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the triple point the tendency was to drift upward. The upward drift may have been due to chemical reaction. For this reason the calorimeter was kept at high temperatures no longer than absolutely necessary, and it is thought that change in chemical composition produced by reaction was not serious. Some tests were made to relate the irregularities in heat capacity with past thermal history, but these were inconclusive.

Considering errors arising from the experimental measurements as well as those resulting

from possible impurities, the data for UF_6 are not considered reliable to much better than one percent. This is about equal to the extreme spread of the points in Fig. 4. The errors in the UF_4 data are probably only about half as large, but the uncertainty resulting from impurity is larger, so that the over-all accuracy for the two compounds is probably about the same. The errors in the other quantities in the tables are probably about the same as those in the heat capacities from which they are derived.

The Vapor Pressure of Uranium Hexafluoride*

B. WEINSTOCK¹ AND R. H. CRIST²

S. A. M. Laboratories, Columbia University, New York, New York

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The vapor pressure of uranium hexafluoride, UF_6 , has been measured from 273°K to 358°K. The measurements were made by a null method in an all metal apparatus with a brass sylphon bellows. The data are represented by the equations:

$$\text{Solid-vapor } \log_{10} P(\text{mm Hg}) = -3.77962 \log_{10} T - (3123.479/T) + 21.87103,$$

$$\text{Liquid-vapor } \log_{10} P(\text{mm Hg}) = -3.72662 \log_{10} T - (2065.679/T) + 18.60033.$$

The constants in the equations were adjusted so that the equations would give the same heat of fusion and triple-point temperature as was determined by Brickwedde, Hoge, and Scott. The vapor pressure at the triple point is 1133 ± 7 mm. The sublimation point at which the vapor pressure is 1 atmosphere is 56.5°C. The heat of vaporization has been calculated using the Berthelot equation to obtain the vapor volume. From this and the entropies measured by Brickwedde, the absolute entropy of the gas has been calculated.

INTRODUCTION

THE vapor pressure of uranium hexafluoride had been previously measured by Ruff and Heinzelmann³ over the temperature range 37–56.2°C. Their results are not precise showing large deviations from linearity in a $\log P$ against $1/T$ plot. The vapor pressures obtained by them are always higher than those obtained in the present work, the percentage differences being

very much greater at lower pressure. This situation could be explained by the presence of a volatile impurity in their sample, e.g., HF. The purpose of the present work was to improve the accuracy of these measurements as well as to extend the range of measurement.

EXPERIMENTAL

The experimental arrangement is shown in Fig. 1. This consists of a reservoir in a thermostat and a brass sylphon bellows for the measurement of pressure by a null method. At the time the experiments were made, it was thought that only a limited number of metals were safe materials for use with UF_6 . Accordingly, the vessels and connecting tubes were of copper, the pack-

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¹ Now at Argonne National Laboratory, Chicago, Illinois.

² Now at Carbide and Carbon Chemical Corporation, South Charleston, West Virginia.

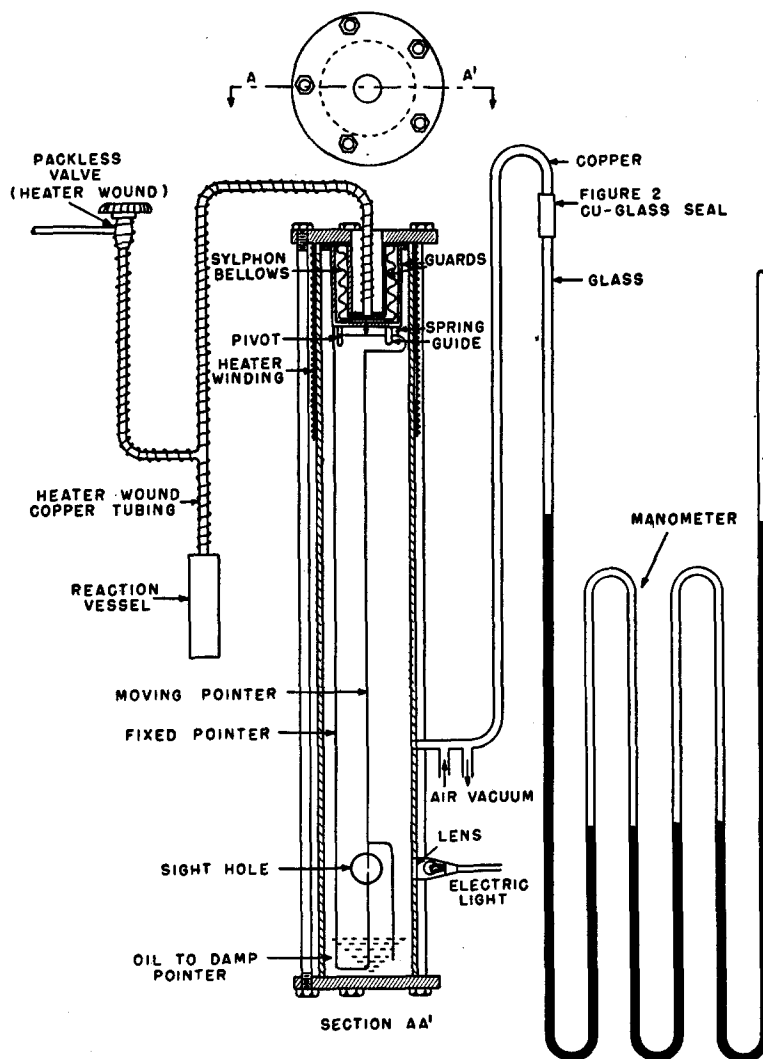
³ Ruff and Heinzelmann, *Zeits. anorg. Chemie* **72**, 63 (1911).

less valves were brass with a silver gasket ring, the sylphon bellows was brass and the whole was joined with silver solder or "Phoscopper." To maintain the characteristics of the sylphon, its vertical motion was restricted to about a millimeter by guards on both sides. The inner one served the additional purpose of decreasing the working volume of the system. The lower end of the sylphon was soldered to a copper plate and the flange at the upper end was attached to the top plate of the pressure can. Butyl rubber served as a gasket. A pointer was attached to the outer sylphon guard and this was moved by a pin soldered to the sylphon. The pointer and reference were damped by dipping into transformer oil as indicated. The pointer was illu-

minated and viewed by appropriately located windows.

The manometer for reading pressures above an atmosphere was of the multiple type and contained mercury and dibutylphthalate. The latter served as a piston liquid providing a very satisfactory meniscus. It was not possible to fill the manometer with the two liquids in proper amounts and at the same time keep the dibutylphthalate free from dissolved air. To avoid release of this gas on evacuating the completed unit for use, a permanent head greater than an atmosphere was furnished by having mercury in the limbs standing to appropriate heights. For measurements up to an atmosphere an ordinary wide tube precision manometer was

FIG. 1. Vapor pressure apparatus. $\frac{1}{4}$ actual size.



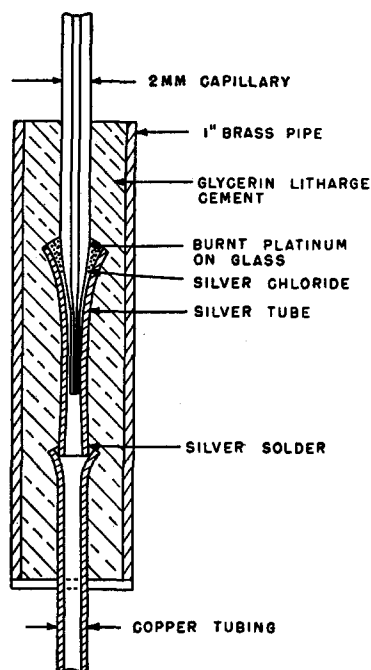


FIG. 2. Metal glass seal.

used. The levels on the multiple manometer were read with a glass plate attached to the sliding arm on the frame of a three-meter Invar scale. All levels were read and the total mercury head was corrected for the difference in the piston liquid levels. All pressure readings were corrected to 0°C .

Two special points in construction might be mentioned. To join copper to thick-walled glass capillary, the latter was drawn down and given a burnt in coating of bright platinum. (See Fig. 2.) This was fitted into a 2-mm wall silver tube to which was soldered the copper stock. The glass silver joint was made vacuum tight by silver chloride. This was done by heating the unit somewhat above the melting point of silver chloride and holding the tip of a stick of the latter to the joint when it filled immediately. The union was very strong but to eliminate any danger of breaking, the whole joint was surrounded with a brass tube which was filled with a litharge-glycerine cement.

The packless "Kerotest" valves used were not vacuum tight. To make them so, a gasket ring of thin annealed silver sheet was put in under the stainless steel diaphragm.

All parts of the apparatus containing the UF_6

to be measured were heated to around 100°C to prevent any condensation of vapor. This included the upper part of the pressure can.

The samples of UF_6 used for the measurements were supplied by Mr. Homer Priest and were resublimed over solid KF several times before using. The first portion was put into the apparatus and left standing for several days to condition the inside surfaces which had baked out as well as possible. An appropriate amount was then sublimed into the reservoir for measurement.

The equilibrium was approached, as indicated in Table I, both by heating and cooling to the desired temperature. Considerable difficulty was experienced in achieving equilibrium for the solid-vapor system at the lower temperatures, in particular at 0°C . Care was taken to maintain the null indicator around the rest point to prevent undue strain on the syphon and pointer system. For a final setting, the null point was always approached from the same direction.

The data are given in Table I and shown on a two-scale plot in Fig. 3. The first measurements indicated by the numeral (I) were made with a sample of UF_6 sublimed a number of times over solid potassium fluoride. On making measurements at higher temperatures and then cooling to -79°C , a non-condensable gas (2-6 mm) remained. This non-condensable gas was removed by repeating heating above room temperature, then cooling to 0°C and pumping. The measurements on the sample from then on are indicated by the numeral (II). A second sample of specially purified UF_6 used for the measurements at high temperature is denoted by (III). The asterisk indicates that the equilibrium was approached from high temperature side. The measurement marked (IV) was made at a later date with a third sample of UF_6 and an equimolar amount of solid potassium fluoride present.

For obtaining number (II) and (III) data, the sample was at equilibrium pressure for 30-60 minutes. The 0°C point was measured many times, the most satisfactory data being those obtained with number (III) sample. The first sample (I) came to equilibrium very slowly when the approach was from room temperature, and much more rapidly when from below 0°C or on a sample pumped around 0°C or lower.

The temperatures were measured to about 0.05°C, but are reported to the nearest 0.1°C. An error of $\pm 0.1^\circ\text{C}$ introduces an error in the pressure of about 3 mm at 60°C and 5 mm at 85°C. The error in reading the manometer was about 2 mm in the higher pressures and less than 0.5 mm at the lower ones.

CALCULATIONS

The data were fitted to equations of the form:

$$\ln P = A/T + B + C \ln T, \quad (1)$$

where A , B , and C are arbitrary constants to be determined from the data, P is the pressure in mm Hg, and T is the absolute temperature. Since it is desirable to have the equations consistent with the measured value of the triple-

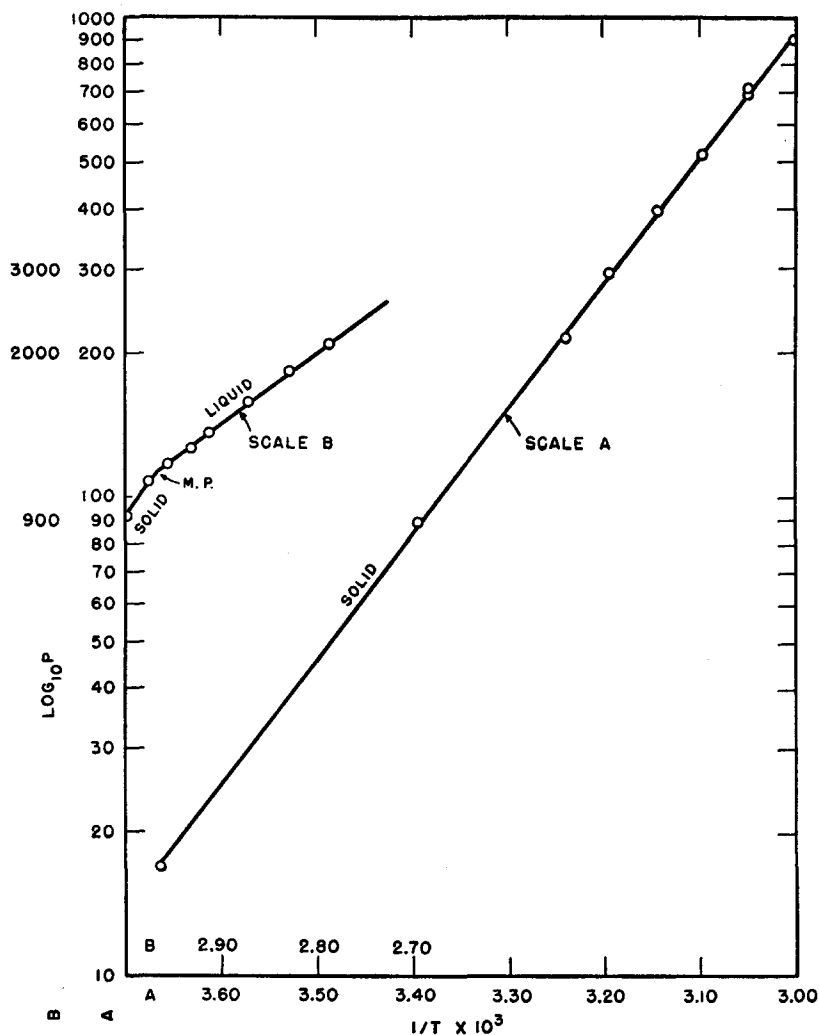
point temperature and the heat of fusion, it was decided to adjust the constants accordingly. This means that the following two relationships among the constants must be satisfied:

$$A_s/T_t + B_s + C_s \ln T_t = A_l/T_t + B_l + C_l \ln T_t, \quad (2)$$

$$\Delta H_f = P_t V_t \left[\frac{A_l - A_s}{T_t} + (C_s - C_l) \right], \quad (3)$$

where the subscript t refers to the triple point, s to the solid, and l to the liquid, and ΔH_f is the measured heat of fusion. It is convenient to have a third relation among the constants in order to put the equations into a form easily adaptable to a least-square determination. This was chosen so that the difference in specific heats between the solid and liquid agree with the measured

FIG. 3. Vapor pressure of UF₆ $\log_{10} P$ (mm Hg) vs. $1/T$ ($^\circ\text{K}$).



value at the triple point. Using the Berthelot equation of state⁴ this can be shown to be:

$$C_s - C_l = \frac{\Delta C_P^{(t)} + (9/128)(P_t/P_c)(T_c/T_t)[1 - (18T_c^2/T_t^2)][\Delta H_f/(1+\alpha)T_t]}{R(1+\alpha)t}, \quad (4)$$

where the subscript *c* refers to the critical point, $\Delta C_P^{(t)}$ is the measured difference in specific heats at the triple point, and $(1+\alpha)$ is the ratio of the actual volume to the ideal volume, as calculated by the Berthelot equation.

The values of T_t , ΔH_f , and $\Delta C_P^{(t)}$ used were those determined by Brickwedde, Hoge, and Scott,⁵ namely, $T_t = 337.213^\circ\text{K}$, $\Delta H_f = 4588$ cal./mole, and $\Delta C_P^{(t)} = -2.10$ cal./mole/ $^\circ\text{C}$. The values of the critical constants used were those given by Kirshenbaum,⁶ namely, $T_c = 518^\circ\text{K}$, and $P_c = 36,000$ mm. The value of the triple-point pressure P_t used was 1130 mm and was determined from a preliminary solution for the con-

stants. Substituting these values, the vapor pressure equations become:

$$\ln P_s = (A_s/T) + B_s + C_s \ln T, \quad (5)$$

$$\ln P_l - (2435.7/T) - 0.053 \ln T + 7.53108 = (A_s/T) + B_s + C_s \ln T.$$

By substituting the observed values of P and T into these equations, a set of equations involving the constants A_s , B_s , and C_s is obtained. The constants are readily obtained from these equations by the method of least squares, both solid and liquid points being taken together. The solution then yields the equations:

$$\begin{aligned} \log_{10} P_s &= -(3123.479/T) \\ &\quad + 21.87103 - 3.77962 \log_{10} T, \\ \log_{10} P_l &= -(2065.679/T) \\ &\quad + 18.60033 - 3.72662 \log_{10} T. \end{aligned} \quad (6)$$

The average deviation of the log of the vapor pressures over the whole range is ± 0.00276 . The triple-point pressure is calculated to be 1133 ± 7 mm, the error being estimated from the average deviation over the whole range.

The heat of vaporization at the vapor pressure can be calculated from the relationship (the volume of the condensed phase being negligible):

$$\Delta H_{\text{vap}} = VT(dP/dT)_V, \quad (7)$$

where $(dP/dT)_V$ is obtained from the vapor pressure equations and V from the Berthelot equation. Four values have been calculated and are tabulated in Table II.

The absolute entropy of the ideal gas at 1-atmosphere pressure, S° , was calculated. The values obtained are listed in Table II and will be compared with those calculated from spectroscopic data in another paper.⁷ The calculation of S° was made from the well known relationship

$$S^\circ = \Delta S_{\text{vap}} + S_s + (S_{\text{ideal}} - S_{\text{actual}}) + R \ln(P_{\text{mm}}/760), \quad (8)$$

where ΔS_{vap} is the entropy change upon va-

⁷ J. Bigeleisen, M. G. Mayer, P. C. Stevenson, and J. Turkevich, J. Chem. Phys. 16, 442 (1948).

TABLE I. Vapor pressure of UF_6 .

	Sample No.	Temp. $^\circ\text{C}$	P_{exp} mm Hg	P_{cal} mm Hg	$P_{\text{cal}} - P_{\text{exp}}$
Solid	III	0.	16.9	16.9	0
	I	21.6	88.3	87.5	-0.8
	I	35.5	216.8	220.5	3.7
	I	40.0	295.4	291.7	-3.7
	I	45.0	397.8	294.2	-3.6
	II		395.8		-1.6
	I	50.0	522.1	527.2	5.1
	I	55.0	711.1	698.2	-12.9
	II		697.2		1.0
	II	60.0	910.0	916.2	6.2
	III	63.1	1072.	1079.	7.0
Liquid	II	65.0	1169.	1167.	-2.
	II	67.9	1273.	1274.	1.
	II	70.1	1360.	1361.	1.
	IV	70.2	1366.	1365.	-1
	III		1370.		5.
	III*		1376.		11.
	III	75.2	1582.	1577.	-5.
	III*	75.3	1568.	1582.	14.
	III*	80.3	1830.	1820.	-10.
	III		1838.		-18.
	III	85.4	2087.	2089.	2.

Note:

- I is first sample
- II is first sample purified
- III is second sample
- IV is a new sample measured one month later with an equimolar amount of KF present
- * indicates that the equilibrium was approached from higher temperatures.

$$^4 V = \frac{RT}{P} \left[1 + \frac{9}{128} \frac{P}{P_c} \frac{T_c}{T} \left(1 - \frac{6T_c^2}{T^2} \right) \right].$$

⁵ Brickwedde, Hoge, and Scott, J. Chem. Phys. 16, 429 (1948).

⁶ I. Kirschenbaum, Columbia Report A753.

porization at the vapor pressure of the actual gas and is equal to $V(dP/dT)_s$; S_s is the entropy of the condensed phase under its own vapor pressure and is taken from Brickwedde's⁵ measurements; $S_{\text{ideal}} - S_{\text{actual}}$ is the entropy change in converting the actual gas to the ideal gas which by the Berthelot equation is given by $(27R/32) \times (P/P_c)(T_c/T)^3$; $R \ln(P_{\text{mm}}/760)$ is the entropy change on taking the ideal gas from its saturation pressure to 1 atmosphere.

The values of these quantities are tabulated in Table II. In Table II, column 1 gives the absolute temperature, column 2, the gas imperfection $1+\alpha$, column 3, the heat of vaporization of the actual gas, column 4, the values of S_s determined by Brickwedde,⁵ column 5, ΔS_{vap} , column 6, $R \ln P/760$, column 7, $(27R/32)(P/P_c) \times (T_c/T)^3$, and column 8, S° . The heat of vaporization is given in cal./mole and the entropy terms in cal./mole/°C.

TABLE II.

$\frac{^\circ\text{K}}{T}$	$1+\alpha$	ΔH_{vap}	S_s	ΔS_{vap}	$R \ln P/760$	$\frac{27R}{32} \frac{P}{P_c} \left(\frac{T_c}{T}\right)^3$	S°
273	.9987	12,220	51.02	44.77	-7.59	0.01	88.21
298	.9936	11,970	54.42	40.18	-3.87	0.03	90.76
323	.9764	11,580	57.73	35.86	-0.75	0.12	92.96
*348	.9441	6,487	74.62	18.64	1.42	0.29	94.97

* Liquid.

The absolute entropy values have a probable error of 0.6 e.u. This arises from a probable error of 0.5 e.u. in S_s reported by Brickwedde⁵ and a probable error of 0.3 e.u. in ΔS_{vap} . The error assigned to ΔS_{vap} is much higher than that calculated from the deviations in ΔH_{vap} . It is based on the usual discrepancy of the order of 100 cal. between calorimetric values of ΔH_{vap} and those obtained from vapor pressure data. The errors in the other two terms used in calculating S° are small in comparison.