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CORRELATION OF CRITICAL TEMPERATURE
WITH THERMAL EXPANSION OF
LIQUID URANIUM HEXAFLUORIDE

AUTHOR:

G. P. Rutledge

CARBIDE AND CARBON CHEMICALS CORPORATION

K-25 PLANT

Oak Ridge, Tennessee

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CARBIDE AND CARBON CHEMICALS CORPORATION
K-25 Laboratory Division

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CARBIDE AND CARBON CHEMICALS CORPORATION
K-25 Laboratory Division

A B S T R A C T

The critical temperature of uranium hexafluoride is predicted to be 218.5°C. using an equation involving the critical temperature as a function of the thermal expansion coefficient of the liquid.

CLASSIFICATION CANCELLED

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CORRELATION OF CRITICAL TEMPERATURE WITH THERMAL EXPANSION COEFFICIENTS OF LIQUID URANIUM HEXAFLUORIDE

G. P. Rutledge

INTRODUCTION

The experimental determination of the critical temperature of uranium hexafluoride is very difficult due to the corrosive properties of the compound, especially at elevated temperatures. Since many thermodynamic properties of uranium hexafluoride are based on the critical temperature, an accurate prediction would be useful.

Among the values obtained by several methods¹ are: 1) 245°C., a preliminary experimental value by Simon; 2) 243°C., calculated from surface tension data; 3) 230 to 249°C., calculated from the empirical relation $T_b/T_c = \text{constant}$, where T_b is the boiling point and T_c is the critical temperature; and 4) 232°C., reported by Cohen. Hoge and Wechsler², using reduced densities and temperatures, as in equation 1, predicted the critical temperature of uranium hexafluoride to be 217°C.

$$\rho_{av} / \rho_c = 1 + m(1 - T/T_c) \quad (1)$$

where ρ_{av} = average density = $(\rho_{\text{liquid}} + \rho_{\text{gas}})/2$

ρ_c = critical density

m = constant

T = temperature of the density measurement

The method of rectilinear diameters was applied and it was assumed that $m = 1$. Hoge and Wechsler stated that the average density of uranium hexafluoride is almost a linear function of temperature and

1. Manhattan Project Technical Series, Argonne National Laboratories, ANL JJK-24, March 10, 1947.
2. Hoge, H. J. and M. T. Wechsler, "Density of Liquid Uranium Hexafluoride From the Triple Point to 162°C. and Density of the Solid Near the Triple Point," National Bureau of Standards, A-1591, December 18, 1943.

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can be represented by equation 2.

$$\rho_{av} = 2.784 - 2.84 \times 10^{-3} T(^{\circ}K) \quad (2)$$

Actually, m varies from 0.85 to 1.0 according to Cragoe and Meyers³ who have plotted rectilinear diameters for a number of substances. Corresponding to Cohen's estimate of T_c ($232^{\circ}C$.) it was found that $m = 1.06$. Hoge and Wechsler² observed that this value is higher than would be expected on the basis of previous observations of the value of m , and stated that the critical temperature probably lies below, rather than above, the value predicted by Cohen. It should be pointed out that the value $217^{\circ}C$. predicted using the method of rectilinear diameters, involved the assumption that equation 2 is valid at the critical temperature of uranium hexafluoride.

In the present investigation the critical temperature of uranium hexafluoride is predicted using thermal expansion data.

DEVELOPMENT OF RELATIONS

In a previous paper⁴ the thermal expansion coefficient of a liquid was expressed as a function of the critical temperature as shown in equations 3 and 4.

$$\beta = .04314 (T_c - T_{av})^{-0.641} \quad (3)$$

$$T_c = \left(\frac{\beta}{.04314} \right)^{-1.56} / T_{av} \quad (4)$$

The thermal expansion coefficient, β , and T_{av} are defined by equations 5 and 6.

$$\beta = \frac{\text{density at } T_1 - \text{density at } T_2}{\text{density at } T_2 (T_2 - T_1)} \quad (5)$$

$$T_{av} = \frac{T_1 + T_2}{2} \quad (6)$$

3. Unpublished work cited by Hoge and Wechsler².

4. Rutledge, G. P., "Correlation of Critical Temperatures with Thermal Expansion Coefficients of Liquid Fluorocarbons", Carbide and Carbon Chemicals Corporation, K-25 Plant, K-419, June 13, 1949.

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If β is known for a given temperature interval it is possible to predict T_c using equation 4. Substituting this value into equation 3 makes it possible to calculate β over other temperature intervals.

APPLICATION TO URANIUM HEXAFLUORIDE

Experimental evidence indicates that uranium hexafluoride may be considered an ideal gas⁵. Equation 3 generally holds for all types of liquids, deviating mostly for associated compounds. Since uranium hexafluoride behaves as an ideal and non-associated gas, the critical temperature predicted by use of equation 4 should be a good approximation of the true value.

The critical temperature of uranium hexafluoride has been predicted using density determinations of the liquid at various temperatures made by the National Bureau of Standards². The results are given in table I. The density measurements of the Bureau were made using glass bobbins of known density immersed in liquid uranium hexafluoride. The temperature was adjusted until each bobbin in turn would just sink and just rise and the average was taken as the temperature at that density.

TABLE I
CRITICAL TEMPERATURE OF URANIUM HEXAFLUORIDE

Temp., °C.	Density, (ρ) gm./cc.	T_{av} , °C.	$\beta \times 10^3$, (Experi- mental) per °C.	$\beta \times 10^3$, (Equation 3, Assuming $T_c = 218.5^\circ\text{C}.$) per °C.	T_c , (Predict- ed Using Equation 4) °C.
68.66	3.604	80.65	1.835	1.834	218.45
92.65	3.452	102.66	2.048	2.051	218.66
112.67	3.316	121.89	2.264	2.303	221.10
131.12	3.183	146.85	2.862	2.792	215.69
162.59	2.920				

Average $T_c = 218.48$

Limit of error, 95% confidence interval ± 3.51

5. Kirshenbaum, I., "The Physical Properties of Uranium Hexafluoride",
SAM Laboratory, A-755, July 1, 1943.

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7

The average of the predicted values in table I of the critical temperature of uranium hexafluoride is 218.5°C . Using this value and equation 3, the expansion coefficients have been calculated. A comparison between predicted and experimental values shows good agreement (see table I and figure 1). The thermal expansion of liquid uranium hexafluoride may now be calculated over temperature intervals for which no density determinations have been made.

DISCUSSION

In a previous paper⁴ it was pointed out that equation 4 gives predictions of the critical temperature in degrees absolute within $\frac{1}{2}\%$ of the experimentally determined value for a number of hydrocarbons and fluorocarbons. It is therefore felt that the value of the critical temperature of uranium hexafluoride that is obtained by this equation can be compared favorably with values obtained by other methods.

The value of 218.5°C . obtained for the critical temperature of uranium hexafluoride using thermal expansion coefficients agrees with the observation of Hoge and Wechsler; namely, that the true value of the critical temperature probably lies below 232°C . even though all previously calculated values have been above this value.

SUMMARY

Using an equation that had been previously derived⁴ in this laboratory, the critical temperature of uranium hexafluoride has been calculated using thermal expansion coefficients obtained from density measurements made by Hoge and Wechsler. The critical temperature of uranium hexafluoride has been calculated to be 218.5°C . Using this value for the critical temperature, it is possible to calculate thermal expansion coefficients for uranium hexafluoride over various temperature intervals.

LABORATORY REFERENCE

Notebook No. 1024 issued to G. P. Rutledge, July 22, 1948, pages 24 to 28.

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LEGEND.

- Expansion coefficients calculated from density measurements.
- Expansion coefficients calculated using equation (3)

FIGURE 1

CHEMISTRY DEPARTMENT LABORATORY DIVISION	
VARIATION OF EXPANSION COEFFICIENTS WITH AVERAGE TEMPERATURE OF URANIUM HEXAFLUORIDE	
K-25 PLANT CARBIDE & CARBON CHEMICALS CORP	
DRWN <u>B. Hammer</u>	APPV'D <u>G. Rutledge</u>
DATE JUNE 8, 1949	DWG NO. LD-A843