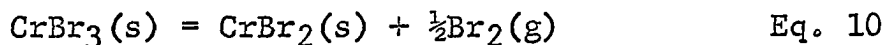


Decomposition vaporization

As its name implies, this type of vaporization involves decomposition of the substance giving a lower valent product, perhaps even the free element. Equation 9 illustrates the process.

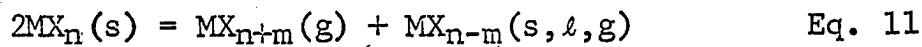


The decomposition of CrBr_3 , as shown by Equation 10, is illustrative of this vaporization mode (4, p. 93).



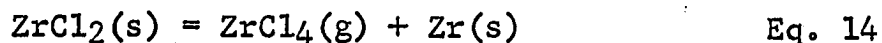
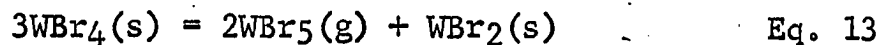
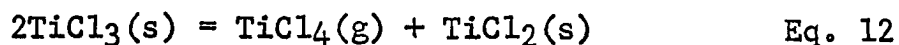
Disproportionation vaporization

Perhaps the most complex vaporization process is disproportionation vaporization. The products of such a reaction are a volatile higher halide and a lower valent product, either volatile or non-volatile. In some cases the lower valent product is the metal. The general process is illustrated by Equation 11.



Typical examples may be found in the TiCl_3 (32), WBr_4 (33) and ZrCl_2 (34) systems, shown in Equations 12, 13 and 14,

respectively.



Closely associated with these processes are equilibrium reactions which include vapor species as reactants. Many transport reactions are known in which this type of equilibria is observed. In fact, a transport reaction is defined as one in which a solid or liquid substance reacts with a gas to form exclusively vapor phase reaction products, which then undergo the reverse reaction at a different place in the system (35).

Vaporization equilibria, then, may include a greater number of reactions than the four basic vaporization processes. Several vanadium halide systems have been studied and their important vaporization modes determined. The number of reports concerned with the vanadium iodides is quite small, however. The objects of the current work are to study the vanadium iodide system, to investigate the equilibrium between VI_2 and iodine and to compare the behavior of this system with that of the vanadium chlorides and vanadium bromides.

Comparison of Properties of Vanadium Halides

Table 1 shows the known or reported halides of vanadium.

Table 1. Halides of vanadium in various oxidation states including physical state at room temperature^a

Oxidation state	F	Cl	Br	I
V	VF ₅ (s) ^b			
IV	VF ₄ (s)	VCl ₄ (l)	VBr ₄ (g) ^c	
III	VF ₃ (s)	VCl ₃ (s)	VBr ₃ (s)	VI ₃ (s) ^d
II		VCl ₂ (s)	VBr ₂ (s)	VI ₂ (s)

^aReferences to all but VBr₄ are given by Sidgwick (21, pp. 815-833).

^bPhysical state designated by (s) solid, (l)liquid and (g) gas.

^cVBr₄ is not stable at room temperature, but may be observed in the vapor phase under the proper conditions (1, p. 57).

^dThere is some doubt about the existence and stability of VI₃.

A brief examination of the table shows that only a very strong oxidizing agent such as fluorine is able to cause vanadium to accept its maximum oxidation state for the halide systems, while the maximum oxidation state reported for the iodides is in VI₃. It is obvious, then, that as one proceeds

down the series fluoride, chloride, bromide, iodide, the higher-valent states become less stable and the lower-valent states more stable. This trend is enhanced, of course, by the absence of a report of VF_2 .

For the fluorides, VF_5 can be easily sublimed without decomposition. Vanadium(IV) fluoride disproportionates significantly at 325° to give $\text{VF}_5(\text{g})$ and $\text{VF}_3(\text{s})$ (20, p. 819). One may compare this behavior with that of VCl_4 and VBr_4 , both of which decompose to give the corresponding vanadium(III) halide and elemental halogen (36; 1, p. 57). Vanadium(III) fluoride is reasonably stable, melting above 800° and beginning to sublime at ca. 600°C . (37). Again the remaining halides differ markedly. Vanadium(III) chloride is practically non-volatile, disproportionating readily at elevated temperatures to give $\text{VCl}_4(\text{g})$ and $\text{VCl}_2(\text{s})$. On the other hand, VBr_3 not only disproportionates under the proper conditions, but undergoes decomposition to $\text{BBr}_2(\text{s})$ and $\text{Br}_2(\text{g})$ as well (2, p. 62). Both VCl_2 and VBr_2 are relatively stable, vaporizing by sublimation (2, p. 61). This behavior is similar to that of VI_2 .

There is a limited amount of thermodynamic data available for the formation and vaporization processes of the vanadium halides. Table 2 gives the heats of formation. The vaporiza-

Table 2. Heats of formation of the vanadium halides

Substance	Heat of formation (kcal/mole)	Reference
VF ₅	(-335 ± 20) ^a	38
	-321 ^b	39
VF ₄	(-325 ± 30)	38, p. 108
	-352 ^b	40
VF ₃	(-285 ± 30)	38, p. 108
VCl ₄	(-141 ± 30)	38, p. 108
	-165 ± 4	41
VCl ₃	(-138)	42
	(-139 ± 20)	38, p. 108
	(-145)	43
	-187 ± 8	41, p. 280
VCl ₂	(-137)	42, p. 52
	-143 ± 1	44
	(-117 ± 20)	38, p. 108
	(-88 to -135) ^b	43, p. 3324
	-147 ± 4	41, p. 300
	(-108)	42, p. 52
VBr ₄	-110 ± 8	45
	-110	46
	(-129 ± 30)	38, p. 108
	(-120 ± 30)	38, p. 108
	(-115 ± 30)	42, p. 52
	-147 ± 1	41, p. 300
VBr ₃	(-108)	47
	-110 ± 1	46, p. 9
	-118	48
	(-104 ± 20)	38, p. 108
VBr ₂	(-62 to -99) ^c	43, p. 3324
	-67 ± 2	27, p. 282
VI ₃	(-77 ± 20)	38, p. 108
VI ₂	-63 ± 3	27, p. 283

^aEstimated values are given in parentheses.

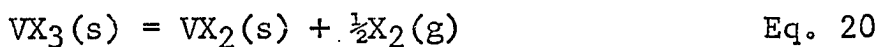
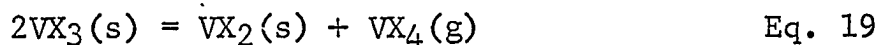
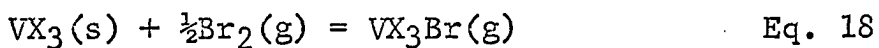
^bThese values are the best accepted values.

^cMaximum and minimum values are given; the calculated values depend on several estimated quantities.

tion and equilibrium data may be represented, in most cases, by the equation:

$$\log P \text{ (or } K) = -\frac{A}{T} + B . \quad \text{Eq. 15}$$

Using an equation of this type the data which have been reported may be tabulated. In Table 3 are listed the data for the vanadium halides undergoing the processes illustrated by Equations 16 through 21.



There are no vaporization data for the vanadium fluorides. The vanadium chlorides have been studied more thoroughly; there is even data available for the vaporization of VCl_4 . Vanadium(III) iodide, although much less stable than VI_2 , is the only vanadium iodide to have its vaporization data reported. The VBr_3 system is most complex, since its vaporization involves processes 17, 19 and 20 simultaneously. It appears that there are some contradictory data, however, and care must be taken to determine which are valid.

Table 3. Thermodynamic data of some vanadium halides

Substance	Process	Temperature range (°K)	ΔH° (kcal/mole)	ΔS° (eu)	A	B	Reference
VC1 ₂	16	750-950	44.8 \pm 1.4	26.6 \pm 0.8	9804	8.71	11,p.163
VC1 ₂	16	910-1100	44 \pm 1	26.1 \pm 0.5	(9720.5)	(5.725)	5,p. 258
VBr ₂	16	750-950	47.8 \pm 1.6	28.3 \pm 0.8	10460	9.08	11,p.163
VC1 ₃	17	625-740	44.7 \pm 1.4	38.0 \pm 0.8	9777	11.20	11,p.163
VC1 ₃	18	525-680	15.8 \pm 1.5	25.0 \pm 2.5	3450	5.48	11,p.163
VC1 ₃	19	625-740	36.0 \pm 1.0	32.0 \pm 1.2	7801	9.84	11,p.163
VC1 ₃	19	600-925	38.0 \pm 1.0	39.6 \pm 5.0	(8350)	(8.70)	49
VBr ₃	19	490-650	38.0 \pm 2	41.5 \pm 2	(8325)	(9.125)	50
VBr ₃	19	590-697	37.7 \pm 1.3	25.5 \pm 0.8	8240	6.47	11,p.163
VBr ₃	17	590-700	43.3 \pm 1.2	37.7 \pm 1.0	9470	11.12	11,p.163
VBr ₃	18	540-680	15.8 \pm 1.5	23.9 \pm 2.4	3465	5.23	11,p.163
VBr ₃	18	523-873	19.1 \pm 1.0	33.1 \pm 1.0	(4200)	(7.2)	48,p.680
VBr ₃	20	590-700	23.1 \pm 0.9	9.3 \pm 0.4	5070	5.02	11,p.163
VI ₃	20	573-803	22.0 \pm 1	27.0 \pm 1	(4800)	(5.9)	27,p.283
VC1 ₂ Br	18	540-680	15.8 \pm 1.5	24.2 \pm 2.3	3460	5.30	11,p.163
VC1 ₄	21	273-363	9.9 \pm 0.1	23.7 \pm 0.5	(2174)	(5.19)	51

^aFor numbers given in parentheses, $\log P \equiv \log P_{\text{atm}}$; for numbers without parentheses, $\log P \equiv \log P_{\text{mm}}$.

de Boer-Van Arkel Process

The vanadium iodide system has a very important use in the purification of vanadium metal starting with crude feed metal. For this reason it is well to discuss the process here.

Although other researchers had begun on the thermal decomposition of various metal halides such as WCl_6 (52), it was Van Arkel and de Boer (53) who extended the work to volatile metal iodides. The process has been called variously the "de Boer," "hot wire," and "iodide" process.

The iodide process is essentially a process of elemental iodine vapor reacting with crude metal to form a volatile iodide and the subsequent thermal decomposition of that iodide into pure metal and elemental iodine. The iodine thus liberated diffuses back to the feed metal where the process is repeated (54).

There are several advantages in using iodine for such a process. Metal iodides exhibit lower thermal stabilities than the corresponding bromides, chlorides or fluorides. Iodine reacts with most elements to yield volatile compounds moderately stable in the vapor phase but thermally dissociable at high temperatures. Iodine reacts with most carbides and nitrides, but not oxides.

Van Arkel has outlined the following conditions which must be fulfilled before a metal can be considered for purifications by the "iodide" process. (55):

1. The metal must form a volatile iodide.
2. The metal must have a melting point greater than the temperature of the deposition element.
3. The volatile iodide must form at a convenient and sensible temperature.
4. The compound must be decomposed easily at a higher temperature.
5. The metal should have a low vapor pressure at the decomposition temperature.

For the reasons stated it becomes important to know as much about the vaporization characteristics of the vanadium iodide system as possible.

EXPERIMENTAL

Materials

Vanadium

The vanadium metal used for all preparations was obtained from Dr. O. N. Carlson (56). It was obtained as a bar, but cold rolled before use. A typical spectrographic analysis showed the following elements present in the indicated amount:

C	154 ppm	Si	<40 ppm
H	<15 ppm	Mg	<15 ppm
O	120 ppm	Mn	<25 ppm
N	<10 ppm	Ni	<50 ppm
Fe	500 ppm	Al	<20 ppm
Cr	700 ppm	Ca	<20 ppm
Ti	100 ppm	Cu	50 ppm

After several of the halide preparations a quantity of metal was found unreacted. This metal was reclaimed by dissolving any surface coating with dilute acid, washing the metal with water, and outgassing in vacuo before further use.

Iodine

Reagent-grade iodine was obtained from the J. T. Baker Chemical Co. It was purified further by outgassing in vacuo to 10^{-5} torr, then stored in sealed glass containers for later use. Whenever it was necessary for the iodine to be pulverized it was ground under an atmosphere of dry nitrogen in a polyethylene bag.

All other chemicals were obtained from commercial sources and were not purified further.

Analytical Procedures

Vanadium

Two procedures were used, one volumetric, the other colorimetric. The former was essentially the method given by Scott (57) for determination of VO^{++} , modified by using cerium (IV) as titrant rather than permanganate ion and detecting the endpoint potentiometrically. Using a saturated calomel reference electrode and a platinum wire indicating electrode an accuracy of at least 0.2 per cent could be obtained, the precision being less than 0.25 per cent.

For small vanadium contents, e.g. in the 0.02 to 4 milligram range, the procedure developed by Wright and Mellon (58) was used. This method was based on the formation of a stable, highly colored, soluble phosphotungstate complex of pentavalent vanadium. Concentrations of the reagents were not particularly critical, but the solutions were made 0.5 molar in nitric acid, 0.5 molar in phosphoric acid and 0.025 molar in sodium tungstate. The solution or precipitate initially obtained was transformed to a clear yellow solution after boiling. The spectrum showed a shoulder at 400 to 450

readings were made at 420 $m\mu$. A blank and standard were measured each time an unknown sample was measured. A calibration curve showed that the solutions obeyed Beer's law within the range of 0.02 to 4 milligrams vanadium per 100 ml. solution.

All spectral measurements were made on a Beckman DU spectrophotometer using matched corex cells having a path length of one centimeter. The method yielded an accuracy on the order of one per cent. The precision was in the same range, usually less than one per cent.

Iodide

Two methods were used for iodide. The first was the titration of iodide ion with standard silver nitrate in acidic solution (59). The end point was determined potentiometrically using a silver wire indicating electrode. With careful attention to detail an accuracy of about one per cent could be obtained.

Secondly, the normal iodimetric method was used (60). The sample was oxidized with potassium iodate before titration with standard thiosulfate. An accuracy of 0.5 per cent was observed, while the precision was on the order of 0.2 per cent.

X-ray diffraction

X-ray powder patterns, used for identification of compounds and phases, were obtained with a 114.59 mm diameter Debye-Scherrer camera. Samples were ground until they passed through a 200 mesh screen before they were packed into a 0.2 mm Lindeman capillary. The capillaries were sealed upon removal from the dry-box.

The material was exposed to nickel-filtered $\text{CuK}\alpha$ radiation for periods of 18-26 hours, depending on the intensity of radiation. Conversion of θ values to interplanar spacings was accomplished by use of tables from the National Bureau of Standards (61).

Whenever precise lattice parameters were needed, as with the samples from equilibration experiments, they were determined by use of either of three methods. The first was an extrapolation of lattice parameter against the Nelson-Riley function (62). Second, the Cohen method was used (63). The third method was a least square curve fitting using the function shown in Equation 22.

$$\frac{1}{d^2} = \frac{4\sin^2\theta}{2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2} \quad \text{Eq. 22}$$

This procedure was performed on an IBM 7074 computer. Data for θ and hkl were fed in. Values for "a" and "c" were

matched with the appropriate $hk\ell$ data to give a calculated value of $\sin^2\theta$ as close to the observed $\sin^2\theta$ as possible. A least-square treatment then gave the best value of "a" and "c".

Preparation of the Halides

Vanadium(II) iodide

Direct combination of the elements gives a black micaeous solid of variable composition. This solid was decomposed under vacuum at 300°C . to give VI_2 . The decomposition to VI_2 was considered complete when no more iodine could be found in a cold trap at -196°C .

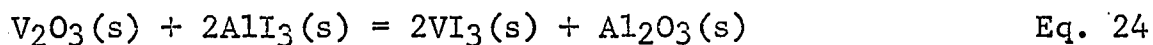
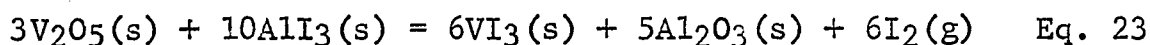
A straight vycor tube was used to prepare the non-stoichiometric iodide in a transport reaction similar to that described by Klemm (22, p. 198). The tube and contents, an excess of iodine being used, were outgassed to 10^{-5} torr and sealed. The tube was placed in a furnace providing a temperature gradient of 600°C (metal) to 180°C (iodine). After a period of about a week, the product was found in the area of the tube bounded by temperatures of 260 and 190° . Excess iodine was then removed by vacuum sublimation.

Vanadium(III) iodide

Preparations of VI_3 proved to be particularly difficult.

The first series of experiments were equilibration studies designed to study the composition of the product as a function of temperature. These experiments will be discussed later in greater detail.

The second method used for the preparation of VI_3 was the reaction between a vanadium oxide, either V_2O_3 or V_2O_5 and AlI_3 as illustrated by Equations 23 and 24.



In either case, the reactants were placed in a Pyrex vessel as shown in Figure 1. The tube was loaded in the dry-box, evacuated, sealed and placed in a furnace so that the small terminal bulb was at room temperature and the remainder of the tube at 230°C . The reaction was terminated after twenty-four hours (25, p. 887). All iodine formed in the reaction sublimed to the cool bulb, but the remaining products were most difficult to separate. Fractional sublimation allowed removal of excess AlI_3 , but the vanadium product did not sublime.

A third experiment utilized a solvent extraction procedure with liquid iodine as the solvent. The apparatus shown in Figure 2, was basically a soxhlet extractor. The

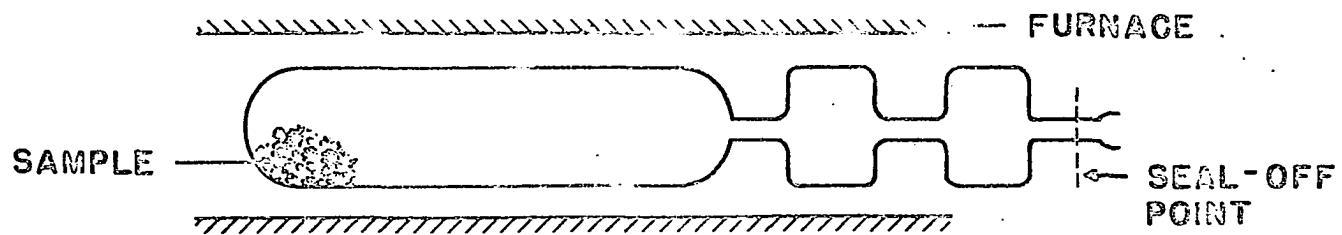


Figure 1. Apparatus for reaction of V_2O_5 or V_2O_3 with AlI_3

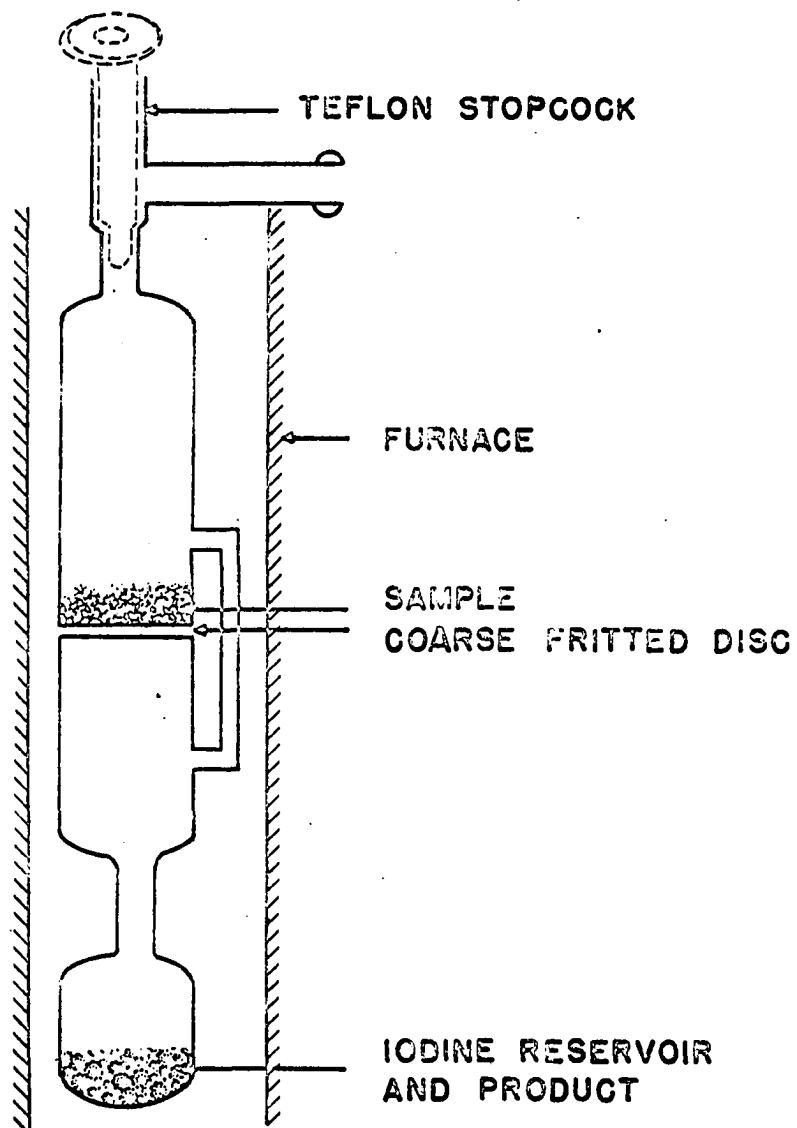


Figure 2. Apparatus for extraction of VI_2 with liquid iodine

extractor, modified from an earlier design (64) was constructed so that it would fit into a furnace with a 30 mm inside diameter. The iodine was held at $182^{\circ}\text{C.} \pm 1^{\circ}$ while the sample temperature was $168^{\circ}\text{C.} \pm 1^{\circ}$; the difference was due to the natural temperature gradient of the furnace. After a ten day reaction period the tube was removed and quenched to room temperature with compressed air. Excess iodine was removed by sublimation in vacuo. Products were observed in the bulb and on the frit. These samples were removed, ground to 200 mesh, analyzed and prepared for x-ray analysis.

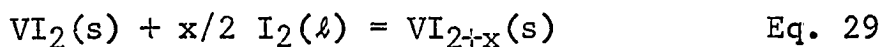
The last method was the reaction between vanadium metal foil and liquid iodine (27, p. 281). A small ampoule was used as a reaction vessel; the vessel was charged with the elements, evacuated, sealed, and suspended in a furnace at 300°C. for two days. The tube was cooled, opened and the sample was placed in a new tube for removal of excess iodine. The product was then removed from the unreacted vanadium.

Equilibration Experiments

In order to study the effect of temperature on the composition of the VI_2 phase in equilibrium with iodine a series of equilibration experiments was completed using the following procedure.

The sample of VI_2 was placed in the equilibration tube, a diagram of which is shown in Figure 3a. The sample was outgassed to at least 4×10^{-5} torr and the tube sealed. The center section was evacuated and sealed. Iodine was placed in the remaining container and outgassed before the tube was sealed. The break-seals were broken and iodine was forced into the tube containing VI_2 . The tube was then sealed off giving an ampoule, as shown in Figure 3b, that was approximately 40 mm. in length by 12 mm. in diameter.

The ampoules were suspended in a resistance furnace, supplied with a stainless steel liner to reduce irregular temperature gradients. The furnace temperature was controlled with a Bristol time-proportioning controller, but the temperature was measured with a calibrated thermocouple hooked to a Rubicon potentiometer. Three tubes were placed in the furnace at the same time; however, each was removed at a different time. Such a procedure was designed to provide data on the length of time necessary to establish an equilibrium according to Equation 29.



Tubes were removed after lengths of time varying from 5 to 21 days.

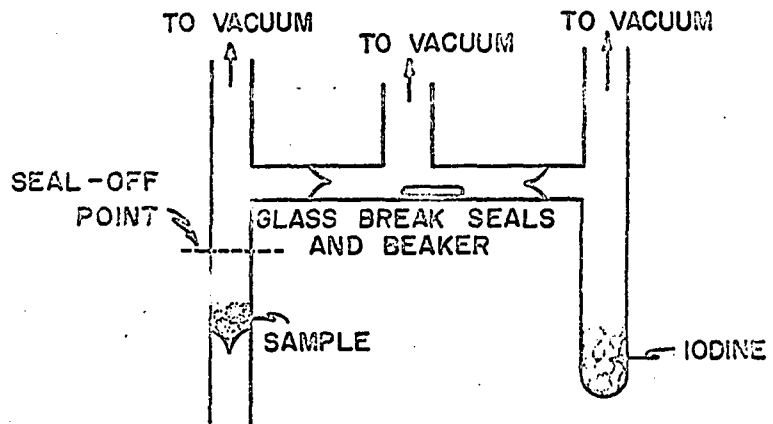


Figure 3a. Apparatus for preparing samples to be equilibrated with liquid iodine

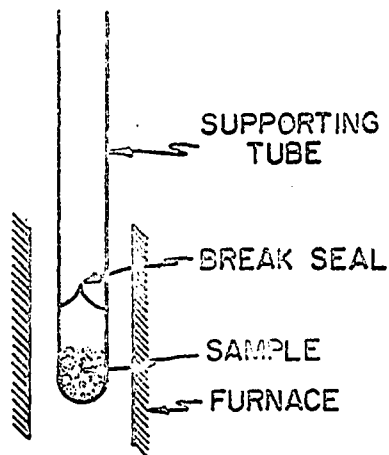


Figure 3b. Sample arrangement during equilibration with liquid iodine

Immediately upon removal from the furnace each ampoule was quenched in a stream of compressed air until the ampoule and contents were at room temperature. The end of the ampoule having the break seal was attached to the vacuum line and evacuated; the seal was broken and iodine removed from the equilibration sample by vacuum sublimation at room temperature. Removal of iodine was considered complete when no more iodine was deposited in a cold trap at -196°C . The tube then was sealed, opened in the dry-box, and samples taken for analyses and x-ray diffraction patterns.

Vapor Pressure Measurements

Transpiration method

A diagram of the transpiration cell, including appropriate condensers, is shown in Figure 4. This cell was a modification of one designed by Mr. W. Tadlock of the Ames Laboratory; his cell, in turn, was modified from a description given by Treadwell and Werner (65). The cell was designed so that the carrier gas flowed through the sample and fritted disc into the condensers.

Figure 5 shows a diagram of the entire transpiration apparatus. Two basic types of experiments could be performed using the transpiration apparatus. That is, the carrier gas

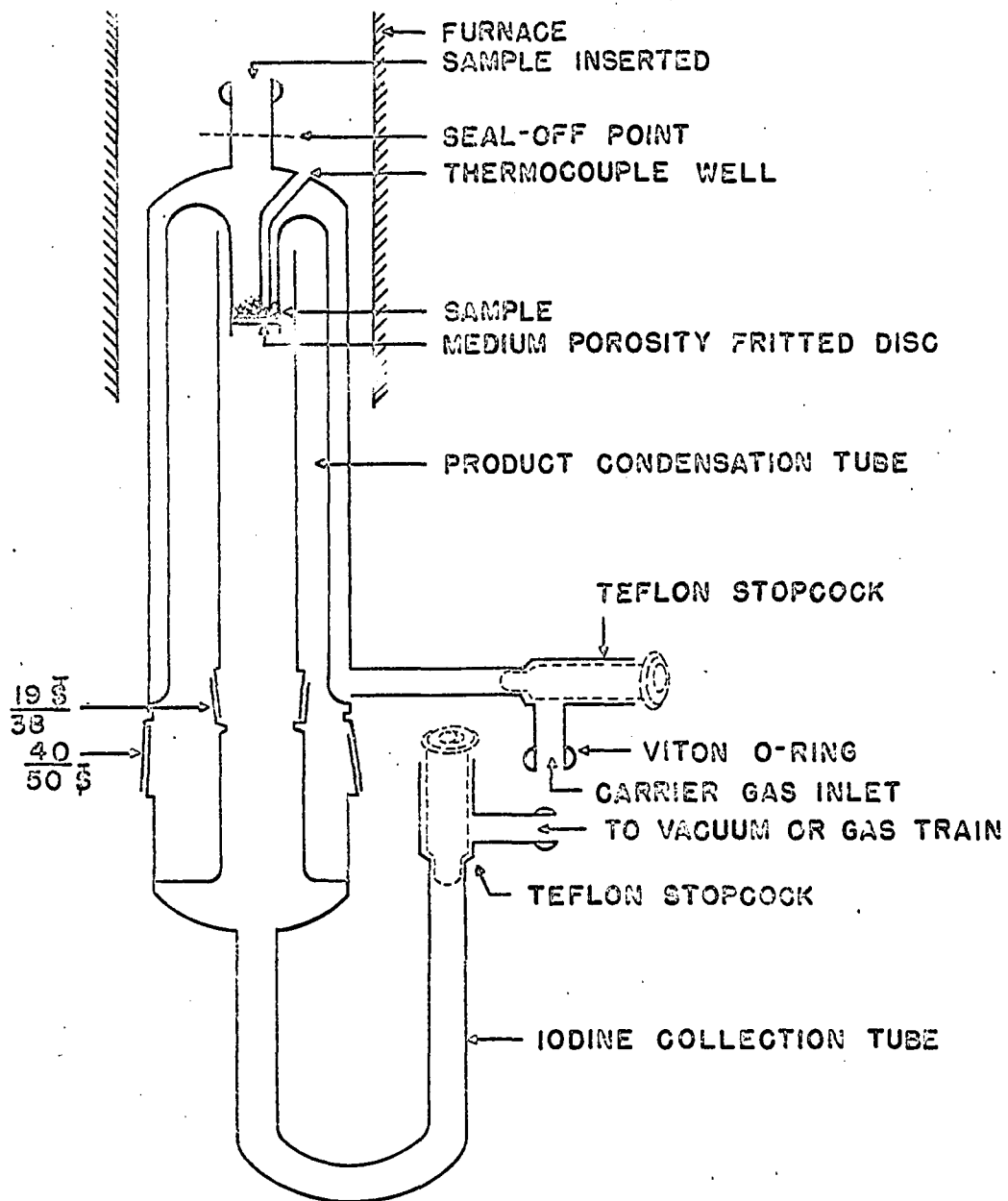


Figure 4. Transpiration cell

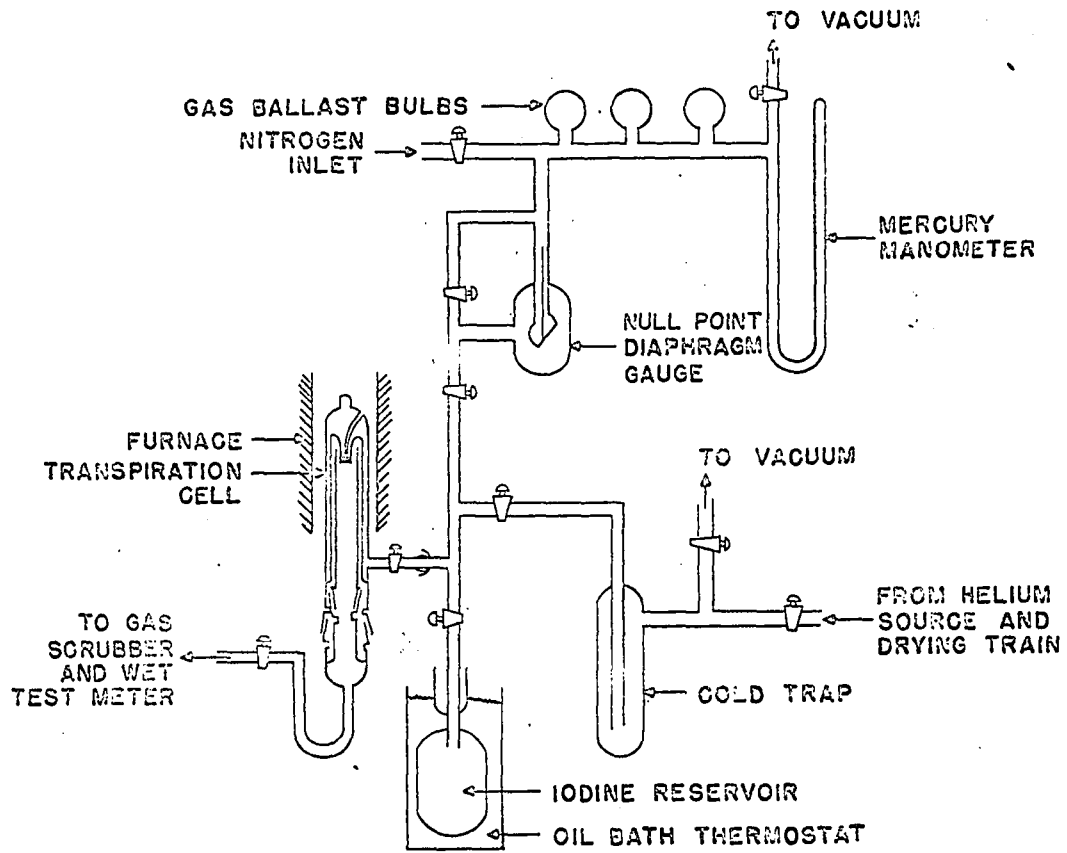


Figure 5. Transpiration cell and associated apparatus

could be either an inert gas, or one which would react with the sample. The carrier gas used in this work was iodine.

Iodine, purified and ground under an atmosphere of dry nitrogen, was placed in the iodine reservoir and outgassed to less than 2×10^{-5} torr. It was also outgassed periodically between experiments to ensure the purity of the supply.

The oil bath, used as a thermostat to control the iodine pressure, was a Pyrex container insulated with layers of aluminum foil and asbestos paper. The bath was heated and cooled with a Cal-rod heater and copper coil, respectively. The temperature was controlled by a microthermoregulator and relay.

The flow rate was controlled by the teflon needle-valve positioned directly above the iodine reservoir. All stopcocks, in fact, were teflon needle-valves of this type. These were necessary because they (as well as all glassware through which iodine vapor passed) had to be heated to prevent condensation of the iodine. This heating was accomplished by wrapping all such glassware with chromel wire. The temperature of this resistance wire was controlled by the input from a variable transformer. The lower part of the transpiration cell, which extended outside of the furnace, was also heated in this way

except an electric heating tape was used instead of the chromel wire.

The total pressure in the transpiration cell was measured by balancing the pressure in the cell against air across a null-indicating diaphragm gauge. The air pressure, in turn, was measured with a mercury manometer. This arrangement prevented problems due to chemical reaction between mercury and iodine.

The diaphragm gauges were tested for sensitivity before being placed into the system by dipping them into water and measuring the deflection with the same 10X telescope used to measure the deflection during the transpiration experiments.

The furnace, obtained from the Marshall Products Company, was mounted in such a manner that it could be easily raised and lowered around the cell, which was placed in a vertical position. This allowed the furnace to be brought to the desired temperature before lowering it into position around the cell for an experiment. A Bristol controller was used to maintain the temperature of the sample to within $\pm 1^{\circ}$. The temperature was measured by a calibrated chromel-alumel thermocouple placed in the recessed thermocouple well in the cell. The thermocouple was calibrated using the melting points of

tin, lead, zinc and aluminum as standards (66). That calibration showed that the calibration data supplied by the manufacturer of the wire was correct. Thereafter, all thermocouples made with the same wire were assumed to have that calibration. The thermocouple potential compensated for cold junction temperature was measured with a Rubicon precision potentiometer.

The cell was filled through an opening in the top of the cell. This, as well as other procedures involving transfer of sample material, was carried out in the dry-box under an atmosphere of argon. The box had a dew point no greater than -45°C . and usually somewhat lower than that. After the cell was removed from the box, evacuated to 10^{-5} torr and sealed, it was mounted in place and connected to the rest of the transpiration apparatus. The entire system was then evacuated to at least 4×10^{-5} torr. The furnace was lowered over the cell and thermal equilibrium established before the carrier gas flow was begun.

At the conclusion of an experiment the gas flow was terminated, the furnace raised and the cell cooled with a stream of compressed air. The iodine condenser was sealed off, the cell removed from its mounting, opened, and the product washed from the condenser tube. The iodine condenser was weighed

and cracked open. The iodine was removed by placing the tube in a vacuum desiccator and outgassing until all of the iodine was gone. The tube was washed to obtain any vanadium product that had not condensed before it reached the iodine condenser. The tubes were dried and reweighed. The amount of iodine was obtained by subtracting the weight of VI_2 , determined spectrophotometrically, from the difference between the weights of the full and empty tubes.

Diaphragm gauge measurements

A diagram of the diaphragm cell is shown in Figure 6. The cell was a quartz, null-type Bourdon gauge. The experiments were performed on an apparatus consisting of the cell and furnace, ballast bulbs, manometer, air inlet and outlet to the vacuum manifold. The gauges displayed sensitivities varying from 0.1 to 0.2 millimeter deflection for each millimeter pressure difference across the diaphragm. Observations of pointer deflection were made with a 10X telescope. The pressures on the manometer could be read to ca. 0.2 millimeter without the aid of a cathetometer.

The cell was well dried by outgassing it for six to twelve hours at $300^{\circ}C$. under a vacuum of 10^{-5} torr. It was removed from the system and taken into the dry box, where the

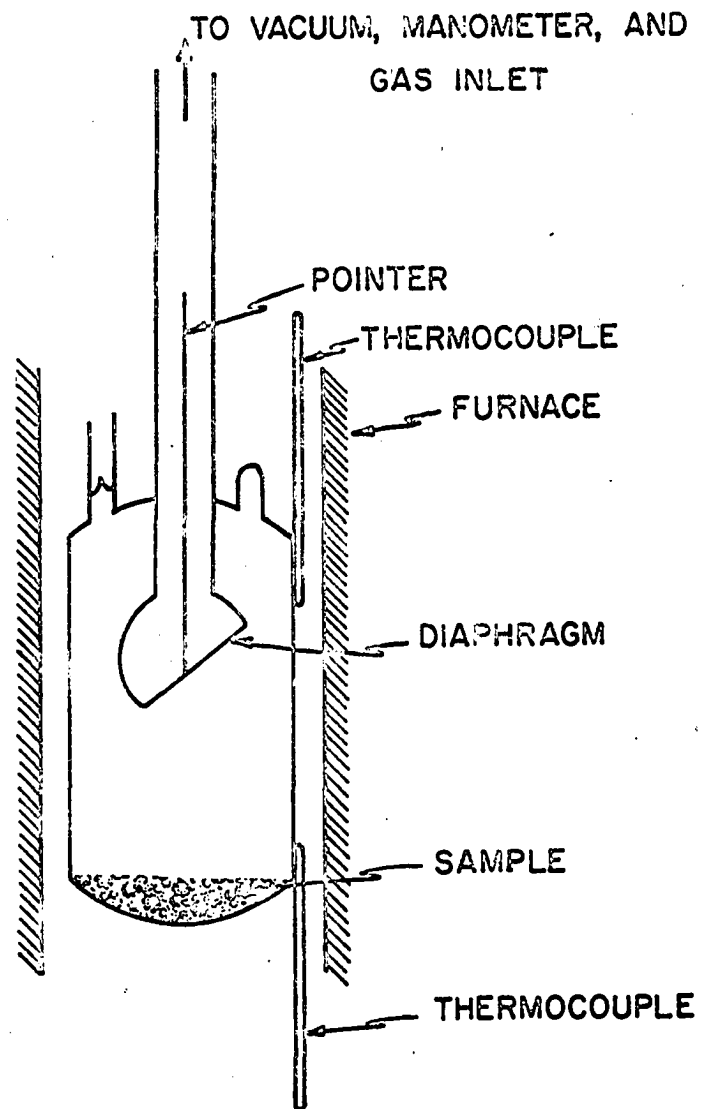


Figure 6. Quartz diaphragm cell

material was introduced. The cell was then re-evacuated for a day at 300°C. A weighed amount of iodine was sublimed into the cell and condensed at the bottom by using a dry ice-acetone bath. The cell was re-evacuated and sealed.

As shown in the figures, the cell was mounted in a vertical position. A nichrome-wound resistance furnace, supplied with a one-eighth inch stainless steel liner, was used to heat the cell. The furnace was insulated at the bottom with a piece of one-quarter inch transite. Heat rising from the furnace tended to reduce possible temperature gradients near the top. The lowest temperature recorded was at the sample. The temperature gradient varied with the temperature, but was never greater than seven degrees.

Two thermocouples were placed along the cell, one in the thermocouple well and the other near the top of the cell. The temperature was measured using a Rubicon precision potentiometer. This gave readings to 0.2°C. when calibrated chromel-alumel thermocouples were used. The temperature was controlled by a Bristol proportional controller.

Measurements were made at 15° to 20° intervals. The cell was heated to the desired temperature and held until a constant value of the pressure was observed. This assured that

equilibrium had been established.

To conclude the experiment the furnace was lowered and the cell quenched to room temperature. The cell was broken in the dry box, the contents placed in a new container and the iodine was sublimed off in vacuo. The product was then analyzed by the titrametric procedures outlined earlier.

RESULTS AND DISCUSSION

The study of the vanadium iodide system proved to be somewhat more complicated than anticipated. Experimental difficulties were solved, but the inconclusive results obtained from some experiments were most frustrating. Although there has been much work done in the area of vaporization reactions of transition metal halides, many areas are still to be explored. As a result some of the data obtained in this investigation, while they appear to be rather surprising at first glance, may be a suggestion of results to be obtained in other systems.

Three types of experiments were performed in the course of this investigation. They are as follows: 1, equilibration experiments between VI_2 and iodine liquid; 2, transpiration experiments; 3, diaphragm gauge experiments.

Preparation of Halides

Vanadium(II) Iodide

While the preparation of VI_2 proved to be reasonably straightforward, the attempted preparation of VI_3 did not succeed.

The preparation of VI_2 by transport in a sealed tube

reaction produced a non-stoichiometric iodide. The composition seemed to depend on the temperature at which the substance deposited. The deposition occurred within a temperature range of ca. 180-280°C. The average composition of the product of such a preparation was ca. VI_{2.25} although it varied slightly from one preparative experiment to another.

The product usually deposited as large black platelets, some of which could be removed without disturbing others. By removing one unusually large crystal it was possible to obtain an X-ray powder pattern of the non-stoichiometric product. During all subsequent preparations the entire mass of product was mixed before an X-ray powder pattern was made. As a result there was some line broadening observed for these patterns. Analysis of the crystal taken for the aforementioned X-ray pattern gave I/V = 2.28.

Anal: V, 15.10%; I, 85.70%; I/V = 2.28.

When a comparison of the X-ray data for this crystal was made with a pattern reported for VI₂ by Klemm (22, p. 200) they were found to be identical. Klemm gives the lattice constants as: $a_0 = 4.00_0$, $c_0 = 6.67_0$, $c/a = 1.667$. The lattice constants obtained for the non-stoichiometric crystal were: $a_0 = 4.00_2$, $c_0 = 6.67_4$, $c/a = 1.667$. Table 4 shows a comparison of observed interplanar spacings for the two substances.

Table 4. A comparison of X-ray data for VI_2 and the non-stoichiometric iodide

Line	hkl	$\sin^2\theta$ this work ($\text{VI}_2.28$)	$\sin^2\theta$ Klemm (VI_2)	$\sin^2\theta$ calculated ^a
1	001	0.0136		0.0133
2	010	.0495		.0494
3	002	.0538	.0529	.0533
4	011	.0629	.0622	.0628
5	012	.1033	.1022	.1028
6	110	.1485	.1483	.1483
7	111	.1614	.1616	.1617
8	013	.1705	.1694	.1695
9	112	.2019	.2011	.2016
10	021	.2109		.2111
11	004	.2148	.2132	.2134
12	022	.2514	.2507	.2511
13	014	.2639	.2622	.2628
14	023	.3182	.3159	.3177
15	005	.3349		.3334
16	120		.3463	.3460
17	121	.3582		.3593
18	114	.3630	.3605	.3617
19	015	.3846	.3815	.3828
20	122	.3991	.3981	.3995
21	024	.4116	.4097	.4111
22	030	.4450	.4461	.4450
23	031	.4545		.4512
24	123		.4642	.4662
25	115	.4826	.4817	.4817
26	032	.4972	.4965	.4982
27	016			.5295
28	025	.5305	.5305	.5310
29	124	.5596		.5596
30	220	.5920	.5920	.5934
31	116	.6311	.6260	.6284
32	130		.6412	.6427
33	007	.6535		.6535

^aThese $\sin^2\theta$ values were calculated by using $a_0 = 4.000$ and $c_0 = 6.670$.

Table 4. (Continued)

Line	hkl	$\sin^2\theta$ this work (VI _{2.28})	$\sin^2\theta$ Klemm (VI ₂)	$\sin^2\theta$ calculated
34	131		.6562	.6562
35	034	.6582		.6583
36	026		.6792	.6777
37	125			.6803
38	132		.7073	.7027
39	223			.8067

From this X-ray data comparison it must be concluded that these are the same compounds.

Vanadium(III) iodide

Several experiments were performed to produce VI₃, but none were fruitful. In all cases the product had a composition between VI₂ and VI₃. Equilibration experiments, which will be discussed later, gave a maximum composition of VI_{2.63}. Extraction of VI₂ with liquid iodine produced compounds on the frit and in the collection bulb having the compositions VI_{2.12} and VI_{2.36} respectively. The final preparative experiment, a repeat of work by Tolmacheva *et al.* (27, p. 281) where vanadium was reacted with iodine at 300°C., produced a solid whose composition was VI_{2.42} in the bulb, while on the surface of the metal the product had a composition of VI_{2.12}.

Anal: (bulb): V, 14.18; I, 85.52; I/V = 2.42.

(surface): V, 15.97; I, 84.33; I/V = 2.12.

Equilibration Experiments

Preparations of VI_2 , as indicated above, afforded a product of indefinite composition when done by a transport technique. No matter what the composition all products appeared to be the same; all showed the same characteristics when dissolved in water and all gave the same X-ray powder pattern. Only when these products were heated in a vacuum so that iodine was liberated did the solid show any change in behavior. After such a heat treatment the solid had a noticeably different color, gave a purplish-gray solution instead of brown and produced an X-ray pattern which, although it could be indexed on the same crystal system, gave different lattice constants. It seemed desirable, then, to determine the variation of composition as a function of the temperature. These experiments were completed at temperatures from 115 to 273°C by allowing VI_2 to equilibrate with liquid iodine.

The products resulting from equilibrations at 115° and 125°C. gave powder patterns nearly identical with that of the starting material, VI_2 . This result was not unexpected since at such low temperatures equilibrium may not have been reached. However it was anticipated that equilibrations at higher temperatures would yield a changed composition,

possibly reaching VI_3 .

Figure 7 shows a plot of the composition as a function of reciprocal temperature. Although there is some scatter in the data, it appears that there is a linear relationship between the two factors. This is somewhat surprising. There appears to be no particular reason why such a relationship should be observed.

As indicated by the figure, a composition of $VI_{2.63}$ was obtained for one sample. Vanadium(III) iodide was never prepared by this method.

The products obtained in experiments with the temperature above $134^{\circ}C$. gave X-ray powder patterns which were very similar. In addition, all patterns were closely related to the pattern of $VI_{2.28}$, with the exception that there were fewer lines on these than for the $VI_{2.28}$. It is interesting that the patterns showed so little change while the composition was changing so drastically. A computer program was used to determine the lattice constants of the samples by a least-square analysis of the data. The biggest source of error in determining lattice constants is the accuracy with which the powder pattern can be read to give the diffraction angle, θ . Although lattice constants for each sample were computed it

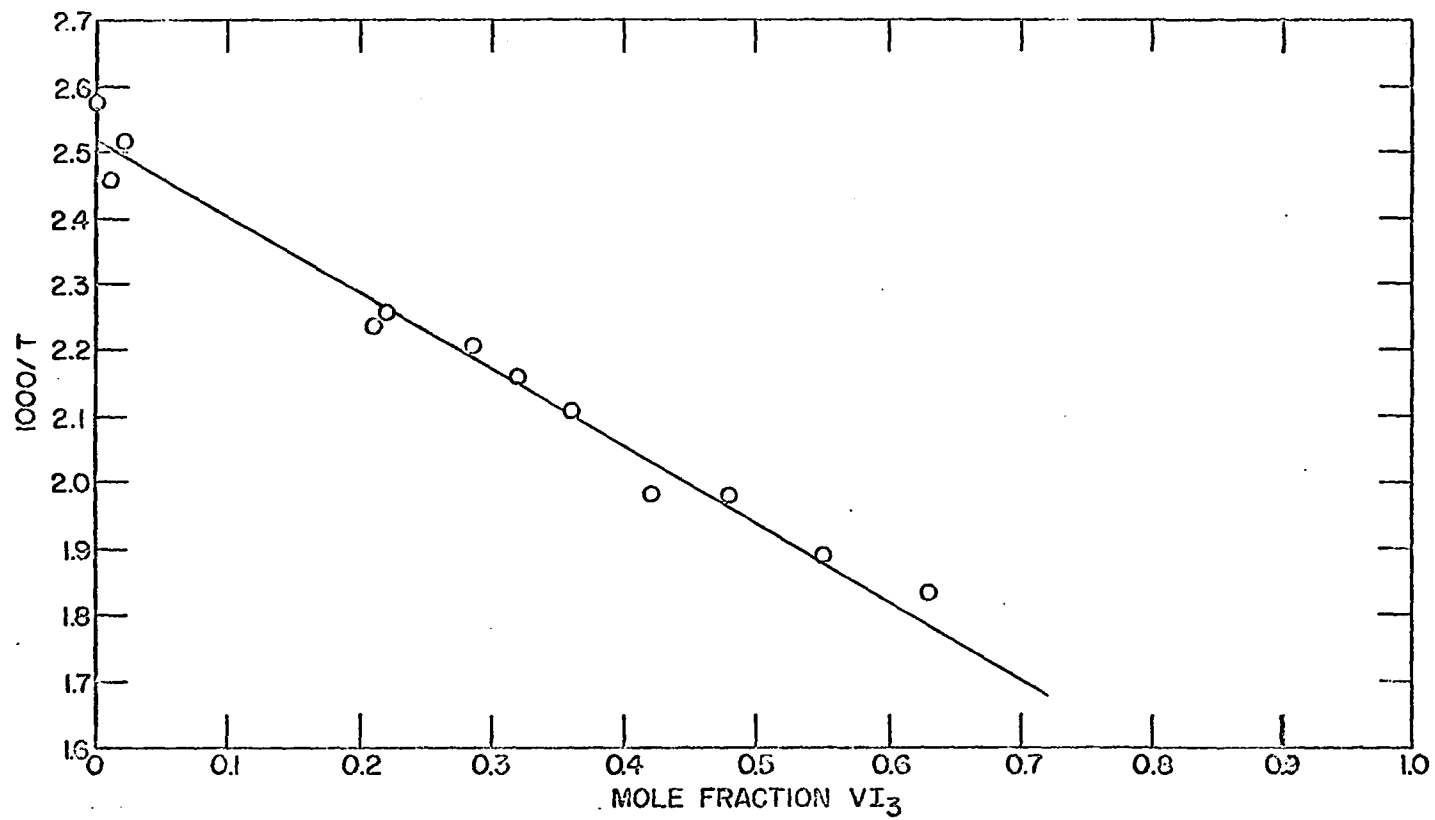


Figure 7. Composition of equilibration product vs. reciprocal temperature for $\text{VI}_2(\text{s}) + \text{I}_2(\ell)$

appeared that any discrepancies or differences in values were within experimental error.

A most interesting result was the constancy of the c/a ratio. For $\text{VI}_{2.28}$, $a_0 = 4.00\text{\AA}$, $c_0 = 6.67\text{\AA}$, $c/a = 1.667$. For $\text{VI}_{2.00}$, $a_0 = 4.07\text{\AA}$, $c_0 = 6.78\text{\AA}$, $c/a = 1.665$. The ratio of lattice constants, then, did not show any great change. The lattice constants varied as follows: $4.00 < a_0 < 4.04$, $6.63 < c_0 < 6.67$. These lattice constant limits are valid over the composition of $\text{VI}_{2.02}$ to $\text{VI}_{2.63}$. These limits were judged to be within experimental error after a careful and critical examination of the data for interplanar spacings. Table 12 gives the interplanar distances for the various solid solutions.

The most startling aspect of this investigation was, of course, the great homogeneity range. Table 5 gives the composition-temperature data obtained as well as data to be discussed later. While the concept of nonstoichiometric compounds is not new, the idea that such a long range of compositions could exist is, to say the least, quite unexpected. There are several similar systems which exhibit homogeneous ranges of varying lengths. Some of these will be noted and appropriate comparisons drawn.

Table 5. Equilibration experiment data

Run	t(°C.)	T(°K.)	1000/T	Composition (I/V)	K ^a	log K
1	115	388	2.577	2.00 ^b		
2	125	398	2.513	2.02		
3	134	407	2.457	2.01		
4	170	443	2.257	2.22	.282	-.550
5	174	447	2.237	2.21	.266	-.575
6	180	453	2.208	2.28	.389	-.410
7	190	463	2.160	2.32	.471	-.327
8	202	475	2.105	2.36	.562	-.249
9	232	505	1.980	2.42 ^c	.724	-.140
10	232	505	1.980	2.48	.923	-.038
11	256	529	1.890	2.55	1.222	+.087
12	273	546	1.832	2.63	1.703	+.231

^aCalculated from the equation $K = X_{VI_3}/1-X_{VI_3}$ where X_{VI_3} is the mole fraction of VI_3 in the solid solution.

^bEstimated error for the composition is ± 0.03 .

^cIt is doubtful that this is equilibrium data.

Schäfer (67) has shown that the solid $NbCl_3$ exhibits a homogeneous phase with compositions ranging between the limits $NbCl_{2.67}$ and $NbCl_{3.13}$. This system is closely related to the vanadium iodides, the metal being in the same family. Schäfer has also reported subsequently that homogeneous phase regions have been observed in the $NbBr_3$ (68) and $TaCl_3$ (35, p. 95) systems. These serve to illustrate the existence of homogeneous phase regions in transition metal halide systems, particularly those of Group V. It is interesting to note that in all

of these cases the metal is in one of its lower oxidation states.

Other examples of non-stoichiometry are perhaps more familiar. Interstitial compounds are well known but have little resemblance to the non-stoichiometric halides. Cotton has discussed the non-stoichiometric sulfide FeS (7, p. 415). Over the composition range 50-50.5 atom per cent sulfur FeS assumes the nickel arsenide structure. When the S/Fe ratio is greater than one, some of the iron positions in the lattice are vacant in a random manner.

Again, the iron oxide system (7, p. 708) shows many of the same characteristics as does the vanadium iodide system. Fe₃O₄ is, of course, a mixed Fe^{II}-Fe^{III} oxide; Fe₂O₃ is also well known. Cotton suggests that the tendency toward non-stoichiometry is a result of the close resemblance of their structures. This may be compared with the vanadium iodide system. The structure of VI₃ is not known; however, one may postulate, with some justification, that it would have the BiI₃ structure. Most 3d-transition metal trihalides whose structures have been determined have the BiI₃ structure. There is one other possible structure type, that of CrCl₃, but few transition metal trihalides crystallize with that

structure.

The structure of a given iron oxide may be thought of as a cubic close packed arrangement of oxide ions with a certain number of Fe^{II} or Fe^{III} ions distributed among the octahedral and tetrahedral holes of the lattice. A redistribution of metal atoms to appropriate lattice positions in the proper ratio is all that is necessary for a conversion to one of the other known iron oxides. Just as the structures of the iron oxides have a cubic close packed array of oxide ions, so the vanadium iodides, assuming VI_3 has the BiI_3 structure, both have hexagonal close packed arrays of iodide ions. (Although the term "ion" is used, one must recognize that the vanadium iodides are covalent in nature.)

It has been shown by Klemm (22, p. 200), and again in this study, that VI_2 has the CdI_2 structure. This structure consists of a hexagonal close packed arrangement of iodide ions with metal ions in all of the octahedral holes of alternate layers (69). The BiI_3 structure also has a hexagonal close packed array of halide ions but has only two-thirds of the octahedral holes in alternate layers filled (69, p. 344). The question then becomes one of how the vanadium ions redistribute themselves within the halide framework.

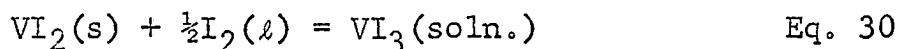
Since a long homogeneous composition range was observed, X-ray powder patterns were made of various samples within the homogeneity range. These patterns indicated that there was a large change in the lattice constants at a low ($I/V = 2.02$) composition. However, all patterns could be indexed on the same crystal system. The c/a ratio was nearly the same in all cases. The space groups for the CdI_2 and BiI_3 structures are D_{3d}^3 (70) and D_{3d}^1 (71), respectively. According to X-ray crystallographic tables (72), there are no special limiting conditions on reflections for either space group. In most cases there were more lines visible for samples at higher compositions, but all extra lines still could be indexed as though it were VI_2 .

The similarity between the CdI_2 structure and BiI_3 structure goes further, however. Both are layer structures made up of repeating layers of the type $ABAB\cdots$ (69, p. 344). Both unit cells contain one molecule, thus suggesting that a conversion from one structure to the other may be the result of increasing or decreasing the number of vacancies at the metal positions. If the extra metal atoms present were in certain restricted lattice holes, a systematic array of lines should have appeared on the X-ray patterns. This was not observed;

in fact, there were fewer reflections in the pattern of pure VI_2 than on most other patterns. This may have been due to the quality of photographic work; the packing of the capillary or slight hydrolysis. Nevertheless the trend persisted throughout the entire composition range. This was born out by the fact that nearly all the lines which appeared for a composition of VI_2 were still observed at a composition of $VI_{2.63}$. In short, only some single crystal X-ray work will be able to delineate a crystal structure shift which may be occurring, since powder pattern data have not been sufficient to clarify the situation.

A model of the VI_2 - VI_3 structure, as described here and by comparison with other systems, consists of a solid solution of VI_3 in VI_2 . This is a result of the random vacancies within the halide lattice.

In order to determine what is going on with these experiments the equation representing the reaction must be considered.



Since the vanadium iodide system is similar to the iron oxide system, we may consider the homogeneous phase to be a solid solution of VI_2 and VI_3 . From all available data the vana-

dium ions seem to be distributed randomly in every other layer of the hexagonal close-packed lattice formed by the iodide ions.

This being the case, it would be desirable to treat these samples as solutions and determine the thermodynamic properties associated with the reaction noted above. Such a treatment requires at least two assumptions: a) the activity of $I_2(l) = 1$. Since there are no data for the solubility of VI_2 in iodine, this must be assumed. It should be valid to the extent that iodine will not dissolve an appreciable amount of VI_{2+X} b) The ratio of activity coefficients is near unity. If the equilibrium constant, K , is

$$K = \frac{a_{VI_3}}{a_{VI_2}} \quad \text{Eq. 31}$$

where a represents the activity of the indicated component of the solid solution, then

$$K = \left(\frac{X_{VI_3}}{X_{VI_2}} \right) \cdot \left(\frac{\gamma_{VI_3}}{\gamma_{VI_2}} \right) = \frac{X_{VI_3}}{1-X_{VI_3}} \quad \text{Eq. 32}$$

$$\text{where } \frac{\gamma_{VI_3}}{\gamma_{VI_2}} \approx 1 \quad \text{Eq. 33}$$

and X is the mole fraction of the appropriate component.

Figure 8 shows a plot of $\log K$ vs reciprocal temperature for most of the samples. Those with $I/V \approx 2.00$ gave values of

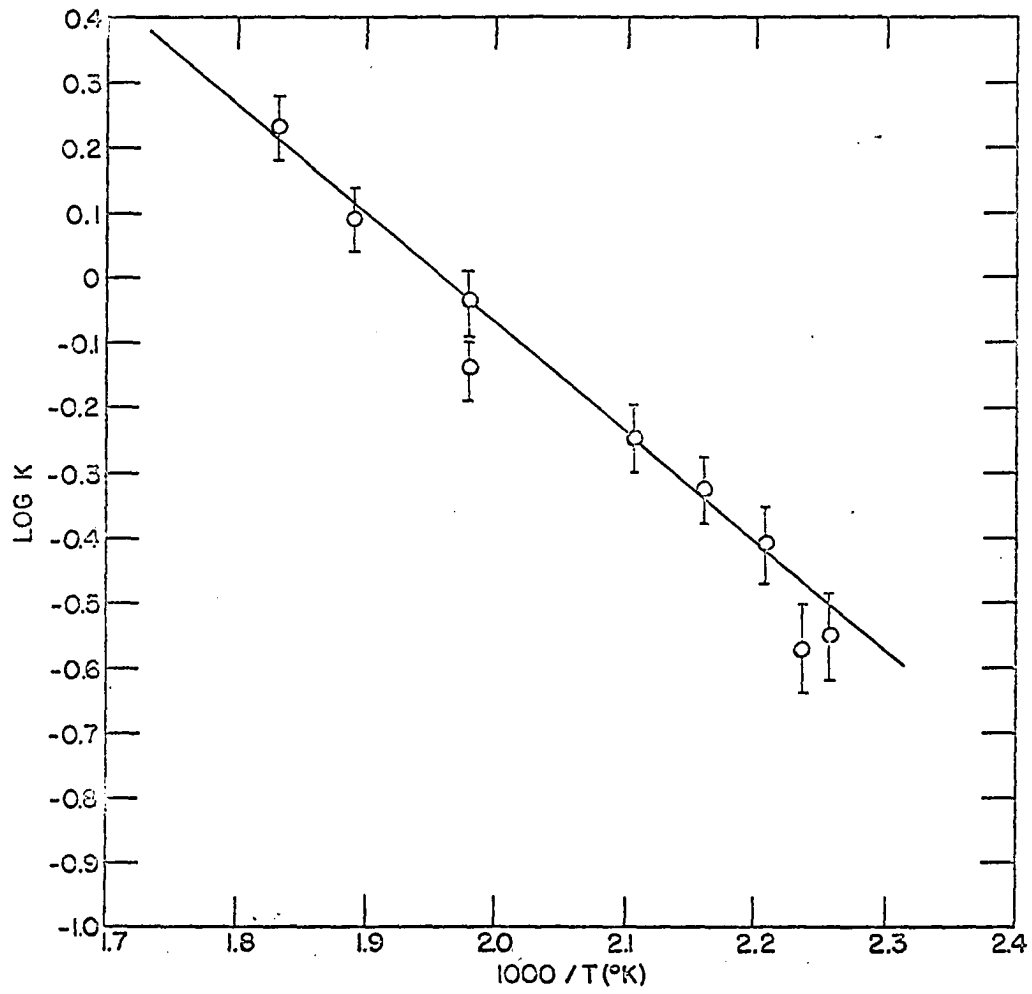


Figure 8. Equilibrium constants for solid solutions between VI_2 and VI_3

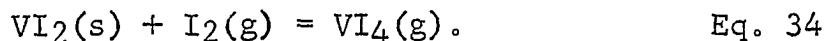
log K which had no meaning (i.e. this magnitude of the mole fraction ratio was such that experimental error was too great to give valid values for K). There are two points which fall off the line. The point at $1000/T = 1.980$, corresponding to a composition of $VI_{2.42}$, has been suspect and it is believed to be a "bad" point, one determined when the equilibrium had not been established. The other two points may represent non-equilibrium data, but it is doubtful. The error bars represent the variation in log K produced by an uncertainty of ± 0.03 in the I/V ratio of the solid solution. One of the two low points falls on the line if the error bar is assumed to be valid. The line was drawn to best fit the remaining data.

In order to determine the thermodynamic properties, the best fit was found by visual observation. No attempt was made to do a least-square analysis of these data. The slope of the line provided a means of determining enthalpy for the reaction. The value obtained was $\Delta H^{\circ} = 7.55$ kcal/mole, while the value for the entropy was $\Delta S^{\circ} = 14.8$ e.u. at $511^{\circ}K$.

Vapor Pressure Data

Transpiration experiments

Transpiration measurements were used to study the reaction between solid VI_2 and iodine vapor. Equilibrium data were obtained which allowed determination of the enthalpy and entropy for the following reaction:



Experiments were conducted to determine the dependence of vapor pressure on flow rate, temperature, and pressure of iodine. Four series of experiments were completed. In the first, second and third series, the pressure of the iodine was set at a certain level while the sample temperature was adjusted for each experiment. The last series of experiments involved holding the sample temperature constant while varying the iodine pressure.

One of the factors of most concern while measuring equilibrium vapor pressures with a flow technique is the degree of saturation of the vapor with the sample vapor. Plots of apparent vapor pressure as a function of flow rate normally show an increase in vapor pressure at low flow rates due to thermal diffusion effects. At high flow rates, on the other hand, the apparent vapor pressure falls off because the

carrier vapor passes over the sample too quickly to become saturated. Between these two extremes the vapor is saturated and no diffusion effects are observed, resulting in a plateau. Figure 9 shows data obtained when only the flow rate was changed with the sample at 608.2°K. The plot was obtained from three points covering a range of flow rates from 14.48 to 54.23 milligrams per minute. The dotted lines on Figure 9 do not show experimental data, but were included only to show what would be expected from the considerations above.

Vapor pressure measurements were made at flow rates greater and less than those within the limits of the runs. Even beyond these limits the data indicate that the iodine vapor was saturated as it should be if the reaction was to be considered to be at equilibrium.

The following parameters were measured during every run: sample temperature, total pressure, length of run in minutes, quantity of vanadium transported and quantity of iodine which passed over the sample. From these data the flow rate (mg. per minute) was calculated. Using Equation 35, the mole fraction, X_V , of transported vanadium was calculated.

$$X_V = \frac{n_V}{n_V + n_I} \quad \text{Eq. 35}$$

where n_V is the moles of vanadium transported and n_I is the

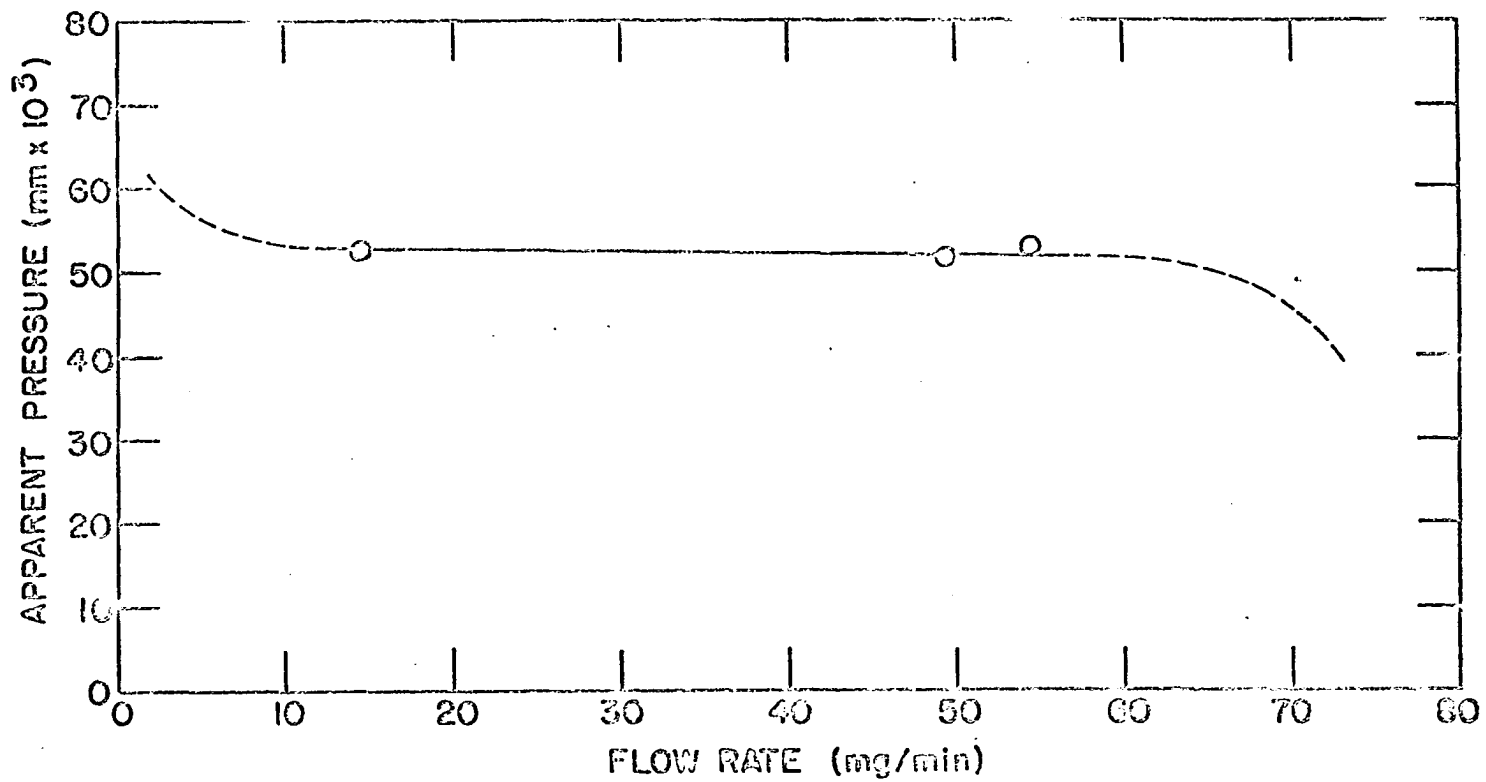


Figure 9. Apparent vanadium iodide pressure vs. iodine flow rate

number of moles of iodine that carried the vanadium. For the reaction between $\text{VI}_2(\text{s})$ and iodine vapor one may assume, for the purpose of simplifying calculations, that the pressure of VI_4 is negligible compared to that of the iodine. According to Dalton's law (73) the sum of the partial pressures is equal to the total pressure, Equation 36.

$$P_T = P_{\text{VI}_4} + P_{\text{I}_2} \quad \text{Eq. 36}$$

Assuming that P_{I_2} is much greater than P_{VI_4} , Equation 36 reduces to

$$P_T = P_{\text{I}_2} \quad \text{Eq. 37}$$

Equation 36 may be written in the form

$$P_T = X_V P_T + X_I P_T \quad \text{Eq. 38}$$

where X_V is the mole fraction of vanadium and X_I the mole fraction of iodine. Equation 39 is obtained from the defini-

$$X_V + X_I = 1 \quad \text{Eq. 39}$$

tion of mole fraction. Making the appropriate substitutions into Equation 36 the following equation may be obtained:

$$P_{\text{VI}_4} = \frac{X_V P_T}{1 - X_V} \quad \text{Eq. 40}$$

This equation was used to calculate P_{VI_4} for each run. When P_{VI_4} was checked with P_{I_2} it was observed that P_{VI_4} was indeed negligible and the earlier assumption was valid. Equation 36 was then used to determine the exact value of P_{I_2} .

The usual method for determining equilibrium thermodynamic data is outlined most clearly by Darken and Gurry (74). It requires the heat capacity of the substances involved so that the sigma function may be calculated as shown in Equations 41 and 42.

$$\sum = -R \ln K + \Delta C_p \ln T = \frac{\Delta H^{\circ}}{T} + I \quad \text{Eq. 41}$$

$$K = \frac{P(\text{products})}{P(\text{reactants})} \quad \text{Eq. 42}$$

In cases where some knowledge of C_p is available this procedure is quite satisfactory. Such data is unavailable for VI_2 and other methods must be used. In this case the enthalpy of reaction was obtained from a plot of $\log K$ vs. $1/T$ where

$$\text{slope} = \frac{d \ln K}{d(1/T)} = - \frac{\Delta H^{\circ}}{R} \quad \text{Eq. 43}$$

Instead of determining the slope graphically, a computer program was used to do a least square analysis of the data.

Experiments were run with several goals in mind. Figure 10 shows a plot of $-\log K$ as a function $1000/T$ for $P_{\text{I}_2} = 21.0 \pm 1.0$ mm. For such a plot, the equation of the line has the form

$$\log K = -A/T + B \quad \text{Eq. 44}$$

where A and B are adjustable parameters. Figures 11 and 12 show similar plots for $P_{\text{I}_2} = 30 \pm 1.0$ mm and 46 ± 1.2 mm,

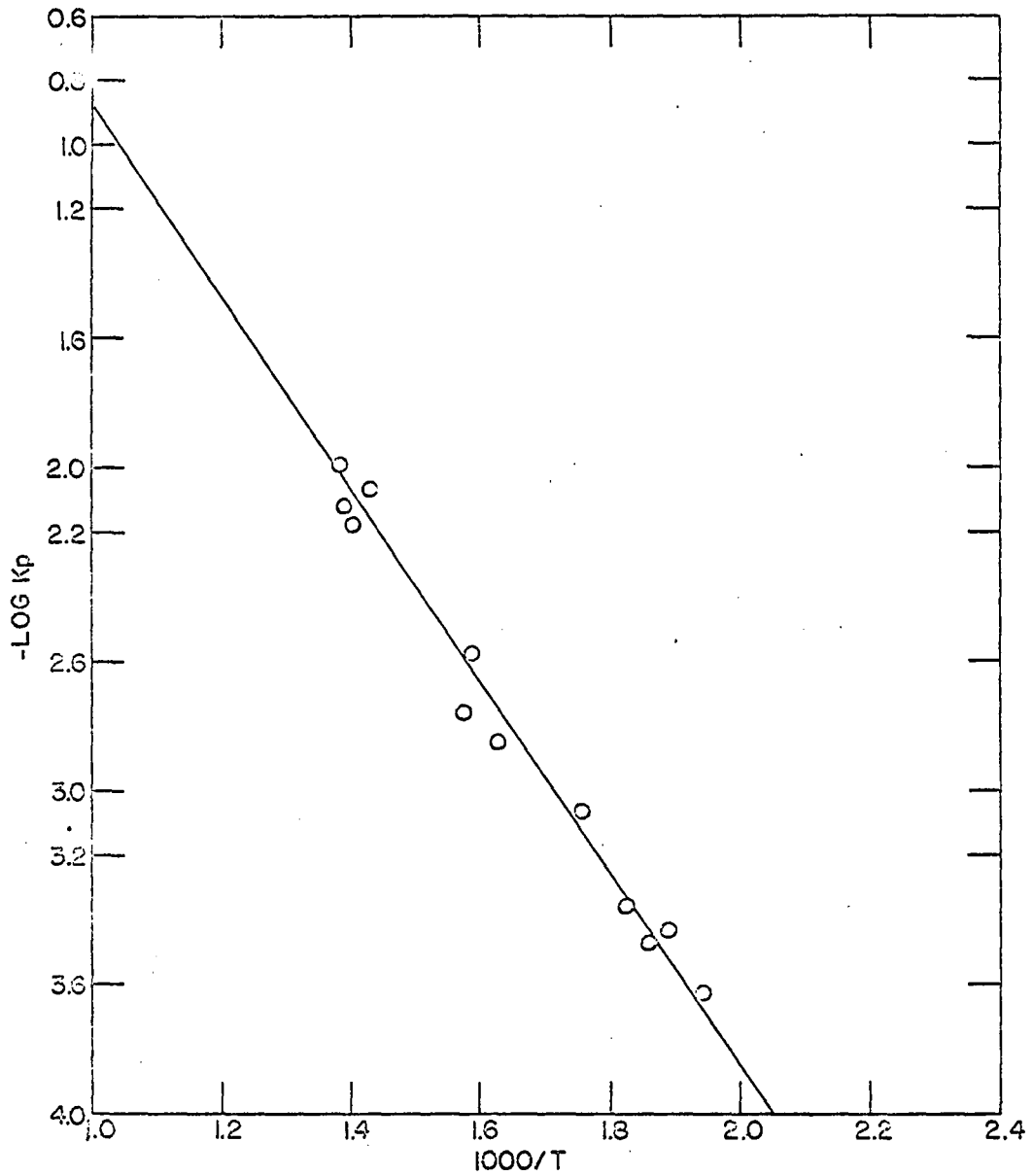


Figure 10. Transpiration equilibrium constants at $P_{I_2} = 21 \pm 1$ mm.

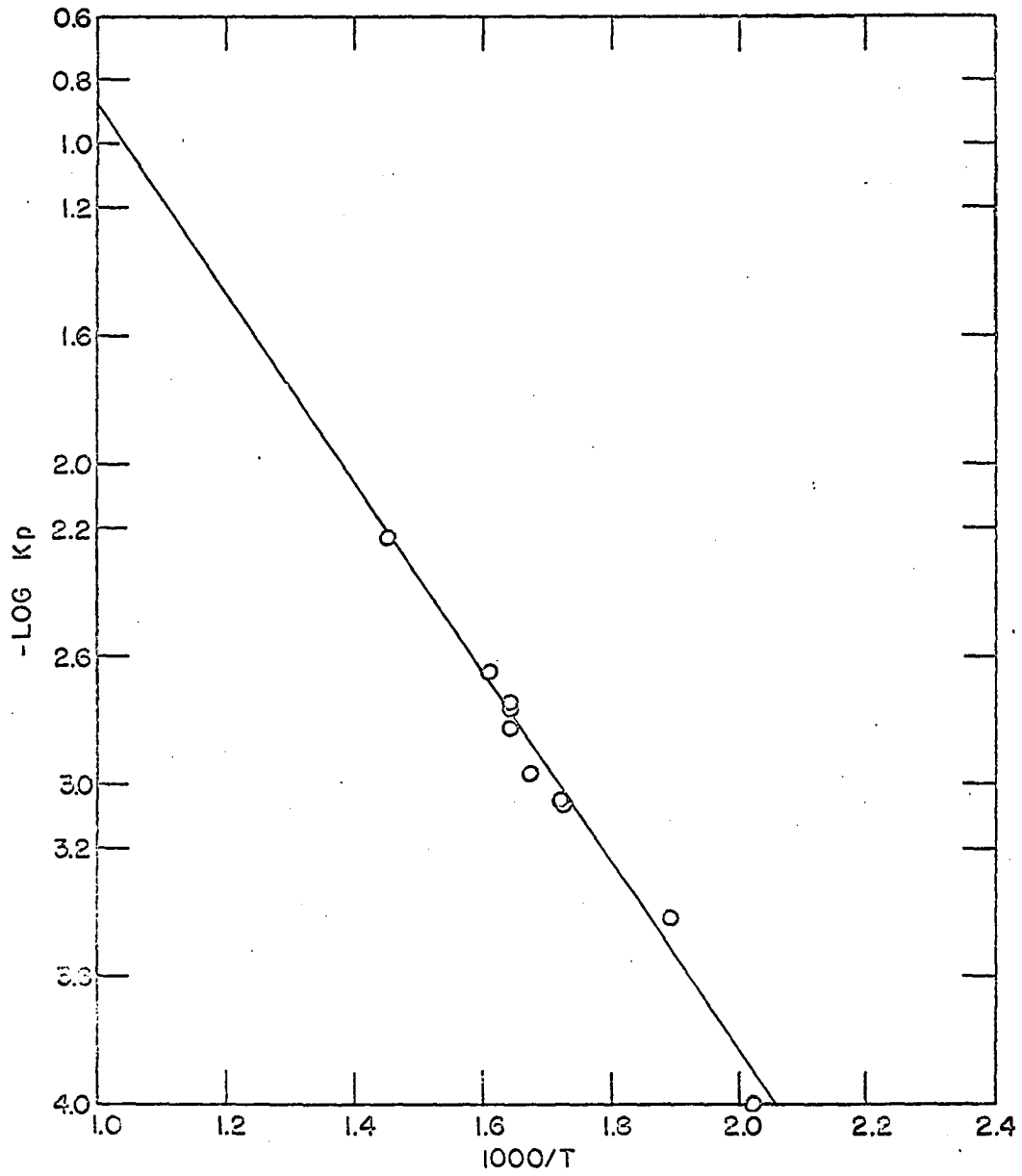


Figure 11. Transpiration equilibrium constants at $P_{I_2} = 30 \pm 1$ mm.

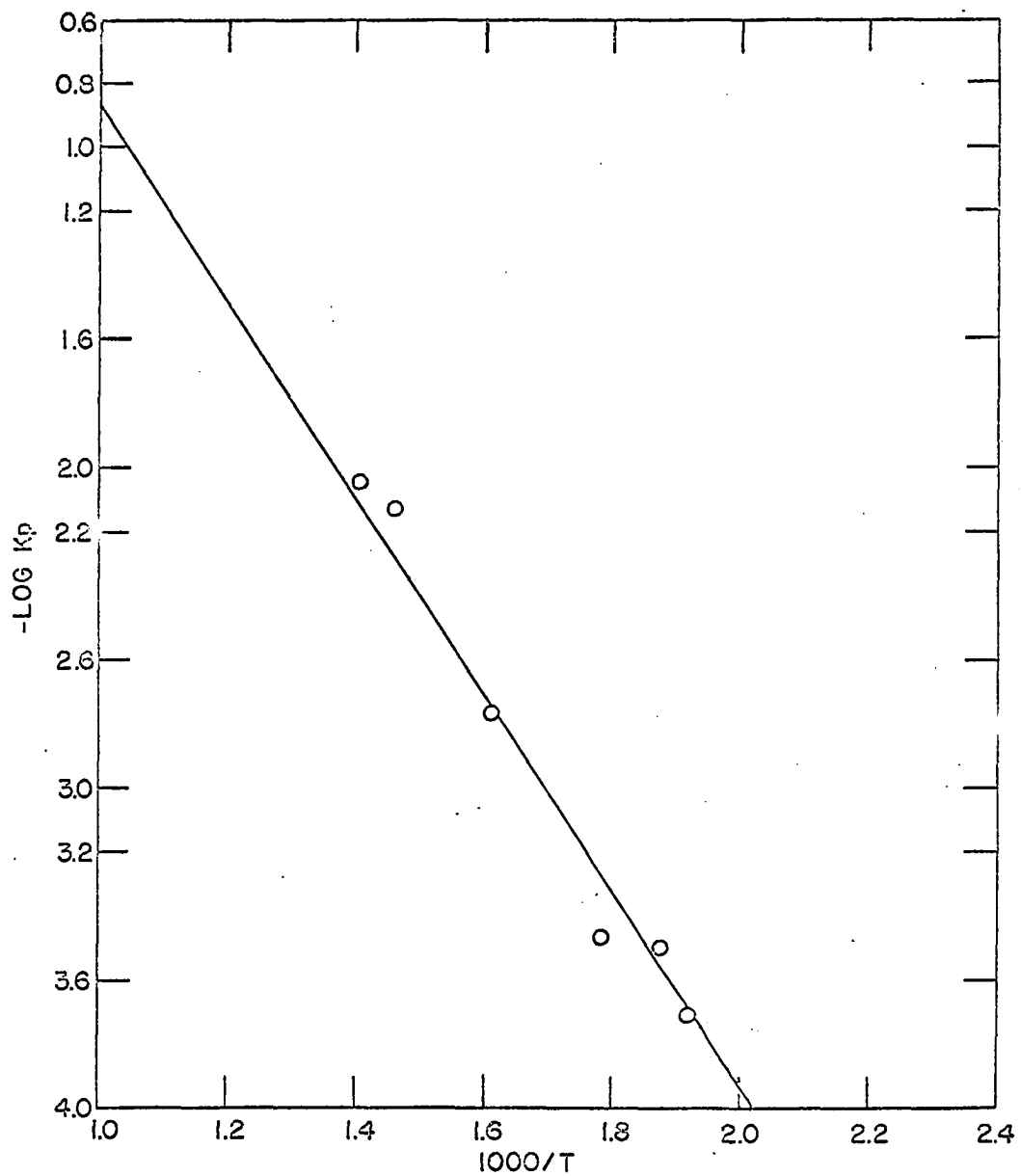


Figure 12. Transpiration equilibrium constants at $P_{I_2} = 46 \pm 1.2$ mm.

respectively. Figure 13 is a plot of all the data combined, including several points not on any of the other three plots. Table 6 gives the results obtained from the least square analysis of each set of data.

Table 6. Data for transpiration equation

Initial P_{I_2}	A	B	ΔH° (kcal/mole)
21.0 ± 1.0	$2.839 \pm 0.125 \times 10^3$	1.861 ± 0.207	13.0 ± 0.6
30.0 ± 1.0	$3.174 \pm 0.099 \times 10^3$	2.420 ± 0.169	15.3 ± 0.8
46.0 ± 1.2	$3.336 \pm 0.241 \times 10^3$	2.650 ± 0.406	14.5 ± 0.4
Combined	$3.040 \pm 0.091 \times 10^3$	2.181 ± 0.152	13.9 ± 0.4

For the reaction illustrated by Equation 34, the equilibrium constant may be determined from the following equation.

$$K = \frac{P_{VI_4}}{P_{I_2}} \quad \text{Eq. 45}$$

Table 13 gives the data obtained for all of the experiments, calculated according to the methods previously described. Table 7 shows the equilibrium constants obtained experimentally and also gives equilibrium constants calculated from the refined equation for the slope, while Table 6 gives the

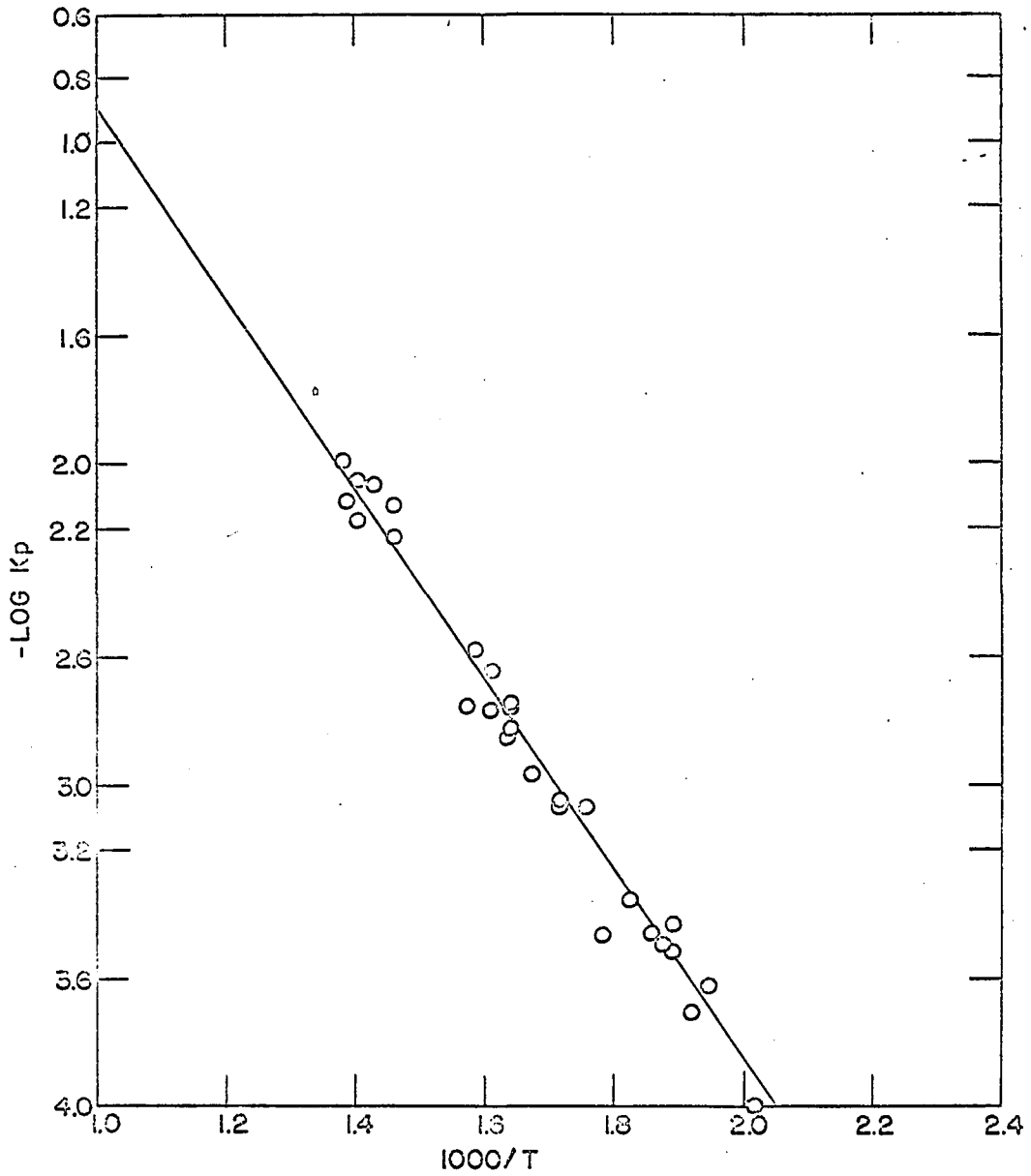


Figure 13. Transpiration equilibrium constants for combined data

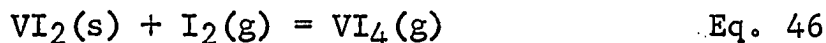
Table 7. Equilibrium constants for the $\text{VI}_2\text{-I}_2$ reaction by transpiration in iodine

Run	T, °K	K_{observed} ($\times 10^3$)	$K_{\text{calculated}}^a$ ($\times 10^3$)
1	630.2	2.623	2.275
2	538.6	.341	.344
3	548.2	.432	.433
4	514.2	.237	.185
5	569.2	.834	.692
6	636.2	1.735	2.524
7	529.2	.364	.272
8	610.4	1.394	1.589
9	719.2	7.543	9.016
10	722.2	10.33	9.419
11	713.2	6.591	8.298
12	699.2	8.561	6.823
13	533.2	.316	.303
14	521.2	.194	.222
15	561.2	.336	.585
16	621.2	1.744	1.936
17	684.2	7.432	5.458
18	712.2	8.780	8.185
19	684.2	5.898	5.458
20	597.2	1.071	1.556
21	620.2	2.262	1.910
22	582.2	.891	.908
23	495.2	.0957	.110
24	528.6	.299	.270
25	581.2	.855	.889
26	608.2	1.718	1.524
27	608.2	1.525	1.524
28	608.2	1.747	1.524
29	608.2	1.700	1.524
30	608.2	1.720	1.524
31	608.2	1.712	1.524
32	608.2	1.715	1.524

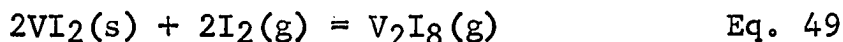
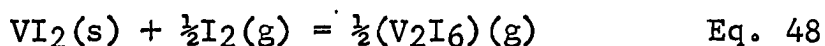
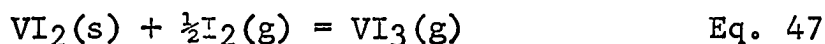
^aCalculated from the equation $\log K = \frac{-3.040 \pm 0.091 \times 10^3}{T} + 2.181 \pm 0.152$.

average enthalpies at each P_{I_2} as well as the average enthalpy calculated from the slope of the combined data.

Until now, it has been tacitly assumed that the vaporization reaction was that shown in Equation 46.



There are, however, several other reactions possible. These may be illustrated here.



The latter reaction was considered to be unimportant because no similar system exhibits such behavior. Either of the other reactions are possible. In order to determine which process was operating, experiments were conducted with a constant sample temperature. The data plotted as P_{VI_4} vs. P_{I_2} are shown in Figure 14. The linear relation between P_{VI_4} and P_{I_2} showed that the reaction represented by Equation 47 was not important, for had it been, a curved line would have resulted. Also the data did not give a linear plot of P_{VI_3} vs. $P_{I_2}^{\frac{1}{2}}$ as required by Equation 50 if the reaction given in Equation 47 prevailed.

$$K = \frac{P_{VI_3}}{(P_{I_2})^{\frac{1}{2}}} \quad \text{Eq. 50}$$

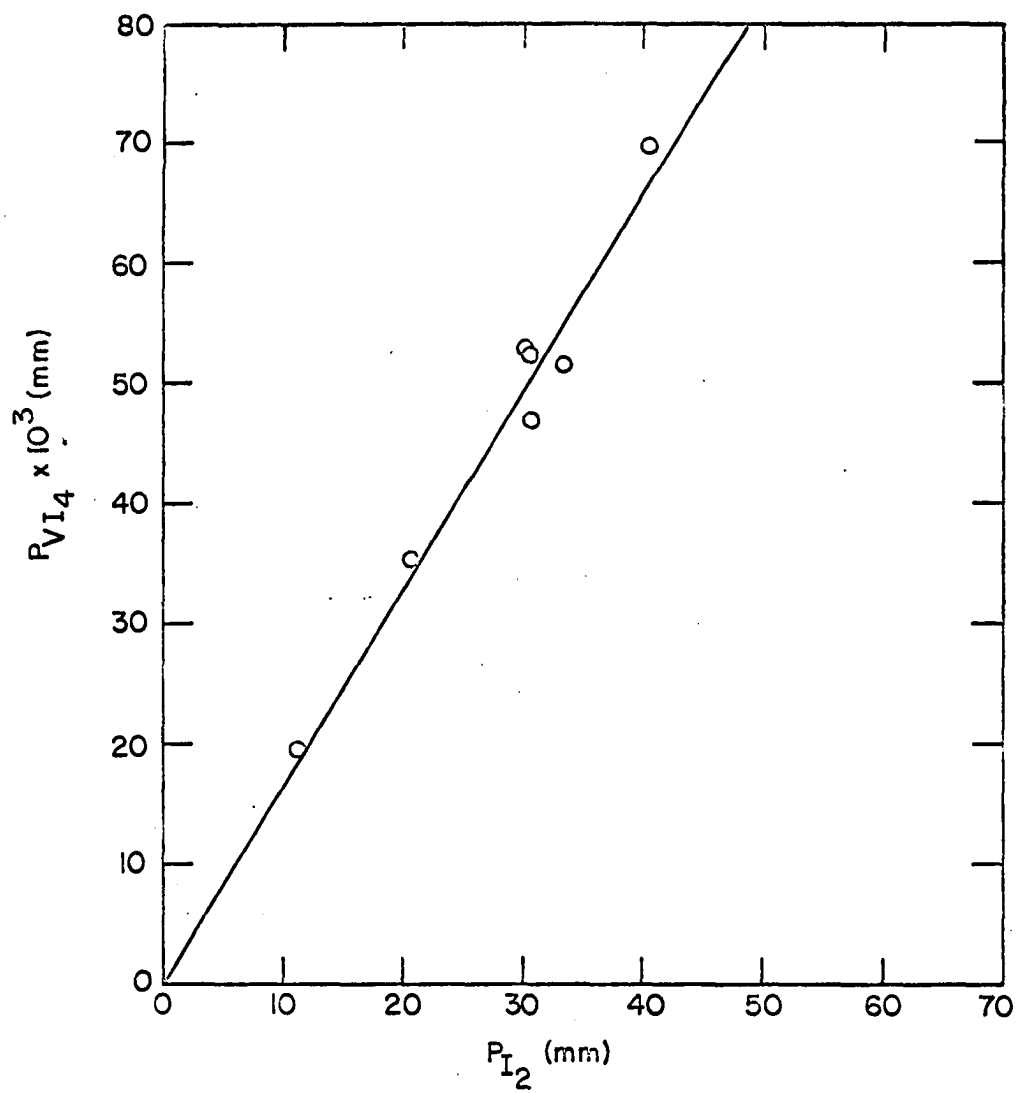


Figure 14. Apparent VI_4 pressure vs. iodine pressure at $608.2^\circ K$

However, this evidence did not eliminate the possibility of the reaction illustrated by Equation 48. In that case a plot of the apparent vanadium iodide pressure vs. P_{I_2} also would give a straight line. A consideration of the magnitude of the vapor pressure suggests a method for distinguishing which reaction is operating. The compounds VCl_3 and VBr_3 have been shown to have quite low vapor pressures in the experimental temperature range (75; 2, p. 62). Table 8 shows a comparison of pressures at various temperatures.

Table 8. A comparison of the vapor pressures of vanadium (III) halides

Compound	T (°K)	P (mmx10 ³)	Reference
VCl_3	624	0.034	2, p. 62
VCl_3	682	.740	2, p. 62
VCl_3	707	2.51	2, p. 62
VBr_3	594	.0151	2, p. 62
VBr_3	634	.153	2, p. 62
VBr_3	685	1.90	2, p. 62
VI_x^a	597	32.96	this work
VI_x	630	57.28	this work
VI_x	684	180.0	this work
VI_x	712	407.3	this work

^a VI_x represents the volatile product of the transpiration experiment.

It can be seen from these data that the pressures observed during the transpiration experiments for VI_2 are on the order of one hundred to one thousand times greater than those observed for VCl_3 and VBr_3 at a corresponding temperature. It might be expected that VI_3 would follow the pattern of the other similar compounds. If so, it would be anticipated that its vapor pressure would be much less than that observed. It is suggested, therefore, that the only reasonable equation is that which yields VI_4 as the gaseous product.

It is interesting to note that the line shown in Figure 14 passes through the origin. This is expected when the sample has a negligible vapor pressure at a given temperature. This behavior was observed in this study as well as by Morette (24, p. 1219), who reports VI_2 as nonvolatile until a temperature near $700^\circ C.$, whereupon it commences to decompose at a rate similar to its rate of sublimation.

For the data shown in Figure 13 the following equation was obtained.

$$\log K = \frac{-3.040 \pm 0.091 \times 10^3}{T} + 2.181 \pm 0.152 \quad \text{Eq. 51}$$

From Equations 51 and 43, the free energy may be expressed as

$$\Delta F^\circ = 13,900 - 10.0T. \quad \text{Eq. 52}$$

It was then possible to calculate average values, $\Delta \bar{H}$ and $\Delta \bar{S}$,

the enthalpy and entropy of vaporization respectively, using Equations 52 and 53. In order to determine a value for the

$$\Delta F^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad \text{Eq. 53}$$

entropy of vaporization a temperature near the middle of the range was selected. The value of ΔS° calculated from that temperature, ΔF_T and ΔH° was considered to be representative and thus was $\Delta \bar{S}$.

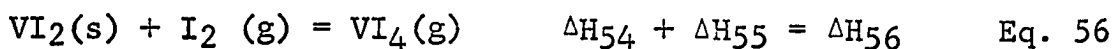
Over the temperature range 495.2-722.2^oK., the following results were obtained for the process shown in Equation 34: $\Delta H^{\circ} = 13.9 \pm 0.4$ kcal/mole, $\Delta S^{\circ} = 10.0 \pm 0.6$ e.u. The temperature chosen to calculate ΔS° was 608.2^oK. These data may be compared with those for VBr₃ reported by Roddy and others as given in Table 9.

Table 9. Thermodynamic data for the reactions $\text{MX}_3(\text{s}) + \frac{1}{2}\text{X}_2(\text{g}) = \text{MX}_4(\text{g})$

M	X	ΔH° (kcal/mole)	ΔS° (e.u.)	T(^o K)	Reference
V	Cl	6.9		453	76
Cr	Cl	28.0	25.4	800	77
V	Br	15.8	23.9	515	2, p. 59
Cr	Br	36.4	27.8	800	4, p. 96
V ^a	I	13.9	10.0	608	this work

^aThe reaction in this case has VI₂ as a reactant. Although the reaction for VI₂ is not represented by the same equation as that of the rest of the compounds, it is well to compare them because the products are similar, e.g. MX₄ (M = V, Cr; X = Cl, Br, I).

Both ΔH° and ΔS° appear to be less than might be expected from the earlier data. There is still some doubt, however, about the validity of such a comparison. If the following reactions are considered

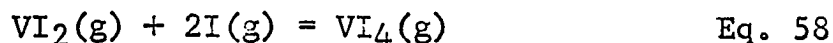


then it can be seen that the net reaction would have a lower ΔH if Reaction 54 is exothermic (i.e. $\Delta H_{54} < 0$). In that case the enthalpy relationships would be: $\Delta H_{54} < 0$, $\Delta H_{55} > 0$, $\Delta H_{55} > \Delta H_{54}$ and $\Delta H_{56} > 0$. There is little data available to indicate what the magnitude and sign of ΔH_{54} might be. By comparison with the other data, however, it seems reasonable that Reaction 54 is indeed exothermic.

In order to consider the total reaction more closely, the following considerations may be helpful.

<u>Reaction</u>	<u>ΔH_{298}° (estimated)</u>	<u>Reference</u>
$\text{VI}_2(\text{s}) = \text{VI}_2(\text{g})$	+55 kcal	by comparison with VBr_2 , VCl_2 (2,p.61)
$\text{VI}_2(\text{g}) + 2\text{I}(\text{g}) = \text{VI}_4(\text{g})$	-86 kcal	see below
$\text{I}_2(\text{g}) = 2\text{I}(\text{g})$	+36 kcal	78
$\text{VI}_2(\text{s}) + \text{I}_2(\text{g}) = \text{VI}_4(\text{g})$	+ 5 kcal	Eq. 57

The heat of reaction for Equation 58 can be estimated if we know average V-I bond energies. Using 1.7 for the average electronegativity of V(III) - V(IV), these may be calculated



using an equation developed by Pauling (78, p. 92):

$$D(\text{V-X}) = \frac{1}{2} [D(\text{V-V}) + D(\text{X-X})] + 23(\text{X}_\text{X} - \text{X}_\text{V})^2 \quad \text{Eq. 59}$$

where $D(\text{V-V}) \approx 20$ kcal (79), $D(\text{I-I}) = 36$ kcal (78, p. 85), $X_\text{I} = 2.5$ (78, p. 93) and $X_\text{V} = 1.7$. Using these quantities $2 D(\text{V-X}) = 86$ kcal.

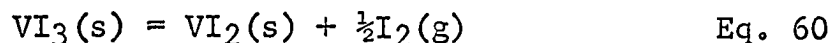
That value is, of course, only approximate but it suggests that the reaction should not be expected to be very endothermic. The actual value observed was 13.9 kcal. It thus appears that the V-I bond energy was overestimated by about 4.5 kcal per bond.

The small entropy change seems to be consistent with the formulation of the reaction. Entropy may be considered to be a measure of the randomness of a system. In the case of a metal trihalide one-half mole of halogen gas produces one mole of gaseous product as shown in Equation 55. In the case of VI_2 , one mole of iodine vapor reacts with VI_2 to produce one mole of VI_4 . Herein lies an explanation for the small value of ΔS obtained in this work: There is the same number

of moles of gas on both sides of the equation.

Diaphragm gauge measurements

Recent work reported by Tolmacheva indicates that the decomposition of VI_3 proceeds according to Equation 60 (27, p. 283).



When the method suggested by Tolmacheva for the preparation of VI_3 was repeated in this work, a product having the composition $VI_{2.43}$ was obtained in the reaction vessel, while the composition $VI_{2.12}$ was obtained for product scraped from the surface of the vanadium foil. Hence the preparation as reported by Tolmacheva could not be repeated to produce VI_3 .

In an effort to establish the vapor species for the reaction between VI_2 and iodine by an independent method, diaphragm gauge experiments were undertaken. Figure 15 presents the data in a plot of $\log P_{\text{mm}}$ vs. reciprocal temperature. The data must be carefully evaluated. The curve obtained for the majority of points is obviously not a straight line, indicating that more than one vaporization process may be important over the temperature range of the experiments. Since the pressure was determined by visual observation of a mercury manometer, the points at $\log P_{\text{mm}} < 0$

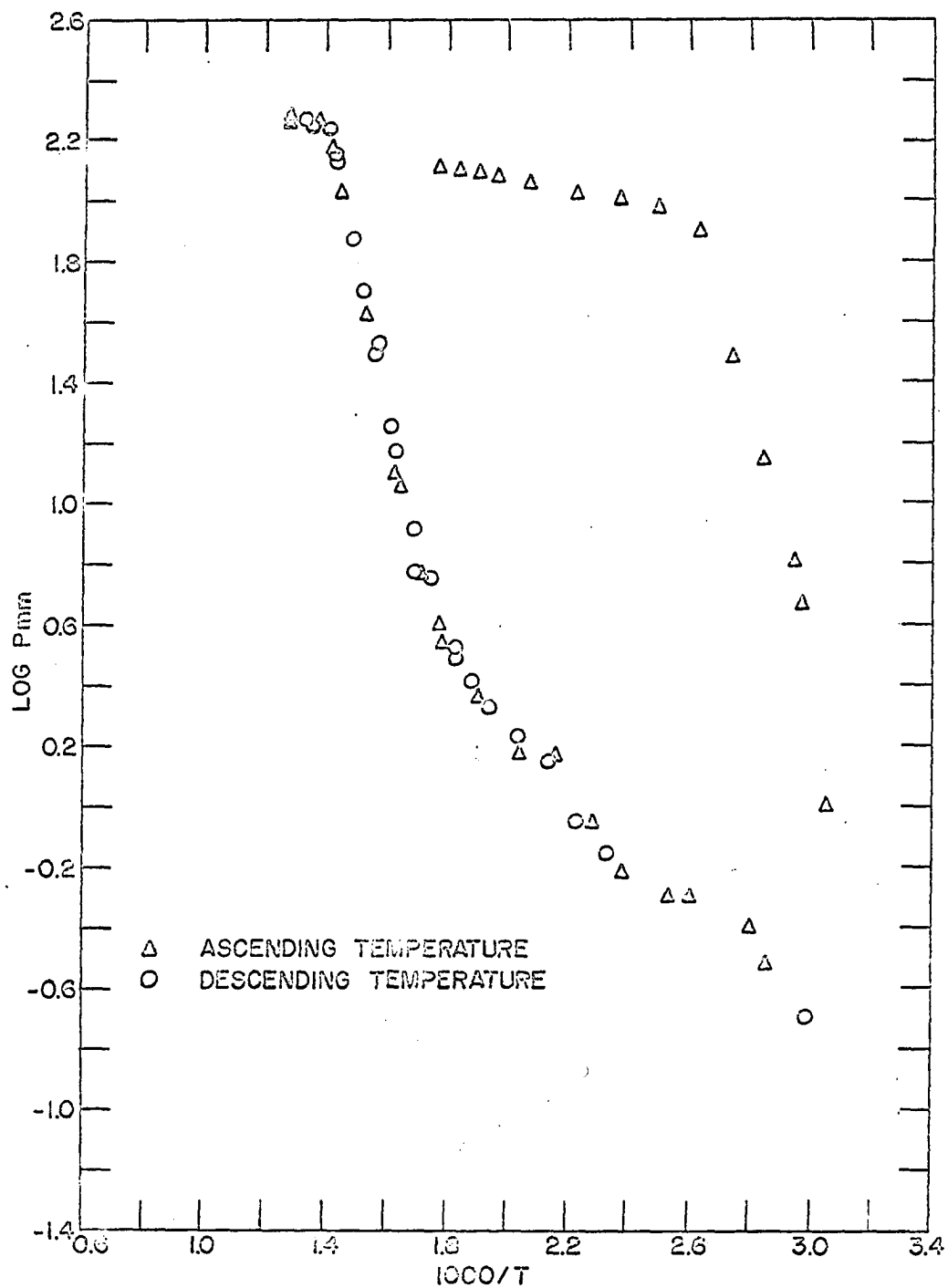


Figure 15. Total pressure measured over initial mixture of VI_2 and I_2 , and over nonstoichiometric reaction product

have little significance. The pressure difference is less than one millimeter and the estimated error of ± 0.5 mm. is much too great to attach any great reliance to that data.

Earlier reports of diaphragm gauge experiments with transition metal halides (4, p. 95; 1, p. 58) indicate a problem of hydrolysis resulting in a residual pressure. This problem did not arise in this investigation, probably because VI_2 is much less susceptible to hydrolysis than the other halides studied above.

Using the procedure outlined in an earlier section, the pressure was observed to rise rapidly on initial heating until a temperature was reached which corresponded to the melting point of iodine. This pressure increase was associated with the normal pressure rise due to the vapor pressure of iodine. At the melting point of iodine the pressure ceased to rise at such a rapid rate and a levelling effect was observed as shown on the figure. At this point reaction ensued between VI_2 and liquid iodine, probably the same effect as observed in the equilibration experiments:



Further heating then caused little change in the pressure.

Readings then were taken as the cell was slowly cooled. As shown, the initial curve was not repeated when points due to descending temperatures were plotted. The pressure eventually fell to zero at room temperature, thus showing no residual pressure effects due to hydrolysis.

Points obtained on the second heating conformed to the curve established by the earlier descending temperature measurements. A second cooling and a third heating again gave data similar to all but the first series. Table 14 gives the data for three ascending and two descending runs.

After concluding the necessary experiments the sample was heated at 338°C and quenched. Analysis of the sample showed the composition to be $\text{VI}_{2.29}$.

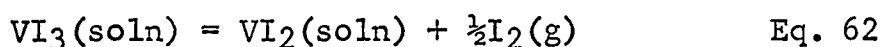
Anal: V, 14.85%; I, 85.15%; $\text{I/V} = 2.29$.

Thus the hypothesis of an interaction as shown in Equation 58 was established.

The composition of the sample indicates, furthermore, that the observed behavior during the diaphragm gauge experiments was not due to the reaction between VI_2 and iodine such as that observed in the transpiration experiments. The explanation for the data, by the very nature of the experiments, is somewhat obscure.

Tolmacheva et al. (27, p. 283) indicate that they measured the decomposition pressure of VI_3 over the temperature range 590-804°K. as shown in Equation 57. If only the data in the reciprocal temperature range of 1.4-1.7 are considered the curve shown in Figure 16 is obtained. These data give a straight line corresponding roughly to the line obtained by the Russian workers. However, it was at a temperature within this range that the cell was finally broken, and the composition of the sample corresponded to $VI_{2.29}$, not VI_3 .

Many experiments, mentioned earlier, showed that VI_2 may be prepared from VI_{2+x} , the non-stoichiometric iodide, by heating in vacuo at temperatures on this same order, 290-440°C. Since the pressures are quite low, the experiments suggest that the important process in this range is decomposition of the non-stoichiometric iodide according to Equation 63.



The explanation for the behavior at lower temperatures can not be explained in terms of such a decomposition reaction, for many experiments during this investigation showed VI_{2+x} to be stable toward the loss of iodine at temperatures less than ca. 250°C. Since the transpiration experiments showed that VI_4 could be formed even at temperatures as low as 250°C., it

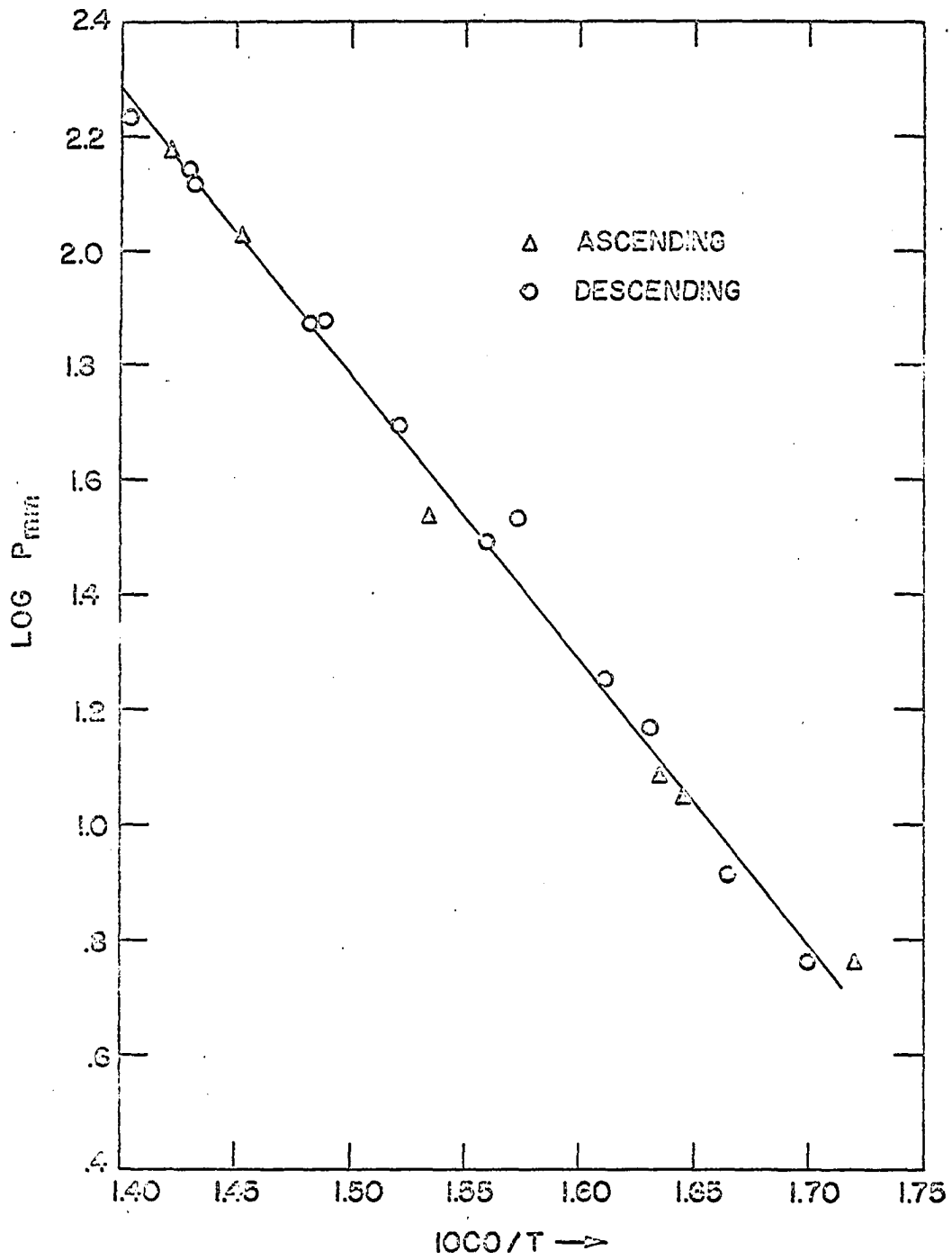
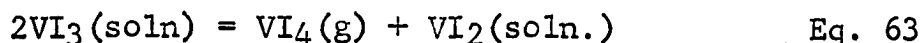


Figure 16. Decomposition pressure over the nonstoichiometric iodide over the range 590 to 715°K.

is likely that some kind of disproportionation such as that shown in Equation 63 is the most important process.



No good explanation is available for the "tailing off" of pressure observed at high temperatures.

Figure 17 shows a comparison of data from this work and that of Tolmacheva et al. (27, p. 283).

A least square analysis of the data from $1.4 < 1000/T < 1.7$ gave the following equation for the line.

$$\log P(\text{atm}) = - \frac{4856 \pm 88}{T} + 6.220 \pm 0.137 \quad \text{Eq. 64}$$

The free energy, obtained from that equation at $T(^{\circ}\text{K}) = 611$ may be expressed as

$$\Delta F^{\circ} = 22221 - 32.9T. \quad \text{Eq. 65}$$

The enthalpy obtained from the slope is $\Delta H^{\circ} = 22 \pm 1$ kcal.

The entropy at $T = 611^{\circ}\text{K}$. is $\Delta S^{\circ} = 32.9 \pm 1$ e.u. Table 10 shows a comparison of these data with that of Tolmacheva et al.

Table 10. Decomposition data for VI_x

Investigator	Compound	Temp. range ($^{\circ}\text{K}$)	A	B	ΔH° (kcal/ mole)	ΔS° (eu)
Tolmacheva	VI_3	591-804	4800	5.9	22 ± 1	27 ± 1
This work	VI_{2+x}	571-713	4856	6.2	22 ± 1	32 ± 1

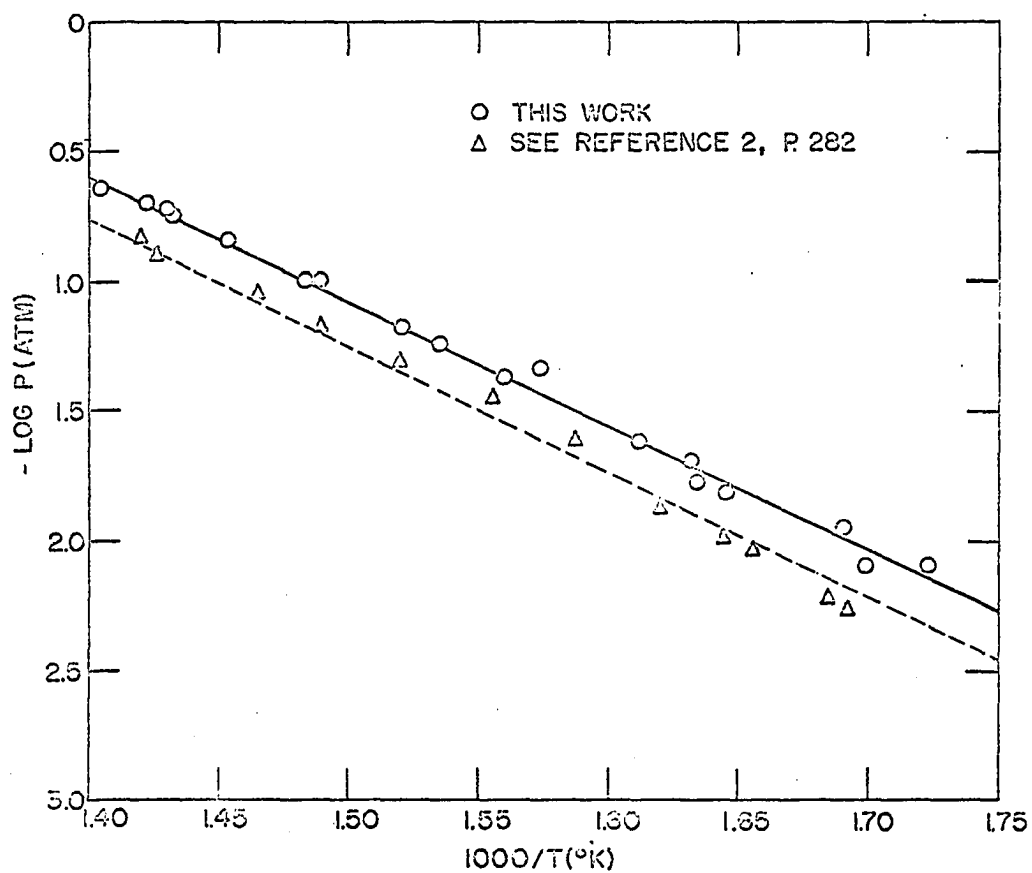


Figure 17. Comparison of decomposition pressure data from this work with data given by Tolmacheva

It seems unlikely, in the light of difficulties in preparing VI_3 , that the data of Tolmacheva are for VI_3 , but are for the non-stoichiometric iodide instead. Of all the reports of VI_3 noted earlier, no one has ever done any structure work with it, nor much chemical work either.

Since the dihalides of vanadium all have extremely low vapor pressures at these temperatures it is likely that VI_3 would be expected to have a greater vapor pressure than VI_2 . This agrees with the observed behavior of VCl_3 - VCl_2 and VBr_3 - VBr_2 (2, p. 62). It would then be expected that the decomposition pressure might increase as the composition increased. If this is valid, the fact that the diaphragm gauge sample had a composition of $VI_{2.29}$ while that scraped from the vanadium foil was $VI_{2.12}$ leads to an explanation why the data obtained here show a higher pressure than that obtained by Tolmacheva et al. Their sample was prepared by scraping sample from the surface of vanadium foil (27, p. 281).

SUMMARY

This study of the vanadium iodide system included both preparative and vapor pressure investigations.

Several different types of experiments were used in an attempt to prepare and isolate VI_3 . They included: a) chemical transport reactions, b) equilibration experiments between VI_2 and liquid iodine, c) solvent extraction using liquid iodine for the solvent and d) direct combination of the metal (as foil) and iodine liquid.

Equilibration experiments between VI_2 and liquid iodine produced products whose composition ranged from $VI_{2.00}$ to $VI_{2.63}$ in the temperature range 495° - $722^{\circ}C$. Although VI_2 was found to have different lattice constants than any non-stoichiometric compound, all compounds within that phase range ($2.02 < I/V < 2.63$) had nearly the same lattice constants. Considering the non-stoichiometric phase to be a solid solution, equilibrium constants and associated thermodynamic data were calculated.

The transpiration technique was used to study the reaction between vanadium(II) iodide and iodine vapor. The principal product was determined to be VI_4 . The pressure of VI_4 resulting from this reaction was determined for the temperature range 581° - $713^{\circ}K$. Equilibrium constants and asso-

ciated thermodynamic data were calculated.

The dissociation of the non-stoichiometric iodide was investigated using the diaphragm gauge technique. A linear portion of that curve was abstracted and thermodynamic calculations made for the data within the temperature range 388°-546°K.

The vaporization or equilibrium data obtained in this investigation may be expressed as $\log P$ (or K) = $-A/T + B$ for the following processes: 1) $VI_2(s) + I_2(g) = VI_4(g)$; 2) $VI_2(\text{soln.}) + \frac{1}{2}I_2(l) = VI_3(\text{soln.})$; 3) $VI_{2+x}(s) = VI_2(s) + I_2(g)$. The values obtained for A and B, along with the temperature range and data are given in Table 11.

Table 11. Thermodynamic data for some vanadium iodides

Process	Temp. range (°K)	A	B	ΔH° (kcal)	ΔS° (e.u.)
1	495-722	3040+91	2.181+0.152	13.9+0.4	10.0
2	388-546	--- ^a	--- ^a	7.55	14.8 ^b
3	581-713	4856+88	6.200+0.137	22.1+0.1	32.9 ^c

^aSince no least square analysis was completed for these data, values for A and B were not determined since their validity would have been questionable.

^bThe value for ΔS° is given for $T = 511^\circ K$.

^cThis value of ΔS° was determined at $T = 611^\circ K$, the graphical value for ΔH° and solving for ΔS° from the equation $\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ$.

SUGGESTIONS FOR FURTHER WORK

More work is being reported on transition metal halide systems than in the past. Increased interest in this area of chemistry is quite evident. Nevertheless, there are still many gaps in the knowledge of these systems, particularly of lower halides.

Basic thermodynamic data are scarce and many areas of investigation are open to workers in this field. Repeating the comment of Roddy (11, p. 164) an investigation of the vanadium fluoride system would be particularly interesting since the stable vapor species over the chlorides, bromides and now iodides of vanadium(II) and (III) include the respective tetravalent halide. The existence of mixed tetravalent halides of vanadium could be determined.

The existence of other systems containing a long homogeneous range should be explored. Good examples of this unusual behavior are few.

In light of the difficulties observed in this study more work on the preparation of higher halides of vanadium is certainly in order.

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ACKNOWLEDGEMENTS

The author wishes to thank Dr. R. E. McCarley for his patience, guidance and understanding during the course of this work.

Appreciation is extended to the members of Physical and Inorganic Group X for their cooperation and generous exchange of ideas and equipment.

Special thanks are extended to Mr. Ron Hogue, who assisted in many ways while this thesis was in its final stages of preparation. No acknowledgement would be complete without thanking Miss Verna Thompson, the finest typist available.

APPENDIX

Table 12. Interplanar spacings for solid solutions in range $2.0 < I/V < 2.63$

Line	hkl	2.00 ^a	2.02 ^b	2.22	2.28	2.36	2.48	2.55	2.63
1	001	6.78	6.72	6.62	6.61	6.70	---	6.65	6.62
2	010	3.52	3.44	3.46	3.46	3.46	3.45	3.47	3.46
3	002	3.39	3.34	3.32	3.32	3.32	3.33	3.33	3.32
4	011	3.13	3.09	3.07	3.07	3.07	3.07	3.08	3.07
5	012	2.45	2.40	2.40	2.40	2.41	2.40	2.41	2.39
6	110	2.04	2.00	2.00	2.00	2.01	2.00	2.01	2.02
7	111	1.90	1.90	---	1.92	---	---	---	---
8	013	---	---	1.87	1.87	1.87	1.87	1.87	1.87
9	112	1.74	1.70	1.71	1.71	1.73	1.72	1.72	1.71
10	021	1.71	1.68	1.68	1.68	1.69	1.68	1.68	1.68
11	004	1.69	---	1.66	1.66	1.66	1.66	1.67	1.67
12	022	1.58	1.56	1.54	1.54	1.54	1.54	1.54	1.54
13	014	---	---	1.50	1.50	1.49	1.50	1.50	1.50
14	023	1.39	1.37	1.36	1.36	1.36	---	1.37	1.36
15	005	---	1.33	---	1.33	---	---	---	---
16	121	1.31	1.30	1.29	1.29	1.29	---	1.29	1.29
17	114	1.30	1.28	1.28	1.28	1.28	---	1.28	1.28
18	015	1.27	1.24	1.24	1.24	1.24	---	1.24	1.24
19	122	1.24	---	---	1.22	1.22	---	1.22	1.22
20	024	1.18	---	---	1.20	---	---	---	---
21	030	---	1.17	---	1.16	---	---	---	1.16
22	031	---	1.14	---	1.14	---	---	---	1.14
23	115	---	---	---	1.11	---	---	---	---
24	032	---	---	---	1.09	---	---	---	---

^aThis sample of VI_{2.00} was prepared by thermal decomposition of the non-stoichiometric iodide.

^bThe sample of VI_{2.28} was made from one crystal which had been ground up.

Table 13. Transport of VI_2 with iodine vapor

Run no.	Sample temp. ($^{\circ}\text{K}$)	$\frac{1000}{T}$	Flow rate (mg/min)	P_{T} (mm)	P_{I_2} (mm)	Moles I_2 ($\times 10^3$)	Moles V ($\times 10^5$)	$P_{\text{VI}_4}^{\text{a}}$ ($\text{mm} \times 10^3$)
1	630.2	1.587	4.47	21.9	21.84	3.155	0.8203	57.28
2	538.6	1.857	8.08	21.7	21.69	4.332	.1476	7.402
3	548.2	1.824	11.98	21.6	21.59	8.968	.3787	9.333
4	514.2	1.945	13.68	21.6	21.59	1.208	.2865	5.120
5	569.2	1.757	20.89	21.8	21.78	1.314	1.151	18.17
6	636.2	1.572	6.42	21.7	21.66	4.453	.7700	37.58
7	529.2	1.890	9.91	21.4	21.39	4.452	.1634	7.782
8	610.4	1.638	16.12	21.3	21.27	7.496	1.043	29.64
9	719.2	1.390	9.74	20.9	20.15	4.491	3.338	152.0
10	722.2	1.384	14.75	21.1	20.39	8.312	8.187	210.7
11	713.2	1.402	8.08	20.9	20.27	3.884	2.480	133.6
12	699.2	1.430	10.05	20.9	20.23	5.612	.4656	173.2
13	533.2	1.875	8.16	44.8	44.79	4.080	1.287	14.16
14	521.2	1.919	43.92	45.6	44.99	14.88	.2855	8.730
15	561.2	1.782	85.94	45.2	45.18	21.98	.7384	15.19
16	621.2	1.610	79.09	45.5	45.42	18.07	3.160	79.19
17	684.2	1.462	35.88	47.0	46.65	12.02	8.871	346.7
18	712.2	1.404	53.10	46.8	46.39	15.06	13.12	407.3
19	684.2	1.462	14.47	30.7	30.52	8.10	4.754	180.0
20	597.2	1.674	15.46	30.8	30.77	5.61	.6009	32.96
21	620.2	1.612	44.45	30.8	30.73	24.87	5.611	69.50
22	582.2	1.718	51.77	30.8	30.77	28.97	2.581	27.42
23	495.2	2.019	21.37	30.5	30.50	12.46	.1181	2.919
24	528.6	1.891	39.66	30.4	30.39	19.69	.5889	9.078
25	581.2	1.721	24.16	30.8	30.77	16.94	1.446	26.30

^aCalculated from $P_{\text{VI}_4} = X_{\text{V}}P_{\text{T}}/1-X_{\text{V}}$, where X_{V} is the mole fraction of vanadium transported, $X_{\text{V}} = n_{\text{V}}/n_{\text{V}}+n_{\text{I}}$.

Table 13. (Continued)

Run no.	Sample temp. ($^{\circ}$ K)	$\frac{1000}{T}$	Flow rate (mg/min)	P_T (mm)	P_{I_2} (mm)	Moles I ($\times 10^3$)	Moles V ($\times 10^5$)	$P_{VI_4}^a$ (mm $\times 10^3$)
26	608.2	1.644	14.48	30.6	30.55	8.90	4.916	52.48
27	608.2	1.644	39.70	30.8	30.75	12.20	5.037	46.89
28	608.2	1.644	54.23	30.3	30.28	28.63	4.318	52.89
29	608.2	1.644	49.37	30.4	30.35	19.25	3.261	51.59
30	608.2	1.644	25.68	40.6	40.53	15.48	2.657	69.71
31	608.2	1.644	7.16	11.4	11.38	4.31	.7452	19.48
32	608.2	1.644	24.51	20.7	20.66	10.72	1.835	35.44

Table 14. Diaphragm gauge data

Run	t (°C)	$\frac{1000}{T}$ (°K)	P _{mm}	log P _{mm}	Ascending or descending temperature
1	22.5	3.382	0.0	---	A
2	43.8	3.058	1.0	0.000	A
3	62.8	2.976	4.6	.664	A
4	66.3	2.945	6.4	.806	A
5	77.8	2.849	13.9	1.143	A
6	91.5	2.742	30.1	1.479	A
7	107.0	2.630	80.1	1.904	A
8	127.5	2.496	92.3	1.965	A
9	148.0	2.374	97.9	1.991	A
10	175.3	2.230	105.3	2.022	A
11	210.0	2.070	112.3	2.050	A
12	236.8	1.961	118.3	2.073	A
13	250.0	1.911	120.1	2.079	A
14	271.0	1.838	124.5	2.095	A
15	274.0	1.827	125.6	2.099	A
16	499.0	1.295	183.2	2.263	A
17	506.0	1.284	195.9	2.292	D
18	499.0	1.295	183.2	2.263	D
19	470.5	1.345	177.3	2.249	D
20	455.8	1.372	175.8	2.245	D
21	439.8	1.403	172.2	2.236	D
22	425.0	1.432	167.8	2.120	D
23	401.0	1.483	75.4	1.877	D
24	368.0	1.560	31.2	1.494	D
25	347.3	1.612	18.0	1.255	D
26	318.5	1.690	8.2	.914	D
27	298.3	1.750	5.7	.756	D
28	272.5	1.832	3.3	.518	D
29	242.0	1.941	2.1	.322	D
30	194.8	2.141	1.4	.146	D
31	174.5	2.233	0.9	-.046	D
32	77.2	2.854	0.3	-0.523	A
33	120.0	2.543	0.5	-0.301	A
34	164.0	2.283	0.9	-0.046	A
35	216.0	2.044	1.5	0.176	A
36	282.8	1.799	3.5	0.544	A
37	334.5	1.645	11.2	1.049	A
38	378.3	1.535	42.1	1.624	A

Table 14. (Continued)

Run	t(°C)	$\frac{1000}{T(^{\circ}\text{K})}$	P _{mm}	log P _{mm}	Ascending or descending temperature
39	415.5	1.452	107.3	2.021	A
40	430.0	1.422	147.8	2.170	A
41	457.8	1.368	182.1	2.258	A
42	474.5	1.337	185.3	2.268	A
43	506.0	1.284	195.9	2.292	A
44	479.3	1.329	185.3	2.268	D
45	447.8	1.387	174.8	2.243	D
46	426.3	1.430	140.4	2.147	D
47	398.8	1.488	74.7	1.873	D
48	384.3	1.521	49.7	1.696	D
49	362.0	1.574	34.0	1.531	D
50	339.4	1.632	14.9	1.173	D
51	315.4	1.699	5.8	0.760	D
52	272.0	1.834	3.1	0.490	D
53	258.5	1.881	2.6	0.415	D
54	216.8	2.039	1.7	0.230	D
55	155.3	2.337	0.7	-0.155	D
56	61.8	2.985	0.2	-0.699	D
57	81.0	2.185	0.4	-0.398	A
58	109.5	2.613	0.5	-0.301	A
59	144.8	2.394	0.6	-0.222	A
60	188.0	2.168	1.5	0.176	A
61	247.3	1.905	2.3	0.362	A
62	288.0	1.782	4.0	0.602	A
63	308.3	1.720	5.8	0.763	A
64	338.3	1.635	12.2	1.086	A