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Knudsen- and Torsion- Effusion Measurements of the Vapor Pressure of Manganese(II) Fluoride

Walter Clayton Hitchingham

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KNUDSEN- AND TORSION- EFFUSION MEASUREMENTS
OF THE VAPOR PRESSURE OF MANGANESE(II) FLUORIDE

by

Walter Clayton Hitchingham

A Thesis
Submitted to the
Faculty of the School of Graduate
Studies in partial fulfillment
of the
Degree of Master of Arts

Western Michigan University
Kalamazoo, Michigan
April 1969

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Dr. Adli S. Kana'an for his direction in the course of this investigation. Further acknowledgement is extended to Dr. Dean Cooke and Dr. Thomas Houser for their constructive evaluation of the manuscript and to Dr. Dale H. Warren and Dr. Robert E. Harmon and the staff of the Department of Chemistry whose training, experience and encouragement have been invaluable to me. The time saving technical assistance obtained from Mr. Dick Durbin and Mr. Fred Ryba of the Physics and Chemistry machine shop is also greatly appreciated. Mr. Max Anable's assistance in preparing the photographs for the thesis is also greatly appreciated.

Walter Clayton Hitchingham

MASTER'S THESIS

M-1844

HITCHINGHAM, Walter Clayton
KNUDSEN- AND TORSION- EFFUSION MEASUREMENTS OF THE VAPOR PRESSURE OF MANGANESE(II) FLUORIDE.

Western Michigan University, M.A., 1969
Chemistry, physical

University Microfilms, Inc., Ann Arbor, Michigan

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INTRODUCTION

The vaporization behavior of many materials must be described in terms of several simultaneous reactions. Even the elements do not necessarily vaporize in a simple, well-defined form, for example sodium vapor contains a mixture of Na and Na₂; the vapor above phosphorous contains various amounts of P₄, P₂ and P, depending upon the temperature; sulfur vapor contains molecules as large as S₈. Some well known compounds are known to vaporize as mixtures of monomers and polymers: e.g., the vapor phase above AlCl₃, P₂O₅, CuCl, and FeCl₃ contains the monomers as well as Al₂Cl₆, P₄O₁₀, Cu₂Cl₂ and Fe₂Cl₆ respectively. Other compounds are known to decompose rather than simply vaporize, for example Ag₂O decomposes to Ag_(s) and O₂, and CaH₂ decomposes to Ca_(s) and H₂.

The investigation of ternary systems may be further complicated by an increase in the number of components. In contrast to binary systems, ternary systems have not been thoroughly investigated although a variety of such compounds has been known for some time. An important class of ternary compounds is that of complex halides of the form $M^{\text{I}}M^{\text{II}}X_3$ and $M^{\text{I}}M^{\text{III}}X_4$, where M^I represents the Alkali metals, M^{II} and M^{III} represent divalent and trivalent metals respectively and X refers to F or Cl. Gaseous ternary compounds of the mentioned types have been reviewed recently by Buchler et al.¹ Information on the volatility and stability of such complexes, in the vapor phase, is limited to measurements of

partial pressures of vapors in equilibrium with the melts of mixtures, of the two binary components $M^I X$ and $M^{II} X_2$, or $M^{III} X_3$. Only in a few cases such studies over the crystalline complex have been reported.

The accumulation of reliable information on the volatility of complexes and its interpretation from the standpoint of thermodynamics, kinetics and chemical bonding is important in understanding the principles of complex formation and the relation between the properties of the simple components with those of their complex species. To study the vaporization behavior of such complex salts, the vapor pressure of the pure components of these salts as well as the partial pressures of the gaseous species are needed. It is the objective of this program to study the vaporization of manganese difluoride by the simultaneous Knudsen-effusion and torsion-effusion techniques, and to evaluate the suitability of the instrument constructed for such simultaneous measurements. The advantage of this instrument is that it provides vapor pressures and estimates of the average molecular weight of the vapors, in a continuous experiment, over a range of temperature and pressure.

CHAPTER I

THEORETICAL

Knudsen-Effusion Method

The Knudsen-effusion method is widely used in measurements of equilibrium vapor- and dissociation- pressures in the 10^{-2} - 10^{-6} Torr range. This method is based on the Kinetic theory of dilute gases.² It utilizes the rate of flow of a vapor through an orifice from a volume saturated with the vapor. This theory indicates that in a closed system the weight of gas molecules, W , striking the walls of a container of surface area A_0 , in time t , is related to the gas density ρ and to the mean velocity of the gaseous molecules \bar{c} by :

$$\frac{W}{A_0 t} = \frac{1}{4} \rho \bar{c} \quad (\text{I-1})$$

Equation (I-1) can be put into a more practical form by substituting for ρ using the ideal gas law, and for \bar{c} from the Kinetic theory :

$$\rho = \frac{\bar{P}\bar{M}}{RT} \quad (\text{I-2})$$

where \bar{M} is the average molecular weight of gaseous molecules;

$$\bar{c} = \left(\frac{8RT}{\pi \bar{M}} \right)^{\frac{1}{2}} \quad (\text{I-3})$$

Thus :

$$\frac{W}{A_0 t} = \frac{1}{4} \frac{\bar{P}\bar{M}}{RT} \left(\frac{8RT}{\pi \bar{M}} \right)^{\frac{1}{2}} \quad (\text{I-4})$$

which rearranges to the Knudsen-effusion equation³:

$$P_k = \frac{W}{A_0 t} \left(\frac{2 \pi R T}{M} \right)^{\frac{1}{2}} \quad (I-5)$$

where P_k is the pressure of gaseous molecules obtained from Knudsen-effusion experiments.

Validity of equation (I-5) is restricted by the following conditions:

- (1) the effusing vapor represents a saturated vapor in equilibrium with the condensed phase in the effusion cell;
- (2) the pressure outside the cell is negligibly low hence no molecules re-enter the cell once they pass through the orifice;
- (3) the flow is free molecular-flow through the orifice — no molecular collisions of vapor within the orifice;
- (4) the fraction of vapor molecules intercepted by the orifice walls and eventually returned to the cell is negligible.

In practice the first three conditions are realized to a reasonable degree. Condition four is influenced by the length to radius ratio of the orifice. An ideal orifice of infinite thinness is almost impossible to attain. A cylindrical orifice may be visualized as a channel with a linear pressure gradient along its axis. A correction for the reflection of molecules in the channel back to the cell was introduced by Clausing⁴. The correction factor, referred to as the Clausing factor, W_0 , represents the "transition probability", the probability that a molecule having entered the orifice inlet will escape through the orifice outlet. It is expressed by:

$$W_0 = \frac{\text{rate at which vapor molecules leave the orifice outlet}}{\text{rate at which vapor molecules enter the orifice inlet}}$$

The Clausing factor is related to the length to radius ratio ℓ/r by:⁵

$$W_0 = \frac{1}{1 + 0.5(\ell/r)} \quad (\text{I-6})$$

for $0 < \ell/r < 1.5$,

and by:

$$W_0 = \frac{1 + 0.4(\ell/r)}{1 + 0.95(\ell/r) + 0.15(\ell/r)^2} \quad (\text{I-7})$$

for $\ell/r > 1.5$.

Accurate values of W_0 were calculated by DeMarcus⁶ and Schulz and Searcy⁷.

The introduction of the Clausing factor modifies equation (I-5) to:

$$P_k = \frac{W}{A_0 t W_0} \left(\frac{2 \pi R T}{\bar{M}} \right)^{\frac{1}{2}} \quad (\text{I-8})$$

Torsion - Effusion Method

An alternative to the Knudsen-effusion method is the torsion-effusion method in which vapor pressures are measured directly by a simple dynamic technique. This method, first developed by Mayer⁸ and Volmer⁹, utilizes a measure of the momentum recoil which can be related to vapor pressures. In this method the sample vapor molecules at saturated equilibrium vapor pressure and at a given temperature are allowed to effuse through the orifices in a cell suspended in such a manner that the recoil force, F , produced by the

effusing vapor molecules applies a torque on the cell. The recoil force is related to the equilibrium vapor pressure, P_{τ} by :

$$P_{\tau} = \frac{2F}{A_0} \quad (I-9)$$

where A_0 is the cross sectional area of the orifice (s). The torque, T_r , generated by the recoil force on the cell is exactly counterbalanced by a restoring torque, T_w , of the suspension wire of the cell. The torque is related to the recoil force by :

$$T_r = Fd \quad (I-10)$$

where d , the moment arm, is the distance between the orifice center and the suspension axis. In the conventional torsion-effusion cell there are two anti-parallel orifices perpendicular to the axis of the suspension wire (torsion fiber). The resultant torques of such two orifices are additive :

$$T_r = (Fd)_1 + (Fd)_2 \quad (I-11)$$

The restoring torque in the torsion fiber is given by :

$$T_w = \tau \theta \quad (I-12)$$

where τ is the torsion constant of the torsion fiber and θ is the angular displacement of the suspension system. Substitution from equation (I-11) and (I-12) into equation (I-9) yields :

$$P_{\tau} = \frac{2 \tau \theta}{(A_0 f)_1 + (A_0 f)_2} \quad (I-13)$$

where f is a correction factor for finite orifice lengths. It is

analogous to the Clausing factor in the Knudsen-effusion equation. It represents the ratio of the recoil force resulting from effusion through an orifice of finite length to that expected if the orifice is of infinitesimal length. This factor, referred to as the pressure factor, had been determined by Searcy and Freeman¹⁰ and a more accurate tabulation of it was reported by Schulz and Searcy⁷.

Correlation of the Knudsen- and Torsion-Effusion Methods

The cell in the torsion-effusion method is a modified Knudsen cell and can be used to measure the torque and the rate of weight loss simultaneously. The torsion pressure calculated by equation (I-13) can be used to calculate the average molecular weight, \bar{M} , of the vapor species. By substitution of P_T for P_K in equation (I-8) and rearrangement one gets:

$$\bar{M} = 2\pi RT \left(\frac{W}{P_T t A_0 W_0} \right)^2 \quad (\text{I-14})$$

If the average molecular weight, \bar{M} , is different from the assumed molecular weight, M , one may speculate on the nature of the vaporization process and deduce whether the effusing vapor consists of a mixture as a result of dissociation or polymerization. The average molecular weight, \bar{M} , is related to the molecular weights, M_i , of the individual vapor species in such a mixture by¹¹:

$$\bar{M} = \left(\sum_i m_i M_i^{-\frac{1}{2}} \right)^{-1} \quad (\text{I-15})$$

where m_i is the mass fraction of vapor species i in the effusing vapor.

Usually the accepted upper pressure limit for an effusion experiment is that pressure for which the mean free path of the molecules is at least ten times the orifice diameter. There is considerable evidence¹²⁻¹⁵ that equation (I-8) is valid at higher pressures than the above restriction permits. Searcy and Schulz¹⁶ have found, by torsion-effusion measurements with orifices of very short channel lengths, that in the transition region the forces exerted by effusing molecules are the same as those predicted by the molecular-flow equation.

Effect of Orifice Dimensions on Equilibrium Pressures

The pressure obtained from an effusion experiment represents the pressure inside the cell which, due to continuous effusion through the orifice, is expected to be less than the equilibrium pressure¹⁷. The equilibrium pressure, P_{eq} , is related to the Knudsen pressure, P_k , by:

$$P_{eq} = \left(1 + \frac{A_0 W_0}{\alpha_c S}\right) P_k \quad (I-16)$$

where S is the sample surface area, α_c the condensation coefficient defined as the fraction of molecules striking the sample that condense. The above equation follows from mass balance considerations where the rate of evaporation equals the sum of the rate of effusion and the rate of condensation. Motzfeldt¹⁸, Whitman¹⁹ and Rosenblatt²⁰ have discussed the theoretical aspects of the treatment which led to equation (I-16). Speiser and Spretnak²¹ introduced

some approximations to the Whitman-Motzfeldt equation which led to equation (I-16). Hildenbrand and Hall²² have demonstrated the utility of equation (I-16) for determination of the equilibrium pressure (P_{eq}) by linear extrapolation of the measured pressure P_k in a series of effusion cells of different orifice areas (A_o). By rearrangement of equation (I-16) it follows that:

$$\frac{1}{P_k} = \frac{1}{P_{eq}} \left(1 + \frac{W_o}{\alpha_c S} A_o \right) \quad (I-17)$$

Thus a plot of $\frac{1}{P_k}$ vs the orifice area A_o , when extrapolated to zero orifice area will yield $\frac{1}{P_{eq}}$ as an intercept and $\frac{W_o}{\alpha_c S P_{eq}}$ as the slope. From the intercept and the slope one may calculate $\frac{1}{\alpha_c S}$, for an orifice of known A_o and W_o , and consequently α_c may be assessed. The sample surface area, S , may be assumed to be equal to the cross sectional area of the cell.

CHAPTER II

EXPERIMENTAL

Description of Apparatus

The experimental system used for simultaneous weight-loss and torsion-effusion measurements is quite simple; it can best be described by consideration of its individual components. The essential parts of the apparatus used (shown in Figure 1-5) include a vacuum recording balance, a torsion-effusion assembly, a vacuum system, a furnace, and a temperature control system. A schematic of the assembly is shown in Figure 6.

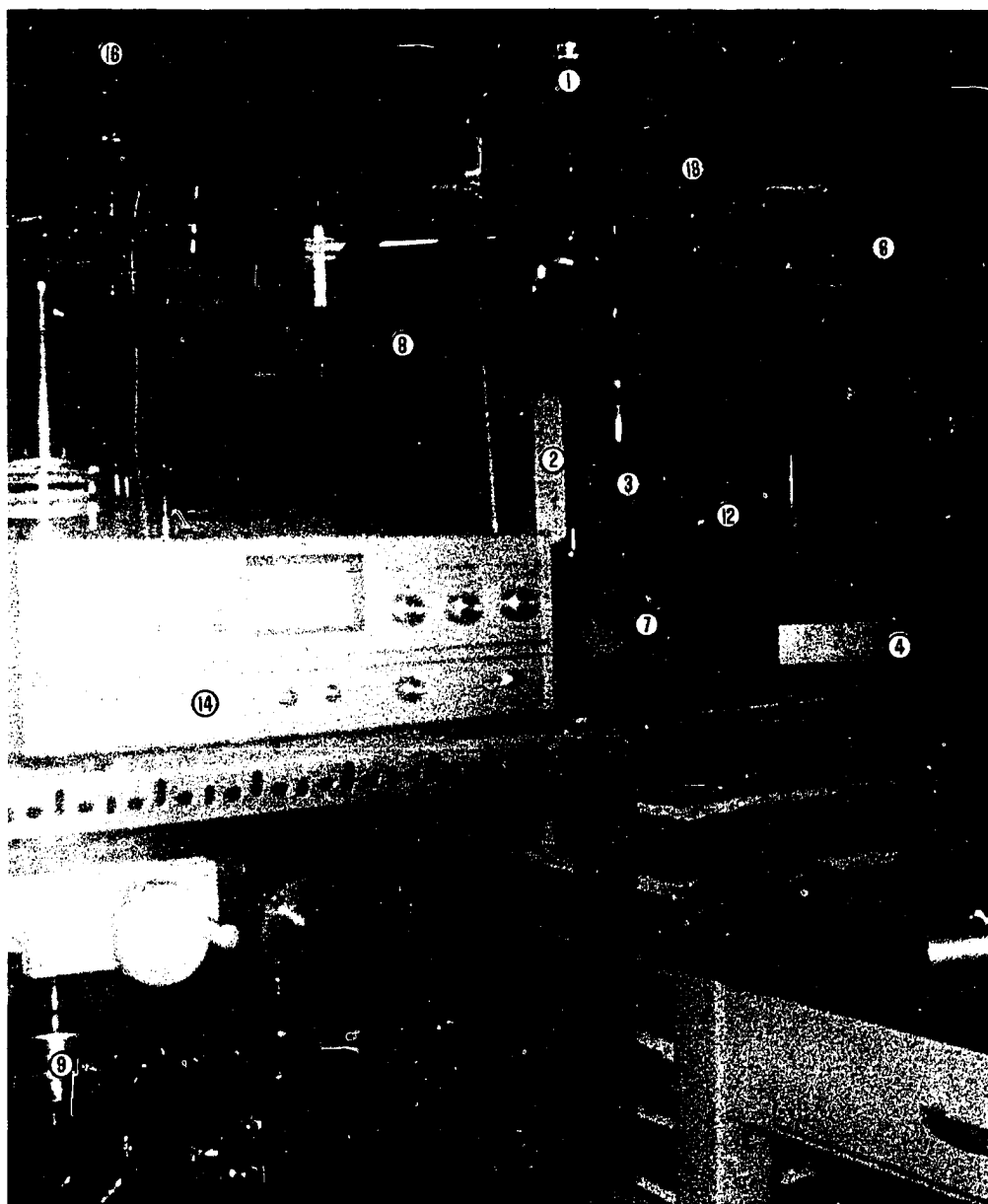
The Balance

The vacuum recording balance used in this work was an Ainsworth semimicro vacuum balance type RV-AU-1. The balance mechanism enables automatic addition or removal of small switch weights in increments of 10 mg up to 400 mg. Small changes in weight are detected by a variable inductance transducer and are recorded on a chart recorder via a bridge circuit. The ten inch span of the chart corresponds to a 10 mg weight change. The reciprocal sensitivity of the balance is 0.03 mg with a reproducibility of ± 0.03 mg. The balance and weight change mechanism are mounted on a base plate and covered by a pyrex bell jar. Connection to the vacuum system and the weighing chamber is through a hole in the base plate beneath the left stirrup.

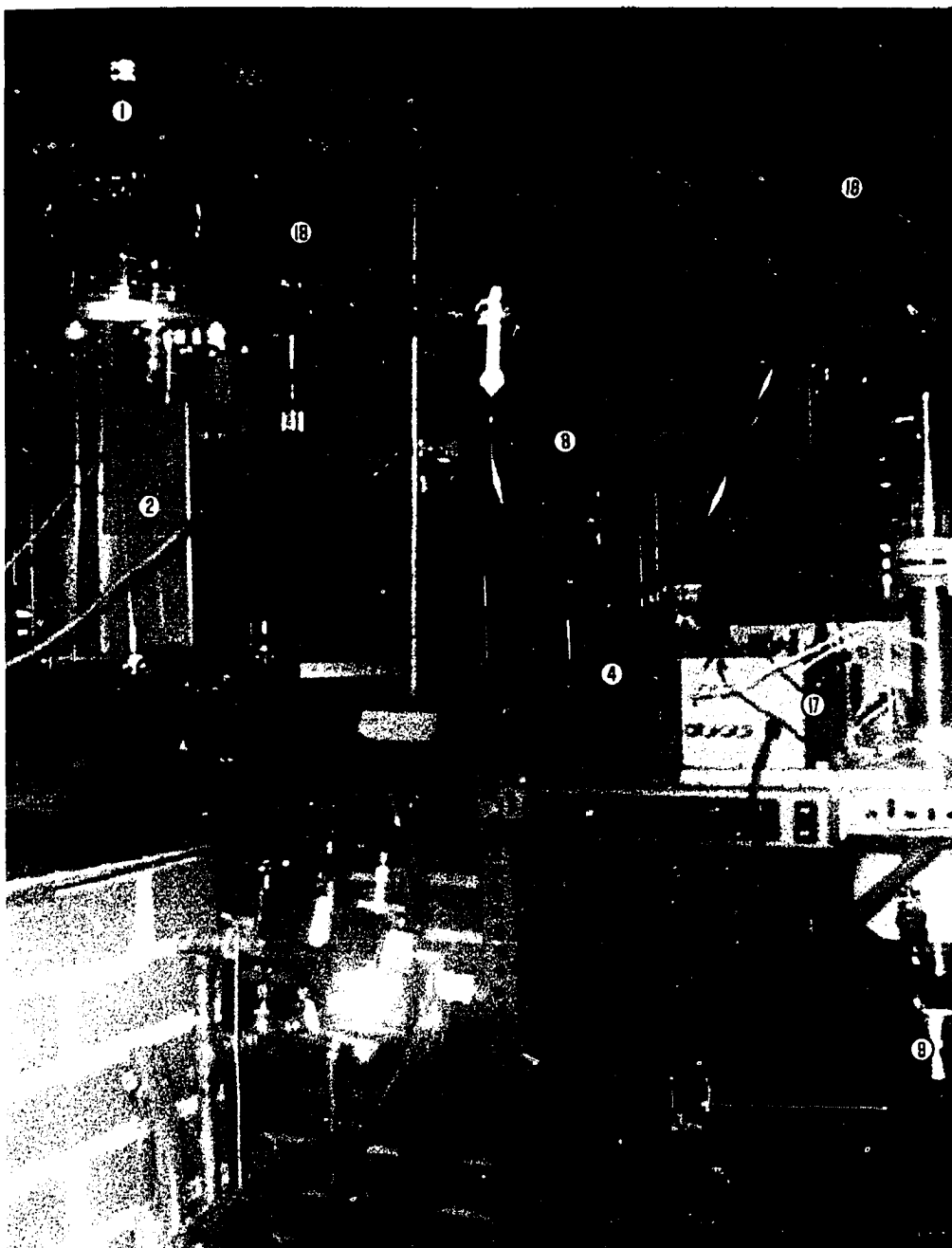
KEY TO FIGURES 1 - 4

TORSION - KNUDSEN EFFUSION APPARATUS

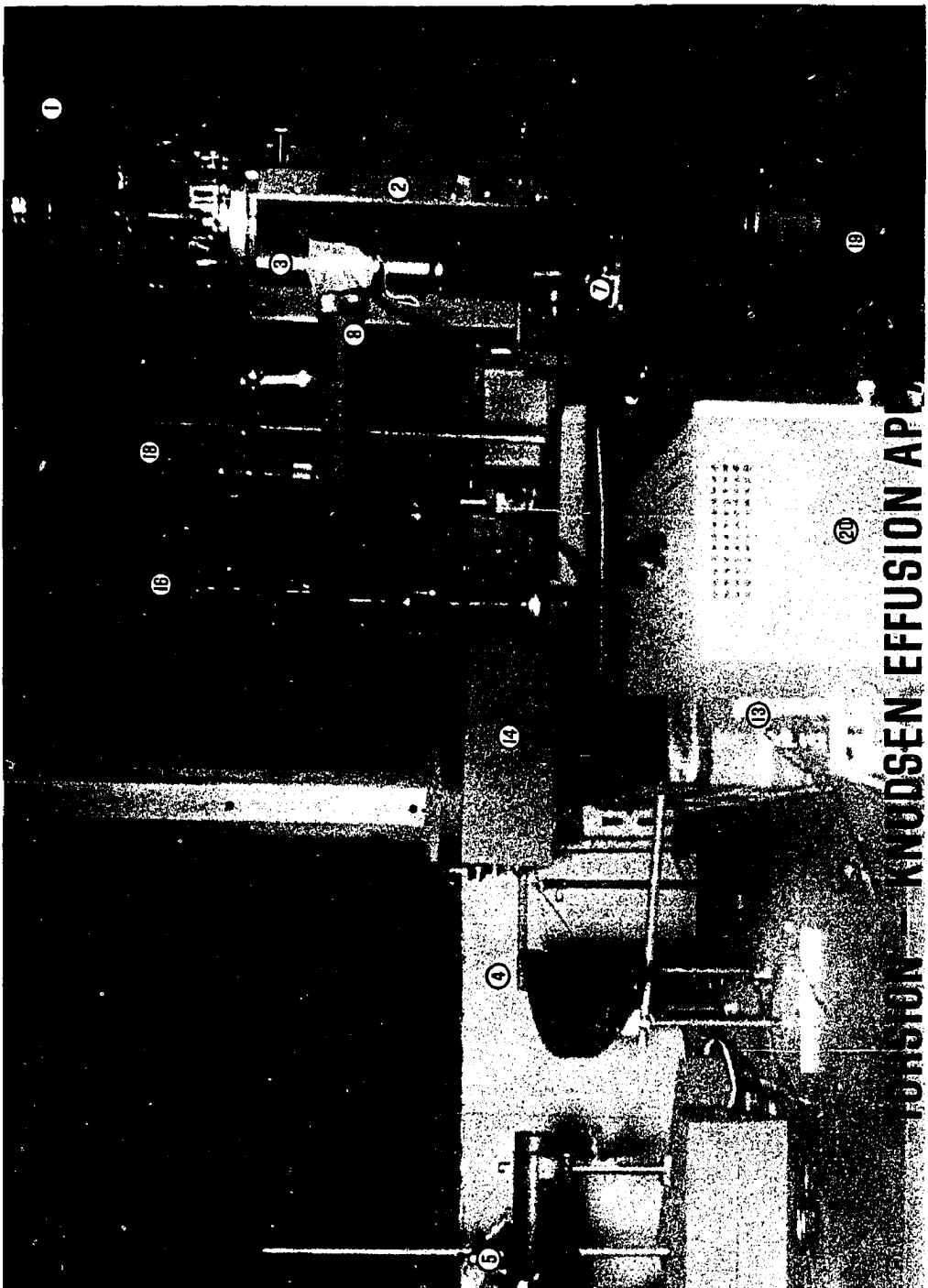
1. Vacuum recording balance
2. Balance stand
3. Brass extension tube
4. Torsion scale
5. Torsion scale and light source
6. Recorder
7. Glass window
8. Brass evacuation line
9. Liquid-nitrogen trap
10. Oil diffusion pump
11. Furnace
12. Potentiometer
13. Temperature Controller
14. Ionization- and thermocouple- gauges console
15. Ice bath
16. Thermocouple gauge
17. Liquid nitrogen feed-control unit
18. Ionization gauge
19. Quartz tube
20. D. C. power supply for electromagnet

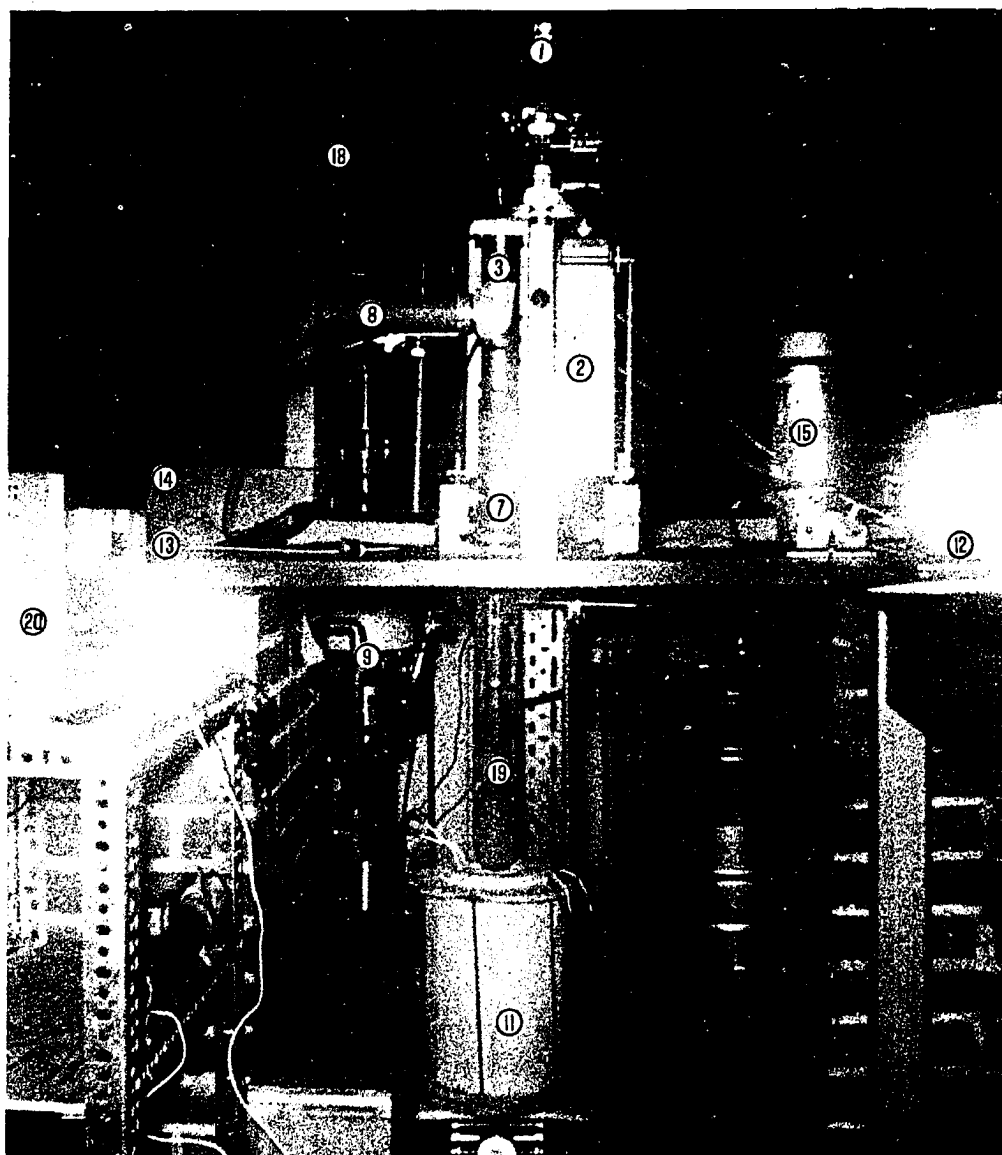


TORSION - KNUDSEN EFFUSION APPARATUS - I



TORSION - KNUDSEN EFFUSION APPARATUS -2



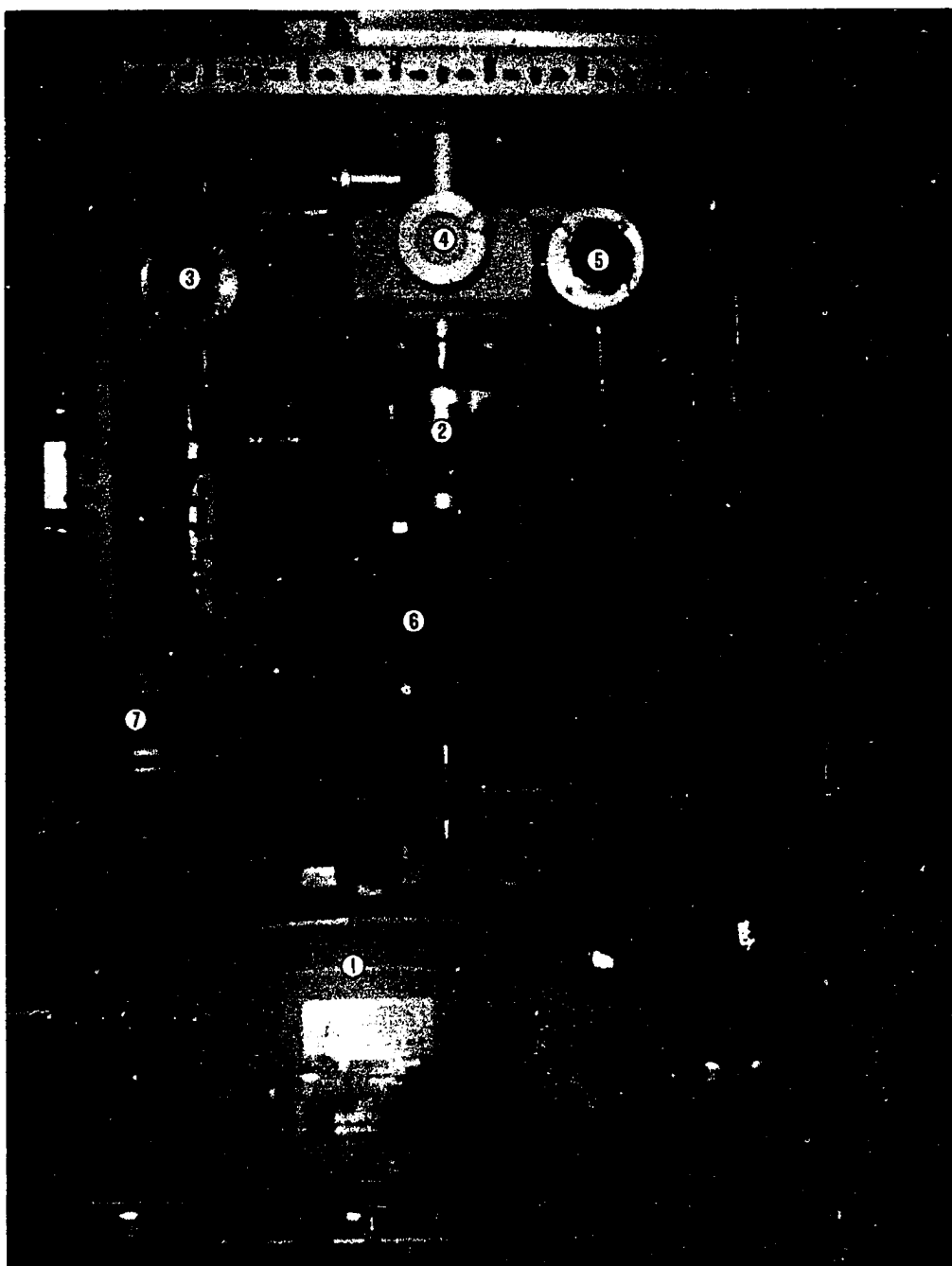


TORSION - KNUDSEN EFFUSION APPARATUS -4

KEY TO FIGURE 5

VACUUM SYSTEM

1. Mechanical pump
2. Diffusion pump and liquid-nitrogen trap
3. Roughing valve
4. Main-gate valve
5. Fore-line vacuum valve
6. Rubber tubing connection between the mechanical and diffusion pumps
7. Liquid-nitrogen Dewar

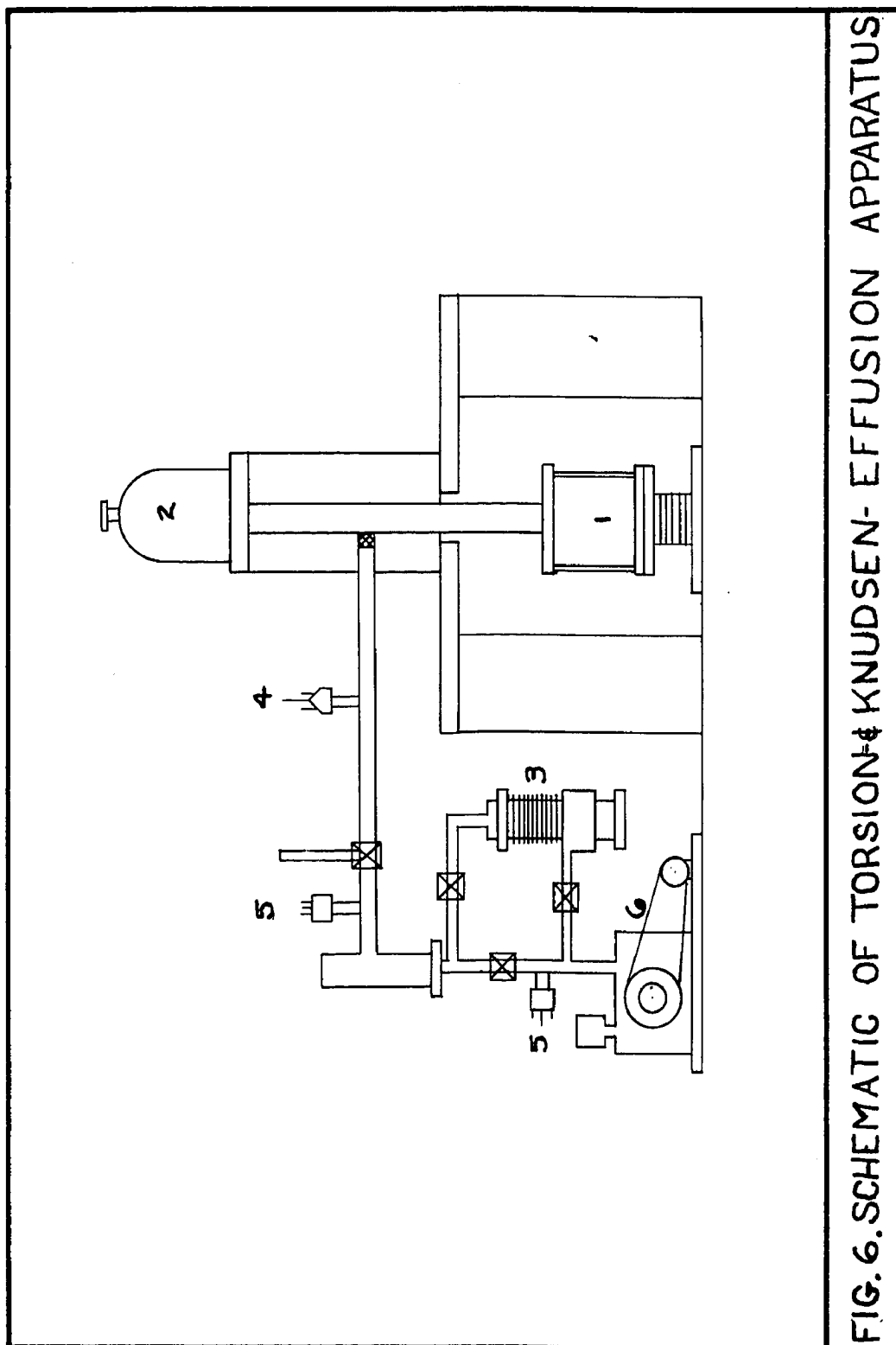


VACUUM SYSTEM

KEY TO FIGURE 6

SCHEMATIC OF TORSION- AND KNUDSEN-EFFUSION APPARATUS

1. Furnace
2. Vacuum recording balance
3. Diffusion Pump
4. Ionization gauge
5. Thermocouple gauges
6. Mechanical Pump



The Torsion-Effusion Assembly

The torsion-effusion assembly (shown in Figure 7) which was suspended from the left beam of the balance consisted of, in the order from top to bottom, a stool and connector, torsion fiber, mirror and damping disc assembly and effusion cell and its suspension assembly.

The stool and connector

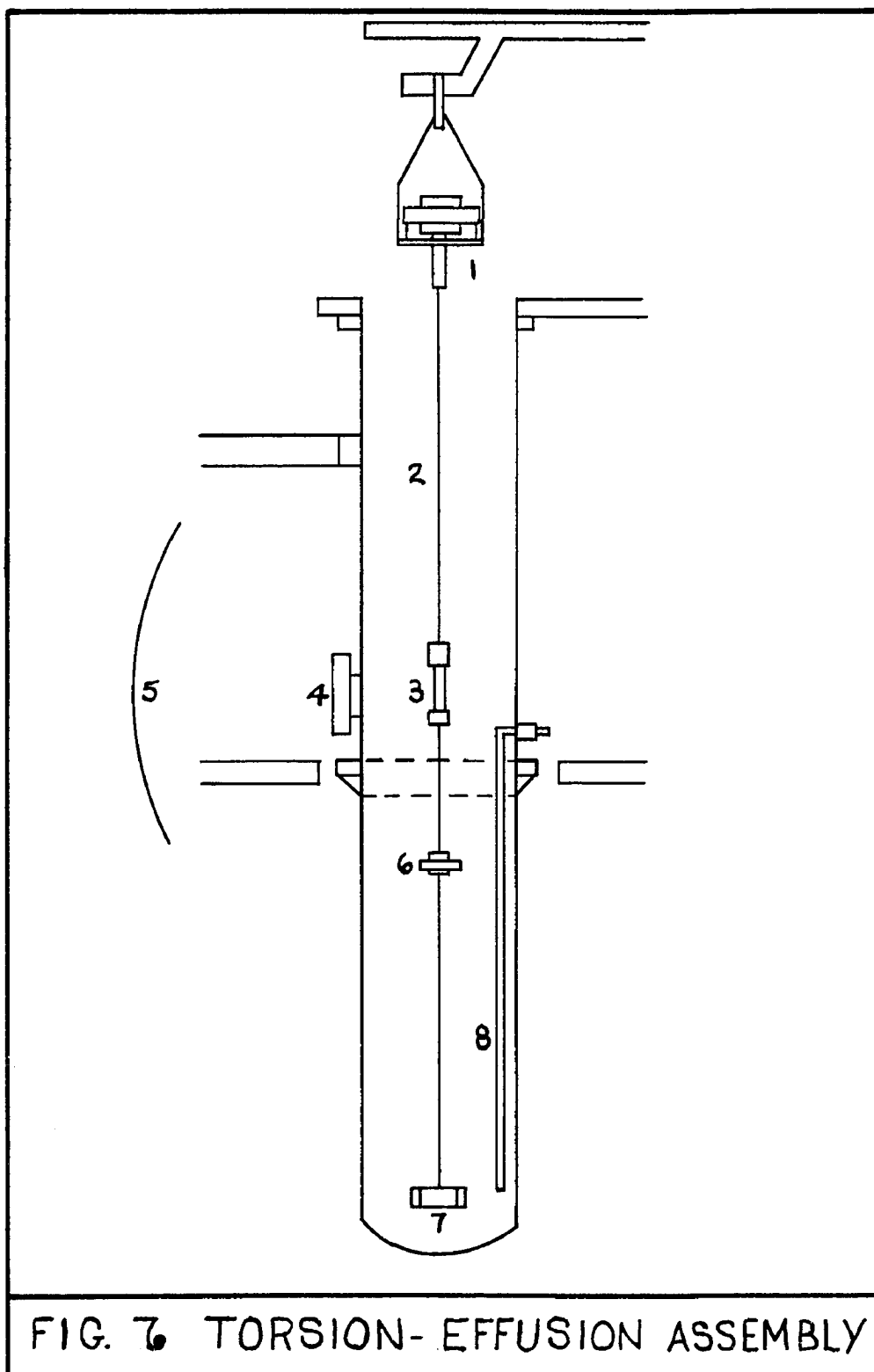
The torsion assembly was connected to the pan of the balance via a small chuck fastened to a rotatable drum fitted into an aluminum stool. The tripod-shaped stool rested on the pan through three equispaced brass pins projected on a circular groove in the pan. The stool and assembly were centered by guiding its pins along the pan groove whose center coincides with the torsion fiber and the axis of the surrounding brass cylinder. Rotation and lateral alignment of the torsion assembly were achieved by rotation of the chuck carrying drum. This arrangement was necessary to direct and position the mirror used to measure the angular deflection of the effusion cell in a direction convenient for measurement.

The torsion filament

An annealed, high purity tungsten wire with a diameter of 0.002 inch or 0.0015 inch and a length of approximately 14 inches, was attached to the above mentioned chuck. At the lower end of

KEY TO FIGURE 7
TORSION-EFFUSION ASSEMBLY

1. Stool and connector
2. Torsion wire
3. Mirror
4. Window
5. Scale
6. Damper
7. Effusion cell
8. Thermocouple



the wire was another chuck which supported a mirror, a damper, and a connecting tantalum tube. Tantalum was chosen because of its relative resistance to corrosion.

The mirror, connector tube and damper

The mirror was cemented with epoxy to an aluminum rod fastened to the lower chuck. A notched position in the aluminum rod allowed positioning of the mirror such that its front surface was approximately in the plane of the torsion assembly axis. The mirror was a front-surface galvanometer type (Leeds and Northrup) 0.5 inches in diameter and concave with a radius of curvature of one meter.

A thin-walled tantalum tube, 0.125 inches in diameter, 0.005 inches in wall thickness, and 15 inches in length, served as a connector to the effusion cell. Its upper end was joined to an aluminum rod supporting the mirror by a tungsten pin. The damper, an aluminum disc, 1.5 inches in diameter and 0.125 inches in thickness, was inserted onto the tantalum tube and positioned at about 6 inches below the mirror by a set screw. The effusion cell was connected to the lower end of a carefully matched graphite dovetail which facilitated assembly and disassembly. Lateral lines were scribed on the dovetail to align the cell with the axis of the suspension system.

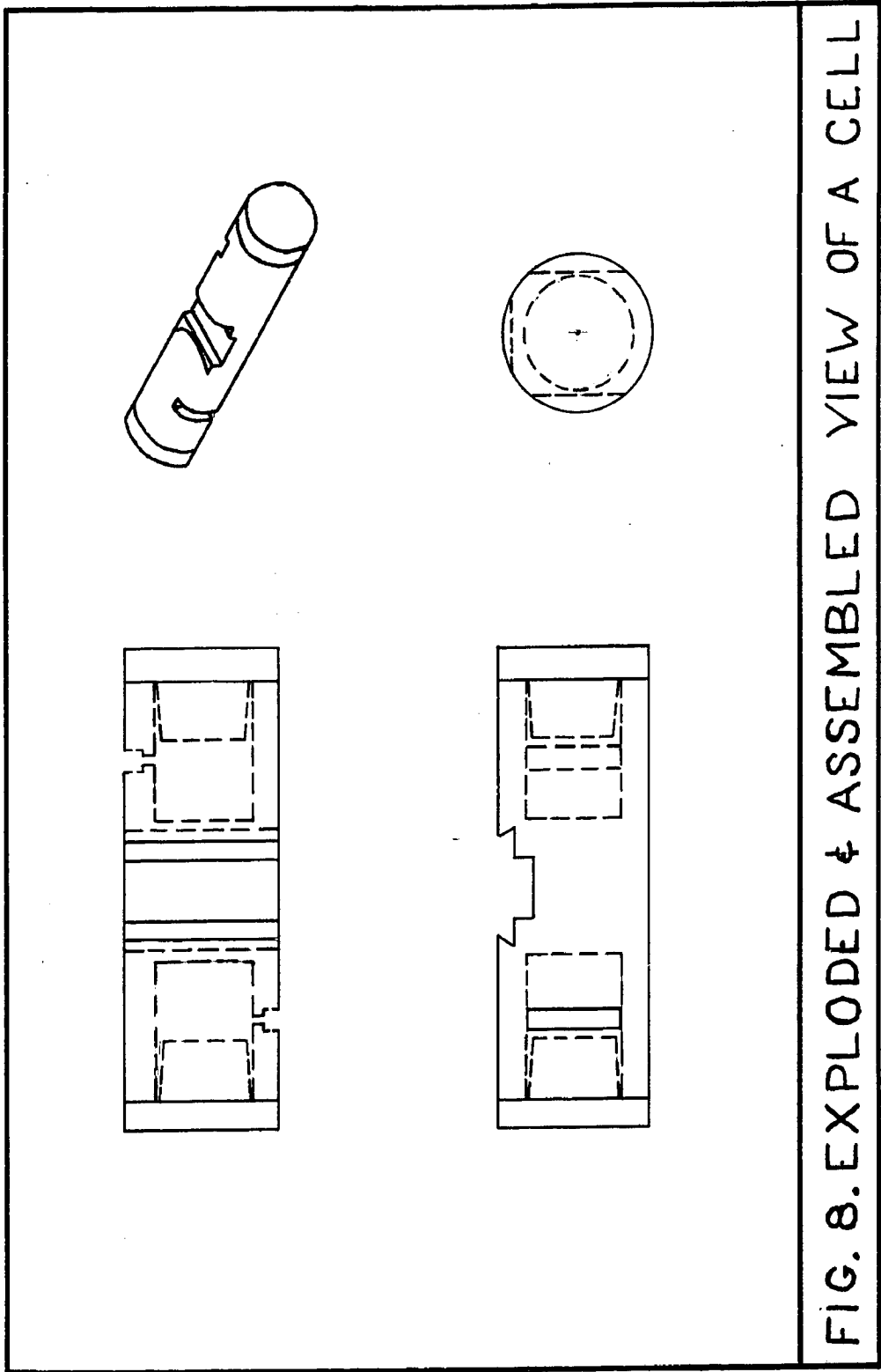
The effusion cell

The effusion cells used in this work were fabricated from spectroscopic grade graphite. The cell, 1.5 inches long, 0.500 inches

in diameter and 0.063 inch wall thickness, had two compartments drilled to a depth of 0.500 inch each from each end. The middle solid section, 0.375 inches long, was machined to match the dovetail of the connecting tube. The cell end openings were fitted with two-degrees tapered graphite plugs. This construction enabled easy loading of the sample. Two holes were drilled on opposite sides of the cell 180° out of phase, antiparallel to each other, and perpendicular to the central axis of the suspension system. A line scribed along the cell's vertical axis extending to the center of the dovetail slot in the cell coincided with the suspension system axis and facilitated the cell alignment by coincidence with the matching lines on the connecting dovetail. The walls in the immediate vicinity of the orifices were thinned down by milling to provide reasonably thin-wall orifices. A sketch is shown in Figure 8.

The Optical Lever System

The optical lever system consisted of a collimated light source, a mirror of the torsion assembly, and a scale. A beam of light from the light source to the scale, after reflection at the mirror, aided in measurement of the cell deflection. The scale was a flexible three foot steel ruler graduated in two hundredths of an inch. This scale was mounted to a plexiglass plate machined to form an arc of a circle. The mounted scale formed an arc of a circle, 36 inches in radius with a center of rotation coincident with the axis of the torsional assembly. The distance of the support for the



plexiglass plate was adjusted to align the scale to the radius cited above. The elevation of the support was adjusted so that the reflected light beam from the mirror would fall on the upper portion of the scale with a minimum lamp adjustment. The lamp used was a conventional galvanometer projector.

The Vacuum System

The balance was connected to the vacuum system through a 2 inch diameter and 18 inches long brass tube which surrounded the torsion assembly. This extension tube was attached to the balance base plate by an O-ring flange. A similar O-ring flange at the other end of the tube joined the quartz heating chamber. The heating chamber was an 18 inch long, 70 mm inside diameter, closed end, quartz tube fitted with a 2 inch grooved flange pipe. A port in the extension tube fitted with a flat glass window, at the same level of the mirror in the torsion assembly, permitted incidence and reflection of the light beam used in deflection measurements. A T-joint soldered to the extension tube at about 4 inches below the balance base plate allowed connection of the balance to the main pumping system through a vacuum coupling.

The main pumping system shown in Figure 5 consisted of a chevron baffle, a cold trap, a 2 inch-four stage fractionating oil diffusion pump with pumping speed of 285 liter/sec (N.R.C. Model HS2-300) and a two stage mechanical fore-pump with a pumping speed of 150 liter/min (Precision Scientific Model D-150). A high vacuum

gate valve separated the balance and weighing extension tube from the diffusion pump. Two, 1 inch vacuum valves were used in roughing- and fore- lines in the all-metal vacuum pumping system. Two ($\frac{1}{8}$ inch) bleeding valves allowed purging the appropriate sections of the system with air dried over dryrite. The pressure in the vacuum system was monitored with one ionization gauge, two thermocouple gauges and a regulated control console (N.R.C.-720).

The Furnace and Temperature Control and Measurement

The furnace and temperature control

The furnace was a resistance wound furnace. The core was a mullite tube 3 inches in diameter and 12 inches long. The heating element was B&S 15 gauge Kanthal wire wound in such a way to compensate for heat loss at the ends and to secure a long hot zone of uniform temperature at the center. A secondary heating element of B&S 18 gauge chromel wire was wound on a 3.75 inch-diameter mullite tube. The windings of the inner tube were insulated by using Norton Alundum refractory cement. The windings of the outer tube were insulated with an asbestos-fiber coating. The concentric ceramic tubes of the main and secondary heating elements were housed in a cold-rolled steel shell, 8 inches in diameter and 11 inches in height. Size 20 abrasive grain Norton Alundum was used for insulation between the outer ceramic tube and the metal housing. The furnace was capped at either end with asbestos discs which were grooved to permit a tight fit with the metal housing.

The upper cap contained a circular opening which allowed insertion of the quartz tube surrounding the effusion cell. The caps were held in place with six threaded rods which passed through the asbestos caps, as shown in Figure 9. Power for the furnace was supplied from a variable transformer. The temperature of the cell was maintained within ± 2.0 degrees by means of a time-proportioning controller (Honeywell Versatronic, Model R7161H).

Temperature measurement

The torsion cell temperature was measured with a chromel-alumel thermocouple encased in a protective refractory tube. The thermocouple was securely fixed approximately 0.5 cm above the top of the effusion cell. The thermocouple leads extended to the outside of the system through a Conax vacuum seal on the suspension housing. The thermocouple cold junction was at the reference temperature of 0°C in an ice-water bath. The thermocouple output was measured by a portable potentiometer (Honeywell No. 2745). The relation between this thermocouple and the temperature in the effusion cell was established by calibration against a prestandardized thermocouple as described in the next section.

Calibration of the Thermocouple

The relation between the output of the experimental thermocouple used for temperature measurements in an experiment and the temperature in the effusion cell was established by calibration

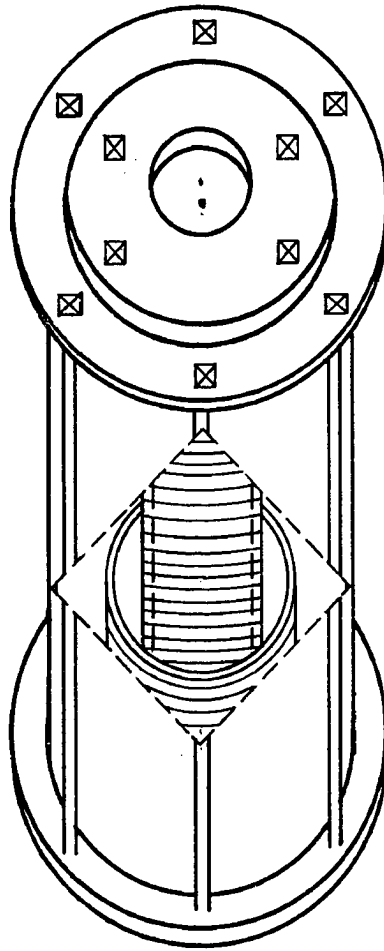


FIG. 9. HIGH TEMPERATURE FURNACE

against a prestandardized thermocouple. The prestandardized thermocouple, referred to as the standard thermocouple, was placed inside a cell through a hole in one of its caps. The cell was suspended in an identical position to that of an actual experiment. The thermocouple wires were passed through a vacuum sealed plug located in the port of the glass window in the suspension housing. The cold joints of the two thermocouples, the standard and the experimental, were at the reference temperature of 0°C in the same ice-water bath. The emf outputs of both thermocouples were read by the same portable potentiometer under virtually the same operating conditions with the system evacuated to a pressure in the normal operating range of 10^{-5} to 10^{-6} Torr. Intercomparison of the two thermocouples was over the range of temperatures used in the effusion studies. After intercomparison, the standard thermocouple was removed from the system. The standard thermocouple was prestandardized against the freezing temperatures of lead, zinc, aluminum, and copper. The resulting standardization of temperature vs. emf of the standard thermocouple was fitted into a linear equation by a least-squares fit according to :

$$T(^{\circ}\text{K}) = 2.75386 \times 10^2 + 2.42216 \times 10 V_s \quad (\text{II-1})$$

Two calibrations were performed; the first was used to calculate the temperatures for experiments I-IV and the second was used to calculate the temperatures for experiment V. The relation between the output voltage of the experimental and standard thermocouples, for each calibration, was fitted into a linear least-squares

equation where :

$$V_s = 0.159822 + 1.00646 V_{\text{exp.}} \quad (\text{II-2A})$$

$$V_s = 0.10917 + 0.99133 V_{\text{exp.}} \quad (\text{II-2B})$$

The final equation for the temperature of the torsional cell in terms of the emf of the experimental thermocouple was derived by substitution for V_s in equation (II-1) from equations (II-2) :

$$T(^{\circ}\text{K}) = 279.257 + 24.378 V_{\text{exp.}} \quad (\text{II-3A})$$

$$T(^{\circ}\text{K}) = 278.030 + 24.012 V_{\text{exp.}} \quad (\text{II-3B})$$

Equations (II-2A) and (II-3A) refer to the first calibration and the respective B equations refer to the second calibration. Propagation of the errors in these constants and the estimated precision of measurement of $V_{\text{exp.}}$ yields an estimated error of $\pm 0.25^{\circ}\text{K}$ in the temperature. The maximum average deviation of all temperatures measured for $V_{\text{exp.}}$ in the experiments was $\pm 2.5^{\circ}\text{K}$; however, the deviation at most temperatures was in the range of $\pm 2.0^{\circ}\text{K}$.

Calibration of the Torsion Fiber

The torsional constant τ was determined by using the assembly as a torsional pendulum in which the cell was replaced by a cross bar which supported a demountable ring of known moment of inertia. The periods of oscillation of the pendulum, with and

without the ring mounted on the cross bar, T_2 and T_1 respectively, were then measured. The torsional constant was calculated from:

$$\tau = \frac{2\pi^2 M (r_1^2 + r_2^2)}{T_2^2 - T_1^2} \quad (\text{II-4})$$

where r_1 and r_2 are the inner and outer radii of the ring and M is the ring mass. The measured torsional constants are listed in Table I. Also listed in this tabulation are the results of the propagated errors. The individual errors in mass, radius and period are those estimated from the precision of the respective measurements. The largest and most decisive of these errors is that associated with the measurement of the periods with the ring in place on the pendulum. The estimated precision in seconds for T_2 and T_1 corresponds to an error in τ of ± 0.0035 , a value which is consistent with the differences obtained from repeated measurements; i.e. ± 0.0010 in the case of the wire used in experiment V. The accuracy in the measured torsional constant is found from these estimated accuracies to be 0.1%. This number is consistent with the results of several measurements of the torsional constants of several samplings of this particular diameter of wire. Table II lists the data of a typical calibration measurement. Since it seemed apparent that the torsional constant of the filament might change with changes in load, it was essential that two rings of different moments of inertia be used. Brass and aluminum rings of masses 39.4653g and 11.9604g respectively were used. The mass of the cells used were within this range. The change in the torsional

Table I
Measurements of Torsional Constants
Characteristics of Aluminum and Brass Rings

Parameter	Aluminum	Brass
inner radius r_1 (cm)	2.699	2.696
outer radius r_2 (cm)	2.858	2.860
mass m (g)	11.9604	39.4653
moment of inertia I (gm cm ²)	92.411	304.83

Torsional Constant Calibration Data					
Wire diameter and Identification	Experiment number	Material of ring and cross bar	Time of Oscillation sec/period		Torsional Constant dyn. cm. rad. ⁻¹
			for cross bar	for cross bar and ring	
			T_1	T_2	
1 (0.002")	III	Aluminum	11.37 ₉ ± 0.01 ₀	38.49 ₁ ± 0.21 ₀	2.700
		Brass	15.32 ₇ ± 0.02 ₄	68.70 ₈ ± 0.16 ₂	2.682
2 (0.002")	IV	Aluminum	11.17 ₆ ± 0.01 ₃	37.91 ₂ ± 0.05 ₇	2.780
		Brass	15.01 ₅ ± 0.01 ₃	67.56 ₀ ± 0.09 ₁	2.774
3 (0.0015")	V	Aluminum	19.41 ₀ ± 0.03 ₁	66.12 ₇ ± 0.12 ₄	0.913 ₁

Table II

Calibration of Torsion Filament used in Experiment V

Run No.	Counts	Time (sec.)	Period	T sec. period ⁻¹
Aluminum Ring and Bar				
1	46	1519.0	23	66.04 ₃
2	48	1586.2	24	66.09 ₂
3	50	1654.4	25	66.17 ₆
4	52	1721.2	26	66.20 ₀
5	54	1784.4	27	66.08 ₉
6	56	1851.0	28	66.10 ₇
7	58	1920.0	29	66.20 ₇
8	60	1987.4	30	66.24 ₇
			Avg.	66.14 ₅
Aluminum Bar				
1	76	737.0	38	19.39 ₅
2	78	756.5	39	19.39 ₇
3	80	778.6	40	19.46 ₅
4	82	798.3	41	19.47 ₁
5	84	817.3	42	19.46 ₀
6	86	836.9	43	19.46 ₃
7	88	854.4	44	19.41 ₈
8	90	873.1	45	19.40 ₂
			Avg.	19.43 ₄

constant due to the change in the load, e.g. using calibration rings of aluminum and brass, is shown in Table I.

The method used to obtain the period of oscillation was as follows: the calibration ring and cross bar suspended from the torsion assembly were set oscillating by passing a magnet near the damping disc and then removing it. The magnitude of oscillation was usually 180° each side of the center. The assembly was allowed to oscillate several times. The period of oscillation was measured from the center point of oscillation using the projector and scale of the optical lever system as an indicating device and a photo cell connected to an electric counter to count the number of oscillations over a period of time. The oscillations time was measured to 0.1 second with an electric timer.

Characteristics of the Effusion Cell

The characteristics of the cells were measured with a travelling microscope which could read to ± 0.0025 mm. The diameter of each orifice was measured at 45° intervals. The average of the measurements was used as the diameter of the orifice. The moment arm was measured from the inside edge of the orifice to the scribed central axis. The radius of the orifice was added to this value to obtain the total moment arm length (d). This represents the perpendicular distance from the axis of the cell to a line through the center of the orifice. The thickness of the orifice was obtained using a micrometer caliper which read to ± 0.0005 inch. The characteristics of the cells used are given in Table III.

Table III
Parameters of Effusion Cells

Expt.-Cell No.	Diameter of orifices (cm)	Areas of orifices (cm ²)	Moment Arm (cm)	Orifice thickness (cm)	Clausing factor W_0	Pressure factor f
I-a	1	0.08298	5.4083 x 10 ⁻³	1.0382	0.0355 ₆	0.7635 ₁
	2	0.08537	5.7240 x 10 ⁻³	1.0606	0.0355 ₆	0.7688 ₇
II-b	1	0.11907	11.136 x 10 ⁻³	1.0370	0.0355 ₆	0.8255 ₂
	2	0.12037	11.380 x 10 ⁻³	1.0375	0.0355 ₆	0.8270 ₉
III-c	1	0.09502	7.0912 x 10 ⁻³	1.0405	0.0254	0.8417 ₇
	2	0.09434	6.9900 x 10 ⁻³	1.0419	0.0254	0.8407 ₂
IV-c	1	0.09502	7.0912 x 10 ⁻³	1.0405	0.0254	0.8417 ₇
	2	0.09434	6.9900 x 10 ⁻³	1.0419	0.0254	0.8407 ₂
V-d	1	0.11877	11.0772 x 10 ⁻³	1.0191	0.0254	0.8708 ₂
	2	0.12235	11.7570 x 10 ⁻³	1.0151	0.0254	0.8742 ₉

Operational Procedure

The operational procedure of a Knudsen-Torsion experiment is comprised of two steps: (1) outgassing of the cell and (2) measurement of the rate of weight loss and torsional deflection of the cell containing the sample being studied.

In the outgassing process, the system was assembled without a sample, as described below, and heated under vacuum to a higher temperature than the maximum temperature of the desired experiment. This step was necessary to insure that no weight loss occurred due to gases adsorbed in the graphite cell.

An effusion measurement, on a sample divided between the two cell chambers, was started by weighing the suspension system. Then approximately one gram of sample, MnF_2 , was introduced into a graphite cell of known weight. The cell was then attached to the suspension system via the dovetail connection. The weights on the pan of the balance were then adjusted to bring the recorder pen to scale. The mirror on the suspension system was adjusted so that a zero point would be near the end of the optical system scale. The bell jar was then placed over the balance. The quartz tube around the cell was bolted in place at the bottom of the brass suspension tube. Once the mirror adjustment had been made, and the system was completely isolated, the system was evacuated to a pressure of about 10^{-6} Torr. The zero point of the torsion apparatus was measured on the torsion scale. At this point, the furnace was

raised into its position around the quartz tube and the system was heated to 473°K where temperature stabilization was allowed to take place. Again a zero point was measured on the torsion scale to obtain the effect of the resistance furnace on the zero point. The temperature was raised in 200° increments to a temperature of 1273°K . After a weight loss of 10-20 mg, the temperature was lowered to a point in the normal working range between 1130°K and 1263°K . The torsion deflection and the rate of weight loss were measured at 10° intervals throughout the above temperature range. These measurements were performed at subsequent temperatures selected at random. This approach was adopted to note the internal consistency of the vapor pressure under such random choice of temperature. Thermal equilibrium was normally established within 20-30 minutes after attaining a given temperature.

Effusion measurements were in the temperature range 1130°K to 1263°K . In one experiment (experiment IV) the sample was heated to about 1153°K , after which it was cooled and the system was opened to observe changes in the characteristics of the sample, such as melting or color changes. After making these observations, the system was closed, in the same manner as described above, and heated above 1153°K where measurements at higher temperatures were taken. The upper temperature limit was imposed by the increase in the rate of weight loss beyond the limits of the validity of the effusion equation. After the upper temperature limit had been reached the system was cooled and opened. The suspension system was weighed and analysis for

manganese was carried out on the sample residue. Torsion deflections were read by employing the galvanometer projector of the optical lever system. The deflection projected on the scale was read to ± 0.02 inch. The projected deflections were twice as great as the rotation of the torsion assembly itself, because the light beam was reflected from the mirror surface. The projected deflection angle at a given temperature, was calculated from the distance between the mirror and the center of scale and the distance between the zero point and the projected image. The projected deflection angle, divided by two, gave the actual angular deflection. The weight loss during a measurement period as recorded on a chart recorder was read to a precision of ± 0.03 mg. The temperature was measured from the output of the experimental thermocouple using the Honeywell portable potentiometer with an ice-water bath as a reference.

CHAPTER III

MEASUREMENT OF THE VAPOR PRESSURE OF MANGANESE (II) FLUORIDE

Introduction

The apparatus to measure the Knudsen and torsion effusion simultaneously was evaluated by measurement of the vapor pressure of manganese (II) fluoride. This compound proved convenient to study for the following reasons :

1. manganese (II) fluoride is known to vaporize as a monomer;
2. the vapor pressure of MnF_2 in the temperature range of interest (1130-1200°K) is within the limits of the validity of the equation of molecular flow (10^{-2} to 10^{-6} Torr);
3. the sublimation pressure of $\text{MnF}_{2(s)}$ is believed to be well established which will allow comparison of the available thermodynamic data of sublimation with the vaporization data from the present investigation;
4. the heat of fusion of $\text{MnF}_{2(s)}$ and the condensation coefficient may be assessed by the above mentioned comparison.

Literature Review

The only previous reports on sublimation and vaporization rates of MnF_2 are the work of Bautista and Margrave²³ and Kent,

Ehlert and Margrave²⁴. Bautista and Margrave²³ investigated the sublimation of a single crystal of MnF_2 in the temperature range 887 to 983°K by the Langmuir technique using a vacuum microbalance. From the second-law least squares treatment of their sublimation data they calculated the enthalpy of sublimation to be 73.5 ± 0.5 Kcal mole⁻¹ at $T_{\text{avg.}} = 939.0^\circ\text{K}$ and 76.0 ± 1.0 Kcal mole⁻¹ at 298°K. Using their data and the computer program written to evaluate the data from this investigation, the linear least-squares equation relating the sublimation pressure and temperature is given in equation (III-1) :

$$\log P \text{ (atm)} = -(1.605 \pm .10) \frac{10^4}{T} + (8.78 \pm 0.11) \quad (\text{III-1})$$

Kent et al.²⁴ investigated both sublimation and vaporization of MnF_2 over an extended temperature range (1054-1193°K) by Knudsen-effusion technique employing a mass spectrometer. The ionic species detected by the mass spectrometer confirmed the absence of dimers and high polymeric species of MnF_2 in the effusate. They calculated the enthalpy of sublimation from the ion intensity data, in the temperature range 1054 to 1128°K to be 73.0 ± 1.5 Kcal mole⁻¹ at $T_{\text{avg.}} = 1103^\circ\text{K}$ and 76.5 ± 1.5 Kcal mole⁻¹ at 298°K. Similarly they calculated the enthalpy of vaporization in the temperature range 1132 to 1193°K to be 71.9 ± 1.4 Kcal mole⁻¹ at $T_{\text{avg.}} = 1159^\circ\text{K}$. They derived the Clausius-Clapeyron equation for sublimation of $\text{MnF}_{2(s)}$ by correlating the ion intensity measurements with the Langmuir sublimation pressure to obtain the mass spectrometer

constant which was then combined with the experimental values from the mass spectrometric measurements to calculate a value for the pressure at each temperature. Their least-squares treatment of the data is presented in equation (III-2).

$$\log P \text{ atm} = -(1.596 \pm 0.031) \frac{10^4}{T} + (8.70 \pm 0.02) \quad (\text{III-2})$$

Also they suggested a value of 1-5 Kcal mole⁻¹ for the enthalpy of fusion of MnF₂ as compared with Brewer's et al.²⁵ estimate of 5.5 Kcal mole⁻¹.

Experiments

The vapor pressure studies of MnF₂ were carried out according to the procedure described in Chapter II. In a typical run 0.7 to 0.8 g of polycrystalline MnF₂ (Purchased from Semi-Elements Inc., Saxonburg, Pa.) used without purification were placed in an outgassed cell. After assembly and evacuation of the system to a pressure of 10⁻⁶ Torr, the sample was heated initially to 473°K for a few hours to outgas the assembly before gradually raising the temperature to 1200°K. Heating at this temperature was continued until a weight loss of about 20 mg was recorded. Then the sample was cooled to a lower temperature within the range 1130 - 1205°K of this investigation.

A few experiments were carried out without measurements of the torsion deflection. This was necessary to select the appropriate cell material and dimensions, the temperature range, and the

stability of torsion deflection and its disturbance by the damping magnet. Cells of stainless steel and Union Carbide graphite (Grade AUC), seemed to affect the steady rate of weight loss due either to their reaction with the sample or to continuous outgassing. A permanent damping magnet interfered with both the balance sensitivity and the torsion deflection. A satisfactory arrangement involved the use of an electromagnet which was powered only after thermal equilibrium at each temperature setting was established, and turned off after a constant torsion deflection was attained.

Five experiments were carried out with spectroscopic graphite cells (Ultra Carbon-high purity, Grade U-7). The first two were limited to measurements of the rate of weight loss. In the third and fifth experiments simultaneous weight loss and torsion deflection measurements were carried out. The fourth experiment was undertaken to check the constancy of the rate of weight loss over relatively longer periods at each of a few temperature settings.

After the last experiment was completed the thermocouple was recalibrated. This calibration was dictated by a suspected change in the relative position of the thermocouple.

The total weight loss in a given experiment was limited to 350-370 mg. This restriction was imposed by the maximum weights of the riders which can be automatically removed from the tare weight without opening the system to atmospheric pressure. This was also desirable to secure sufficient sample residue in the cell to maintain equilibrium between the condensed and vapor phases.

Results

The vapor pressure data of five experiments are tabulated in Table (IV to X) and presented in the form of $\log P$ vs. $\frac{1}{T}$ plots in Figures (10 to 13). Experiment IV is not presented graphically because it represents the data at a few selected temperatures.

The Knudsen vapor pressure at each temperature was calculated according to equation (I-8) on the assumption that only the monomer ($\text{MnF}_2(\text{g})$), of molecular weight (92.9348), makes up the vapor species. The torsion pressures were calculated according to equation (I-13). The parameters of the effusion cells and the torsional constant of the fibers, used in these calculations, are those listed in Tables I and III respectively. The computations were performed on an IBM 1620 computer. A least-squares treatment of the linear relationship between $\log P$ and $\frac{1}{T}$ for each experiment was performed for the Knudsen- and torsion- effusion data independently.

The enthalpies and entropies of vaporization were derived from the linear least-squares analyses of the data according to

$$\log_{10} P_{(\text{atm})} = - \frac{\Delta H_v^\circ}{2.303 RT} + \frac{\Delta S_v^\circ}{2.303 R} \quad (\text{III-3})$$

The results of least-squares analyses of the measurements are summarized in Table XI. The cited errors are the standard deviations obtained in the least-squares analyses.

Table IV

Vaporization Data of MnF_2 by Knudsen Effusion
Experiment I ^a

Pt. No.	Weight Loss $w \times 10^3 (\text{g})$	Time $t(\text{min})$	Temperature (°K)	Pressure (atm)	$\frac{10^4}{T}$	$-\log P$
1	6.65	12.5	1254.9	9.336×10^{-5}	7.9690	4.030
2	1.40	20.0	1166.1	1.184×10^{-5}	8.5754	4.927
3	2.58	107.5	1130.1	3.997×10^{-6}	8.8492	5.398
4	3.39	75.0	1155.4	7.611×10^{-6}	8.6550	5.119
5	4.83	80.0	1165.4	1.021×10^{-5}	8.5807	4.991
6	8.68	107.5	1176.4	1.372×10^{-5}	8.5007	4.863
7	8.29	82.5	1185.3	1.714×10^{-5}	8.4366	4.766
8	10.89	85.0	1195.0	2.194×10^{-5}	8.3684	4.659
9	15.79	97.5	1204.6	2.784×10^{-5}	8.3017	4.555
10	6.52	32.5	1214.5	3.463×10^{-5}	8.2337	4.461
11	10.39	40.0	1224.7	4.503×10^{-5}	8.1652	4.347
12	18.35	57.5	1233.1	5.552×10^{-5}	8.1096	4.256
13	15.53	37.5	1245.0	7.239×10^{-5}	8.0322	4.140
14	10.20	17.5	1262.8	1.026×10^{-4}	7.9187	3.989
15	8.64	12.5	1271.8	1.221×10^{-4}	7.8628	3.913

a) Effective orifice area : $\sum a_i w_{oi} = (7.8725)(10^{-3}) \text{ cm}^2$

Table V
Vaporization Data of MnF_2 by Knudsen Effusion
Experiment II ^a

Pt. No.	Weight Loss $w \times 10^3 (\text{g})$	Time $t (\text{min})$	Temperature (°K)	Pressure (atm)	$\frac{10^3}{T}$	$-\log P$
1	7.67	60.0	1165.5	9.780×10^{-6}	8.5799	5.010
2	3.43	30.0	1161.7	8.733×10^{-6}	8.6078	5.059
3	7.08	112.5	1137.5	4.756×10^{-6}	8.7914	5.323
4	3.87	47.5	1147.1	6.184×10^{-6}	8.7176	5.299
5	6.55	92.5	1144.7	5.369×10^{-6}	8.7361	5.270
6	6.40	75.0	1149.2	6.482×10^{-6}	8.7018	5.188
7	4.48	35.0	1166.7	9.797×10^{-6}	8.5713	5.009
8	11.32	77.5	1172.5	1.121×10^{-5}	8.5290	4.950
9	17.70	97.5	1180.4	1.398×10^{-5}	8.4714	4.855
10	10.71	97.5	1160.3	8.385×10^{-6}	8.6186	5.077
11	35.82	147.5	1190.5	1.878×10^{-5}	8.3998	4.726
12	16.55	90.0	1180.8	1.416×10^{-5}	8.4686	4.849

^a) Effective orifice area: $\sum a_i w_{oi} = (1.7404)(10^{-2}) \text{ cm}^2$

Table VI
Vaporization Data of MnF_2 by Knudsen Effusion
Experiment III^a

Pt. No.	Weight Loss $w \times 10^3 (\text{g})$	Time $t (\text{min})$	Temperature (°K)	Pressure (atm)	$\frac{10^4}{T}$	$-\log P$
1	15.61	195.0	1174.9	9.618×10^{-6}	8.5115	5.017
2	5.18	202.5	1131.0	3.016×10^{-6}	8.8416	5.521
3	5.34	142.5	1143.6	4.442×10^{-6}	8.7445	5.352
4	4.51	150.0	1135.9	3.552×10^{-6}	8.8035	5.450
5	4.77	95.0	1153.5	5.978×10^{-6}	8.6696	5.224
6	3.37	97.5	1140.5	4.092×10^{-6}	8.7679	5.388
7	16.69	187.5	1174.7	1.069×10^{-5}	8.5131	4.971
8	6.78	125.0	1156.9	6.467×10^{-6}	8.6440	5.189
9	7.82	105.0	1168.6	8.924×10^{-6}	8.5575	5.049
10	16.97	172.5	1179.6	1.184×10^{-5}	8.4774	4.927
11	17.06	157.5	1183.7	1.306×10^{-5}	8.4482	4.884
12	16.40	125.0	1191.4	1.587×10^{-5}	8.3938	4.799
13	14.89	97.5	1197.7	1.853×10^{-5}	8.3497	4.732
14	9.34	55.0	1203.1	2.065×10^{-5}	8.3121	4.685

a) Effective orifice area: $\sum a_i w_{oi} = (1.1126)(10^{-2}) \text{ cm}^2$

Table VII
Vaporisation Data of MnF_2 by Torsion Effusion
Experiment III ^a

Pt. No.	Linear deflection ΔS (in)	Temperature (°K)	Pressure (atm)	$\frac{10^5}{T}$	$-\log P$
1	2.133	1174.9	1.277×10^{-5}	8.5115	4.894
2	0.564	1131.0	3.377×10^{-6}	8.8416	5.471
3	0.815	1143.6	4.880×10^{-6}	8.7445	5.312
4	0.693	1135.9	4.150×10^{-6}	8.8036	5.382
5	1.107	1153.5	6.629×10^{-6}	8.6696	5.179
6	2.093	1174.7	1.253×10^{-5}	8.5131	4.902
7	1.321	1156.9	7.910×10^{-6}	8.6440	5.102
8	1.723	1168.6	1.032×10^{-5}	8.5575	4.986
9	2.270	1179.6	1.359×10^{-5}	8.4774	4.867
10	2.492	1183.7	1.492×10^{-5}	8.4482	4.826
11	3.015	1191.4	1.805×10^{-5}	8.3938	4.743
12	3.515	1197.7	2.105×10^{-5}	8.3497	4.677
13	3.970	1203.1	2.377×10^{-5}	8.3121	4.624

a) Effective orifice area x moment arm: $\sum A_1 d_1 f_1 = (1.23336)(10^{-2}) \text{ cm}^3$

Torsional Constant: $\tau = 2.6940 \text{ dyn cm rad}^{-1}$

Table VIII

Knudsen - Effusion Data of Vaporization for MnF_2

Pt. No.	Weight Loss $w \times 10^3 (\text{g})$	Experiment IV ^a				$-\log P$
		Time $t (\text{min})$	Temperature (°K)	Pressure (atm)	$\frac{10^4}{T}$	
1	2.25	60.0	1152.2	4.462×10^{-6}	8.6788	5.351
2	3.38	90.0	1151.0	4.466×10^{-6}	8.6880	5.350
3	8.83	225.0	1154.7	4.674×10^{-6}	8.6605	5.330
4	2.80	70.0	1155.7	4.767×10^{-6}	8.6531	5.321
5	9.59	65.0	1203.8	1.794×10^{-5}	8.3079	4.746
6	7.37	50.0	1204.2	1.793×10^{-5}	8.3045	4.746
7	5.76	40.0	1202.9	1.751×10^{-5}	8.3130	4.764
8	9.21	65.0	1203.7	1.723×10^{-5}	8.3079	4.764

a) Effective orifice area: $\sum a_i w_{oi} = (1.1126)(10^{-2}) \text{ cm}^2$

Table IX
Vaporization Data of MnF_2 by Knudsen Effusion
Experiment V^a

Pt. No.	Weight Loss $w \times 10^3 (\text{g})$	Time $t(\text{min})$	Temperature (°K)	Pressure (atm)	$\frac{10^4}{T}$	$-\log P$
1	23.08	145.0	1166.4	1.123×10^{-5}	8.5731	4.950
2	6.69	90.0	1138.3	5.179×10^{-6}	8.7847	5.286
3	10.66	110.0	1147.5	6.779×10^{-6}	8.7148	5.169
4	11.72	95.0	1156.6	8.664×10^{-6}	8.6461	5.062
5	19.87	62.5	1193.1	2.268×10^{-5}	8.3816	4.644
6	12.11	62.5	1173.6	1.371×10^{-5}	8.5205	4.863
7	14.45	60.0	1182.5	1.710×10^{-5}	8.4565	4.767
8	10.61	130.0	1142.4	5.697×10^{-6}	8.7533	5.244
9	6.28	45.0	1161.9	9.823×10^{-6}	8.6068	5.008
10	4.36	42.5	1151.3	7.188×10^{-6}	8.6858	5.143

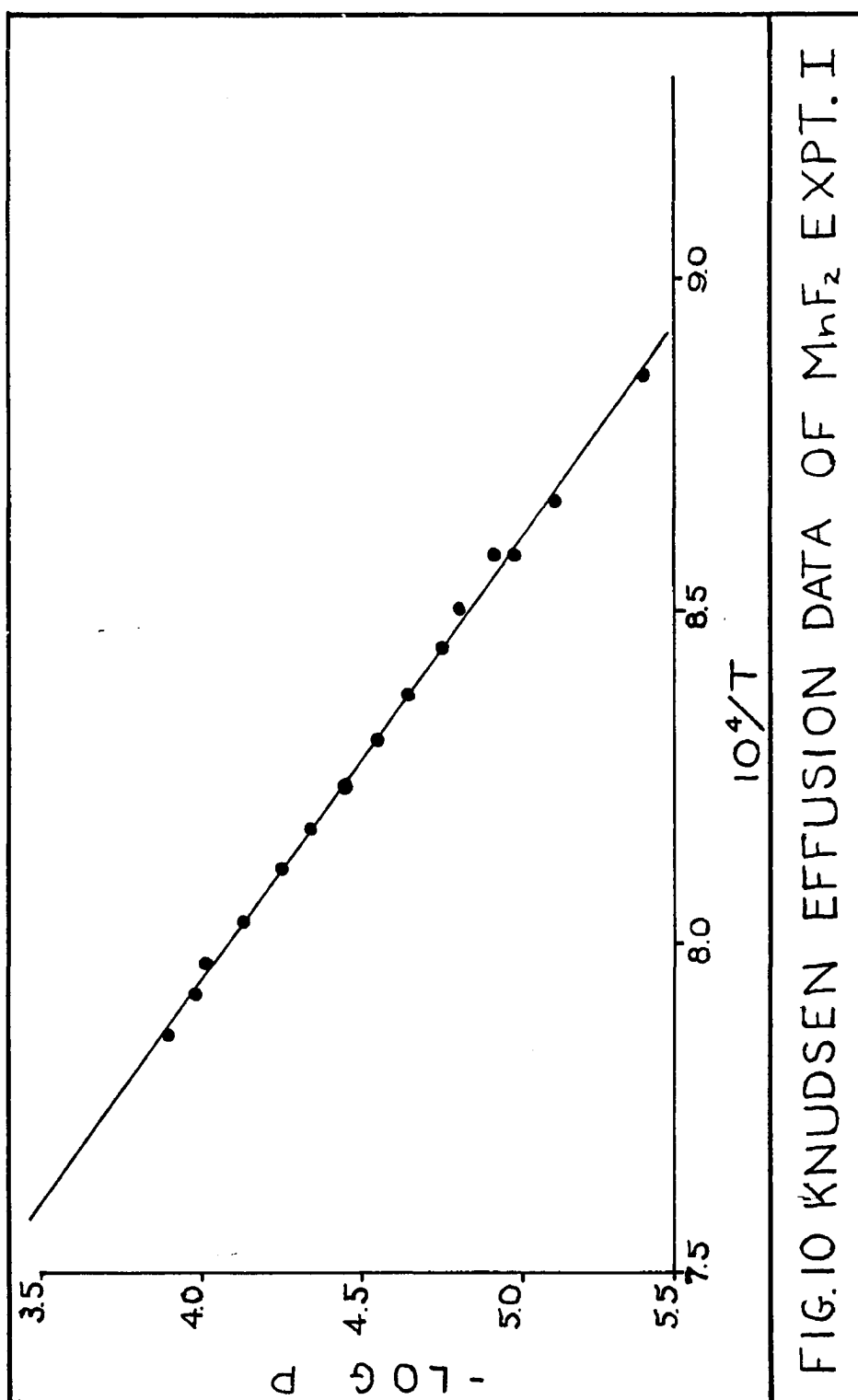
^a) Effective orifice area : $\sum a_i w_{oi} = (1.8886)(10^{-2}) \text{ cm}^2$

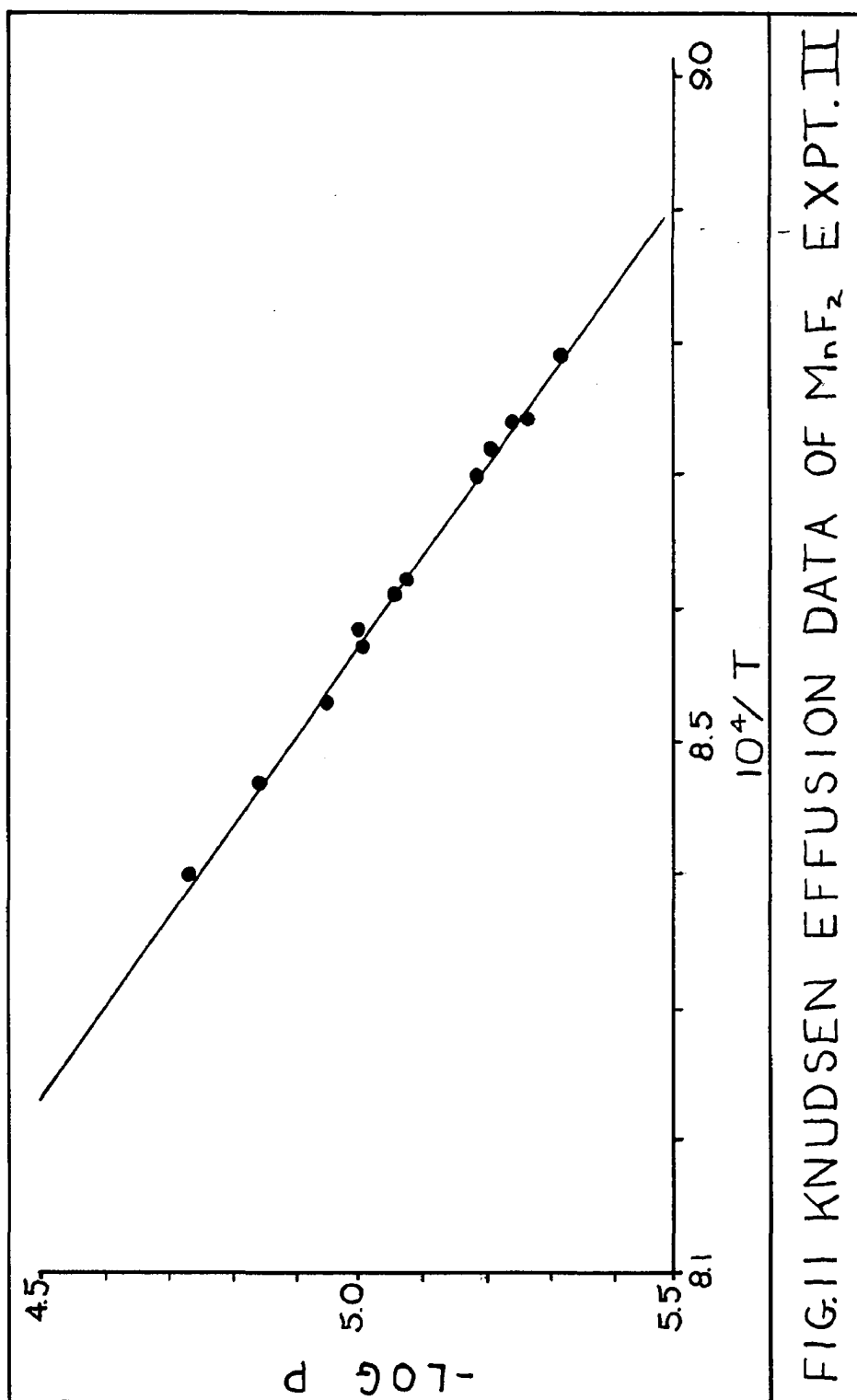
Table X
Vaporization Data of MnF_2 by Torsion Effusion
Experiment V^a

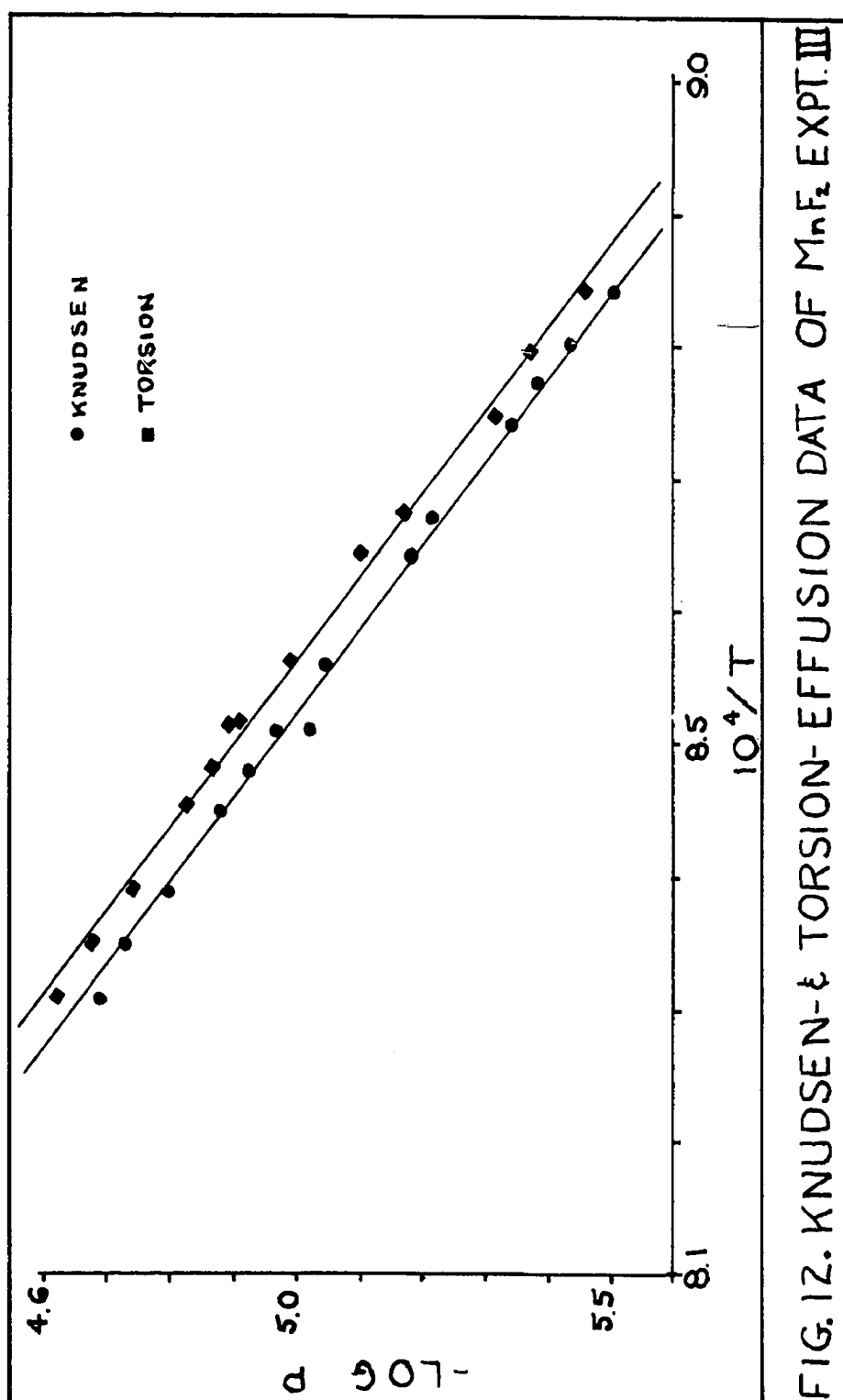
Pt. No.	Linear deflection S (in)	Temperature (°K)	Pressure (atm)	$\frac{10^4}{T}$	-log P
1	10.49	1166.4	1.296×10^{-5}	8.5731	4.887
2	4.78	1138.3	5.904×10^{-6}	8.7847	5.229
3	6.16	1147.5	7.609×10^{-6}	8.7148	5.119
4	7.94	1156.6	9.808×10^{-6}	8.6461	5.008
5	20.71	1193.1	2.558×10^{-5}	8.3816	4.592
6	12.46	1173.6	1.539×10^{-5}	8.5205	4.813
7	15.64	1182.5	1.932×10^{-5}	8.4565	4.714
8	5.30	1142.4	6.547×10^{-6}	8.7533	5.184
9	9.05	1161.9	1.118×10^{-5}	8.6068	4.952
10	6.89	1151.3	8.511×10^{-6}	8.6858	5.070

^a) Effective orifice area x moment arm: $\sum a_1 d_1 f_1 = (2.0265)(10^{-2}) \text{ cm}^3$

Torsional constant: $\tau = 0.9131 \text{ dyn cm rad}^{-1}$







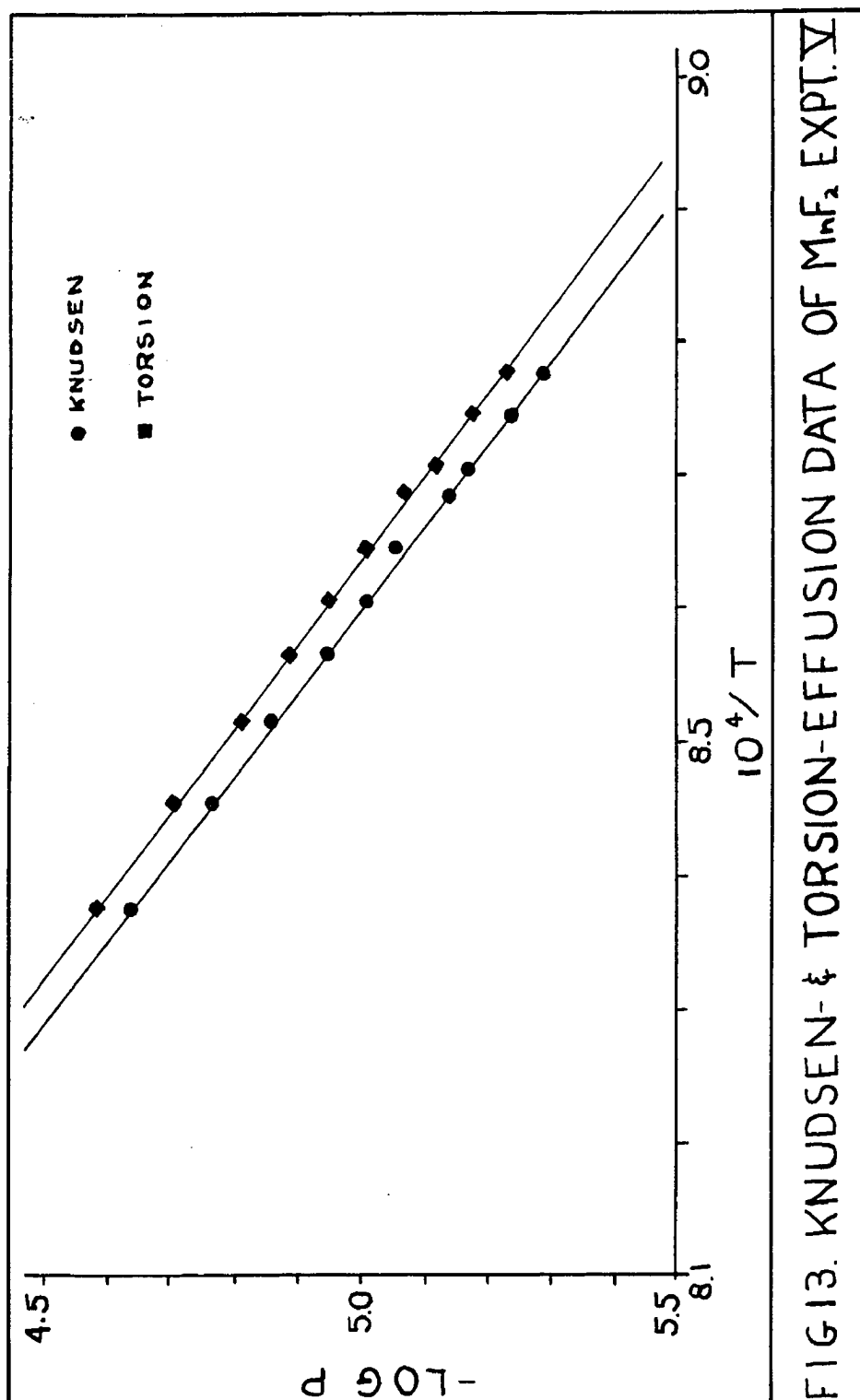


Table XI
Summary of Vapor Pressure Measurements of MnF_2

Experiment Number	Temperature Range °K	Method	ΔH° Kcal mole ⁻¹	ΔS° eu	$-\log P$ at \bar{T}	P at \bar{T} (atm)	\bar{T} (°K)
I	1130-1272	Knudsen	69.6 ± 0.8	36.9 ± 2.0	4.986	1.033×10^{-5}	1165
II	1137-1190	Knudsen	68.9 ± 1.3	36.2 ± 1.1	5.020	9.991×10^{-6}	1165
III	1131-1203	Knudsen Torsion	72.0 ± 0.9 72.8 ± 1.5	38.5 ± 0.8 39.5 ± 1.3	5.100 5.037	7.939×10^{-6} 9.191×10^{-6}	1165
IV	1151-1203	Knudsen	73.9 ± 1.1	39.6 ± 1.5	5.198	6.313×10^{-6}	1165
V	1131-1203	Knudsen Torsion	73.2 ± 0.7 72.3 ± 0.4	40.1 ± 0.6 39.6 ± 0.3	4.968 4.912	1.077×10^{-5} 1.226×10^{-5}	1165
Kent (24)	1132-1193	Mass Spec. (Vaporiz.)	71.9 ± 2.4				1159
Kent (24)	1054-1128	Mass Spec. (Sublim.)	73.0 ± 1.5	39.8 ± 0.1	5.902	1.253×10^{-6}	1093
Bautista (23)	887 - 983	Langmuir (Sublim.)	73.5 ± 0.1	40.2 ± 3.2	8.313	4.859×10^{-9}	939
Composite of I and II		Knudsen	69.7 ± 1.5	36.0 ± 2.3	5.017	9.607×10^{-6}	1165

Discussion

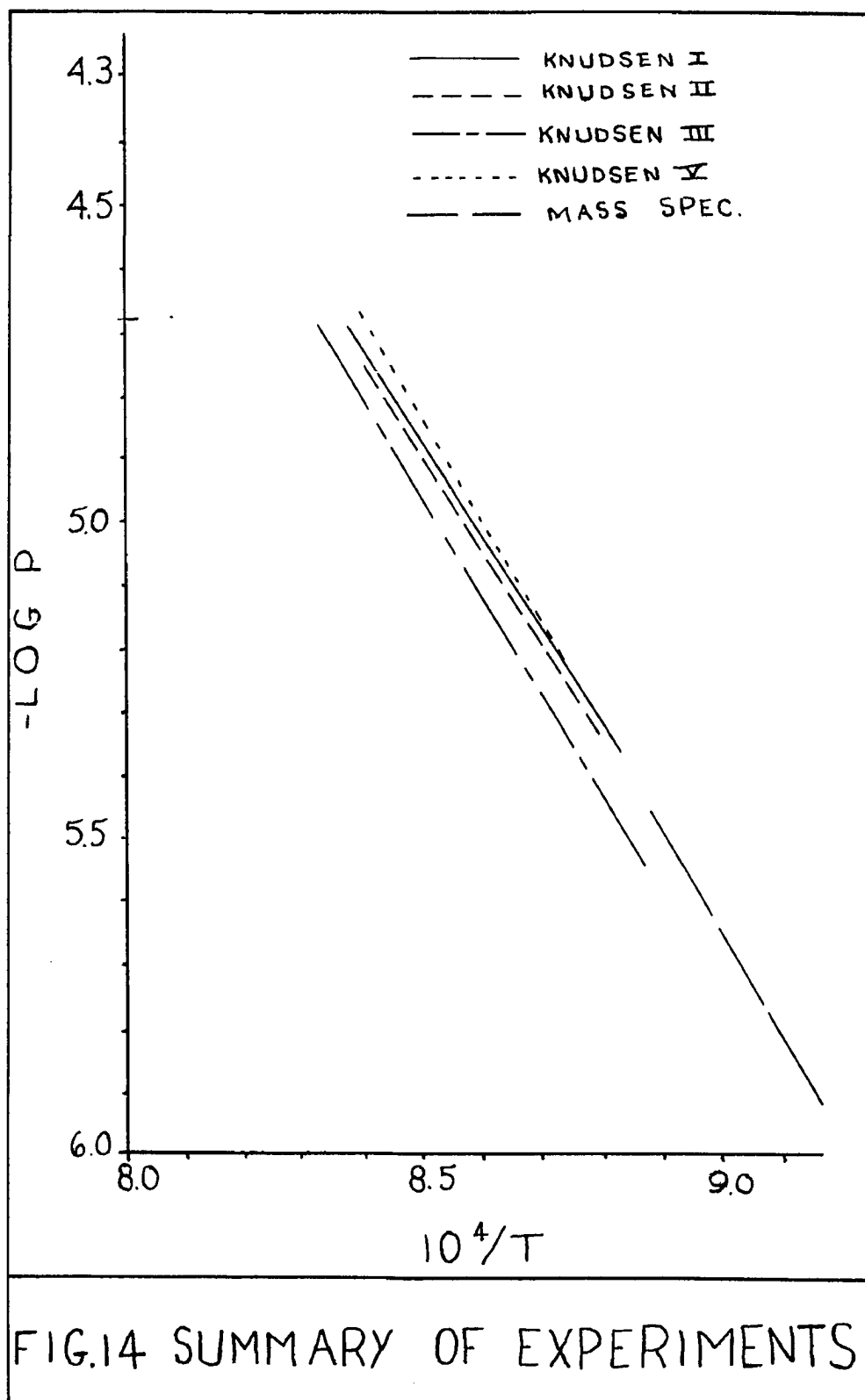
Clausius-Clapeyron plots for the Knudsen-effusion data of experiments I-III and V and for the mass spectrometric sublimation data are presented in Figure 14. For a meaningful analysis of the data and a clarification of these plots the four experiments are treated as three separate groups: I and II, III, and V. Experiment IV is excluded for the consideration mentioned before.

Experiments I and II

These two experiments were performed in succession shortly after the initial calibration of the thermocouple. The same torsion assembly was used except for the cells. Inspection of Figure 14 and Table XI shows the close agreement of the vapor pressures and the derived enthalpies and entropies of vaporization from the experimental data. In addition, a composite least-squares analysis of all the points, except those obtained at the highest temperatures, yields the following Clausius-Clapeyron equation:

$$\log_{10} P_{(\text{atm})} = - \frac{(1.524 \pm 0.032)10^4}{T} + (8.067 \pm 0.5) \quad (\text{III-4})$$

Using equation (III-4) the calculated enthalpy and entropy of vaporization are in close agreement with those derived from the same treatment of the individual experiments independently. The melting point of MnF_2 , calculated from the analytical solution of the vaporization equation, (III-4), and the mass spectrometric



sublimation equation, (III-2), at the intersection point of equal pressures, is 1137°K. The literature value cited by Brewer²⁶ is 1129°K.

Equation (III-4) yields for the enthalpy of vaporization of $\text{MnF}_2(l)$, $\Delta H_{1165}^\circ = 69.7 \pm 1.5 \text{ Kcal mole}^{-1}$ and for the entropy of vaporization, $\Delta S_{1165}^\circ = 36.9 \pm 2.3 \text{ eu}$, in the temperature range 1130 - 1200°K. The enthalpy value is lower than the value, $\Delta H_{1159}^\circ = 71.9 \pm 2.4 \text{ Kcal mole}^{-1}$, obtained mass spectrometrically²⁴.

Assuming the enthalpy of vaporization value of this study and that of sublimation reported by Kent et al.²⁴ to apply adequately at the melting point, their difference yields an enthalpy of fusion $\Delta H_{1129}^\circ = 3.2_5 \pm 2.0 \text{ Kcal mole}^{-1}$ and an entropy of fusion $\Delta S_{1129}^\circ = 3.0 \pm 1.8 \text{ eu}$. This value for the enthalpy of fusion is within the range of 1-5 Kcal mole⁻¹ suggested by Kent et al.²⁴ and is in fair agreement with 5.5 Kcal mole⁻¹, the value estimated by Brewer et al.²⁵. There are no reported values for the entropy of vaporization with which to compare the present value.

Experiment III

This experiment was carried out with a new torsion filament and tantalum-connector tube in the torsion assembly. Due to these changes in the system and to the use of the apparatus by another investigator during the interruption period, it was suspected that the position of the cell relative to the thermocouple and furnace had changed. Such a change would lead to an error in the calculated

temperature based on equation (II-3A) of the initial thermocouple calibration.

Inspection of Figure 14 and Table XI shows that the Knudsen and torsion vapor pressures calculated from the data of this experiment are relatively low. The value of enthalpy of vaporization, although higher than that calculated from experiments I and II, agrees well with the value cited by Kent et al.²⁴. By the same reasoning applied to experiments I and II the melting point of MnF_2 , calculated from the solution of the proper vaporization and sublimation equations is 756°K , from the Knudsen-effusion data, and 555°K , from the torsion-effusion data. These values fall far below the literature value of 1129°K ²⁶.

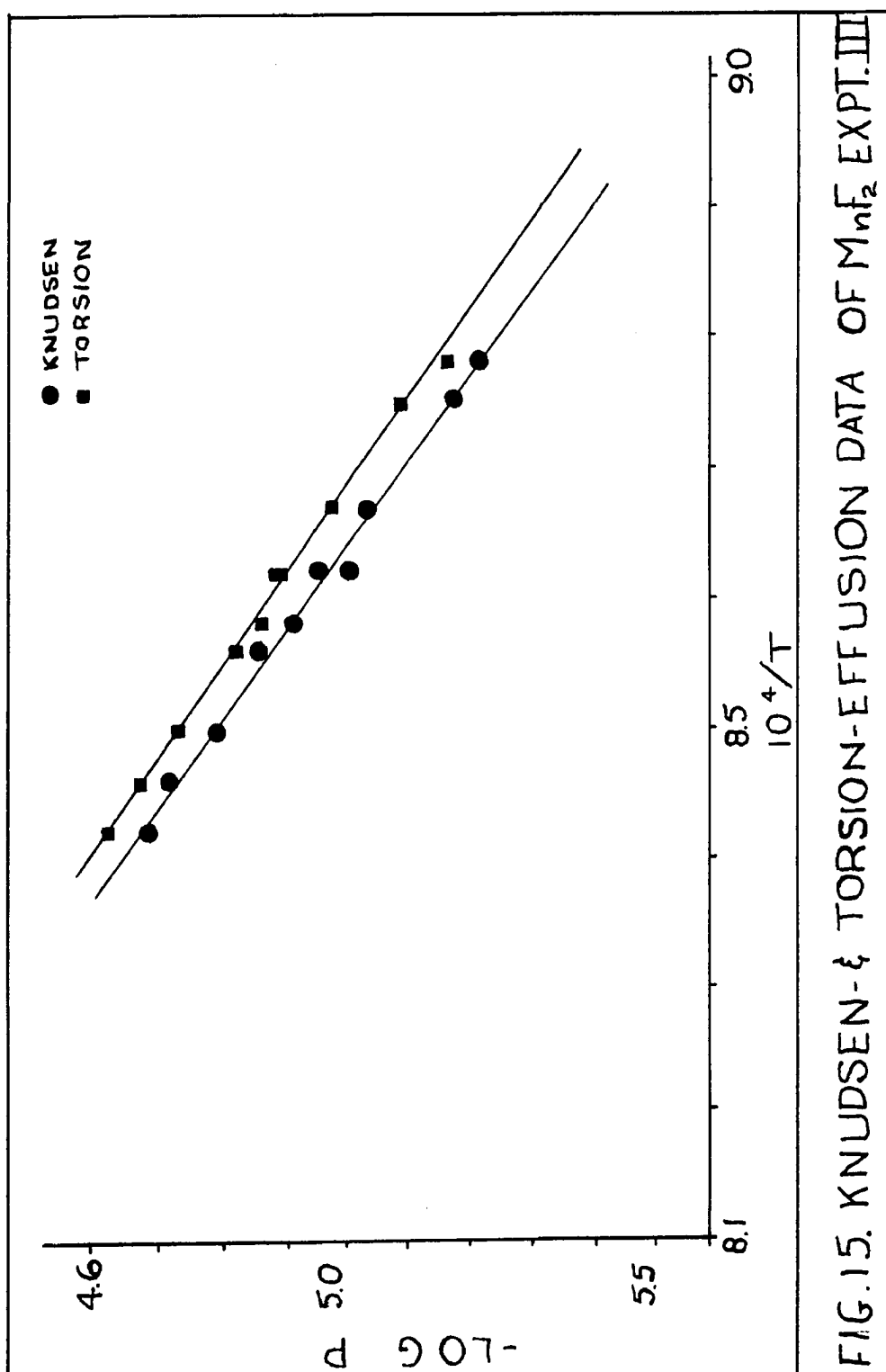
A correction for the temperature by using equation (II-3B), derived from the final thermocouple calibration, yields the following Clausius-Clapeyron equations:

$$\log_{10} P_{(\text{atm})} = - \frac{1.515 \times 10^4}{T} + 8.074 \quad (\text{III-5})$$

from Knudsen-effusion measurements, and

$$\log_{10} P_{(\text{atm})} = - \frac{1.480 \times 10^4}{T} + 7.844 \quad (\text{III-6})$$

from torsional-recoil measurements. The corresponding Clausius-Clapeyron plots are shown in Figure 15. The enthalpies and entropies of vaporization, derived from the above equations, are $\Delta H_{1165}^\circ = 69.3 \text{ Kcal mole}^{-1}$ and $\Delta S_{1165}^\circ = 36.9 \text{ eu}$, from



equation (III-5), and $\Delta H_{1165}^{\circ} = 67.7 \text{ Kcal mole}^{-1}$ and

$\Delta S_{1165}^{\circ} = 35.9 \text{ eu}$, from equation (III-6). Although such correction brings the enthalpy and entropy of vaporization, derived from the Knudsen-effusion data, into better agreement with experiments I and II, the corresponding vapor pressures are relatively higher ($1.166 \times 10^{-3} \text{ atm}$ at 1165°K).

Experiment V

Experiment V was performed with the same torsion assembly used in experiment III except for a new torsion filament and the cell. Having suspected the validity of the initial calibration of the thermocouple, a recalibration was made after the completion of the experiment. Equation (II-3B) of this new calibration was employed to calculate the temperatures of this experiment. Inspection of Figure 14 and Table XI shows that the Knudsen and torsion vapor pressures are higher than those of experiments I and II. The value of the enthalpy of vaporization is in agreement (within experimental errors) with the value from the mass spectrometric measurements; however, it is higher than the value calculated from the data of experiments I and II. The analytical solution of the proper vaporization and sublimation equations yields a rather low value for the melting point of MnF_2 (500°K from Knudsen and 320°K from torsion data).

Comparison of mass-effusion and torsion-recoil pressures

There have been published several reports^{11,27,31} in which the Knudsen-effusion and torsion-recoil methods have been used in vapor pressure measurements of the same substance. In each reported case the measured torsion pressure was greater than the Knudsen pressure, even when such measurements were performed simultaneously in the same apparatus²⁷. Inspecting the values of the Knudsen and torsion pressures of experiments III and V it is observed that the torsion pressures are larger than the corresponding Knudsen pressures. The average value of the ratio P_T/P_K is 1.15. This value is within the range of 1.05 to 1.17 of the same ratio in the cited references.

The lack of agreement between P_T and P_K may be attributed to the surmise that the torsion pressure is larger than the Knudsen pressure because of the effusate which returns preferentially to the same side of the cell from which it originated²⁷. The effusate molecules rebound from the walls of the quartz enclosure against the side of the cell from which they originated. Their impacts, on this side, increase the deflection of the torsion assembly. Also, the returning effusate molecules decrease the observed rate of weight loss. The increased deflection leads to a higher apparent torsion pressure while the reduced rate of mass effusion leads to a lower Knudsen pressure.

The observation that P_T is greater than P_K rules out the

presence of the dimer. If only monomers and dimers are present, then:²⁷

$$P_T - P_K = (2\pi RTM_2)^{\frac{1}{2}} \left[1 - (M_2/M_1)^{\frac{1}{2}} \right] Z_2 \quad (\text{III-7})$$

where the M's are molecular weights and Z_2 is the molar rate of effusion of the dimer. Since $Z_2 \geq 0$ and $M_2 > M_1$, then $P_T - P_K$ would be ≤ 0 if the dimer were present. Support of the absence of dimer in the vapor species was reported by Kent et al.²⁴ in their mass spectrometric studies.

Conclusions

Comparison of the vaporization data of MnF_2 , summarized in Table XI, shows that, within experimental errors, only experiments I and II yield reproducible vapor pressures and enthalpy and entropy of vaporization. The close agreement between these two experiments permitted a composite least-squares analysis of all the points, except those obtained at the highest temperatures. The Clausius-Clapeyron equation and the enthalpy and entropy of vaporization of $\text{MnF}_2(\ell)$, in the temperature range 1130 - 1200°K, obtained from the combined data of these two experiments are:

$$\log_{10} P_{(\text{atm})} = -\frac{(1.524 \pm 0.032)10^4}{T} + (8.067 \pm 0.5) \quad (\text{III-4})$$

$$\Delta H_{1165}^\circ = 69.7 \pm 1.5 \text{ Kcal mole}^{-1}$$

and

$$\Delta S_{1165}^\circ = 36.9 \pm 2.3 \text{ eu}$$

Additional criteria, considered in accepting these data as the most reliable are presented below.

1) The melting point of MnF_2 , calculated from the analytical solution of the vaporization equation, (III-4), and the sublimation equation, (III-2), at the intersection point of equal pressures, is consistent with the literature value. Similar calculations, using the vaporization equations based on experiments III and V, gave melting points which are too low.

2) The enthalpy of fusion derived from vaporization data, based on equation (III-4), and the sublimation data is consistent with the value estimated by Brewer²⁵. The values of the enthalpy and entropy of fusion, arrived at in this investigation are :

$$\Delta H_{1129}^{\circ} = 3.2_5 \pm 2.0 \text{ Kcal mole}$$

and

$$\Delta S_{1129}^{\circ} = 2.9 \pm 1.8 \text{ eu.}$$

3) The validity of the thermocouple calibration, represented by equation (II-3A) when applied to the data of experiment III, is suspected. Neither of the two calibration equations (II-3A and II-3B) can be considered as reliable since the calibrations and the vaporization measurements were interrupted by unavoidable replacements of the torsion fiber. The same arguments do not apply to experiment V since the final calibration was performed immediately after completion of the experiments. However, the non-conformity of this experiment escapes an explanation on

a thermodynamic basis.

4) The vaporization data of Kent et al.²⁴ is based on an extrapolation of their sublimation data. The cited reference failed to present a Clausius-Clapeyron equation, for the vapor pressure of MnF_2 (ℓ), and a value for the entropy of vaporization.

Although experiments III and V failed to contribute acceptable thermodynamic functions for MnF_2 , they still served to prove the utility of the present apparatus for simultaneous measurements of the torsional recoil and mass effusion as a means of direct and indirect determinations of vapor pressures. However, improvements in the apparatus are needed so that more reliable and reproducible information will become available by its use.

Suggested Apparatus Improvements

The improvements considered as necessary for this apparatus to be capable of yielding reliable and reproducible data are outlined below:

- 1) the experimental thermocouple should be fixed in a permanent position;
- 2) the experimental thermocouple should be periodically checked during an investigation;
- 3) the scale and light source of the optical lever system should be mounted on a rigidly fixed frame;
- 4) a fast responding furnace is recommended.

Suggestions for Future Work

As pointed out earlier the apparatus, after the suggested improvements, should be fruitful not only in determining vapor pressures directly and indirectly but also in investigating dissociation and disproportionation reactions. Before the discrepancy between the torsion pressure and the Knudsen pressure can be utilized to indicate simple vaporization, dissociation or polymerization, it is essential to determine if the discrepancy is inherent in the method by a study involving a substance known to vaporize as a monomer and of known vapor pressure. Cadmium, zinc and silver are such substances which are available with high purity.

Once the instrumental correction factor is established, the vaporization behavior of several double salts, e.g. RbMnF_3 , may be elucidated and thermodynamic functions of such salts may be derived from their vapor pressure data.

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