

CONTRIBUTION FROM UNION CARBIDE CORPORATION,
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α -Uranium Pentafluoride. I. Characterization¹

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Using uranium hexafluoride as the carrier gas, under sufficient pressure to prevent disproportionation of the uranium pentafluoride, the vapor pressure of this intermediate fluoride was determined by measurement of the transpiration rates over the temperature range from 282 to 412°. From these data, confirmation of the observed melting point was obtained and the heats of fusion and vaporization were derived.

Introduction

Although uranium pentafluoride has been known almost as long as uranium hexafluoride, detailed study of this intermediate fluoride of uranium has been much less extensive.³ The complicated nature of the compound, which is exemplified by its tendency to disproportionate,³ is undoubtedly a contributing factor to the limited amount of thermodynamic data available.

Early estimates of the vapor pressure of uranium pentafluoride were calculated from a compilation of thermodynamic relationships developed by Brewer and co-workers on the basis of analogy to other pentafluorides.⁴ Later observations in connection with studies being made at Oak Ridge by Cameron,⁵ Gilpatrick, Baldock, and Sites,⁶ Crews and Davis,⁷ and Kobisk and associates⁸ produced various experimental estimates for specific points which not only differed by several orders of magnitude from the values predicted by Brewer's derivations but also differed widely among themselves.

In agreement with the general prediction for binary pentafluorides, all the values lay between the known vapor pressures of uranium tetrafluoride⁹ and uranium hexafluoride¹⁰ and were of such magnitude as to indicate that the vapor pressure of uranium pentafluoride would be measurable by the transpiration process.

Results

Using uranium hexafluoride as an inert carrier gas under sufficient pressure to prevent disproportionation of the uranium pentafluoride, transpiration rates were measured at intervals over a temperature range which included the melting point. The relationship expressed by eq. 1 was used to calculate the vapor pressure of

uranium pentafluoride at each of the transpiration temperatures.

$$P_{\text{UF}_5} = \frac{N_{\text{UF}_5} P_{\text{UF}_6}}{N_{\text{UF}_6}} \quad (1)$$

where P_{UF_5} and P_{UF_6} are the pressures of uranium pentafluoride and uranium hexafluoride, respectively, N_{UF_5} is the amount of UF_5 transpired during the experiment expressed in moles, and N_{UF_6} is the corresponding amount of UF_6 used as the carrier gas expressed in moles.

Since the uranium pentafluoride melted within the selected experimental temperature range, it was necessary to determine the melting point in order to correlate the vapor pressure data with temperature. This was done by observation of the cooling rate and allowed a separation of the vapor pressure data into two groups, one for the solid phase and one for the liquid phase.

Applying the statistical treatment reported by Kastenbaum¹¹ to the two groups of data, vapor pressure-temperature relationships based on the Clausius-Clapeyron equation were developed. These are given by eq. 2 and 3. For solid UF_5

$$\log p = -\frac{(8001 \pm 664)}{T} + (13.994 \pm 1.119) \quad (2)$$

For liquid UF_5

$$\log p = -\frac{(5388 \pm 803)}{T} + (9.819 \pm 1.236) \quad (3)$$

where p is the vapor pressure expressed in mm. and T is the temperature expressed in °K. The indicated experimental limits of error are applicable at the 95% level of confidence. The experimentally determined melting point, 348°, was consistent with the value derived by simultaneous solution of the vapor pressure equations, 353° (+13°; -16°).

Assuming the vapor to behave ideally, heats of vaporization were calculated from the vapor pressure equations: for the solid, $\Delta H_{\text{vap}} = 36.6 \pm 3.0$ kcal./mole; for the liquid, $\Delta H_{\text{vap}} = 24.7 \pm 3.8$ kcal./mole. The difference between these values is the heat of fusion, $\Delta H_{\text{fus}} = 11.9 \pm 4.2$ kcal./mole.

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(2) To whom correspondence should be addressed.
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(4) L. Brewer, L. A. Bromley, P. W. Giles, and N. L. Lofgren, U. S. Atomic Energy Commission, MDDC-1543, Sept. 20, 1945.
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(6) L. O. Gilpatrick, R. Baldock, and J. R. Sites, U. S. Atomic Energy Commission, ORNL-1376, Aug. 29, 1952.
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(8) E. H. Kobisk, R. L. Farrar, D. E. Ham, and W. Davis, Jr., unpublished data, 1957.
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TABLE I
 TRANSPIRATION DATA FOR URANIUM PENTAFLUORIDE

Temp., °C.	Press., atm.	Flow rate of carrier, cc./min.	Wt. of UF ₆ , g.	Wt. of UF ₆ , g.	Cor. wt. of UF ₆ , g.	Cor. vap. press. of UF ₆ , mm.
282.0	1.27	12.87	151.67	0.0819	0.0619	0.42
299.0	0.88	26.60	62.83	0.0843	0.0778	0.88
307.0	1.35	21.52	80.05	0.1360	0.1286	1.74
313.0	0.77	13.50	73.34	0.2157	0.1967	1.66
316.8	1.73	25.38	115.00	0.2601	0.2527	3.05
317.3	1.46	12.60	52.16	0.1353	0.1273	2.86
323.5	1.46	11.52	43.53	0.1580	0.1503	4.05
333.0	1.81	10.92	50.36	0.2242	0.2158	6.23
343.3	1.76	14.19	72.98	0.5852	0.5745	11.13
345.3	1.60	18.26	85.20	0.7517	0.7407	11.17
349.0	1.81	12.39	51.03	0.4685	0.4596	13.10
354.0	1.83	27.90	136.26	1.5290	1.5179	16.38
361.0	2.33	12.06	68.47	0.7149	0.7039	19.24
366.5	2.78	12.71	71.16	0.8945	0.8848	27.77
374.0	2.37	12.70	77.87	1.2669	1.2534	30.64
381.0	2.41	6.58	31.19	0.6717	0.6603	40.99
392.0	2.58	10.70	64.09	1.5208	1.5055	48.69
412.0	3.13	10.55	62.06	2.2189	2.2030	89.26

The data obtained from this investigation are presented in Table I. Direct comparison with the results of the earlier works is made on the graphic representation of eq. 2 and 3 shown in Figure 1.

Experimental

Equipment. Transpiration Apparatus.—The transpiration chamber was a 1-in. nickel tube approximately 15 in. in length with a nickel thermowell extending axially from the closed end to the middle of the tube. A gas manifold was connected to the chamber by a tube entering the closed end for the purpose of introducing uranium hexafluoride or nitrogen. A brass refrigeration flange closure was silver soldered at the other end to provide an opening through which a nickel boat containing uranium tetrafluoride could be inserted. Close-fitting nickel rings were located at both ends of the boat to center the boat in the heated zone and to reduce diffusion of uranium pentafluoride vapor toward the cooler ends of the chamber. The uranium penta-

fluoride condenser, made of 0.25-in. nickel tubing, 11 in. long with a nozzle tip to minimize diffusive effects, was inserted through the seal plate of the flange by means of a Teflon-packed compression seal. It was necessary only that this condenser be maintained at some temperature cooler than the vaporization section of the reactor.

The external uranium hexafluoride condensing trap was cooled in Dry Ice-trichloroethylene slush. A jacket of 1-in. copper pipe, split longitudinally, was placed around the vaporization chamber to distribute the heat supplied by a 750-watt Hevi-Duty electric tube furnace evenly over a greater portion of the chamber. The temperature of the furnace was controlled by the output of an 18-amp. Variac fed by a 6-kva. Seco automatic voltage regulator. An iron-constantan thermocouple, previously calibrated, was placed in the thermowell to monitor the vapor temperature. All parts of the system were pretreated with fluorine at temperatures equal to the maximum to which the various parts would be exposed during the experiments.

The uranium hexafluoride source cylinder was supported in a liquid bath heated to maintain the cylinder pressure constant at the desired level. For the lower temperature experiments, water filled the bath, while Dowtherm A was used where higher uranium hexafluoride pressures were required. A Bourdon tube pressure gauge was used to measure the pressure of uranium hexafluoride vapor supplied to the system. A dry nitrogen source was available for purging uranium hexafluoride from the partially cooled chamber prior to removal of the uranium pentafluoride condenser.

Melting Point Apparatus.—The design of the melting point tube is shown in Figure 2. The tube was made of commercially pure wrought nickel, and all joints were nickel welded. The tube was pretreated with fluorine at temperatures up to 490° for a period of several hours before use. The temperature of the material around the thermowell could be monitored continuously by means of an iron-constantan thermocouple and a Brown Elektronik recorder.¹² This combination gave no significant temperature error when calibrated with reagent grade potassium dichromate at its melting point. The melting point tube was insulated from direct thermal radiation by a wrapping of alternate layers of glass wool and aluminum foil and was heated in a vertically mounted 2-in. tube furnace, the temperature of which was controlled by the output of a 5-amp. Variac. The insulated tube was flexibly suspended inside the furnace so that manual agitation of the tube was possible. By means of the 0.25-in. flare Tee¹³ at the top of the tube, connection was

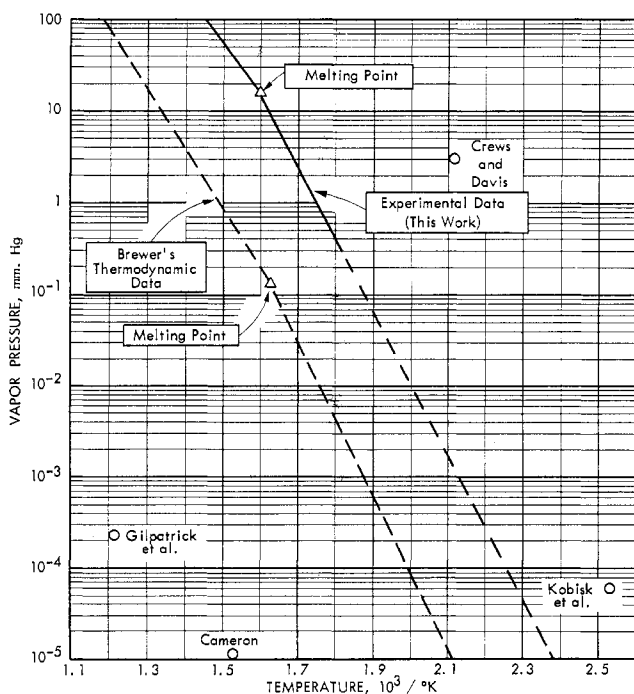


Figure 1.—Vapor pressure of uranium pentafluoride.

(12) An electronically operated, strip chart recording potentiometer manufactured by Minneapolis-Honeywell.

(13) American Standards Association B-70.1, Figure 9A.

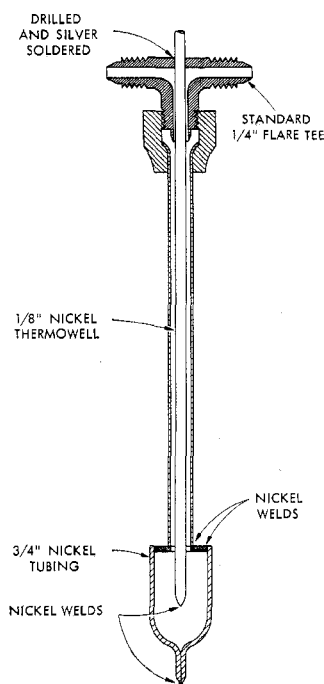


Figure 2.—Melting point tube.

made to both a source of uranium hexafluoride vapor and a trapped evacuation system. The desired pressure of uranium hexafluoride vapor was generated by a cylinder, containing solid uranium hexafluoride, which was equipped with a pressure gauge and placed in an air bath capable of being maintained at temperatures up to 400° . The connecting lines to the melting point tube which were outside the oven were heated with insulated resistance wire to prevent condensation of the uranium hexafluoride vapor, and valves at appropriate locations permitted isolation of the melting point tube from the rest of the system.

Materials. Uranium Pentafluoride.—The uranium pentafluoride for both the melting point and vapor pressure determinations was produced *in situ* by the reaction of finely divided uranium tetrafluoride and gaseous uranium hexafluoride maintained at a pressure of 1 atm. over a period of approximately 16 hr. at temperatures between 230 and 250° . The product of the reaction consisted of large, white to ice-blue crystals which gave an X-ray pattern of pure α -uranium pentafluoride when reaction with atmospheric moisture was prevented.

Uranium Tetrafluoride.—The uranium tetrafluoride used in the above synthesis had been prepared by the gas phase reduction of uranium hexafluoride with hydrogen. It consisted of finely divided green crystals, the purity of which is indicated by the absence of foreign lines in the X-ray diffraction pattern and the analysis for total uranium. *Anal.* Calcd.: total U, 75.8. Found: total U, 75.4; U(IV), 73.0. Spectrochemical analysis showed a total cationic impurity level of 0.1%.

Uranium Hexafluoride.—The uranium hexafluoride was a typical sample of gaseous diffusion plant "tails." Prior to use it was heated above its melting point, and the inert gases were flashed off until the measured cylinder pressure agreed with the reported vapor pressure of pure uranium hexafluoride.¹⁰

Procedure. Vapor Pressure Measurement.—Prior to the start of a transpiration experiment, tare weights were obtained for both the uranium pentafluoride condenser tube and the uranium hexafluoride condensing trap. At all times when the vaporization chamber was open to the atmosphere a stream of dry nitrogen was maintained so that atmospheric hydrolysis and/or oxidation of the uranium pentafluoride were prevented.

With the throttle valve (located between the two condensers) closed, the sample temperature was brought to the desired level. At the same time the uranium hexafluoride source cylinder was heated to supply uranium hexafluoride vapor at the required

pressure. When these conditions were attained, the throttle valve was opened sufficiently for a predetermined flow of gas through the chamber, yet providing enough back pressure to maintain the uranium hexafluoride pressure within the chamber. The position of the throttle valve permitted an estimate of the flow rate upon which to base the duration of the experiment. Exact flow rates were later calculated from the weight of uranium hexafluoride collected.

At the end of each run, the throttle valve and uranium hexafluoride cylinder valve were closed simultaneously. After the transpiration chamber was allowed to cool partially, the throttle valve was reopened and the gases within the chamber were swept out by a flow of dry nitrogen. With nitrogen still flowing, the uranium hexafluoride trap was isolated and removed for weighing. The flange bolts were loosened and a sleeve of polyethylene tubing was placed over the flange and the uranium pentafluoride condenser. When the tube was thoroughly purged of air, the open end was tied off, the flange and condenser were removed, and the other end was tied off. In this condition the condenser was moved to a drybox where it was carefully removed from the flange and reweighed. When the weight of uranium pentafluoride in the condenser was established, the material was partially removed by tapping the condenser sharply so that crystals fell into a vial which was then sealed; these crystals were used for subsequent X-ray examination. The remaining material was removed from the condenser by soaking overnight in a solution of sodium carbonate containing hydrogen peroxide. When the condenser had been rinsed and oven dried, it was weighed and reassembled for the next run. This procedure was repeated for each of the vapor pressure points measured.

Melting Point.—After the melting point apparatus was charged with uranium tetrafluoride, the conversion to α -uranium pentafluoride was performed as previously described. With a pressure of uranium hexafluoride in excess of the disproportionation pressure of α -uranium pentafluoride, the prepared sample was heated to 370° . Allowing the molten sample to cool slowly, the temperature was observed at which the phase change (freezing) occurred. This was indicated by a period during which the temperature remained constant and after which the previously observed cooling rate was resumed. The procedure was repeated with various uranium hexafluoride pressures in the range between 0.7 and 4.6 atm. As seen in Table II, identical melting points were observed at uranium hexafluoride pressures greater than 1.6 atm.

TABLE II
MELTING POINT OF URANIUM PENTAFLUORIDE
UNDER VARIOUS PRESSURES OF URANIUM HEXAFLUORIDE

UF ₆ press., atm.	M.p., °C.	UF ₆ press., atm.	M.p., °C.
4.6	348	1.7	348
3.4	348	1.4	345
3.0	348	1.2	346
2.9	348	0.9	345
2.5	348	0.7	346
2.1	348		

After all the experimental measurements were made, the melting point tube was thoroughly cleaned with a neutral solution of sodium dichromate. The total loss in weight resulting from the fluorine pretreatment, approximately 3 weeks of exposure to liquid uranium pentafluoride, and cleaning with the solution of sodium dichromate was 0.059 g.

Discussion

Brewer⁴ reported a melting point for uranium pentafluoride of 600°K. , but simultaneous solution of the vapor pressure equations he presents for liquid and solid uranium pentafluoride shows the point of intersection to be 615°K. or 342°C.

Both Cameron⁵ and Gilpatrick⁶ based their estimates upon observations of ion intensities made with a mass spectrometer and attributed to uranium pentafluoride. In view of the nature of their experiments and the assumptions made, it is not surprising that both values are low.

Although Crews and Davis⁷ and Kobisk, *et al.*,⁸ were not seeking a direct measurement of the vapor pressure of uranium pentafluoride, both studies involved a vapor transport of this material. Considering the experimental conditions under which their transport measurements were made and that certain corrections might have been applied had the data been available, it is normal that the values proposed by these investigators may well be higher than the more refined and direct measurements reported here. Noting that Kobisk's value lies almost upon an extrapolation of our liquidus vapor pressure curve, an interesting speculation arises: that transpiration from a thin adsorbed film of uranium pentafluoride exhibits the characteristics of vaporization from a liquid surface even though the ambient temperature is well below the melting point of uranium pentafluoride.

Several sources of possible error were considered in this investigation. Even though all parts of the equipment were pretreated with fluorine at some elevated temperature, it was recognized that any reduction of uranium hexafluoride on the surfaces of the uranium pentafluoride condenser would bias the amount of material collected in an upward direction. This was also true for any uranium pentafluoride which was caused to migrate to the condenser by purely diffusive forces. An empirical correction for both these factors was derived from a series of static exposures made at different temperatures and for varying periods of time. Table III contains the smoothed data from these static exposures typifying the corrections applied to the vapor pressure data.

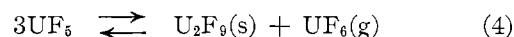
TABLE III
EMPIRICAL CORRECTIONS FOR REDUCTION-DIFFUSION ERRORS

Temp., °C.	UF ₅ coll. rate, mg./hr.	Temp., °C.	UF ₅ coll. rate, mg./hr.
240	0.90	340	1.49
260	0.93	360	1.82
280	1.00	380	2.24
300	1.10	400	2.78
320	1.26		

Two assumptions on which this work is based are that uranium pentafluoride is a monomer in the temperature range studied and that the heat of vaporization is a constant. Although these are not experimentally established facts, the assumptions appear to be valid. Failure to saturate the carrier gas with uranium pentafluoride and incomplete collection of the uranium

pentafluoride in the first condenser constituted other possible sources of error; however, the measured vapor pressure was independent of the uranium hexafluoride flow rate over the range of 5 to 28 cc./min. used in the experiments, and no trace of deposited material was found beyond the first 4 in. of the condenser tube.

Certain unique problems existed in the determination of the melting point of α -uranium pentafluoride. Disproportionation at elevated temperatures occurs according to eq. 4



When the uranium pentafluoride is molten, the concentration of diuranium ennefluoride in the melt will depend on its solubility. Within the range of complete solubility, the concentration is inversely proportional to the uranium hexafluoride pressure. However, the existence of pure uranium pentafluoride cannot be assumed at high pressures of uranium hexafluoride due to the increased solubility of this gas in the molten salt with increased pressure. Because of these facts, it is impossible to measure experimentally the melting point of pure uranium pentafluoride; however, measurement of the melting point under the same conditions imposed for the vapor pressure determination should give a value differing only slightly from that of the pure material providing the solubilities of both uranium hexafluoride and diuranium ennefluoride in the molten salt are not high.

As shown in Table II, the melting points were constant at all uranium hexafluoride pressures above 1.6 atm. This indicates that the diuranium ennefluoride concentration becomes significant only at the lower pressures and that the solubility of uranium hexafluoride gas in molten uranium pentafluoride is not particularly high. The slightly lower melting points observed at the lower pressures of uranium hexafluoride were probably due to the presence of diuranium ennefluoride. This conclusion is supported by the fact that the disproportionation pressure of uranium pentafluoride is 1.5 atm. at 370°, the highest temperature attained by the molten salt before observation of the cooling rates was undertaken.

Finally, there was the possibility that nickel fluoride, formed as a result of the fluorine pretreatment and by subsequent reaction with the uranium fluorides, might affect the accuracy of the melting point determination. A small weight gain in excess of that for the stoichiometric conversion of uranium tetrafluoride to uranium pentafluoride was noted. This was attributed to reaction of uranium hexafluoride with the nickel of the melting point tube to form nickel fluoride and additional uranium pentafluoride. However, the total weight lost by the melting point tube during its use indicates that the attack upon the nickel was small.