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The Heats of Vaporization of Uranium Hexafluoride*

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Vaporizations of uranium hexafluoride were carried out in a heavy-wall, nickel-plated calorimeter. Measurements of the heat of vaporization of the solid were made at seven temperatures and of the liquid at four temperatures, covering the range from 4° to 90°C. The apparatus was tested before beginning the measurements by obtaining the heats of vaporization of water at three temperatures.

The scattering of the data on UF_6 is about one percent. The measured heats of vaporization have been used to obtain a consistent correlation of the vapor pressures, heat of fusion, and triple point given in the literature. The results are expressed as vapor pressure equations and an equation of state for the saturated vapor. From these equations and the National Bureau of Standards values for the thermodynamic properties of the solid and liquid, the entropies of the ideal gas are calculated and compared with those given in the literature from spectroscopic data and molecular structure.

INTRODUCTION

URANIUM hexafluoride has been extensively investigated. The heat capacities of the solid and liquid from 15° to 370°K were measured at the National Bureau of Standards by Brickwedde, Hoge, and Scott;¹ the vapor pressures of the solid and liquid from 0° to 85°C were measured by Weinstock and Crist;² and the calculation of thermodynamic properties of the ideal gas from structural and spectroscopic data have been reported by Bigeleisen, Mayer, Stevenson, and Turkevich.³ The heats of vaporization of the solid and liquid from 4° to 90°C have now been measured, thereby providing the data required for a consistent correlation of the other thermal data and a critical analysis of the thermodynamic properties of UF_6 .

APPARATUS

The apparatus used for measuring the heats of vaporization is shown in Fig. 1. The vaporization chamber was made of copper $\frac{1}{8}$ inch thick, nickel-plated on all interior surfaces. The lower part, containing the solid or liquid material, had vanes of nickel-plated copper for conducting heat to the sample. The copper block in the upper portion of the chamber forced the vapor to take a long path near the heated wall of the container, bringing it up to temperature after the cooling effect of vaporization. The throttling valve for controlling the flow of vapor was made of brass with a nickel stem. The numbers indicate location of the elements of a multi-junction Chromel-Constantan thermocouple. Copper leads were located at the points numbered 1, 3, 4, and 5, and four readings of the temperature difference between the calorimeter and the jacket could be obtained by using the pairs of leads 1-3, 3-4, 4-5, and 1-5. A nickel thermometer on the

copper-nickel tube (*N*) was used to observe changes in temperature of the emergent vapor during a vaporization experiment. A brass vacuum-jacket (*J*), with a ring (*R*) on which leads were wound for tempering, surrounded the vaporization chamber. The whole apparatus was suspended in a stirred bath, which was maintained at a constant temperature within 0.002°C by use of a copper resistance thermometer. The temperature of the bath was measured with a platinum resistance thermometer.

The receiving cans (*C*) were chilled to about -25°C. The copper-nickel tube leading to the cans was wound with a heater, and the tube and valves were kept hotter than the bath to avoid condensation. The connection

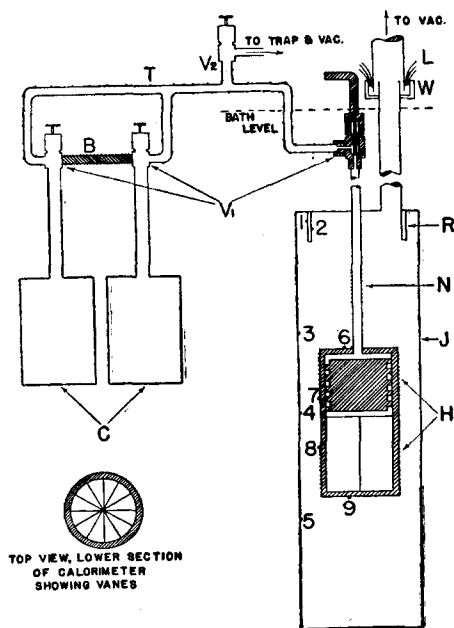


FIG. 1. Apparatus for heat of vaporization of UF_6 .

B Heated support
C Receiving cans
H Heaters
J Brass jacket
L Leads
N Nickel thermometer
R Ring
T Heated tube
V1 Valves, nickel stems
V2 Valve, steel stem
W Wax seal
Numbers give location of thermocouple junctions

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¹ Brickwedde, Hoge, and Scott, *J. Chem. Phys.* **16**, 429 (1948).

² B. Weinstock and R. H. Crist, *J. Chem. Phys.* **16**, 436 (1948).

³ Bigeleisen, Mayer, Stevenson, and Turkevich, *J. Chem. Phys.* **16**, 442 (1948).

to the vacuum system was through a U-shaped trap, kept in liquid air.

The circuits for controlling and measuring the electrical energy supplied to the heater (H), and for measuring the resistances of the platinum and nickel thermometers, have been previously described.⁴ The

TABLE I. Experimental and calculated values of γ for UF_6 . The fourth column gives the sum of corrections for heat leak, drift, and difference between initial and final temperature. The calculated values ($\gamma_{\text{calc.}}$) are obtained from Eqs. (4) and (6).

Temp. °C	Sam- ple No.	$\gamma_{\text{obs.}}$ cal mole ⁻¹	$\Sigma \text{corr.}$ cal mole ⁻¹	$\gamma_{\text{corr.}}$ cal mole ⁻¹	$\gamma_{\text{calc.}}$ cal mole ⁻¹	$\gamma_{\text{corr.}}$ - $\gamma_{\text{calc.}}$ cal mole ⁻¹
Solid						
4.32	6	12,085	-27	12,058	12,002	56
	6	12,120	7	12,127		125
	6	12,038	-5	12,033		31
	6	12,012	29	12,041		39
14.71	6	12,159	-77	12,082	11,945	137
24.38	6	11,988	3	11,991	11,882	109
	6	11,860	22	11,882		0
	6	11,881	2	11,883		1
41.72	1	11,907	11	11,918	11,736	182
	2	11,688	37	11,725		-11
	2	11,683	43	11,726		-10
	2	11,748	103	11,851		115
	2	11,666	38	11,704		-32
47.42	2	11,724	18	11,742	11,678	64
	2	11,581	175	11,756		78
48.18	2	11,463	94	11,557	11,670	-113
	2	11,451	85	11,536		-134
54.80	2	11,427	125	11,552	11,593	-41
	2	11,400	105	11,505		-88
	2	11,490	31	11,521		-72
	2	11,503	17	11,520		-73
Mean ± 72						
Liquid						
65.19	3	6,972	-75	6,897	6,880	17
	3	6,982	76	7,058		178
	5	6,900	-85	6,815		-65
	5	6,884	-40	6,844		-36
70.14	3	6,838	-60	6,778	6,811	-33
	4	6,923	-45	6,878		67
	4	6,860	5	6,865		54
	4	6,775	-28	6,747		-64
	4	6,854	-38	6,816		5
80.28	4	6,718	6	6,724	6,679	45
	4	6,714	-22	6,692		13
	5	6,866	-40	6,826		147
	5	6,662	2	6,664		-15
	5	6,667	12	6,679		0
	5	6,629	40	6,669		-10
	6	6,669	23	6,692		13
	6	6,668	-11	6,657		-22
	6	6,623	27	6,650		-29
90.26	6	6,541	24	6,565	6,559	6
	6	6,568	-14	6,554		5
Mean ± 41						

⁴Scott, Meyers, Rands, Brickwedde, and Bekkedahl, J. Research Nat. Bur. Stand. 35, 39 (1945) RP1661.

TABLE II. Heats of vaporization of UF_6 and entropies of the ideal gas.

Temp. °K	L cal mole ⁻¹	L/T cal mole ⁻¹ deg ⁻¹	S° cal mole ⁻¹ deg ⁻¹	S°_{spect} cal mole ⁻¹ deg ⁻¹
Solid				
273.16	12,023	44.02	87.56	87.65
280	11,988	42.81	88.39	88.30
290	11,929	41.13	89.57	89.48
298.16	11,872	39.82	90.50	90.34
300	11,858	39.53	90.70	90.50
310	11,772	37.97	91.80	91.56
320	11,666	36.46	92.86	92.58
330	11,537	34.96	93.87	93.54
337.21	11,429	33.89	94.59	94.20
Liquid				
337.21	6859	20.34	94.59	94.20
340	6817	20.05	94.88	94.47
350	6671	19.06	95.90	95.40
360	6533	18.15	96.91	96.30
370	6404	17.31	97.95	97.20

galvanometer used for the thermocouple indications was sensitive enough to give deflections of 1 to 4 millimeters per millidegree, depending on the number of junctions being used. A synchronous electric timer operated by a controlled 60-cycle signal measured the heating intervals with an accuracy of 0.01 or 0.02 second.

EXPERIMENTAL

Samples of UF_6 were prepared for the calorimeter by three successive sublimations and condensations. The purification train consisted of Pyrex traps, connected in series, which were carefully outgassed by heating and evacuating before the UF_6 was introduced. Six fillings of the calorimeter were made.

Analyses of the samples as introduced into the calorimeter indicated an average of about one percent impurity. Most of this could be attributed to non-volatile material, such as UO_2F_2 , which would have a negligible effect on the heat of vaporization. Possible volatile impurities are HF and SiF_4 .

Each sample was introduced into the vaporization chamber by melting and allowing it to flow in under the vapor pressure of the liquid.

In preparation for a heat of vaporization experiment, the evacuated and weighed receiving cans were put in place and chilled, the vapor line was evacuated, and usually the sample in the calorimeter required some pumping to remove gas. The calorimeter was warmed to the temperature of the bath and allowed to come to thermal equilibrium as evidenced by the constancy of the indications of the four thermo-element combinations and the resistance thermometers. A determination was begun by turning on the timer and heater current simultaneously and opening the throttle valve very gradually. The valve was adjusted as necessary during the run to keep the temperature of the calorimeter slightly lower than that of the surrounding jacket,

to prevent condensation in the tube. Data taken continuously during a determination were the readings of nickel thermometer resistance, heater current and potential, and deflections of thermocouples 1-3, 3-4, 4-5, 1-5. The time required to vaporize a 10g portion of the sample was 15 to 40 minutes, depending on rate of heating. At the end of an experiment the temperature of the calorimeter was adjusted to reproduce the starting conditions as closely as possible. This was done by supplying energy to the calorimeter for a short measured period. After two successive vaporizations, the receiving cans were removed and weighed.

The accuracy of the calorimeter was tested, and the best method of operation was found, by a series of experiments on the heat of vaporization of water. By the procedure described above, there were 12 determinations at 60°C, one at 70°C, and three at 95°C. The average deviations from the means of the determinations at 60° and 95°C were 0.12 and 0.20 percent, respectively. The mean values at 60° and 95°C were 0.05 percent smaller and 0.07 percent smaller, respectively, than the values at those temperatures given by Osborne, Stimson, and Ginnings.⁵ Thus, the consistent error was not large.

RESULTS AND CALCULATIONS

The quantity measured in heat of vaporization experiments is γ in the equation

$$L = \gamma[1 - (V_c/V_g)] \quad (1)$$

where L is the latent heat of vaporization and V_c and V_g are the molar volumes of the condensed phase and vapor, respectively. Forty-one acceptable values of γ for UF_6 were obtained; these are listed in the second column of Table I. The sum of the calculated corrections for heat leaks, drifts, and differences in beginning and ending temperature is given in the third column. The corrected values of γ are given in the fourth column of Table I and plotted in Fig. 2. All results are expressed in the defined calorie, equivalent to 4.1840 absolute joules.

The only previously available heats of vaporization of UF_6 are those calculated from the vapor pressure data of Weinstock and Crist.² These calculated results are represented in Fig. 2 by curve B , which assumes the ideal gas law for the vapor, and by curve C , which assumes the Berthelot equation and the critical constants given by Kirschenbaum.⁶ The vapor pressure data have about the same precision as the measured heats of vaporization. The two sets of data can be reconciled, as can be seen in Fig. 2, by using an equation of state somewhat less drastic than the Berthelot. Consequently, an equation of state of the form $PV = RT + BP$ was assumed, and the virial coefficient B was

investigated both as functions of T^{-1} and T^{-2} . It was found that the function

$$B(\text{cm}^3) = 1082 - (1.81 \times 10^8)T^{-2} \quad (2)$$

produced the best agreement between the measured heats of vaporization and the vapor pressure data of Weinstock and Crist.

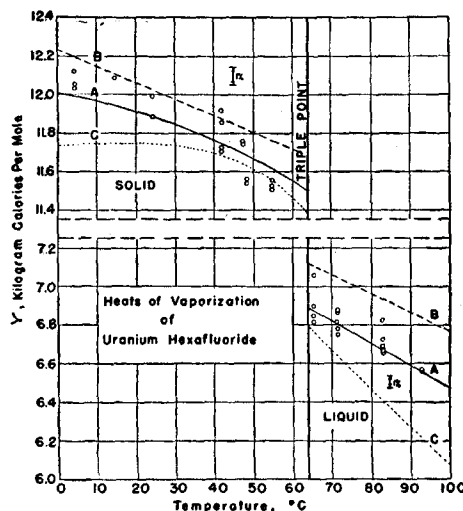


FIG. 2. Heats of vaporization of UF_6 . The circles are the experimental values (γ_{corr}) given in the fifth column of Table I. Curve A is calculated from Eqs. (4) and (6). Curves B and C are calculated from the vapor pressure data of Weinstock and Crist assuming (B) the ideal gas law and (C) the Berthelot equation.

Curve A of Fig. 2 was obtained from the following set of equations:

Solid:

$$\log_{10} P_{\text{mm}} = -(2858.2/T) + 16.3619 - 1.9116 \log_{10} T \quad (3)$$

$$\gamma = RZ(6581.2 - 1.9116T) \quad (4)$$

Liquid:

$$\log_{10} P_{\text{mm}} = -(2466.0/T) + 26.1868 - 6.2582 \log_{10} T \quad (5)$$

$$\gamma = RZ(5678.2 - 6.2582T) \quad (6)$$

where

$$Z = 1 + (BP/RT)$$

and B is obtained from Eq. (2). Equations (4) and (6) are obtained directly from Eqs. (3) and (5), respectively, by the Clausius-Clapeyron equation.

These equations are made to reproduce the heats of fusion (4588 cal mole⁻¹) found by Brickwedde, Hoge, and Scott within their experimental error of about 0.5 percent. The vapor pressure data of Weinstock and Crist are represented by these equations as closely as by their own. The heats of vaporization are reproduced satisfactorily within the experimental accuracy.

Calculated values of the heat of vaporization were obtained by substituting the values of γ obtained from Eqs. (4) and (6) in Eq. (1), and are tabulated at ten-degree intervals in the second column of Table II.

⁵ N. S. Osborne, H. F. Stimson, and D. C. Ginnings, J. Research Nat. Bur. Stand. 23, 256 (1939).

⁶ I. Kirschenbaum, Columbia Report A753.

The corresponding entropies of vaporization are given in the third column.

The molar volume of the solid was assumed constant at 70.42 cc. Its variation would be expected to be small, and would have a negligible effect in calculating L . The volumes of the liquid were obtained from the density measurements of Hoge and Wechsler.⁷

The entropies of the ideal gas at one atmosphere were obtained by the usual third-law addition of entropies,

$$S^\circ = S_{\text{sat}} + (L/T) + \Delta S(\text{ideal-real}) + R \ln(P_{\text{mm}}/760) \quad (7)$$

and are tabulated in the fourth column of Table III. The required values of S_{sat} are taken from Brickwedde, Hoge, and Scott,¹ except that those for the liquid have been lowered by 0.05 cal mole⁻¹ deg⁻¹ corresponding to a change in the heat of fusion from 4588 to 4570 cal mole⁻¹. In the last column of Table III are tabulated for comparison the values of S° obtained by interpolating in the table calculated by Bigeleisen, Mayer,

Stevenson, and Turkevich³ from the spectroscopic data.

The steadily increasing difference between the third-law and spectroscopic entropies, and the extremely low Boyle point calculated from Eq. (2), seem to indicate that there is a consistent temperature-dependent error in the experimental measurements. The tests with water indicate that this is not due to the vaporization calorimeter. The determination of the accuracy of the equations presented here may have to await measurements of the P - V - T relationships of UF_6 gas. From a consideration of the estimated errors of the present measurements and the consistency of the correlation of these results with other thermal data, it appears reasonable to assign a probable error of about one percent to the tabulated values of latent heat of vaporization. This accuracy is an order of magnitude worse than is usually obtained in this laboratory, but it seems to be comparable with that obtained in measuring other properties of UF_6 ; and, in view of the refractory nature of this compound, an error of one percent is not excessive.

⁷ H. J. Hoge and M. T. Wechsler, *J. Chem. Phys.* (in press).

Catalysis on Non-Uniform Surfaces

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Using the ammonia decomposition as an example, the kinetics of a heterogeneous reaction are discussed. On a continuously non-uniform surface, no single reaction step is the limiting one; on the optimum sites two reaction steps are equally slow. The expression for over-all velocity is developed, and solved exactly for the case of an exponential distribution of activation energies. It appears that if the distribution is broad, its exact shape is unimportant, but that a factor r , connected with the amount of adsorption energy available for catalytic work, is important. It is shown that for a broad distribution, the pressure dependence of the over-all rate is the same as the pressure dependence on the optimum sites. Because the position of the optimum depends on pressure, one cannot assume that the surface is "effectively uniform." The simplest of ammonia kinetics is discussed, but it appears that on a non-uniform surface, much more extensive experiments than have been available are necessary to elucidate properly the kinetics of a reaction.

I. INTRODUCTION

IT is generally recognized that from the standpoint of gas adsorption studies, the surface of a catalyst is often quite non-uniform. That is, heats of adsorption and energies of activation for adsorption and desorption vary widely over the surface.¹

When catalytic reactions are studied, it is equally well known that the same surface often is treated as if it were uniform; from this apparent contradiction, it emerges that often only a small fraction of the surface available for gas adsorption is effective in bringing about a reaction. This contention is supported by the investigation of catalytic poisoning, when it is found that a

small fraction of the amount of poison necessary to saturate the surface will stop reaction. A consideration of these phenomena leads to the "Theory of Active Centers" (H. S. Taylor).

Constable² attempted to reconcile the dualism between the data of adsorption and catalysis. He postulated an exponential distribution of the values of the activation energy over the surface, and assumed that there existed a "lowest value" for this energy, below which reaction would not proceed. He was thus able to show that the effective value of the activation energy for reaction was little different from the minimum value. His treatment is essentially incomplete in that it leaves unexplained the factors that determine the "minimum activation energy." The factors will now be considered.

* Junior Fellow, Harvard Society of Fellows, 1948-

¹ G. M. Schwab, H. S. Taylor, and R. Spence, *Catalysis* (D. Van Nostrand Company, New York, 1937).

² F. H. Constable, *Proc. Roy. Soc. A108*, 355 (1925).