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CHEMISTRY-GENERAL

URANIUM HEXAFLUORIDE: A SURVEY  
OF THE PHYSICO-CHEMICAL PROPERTIES

by

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## INTRODUCTION

Although data on the physical properties of  $UF_6$  have been compiled in a number of sources, none of the compilations\* are both thorough and up-to-date. Most of the available compilations do not cover literature published after 1950. In the last ten years some of the discrepancies in the reported values of various properties of  $UF_6$  have been resolved and new, more exact data have been added to the literature. In addition, values of the physical properties taken from different compilations often show striking and unexplained differences. For these reasons this handbook has been compiled in an attempt to collect all of the current physico-chemical data on  $UF_6$  in one useful volume and to highlight apparently contradictory results.

It is hoped that this handbook will serve both to acquaint technical personnel with the physico-chemical character of  $UF_6$  and to display the status of current knowledge of the values of each physical property. In many cases both preliminary and final values are tabulated herein to facilitate evaluation of the data by the reader, the preliminary values serving also to trace the history of some of the investigations which produced the now accepted values. The more reliable data for most properties are expressed as functions of their variables (e.g., temperature or pressure) to aid the user in quick extraction from the text. These functions are plotted in the form of graphs, given as equations, or both. In the case of most of the reliable data, a brief description is given of the experimental method which the investigator used. The reader is urged, however, to consult the investigator's publications for more complete information on the property reported and for a more authoritative interpretation of the results. Although no special effort was made to correlate all the data reported in this compilation for purposes of inter-comparing deduced values of other properties, the data have been correlated for a few properties using various of the well-known empirical relations.

The bibliography near the end of the text is arranged alphabetically according to the first author, and then chronologically. Although every effort has been made to obtain and consider all reports of original data on the physical properties, references to preliminary results were often omitted and the source for the final results given. This avoids many citations to obscure, early progress reports of both the American and British atomic energy projects.

Only those papers published between 1940 and the present were used in the compilation. Data published prior to 1940 are generally considered unreliable because of the crude techniques used in the purification of  $UF_6$ . However if need be, much of the earlier information can be obtained from the "Uranium" volume of Gmelin's Handbuch der Anorganischen Chemie. Library sources utilized in the present compilation included: Chemical Abstracts, Science Abstracts, Nuclear Science Abstracts, and books of the National Nuclear Energy Series. Bibliographic tools covering classified reports of the U.S. Atomic Energy Commission were also used to supplement the publications mentioned above, as were earlier compilations and bibliographies. In all cases, however, the data incorporated herein was obtained from the original source when it could be obtained.

\*See References 9, 17, 20, 28, 46, 65, 82, 87, 88, 93, 107, 111, 115 and 135.

The symbols used in this compilation are generally those given in the original sources. When two or more symbols were used in different papers to identify a single property, an arbitrary selection was made. Unfortunately, one symbol may represent more than one property. However, this should not present any real problem since symbol identification is covered in the List of Symbols at the end of the text.

It is hoped that the methods of presenting and correlating data used in this compilation have not distorted any of the experimental data. As it is quite human to initiate and propagate typographical errors, as well as to incorporate some errors stemming from ignorance in compilations of this type, it will be appreciated if these errors are called to the attention of the compiler.

## MOLECULAR PROPERTIES

### STRUCTURE

The molecular structure of the  $\text{UF}_6$  molecule has been investigated in the solid state by x-ray crystallography, in the liquid state by Raman spectroscopy, and in the vapor state by infrared spectroscopy, by electron diffraction, and by dipole moment techniques. These data are consistent.

Hoard and Stroupe<sup>80, 81, 89</sup> used x-ray diffraction techniques to determine the parameters of crystalline  $\text{UF}_6$  and to reach a somewhat more definite conclusion regarding the configuration of the  $\text{UF}_6$  molecule. It was found by x-ray analyses that cylindrical single crystals of  $\text{UF}_6$  possess an orthorhombic unit structure with the lattice constants  $a = 9.900 \text{ \AA}$ ,  $b = 8.962 \text{ \AA}$ , and  $c = 5.207 \text{ \AA}$ , each with an estimated probable error of  $0.002 \text{ \AA}$ . The orthorhombic unit structure has the space grouping  $D_{2h}^{16}$  Pnma and contains four molecules of  $\text{UF}_6$ . The uranium atoms were found to occupy the 4c positions in the mirror planes of  $D_{2h}^{16}$  with the parameters  $X = 0.1295 \pm 0.0005$  and  $Z = 0.081 \pm 0.001$ .

Hoard and Stroupe also conducted modified Fourier analyses of the  $(hk0)$  and  $(h0l)$  data and described the geometrical positions of the fluorine atoms. They state that the x-ray data do not indicate a completely regular octahedral configuration for the molecule as it exists within the crystal; however, it is quite likely that conditions are modified upon vaporization of the material. None of the U-F bands were found to be larger than  $2.0 \text{ \AA}$  in the case of the crystal, and the authors felt that the slight distortion in the crystal is compatible with a regular configuration for the molecule in the vapor state.

In an effort to resolve the apparent discrepancy which existed at that time between the structure proposed for  $\text{UF}_6$  as deduced from x-ray analysis of single crystals and that deduced from electron diffraction analysis of the vapor, Bauer and Palter<sup>16, 17</sup> investigated x-ray powder photographs of crystalline  $\text{UF}_6$ . Although the discrepancy was not eliminated, a rather extensive powder diffraction pattern for  $\text{UF}_6$  was reported. The pattern was obtained by using nickel-filtered copper  $K\alpha$  radiation with a camera having a radius of  $57.25 \pm 0.010 \text{ cm}$ . The diffraction pattern, consisting of 91 lines, is presented in Table 1.

The structures of the  $\text{UF}_6$  molecule in the liquid and in the vapor states were determined by an investigation of the Raman spectrum of the liquid and by several individual investigations of the infrared spectrum of the vapor. These investigations yielded data which are completely in accord with each other and which can best be accounted for by assuming regular octahedral symmetry. In addition to these data, an inferred zero dipole moment obtained from dielectric constant measurements (see Dipole Moment, page 16) gives strong evidence in support of the  $O_h$  point group symmetry in which all U-F bond distances are the same.

Bigeleisen, Mayer, Stevenson, and Turkevich<sup>20</sup> were able to interpret the observed vibration spectrum of  $\text{UF}_6$  vapor on the basis of a totally symmetrical structure. Although the fundamental assignments were slightly different, the interpretation of the infrared spectrum made by Bigeleisen and his co-workers was verified by Burke, Smith, and Nielsen<sup>29</sup>; by Gaunt<sup>65</sup>; and finally by Hawkins, Mattraw and Carpenter<sup>74</sup>. Values of the fundamentals deduced from the infrared spectra compare favorably with those obtained from the Raman spectra<sup>20, 35</sup>.

Table 1  
DIFFRACTION PATTERN OF THE CRYSTALLINE POWDER

Line Number	<u><math>\frac{\sin \Theta^*}{\lambda}</math></u>	<u>d (Å)</u>	<u><math>I/I_1</math></u>	Line Number	<u><math>\frac{\sin \Theta^*}{\lambda}</math></u>	<u>d (Å)</u>	<u><math>I/I_1</math></u>
1	.1109	4.510	113	47	.3924	1.274	9
2	.1138	4.394	75	48	.4021	1.243	15
3	.1172	4.266	116	49	.4047	1.235	18
4	.1244	4.019	118	50	.4138	1.208	9
5	.1422	3.516	22	51	.4186	1.195	13
6	.1577	3.171	48	52	.4235	1.182	8
7	.1807	2.767	36	53	.4298	1.164	8
8	.1870	2.674	33	54	.4341	1.152	7
9	.1943	2.573	37	55	.4478	1.117	11
10	.1976	2.530	3	56	.4507	1.109	7
11	.2011	2.486	22	57	.4552	1.098	5
12	.2051	2.438	3	58	.4620	1.082	16
13	.2082	2.402	34	59	.4700	1.064	6
14	.2126	2.352	24	60	.4743	1.054	7
15	.2195	2.278	13	61	.4785	1.045	3
16	.2258	2.214	36	62	.4865	1.028	5
17	.2297	2.177	32	63	.4910	1.018	5
18	.2332	2.144	38	64	.5007	0.999	3
19	.2474	2.021	39	65	.5046	0.991	3
20	.2497	2.002	7	66	.5130	0.975	3
21	.2532	1.975	22	67	.5180	0.965	3
22	.2618	1.910	10	68	.5247	0.953	9
23	.2659	1.880	5	69	.5271	0.949	5
24	.2705	1.848	15	70	.5321	0.940	7
25	.2764	1.809	19	71	.5363	0.932	5
26	.2808	1.781	13	72	.5416	0.923	7
27	.2880	1.736	13	73	.5485	0.912	7
28	.2953	1.693	44	74	.5516	0.906	3
29	.2983	1.676	21	75	.5593	0.894	3
30	.3016	1.658	33	76	.5685	0.880	14
31	.3072	1.628	26	77	.5767	0.867	12
32	.3103	1.611	3	78	.5795	0.863	5
33	.3193	1.566	23	79	.5881	0.850	19
34	.3232	1.548	7	80	.5911	0.846	17
35	.3270	1.529	29	81	.5940	0.835	3
36	.3348	1.493	33	82	.6068	0.824	3
37	.3384	1.478	17	83	.6089	0.821	5
38	.3438	1.451	11	84	.6104	0.819	16
39	.3481	1.436	19	85	.6136	0.815	5
40	.3537	1.415	10	86	.6185	0.808	5
41	.3582	1.396	22	87	.6212	0.805	14
42	.3638	1.374	8	88	.6303	0.793	3
43	.3726	1.342	7	89	.6317	0.792	11
44	.3800	1.317	16	90	.6358	0.786	11
45	.3846	1.301	6	91	.6421	0.776	3
46	.3891	1.286	19				

\*A discrepancy exists in the column headings in two similar reports by Bauer, References 16 and 17. In the first the heading is  $\frac{\sin \Theta^*}{\lambda}$ ; in the second  $\frac{\sin \Theta^*}{2}$ . Experimental data obtained in our laboratory indicates  $\frac{\sin \Theta^*}{\lambda}$  is correct.

Glauber and Schomaker<sup>68</sup> eliminated an apparent discrepancy between the interpretation of the structure which was based on vibrational data and that which was based on electron diffraction data by an improvement in the theory of electron diffraction. Bauer<sup>18</sup>, on the basis of available electron diffraction theory, proposed an irregular octahedral structure for  $\text{UF}_6$  with three short (1.87 Å) and three long (2.17 Å) bonds. Upon improving the Born approximation as customarily applied to electron diffraction experiments, Glauber and Schomaker were able to show that  $\text{UF}_6$  need not be considered as having a distorted structure. Recent electron diffraction studies by Weinstock and Malm<sup>143</sup> also provide strong evidence for the octahedral nature of the  $\text{UF}_6$  vapor molecule.

### FORCE CONSTANTS

Force constants have been calculated from the fundamental vibration frequencies which were proposed on the basis of the regular octahedral symmetry ( $\text{O}_h$  point group). Values of the calculated force constants are presented in Table 2.

Gaunt<sup>66</sup> estimated the stretching force constant ( $k_1 = 2.47 \times 10^5$  dynes/cm.) and bond length of the uranium atom to the fluorine atom (2.04 Å) by using the frequency formulae\* which were derived by Heath and Linnett. The approximate value of  $k_1$  is not in agreement with other calculated values. A preliminary value of the U-F bond distance (1.994 Å) was obtained from electron diffraction measurements by Schomaker, Kimura, and Weinstock†.

Pistorius<sup>121</sup> calculated the force constants by using Wilson's F-G matrix method, the infrared data which were obtained by Gaunt<sup>65</sup> and by Hawkins and his co-workers<sup>74</sup>, and the Raman data which were obtained by Claassen and his co-workers<sup>35</sup>. From the vibration data, the following fundamentals were obtained by averaging:  $\nu_1 = 666.5 \text{ cm.}^{-1}$ ,  $\nu_2 = 534 \text{ cm.}^{-1}$ ,  $\nu_3 = 624.5 \text{ cm.}^{-1}$ ,  $\nu_4 = 187.5 \text{ cm.}^{-1}$ ,  $\nu_5 = 202 \text{ cm.}^{-1}$  and  $\nu_6 = 140 \text{ cm.}^{-1}$ . Values of the force constants, shown in Table 2, were calculated on the basis of these fundamentals and found to compare favorably with values calculated by Claassen.

Claassen<sup>36</sup> derived a general quadratic potential function for  $\text{UF}_6$ -type molecules which relates the force constants to the fundamental frequencies. He determined values of the fundamentals  $\nu_1 = 667 \text{ cm.}^{-1}$ ,  $\nu_2 = 535 \text{ cm.}^{-1}$ ,  $\nu_3 = 623 \text{ cm.}^{-1}$ ,  $\nu_4 = 181 \text{ cm.}^{-1}$ ,  $\nu_5 = 202 \text{ cm.}^{-1}$  and  $\nu_6 = 140 \text{ cm.}^{-1}$  from the existing infrared and Raman data and calculated the force constants which are listed in Table 2. Values of the force constants, as well as the formulae derived by Claassen, agree with the data proposed by Linnett and Simpson<sup>103</sup>.

Linnett and Simpson proposed limited ranges for the possible values of the force constants by making various assumptions, whereas both Pistorius and Claassen attempted to set definite values to the constants on the basis of a regularity that appears in the series of molecules they studied. The conditions and the limited range of the values for the various force constants are listed in Table 2.

Califano<sup>32</sup> used a quadratic potential made up of four-interaction constants to calculate the force constants for  $\text{UF}_6$ . The force constants listed in Table 2 were calculated using the following values for the fundamental vibrational frequencies:  $\nu_1 = 665 \text{ cm.}^{-1}$ ,  $\nu_2 = 536 \text{ cm.}^{-1}$ ,  $\nu_3 = 623 \text{ cm.}^{-1}$ ,  $\nu_4 = 186 \text{ cm.}^{-1}$ ,  $\nu_5 = 202 \text{ cm.}^{-1}$ , and  $\nu_6 = 136 \text{ cm.}^{-1}$ .

\*Claassen and his co-workers<sup>35</sup> reported that Gaunt erred in applying the equations of Heath and Linnett to the data on  $\text{UF}_6$ . The values of the calculated frequencies,  $\nu_3 = 626 \text{ cm.}^{-1}$  and  $\nu_4 = 190 \text{ cm.}^{-1}$ , should have been  $606 \text{ cm.}^{-1}$  and  $265 \text{ cm.}^{-1}$ , respectively.

†Unpublished work; see Ref. 143.

Table 2  
FORCE CONSTANTS IN  $10^5$  DYNES/CM.

Force Constants <sup>t</sup>	Linnett et al.* (Ref. 103)	Claassen (Ref. 36)	Pistorius (Ref. 121)	Califano (Ref. 32)
$k_1$	2.07 to 3.85 <sup>a</sup> 2.07 to 3.78 <sup>b</sup> 2.07 to 3.78 <sup>c</sup> 3.78 <sup>d</sup> or 3.68 to 3.78 <sup>d</sup>	3.78 3.80 <sup>†</sup>	3.78	3.795
$k_{11}$	0.30 <sup>a, b, c, d</sup>	0.296 0.296 <sup>†</sup>	0.296	0.289
$k'_{11}$	- 0.07 to 1.71 <sup>a</sup> 0.00 to 1.71 <sup>b, c</sup> 0.00 <sup>d</sup> or 0.00 to 0.10 <sup>d</sup>	0.00 <sup>†</sup>		
$k_a$				0.129
$k_{1a}$				0.058
$k_{aa}$				0.013
$k'_{aa}$				0.007
$\frac{k_{1a} - k'_{1a}}{r}$	- 0.46 to 0.72 <sup>a, b</sup> 0.00 to 0.72 <sup>c</sup> 0.00 to 0.01 <sup>d</sup> or 0.45 to 0.55 <sup>d</sup>	0.03 <sup>†</sup>	0.426 0.032	
$\frac{k_a - k_{aa}}{r^2}$	0.13 to 0.52 <sup>a</sup> 0.13 to 0.52 <sup>b</sup> 0.13 <sup>c</sup> or 0.18 to 0.52 <sup>c</sup> 0.13 <sup>d</sup> or 0.18 to 0.21 <sup>d</sup>	0.120 <sup>†</sup> 0.125 <sup>†</sup>		0.116 <sup>‡</sup>
$\frac{k_{aa} - k''_{aa}}{r^2}$	0.01 to 0.40 <sup>a</sup> 0.01 <sup>b</sup> or 0.06 to 0.40 <sup>c</sup> 0.01 <sup>d</sup> or 0.06 to 0.10 <sup>d</sup>	0.011 <sup>†</sup>	-0.119 -0.045	
$\frac{k'_{aa} - k''_{aa}}{r^2}$	0.01 to 0.40 <sup>a, b</sup> 0.01 <sup>c</sup> or 0.06 to 0.40 <sup>c</sup> 0.01 <sup>d</sup> or 0.06 to 0.10 <sup>d</sup>	0.009 <sup>†</sup> 0.010 <sup>†</sup>	0.096 0.022	
$k_a - k''_{aa}$			0.227	
$k_a + k'''_{aa} - 2 k_{aa}$		0.114	0.132	
$k_a - k'''_{aa} - 2 k'_{aa} + 2 k''_{aa}$		0.110		

\*Assumptions: (a)  $k'_{11}$  positive (b)  $\frac{k_{1a} - k'_{1a}}{r}$  (c)  $k_{aa} - k''_{aa}$  (d)  $k'_{11} < k_{11}$ .

<sup>†</sup>Given by Linnett and Simpson (Ref. 103).

<sup>‡</sup>Calculated on basis of values given.

$\xi_{k_1}$  bond stretching

$k_{11}$  bond-bond (adjacent) (e.g. between  $UF_x$  and  $UF_y$ )

$k'_{11}$  bond-bond (opposite) (e.g. between  $UF_x$  and  $UF_{-x}$ )

$k_a$  angle bending

$k_{1a}$  bond-angle (adjacent) (e.g. between  $UF_x$  and  $F_xUF_y$ )

$k'_{1a}$  bond-angle (opposite) (e.g. between  $UF_x$  and  $F_{-x}UF_y$ )

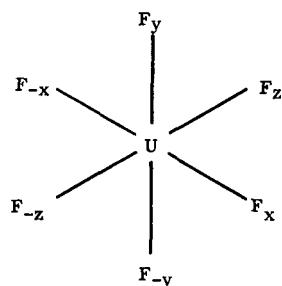
$k_{aa}$  angle-angle (planar-adjacent) (e.g. between  $F_xUF_y$  and  $F_{-x}UF_z$ )

$k''_{aa}$  angle-angle (angled-adjacent) (e.g. between  $F_xUF_y$  and  $F_xUF_z$ )

$k'''_{aa}$  angle-angle (angled-opposite) (e.g. between  $F_xUF_y$  and  $F_{-x}UF_z$ )

$k_{aq}$  angle-angle (planar-opposite) (e.g. between  $F_xUF_y$  and  $F_{-x}UF_{-y}$ )

$k_{1c}$  angle-bond (perpendicular) (e.g. between  $F_xUF_z$  and  $F_{-y}$ )



## CRITICAL IONIZATION POTENTIALS

Cameron and White<sup>146</sup> determined the critical ionization potentials of  $\text{UF}_6$  with a Nier-type mass spectrometer in which the emission regulator unit had been modified to permit variation of electron energy without disturbance to total emission from the filament. The data, which are listed in Table 3, have a probable error range of from 5 percent for the  $\text{UF}_5^+$  ion to 15 percent for the  $\text{U}^+$  ion.

Table 3  
CRITICAL IONIZATION POTENTIALS

<u>Ion</u>	Critical Ionization Potential (volts)
$\text{UF}_5^+$	15.5
$\text{UF}_4^+$	20.1
$\text{UF}_3^+$	23.5
$\text{UF}_2^+$	29.9
$\text{UF}^+$	37.9
$\text{U}^+$	50.3

## MAGNETIC SUSCEPTIBILITY

No recent data on the measurements of the magnetic susceptibility have been reported. The information appearing in previous compilations<sup>88, 93</sup> is all that has been found in literature.

It has been reported that  $\text{UF}_6$  appears to be paramagnetic. Henkel and Klemm<sup>77</sup> reported that the specific susceptibility of solid  $\text{UF}_6$  is  $0.12 \times 10^{-6}$  and that the molar susceptibility is  $43 \times 10^{-6}$ . Correcting the molar susceptibility for diamagnetism, Tilk<sup>139</sup> obtained a value of  $106 \times 10^{-6}$ . The paramagnetism seems to be independent of the temperature.

## SURFACE TENSION

The surface tension of liquid  $\text{UF}_6$  in contact with its vapor was measured in the 70° to 100°C. range<sup>107</sup> and at 65° and 72.5°C.<sup>125</sup> by the capillary rise method. The latter results are reported with an estimated accuracy of  $\pm 0.3$  dynes/cm. (between 1.8 and 2.3 percent of the results reported) while the former are reported as accurate to  $\pm 3$  percent of the reported surface tension. The results, which are in agreement with each other, are summarized in Table 4 and presented in Figure 1.

## POLARIZATION

The dielectric constant,  $\epsilon$ , of the vapor has been determined at various temperatures by both the heterodyne beat method and the resonance method. A comparison of the various

Table 4  
SURFACE TENSION OF THE LIQUID

Temperature (°C.)	Surface Tension (dynes/cm.)	Reference
65	17.66 ± 0.5	125
70	16.8 ± 0.3	107
72.5	16.48 ± 0.5	125
80	15.6 ± 0.3	107
90	14.3 ± 0.3	107
100	13.1 ± 0.3	107

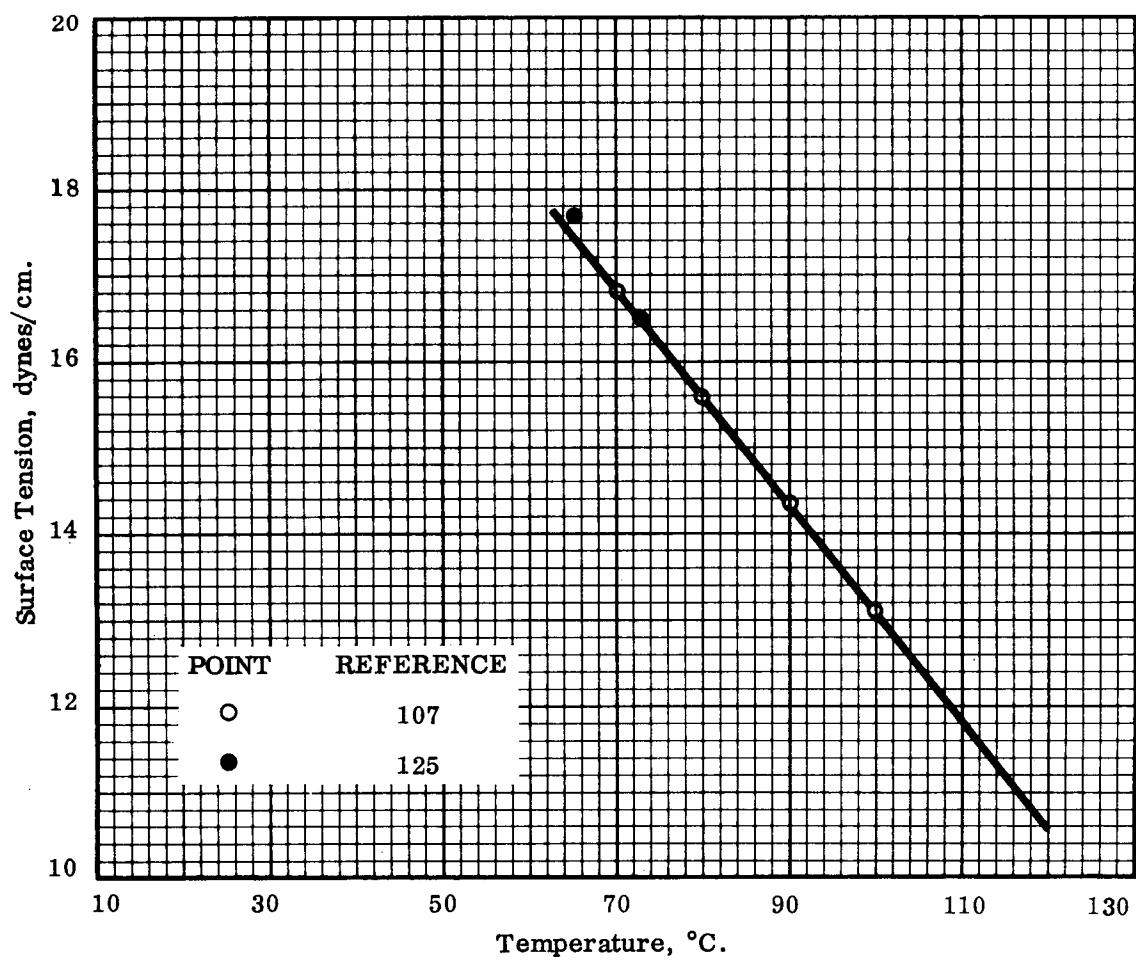


FIG. 1. SURFACE TENSION OF THE LIQUID

experimental values of the dielectric constant of the vapor is presented in Table 5; some of the more reliable data  $[(\epsilon - 1) \times 10^6]$  are plotted versus temperature in Figure 2. Molar polarization,  $P_m$ , and the dipole moment,  $\mu$ , have been determined from experimental values of the dielectric constant of the vapor using the Debye equation:

$$P_m = \frac{\epsilon - 1}{\epsilon + 2} \times M/\rho = \frac{4\pi N}{3} (\alpha + \mu^2/3kT) \quad (1)$$

where:  $M$  = the molecular weight

$\rho$  = the vapor density

$N$  = the Avogadro number

$\alpha$  = the molecular polarizability

$k$  = the Boltzmann constant

Table 5

DIELECTRIC CONSTANT AND MOLAR POLARIZATION OF THE VAPOR

Temperature (°C.)	Dielectric Constant, $(\epsilon - 1) \times 10^6$		Polarization (cc.)	Reference
	Observed	Calculated*		
19.6	3800 $\pm$ 400		30.7 $\pm$ 1.0	9
28.2	3815.4 $\pm$ 5.7	(3816)	31.448 $\pm$ 0.047	108, 109, 110
40.0	3676.5 $\pm$ 3.8	(3672)	31.490 $\pm$ 0.033	108, 109, 110
50.0		(3558)		
59.5	2970		27.0 $\pm$ 0.2	137
60.0		(3452)		
61.1	3441.5 $\pm$ 4.5	(3440)	31.463 $\pm$ 0.041	108, 109, 110
67.4	2920		27.2 $\pm$ 0.3	137
70.0		(3351)		
80.0		(3256)		
83.1	3229.5 $\pm$ 3.7	(3228)	31.468 $\pm$ 0.036	108, 109, 110
	3221.9 $\pm$ 4.1		31.394 $\pm$ 0.040	108, 109, 110
89.0	2730		27.0 $\pm$ 0.2	137
90.0		(3166)		
100.0		(3082)		
110.0		(3001)		
120.0		(2925)		
130.0		(2888)		
140.0		(2783)		
150.0		(2718)		

\*On the basis of  $(\epsilon - 1) \times 10^6$   $T/T_0 = 4209.8$  (Ref. 108, 109).

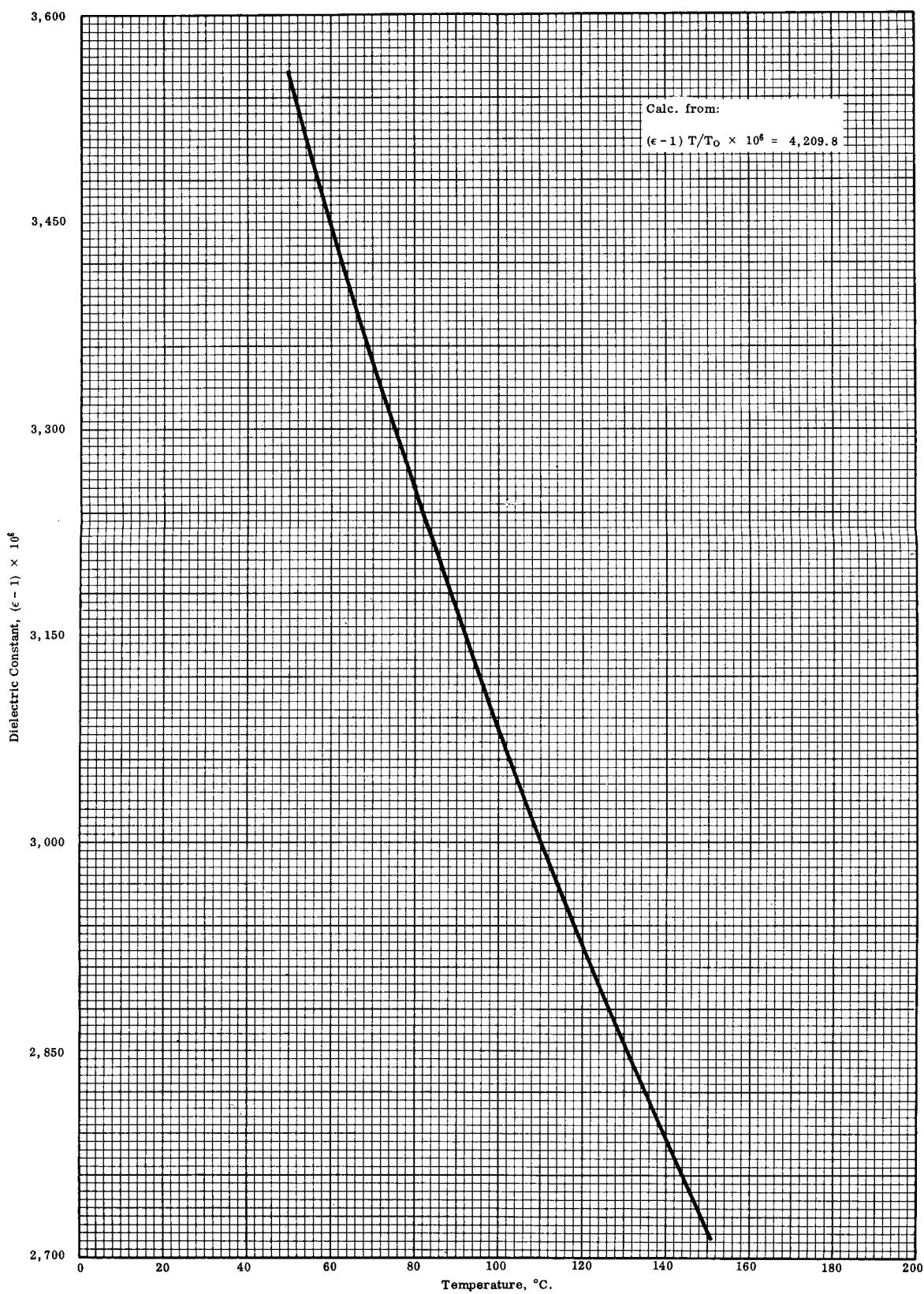


FIG. 2. DIELECTRIC CONSTANT OF THE VAPOR

From the calculated value of  $P_m$ , values of the dielectric constant of the liquid were determined. A comparison with the experimental value, which is not very good, is presented in Table 6. The calculated dielectric constant values are plotted in Figure 3.

Table 6  
DIELECTRIC CONSTANT OF THE LIQUID

Temperature (°C.)	Dielectric Constant	
	Observed (Ref. 30)	Calculated*
65		2.41
70	2.57	2.39
90		2.32
120		2.21
140		2.13
160		2.05

\*Using Clausius-Mosotti equation, molar polarization value 31.034 cc., and Wechsler and Hoge (Ref. 140, 141) liquid density values.

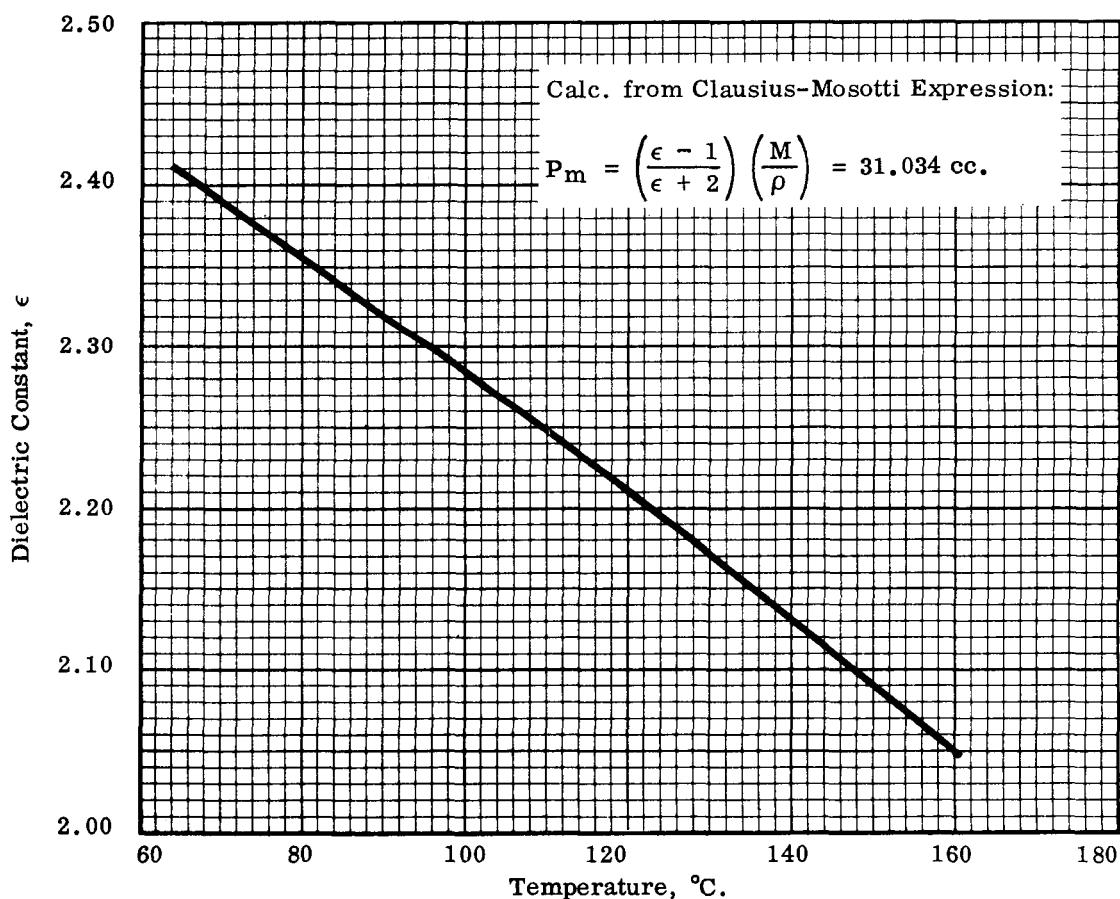


FIG. 3. DIELECTRIC CONSTANT OF THE LIQUID

### DIPOLE MOMENT

From Equation 1 it is obvious that if the molar polarization does not vary with temperature, the dipole moment must be considered zero. Smyth and Hannay<sup>137</sup> and later Magnuson<sup>110</sup> failed to find any detectable variation of the polarization of  $\text{UF}_6$  with temperature. They reported that the dipole moment of  $\text{UF}_6$  is essentially zero (less than  $10^{-18}$  esu., cm.) and therefore the  $\text{UF}_6$  molecule could be a regular octahedron. The polarization values were calculated from dielectric constant measurements on the vapor taken at various temperatures and pressures.

### DIELECTRIC CONSTANT AND MOLAR POLARIZATION OF THE VAPOR

The most recent and comprehensive dielectric constant data are those of Magnuson<sup>110</sup>. Dielectric constants were obtained from a ratio of the measured resonant frequency of an evacuated cavity to that of the cavity when filled with  $\text{UF}_6$  vapor. The Debye equation was then used to determine the molar polarization,  $P_m$ , and the dipole moment,  $\mu$ . Since the variation of vapor density with pressure,  $P$ , was not well known, a non-ideality parameter (see Non-ideality of  $\text{UF}_6$  Vapor, page 98) as well as the above-mentioned properties were calculated from a series of dielectric measurements taken at a constant temperature and at different pressures. The quantity  $[(\epsilon - 1)/(\epsilon + 2)][1/P]$  was plotted against  $P$  and a straight line was fitted to the experimental data. The slope of the straight line defined the non-ideality parameter,  $A$ , and the intercept defined the molar polarization,  $P_m$ . All pressure measurements were corrected to the density of mercury at 0°C. and the limit of error of the results is stated as being at the 95 percent confidence interval. Magnuson reported the results as follows:

$$(\epsilon - 1) = 4202.8 \times 10^{-6} \text{ per atm. at } 61.1^\circ\text{C.} \quad (2)$$

$$P_m(\text{av.}) = 31.034 \text{ cc.}$$

(averaged over the range 53° to 153°C.)

Other dielectric constant investigations<sup>108, 109</sup> which were previously conducted by Magnuson at lower pressures (< 40 cm. Hg) did not reveal the effects of non-ideality because of the low pressure. He measured the dielectric constants at five temperatures and made corrections to standard conditions by means of the general gas laws. He averaged the results and reported them as follows:

$$[(\epsilon - 1) T/T_0] \times 10^6 = 4209.8 \pm 3.4 \text{ (corrected to standard conditions)} \quad (3)$$

$$P_m = 31.453 \pm 0.025 \text{ cc.}$$

The slight discrepancy between these results and those previously given by Magnuson can be attributed to the different calculating procedures he used in each case. Magnuson's later results are listed in Table 5 along with earlier data obtained by other investigators. Values of  $(\epsilon - 1) \times 10^6$  were calculated from Equation 3 and are shown plotted against temperature in Figure 2.

Some of the earlier dielectric constant measurements made by other investigators do not compare favorably with those of Magnuson. Amphlett, Mullinger and Thomas<sup>9</sup> measured the dielectric constant by the heterodyne beat method and reported a value of  $\epsilon = 1.0038 \pm 0.0001$  at 19.6°C. and 760 mm. Hg. They determined the total polarization from the Clausius-Mosotti relationship:

$$P_m = [(\epsilon - 1)/(\epsilon + 2)] \times M/\rho = [(\epsilon - 1)/3] \times (RT/P) = 30.7 \pm 1.0 \text{ cc.} \quad (4)$$

The value of  $\epsilon$  thus obtained is slightly higher than that obtained by Magnuson. Smyth and Hannay<sup>89, 137</sup> measured the dielectric constant with an apparatus similar to that used by McAlpine and Smyth\*. Five measurements of the dielectric constant of  $\text{UF}_6$  made at each of three temperatures, 59.5°, 67.4° and 89.0°C., were used to calculate the molar polarization. Smyth and Hannay's results, also listed in Table 5, are lower than those of Amphlett and his co-workers as well as those of Magnuson<sup>110</sup>.

#### DIELECTRIC CONSTANT OF THE LIQUID

The dielectric constant of the liquid has not been very thoroughly investigated. The only study found in the literature was that reported by Burns, McKown, and Asbury<sup>30</sup>. From resistance measurements at 70°C., they found that the coefficient of electrical resistance was of the order of  $10^{14}$  ohms and that the dielectric constant was 2.57 at 500, 1000 and 2000 cycles per second. Their molar polarization value (33.6 cc.) calculated from the dielectric constant does not appear to be in agreement with that (31.034 cc.) obtained from the dielectric constant measurements on the vapor by Magnuson.

The dielectric constant of a non-polar liquid such as  $\text{UF}_6$  can also be obtained from the Clausius-Mosotti equation (Equation 4) if the molar polarization and the liquid density at a given temperature are known. Smyth and Hannay<sup>89, 137</sup> made such a calculation using their average molar polarization value of 27.1 cc. and found the dielectric constant of the liquid at 65°C. to be 2.18. They considered this value typical for non-polar liquids.

Using the average molar polarization value (31.034 cc.) obtained by Magnuson and the liquid density values obtained by Hoge and Wechsler<sup>140, 141</sup> approximate dielectric constants of the liquid for various temperatures were calculated for this report. These are presented in Table 6 and Figure 3.

#### DENSITY

The density values of solid  $\text{UF}_6$  which have been determined by various methods appear to vary linearly with temperature in the 20° to 62.5°C. range. These values, which are given in Table 7 and Figure 4, indicate a rather high coefficient of expansion for the

Table 7  
DENSITY OF THE SOLID

Temperature (°C.)	Density (g./cc.)	Remarks	Reference
20.7	$5.09 \pm 0.06$	From British tube alloy data sheets	46
$24 \pm 1$	(4.95)	Preliminary value calculated from lattice constants	80
25	$5.06 \pm 0.005$	Final value calculated from lattice constants	81
62.5	(4.93)	Preliminary value calculated from ratio of liquid volume to solid volume	140
62.5	4.87	Final value calculated from ratio of liquid volume to solid volume	141

\*McAlpine, K. B. and Smyth, C. T. J. Am. Chem. Soc. 55, 453 (1933).

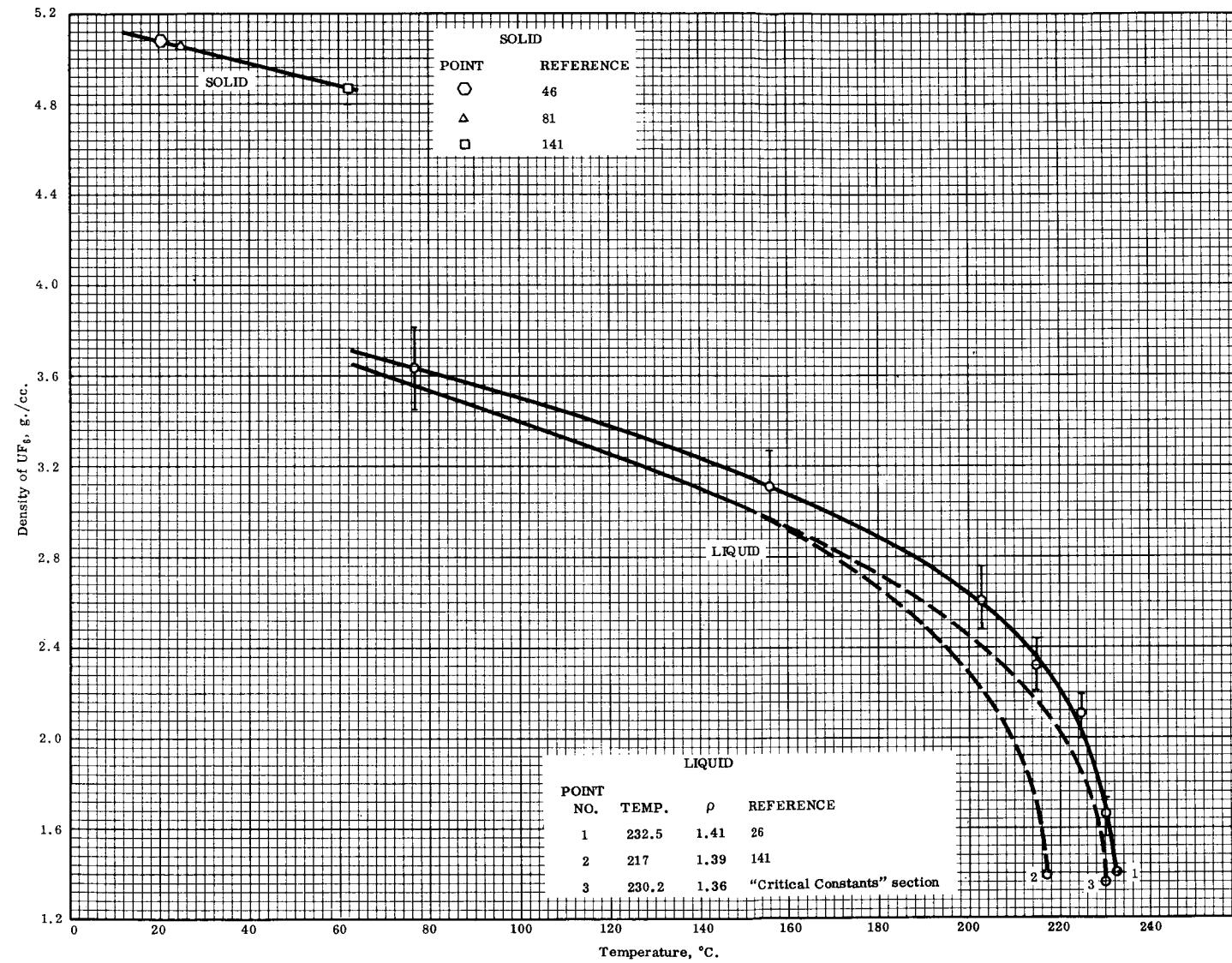


FIG. 4. DENSITIES OF THE SOLID AND THE LIQUID

solid. Reliable density values of the liquid have been determined in the 65° to 163°C. range and are presented in Table 8 and in Figure 4.

Reasonably accurate vapor density values can be calculated either from the equation of state proposed by Magnuson or the one proposed by Weinstock (see Equations of State, page 97). The data presented in Tables 9 and 10 and Figures 5 and 6 can be used in comparing the density values of the vapor calculated from both equations of state with those values derived from the ideal gas law.

### SOLID DENSITY

British data sheets<sup>48</sup> give a solid density value of  $5.09 \pm 0.06$  g./cc. at 20.7°C. Hoard and Stroupe<sup>80</sup> estimated a value of 4.95 g./cc. at 24°C. from approximate lattice constants of the orthorhombic unit structure of the  $\text{UF}_6$  molecule. From more accurately determined constants<sup>81</sup>, they recalculated the density at 25°C. and found it to be  $5.06 \pm 0.005$  g./cc.

Wechsler and Hoge<sup>140</sup> reported a preliminary density value of 4.93 g./cc. at 62.5°C. This value was based on their observation of the ratio of the liquid volume at 65.1°C. to the solid volume at 62.5°C. and upon Priest's value<sup>123</sup> (3.667 g./cc.) for the density of the liquid. The ratio of the liquid volume to the solid volume at the previously mentioned temperatures was reported as  $1.343 \pm 0.002$ . The authors<sup>141</sup> later redetermined the value for the density of the liquid at 65.1°C. and reported it as 3.624 g./cc. Using this value for the density of the liquid, they recalculated the density of the solid and found it to be 4.87 g./cc. at 62.5°C.

It is interesting to note that the final values of the density at 20.7°, 25°, and 62.5°C., which were obtained in three independent investigations, form a straight line, vaguely indicating that these data are in agreement and that  $\text{UF}_6$  solid has a rather high coefficient of expansion (see Figure 4).

### LIQUID DENSITY

The density of liquid  $\text{UF}_6$  has been determined by a number of different investigators, and the reported values are in fair agreement. Hoge and Wechsler<sup>141</sup> determined the absolute densities of the saturated liquid in the 65° to 162°C. range. Measurements were made by immersing glass bobbins of known density into liquid  $\text{UF}_6$ . The bobbin densities were corrected for thermal expansion. The temperature was recorded just when a bobbin would start to sink and just when it would start to rise. The average of the two temperatures represents the point at which the density of the liquid and that of the glass bobbins became equal. The results are represented by the equation:

$$\rho(\text{g./cc.}) = 3.630 - 5.805 \times 10^{-3} (t-t_f) - 1.36 \times 10^{-5} (t-t_f)^2 \quad (5)$$

where  $\rho(\text{g./cc.})$  is the density at a stated temperature and where  $t$  values are in degrees centigrade ( $t_f$  is taken as 64.052°C.). Previously Hoge and Wechsler<sup>140</sup> determined liquid densities from measurements of the ratio of the volume of the saturated liquid at temperatures ranging from 64.052° to 92°C. to the volume at the triple point,  $t_f$  (64.052°C.). This ratio was expressed by the equation:

$$V/V_f = 1 + 1.727 \times 10^{-3} (t-t_f) + 3.59 \times 10^{-6} (t-t_f)^2 \quad (6)$$

where the subscripts indicate values at the triple point.

Llewellyn<sup>107</sup> determined the liquid density from 70° to 100°C. by sealing  $\text{UF}_6$  of a known weight in a calibrated tube and measuring the volume at various temperatures. Results are given in Table 8. These values are within 0.5 percent of those given by Hoge and Wechsler also appearing in this table.

Table 8  
DENSITY OF THE LIQUID

Temperature (°C.)	Density (g./cc.)			
	Hoge and Wechsler (Ref. 141)	Llewellyn (Ref. 107)	Priest (Ref. 123)	Abelson et al. (Ref. 1,128)
64. 052			3. 674	
65	3. 624	3. 63†		
65. 1			3. 667 ± 0. 05	
68		3. 620		
68. 66	3. 604*			
70	3. 595	3. 60†		
71. 6		3. 582		
72. 91	3. 576*			
74		3. 581		
75	3. 565			
76		3. 560		
77				3. 63
78. 2		3. 542		
80	3. 532	3. 54†		
81		3. 525		
84		3. 520		
85	3. 502			
87. 8		3. 484		
90	3. 470	3. 48†		
91. 6		3. 455		
92. 65	3. 452*			
93. 8		3. 448		
95	3. 437			
98. 6		3. 427		
98. 9		3. 416		
100	3. 404	3. 41†		
112. 67	3. 316*			
120		3. 263		
131. 12	3. 183*			
140		3. 111		
156				3. 11
160	2. 948			
162. 59	2. 920*			
203				2. 62
215				2. 32
225				2. 09
230				1. 63
232. 5				1. 41
				1. 373

\*Experimental value.

†Value rounded off.

‡See Critical Constant Section, page 89.

Table 9  
COMPARISON OF VAPOR DENSITIES AT 49.2 °C.

Pressure (mm. Hg)	Density (g./cc. $\times 10^3$ )			Experimental (Ref. 9)	
	Equation of State				
	Weinstock	Magnuson	Ideal Gas Law		
523	9.425	9.391	9.1585	9.016	
470	8.445	8.418	8.2306	8.119	
350.0	6.247	6.233	6.1292	-----	
259.3	4.627	4.598	4.5408	4.278	
186.4	3.297	3.294	3.2642	3.130	

Table 10  
VAPOR DENSITY CALCULATED ON THE BASIS OF THE  
PROPOSED EQUATION OF STATE

Temperature (°C.)	Temperature (°K.)	Density, $\rho$ (g./cc.)			Ideal Gas Law
		Weinstock	Magnuson		
50	323.2	0.01384	0.01376	0.01328	
60	333.2	0.01338	0.01335	0.01288	
80	353.2	0.01254	0.01249	0.01215	
100	373.2	0.01180	0.01176	0.01149	
120	393.2	0.01116	0.01113	0.01091	
140	413.2	0.01059	0.01056	0.01038	

Priest<sup>123</sup> determined the liquid density by using a glass apparatus consisting of a calibrated Pyrex tube of uniform bore. The tube, containing accurately weighed  $\text{UF}_6$ , was sealed and immersed in a bath at 65.1°C. The height of the column of liquid was measured with a precision cathetometer. The density was reported as  $3.667 \pm 0.05$  g./cc. Using this value and Equation 6, Brickwedde, Hoge and Scott<sup>24</sup> calculated the density of the liquid (3.674 g./cc.) at the triple point. A comparison of the experimental density values of the saturated liquid with those calculated from Equation 5 as well as the density values reported by Abelson and his co-workers<sup>1</sup> can be made from the data presented in Table 8 and Figure 4. Details of the density investigations of Abelson and his co-workers were not available, and the density values given in this report were obtained from secondary literature sources<sup>1, 26</sup>.

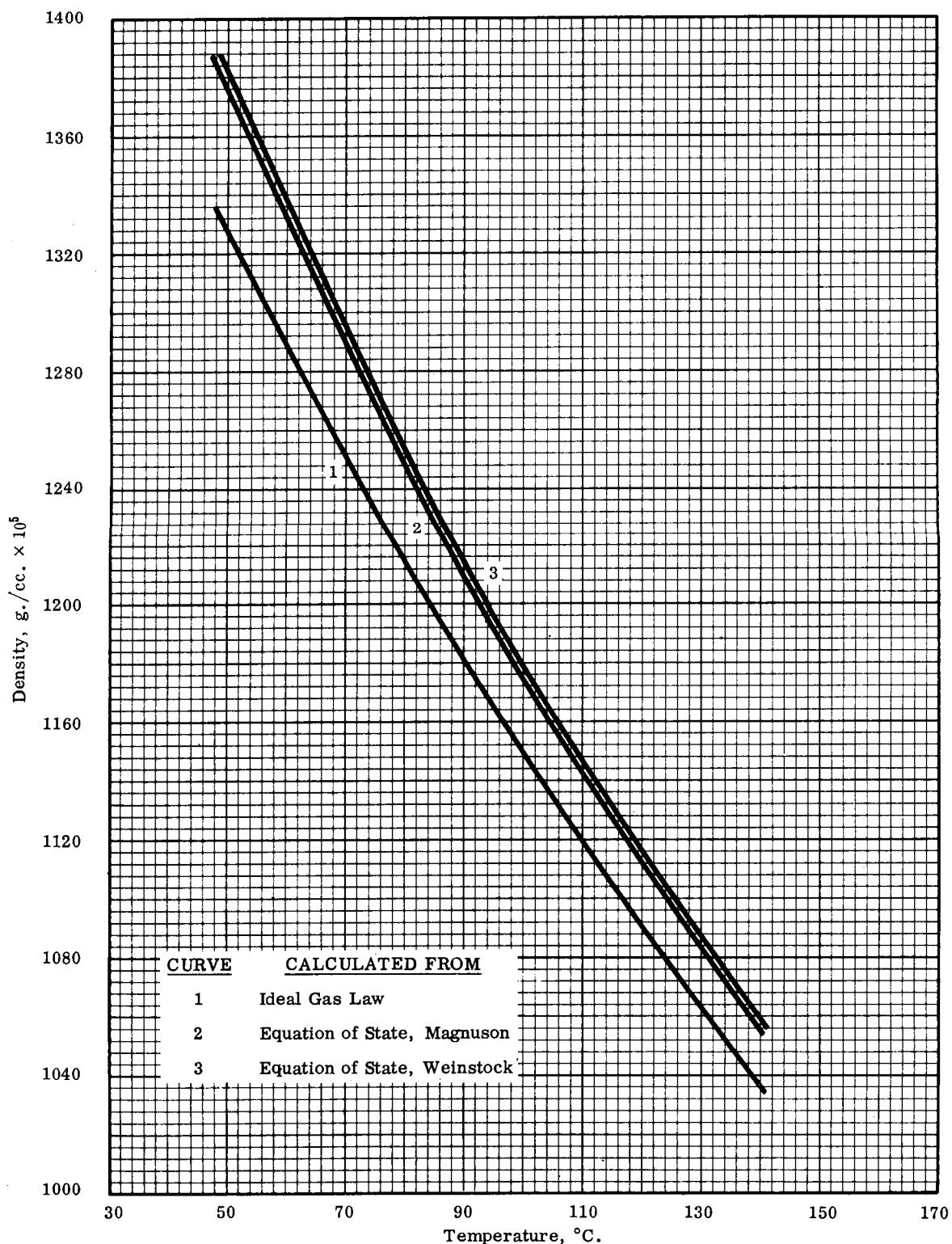


FIG. 5. VAPOR DENSITY CALCULATED AT ATMOSPHERIC PRESSURE

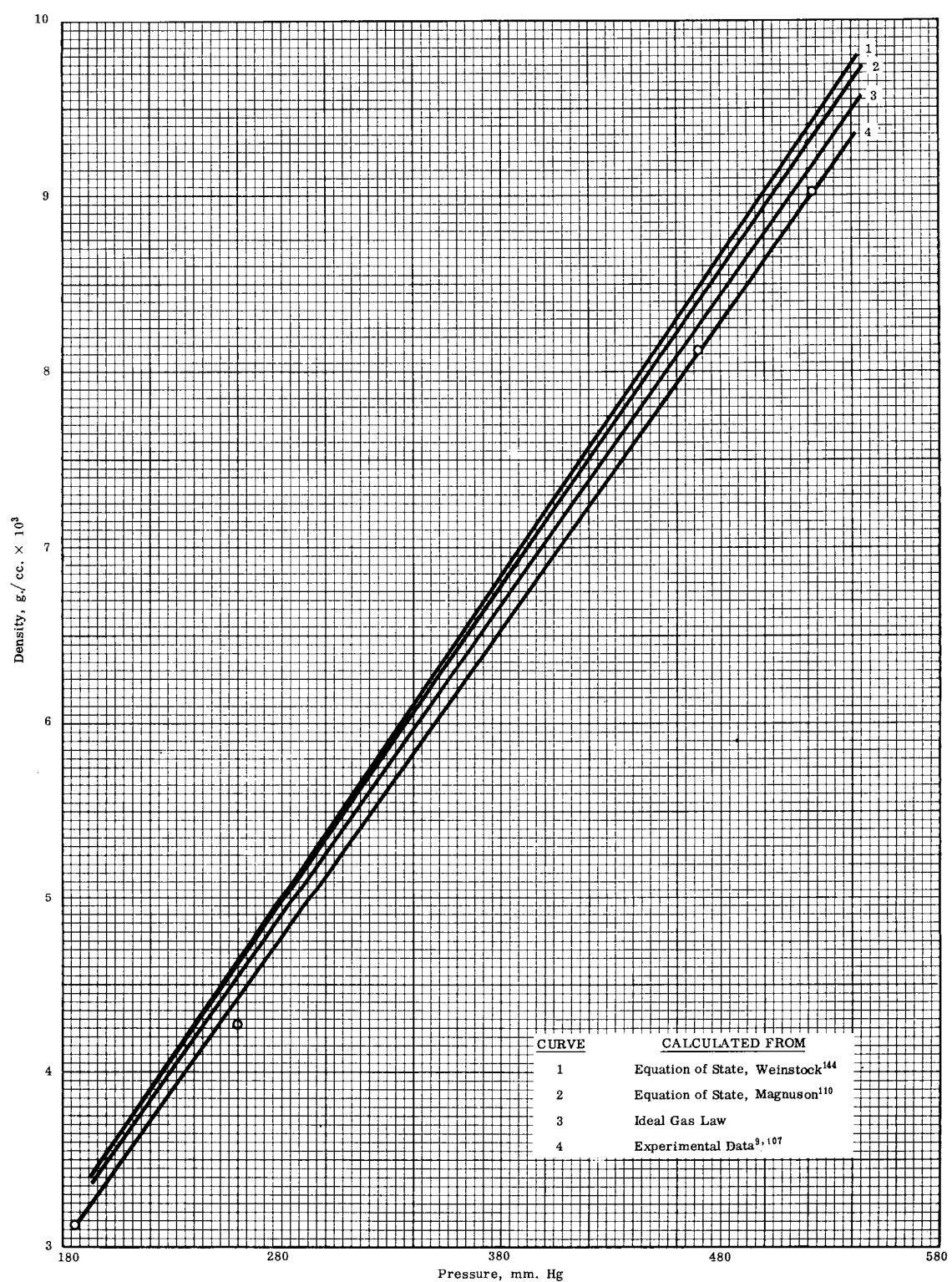


FIG. 6. VAPOR DENSITIES - CALCULATED COMPARED WITH EXPERIMENTAL AT 49.2°C.

### VAPOR DENSITY

Amphlett, Mullinger, and Thomas<sup>9</sup> (see also Llewellyn<sup>107</sup>) reported that at 49.2°C. and at low pressures, UF<sub>6</sub> vapor is essentially ideal, at least within the presumed experimental error (one percent) of their measurements. Therefore the density of vapor should be approximately derived by using the ideal gas law:

$$\rho = MP/RT = 4.291 P/T \text{ g./cc.} \quad (7)$$

where P is in units of atmospheres and T is in degrees Kelvin. However, at pressures slightly higher than those used in the earlier investigations, it was definitely established by accurate pressure-volume-temperature measurements and by studies of the dielectric constant and thermodynamic properties that UF<sub>6</sub> does not behave as an ideal gas. From the dielectric constant studies a non-ideality parameter was proposed by Magnuson<sup>110</sup> which yields the following expression for the density of vapor for the 50° to 140°C. range:

$$\rho = 4.291(P/T) (1 + 1.2328 \times 10^6 P/T^3) \text{ g./cc.} \quad (8)$$

From studies of the thermodynamic properties, Weinstock and his co-workers<sup>144</sup> proposed a non-ideality parameter which yields the following vapor density expression:

$$\rho = \frac{4.291 P}{T[1 + (-1.3769 \times 10^6 P/T^3)]} \text{ g./cc.} \quad (9)$$

Comparison of the values of the vapor densities at one atmosphere calculated on the basis of Equations 7, 8, and 9 are presented in Table 10 and in Figure 5. Comparison of the density values calculated on the basis of Equations 7, 8 and 9 with the experimental values obtained by Amphlett and his co-workers are presented in Table 9 and Figure 6.

## OPTICAL PROPERTIES

### REFRACTIVE INDEX

Both Llewellyn<sup>107</sup> and Simon<sup>135</sup> have reported index of refraction values of liquid UF<sub>6</sub> in the 70° to 100°C. range. These values, which are listed in Table 11, were determined from measurements of the angle of total reflection and are estimated to be accurate within 0.4 percent. Values of the molecular refraction at 85°C. calculated from these index values were determined as 22.59 ± 0.1 at the 4360 Å wave length and as 21.83 ± 0.1 at the 5890 Å wave length. Assuming that the molecular refraction of the vapor is the same as that of the liquid, both authors reported an expression for the refractive index of the vapor:

$$\eta - 1 = 5.2 \times 10^{-4} \frac{P(\text{mm. Hg})}{T(\text{°K.})} \quad (\text{at } 5100 \text{ Å}) \quad (10)$$

Table 11  
REFRACTIVE INDEX OF THE LIQUID

Temperature (°C.)	Refractive Index	
	4360 Å	5890 Å
66.0	1.385	
68.0	1.386	
69.4		1.367
70.0	1.383	1.367
72.2		1.366
72.3	1.382	
73.5		1.367
75.2	1.377	
77.5		1.360
79.2	1.376	
80.0	1.374	
84.0	1.371	
84.7	1.369	
85.2		1.353
87.2		1.354
90.0	1.365	1.342
90.5	1.364	1.350
91.0	1.364	
95.1		1.347
100.0	1.355	1.342

The refractive index of a  $\text{UF}_6\text{-BrF}_5$  mixture has been determined with the hollow prism spectrometer described by Stein and Vogel<sup>138</sup> as a function of composition. The refractive index values obtained at 70°C., using the  $\text{Na}_D$  line, for the entire range of concentration of the  $\text{UF}_6\text{-BrF}_5$  system are listed in Table 12. These are represented by the equation:

$$\eta_D^{70} = 1.3275 + 0.0380N - 0.065N^2 - 0.0010N^3 \quad (11)$$

where  $N$  is the mole fraction of  $\text{UF}_6$  in  $\text{BrF}_5$ .

Table 12

REFRACTIVE INDEXES OF URANIUM HEXAFLUORIDE -  
BROMINE PENTAFLUORIDE MIXTURES AT 70°C.

Mole Fraction $\text{UF}_6$ in $\text{BrF}_5$	Refractive Index
0.0000	1.3275
0.1684	1.3338
0.3153	1.3388
0.4354	1.3428
0.5134	1.3449
0.5965	1.3477
0.7607	1.3522
0.9069	1.3560
1.0000	1.3580

## MOLECULAR SPECTRA

### VIBRATIONAL SPECTRA

The infrared and Raman spectra of  $\text{UF}_6$  have been studied rather intensively by several investigators. The data obtained indicate that the  $\text{UF}_6$  molecule has an  $\text{O}_h$  point group symmetry (regular octahedral symmetry). The  $\text{O}_h$  group possesses six fundamental modes of which only two are active in the infrared\*. Values of the other fundamentals were obtained either from the Raman spectrum, in which three are active, or by deduction from the binary and ternary combinations of the infrared bands. A summary of the various reported values of the fundamentals which have been assigned by the various investigators is given in Table 13. Values assigned by Gaunt<sup>65</sup> compare favorably to those deduced by Hawkins and his co-workers<sup>74</sup>. These values are in agreement with findings in the latest Raman investigations<sup>35</sup>. Summaries of the observed infrared spectrum and the observed Raman spectrum are given in Tables 14 and 15, respectively.

### Infrared Spectrum

The infrared spectrum of  $\text{UF}_6$  vapor has been investigated recently by Hawkins, Mattraw, and Carpenter<sup>74</sup> at temperatures up to 100°C. Originally the spectrum was studied at

\*Herzberg, G. Infrared and Raman Spectra. New York, Van Nostrand Co., Inc., 1945.

Table 13  
FUNDAMENTAL VIBRATION FREQUENCIES

Assignment	Symmetry	Activity	Degeneracy	Frequencies, cm. <sup>-1</sup>			
				Hawkins, et al. (Ref. 74)	Weinstock (Ref. 144)	Gaunt (Ref. 65)	Bigeleisen (Ref. 20)
$\nu_1$	A <sub>1g</sub>	Raman	1	665	667	668	656
$\nu_2$	Eg	Raman	2	536	535	532	511
$\nu_3$	F <sub>1u</sub>	Infrared	3	623	623	626	640
$\nu_4$	F <sub>1u</sub>	Infrared	3	186	181	189	200
$\nu_5$	F <sub>2g</sub>	Raman	3	202	202	202	200
$\nu_6$	F <sub>2u</sub>	Inactive	3	136	140	144	130

room temperature by Bigeleisen, Mayer, Stevenson, and Turkevich<sup>20</sup>. It was reinvestigated by Burke, Smith, and Nielsen<sup>29</sup> and by Gaunt<sup>65</sup>. The findings in the investigations at elevated temperatures are much the same as the findings in investigations at room temperature, except that six new bands were revealed in the former case. Assignments of the fundamental vibrations were made on the assumption that the structure of the UF<sub>6</sub> molecule is that of a regular octahedron.

Hawkins and his co-workers<sup>74</sup> studied the infrared spectrum from 2 to 23 microns with a Baird double-beam model AB2-195 spectrometer which employed sodium chloride and potassium bromide optics. The cell was constructed of copper and contained silver chloride windows which apparently did not change in transmissive properties at 100°C. The recorded spectra were calibrated with polystyrene in the sodium chloride region and with 1, 2, 4-trichlorobenzene in the potassium bromide region. The results obtained by Hawkins and his co-workers are summarized in Table 14. In addition to the six new bands reported in the spectrum made at the elevated temperatures, they found all the bands reported by Burke and his co-workers but did not find the 547 and 587 cm.<sup>-1</sup> bands reported by Gaunt. However, they felt that the band at 587 cm.<sup>-1</sup> was real and believed that Gaunt was able to detect this weak band by using a long path technique. The fundamental vibrations of UF<sub>6</sub> which they assigned on the basis of regular octahedral structure and the observed infrared spectrum are presented in Table 13. These values compare favorably with the values previously proposed by Gaunt<sup>65</sup>.

Gaunt studied the infrared spectrum at room temperature from 2 to 25 microns with a Hilger D 209 single-beam spectrometer which employed lithium fluoride, sodium chloride, and potassium bromide prisms as its optics<sup>65</sup>. The cells, which ranged from 10 to 186 centimeters in length, were fitted with windows of potassium bromide. The results summarized in Table 14 fully confirm the original measurements of Bigeleisen and his co-workers and agree with the reinvestigation by Burke and his co-workers<sup>29</sup>. The interpretation of the spectrum made by Gaunt differs slightly from the interpretation made by Bigeleisen and his co-workers<sup>20</sup>. The assignments of the fundamentals made by Gaunt are shown in Table 13.

Table 14  
INFRARED SPECTRUM OF THE VAPOR

Frequencies (cm. <sup>-1</sup> ) *				Assignments	Symmetry (Ref. 20, 74)	Intensity, Percent Absorption (Ref. 74)	
A (Ref. 74)	B (Ref. 29)	C (Ref. 65)	D (Ref. 20)			Room Temperature	100°C.
1869 (1869)				$3\nu_3$ (A)	$A_2 + 2F_1 + F_2$		3
1808 (1782) or (1824)				$2\nu_3 + \nu_2$ (A) or $\nu_1 + \nu_2 + \nu_3$ (A)	$A_1 + A_2 + 2E + F_1 + F_2$ or $F_1 + F_2$		3
1684 (1695)				$2\nu_2 + \nu_3$ (A)	$2F_1 + F_2$		8
1337 (1337) or (1345)				$\nu_1 + \nu_2 + \nu_6$ (A) or $\nu_2 + \nu_3 + \nu_4$ (A)	$F_1 + F_2$		9
1288	1288 (1296)	1294 (1294)	1295 (1295)	$\nu_1 + \nu_3$ (A, B, C) $\nu_6 + \nu_1$ (D)	$F_1$	52	90-100
1159	1159 (1151)	1158 (1158)	1163 (1151)	$\nu_2 + \nu_3$ (A, B, C) $\nu_6 + \nu_2$ (D)	$F_1 + F_2$	59	90-100
852 (851)	850 (856)	854 (857)	850 (856)	$\nu_1 + \nu_4$ (A, B, C) $\nu_5 + \nu_1$ (D)	$F_1$	12	59
825	825 (840)	825 (828)	825 (840)	$\nu_3 + \nu_5$ (A, B, C) $\nu_6 + \nu_3$ (D)		33	90-100
755 (752)		756 762		$\nu_1 - \nu_2 + \nu_3$ (A, C)	$F_1 + F_2$		14
715 (722)	715 (711)	717 (721)	713-719 (711)	$\nu_2 + \nu_4$ (A, B, C) $\nu_5 + \nu_2$ (D)	$F_1 + F_2$	16	67
672	674 641	676 676	641 675	$\nu_2 + \nu_6$ (A, B, C) $\nu_4 + \nu_2$ (D)	$F_1 + F_2$	73	90-100
623	623	626	623 640	$\nu_3$ (A, B, C) $\nu_6$ (D)	$F_1$	90-100	90-100
		587		$2\nu_5 + \nu_4$ (C)			
		593		$\nu_3 + \nu_6 - \nu_4$ (C)			
		574					
		581					
571 (558)		547 567		$3\nu_4$ (A, C)	$A_1 + 2F_1 + F_2$		67 Broad
533 (524) or (540)				$\nu_4 + \nu_5 + \nu_6$ or $2\nu_5 + \nu_6$	$A_1 + A_2 + 2E + 4F_1 + 3F_2$ or $A_1 + E + 2F_1 + 3F_2$		
479 (479)				$\nu_1 - \nu_4$ or	$F_1$		14
(388) or (400)	392 (400)	394 (391)	(400)	$\nu_4 + \nu_5$ (A, B, C) $\nu_2 - \nu_6$ (A) $\nu_5 + \nu_3$ (D)	$A_2 + E + F_1 + F_2$ or $F_1 + F_2$		
(350) <sup>†</sup> or (338)	350 (330)		(330)	$\nu_2 - \nu_4$ (A) or $\nu_5 + \nu_6$ (B) $\nu_4 + \nu_6$ (D) $\nu_4 + \nu_3$ (D)	$F_1 + F_2$ <sup>†</sup> or $A_1 + E + F_1 + F_2$		
(273) or (289) or (268)	279 (270)		(200)	$-\nu_2 + \nu_3 + \nu_4$ (A) or $\nu_2 + \nu_3 + \nu_5$ (A) or $2\nu_5 - \nu_6$ (A) or $2\nu_4 - \nu_6$ (B) $\nu_5$ (D)	$A_2 + A_2 + 2E + 2F_1 + 2F_2$ or $A_1 + A_2 + 2E + 2F_1 + 2F_2$ or $A_1 + E + 2F_1 + 3F_2$		

\*Values in parentheses are calculated values.

<sup>†</sup>Preferred value.

Table 15  
OBSERVED RAMAN SPECTRUM

Designation	Frequencies (cm. <sup>-1</sup> )			Bigeleisen et al. (Ref. 20)
	Duncan (Ref. 44)	Claassen et al. (Ref. 35)		
	Liquid	Vapor - 1200 mm. Hg (70°C.)		
$\nu_1$	603	666.6 $\pm$ 0.3	656 $\pm$ 3	666 $\pm$ 3
$\nu_2$		535 $\pm$ 5	511 $\pm$ 3	
$\nu_5$	228			202 $\pm$ 3

Burke, Smith, and Nielsen<sup>29</sup> observed the infrared spectrum from 2 to about 40 microns with Perkin-Elmer spectrometer models 12C and 21 equipped with sodium chloride, potassium bromide, and KRS-5 prisms. The cell was constructed of fluorothene and contained windows of silver chloride, potassium bromide, or KRS-5 depending upon the region investigated. A modified Perkin-Elmer one-meter cell was also used, but no additional information was obtained. The results, which are summarized in Table 14, were found to be virtually identical with the measurements of Bigeleisen and his co-workers except that three new bands at 279 cm.<sup>-1</sup>, 350 cm.<sup>-1</sup> and 392 cm.<sup>-1</sup> were located in the extended 17-to-40 micron region.

Bigeleisen, Mayer, Stevenson and Turkevich<sup>20</sup> conducted the original study of the infrared spectrum in the region between 2 and 17 microns at room temperature. A rock-salt spectrometer and a 20-centimeter cell fitted with rock-salt windows were used to obtain the spectrum at several pressures. The results are summarized in Table 14. The fundamentals, which were assigned on the basis of the O<sub>h</sub> point symmetry, are listed in Table 13.

#### Raman Spectrum

The Raman spectrum was studied by Duncan<sup>44</sup> and by Bigeleisen, Mayer, Stevenson, and Turkevich<sup>20</sup> and rather recently by Claassen, Weinstock, and Malm<sup>35</sup>. These studies, the results of which are given in Table 15, revealed only three Raman lines. This is in agreement with the number of Raman lines predicted if it is assumed that UF<sub>6</sub> has an O<sub>h</sub> point symmetry. The fundamentals  $\nu_1$  and  $\nu_2$ , which were observed by Claassen and his co-workers, compare very well with those deduced from the observed combination bands of the infrared spectrum, especially those reported by Gaunt<sup>65</sup> and by Hawkins and his co-workers<sup>74</sup>.

In the investigation of the Raman spectrum of UF<sub>6</sub> vapor at 70°C. and 1200 mm. Hg by Claassen and his co-workers<sup>35</sup>, the Raman tube, 20 centimeters long and made of 14-millimeter pyrex tubing, contained a plane window on one end and a break seal on the other. The tube was irradiated (4358 Å) by an Applied Research Laboratories excitation unit and the spectrum was obtained using a Hilger E 612 instrument with two 63° glass prisms, a camera aperture of f/6.7, and an inverse dispersion of 16 Å per millimeter at 4358 Å. The results, with estimated uncertainties, are in agreement with the values chosen on the basis of infrared combination bands and compare favorably with other observed values. Using the frequency values obtained from the Raman spectrum and assuming that the UF<sub>6</sub> molecule has octahedral symmetry, Weinstock<sup>144</sup> later calculated values of the other four fundamental vibrational frequencies. These values are listed in Table 13.

Duncan<sup>44</sup> obtained the Raman spectrum of liquid  $\text{UF}_6$  using a glass Raman tube 6 millimeters in diameter and 20 centimeters long, with a flat end window. The tube containing the liquid  $\text{UF}_6$  was irradiated at 4358.34 Å with the mercury line filtered by cobalt blue. Two "strong" Raman lines, the more intense one at  $603 \text{ cm.}^{-1}$  and the other at  $228 \text{ cm.}^{-1}$ , were observed.

Bigeleisen and his co-workers<sup>20</sup> reported that their Raman spectrum values for liquid  $\text{UF}_6$  at  $70^\circ\text{C}$ . were obtained using 4358 Å excitation. In addition to the Raman spectrum of liquid  $\text{UF}_6$ , the Raman spectrum of a solution of  $\text{UF}_6$  in  $\text{C}_7\text{F}_{16}$  was obtained by using both 4358 Å and 5461 Å excitations. The Raman lines obtained from these studies also are summarized in Table 15.

#### VISIBLE AND NEAR - ULTRAVIOLET SPECTRA

The ultraviolet absorption spectrum of  $\text{UF}_6$  has been studied by Lipkin and Weisman<sup>104</sup>, by Duncan<sup>43</sup>, by Martin and Amphlett<sup>55, 112</sup> and by Amphlett, Mullinger, and Thomas<sup>9</sup>. Most of their data, which are presented in Tables 16 and 17, have been summarized in a number of earlier compilations<sup>45, 88, 93, 115, 135</sup>. Recently an article concerning the absorption spectrum in the visible and near-ultraviolet region has appeared in the Russian literature<sup>136</sup>. The author of the Russian article, Sheremet'ev, stated that the absorption spectra of  $\text{UF}_6$  are considerably more complicated than those reported as a result of the previously mentioned investigations. His data are presented in Tables 18, 19, 20, and 21.

Amphlett, Mullinger, and Thomas<sup>9</sup> obtained a qualitative picture of the absorption of  $\text{UF}_6$  vapor between 2000 Å and 4000 Å. A medium-sized Hilger quartz spectrograph with a hydrogen lamp as source and a copper arc for producing reference lines of known wave length was used to obtain the spectra. Two cells were used, a 15-centimeter pyrex cell with silica windows and a 5-centimeter cell of fused silica. The cells were attached by a T-piece to a bulb which contained the sample.

Preliminary results obtained by these investigators are somewhat different from those obtained earlier by Lipkin and Weisman<sup>104</sup>. The data of Amphlett and his co-workers indicate continuous absorption with complete extinction below 3100 Å; the extinction wave lengths of the vapor at various temperatures and pressures are listed in Table 16.

Lipkin and Weisman<sup>104</sup> obtained the absorption spectrum of  $\text{UF}_6$  at room temperature by use of a large Hilger instrument (dispersion 5 Å per millimeter). They found a region of strong continuous absorption at about 3300 Å and a region of structure absorption at about 3400 Å to 3800 Å. No detailed analysis of the spectrum was made.

Duncan<sup>43, 45</sup> reinvestigated the absorption spectrum of  $\text{UF}_6$  at a pressure of 36 mm. Hg. The spectrum was studied in the 4000 Å to 3400 Å region using a cell of 1-meter path length. It was found that the spectrum of  $\text{UF}_6$  vapor contained ultraviolet edges which appeared slightly sharper than the long wave-length edges. The position of these absorption bands, which are rather diffuse, are listed in Table 17. Duncan expressed the belief that in addition to the strong continuous absorption below 3300 Å there probably exists a continuum underlying the diffuse bands. The absorption spectrum of  $\text{UF}_6$  in Indies oil (a branched-chain fluorinated hydrocarbon) at  $77^\circ\text{K}$ . showed essentially the same structure as the spectrum of the vapor except for a uniform shift by about 450  $\text{cm.}^{-1}$  of all bands to lower frequencies.

Sheremet'ev<sup>136</sup> obtained the absorption of  $\text{UF}_6$  vapor in the visible and neighboring regions of the spectrum. The material used in the experiments was separated from volatile impurities by sublimation in a vacuum, first at  $-70^\circ\text{C}$ . and then at  $-50^\circ\text{C}$ ., and by gradually passing the vapor through a 1-meter-long quartz column filled with recrystallized

Table 16  
EXTINCTION WAVE LENGTHS OF THE VAPOR

Bulb Temperature (°C.)	Vapor Pressure (mm. Hg)*	Extinction Wave Length (Å)
17	65	3100
- 18	3.8	2400
- 48	0.17	2270
- 58	0.05	2180
- 77	0.003	2130
-180		2130

\*Obtained by extrapolation from the vapor pressure equation:  
 $\text{Log}_{10} P(\text{mm.}) = 10.74 - 2592/T$

Table 17  
ABSORPTION SPECTRUM OF THE VAPOR\*  
(Reference 45)

Wave Number, (cm. <sup>-1</sup> )	Remarks	Wave Number, (cm. <sup>-1</sup> )	Remarks
24364	Bands measured only at 144.5	26379	
24440	mm. Hg	26573	
		26644	
24504	Very weak	26756	
		26935	Doubtful
24794	Somewhat sharper bands measured	27015	Violet edge of moderately
24860	in pressure range 44.7 - 61.7		strong absorption
24972	mm. Hg at 12 - 18°C.	27135	
		27134	
25108		27334	
25211		27342	
25344		27420	
25478		27490	
25538		27568	
25720		27655	
26031		27820	Violet edge of strong
26175		27907	absorption
26277		28080	
		28415	Center

\*Measured at 293°K. with a Hilger E-1 spectrograph.

Table 18  
 VISIBLE AND ULTRAVIOLET ABSORPTION SPECTRUM OF THE VAPOR  
 (Reference 136)

Band	Wavelength, Å	Frequency (cm. <sup>-1</sup> )	Frequency Difference	
			cm. <sup>-1</sup>	Between Bands
1a	4068	24582	513	1a and 3b
1b		24661		
2a		24746		
2b	4040	24875	570	2b and 4b
2c		24981		
3a		25031		
3b		25095*	645	3b and 5b
3c		25220		
4a		25348		
4b	3930	25445	583	4b and 6b
4c		25510		
5a		25608		
5b		25740*	645	5b and 7b
5c		25839		
6a		25966		
6b	3842	26028	603	6b and 8b
6c		26178		
7a		26281		
7b		26385*	533	7b and 9b
7c		26490		
7d		26560		
8a		26595		
8b	3755	26631	617	8b and 10b
9a		26845		
9b		26918*	630	9b and 11b
9c		27027		
10a		27134*	576	10b and 12b
10b	3690	27248*		
11a		27462		
11b		27548*	636	11b and 13c
11c		27662		
12a		27754		
12b	3594	27824*	585	12b and 14b
12c		27932		
13a		28050		
13b		28074		
13c		28184*	634	13c and 15c
14a		28272		
14b	3520	28409*		
14c		28530		
15a		28637		
15b		28710		
15c	3470	28818*		

\*Strongest band of group.

Table 19  
FREQUENCY DIFFERENCES NEAR 200 AND 104 CM.<sup>-1</sup>  
(Reference 136)

Frequency (cm. <sup>-1</sup> )	Difference (cm. <sup>-1</sup> )	Frequency (cm. <sup>-1</sup> )	Difference (cm. <sup>-1</sup> )
24528		25095	
24746	218	25220	125
24981	235	25348	
25220	239	25445	97
25445	225	25608	
25608	163	25740	132
25839	231	25839	99
26028	189	26028	
26281	253	26178	150
26490	209	26281	
26631	141	26385	104
26845	214	26490	105
27027	182	26918	
27248	221	27027	109
27462	214	27134	
27662	200	27248	114
27824	162	27548	
28050	226	27662	114
28272	222	27824	
28530	258	27932	108
28710	180	28074	
24582		28184	110
24661	79	28409	
24756		28530	121
24875	119	28710	
24981	106	28818	108

potassium bifluoride which had been dried at 150°C. The UF<sub>6</sub> purified in this manner consisted of colorless 3- to 4-millimeter orthorhombic crystals. Sheremet'ev reported a melting point of 69.2°C. at approximately 2 atmospheres. (At approximately 2 atmospheres the melting point is 64.02 ± 0.05°C., [see Triple Point of UF<sub>6</sub>, page 89].) The spectra were obtained by use of a quartz spectrograph ISP-22 with an average linear dispersion of 25 Å per millimeter in the interval of the wave length from 4100 Å to 3400 Å. The absorption cells were made of quartz (100 millimeters long and 400 millimeters in diameter) with parallel optical grade quartz windows. Sheremet'ev obtained the absorption spectra of UF<sub>6</sub> vapor in the 5 to 94 mm. Hg pressure range. He determined the vapor pressure by extrapolation from the experimental values obtained by Amphlett and his co-workers<sup>9</sup> (see Vapor Pressure, page 87, Equation 86).

The spectrogram obtained by Sheremet'ev indicates that there is continuous absorption which begins near 3341 Å and proceeds toward the shorter wave lengths. It also indicates that there is an absorption zone in the interval from 4050 Å to 3470 Å. The whole absorption zone was measured from negatives with a Zeiss microphotometer. Results are given in Table 18. Sheremet'ev states that the most intense absorption in the vapors takes place near the 27,134 cm.<sup>-1</sup> frequency, while other comparatively intense absorptions take place near the 26,631 cm.<sup>-1</sup>; 26,918 cm.<sup>-1</sup>; 27,548 cm.<sup>-1</sup>; 27,824 cm.<sup>-1</sup>;

Table 20  
VISIBLE AND ULTRAVIOLET ABSORPTION OF THE SOLID AT 88°K.  
(Reference 136)

Band	Frequency (cm. <sup>-1</sup> )	Frequency Difference		Band	Frequency (cm. <sup>-1</sup> )	Frequency Difference	
		cm. <sup>-1</sup>	Between Bands			cm. <sup>-1</sup>	Between Bands
1a	24539			9a	26809		
1b	24606*	614	1b and 3c	9b	26980*		
1c	24636			9c	27041	551	9e and 11e
2a	24721*			9d	27071		
2b	24764			9e	27134†		
2c	24844	638	2d and 4c	10a	27172		
2d	24937*			10b	27322*	650	10b and 12d
3a	25029			11a	27397		
3b	25150*			11b	27510†		
3c	25220*	566	3c and 5c	11c	27548	643	11e and 13e
3d	25316			11d	27586		
4a	25393			11e	27685*		
4b	25412			12a	27772†		
4c	25575*	616	4c and 6d	12b	27840		
5a	25608			12c	27894	665	12d and 14c
5b	25693			12d	27972*		
5c	25786*	634	5c and 7b	13a	28034		
5d	25808			13b	28105*		
6a	25987			13c	28231	574	13d and 15c
6b	26055*			13d	28328†		
6c	26144	582	6d and 8b	13e	28425*		
6d	26191*			14a	28490		
7a	26315			14b	28520*		
7b	26420*			14c	28637*		
7c	26455	572	7e and 9e	15a	28752*		
7d	26476			15b	28776		
7l	26562†			15c	28902*		
8a	26666			15d	29070		
8b	26773*	549	8b and 10b	15e	29200		

\*Relatively strong bands.

†Very strong bands.

Table 21  
THE VISIBLE AND ULTRAVIOLET ABSORPTION OF THE SOLID AT 293°K.  
(Absorption Zone 4070-3470 Å)  
(Reference 136)

Frequency (cm. <sup>-1</sup> )			
25297	26095	26918*	27800
25384	26178	26976	27894
25477	26246	27063	28050
25542	26385	27134	28090
25608	26455	27249	28129
25693	26574	27322	28288
25813	26631	27510	28441
25839	26737	27548	28612
25927	26773	27700	28653

\* Strong band.

28,184 cm.<sup>-1</sup> and 28,409 cm.<sup>-1</sup> frequencies. He also states that "most of the intervals between neighboring groups (even as well as uneven) of bands represent the differences of frequencies, which differ from 603 cm.<sup>-1</sup> by no more than a double error of measure- ( $\pm 2.15$  cm.<sup>-1</sup>)" and that "the differences of frequencies near 200 and 104 cm.<sup>-1</sup> are also systematically found." The regularity which is mentioned in the latter statement is supposedly shown in the differences which are listed in Table 19. This regularity indicates that there is well-expressed harmony only in regard to the frequency 100 cm.<sup>-1</sup>. For the frequencies 600 cm.<sup>-1</sup> and 200 cm.<sup>-1</sup>, many values were observed which ranged between 570 cm.<sup>-1</sup> and 650 cm.<sup>-1</sup> and between 180 cm.<sup>-1</sup> and 260 cm.<sup>-1</sup>, respectively. On the basis of these findings, Sheremet'ev concluded that the structure of the UF<sub>6</sub> molecule does not completely correspond to the model of a regular octahedron.

Dieke and Duncan<sup>45</sup> reported that the absorption spectra of thin films of solid UF<sub>6</sub> showed no discrete bands, although the film may not have been of a favorable thickness.

Sheremet'ev obtained an absorption spectrum of solid UF<sub>6</sub> in the visible and in the neighboring ultraviolet regions at 88° and 293°K. using thin (about 0.1 millimeter) films. The results of the measurement at 88°K. are presented in Table 20 in which the second column gives the maximal frequencies of separate bands. The results of the measurements at 293°K. are listed in Table 21. At 88°K. the absorption spectrum consists of about 60 narrow bands of which nearly half are rather intense. At 293°K. the spectrum begins to blur, yielding only about 36 narrow bands. The strongest band at 88°K. is found near the 27,134 cm.<sup>-1</sup> frequency, while at 293°K. the most intense band is found near the 26,918 cm.<sup>-1</sup> frequency. The visible and ultraviolet absorption spectra of fused UF<sub>6</sub> at 353°K. obtained using a layer of fused UF<sub>6</sub> 1 millimeter thick were reported as a continuum with a clear long wave border near 4210 Å.

## FLUORESCENCE SPECTRA OF THE SOLID

The powder fluorescence spectrum (unpolarized) of the  $\text{UF}_6$  solid was obtained by Dieke and Duncan<sup>45</sup> with a Hilger E-1 prism spectrograph at 77°K. At this temperature, solid  $\text{UF}_6$  which has been excited chiefly by the mercury 3660 Å line shows a bright violet fluorescence. At room temperature the fluorescence disappears. No fluorescence was observed in the vapor after even very long exposures. The fluorescence spectrum reported is presented in Table 22.

Table 22  
FLUORESCENCE SPECTRUM OF THE SOLID AT 77°K.

Bands (cm. <sup>-1</sup> )	
22230	23319
22450	23537
22662	23739
22883	23994
23098	24166

## TRANSPORT PHENOMENA

### DIFFUSION COEFFICIENTS

#### SELF-DIFFUSION COEFFICIENT OF THE VAPOR

Ney and Armistead<sup>117</sup> determined the quantity  $\rho D$  at 30°C. in which  $\rho$  is the vapor density and  $D$  is the diffusion coefficient of material enriched in one isotope which diffuses into normal material contained in an apparatus of known geometry. The enrichment of the vapor was measured with a mass spectrometer. Although  $D$  as determined by Ney and Armistead cannot be rigorously defined as a self-diffusion coefficient, it does approximate it. The value of  $\rho D$  at 30°C. was calculated from the experimental  $\rho D$  values which were obtained at temperatures between 23.9° and 27.6°C. by utilizing a relationship between viscosity and temperature. The authors justified the use of the viscosity-temperature relationship on the basis of the small size of the correction necessary. The value of  $\rho D$  at 30°C. was reported as  $234 \pm 9$  micropoises. Since the investigations were conducted at 30°C. and approximately 10 mm. Hg pressure, the approximate density of the vapor under these conditions may be calculated from the ideal gas law (see page 49). The self-diffusion coefficient at 30°C. and 10 mm. Hg is then:

$$D = \frac{2.34 \times 10^{-4}}{1.86 \times 10^{-4}} = 1.26 \text{ cm.}^2/\text{sec. at 30°C. and 10 mm. Hg} \quad (12)$$

Using the value 1.32 as the "dimensionless quantity",  $\epsilon$ , which is equivalent to  $\rho D / \eta$  (kinetic theory) as derived by DeMarcus and Starnes<sup>42</sup> (see page 49), the quantity  $\rho D$  can be determined from the equation:

$$\rho D / \eta = 1.32 \quad (13)$$

where viscosity,  $\eta$ , =  $0.6163T^{0.933} \times 10^{-6}$  poise. Values of  $\rho D$  calculated from Equation 13 for temperatures ranging from 30° to 200°C. are listed in column 4 of Table 23. Values of  $\rho D$  calculated by McMillan<sup>114</sup> are listed in column 3. Jacobsohn<sup>82</sup> showed that the

Table 23  
SELF-DIFFUSION COEFFICIENT VALUES

Temperature (°K.)	$\rho D \times 10^6$ (poise)		
	Observed (Ref. 117)	McMillan* (Ref. 114)	Calculated Values†
303	234	265	236
313		274	
333		290	250
353		306	264
383		330	285
413		352	305
443		378	326
473		402	347

\*Calculated from  $\rho D = (1.529)(0.6163T^{0.933})$

†Calculated from  $\rho D = (1.32)(0.6163T^{0.933})$

relationship  $D = \epsilon \eta / \rho$  and the assumption  $\epsilon = 1.50$  were used to derive an expression for the diffusion coefficient D:

$$D = 0.0606 \frac{20 \text{ cm.}}{P(\text{cm.})} \left[ 1 + 6.29(t \times 10^{-3}) + 9.6(t \times 10^{-3})^2 \right] \text{ cm.}^2/\text{sec.} \quad (14)$$

However, the uncertainty of the viscosity-temperature relationship and of the value of  $\epsilon$  used in the Equation 14 limit its usefulness.

#### DIFFUSION COEFFICIENT INTO AIR

The coefficient of diffusion of  $\text{UF}_6$  into air at atmospheric pressure was measured by British workers in 1944.<sup>53</sup> The  $\text{UF}_6$  was allowed to diffuse upwards through air in a straight vertical tube and was carried away by a steady flow of air across the top of the tube. The rate of flow was determined and the concentrations at two points of the tube were measured by Katharometers. The diffusion coefficient reported at  $19^\circ\text{C}$ . for concentrations between 3.5 and 6.5 mole percent  $\text{UF}_6$  was  $0.072 \pm 0.006 \text{ cm.}^2/\text{sec.}$

#### SELF-DIFFUSION COEFFICIENT OF THE LIQUID

Rosen and Whybrew<sup>128</sup> determined the diffusion coefficient of liquid  $\text{UF}_6$  at approximately  $70^\circ\text{C}$ . in a manner similar to that used by Ney and Armistead to determine the diffusion coefficient of  $\text{UF}_6$  vapor. Two halves of a long narrow tube were filled with material having two different concentrations of light constituent, and diffusion was allowed to take place for a definite period of time at a constant temperature. The diffusion coefficient was calculated from the change in mean concentration in each half of the tube. Mass spectrometer techniques were used to measure the change. The result,  $1.90 \pm 0.13 \times 10^{-5} \text{ cm.}^2/\text{sec.}$ , was reported at a mean temperature of  $69.5^\circ\text{C}$ . The authors state that if the coefficient is in error, "it is more likely to be too high than too low, because, if any disturbing factor were present that tended to bring about mixing, its effect on the concentration distribution would be more or less equivalent to that of an increase in the rate of diffusion." The authors also noted that Cohen's calculated value<sup>38</sup> for the diffusion coefficient of the liquid is about  $5 \times 10^{-5} \text{ cm.}^2/\text{sec.}$ , which is in the same order of magnitude as the experimental results. The diffusion coefficient was calculated by using an approximate formula given by Powell, Roseveare and Eyring.\*

#### THERMAL DIFFUSION COEFFICIENT

Nier<sup>118</sup> attempted to determine the thermal diffusion coefficient in the range between  $65^\circ$  and  $480^\circ\text{C}$ . by means of a Clausius-type thermal diffusion column. As no appreciable separation was observed, he concluded that the method was not sensitive enough for separation of quantities of  $\text{U}^{235}$ .

That this conclusion is questionable is proved by the temporary use in the United States of a full-scale thermal diffusion plant in the mid-1940's. Some of the major results of the work required to design this plant are referred to elsewhere in this compilation.

#### VISCOSITY

##### VISCOSITY OF THE VAPOR

The viscosity of  $\text{UF}_6$  vapor has been investigated a number of times by the capillary flow and the oscillating disk methods. Early reports of viscosity measurements which were obtained by the capillary flow method showed large discrepancies (10 to 20 percent) between the values obtained by the different investigators. After these discrepancies

\*Powell, R. E., Roseveare, W. E. and Eyring, H. Ind. Eng. Chem. 33, 430 (1941).

were resolved, fairly accurate viscosity data in the 40° to 200°C. range were obtained by this method. The experimental results are in fair agreement with viscosity data obtained by the oscillating disk method, although the slopes of the viscosity versus temperature curves obtained by the two different methods do not agree. Summaries of the viscosity data are presented in Table 24 and in Figure 7. Some of the details of the various investigations are discussed below.

Fowler<sup>61</sup> determined the viscosity of UF<sub>6</sub> vapor by capillary flow measurements at pressures greater than 760 mm. Hg, whereas Llewellyn and Swaine<sup>54</sup>, Llewellyn<sup>106</sup>, and Roberts<sup>127</sup> determined its viscosity by the same method but at pressures less than 50 mm. Hg. The results of the investigations conducted at different pressure levels are not in agreement. Fowler's results are considerably higher than those of Llewellyn and Swaine and others.

Cohen<sup>37</sup> attempted to resolve the differences between the results obtained by Fowler and those of Llewellyn and Swaine. He summarized their data using the following empirical formulae:

For Llewellyn's data:\*

$$\eta = 2.10 \times 10^{-6} T^{0.779} \quad (0 \text{ to } 200^\circ\text{C.}) \quad (15)$$

For Fowler's data:

$$\eta = 2.46 \times 10^{-6} T^{0.772} \quad (85 \text{ to } 165^\circ\text{C.}) \quad (\text{calibrated with air}) \quad (16)$$

$$\eta = 1.78 \times 10^{-6} T^{0.827} \quad (150 \text{ to } 260^\circ\text{C.}) \quad (\text{calibrated with N}_2) \quad (17)$$

Upon correlating the two sets of viscosity data with the thermal conductivity and the self-diffusion coefficients, he found that Llewellyn's results formed a picture more in conformity with what was known about the two mentioned properties. However, since Fowler's data were examined rather rigorously and no systematic errors could be found, Cohen recommended further investigation of all three fundamental constants.

Only after an intensive investigation of the viscosity were Myerson and Eicher<sup>116</sup> able to determine the cause of the large discrepancies in the viscosity data. They showed that the viscosity of the vapor is essentially independent of pressure under the conditions prevailing during the various investigations, while the Reynolds number is a direct function of pressure. They attributed Fowler's high results to the effect of non-laminar flow. Upon further investigation with a platinum capillary of small diameter, they found that the Reynolds number varies linearly with the time ratio of the flow. Therefore, they determined the viscosities using a platinum capillary, 75 centimeters in length with an inside diameter of 0.03 centimeters. These determinations were made at a Reynolds number less than 100 and in regions of experimentally established non-turbulent flow over the 40 to 200°C. range. McMillan<sup>114</sup> expressed Myerson and Eicher's results as:

$$\eta = 0.6163 T^{0.933} \text{ micropoise} \quad (18)$$

DeMarcus and Starnes<sup>42</sup>, in their report on the intermolecular action of UF<sub>6</sub>, commented on Myerson and Eicher's viscosity data. They stated that since the capillary flow method does not provide a direct measurement of viscosity, but instead gives a measure of viscosity which is relative to that of air as the standard, the viscosity data of air which was used by Myerson and Eicher should also have been screened according to the Reynolds number criterion. They felt that the reported viscosities of UF<sub>6</sub> vapor might have systematic errors because of some uncertainty in the values for the viscosity of air which

\*Llewellyn's formula for his own data:  $\eta = 1.67(1 + 0.0026 t) \times 10^{-4}$  poise (0 to 200°C.)

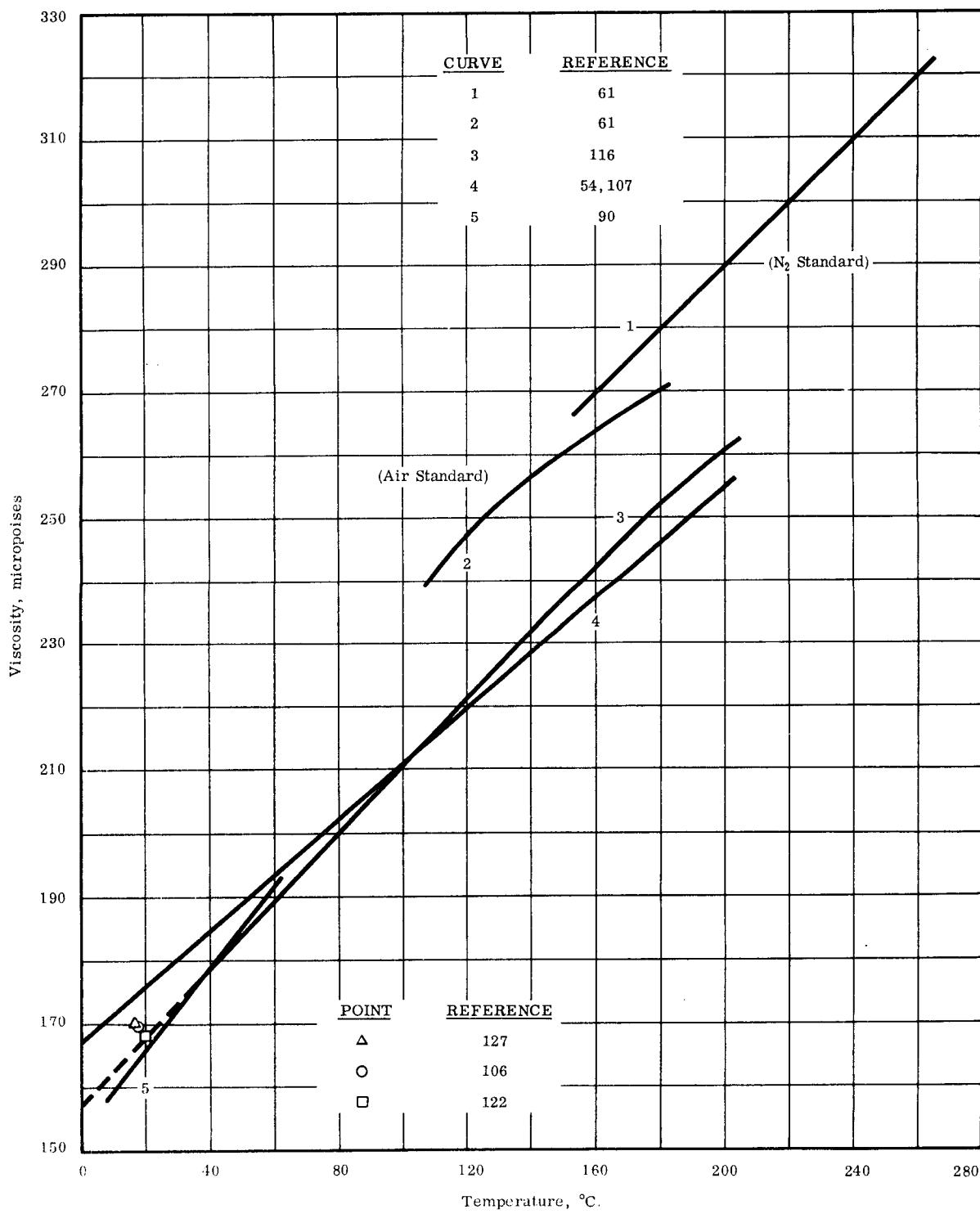


FIG. 7. VISCOSITY OF THE VAPOR

Table 24  
VISCOSITY OF THE VAPOR  
 $\eta$  (micropoises)

Temperature (°C.)				Fowler (Ref. 61)			Present (Ref. 122)	Roberts (Ref. 127)	Llwellyn (Ref. 106)
	Myerson and Eicher (Ref. 116)	Kigoshi (Ref. 90)	Llwellyn and Swaine (Ref. 54, 107)	Air Std.	N <sub>2</sub> Std.				
0			167						
14.5		162.4							
17							170 ± 3		
18								169 ± 3	
20						168			
25			176						
26.3		170.1							
35.2		176.0							
40	178.7								
44.7		182.2							
50			189						
60	189.0								
80	199.9								
84.9				239.8					
100.0			211						
104					239.9				
110	216.1								
123.9					249.6				
140	231.9								
144.5				258.8					
150			233						
153.9					266.7				
164.5						271.9			
165.8				269.0					
170	248.0								
186					283.1				
196.3						288.4			
200	261.1		255						
210					295.6				
219						299.7			
232.2					305.6				
248.0						315.0			
263.0						321.6			

were used as standards. Upon comparing the viscosity of air values used by Myerson and Eicher against more recent values which have appeared in the literature, they found agreement up to about 300°K.; however, values ranged generally between 0.5 percent low at 300°K. and possibly 1.5 percent high at the upper temperature limit of about 400°K. They consider it reasonable to assume that the slope of the Myerson-Eicher viscosity-temperature curve might be in error by as much as 1.4 percent.

Although Myerson and Eicher's results are in agreement with the results of Fleischman<sup>122</sup> which were determined by the oscillating disc method, they do not compare as favorably with the results of Kigoshi<sup>90</sup>, which were also determined by the oscillating disc method. Disagreement between the data of Kigoshi and those of Myerson and Eicher is especially apparent in the slopes of the viscosity-temperature curves, which are shown in Figure 7. Since it is not known which of the slopes is the more accurate, the related physical properties of the UF<sub>6</sub> molecule, such as molecular diameter, rigidity, etc., which were calculated from the viscosity data by Kigoshi must be considered to be somewhat uncertain.

### VISCOSITY OF THE LIQUID

The data on the viscosity of liquid UF<sub>6</sub> in the literature are rather scanty and not in agreement. A summary of the viscosity values of the liquid, some which were calculated for this report from proposed viscosity-temperature relationships, is presented in Table 25 and in Figure 8.

Table 25

### VISCOSITY OF THE LIQUID $\eta$ (centipoises)

Temperature (°C.)	Kirshenbaum* (Ref. 92)	Simon (Ref. 135)	Blatt (Ref. 21)	Llewellyn (Ref. 107)	Calculated†
67.2	0.731*				
67.9				0.924	
70.0		0.91		0.910	0.84
71.5				0.902	
72.5	0.692*				
72.6		0.687 ± 0.007			
72.9		0.685*			
73.4	0.679*				
73.9				0.892	
74.5				0.880	
74.6			0.788 at 347 psi.		
74.7	0.669*				
75.0	0.663*				
75.8			1.035 at 3000 psi.*		
76.5				0.876	
78.8				0.870	
80.0		0.85			
83.3				0.834	
84.9				0.832	
88.3				0.815	
90.0		0.80			0.77
92.2				0.794	
95.7				0.770	
97.8				0.766	
99.0				0.752	
100.0		0.75			
110.0					0.71
130.0					0.66
150.0					0.61
153.0			0.668 at 400 psi.		
153.5			0.689 at 3200 psi.		
170.0					0.57
190.0					0.54
210.0			Critical point 230.2°C.		0.51
248.0			0.552 at 3000 psi.		
250			0.505 at 1000 psi.		

\*Preliminary values.

†From Equation 22 using vapor pressure values of the liquid as obtained by Oliver et al. (Ref. 119).

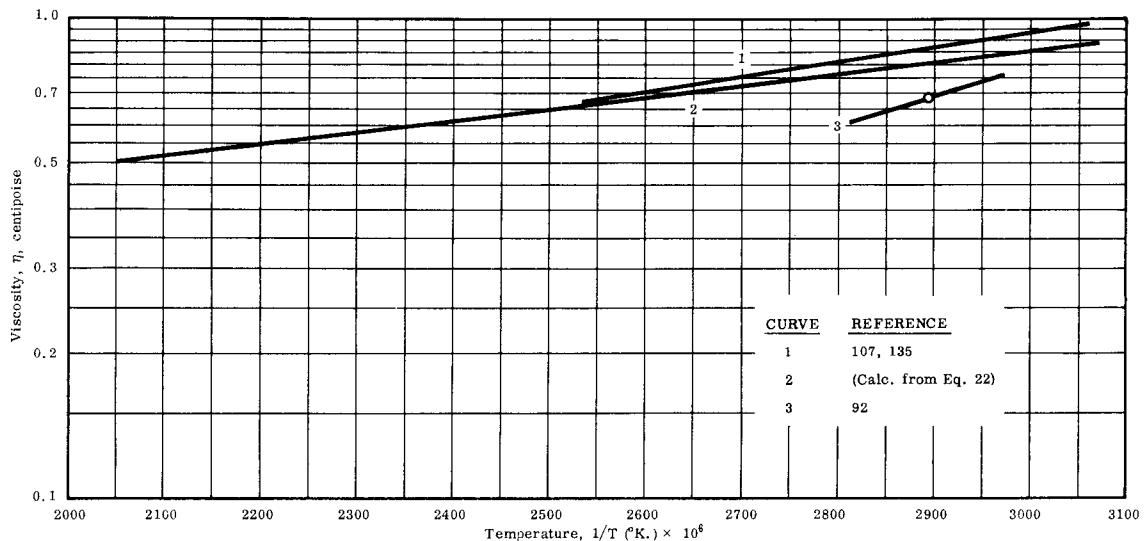


FIG. 8. VISCOSITY OF THE LIQUID

Kirshenbaum<sup>92</sup> determined the viscosity of liquid  $\text{UF}_6$  in the  $67^\circ$  to  $75^\circ\text{C}$ . range by using a modified Ostwald viscosimeter. He stated that since the temperature measurements were uncertain and the total temperature range was small, only a single value of the viscosity at the average temperature should be considered as the final result. The absolute viscosity at  $72.6^\circ\text{C}$ . was reported as  $0.687 \pm 0.007$  centipoise. He checked the validity and accuracy of his measurements using the same apparatus to determine the viscosity of known liquids.

Cohen<sup>38</sup> used an expression:

$$\eta = Ae^{(\Delta H(v)/T)B} \quad (19)$$

and assumed that the viscosity of  $\text{UF}_6$  vapor at its boiling point is the same as that of carbon tetrachloride at its boiling point. From this assumption, he determined the constants A and B for liquid  $\text{UF}_6$  and obtained the following expression from which he calculated the viscosities of liquid  $\text{UF}_6$ :

$$\eta = 0.1271 \times 10^{-3} e^{(1.217 \times 10^3 / T^\circ\text{K.})} \text{ poise} \quad (20)$$

According to Kirshenbaum<sup>93</sup>, this expression gives a viscosity value of 0.43 centipoise at  $72.6^\circ\text{C}$ . compared to the experimental value of 0.687 centipoise.

Blatt<sup>21</sup> measured the viscosity of the liquid by passing  $\text{UF}_6$  through a tube of known length and diameter. The material was drawn through the tube by a thermal siphon, and the rate of flow measured by heating the material to a constant temperature and extracting the heat in a calorimeter bath. Blatt discussed the Cohen expression of the data:

$$\eta = Ae^{(\Delta F - P\Delta V)/RT} \quad (21)$$

where:  $A = 1.67 \times 10^{-3}$  poise

$$\Delta F = 1100 \text{ cal./mole}$$

$$\Delta V = 28 \text{ cc.}$$

Blatt put the expression into the form:

$$\eta = 1.67 \times 10^{-3} e^{\left(\frac{554 - 0.023P}{T^{\circ}K.}\right)} \quad (22)$$

where P is in pounds per square inch.

Equation 22 was used to calculate viscosity values of the liquid between 70° and 210°C. using the vapor pressure values of Oliver and his co-workers<sup>119</sup>. They are presented in Table 25 and in Figure 8. Viscosity values for the temperatures between 70° and 100°C. were reported by Simon<sup>135</sup> and are presented in the same table. These values also were later included by Llewellyn<sup>107</sup>.

#### KINEMATIC VISCOSITY OF MIXTURES OF URANIUM HEXAFLUORIDE AND C<sub>8</sub>F<sub>16</sub>

DeMarcus and Hopper<sup>41</sup> used Eyring's viscosity formula:

$$\eta = \frac{hN}{V} e^{(\Delta F/RT)} \quad (23)$$

where: h is Planck's constant

N is the Avogadro number

V is the molar volume

R is the gas constant

T is the absolute temperature

to derive an expression for determining the kinematic viscosity of UF<sub>6</sub>-C<sub>8</sub>F<sub>16</sub> mixtures. By converting viscosity to kinematic viscosity and using Eyring's viscosity formula for ideal mixtures, the authors showed that the kinematic viscosity can be represented by:

$$\eta \text{ (mixture)} = \eta_1^{x_1} \eta_2^{x_2} \left( \frac{M_1^{x_1} M_2^{x_2}}{X_1 M_1 + X_2 M_2} \right) \quad (24)$$

where subscripts 1 and 2 refer to the pure liquids, X<sub>1</sub> and X<sub>2</sub> being the respective mole fractions. Since the necessary data for calculating the kinematic viscosities from the above equation were not available, calculation of actual kinematic viscosity values of the mixtures was not attempted.

#### THERMAL CONDUCTIVITY

##### THERMAL CONDUCTIVITY OF THE VAPOR

The thermal conductivity values of UF<sub>6</sub> vapor have been determined by various investigators with respect to known conductivities of other vapors at temperatures ranging between 0° and 125°C. The experimental values, most of which were obtained by the "hot wire" method, were reported to compare favorably with the values calculated from viscosity and heat-capacity data. The average of the experimental and calculated values, which was taken on an equal-weight basis, is represented by the following equation:

$$K_{av} = 1.46 (1 + 0.0042 t^{\circ}C.) \times 10^{-5} \text{ cal./cm. sec. } ^{\circ}C. \quad (25)$$

Equation 25 was reported as representing the most reliable thermal conductivity values for temperatures between 0° and 100°C. A summary of all the reported experimental and calculated results is presented in Table 26 and Figure 9. The individual thermal conductivity investigations are discussed in more detail below.

Table 26  
THERMAL CONDUCTIVITY OF THE VAPOR

$K \times 10^5$  (cal./cm. sec.  $^{\circ}$ C.)

Temperature ( $^{\circ}$ C.)	Calculated from Equation 125	Hot Wire Determinations				Viscosity Calculations*	
		Taylor and Agron (Ref. 4, 5, 78, 89)	Llewellyn (Ref. 105)	Llewellyn (Ref. 107)	Fleischmann (Ref. 122)	Myerson and Eicher (Ref. 4, 89)	Llewellyn and Swaine (Ref. 4, 89)
0	1.46	1.44*	1.39 $\pm$ 0.03			1.46	1.55
5				1.42			
49.2		1.79 $\pm$ 0.03					
50	1.76	1.79*	1.65*			1.79	1.84
88.9		2.07 $\pm$ 0.03					
100	2.07	2.14*	1.91 $\pm$ 0.03			2.12	2.12
105				1.94			
125	2.23	2.32*	2.04*		2.05 $\pm$ 0.1†	2.28	2.26

\*Calculated from the representative equations.

†Obtained by R. D. Present.

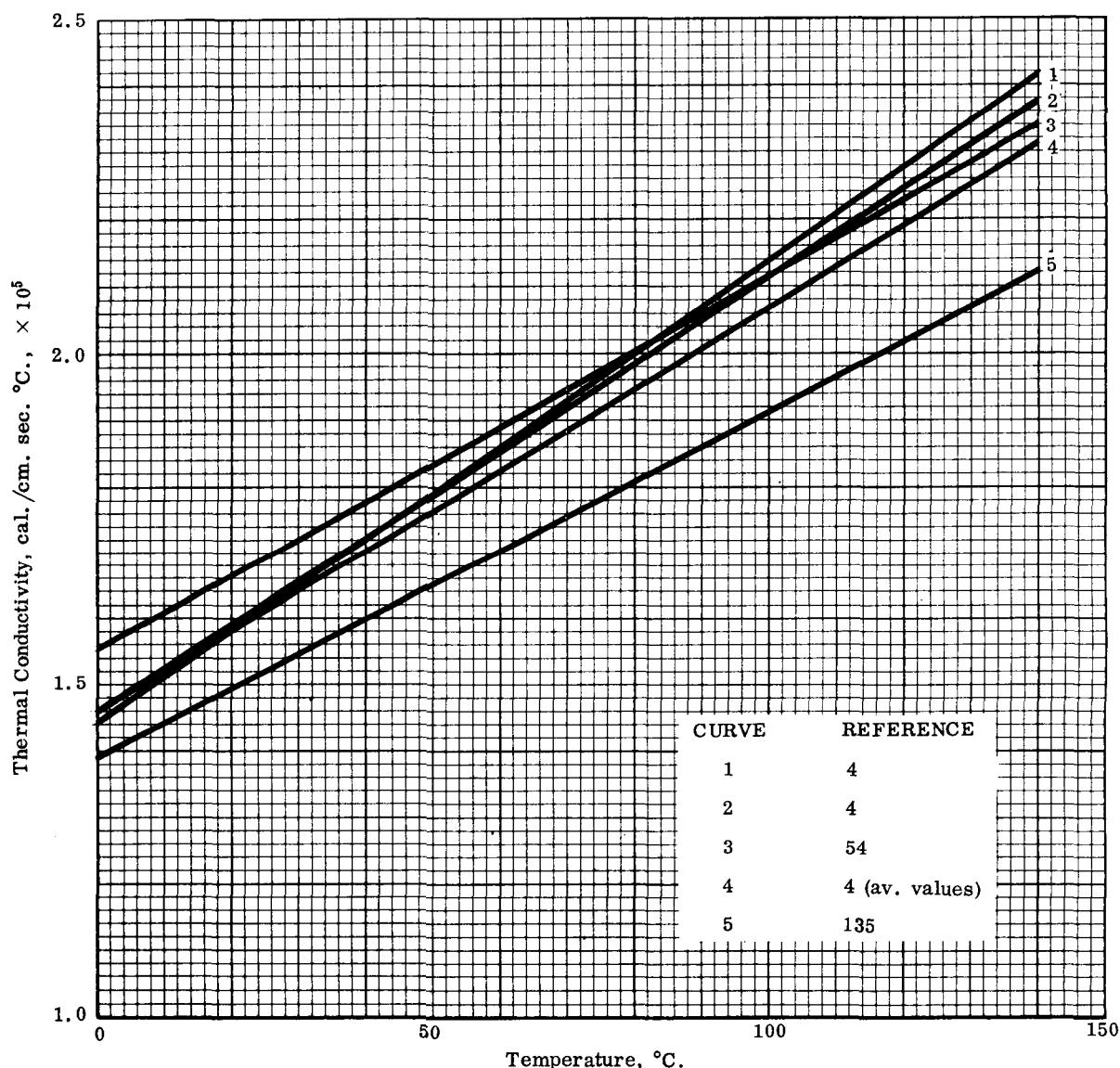


FIG. 9. THERMAL CONDUCTIVITY OF THE VAPOR

Agron and Taylor<sup>4, 5, 78, 89</sup> found, by the "hot wire" method, that the thermal conductivities of  $\text{UF}_6$  vapor measured relative to argon and nitrogen at  $49.2^\circ$  and  $88.9^\circ\text{C}$ . were  $1.79 \pm 0.03 \times 10^{-5}$  and  $2.07 \pm 0.03 \times 10^{-5}$  cal./cm. sec.  $^\circ\text{C}$ ., respectively. The thermal conductivity values of the standards, argon and nitrogen, which were used in these determinations were  $K = 3.850 (1 + 0.0031 t^\circ\text{C})$  and  $K = 5.760 (1 + 0.0027 t^\circ\text{C})$ , respectively. The authors expressed their results for temperatures between  $0^\circ$  and  $100^\circ\text{C}$ . by the following equation:

$$K = 1.45 (1 + 0.0048 t^\circ\text{C}) \times 10^{-5} \text{ cal./cm. sec. } ^\circ\text{C.} \quad (26)$$

The results of Llewellyn<sup>107, 135</sup> which were  $1.42 \pm 0.03$  and  $1.94 \pm 0.03$  cal./cm. sec.  $^\circ\text{C}$ . at  $5^\circ$  and  $105^\circ\text{C}$ ., respectively, are somewhat lower than those of Agron and Taylor. Since the method of measurement is the same in each case, the discrepancy between the results of Llewellyn and those of Agron and Taylor may have been caused by a different choice of thermal conductivity values for the standards. Agron and Taylor represented Llewellyn's results<sup>107</sup> (see also Simon<sup>135</sup>) by the following expression:

$$K = 1.39 (1 + 0.0037 t^\circ\text{C}) \times 10^{-5} \text{ cal./cm. sec. } ^\circ\text{C.} \quad (27)$$

Present<sup>122</sup>, in his report on Fleischmann's measurement of thermal conductivity, showed that Fleischmann's reported value is in error because of the temperature and pressure corrections and the neglect of convection losses. With the proper correction and with  $7.3 \times 10^{-5}$  cal./cm. sec.  $^\circ\text{C}$ . as the thermal conductivity of the  $\text{N}_2$  standard, the thermal conductivity of  $\text{UF}_6$  at  $100^\circ\text{C}$ . was established as  $2.05 \pm 0.10 \times 10^{-5}$  cal./cm. sec.  $^\circ\text{C}$ . and found to compare favorably with other values of the vapor from viscosity values, heat capacity values which were obtained from spectroscopic data<sup>24</sup>, and the Eucken equation:

$$K = \frac{1}{4} (9 C_p/C_v - 5) \eta C_v \quad (28)$$

Conductivity values obtained from Myerson and Eicher's Viscosity data<sup>116</sup> and the Eucken equation are in agreement with Agron and Taylor's experimental results. The results calculated from viscosity data are given in Table 26 and are expressed by the following equations:

$$K = 1.46 (1 + 0.0045 t^\circ\text{C}) \times 10^{-5} \text{ cal./cm. sec. } ^\circ\text{C.} \quad (\text{Myerson and Eicher}^{116}) \quad (29)$$

$$K = 1.55 (1 + 0.0037 t^\circ\text{C}) \times 10^{-5} \text{ cal./cm. sec. } ^\circ\text{C.} \quad (\text{Llewellyn and Swaine}^{54}) \quad (30)$$

Taylor and Agron averaged Equations 26, 27, 29 and 30 on an equal-weight basis to obtain the most probable values for the thermal conductivity of  $\text{UF}_6$  vapor between  $0^\circ$  and  $100^\circ\text{C}$ . (see Equation 25).

#### THERMAL CONDUCTIVITY OF THE LIQUID

Priest<sup>123</sup> found that the thermal conductivity of liquid  $\text{UF}_6$  at  $72^\circ\text{C}$ . was  $3.83 \times 10^{-4}$  cal./cm. sec.  $^\circ\text{C}$ .  $\pm 3$  percent. This value was obtained by averaging the results calculated from heat input over a temperature range the midpoint of which was  $72^\circ\text{C}$ . A liquid, said by Priest to have properties known to be similar to those of  $\text{UF}_6$ , was used to check the apparatus.

Cohen<sup>38</sup> used the Bridgeman-Eyring formula to represent the thermal conductivity of the liquid. He found that the thermal conductivity of the liquid varied linearly with temperature.

#### THERMAL CONDUCTIVITY OF $\text{UF}_6$ -GAS MIXTURES

Llewellyn<sup>105</sup> determined the variation of thermal conductivity with composition of  $\text{UF}_6$ -air mixtures at  $5^\circ\text{C}$ . by a "hot wire" method. The results, which were read from a smooth curve, are shown in Table 27 and plotted in Figure 10.

Table 27  
THERMAL CONDUCTIVITY OF URANIUM HEXAFLUORIDE - AIR MIXTURES

Percent $\text{UF}_6$	Conductivity (cal./cm. sec. $^{\circ}\text{C}.$ )
0	$5.90 \times 10^{-5}$
20	$4.50 \times 10^{-5}$
40	$3.45 \times 10^{-5}$
60	$2.60 \times 10^{-5}$
80	$2.00 \times 10^{-5}$
100	$1.42 \times 10^{-5}$

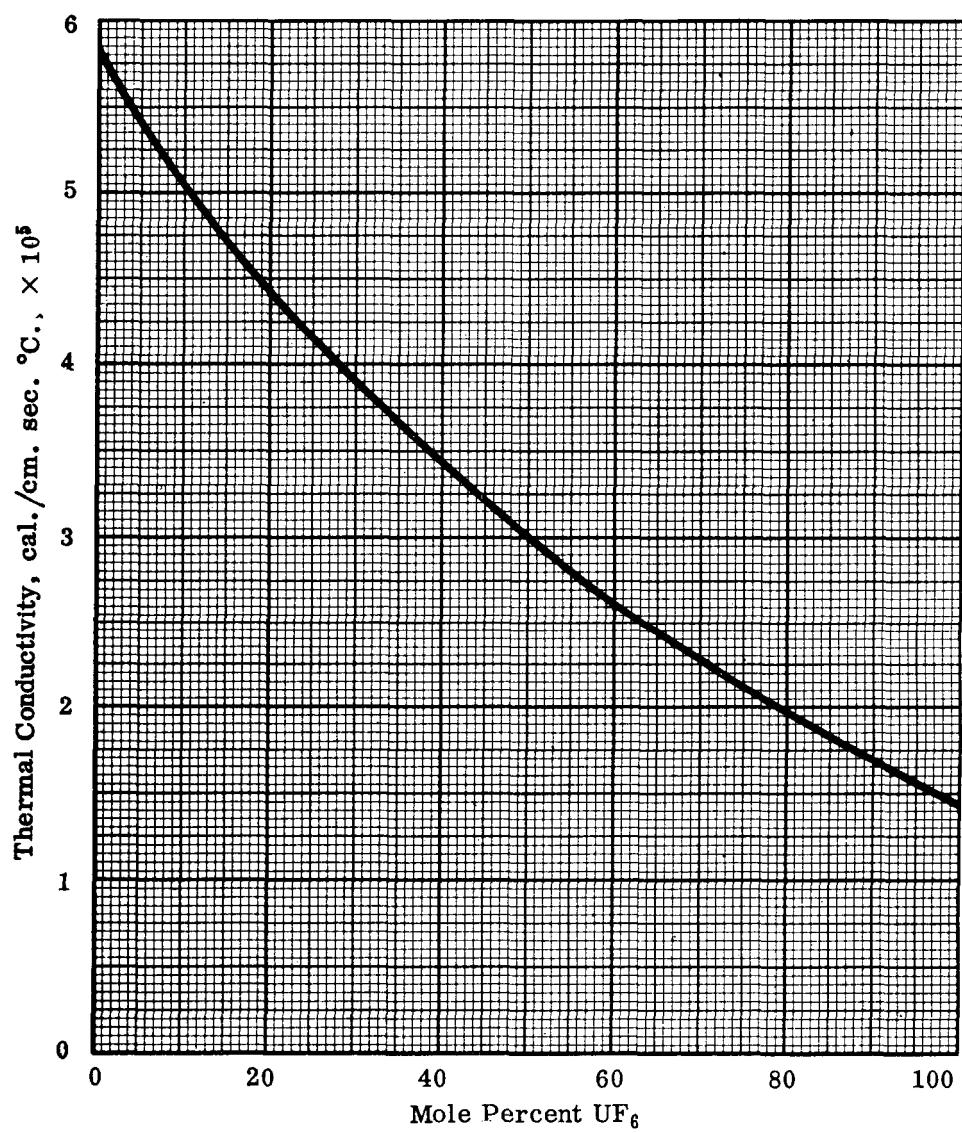


FIG. 10. THERMAL CONDUCTIVITY OF URANIUM HEXAFLUORIDE - AIR MIXTURES

Greenspan, Roach, and Riseman<sup>69</sup> found that thermal conductivity of  $\text{UF}_6$ -nitrogen mixtures could be used to make continuous analyses of flowing  $\text{UF}_6$ -nitrogen mixtures. For the pure components they obtained a reproducibility of at least 0.1 mole percent. They did not report actual thermal conductivity values.

### MEAN FREE PATH

An expression has been reported<sup>88</sup> from which values of the mean free path at various temperatures and pressures can be calculated, although no reference is given to indicate the source. Approximate values of the mean free path which were independently calculated from related physical properties are presented at various temperatures and pressures. The values presented here were calculated to establish the order of magnitude of the mean free path. Values calculated at standard temperatures and pressures are given in Table 28. Values calculated at temperatures of 0°, 30° and 130°C. and at pressures from 0.2 to 2.0 atmospheres are presented in Table 29 and in Figure 11.

Table 28  
CALCULATED MEAN FREE PATHS AT STANDARD  
PRESSURE AND TEMPERATURE\*

Relationship	Values at 0°C.	Mean Free Path ( $\times 10^6$ )
Viscosity	$1.55 \times 10^{-4}$ g./cm. sec.*	2.31
Thermal conductivity	$1.46 \times 10^{-5}$ cal./cm. sec.†	2.70
Thermal diffusion	$1.59 \times 10^{-2}$ cm. <sup>2</sup> /sec.‡	3.73
Molecular diameter	$4.20 \times 10^{-8}$ cm.ξ	4.73
Dimensionless quantity	$\epsilon = 1.32$ //	3.05
Equation 31		1.66

\*Obtained by averaging the viscosity value of Myerson and Eicher with that of Kigoshi.

†Obtained from the equation:  $K_{(av)} = 1.46 (1 + 0.0042 t^{\circ}\text{C.}) 10^{-5}$  cal./cm. sec. °C.

‡Obtained from equation:  $D = 0.0606 \frac{20 \text{ cm.}}{\rho \text{ cm.}} [1 + 6.29 (t \times 10^{-3}) + 9.6 (t \times 10^{-3})^2]$   
cm.<sup>2</sup>/sec.

ξObtained from Kigoshi.<sup>90</sup>

//Suggested by DeMarcus and Starnes (Ref. 42). Values of the other constants used in the calculations are:

$$\bar{c} = 1.281 \times 10^4 \text{ cm./sec.}$$

$$\rho = 1.57 \times 10^{-2} \text{ g./cm.}^3$$

$$C_V = 28.3 \text{ cal./g.}$$

Table 29  
MEAN FREE PATHS CALCULATED ON THE BASIS  
OF THE TRANSPORT PROPERTIES

Temperature (°C.)	Pressure (atm.)	Dimensionless Quantity <sup>†</sup>	1 × 10 <sup>6</sup> (cm.)*		
			Thermal Conductivity <sup>‡</sup>	Viscosity <sup>ξ</sup>	ρD = 234 Micropoise
0	0.2	15.26	13.49	11.56	
	0.6	5.09	4.49	3.85	
	1.0	3.05	2.29	2.31	
	1.4	2.18	1.97	1.65	
	2.0	1.53	1.38	1.16	
30	0.2	17.13	14.76	12.94	17.55
	0.6	5.54	4.77	4.18	5.67
	1.0	3.27	2.81	2.47	3.35
	1.4	2.29	1.98	1.73	2.35
	2.0	1.57	1.35	1.18	1.61
130	0.2	26.99	--	20.40	
	0.6	8.93	--	6.76	
	1.0	5.32	--	4.03	
	1.4	3.75	--	2.84	
	2.0	2.61	--	1.98	

\*Density of UF<sub>6</sub> vapor at 0° calculated from ideal gas law. Density of UF<sub>6</sub> vapor at 30° and 130° calculated from Magnuson equation of state (Ref. 110).

<sup>†</sup> $\frac{\rho D}{\eta}$  = 1.32 value suggested by DeMarcus and Starnes (Ref. 42).

<sup>‡</sup>K values obtained from the equation:  $K_{(av)} = 1.46(1 + 0.0042 t^{\circ}\text{C.}) \times 10^{-5}$  cal./cm.sec.°C.

<sup>ξ</sup> $\eta$  values at 0° and 30° are averages of Myerson and Eicher data with those of Kigoshi.  
 $\eta$  values at 130° are Myerson and Eicher data.

Values of the mean free path are reported in the Kellex Corporation Technical Data Book and the Carbide and Carbon Chemicals Corporation Technical Data Book.<sup>120</sup> No information is given in either book to indicate where or how the figures were obtained. Jacobsohn<sup>82</sup> reported the following equation which represents the mean free path values for temperatures from 0° to 200°C.:

$$l = \frac{20 \text{ cm.}}{p \text{ cm.}} \quad (6.32) \quad [1 + 4.45 (t \times 10^{-3}) + 3.1 (t \times 10^{-3})^2] \times 10^{-6} \text{ cm.} \quad (31)$$

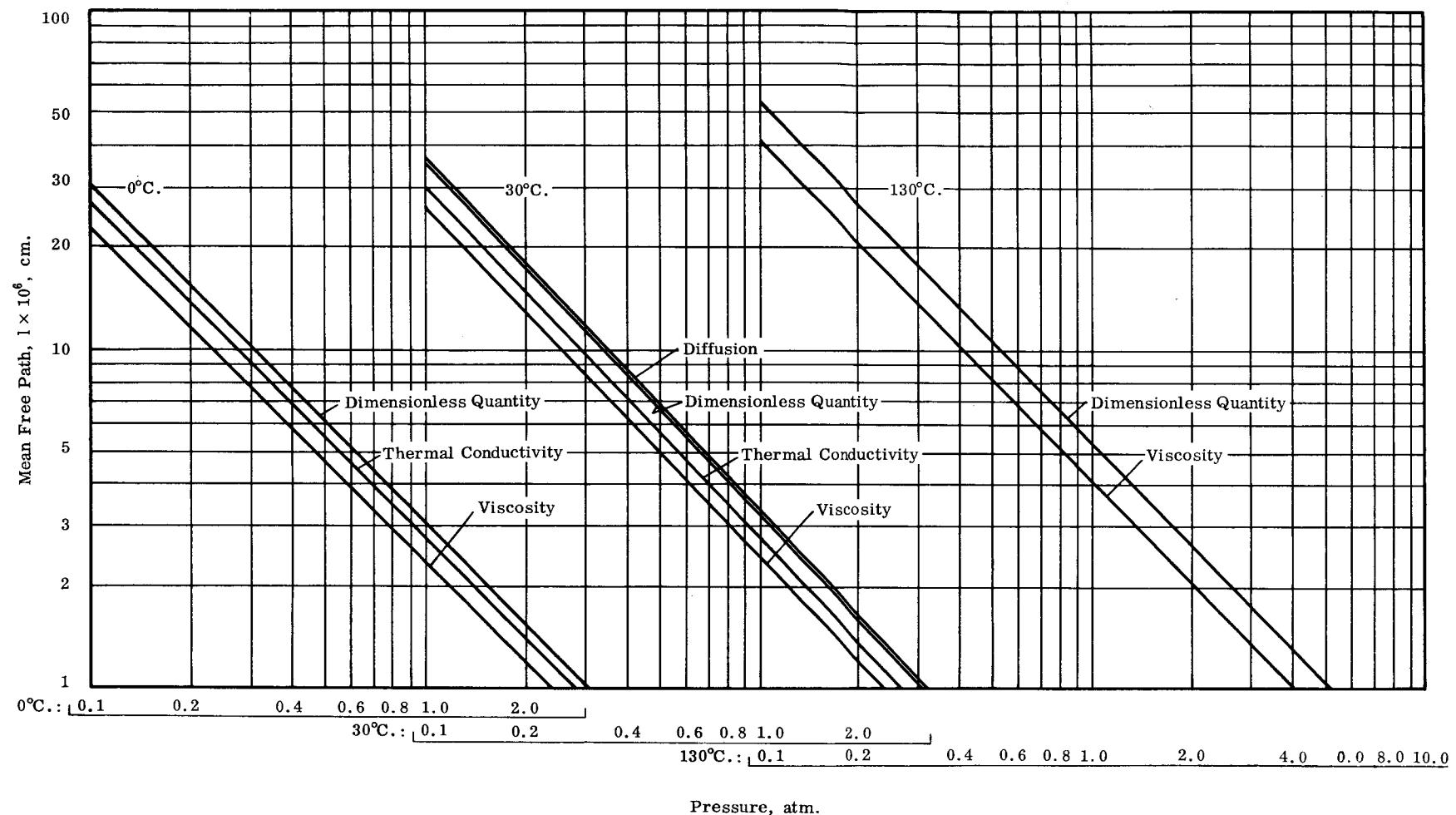


FIG. 11. ESTIMATED MEAN FREE PATHS AT VARIOUS TEMPERATURES

Values of the mean free path calculated from this equation are lower than the estimates given in this report but are of the same order of magnitude.

The mean free path can be related to the viscosity,  $\eta$ ; the thermal conductivity,  $K$ ; the coefficient of self-diffusion,  $D$ ; and the molecular diameter,  $\sigma$ ; by application of the kinetic theory as shown by Jeans.\* The relationships, which are only first approximations, are as follows:

$$\text{Viscosity} \quad \eta = 1/3 \rho \bar{c}l \quad (32)$$

$$\text{Thermal conductivity} \quad K = 1/3 \rho \bar{c}l C_v \quad (33)$$

$$\text{Diffusion} \quad D = 1/3 \bar{c}l \quad (34)$$

$$\text{Molecular diameter} \quad \sigma^2 = 1/\sqrt{2\pi} \eta l \quad (35)$$

where  $\rho$  is the density of the gas,  $\bar{c}$  is the mean velocity which can be calculated from the equation:

$$\bar{c} = \sqrt{8RT/\pi M}, \quad (36)$$

$\eta$  is the number of molecules in a unit volume, and  $C_v$  is the heat capacity at constant volume.

Comparison of Equations 32 and 33 indicates that  $K$  should be equal to  $\eta C_v$ , although the experimental measurements indicate that  $K$  is slightly greater. Comparison of Equations 32 and 34 indicates that  $\rho D/\eta = 1$ , but, as might be expected, the experimental data indicate that the ratio should be greater than 1. These differences are shown by Jeans to be caused by factors which are neglected in the simple kinetic theory. Jeans also shows that Equations 32 and 34 contain two sources of error, the first error arising from the assumption that the mean free path is the same for all velocities, and the second from neglect of the persistence of velocities.

Upon correcting  $D$  and  $\eta$  for persistence, Jeans found that:

$$\rho D/\eta = 1.34 \quad (37)$$

The value of this quantity, the "dimensionless quantity" (see page 49), is in agreement with the experimental results ( $1.35 \pm 0.05$ ) and the calculated results of DeMarcus and Starnes<sup>42</sup> (1.32).

Mean free path values obtained through the relationships listed above at standard conditions are presented in Table 28. Also given are values which were used in the calculations of the physical properties and constants at standard conditions. In the list of the mean free path values, it is apparent that values are of the same order of magnitude. The values obtained from viscosity and thermal conductivity data agree with those obtained from the dimensionless quantity. The mean free path values calculated from thermal conductivity and viscosity data are 13 and 30 percent lower, respectively, than those calculated using the dimensionless quantity. Values were also obtained from viscosity, thermal conductivity, and dimensionless quantity data at temperatures of  $0^\circ$ ,  $30^\circ$  and  $130^\circ\text{C}$ . for pressures ranging from 0.2 to 2.0 atmospheres. These values are presented in Table 29 and Figure 11.

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\*Jeans, J. H. The Dynamic Theory of Gases. 4th ed. London, Dover Publications, Inc., 1954.

## INTERMOLECULAR FORCE MODELS

A number of force models for  $\text{UF}_6$  molecules have been proposed by various investigators in their attempts to describe the behavior of the vapor by correlating experimental values of the transport properties; i.e., viscosity, self-diffusion, and thermal conductivity. The force models and the values of the constants which were employed are listed in Table 30.

Even though on the basis of the kinetic theory of gases it appears that the dimensionless quantity,  $\rho D/\eta$ , should be equal to a constant,  $\epsilon$ , which is dependent on the forces between the molecules in a vapor, force laws based on values of the dimensionless quantity alone are likely to give ambiguous results. Amdur<sup>6</sup> briefly summarized the reasons for the ambiguity as follows: "First at laboratory temperatures, the transport properties of gases depend upon molecular inter-actions which must be represented as a combination of attractive and repulsive forces. Second, it is possible to obtain essentially the same  $\rho D/\eta$  values for different molecular-force models which are not demonstrably equivalent." Since most of the force models which have been proposed for  $\text{UF}_6$  are based, primarily, on viscosity data, the models and data based on them should be used with caution. Of the force models which have been proposed, the Lennard-Jones 6-12 model, fitted with force constants which were estimated from viscosity measurements, from empirical correlations, from the free-volume theory of liquids, and from existing estimates of the second virial coefficient, appears to describe the behavior of  $\text{UF}_6$  molecules most satisfactorily.

DeMarcus and Starnes<sup>42</sup> employed the Lennard-Jones 6-12 force model to derive an approximate expression for the intermolecular potential between two  $\text{UF}_6$  molecules the mass centers of which are  $R(\text{cm.})$  apart:

$$\phi(R) = \frac{9.9937 \times 10^{-101}}{R^{12}} - \frac{4.9216 \times 10^{-57}}{R^6} \text{ ergs} \quad (38)$$

This expression was estimated from viscosity measurements obtained from empirical correlations, from the free-volume theory of liquids, and from existing estimates of the second virial coefficient. The expression is reported to be independent of isotopic species and of relative orientation of the two molecules. The dimensionless quantity,  $\rho D/\eta$ , was determined by using theoretically derived values of the parameters  $\epsilon$  and  $R_0$  of the Lennard-Jones 6-12 model in the form:

$$\phi(R) = 4\epsilon [ (R_0/R)^{12} - (R_0/R)^6 ] \text{ ergs} \quad (39)$$

For the values  $\epsilon/k = 439^\circ\text{K}$ . and  $R_0 = 5.2232 \times 10^{-8} \text{ cm.}$ , the dimensionless quantity was determined to be 1.32. This value was found to be in agreement with the experimental results (1.36) which were calculated from the viscosity data of Myerson and Eicher<sup>116</sup> and the  $\rho D$  data of Ney and Armistead<sup>117</sup>. Values of theoretical viscosities, computed using the above values of  $\epsilon/k$  and  $R_0$  and the equation given by Hirschfelder, Bird, and Spots\* for the viscosity of a single component gas, were found to compare favorably with the experimental viscosity values obtained by Myerson and Eicher.

McMillan<sup>114</sup> applied the inverse force model, in which the interaction force has only one repulsion term,  $F = Xr^{-9}$ , in an attempt to explain the behavior of  $\text{UF}_6$  vapor between 40° and 200°C. From this force model, the viscosity can be represented by:

$$\eta = AT^n = \frac{5}{8} \left( \frac{kmT}{\pi} \right)^{1/2} \left( \frac{2kT}{X} \right)^{2/\nu-1} A_2(\nu) \Gamma \left( 4 - \frac{2}{\nu-1} \right) \quad (40)$$

\*Hirschfelder, J. O., Bird, R. D., and Spots, E. L. J. Chem. Phys. **16**, 968(1948).

Using the viscosity data reported by Myerson and Eicher, McMillan obtained  $A = 0.6163$  and  $n = 0.933$ , or:

$$\eta = 0.6163 T^{0.933} \quad (41)$$

From Equation 40 and the equations for force and the potential energy of the inverse force model, McMillan obtained the values  $\nu = 5.6$  and  $\epsilon = 1.529$  or:

$$\rho D/\eta = 1.529 \quad (42)$$

The value of  $\rho D$  at 30°C. calculated from Equation 42 does not compare favorably with the experimental value.

Treating the potential energy function,  $U(r) = \lambda r^{-8}$ , of the inverse force model as having spherical symmetry, McMillan calculated the second virial coefficient,  $B_V$ , in the equation of state:

$$PV = A_V + B_V V^{-1} + C_V V^{-2} \quad (43)$$

by means of the expression:

$$B = \frac{2\pi}{3} \Gamma \left[ \frac{S-3}{8} \right] \left[ \frac{\lambda}{kT} \right]^{3/8} \quad (44)$$

in which  $B_V/A_V = B\nu_O$  and  $\nu_O$  is the density of molecules for each cubic centimeter under normal conditions, resulting in:

$$\log B_V/A_V = -1.383 - 0.653 \log T \quad (45)$$

From Equation 45, the value of  $B_V/A_V$  at 0°C. is of the order of  $10^{-3}$ , indicating that  $UF_6$  behaves as an ideal gas in the first approximation.

Kigoshi<sup>30</sup> obtained estimates of the molecular diameter, the rigidity, and the Sutherland constant for  $UF_6$  vapor by fitting the experimental viscosity values to the Sutherland formula:

$$\eta = C T^{3/2} / (T + S) \quad (46)$$

by using the constants  $C = 28.44 \times 10^{-6}$  and  $S = 566.8$

where:

$$C = 5/16 \sigma^2 (km/\pi)^{1/2} \quad (47)$$

From Equation 47, where  $k$  is the Boltzmann constant,  $\sigma$  is the molecular diameter, and  $m$  is the mass of the molecule, the value of the molecular diameter,  $\sigma = 4.29 \text{ \AA}$ , of  $UF_6$  was obtained. Assuming the observed viscosities are proportional to  $T^S$ , Kigoshi set  $S$  equal to 1.16 and determined the rigidity,  $\nu$ , of the molecule from the equation:

$$S = 1/2 + 2/(\nu-1) \quad (48)$$

and

$$\nu = 4.03$$

These values should be also used with caution, for as Amdur<sup>6</sup> pointed out, the temperature variation of the coefficient of viscosity,  $\eta \propto T^{[1 + 2/(\nu-1)]}$ , for point-repelling molecules provides no better information about the law of force than does the ratio  $\rho D/\eta$  or the temperature dependence of "D" if it were known.

Cohen<sup>37</sup> employed the repulsive force law,  $f = \lambda_n/r^n$ , where  $\lambda_n$  is the force constant and  $r$  is the distance between molecules, and the viscosity data which was then available to determine the values of the dimensionless quantity and the values of  $n$ . These values are listed in Table 30. Cohen also employed the attraction-repulsion force law,

Table 30  
FORCE LAW CONSTANTS

Temperature (°C.)	Force Model	$\rho D/\eta$	$\eta$	S	$\lambda$ (erg cm. <sup>12</sup> )	$\mu$ (erg cm. <sup>6</sup> )	Reference
30	Inverse Force (Eq. 38) and the Attractive-Repulsive type (Eq. 39).	1.31	20	29	--	--	38
		1.16	--	--	--	--	38
		1.18	--	--	--	--	38
30 to 200	Lennard-Jones 6-12 (Eq. 40)	1.32	--	--	$9.9937 \times 10^{-101}$	$4.9216 \times 10^{-57}$	42
15 to 50	Sutherland (Eq. 41)	--	--	566.8	--	--	90
40 to 200	Inverse Force (Eq. 38)	1.529	8	--	--	--	114
0 to 200	Sutherland (Eq. 41)	--	--	101	--	--	135

$f = \lambda_n/r^n - \lambda_3/r^5$ , where  $\lambda_n$  and  $\lambda_3$  are the force constants for attraction and repulsion, respectively. Using this force law, the viscosity can be represented by:

$$\eta = (C T^{1/2} b) / (T^b + S) \quad (\text{poise}) \quad (49)$$

where C is a constant, S is the Sutherland constant, and  $b = 1/2 + 2/(n-1)$ . Taking  $n = 20$ , Cohen found that  $S = 29$ . The constant C was chosen so that the viscosity values calculated from Equation 49 agree with those reported by Llewellyn. However, despite this agreement, Cohen felt that a repulsive force field varying as  $1/r^{20}$  seemed rather "hard" for the  $UF_6$  molecule and therefore recommended further measurement of the transport properties.

## THERMODYNAMIC PROPERTIES

The thermodynamic properties of  $UF_6$  discussed here have been obtained mostly from primary literature sources. These properties, in some cases, have been determined directly by experimentation. An indirect method, using other related data, was resorted to in other cases.

The heat capacities of the solid and of the liquid have been measured from  $14^\circ$  to  $370^\circ K$ . These values are reported as being reliable within one percent. The entropies, enthalpies, and free energy functions of the solid and of the liquid have been calculated from the experimental values of the heat capacity.

The thermodynamic properties of the vapor have been determined over the range  $100^\circ$  to  $1000^\circ K$ . from vibrational spectra together with the interatomic distances using statistical mechanics. These properties have also been determined using the heats of vaporization and sublimation, and the third law addition of entropies. The original comparison<sup>20</sup> of the thermodynamic properties obtained by these two methods in the range from  $273^\circ$  to  $348^\circ K$ . revealed slight discrepancies, although a recent comparison<sup>144</sup> of these properties in the range from  $273^\circ$  to  $370^\circ K$ . using later and more precise data revealed a more favorable agreement. In the latter comparison a non-ideality parameter was used to define the gas imperfection.

The heats of vaporization and sublimation have been measured experimentally from  $273^\circ$  to  $370^\circ K$ . and have also been calculated from vapor pressure data using the Clapeyron equation. The values obtained experimentally do not compare favorably with the calculated values which should be considered more reliable. From the heat values, the entropies of vaporization and sublimation have been calculated assuming that the heat change involved is both isothermal and reversible.

The heat of fusion has been measured calorimetrically and has also been calculated from the heats of vaporization and sublimation. The value obtained by measurement is in agreement with the calculated value.

Some of the basic thermodynamic properties have been covered in fairly recent compilations by others. These sources contain "selected" thermodynamic properties, with extrapolations to cover a larger temperature range. They contain useful applications of the thermodynamic data. Therefore, a few of them should be mentioned. The National Bureau of Standards circular, The Selected Values of Chemical Thermodynamic Properties<sup>22</sup>, contains a tabulation of the "best" thermodynamic values of  $UF_6$  for such properties as the heats of transition, fusion and vaporization.

An Argonne National Laboratory survey, The Thermodynamic Properties of the Fluorides, Chlorides, and Oxides of the Elements to  $2500^\circ K$ ,<sup>67</sup> lists empirical heat capacity equations which are used to determine the free energy of formation of the various fluorides, chlorides, and oxides of the elements. The constants of the empirical equations were obtained either from experimental data or by some theoretical, semi-empirical approach. Other thermodynamic data relating to enthalpy, entropy, free energy functions, and the like were obtained by the appropriate integrations. The Argonne publication also contains diagrams showing the free energy of formation versus temperature from which stability relations existing between compounds of a given type can be quickly obtained. A less recent report, The Thermodynamic Properties of Uranium Halides, Oxides, Nitrides, and Carbides<sup>23</sup>, also contains some rather useful applications of the thermodynamic properties.

The Carrier report, P. G. Thermodynamic Properties<sup>131</sup>, is an attempt at establishing a self-consistent set of thermodynamic data for the vapor to fit the various known isolated data. Assuming that  $\text{UF}_6$  behaves nearly as a perfect gas, enthalpy, relative pressure, relative volume, specific heat, ratio of specific heats, viscosity, and acoustic velocity were derived and tabulated as a function of temperature.

### HEAT CAPACITY

The heat capacity of solid and liquid  $\text{UF}_6$  which have been measured in the temperature range from  $14^\circ$  to  $370^\circ\text{K}$ . are represented, in part, by Equations 50 and 51. These values, which are reliable to within one percent, are presented in Table 31 and Figures 12 and 13. Other less reliable values are listed in Table 32.

The heat capacity values of  $\text{UF}_6$  vapor have been determined by two methods: first, from thermodynamic functions of the solid and liquid and vapor pressure data utilizing the third law addition of entropies; and second, from the vibrational spectra using statistical mechanics. Although the more reliable values (listed in the first three columns of Table 33) obtained by using these two methods are in reasonable agreement, it should be kept in mind that even better agreement<sup>144</sup> could be obtained if the most recent data reported were employed in the computations.

### HEAT CAPACITY OF THE SOLID AND THE LIQUID

Brickwedde, Hoge, and Scott<sup>24</sup> measured the heat capacity,  $C_p$ , of solid and liquid  $\text{UF}_6$  under its own vapor pressure from  $14^\circ$  to  $370^\circ\text{K}$ . using a special fluted copper calorimeter. The corrugations in the calorimeter allowed for a ten percent increase in the volume of the material at temperatures near its melting point. Vapor corrections to both the heat capacity and the heat of fusion values were applied according to the procedure outlined by Hoge\*.

The vapor pressure data of Crist and Weinstock and those of Simon (see page 86) were found to intersect at  $64.052^\circ\text{C}$ ., the triple point temperature. At this temperature, the vapor pressure equations yield a triple point pressure of 1142 mm. Hg. A maximum vapor pressure correction of 5 percent was determined near the triple point. Extrapolation of the molar heat capacity of  $\text{UF}_6$  from  $14^\circ$  to  $0^\circ\text{K}$ . was made on the basis of the Debye-Einstein specific heat functions. In considering the error arising from experimental measurements and from possible impurities, the authors felt that the  $C_p$  data should be reliable to approximately one percent.

Kirshenbaum<sup>93</sup> converted the units of the original heat capacity data which are joules/mole deg. to units of cal./mole deg. by use of the factor 4.1833 calories = 1 international joule. The values derived are presented in Table 31.

The heat capacity-temperature relationships of solid and liquid  $\text{UF}_6$  determined from the enthalpy-temperature equations obtained by Kirshenbaum<sup>93</sup> from the experimental data of Brickwedde and his co-workers are:

#### Solid ( $250^\circ$ to $337.212^\circ\text{K}$ .)

$$C_p = [20.0827 + 161.158 \times 10^{-3}T + 104.792 \times 10^4/T^2] \text{ cal./mole deg.} \quad (50)$$

(deviates less than one percent from the experimental results for the stated temperature range)

\*Hoge, H. J. J. Research Natl. Bur. Standards **36**, 111 (1946).

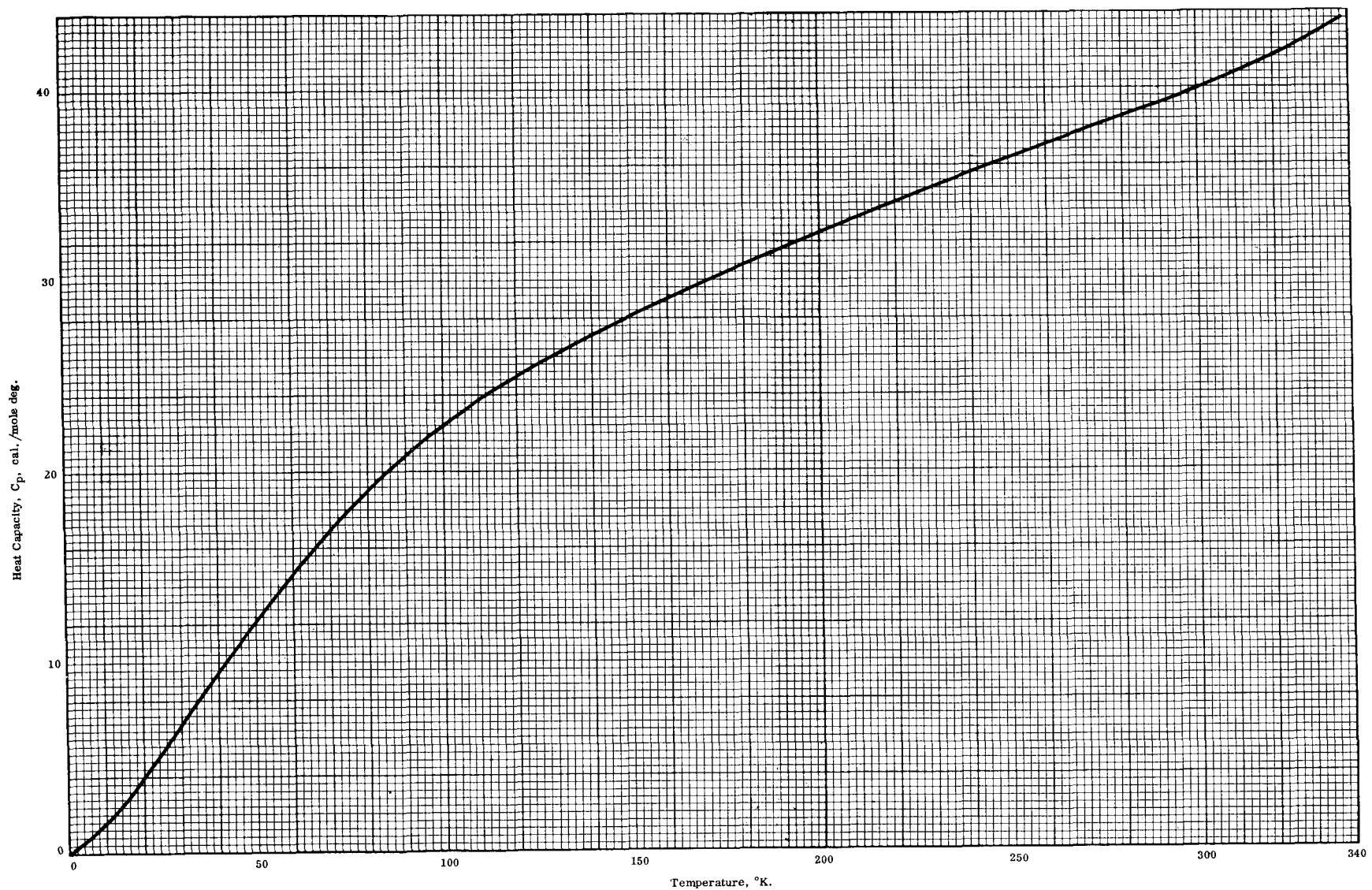


FIG. 12. HEAT CAPACITY OF THE SOLID  
(Reference 24)

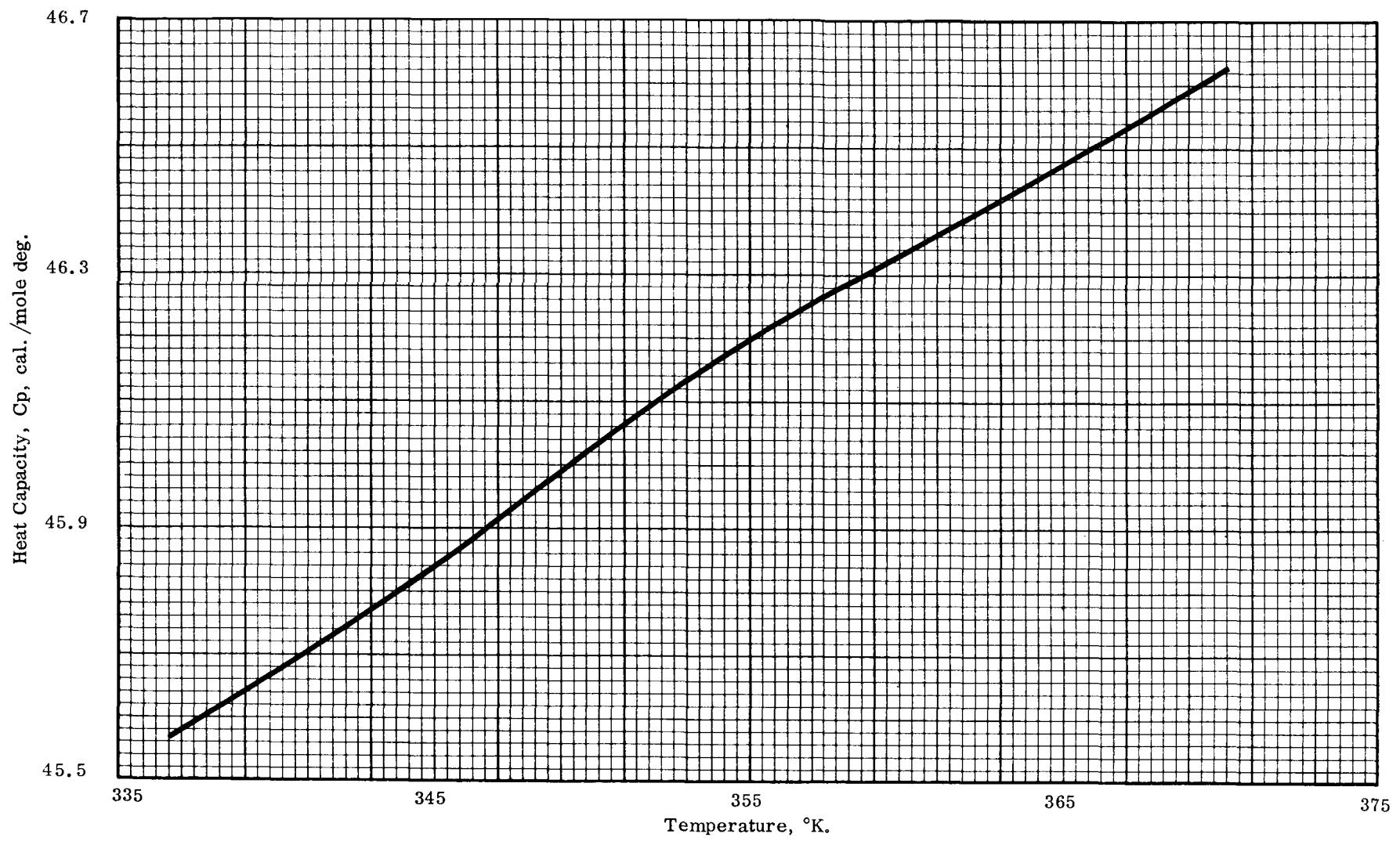


FIG. 13. HEAT CAPACITY OF THE LIQUID  
(Reference 24)

Table 31  
THERMODYNAMIC PROPERTIES OF THE SOLID AND THE LIQUID  
(Reference 88)

Temperature (°K.)	Cp (cal./mole °C.)	H - H <sub>0</sub> (cal./mole)	S - S <sub>0</sub> (cal./mole °C.)	T (S - S <sub>0</sub> ) (cal./mole)
SOLID				
0	0	0	0	0
20	4.06	28.0	1.96	39
25	5.53	52.0	3.04	76
30	6.92	83.2	4.16	125
35	8.27	121.1	5.33	187
40	9.64	165.9	6.53	261
45	11.00	217.5	7.72	347
50	12.34	275.9	8.96	448
55	13.66	304.9	10.21	562
60	14.90	412.4	11.45	687
65	16.07	489.8	12.69	825
70	17.16	572.8	13.91	974
75	18.22	661.4	15.13	1,135
80	19.20	754.9	16.35	1,308
85	20.14	853.9	17.55	1,492
90	20.99	956.2	18.72	1,685
95	21.76	1,063	19.86	1,887
100	22.49	1,174	20.99	2,099
105	23.17	1,288	22.11	2,322
110	23.82	1,405	23.21	2,553
115	24.46	1,526	24.29	2,793
120	25.08	1,650	25.34	3,041
125	25.66	1,777	26.37	3,296
130	26.23	1,907	27.39	3,561
135	26.77	2,039	28.40	3,834
140	27.30	2,174	29.38	4,113
145	27.80	2,312	30.33	4,398
150	28.30	2,452	31.29	4,694
155	28.78	2,595	32.22	4,994
160	29.24	2,740	33.16	5,306
165	29.71	2,887	34.04	5,617
170	30.15	3,037	34.95	5,942
175	30.60	3,189	35.83	6,270
180	31.03	3,343	36.69	6,604
185	31.42	3,499	37.55	6,947
190	31.87	3,657	38.39	7,294
195	32.27	3,818	39.23	7,650
200	32.65	3,980	40.04	8,008
205	33.05	4,144	40.85	8,374
210	33.46	4,310	41.67	8,751

Table 31 (Continued)  
 THERMODYNAMIC PROPERTIES OF THE SOLID AND THE LIQUID  
 (Reference 88)

Temperature (°K.)	Cp (cal./mole °C.)	H - H <sub>0</sub> (cal./mole)	S - S <sub>0</sub> (cal./mole °C.)	T (S - S <sub>0</sub> ) (cal./mole)
SOLID				
215	33.78	4,479	42.45	9,127
220	34.22	4,648	43.24	9,513
225	34.60	4,820	44.01	9,902
230	34.96	4,994	44.77	10,296
235	35.34	5,170	45.51	
240	35.70	5,348	46.28	11,107
245	36.07	5,527	47.02	11,520
250	36.43	5,708	47.74	11,935
255	36.78	5,892	48.48	12,362
260	37.14	6,067	49.20	12,792
265	37.50	6,263	49.89	13,221
270	37.86	6,451	50.61	13,665
273.16	38.08	6,571	51.05	13,942
275	38.22	6,640	51.30	14,108
280	38.56	6,833	51.99	14,557
285	38.90	7,027	52.69	15,017
290	39.24	7,223	53.36	15,474
295	39.61	7,420	54.02	15,936
298.16	39.86	7,545	54.45	16,235
300	40.00	7,619	54.69	16,407
305	40.42	7,820	55.36	16,885
310	40.87	8,023	56.03	17,369
315	41.33	8,229	56.68	17,854
320	41.80	8,437	57.35	18,352
325	42.27	8,648	57.99	18,847
330	42.77	8,860	58.64	19,351
335	43.27	9,076	59.28	19,859
337.212	43.49	9,172	59.57	20,088
LIQUID				
337.212	45.59	13,760	73.17	24,674
340	45.68	13,888	73.55	25,007
345	45.84	14,118	74.22	25,606
350	46.02	14,348	74.89	26,212
355	46.20	14,579	75.54	26,817
360	46.33	14,811	76.18	27,425
365	46.48	15,044	76.83	28,043
370	46.62	15,278	77.45	28,657

Liquid (337.212° to 370°K.)

$$C_p = [17.954 + 65.028 \times 10^{-3}T + 66.699 \times 10^4/T^2] \text{ cal./mole deg.} \quad (51)$$

$$C_p = [18.0855 + 0.126985T - 1.3476307 \times 10^{-4}T^2] \text{ cal./mole deg.} \quad (51a)$$

(Values calculated from Equation 51 deviate less than 0.6 percent from the experimental values for the stated temperature range)

Equation 51a was obtained by fitting the actual heat capacity values to a temperature function. This equation is more representative of the experimental heat capacity values than is Equation 51.

Glassner<sup>87\*</sup> expressed the experimental heat capacity data of solid  $UF_6$  by the equation:

$$C_p = [12.34 + 92.23 \times 10^{-3}T] \text{ cal./mole deg.} \quad (52)$$

which represents the experimental data within 0.2 percent in the temperature range 300°K. to 337.212°K.

Other reported values of the heat capacity of the solid and liquid found in the literature differ somewhat from those reported by Brickwedde and his co-workers. Llewellyn<sup>107</sup> determined the heat capacity values of the solid and the liquid using a copper calorimeter. The results, which are reported to have an estimated error of one percent, deviate from the results of Brickwedde and his co-workers for the solid at 333°K. and for the liquid at 373°K. by approximately 5 percent. The heat capacity values of the solid reported by Llewellyn<sup>107</sup> and others<sup>47, 50</sup> are listed in Table 32. Heat capacity values of the liquid in the temperature range 343° to 373°K. are expressed by the equation:

$$C_p = [47.3 + 0.347(t^{\circ}\text{C.} - 70)] \text{ cal./mole deg.} \quad (53)$$

Values of the heat capacity obtained from Equation 53 are somewhat higher than those given by Brickwedde and his co-workers.

HEAT CAPACITY OF THE VAPOR

Bigeleisen and his co-workers<sup>20</sup> and more recently Gaunt<sup>65</sup> calculated the heat capacity of the vapor from the fundamental frequencies which were assigned to the vibrational spectra of  $UF_6$ . For calculation of the heat capacity from fundamental frequencies, the structure of  $UF_6$  was taken as that of a regular octahedron in which the uranium-to-fluorine distance is 2.00 Å and the symmetry number is 24. Since the fundamentals assigned by Bigeleisen and his co-workers differ only slightly from those assigned by Gaunt, the thermodynamic functions calculated from the two sets of fundamentals are in agreement. Claassen, Weinstock, and Malm<sup>38</sup> confirmed the thermodynamic functions obtained by Gaunt. Since they obtained, from the Raman spectrum, fundamentals which agreed very well with those determined by Gaunt, they found no need to revise Gaunt's thermodynamic calculations.

\*Glassner stated in a private communication that values of the constants a and b for  $UF_6$  (solid) given on the last page of Table III of his report are incorrect. The correct values may be obtained by dropping the entire tabulation for columns a, b, c, and d two lines, beginning with  $UF_3$ . The insertions intended for  $UF_3$  are as follows:

	<u>a</u>	<u>b</u>	<u>c</u>	<u>d</u>	<u>A</u>	<u>B</u>
solid	20.8	7.2			6.522	94.6
liquid	34				7.596	175.5

Table 32  
OTHER SOLID AND LIQUID HEAT CAPACITY VALUES

Temperature (°K.)	<u>C<sub>p</sub> (cal./mole deg.)</u>	
	Llewellyn (Ref. 107)	Simon (Ref. 135)
<u>SOLID</u>		
213.2	--	29.5
223.2	34.2	--
233.2	34.6	30.4
253.2	35.7	31.7
273.2	37.0	33.5
293.2	39.0	36.2
303.2	--	38.0
313.2	41.8	40.5
323.2	--	44.0
333.2	44.5	--
<u>LIQUID</u>		
343.2	47.4	--
353.2	48.1	--
363.2	48.8	--
373.2	49.5	--

However, it should be mentioned that Weinstock and his co-workers<sup>144</sup> re-evaluated both the fundamental frequencies and the U-F distance. They found that the thermodynamic data calculated by using the new frequencies gave better comparisons than were made by earlier workers. Their calculations of the thermodynamic data based on the third law of thermodynamics were made using the vapor pressure data of Oliver and his co-workers<sup>119</sup> and a correction for the gas imperfection.

The heat capacity values determined by Gaunt<sup>65</sup> were found to agree with the corrected experimental data of Arms<sup>135</sup>, who determined the heat capacity of the vapor using an apparatus of the type devised by Blackett, Henry, and Rideal\*. The method used gives values which are relative to those of vapors of known heat capacity. Arms' results, however, were shown to be erroneous. Gaunt found that the errors in Arms' results were caused by neglect of a factor which depends on the nature of the vapor. By making the proper corrections and using the value 6.98 cal./mole deg. for the heat capacity of air at 25°C., Gaunt calculated the corrected experimental heat capacity value for UF<sub>6</sub> at 25°C. as 30.5 cal./mole. This value compares favorably with the value of 30.9 cal./mole

\*Blackett, P. M. S., Henry, P. S. H. and Rideal, E. K. Proc. Roy. Soc. 126A, 319 (1930).

which was determined from the spectral data. Unfortunately, the data available to Gaunt were not sufficient for complete revision of the heat capacity values which were determined by Arms at other temperatures.

Booth, Callihan, and Haggstrom<sup>22</sup> also measured the heat capacity of  $\text{UF}_6$  vapor by a continuous flow method similar to that described by Blackett, Henry, and Rideal. The investigation was conducted at 52.5°C. and 12.7 cm. Hg. The measurement of the heat capacity was related to hydrogen and to air which at the conditions of the investigation have specific heats of  $4.36 \times 10^{-5}$  and  $4.29 \times 10^{-5}$  cal./deg., respectively. They reported a value of  $29 \pm 1$  cal./mole. Nordsieck<sup>22</sup> also estimated the heat capacity of the vapor from the molecular data. Vibrational frequencies of  $\text{UF}_6$  were estimated by extrapolation from the known series of molecules of  $\text{SF}_6$ ,  $\text{SeF}_6$  and  $\text{TeF}_6$ . The averaged distance,  $d$ , from the central atom to fluorine was also determined by extrapolation and found to be 1.98 Å. The structure of  $\text{UF}_6$  was assumed to be a regular octahedron. The values of the heat capacities along with the estimated deviation of the mean which were obtained by Nordsieck are presented in column 6 of Table 33.

Duncan<sup>44</sup> calculated heat capacity values at various temperatures from estimated frequencies of Raman spectra, moments of inertia, and a symmetry number of 24. These values are presented in column 8 of Table 33.

Kirshenbaum<sup>93</sup> derived Equation 54 for the heat capacity of  $\text{UF}_6$  vapor from thermodynamic functions and the vapor pressure-temperature relationships of the condensate:

$$C_p \text{ (vapor)} = [32.43 + 7.936 \times 10^{-3}T - 32.068 \times 10^4/T^2] \text{ cal./mole deg.} \quad (54)$$

Values of the heat capacity are presented in column 4 of Table 33. The more reliable values are shown in Figure 14.

Table 33  
HEAT CAPACITY OF THE VAPOR

Temperature (°K.)	Bigeleisen and Mayer* (Ref. 20)	Gaunt† (Ref. 65)	Calculated from Equation 54 (Ref. 65)	Arms (Ref. 135)	Nordsieck (Ref. 22)	Booth, et al.‡ (Ref. 22)	Duncan§ (Ref. 44)
100	18.93	16.76					
150	23.45	23.32					
200	26.74	26.62					
250		29.12	29.28				
273	30.13	30.05	30.29				29.7
273.2					29.2 ± 1.0		
298	31.00	30.93	31.18				
298.2					33.5 ± 1 <sup>†</sup> (30.5) <sup>‡</sup>		
323	31.75	31.68	31.92				31.4
323.2					30.1 ± 1.0	29 ± 1	
348	32.38	32.32	32.54	34.5 ± 1 <sup>†</sup>			
348.2					30.8 ± 0.5		
373	32.93						32.8
398		33.36	33.56				
398.2					35.5 ± 1 <sup>†</sup>		
400	33.46	33.40					
500	34.80	34.77	35.12				
650			36.83				
750	36.35						
1000	36.94						

\*Calculated from vibration spectra.

†Calculated from infrared spectra.

‡Experimental values.

§Corrected value calculated by Gaunt.

¶Estimated from measured vibrational frequencies of  $\text{SF}_6$ ,  $\text{SeF}_6$ ,  $\text{TeF}_6$  and  $\text{UF}_6$ .

†Measured relative to both hydrogen and air heat capacity values.

‡Calculated from Raman spectra.

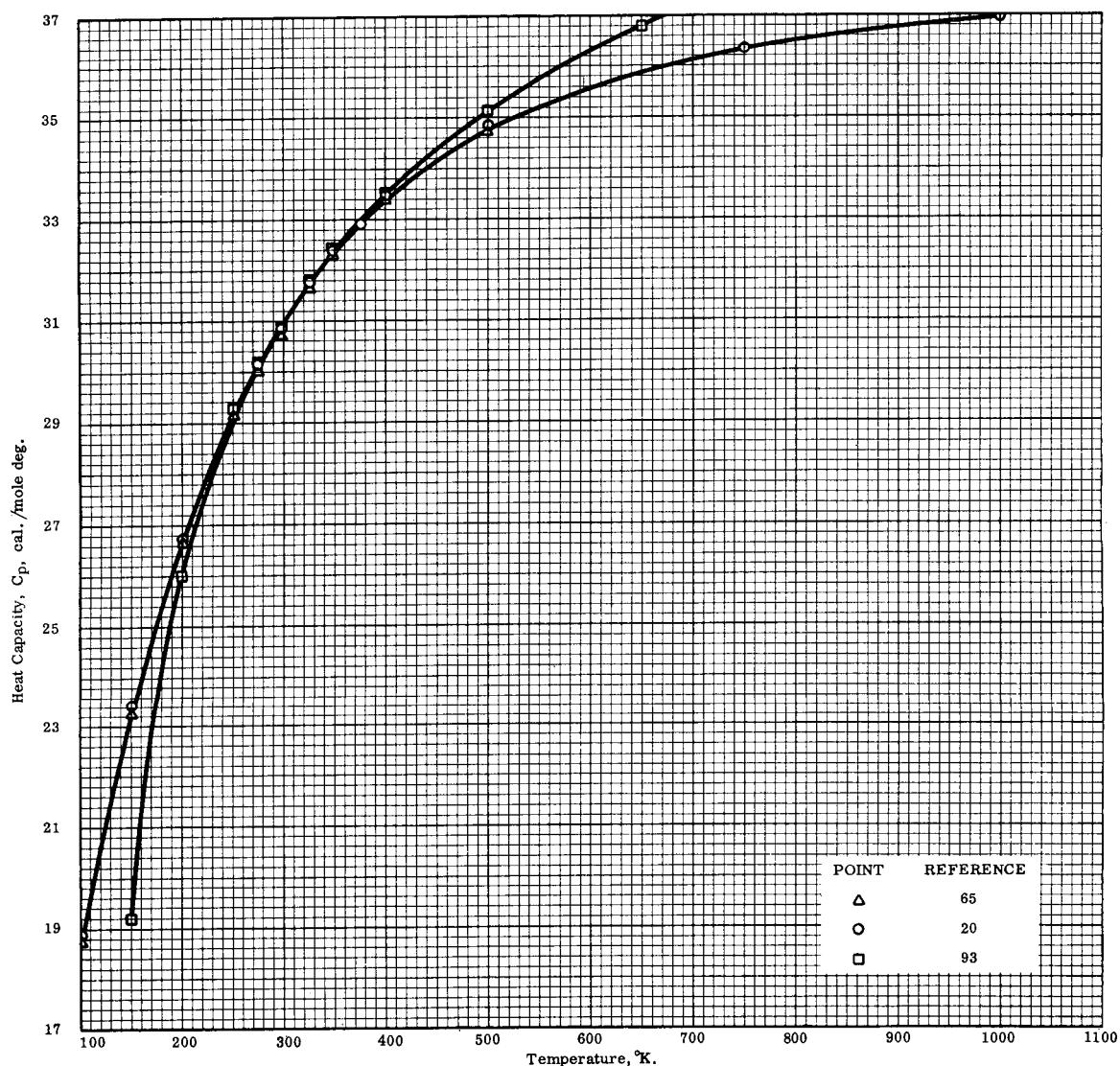


FIG. 14. CALCULATED HEAT CAPACITY OF THE VAPOR

#### HEAT CAPACITY RATIO

Values of the heat capacity ratio reported in the literature were estimated in two ways:

(1) from experimental values of the velocity of sound,  $\mu$ , using the equation:

$$C_p/C_v = \mu^2 (\partial P/\partial T)_P \quad (55)$$

where  $P$  is the pressure and  $\rho$  is the vapor density; and

(2) from the heat capacity at constant pressure,  $C_p$ , using the equation:

$$C_p/C_v = C_p / (C_p - R) \quad (56)$$

where  $R$  is the gas constant. Equation 56 is based on the assumption that the behavior of  $UF_6$  vapor is the same as that predicted by the ideal gas law.

Values of  $C_p/C_v$  at 49.2°C. obtained using Equation 55 are in agreement with those obtained using Equation 56 and are found to range between 1.062 and 1.067.

The quantity  $(\partial\rho/\partial P)_{49.2^\circ\text{C}}$  was experimentally determined at various pressures by Amphlett, Mullinger, and Thomas<sup>9</sup>. It was found that

$$(\partial P/\partial\rho)_{49.2^\circ\text{C.}} = 1.32 \times 10^{-8} \text{ sec.}^2/\text{cm.}^2 \quad (57)$$

which is nearly the same, at least within experimental error, as the value predicted by the kinetic theory of gases:

$$(\partial\rho/\partial P)_{49.2^\circ\text{C.}} = 1.314 \times 10^{-8} \text{ sec.}^2/\text{cm.}^2 \quad (58)$$

Chackett<sup>34</sup> determined the velocity of sound in  $\text{UF}_6$  vapor as 8,990 cm./sec. at 49.2°C. with an estimated error of  $\pm 0.2$  percent. Previously, a preliminary mean value of 8,870 cm./sec. was reported<sup>49</sup>. The latter value was determined at 49°C. and at pressures of 326 and 539 mm. Hg using a resonance tube 25 centimeters long and 1.6 centimeters in diameter. The former value was determined at 420 mm. Hg using a similar tube, except that it was wider and longer. Using the value  $\mu = 8,990 \text{ cm.}/\text{sec.}$  and assuming that  $\text{UF}_6$  vapor is ideal, Chackett found that:

$$\begin{aligned} C_p/C_v &= (8,990)^2 (1.314 \times 10^{-8}) \\ &= 1.062 \pm 0.5 \text{ percent*} \end{aligned} \quad (59)$$

Using the experimental value of  $(\partial\rho/\partial P)_{49.2^\circ\text{C.}}$ , the ratio  $C_p/C_v$  was found to be 1.067. From the heat capacity value of  $\text{UF}_6$  vapor at 49.2°C., which was obtained from the heat capacity equation of Kirshenbaum (see page 63) and Equation 51, it was found that  $C_p/C_v = 1.066$ . This value compares favorably with the values given above. Booth and his co-workers reported that an average of the experimental and theoretical values of  $C_p$  at 50°C. yields a value of  $C_p/C_v = 1.073$ .

## ENTHALPY

The enthalpy values of the solid and of the liquid were calculated from the measured heat capacity values by integrating along the saturation curve. The values for the solid which are represented, in part, by Equation 61 and the values for the liquid which are represented by Equation 62 are presented in Table 31 and in Figure 15. The enthalpy of the vapor which was obtained from the calculated entropy function is expressed by Equation 63.

Brickwedde, Hoge, and Scott<sup>24</sup> determined the enthalpies of solid and liquid  $\text{UF}_6$  by integrating

$$dH = C_{\text{sat}} dT + VdP \quad (60)$$

along the saturation curve.  $C_{\text{sat}}$  is the heat capacity of the condensed phase in equilibrium with the saturated vapor. Values of the enthalpies of the liquid and solid are presented in Table 31. Kirshenbaum<sup>93</sup> fitted the enthalpy values of the solid and liquid which were calculated by Brickwedde and his co-workers to the following representative equations:

---

\*The value actually reported by Chackett ( $1.063 \pm 0.5$  percent) was found to contain a slight rounding-off error. Although this error falls within the estimated 0.5 percent error, for mathematical consistency the value has been changed to 1.062 for this report.

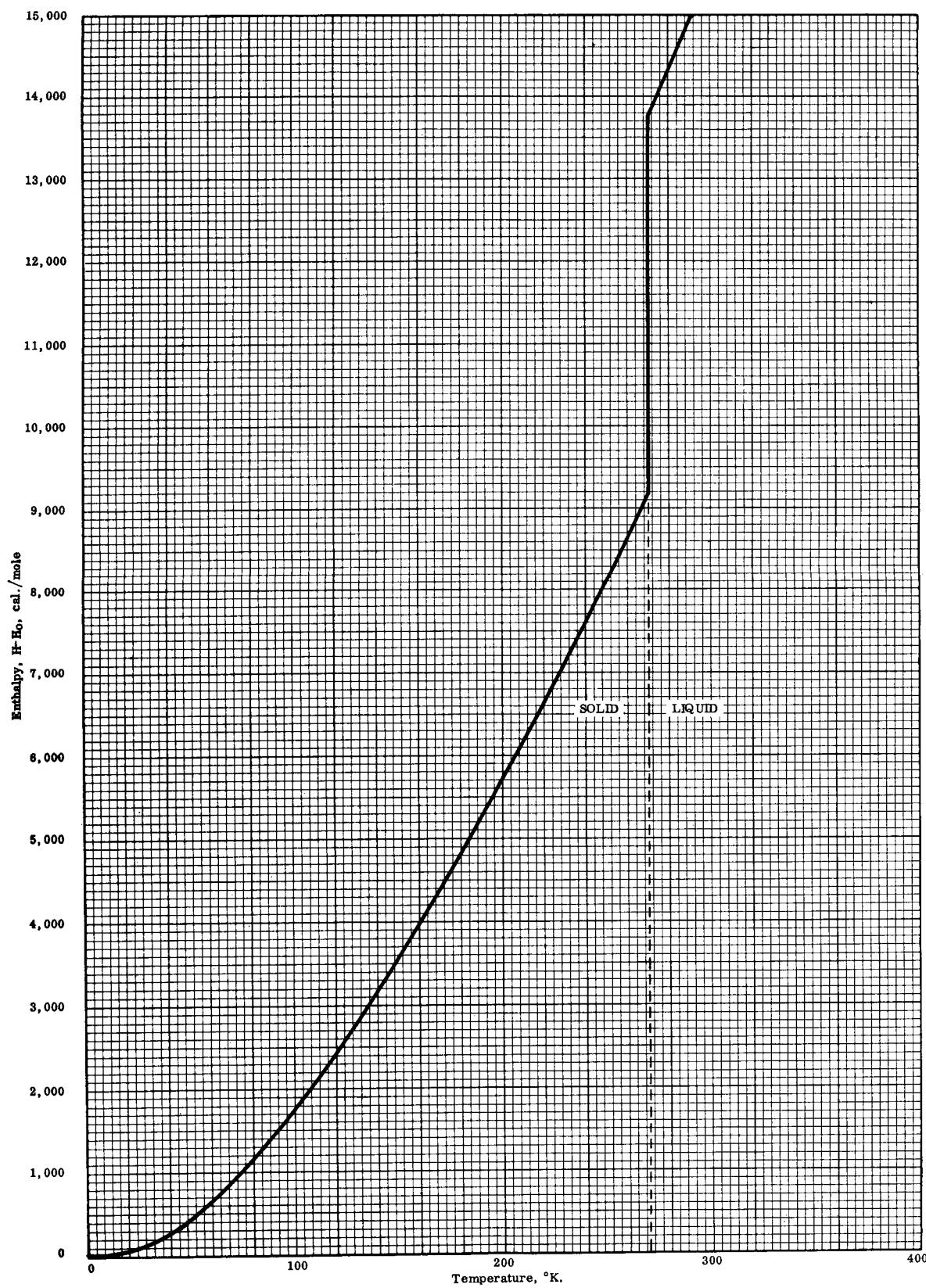


FIG. 15. ENTHALPY OF THE SOLID AND THE LIQUID  
(Reference 24)

Solid

$$H - H_0 = 9865 - 20.082T + 80.790 \times 10^{-3}T^2 - 104.7920 \times 10^4 T^{-1} \text{ cal./mole deg.} \quad (61)$$

(deviates from experimental values by  $\pm 0.01$  percent from  $337.21^\circ$  to  $265^\circ\text{K}$ .  
and by  $\pm 1$  percent from  $265^\circ$  to  $225^\circ\text{K}$ .)

Liquid

$$H - H_0 = 5986.6 + 17.954T + 32.514 \times 10^{-3}T^2 - 66.6990 \times 10^4 T^{-1} \text{ cal./mole deg.} \quad (62)$$

(deviates from experimental values by  $\pm 0.01$  percent).

Vapor

$$H = 8460 + 32.43T + 3.968 \times 10^{-3}T^2 + 32.0680 \times 10^4 T^{-2} \text{ cal./mole deg.} \quad (63)$$

This equation was obtained from the entropy equation of the vapor which was derived from thermodynamic data and vapor pressure equations of the condensate.

**ENTROPY**

An approximate entropy diagram for  $\text{UF}_6$  was constructed by Havlicek<sup>73</sup> from the critical data and the saturated vapor pressure data in the low temperature range. These data are given in a monograph by Katz and Rabinowitch<sup>88</sup>. The diagram shown by Havlicek is reproduced in Figure 16. This diagram should be used with caution, since it was determined using physical constants of uncertain value.

The entropy values of the solid and of the liquid were calculated by Brickwedde and his co-workers<sup>24</sup> from the measured heat capacity values. Entropy values of the vapor were obtained from the vapor pressure data using the third law of thermodynamics and from the fundamental vibrational frequencies using statistical mechanics. These values, which are listed in Table 34, are found to be in reasonable agreement. However, as pointed out before, even better agreement could be obtained if the latest values of the necessary properties<sup>144</sup> (fundamental vibration frequencies, vapor pressure data, etc.) and the non-ideality factor of the vapor are used in calculating the thermodynamic properties.

**ENTROPY OF THE SOLID AND OF THE LIQUID**

Brickwedde and his co-workers<sup>24</sup> determined the entropies of solid and liquid  $\text{UF}_6$  from the experimental values of the heat capacity by integrating the equation:

$$dS = (C/T) dT. \quad (64)$$

Values of the entropy of the solid and of the liquid obtained from Equation 64 are presented in Table 33. Kirshenbaum<sup>93</sup> fitted these values to the following representative equations:

Solid

$$S - S_0 = [126.082 \ln T + 0.16162T - 523,960T^{-2}] \text{ cal./mole deg.} \quad (65)$$

(deviates from experimental results by  $\pm 0.01$  percent  
from  $337.21^\circ$  to  $273.16^\circ\text{K}$ .)

Liquid

$$S - S_0 = [-50.33 + 17.954 \ln T + 0.065028 T - 333,490T^{-2}] \text{ cal./mole deg.} \quad (66)$$

(deviates from experimental results  $\pm 0.01$  percent).

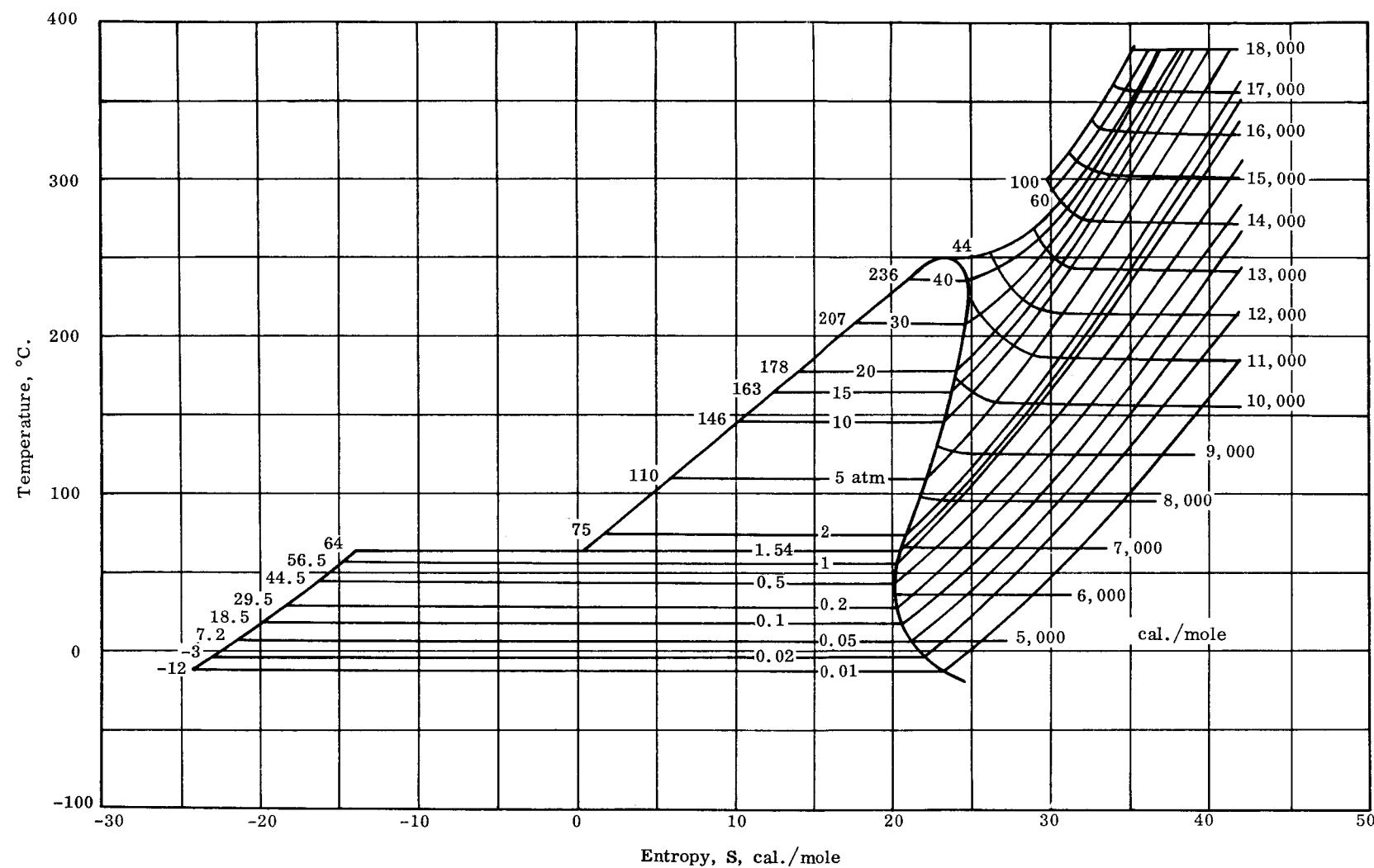


FIG. 16. AN APPROXIMATE ENTROPY DIAGRAM  
(Reference 73)

Table 34  
ENTROPY OF THE VAPOR  
 $S^\circ$  (cal./mole deg.)

Temperature (K.)	Bigeleisen* et al. (Ref. 20)	Masi† (Ref. 113)	Gaunt‡ (Ref. 65)	Weinstock§ et al. (Ref. 142)	Duncan   (Ref. 44)	Kirshenbaum¶ (Ref. 93)	Calculated# Values
100	62.99		62.64				
150	71.58		71.27				
200	78.81		78.34				
250			84.56				
273	87.65		87.19	88.21	86.07	82.27	
273.16	(87.65)	87.56					87.83
280	(88.30)	88.39					88.80
283.16							
290	(89.48)	89.57					89.87
293.16							
298	90.34		89.86	90.76			
298.16	(90.34)	90.50					
300	(90.50)	90.70					90.76
303.16							
310	(91.56)	91.80					91.84
313.16							
320	(92.58)	92.86					92.93
323	92.89		92.39	92.96	91.32	93.59	
323.16							
330	(93.54)	93.87					93.83
333.16							
337.21	(94.20)	94.59					
340	(94.47)	94.88					94.87
343.16							
348	95.22		94.75	94.97			
350	95.40	95.90	94.95				95.84
353.16							
360	(96.30)	96.91					96.75
363.16							
370	(97.20)	97.95					
373	97.47				95.86	98.46	
373.16							97.68
398			99.16				
400	99.86		99.34			100.46	
500	107.45		106.95				
750	122.37						
1000	132.58						

\*Calculated from vibrational spectra. Values in parentheses interpolated from Bigeleisen's entropy table by Masi (Ref. 113) for comparison purposes.

†Calculated from third-law addition of entropies using  $C_{\text{sat}}$  of Brickwedde et al. and assuming  $\text{UF}_6$  an ideal gas. (Ref. 24)

‡Calculated from vibrational spectra (See also Ref. 65).

§Calculated from third-law addition of entropies using  $C_{\text{sat}}$  of Brickwedde et al. and using the Berthelot equation.

||Calculated from estimated Raman frequencies, moments of inertia and symmetry number equal to 24.

¶Calculated from Equation 67, which was derived on the basis of vapor pressure data and other thermodynamic functions.

#Values calculated using the Clapeyron equation, the third-law addition of entropies and the vapor pressure data obtained by Oliver et al.

### ENTROPY OF THE VAPOR

Entropy values of the vapor, which were determined by various methods, are presented in Table 34. Kirshenbaum<sup>93</sup> derived an expression, Equation 67, for the entropy of the vapor from thermodynamic data and vapor pressure equations of the condensate:

$$S_{(1 \text{ atm.})} = [74.69 \log T + 7.935 \times 10^{-3} T + 16.034 \times 10^4 T^{-2} - 98.05] \text{ cal./mole deg.} \quad (67)$$

Values obtained from this equation are in reasonable agreement with those obtained from other sources. Approximate entropy values can be obtained from the curve given in Figure 17.

The entropy of the vapor has been calculated at one atmosphere for temperatures ranging from 0° to 100°C. using the third-law addition of entropies and Equation 68:

$$S^\circ = S_{\text{sat}} + \Delta S_v + \Delta S_{(\text{ideal-real})} + R \ln P \text{ (atm.)} \quad (68)$$

where  $\Delta S_{(\text{ideal-real})} = 27RP(T_c)^3/32P_c(T)^3$

The values of  $S_{\text{sat}}$  are those obtained by Brickwedde and his co-workers. The  $\Delta S_v$  values were obtained from the calculated values of the heats of vaporization and sublimation based on Magnuson's non-ideality parameter and are listed in Table 36 and in Table 37, respectively. The values of the critical constants and the vapor pressure data are those obtained by Oliver and his co-workers<sup>119</sup>.

Weinstock and Crist<sup>142</sup> calculated the entropy of the vapor at several temperatures using measurements of the vapor pressure and a form of the Berthelot equation which incorporated values of the heat of fusion and the heat capacity at the triple point. The values of the various constants used in the calculations are: the triple point temperature,  $T_t = 337.213^\circ\text{K.}$ ; the heat of fusion,  $\Delta H_f = 4588 \text{ cal./mole}$ ; the heat capacity at the triple point,  $\Delta C_p^t = 2.10 \text{ cal./mole}$ ; the critical temperature  $T_c = 518^\circ\text{K.}$ ; and the critical pressure,  $P_c = 36,000 \text{ mm. Hg.}$  Values of the entropy of the vapor determined by Weinstock and Crist are given in Table 34.

Masi<sup>113</sup> calculated the entropy,  $S^\circ$ , of  $\text{UF}_6$  gas (ideal) at one atmosphere from the third-law addition of entropies using entropy values which were calculated from the experimentally determined heats of vaporization and sublimation, using Equation 68 where the  $S_{\text{sat}}$  values used were those obtained by Brickwedde and his co-workers except that values for the liquid were lowered by 0.05 cal./mole deg., corresponding to a change in the heat of fusion from 4588 to 4570 cal./mole. For comparison Masi obtained values of  $S^\circ$  for corresponding temperatures by interpolating in the table calculated by Bigeleisen and his co-workers<sup>20</sup>. These values are listed in parentheses in column 2 of Table 34.

Entropy values calculated from vibrational spectra compare favorably with those obtained by Weinstock and Crist from vapor pressure data. This comparison was first made by Bigeleisen and his co-workers. Entropy values calculated by Bigeleisen and his co-workers are given in column 2 of Table 34; those calculated by Gaunt<sup>65</sup> are given in column 4; and those calculated by Duncan<sup>44</sup> are given in column 6.

### **FREE ENERGY OF THE VAPOR**

The free energy function,  $-(F^\circ - E_0^\circ)/T$ , for  $\text{UF}_6$  vapor was calculated by Bigeleisen and others<sup>20</sup> and more recently by Gaunt<sup>65</sup>. These values, as well as other values calculated by Bigeleisen and his co-workers such as for the thermodynamic properties determined on the basis of the spectral data, compare favorably with each other. Values of  $-(F^\circ - E_0^\circ)/T$  in units of cal./mole deg. for temperatures between 100° and 1000°K. are presented in Table 35.

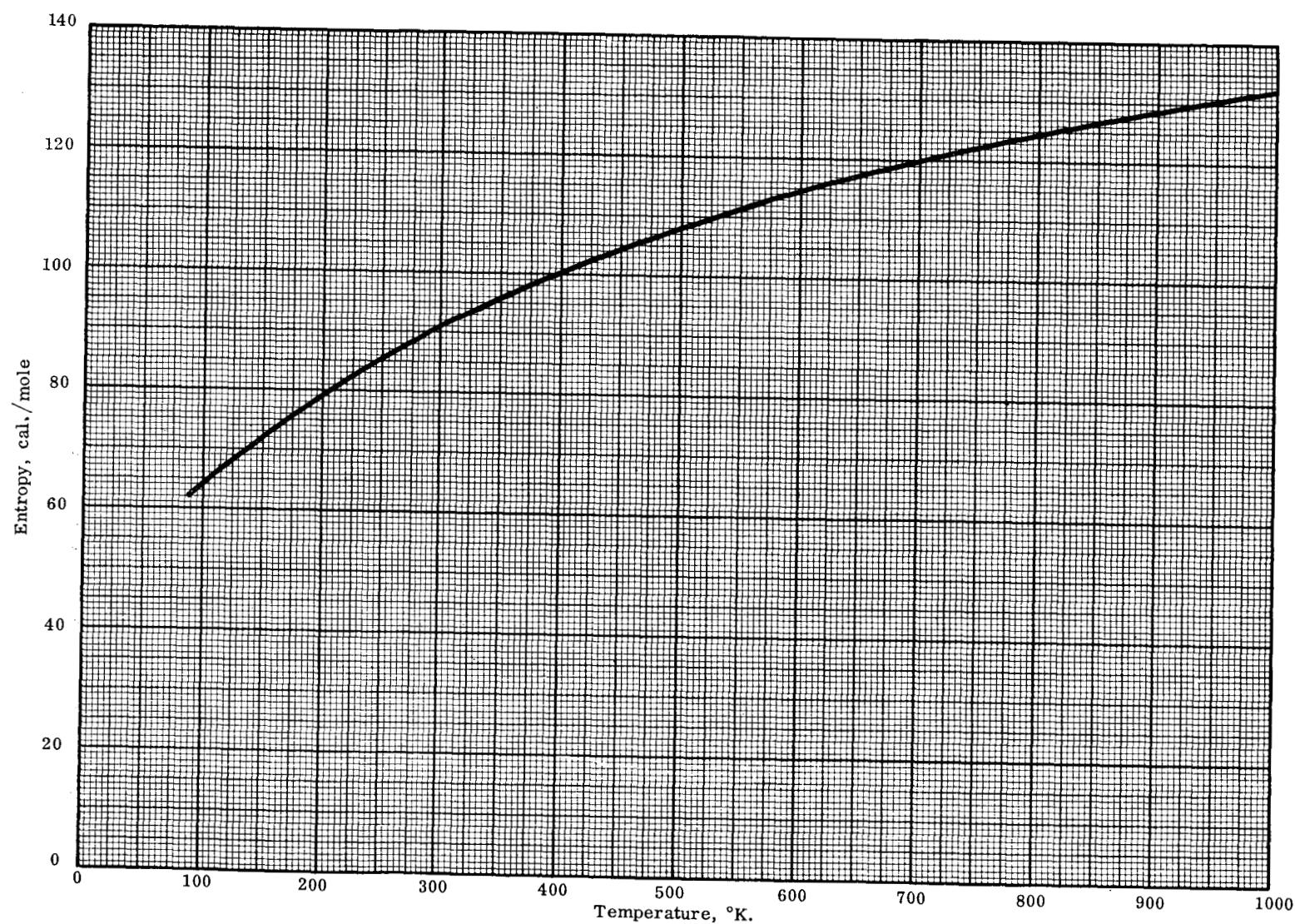


FIG. 17. ENTROPY OF THE VAPOR  
(Reference 20)

Table 35  
FREE ENERGY OF THE VAPOR

Temperature (°K.)	- (F° - E° <sub>0</sub> )/T (cal./mole deg.)	
	Bigeleisen, et al. (Ref. 20)	Gaunt (Ref. 65)
100	50.91	50.74
150	56.41	56.18
200	61.14	60.84
250		64.98
273	67.08	66.75
298	68.92	68.57
323	70.69	
348	72.33	
350		72.12
373	73.93	
400	75.65	72.25
500	81.25	80.85
750	92.99	
1000	101.37	

#### HEATS OF VAPORIZATION AND OF SUBLIMATION

The heats of vaporization and sublimation have been determined by two methods, one a direct calorimetric measurement and the other an indirect method based on vapor pressure data and the Clapeyron equation. Values obtained by these methods are not in the best agreement. Summaries of values for the heat of vaporization and the heat of sublimation are presented in Tables 36 and 37 respectively. Comparisons of the experimental values with values calculated on the basis of the most recent vapor pressure data are presented in Figures 18 and 19.

Masi<sup>113</sup> measured the heats of sublimation and vaporization at temperatures between 4° and 90°C. From these data he calculated the entropies of vaporization and sublimation and the entropy of the ideal gas at one atmosphere (see page 70).

The apparatus, which consisted of a heavy-wall, nickel-plated calorimeter, was tested by obtaining a number of values for the heat of vaporization of water at various temperatures before the measurements were begun. The mean values at 60° and 95°C. were reported to be 0.05 and 0.07 percent smaller, respectively, than the values given by Osborne, Stimson and Ginnings\*.

\*Osborne, N. S., Stimson, H. F. and Ginnings, D. C. J. Research Natl. Bur. Standards 23, 256(1939).

Table 36  
HEATS OF VAPORIZATION  
 $\Delta H_v$  (kcal./mole)

Temperature (°K.)	Calculated on Basis of Vapor Pressure Data of Oliver et al. <sup>119</sup> and the Non-ideality Parameters Proposed by		Weinstock and Crist (Ref. 142)	Simon (Ref. 135)*	Kirshenbaum (Ref. 93)	Masi (Ref. 113)	Cohen (Ref. 38)
	Magnuson	Weinstock					
337.18	6.792						
337.21				6.920 $\pm$ 0.1	7.038	6.859	
338.16	6.764						6.950
340					7.000	6.817	
343.16	6.699	6.634		6.890			6.890
345					6.933		
348			6.487				
348.16							6.820
350					6.865	6.671	
355					6.797		
353.16	6.542	6.470					6.740
360					6.729	6.533	
363.16	6.374	6.264		6.670			6.570
365					6.660		
368.16							6.460
370					6.591	6.404	
373.16	6.206	6.067			6.547		
383.16	6.042	5.867		6.310			
393.16	5.875	5.661					
403.16	5.708	5.446		5.800			
413.16	5.536	5.219					

\*See also Llwellin<sup>107</sup>.

Table 37

HEAT OF SUBLIMATION  
 $\Delta H_s$  (kcal./mole)

Temperature (°K.)	Calculated on Basis of Vapor Pressure Data of Oliver et al. <sup>119</sup> and the Non-ideality Parameters Proposed by			Weinstock and Crist (Ref. 142)	Simon (Ref. 135)*	Kirshenbaum (Ref. 93)	Masi (Ref. 113)
	Berthelot	Magnuson	Weinstock				
198.16					12.20		
223.16					12.15		
248.16					12.08		
273				12.22			
273.16	12.086	12.082	12.080		11.98	12.22	12.023
275						12.20	
280						12.16	11.988
283.16	11.973	11.969	11.965			12.12	
285						12.08	
290						11.929	
293.16	11.857	11.849	11.842		11.87		
295						12.04	
298				11.97			
298.16	11.80 <sup>†</sup>					12.01	11.872
300						12.00	11.858
303.16	11.764	11.753	11.739			11.95	
305						11.91	11.772
310						11.86	
313.16	11.676	11.660	11.636		11.73	11.81	11.666
315						11.76	
320						11.71	11.537
323				11.58			
323.16	11.574	11.547	11.506			11.53	
325						11.65	
329.7	11.50 <sup>(1 atm.)†</sup>						
330						11.63	11.429
333.16	11.440	11.404	11.331		11.47		
335							
337.18	11.372	11.38 <sup>†</sup>					
337.21							
338.16							

\*See also Reference 107.

<sup>†</sup>Calculated by Oliver, et al.

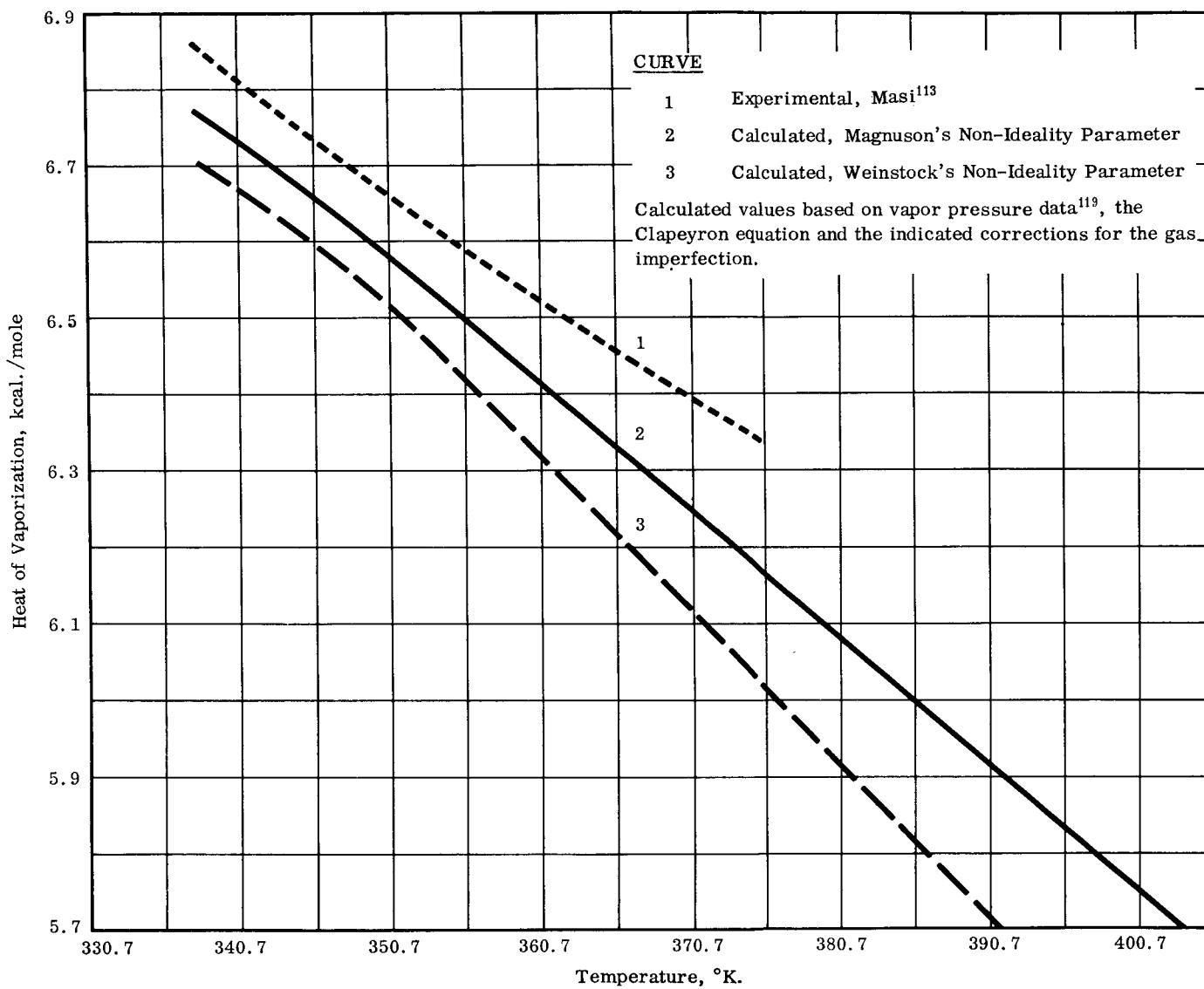


FIG. 18. HEATS OF VAPORIZATION

The measured quantities,  $\nu$ , in the heat of vaporization experiments with  $\text{UF}_6$  were found by Masi to compare favorably with values of  $\nu$  calculated from the Clapeyron equation and the vapor pressure data of Weinstock and Crist<sup>142</sup>. The vapor pressure data were reconciled with the measured heat data by using an equation of state of the form  $PV = RT + BP$ , where the virial coefficient  $B_{CC} = 1082 - (1.81 \times 10^8)T^{-2}\text{cc}$ .

From the equations:

$$\text{Solid: } \nu = RZ (6581.2 - 1.9116T) \quad (69)$$

$$\text{Liquid: } \nu = RZ (5678.2 - 6.2582T) \quad (70)$$

where  $Z = 1 + (B_p/RT)$

and the Clapeyron equation in the form:

$$\Delta H = \nu [1 - (V_c/V_g)] \quad (71)$$

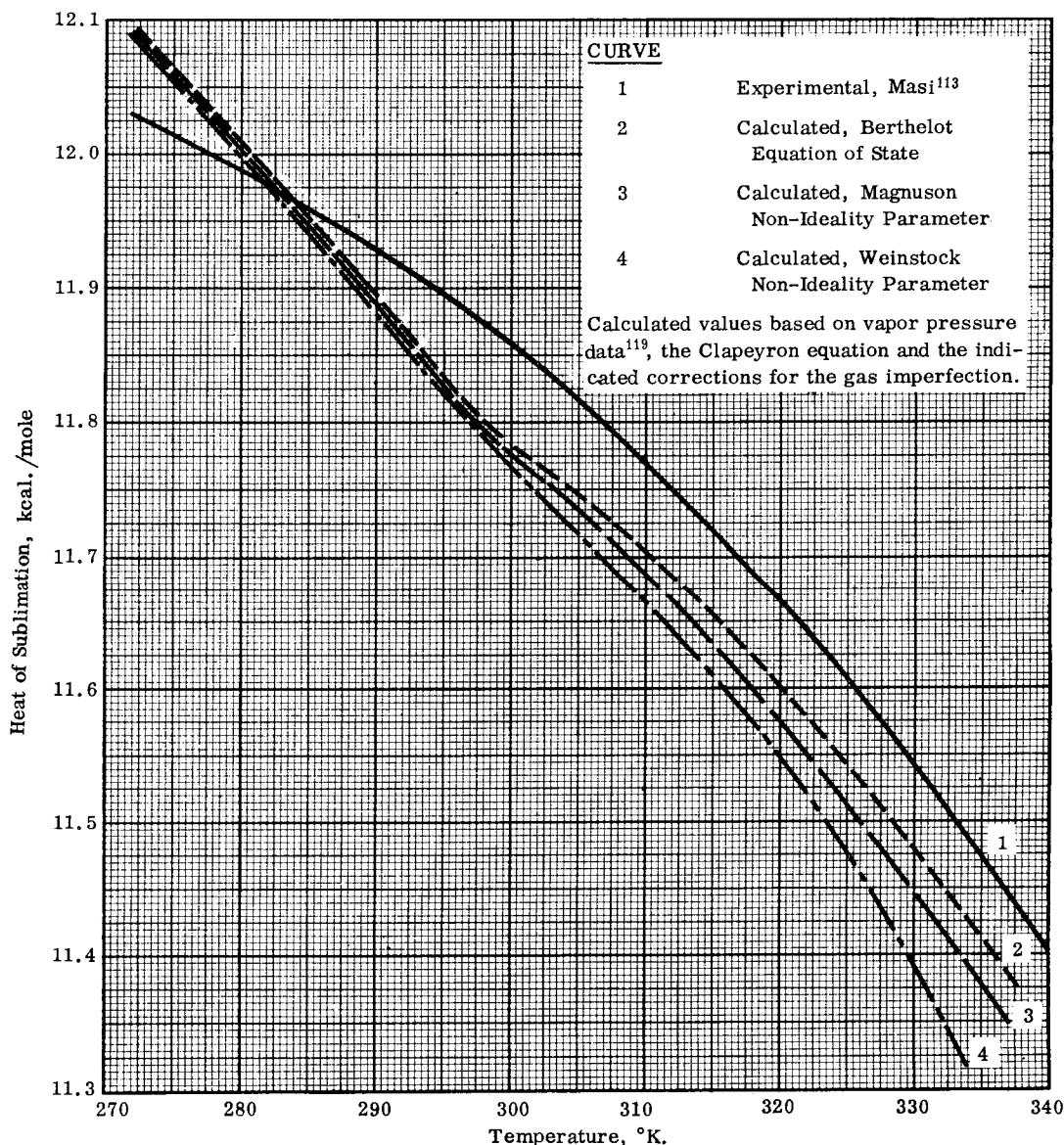


FIG. 19. HEATS OF SUBLIMATION

he calculated the heats of vaporization and sublimation. The calculated values are tabulated in Tables 36 and 37, respectively. Masi assigned a probability error of about one percent to the latent heat values. However, he also mentioned an unexplained phenomenon of an increasing difference between the third-law entropies and the spectroscopic entropies which were calculated by Bigeleisen and his co-workers.

The Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \quad (72)$$

is applicable to the equilibrium between any two phases of one component and can be used to determine the heats of vaporization or sublimation whenever the vapor pressure-temperature relationships of a system are accurately known and the difference in the volumes of the two phases,  $\Delta V$ , can be determined.

If the equilibrium under consideration is that between an ideal gas and the condensed phase, the equation of state of the ideal gas may be substituted to remove the volume term in Equation 72. The resulting equation is, of course, the Clausius-Clapeyron equation.

Heat values calculated using Equation 72 and the vapor pressure-temperature relationships reported by Oliver and his co-workers<sup>119</sup> are listed in parentheses in the last columns of Tables 36 and 37. Vapor volumes needed for the determination of the heats of sublimation were calculated on the basis of Magnuson's proposed non-ideality parameter and the Berthelot equation;  $V = [RT/P][1 + 9PT_c/128 P_c T(1 - 6 T_c^2/T^2)]$  where  $T_c = 503.36^\circ\text{K}$ . and  $P_c = 45.5$  atmospheres. Volumes needed for the calculation of the heat of vaporization were determined in the same way using Weinstock's non-ideality parameters as well. The volumes of the liquid were calculated from the density values obtained by Wechsler and Hoge<sup>141</sup>. The volume of the solid was assumed to be constant over the  $0^\circ$  to  $60^\circ\text{C}$ . range and was calculated from the density value of 4.87 grams per cubic centimeter.

Oliver and his co-workers calculated the heat values from vapor pressure data, the Clapeyron equation, and the Berthelot equation. These values also are listed in the last column of Tables 36 and 37.

In addition, other heat values have been calculated in a manner similar to that described above. Formulae representing the heats of vaporization reported, first by Simons<sup>135</sup> and later by Llewellyn<sup>107</sup>, are as follows:

$$\Delta H_v = [8890 - 0.0225 T^2 + 1.85 T] \text{ cal./mole deg.} \quad (73)$$

$$\Delta H_v = [6920 - 5.3(t - 65) - 0.184(t - 65)^2] \text{ cal./mole deg.} \quad (74)$$

Equation 74 satisfies the condition that  $\Delta H_v = 0$  at the critical temperature ( $t_c$ ),  $245^\circ\text{C}$ . Values of the heats obtained from these expressions are reported to agree with the experimental values of Masi<sup>113</sup> to within two percent at  $100^\circ\text{C}$ . These values are listed in Table 36. The heats of sublimation are expressed by the equation:

$$\Delta H_s = [12,600 - 875,600 e^{-2560/T} - 2T] \text{ cal./mole deg.} \quad (75)$$

Values of the heats obtained from this expression are reported to agree with those obtained by Masi to within one percent and are shown in Table 37.

Kirshenbaum<sup>93</sup> also calculated the heats of vaporization and sublimation from vapor pressure data. He obtained the following representative equations:

$$\Delta H_v = [2473.4 + 14.476 T - 0.028546 T^2 + 987,670 T^{-1}] \text{ cal./mole deg.} \quad (76)$$

$$\Delta H_S = [-1405 + 52.512 T - 0.076822 T^2 + 1,368,000 T^{-1}] \text{ cal./mole deg.} \quad (77)$$

Values obtained from these equations are also in agreement with those obtained experimentally by Masi. These values are also included in Tables 36 and 37.

Weinstock and Crist<sup>142</sup> calculated the heat of vaporization from the Clapeyron equation, except that they neglected the volume of the condensed phase. The quantity  $dP/dT$  was calculated from vapor pressure expressions and the values of vapor volumes were determined from the Berthelot equation of state. These values too are found in Tables 36 and 37.

Cohen<sup>38</sup> reported values for the heats of vaporization for the range between 65° and 95°C. These values were extrapolated as a function of temperature over the 60° to 232°C. range by utilizing the fact that  $\Delta H_V = 0$  at the critical point. Only the experimental values are given in this report. The extrapolated values can be found in the original work.

### HEAT OF VAPORIZATION AT 0°K

Weinstock, Weaver, and Malm<sup>144</sup> evaluated the heat of vaporization,  $\Delta H_0^\circ$ , at 0°K. using two methods. One was based on the fundamental vibrational frequencies and utilized the methods of statistical mechanics. The other utilized vapor pressure data, the Clapeyron equation, and the third law of thermodynamics. In the case of their determinations based on statistical mechanics (Equation 78), using a virial coefficient  $b = 3.6 \times 10^3 T^{-2}$  cal. mole<sup>-1</sup> (mm. Hg)<sup>-1</sup> and the equation of state,  $PV = RT + bP$ , instead of the Berthelot equation of state to define the non-ideality of the vapor, it was found that a constant value,  $\Delta H_0^\circ = 12,965 \pm 2$  cal. mole<sup>-1</sup>, was obtained from 280° to 370°K. In general, the agreement between the values of  $\Delta H_0^\circ$  obtained by the two methods was especially good when the gas imperfection was taken into account through use of the virial coefficient. A slight discrepancy at the lower pressure was accounted for by a slight systematic error in the vapor-pressure measurements of Oliver and his co-workers<sup>119</sup> near 0°C. (see Vapor Pressure, page 81).

Only the most recent data were used for the computations. The heat of vaporization at 0°K. was evaluated using the fundamental vibrational frequencies proposed by the authors (see Table 13) and the relation

$$\Delta H_0^\circ = -(F^\circ - H_0^\circ)g + (F - H_0^\circ)_C - RT \ln P - (F - F_{ideal})g \quad (78)$$

in which the free energy function of the ideal gas,  $-(F^\circ - H_0^\circ)g$ , was calculated by means of statistical mechanics using 1.994 Å for the U-F distance<sup>145</sup> and in which the free energy function for the condensed phases,  $(F - H_0^\circ)_C$ , was taken from the heat capacity measurements of Brickwedde and his co-workers<sup>24</sup>. The vapor pressure equations and critical constants of Oliver and his co-workers were used in all the necessary calculations. The  $\Delta H_0^\circ$  calculated from Equation 78 was then compared to the values obtained from Equation 79:

$$\Delta H_0^\circ = \Delta H - (H^\circ - H_0^\circ)g - (H - H_0^\circ)_C - (H - H^\circ)g \quad (79)$$

where the heats of vaporization and sublimation,  $\Delta H$ , were evaluated using the vapor pressure equation of Oliver and his co-workers and the Clapeyron equation. Both the proposed equation of state and the Berthelot equation of state were used to determine  $\Delta H$  values. The other thermodynamic quantities used in the equation were derived in a manner similar to that used above.

### ENTROPIES OF VAPORIZATION AND OF SUBLIMATION

For a small reversible change, the entropy of sublimation or vaporization,  $dS$ , can be calculated by use of the following equation:

$$dS = \frac{dq}{T} \quad (80)$$

where  $dq$  is the heat absorbed. It must be emphasized that Equation 80 is applicable to the phase changes in which  $dq$  is taken up isothermally and reversibly as the heat absorbed in the isothermal stage of a Carnot cycle.

Masi<sup>113</sup> calculated the entropies of vaporization and of sublimation from the experimental heat values. The entropy values are given in Table 38 and Figure 20 along with values calculated from heat values determined from recent vapor pressure data and values calculated from heat values reported by Crist and Weinstock<sup>142</sup>.

#### HEAT OF FUSION

The heat of fusion of  $UF_6$  was determined calorimetrically by Brickwedde and his co-workers<sup>24</sup>. They reported a value of 19,193 joule  $\text{mole}^{-1}$  or 4588 cal.  $\text{mole}^{-1}$ . Oliver and his co-workers<sup>119</sup> determined the heat of fusion,  $\Delta H_f$ , from the heat of vaporization,  $\Delta H_v$ , and the heat of sublimation,  $\Delta H_s$ , at the triple point in the straightforward manner:

$$\begin{aligned} \Delta H_f &= \Delta H_s - \Delta H_v \\ &= 4.56 \text{ kcal. mole}^{-1} \end{aligned} \quad (81)$$

Weinstock and his co-workers<sup>144</sup> also calculated the heat of fusion in the same manner as described above, that is, from the difference between the calculated heats of sublimation and vaporization. The value, 4.555 kcal.  $\text{mole}^{-1}$ , compares favorably with the measured value. All of the above-mentioned values are in agreement with the earlier results reported as  $4.5 \pm 0.5$  kcal.  $\text{mole}^{-1}$  at  $64.5^\circ\text{C}$ . by British workers<sup>47, 48, 50, 51, 55</sup>.

Table 38  
ENTROPIES OF VAPORIZATION AND SUBLIMATION

Temperature (°K.)	Entropy, S (cal./mole deg.)		
	Masi (Ref. 113)	Weinstock and Crist (Ref. 142)	Calc. on Basis of Data from Oliver et al. (Ref. 119)
<u>SUBLIMATION</u>			
273.16	44.02	44.77	44.25
280	42.81		
283.16			42.28
290	41.13		
293.16			40.45
298		40.18	
298.16	39.82		
300	39.53		
303.16			38.81
310	37.97		
313.16			37.28
320	36.46		
323		35.86	
323.16			35.82
330	34.96		
333.16			34.34
337.18			33.73
337.21	33.89		
<u>VAPORIZATION</u>			
337.18			20.06
337.21	20.34		19.99
338.16			
340	20.05		
343.16			19.52
348		18.64	
350	19.06		
353.16			18.53
360	18.15		
363.16			17.55
370	17.31		
373.16			16.64
393.16			14.94
403.16			14.16
413.16			13.40

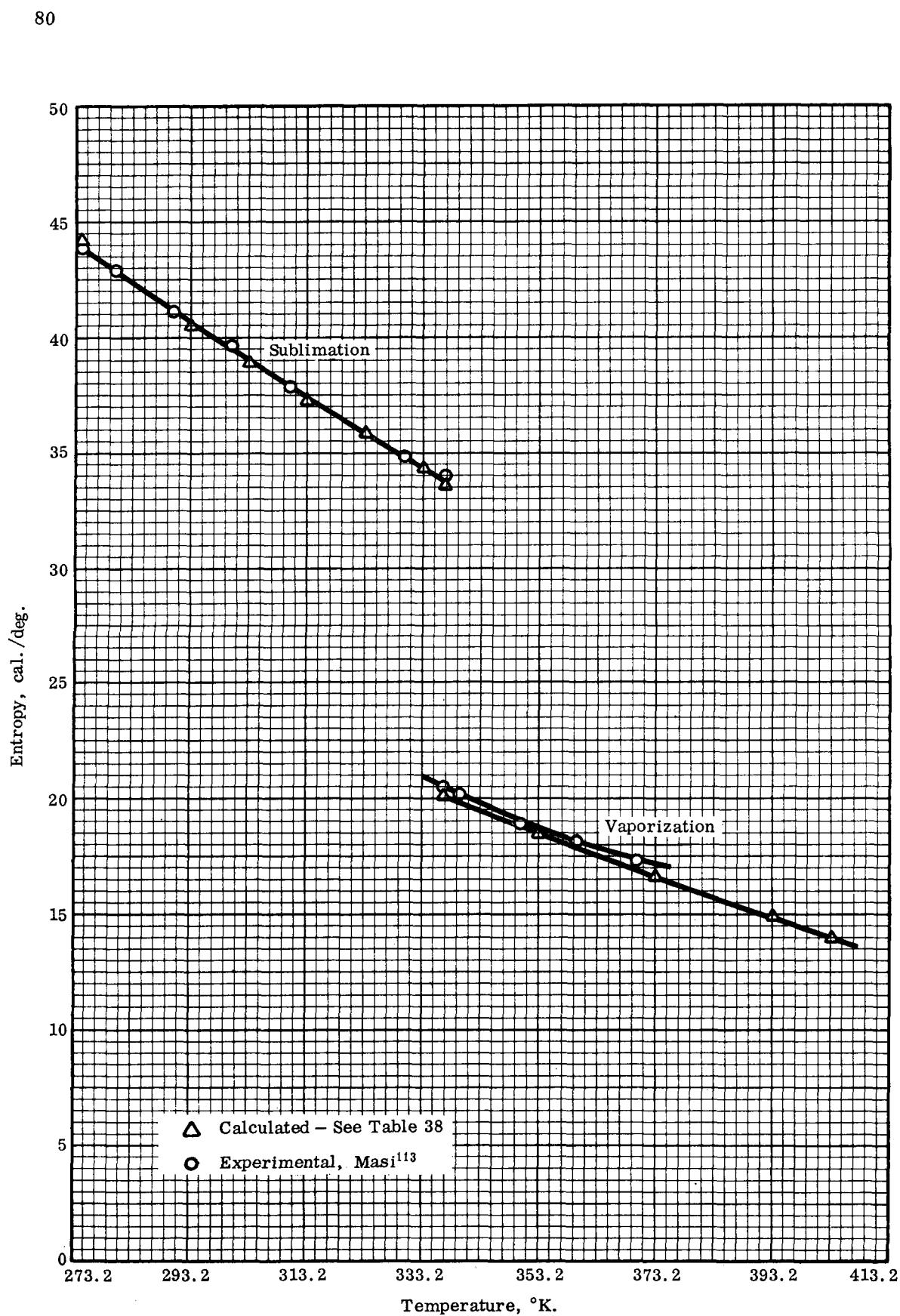


FIG. 20. ENTROPIES OF SUBLIMATION AND VAPORIZATION

## PHASE RELATIONS

### VAPOR PRESSURE

The vapor pressure of  $\text{UF}_6$  has been investigated many times, especially in the low pressure range. Most of the early vapor pressure data appeared in the report literature of the atomic energy projects of the United States and Great Britain with summaries of the more reliable data appearing in the open literature. Of the more reliable data, those obtained by Oliver, Milton, and Grisard<sup>119</sup> are the most extensive, covering temperatures ranging from 0° to near the critical point, 230.2°C. These data, which are accurately represented by three Antoine vapor pressure-temperature expressions, are found to compare favorably with other less extensive but, nevertheless, reliable data. However, Weinstock and his co-workers<sup>144</sup> recently pointed out that a slight systematic error appears in the vapor-pressure measurements of Oliver and his co-workers near 0°C. By using the Clapeyron equation and a value for  $\Delta H^\circ$  of 12,965 cal. mole<sup>-1</sup>, they calculated that the vapor-pressure of  $\text{UF}_6$  at 0°C. is 17.70 mm. Hg. This compares favorably with the value 17.65 mm. Hg obtained at the ice point which was reported to Weinstock by Plurien in a footnote in the previous article<sup>144</sup>.

The observed vapor pressure data for the solid are listed in Tables 39 and 40 while those for the liquid are listed in Table 41. The representative expressions for the recent reliable data along with some of the experimental methods used to obtain them, are presented below. Earlier data, mostly of a preliminary nature, are referred to and summarized by their representative equations in Table 42.

Oliver and his co-workers<sup>119</sup> measured the vapor pressure of the solid from 0° to 64.02°C. by both static and ebulliometric methods. They measured the vapor pressure of the liquid from 64°C. to the critical temperature by the ebulliometric method alone. The two methods of measuring pressure yielded results consistent within the experimental error (Tables 39 and 41). The temperatures were accurately measured within  $\pm 0.01^\circ\text{C}.$ , but the accuracy of the ebulliometric pressure measurements depended upon the accuracy of the reference, the boiling point of water. This was taken from the Osborne-Meyers steam tables\*.

The vapor pressure of the solid is represented by a modified Antoine equation, Equation 82, which has an estimated uncertainty, based on a 95 percent confidence level, of  $\pm 0.05$  percent. The vapor pressure of the liquid from 64° to 116°C. is represented by Equation 83, and above 116°C. by Equation 84. The uncertainties of these equations are  $\pm 0.03$  percent and  $\pm 0.3$  percent, respectively at the same confidence level.

#### Solid, Vapor; 0° to 64°C.

$$\log_{10} P(\text{mm.}) = 6.38353 + 0.0075377t - 942.76/(t + 183.416) \quad (82)$$

#### Liquid, Vapor; 64° to 116°C.

$$\log_{10} P(\text{mm.}) = 6.99464 - 1126.288/(t + 221.963) \quad (83)$$

#### Liquid, Vapor; 116°C. to critical point

$$\log_{10} P(\text{mm.}) = 7.69069 - 1683.165/(t + 302.148) \quad (84)$$

\*Osborne, N. S. and Meyers, C. H. J. Research Natl. Bur. Standards 13, 1-20(1934).

Table 39

## EXPERIMENTAL VALUES OF THE VAPOR PRESSURE OF THE SOLID

Table 40  
VAPOR PRESSURE OF THE SOLID AT LOW TEMPERATURES

Temperature (°C.)	Pressure (mm. Hg)		
	Awbery (Ref. 11)	Llewellyn* (Ref. 107)	Haworth† (Ref. 75)
-200	$2 \times 10^{-25}$	$10^{-26}$	
-183	$9 \times 10^{-19}$		
-150	$5 \times 10^{-11}$	$10^{-11}$	
-100	$5.8 \times 10^{-5}$	$4.3 \times 10^{-5}$	
-90		$3.0 \times 10^{-4}$	
-80		$1.7 \times 10^{-3}$	
-78	$2.8 \times 10^{-3}$		
-70		$8.2 \times 10^{-3}$	
-60	0.037	0.034	
-50		0.173	
-40	0.414	0.369	
-30		1.16	
-25	1.949		
-20	3.136	3.11	
-15	4.953	5.00	
-14		5.42	
-14.2			6.85
-13		5.93	
-12.4			7.80
-11		7.08	
-10	7.688	7.73	
-5	11.739	11.9	
-2		15.2	
-1.5			17.80
-1		16.5	
0	17.65	17.9	

\*Calculated values. See Equation 91; see also Ref. 135.

†Experimental values.

Table 41  
VAPOR PRESSURES OF THE LIQUID

Temperature (°C.)	Pressure (mm. Hg)				
	Oliver et al. (Ref. 119)	Llewellyn (Ref. 107)	Weinstock (Ref. 142)	Abelson* (Ref. 1)	Awbery† (Ref. 11)
64.2	1,145.2				
64.7					1,157
64.8		1,161			
65.0			1,169	1,189	1,169
65.99	1,211.4				
66.18	1,218.8				
67.06	1,252.2				
67.9			1,273		
68.59	1,313.1				
69.55	1,352.2				
69.7		1,338			
70.0		1,350			1,369
70.1			1,360		
70.2			1,366		
			1,370		1,377
			1,376		
70.79	1,404.3				
71.86	1,450.4				
72.8		1,470			
72.82	1,492.3				
74.11	1,550.7				
74.75	1,580.3				
75.0		1,566			1,594
75.2			1,582		1,603
75.3			1,568		1,608
76.52	1,164.2				
78.25	1,750.1				
79.1		1,752			
80.0				1,913	1,845
80.19	1,849.2				
80.3			1,830		
			1,838		1,861
82.0		1,905			
82.08	1,951.2				
83.5		1,970			
83.87	2,050.8				
85.0		2,058			2,126
85.4			2,087		2,150
85.54	2,147.8				
86.63	2,212.8				
87.20	2,247.0				
88.84	2,348.7				
89.3		2,300			
90.0				2,437	

\*Values reported to have a probable error of 5 percent.

†Values calculated from Equation 105.

Table 41 (Continued)  
VAPOR PRESSURES OF THE LIQUID

Temperature (°C.)	Pressure (mm. Hg)				
	Oliver et al. (Ref. 119)	Llewellyn (Ref. 107)	Weinstock (Ref. 142)	Abelson* (Ref. 1)	Awbery† (Ref. 11)
90.35	2,445.3				
91.35	2,511.1				
91.88	2,546.5				
95.00		2,648			2,781
99.94	3,131.1				
100.00		2,985		3,258	3,160
108.07	3,818.4				
116.03	4,596.8				
118				5,016	
120					5,074
124.17	5,512.3				
133.19	6,669.7				
137				6,878	
140					7,751
141.44	7,888.6				
149.50	9,226.0				
157.83	10,773				
160					11,410
170.64	13,528				
162			11,377		
180					16,347
180.57	15,986				
188.85	18,294				
196.02	20,477				
199.85	21,735				
200				22,755	22,988
207.32	24,329				
213.82	26,779				
218.74	28,773				
220					31,954
220.52	29,468				
224.76	31,409				
225.14	31,611				
225.57	31,781				
227.93	32,908				
228.38	33,260				
229.11	33,740				
230.2	34,580			37,235	
240					44,168
245					47,880

\*Values reported to have a probable error of 5 percent.

†Values calculated from Equation 105.

Table 42  
SUMMARY OF EARLIER DATA  
ON VAPOR PRESSURE-TEMPERATURE RELATIONSHIPS

<u>Expression</u>	<u>Equation</u>	<u>Reference</u>
SOLID-VAPOR		
$\text{Log}_{10}P(\text{mm.}) = 10.8407 - 2623.3/T$ (superseded by Equation 87)	95	142
$\text{Log}_{10}P(\text{mm.}) = 11.19 - 2714/T$ (low temperature)	96	51
$\text{Log}_{10}P(\text{mm.}) = 4460/T + 119.95 - (0.0000571T^2 - 0.0854T + 49.85 \text{ Log}_{10}T)$	97	50
$\text{Log}_{10}P(\text{mm.}) = 10.76 - 2600/T$	98	52
$\text{Log}_{10}P(\text{mm.}) = 10.97 - 2600/T$	99	7
$\text{Log}_{10}P(\text{mm.}) = 10.76 - 2600/T$	100	8
$\text{Log}_{10}P(\text{mm.}) = 10.74319 - 2593.48/T$	101	11
LIQUID-VAPOR		
$\text{Log}_{10}P(\text{mm.}) = 7.5223 - 1505.9/T$	102	142
$\text{Log}_{10}P(\text{mm.}) = 7.73 - 1575/T$ (between 65° and 95°C.)	103	51
$\text{Log}_{10}P(\text{mm.}) = 131.64 - 2170/T + 56.0 - 0.0394T$	104	51
$\text{Log}_{10}P(\text{mm.}) = 17.81264 - 2916.9127 + 0.107489 \text{ Log}_{10}T$ - 0.026137715T + $2.14125 \times 10^{-5}T^2$	105	10

Brooks and Wood<sup>27</sup> fitted the liquid  $\text{UF}_6$  vapor pressure data of Oliver, Milton, and Grisard over the 64° to 226°C. range with a sixth-order polynomial in  $1/T^{\circ}\text{K}$ . The equation which represents the data to  $\pm 0.0005$  (standard deviation of  $\ln P$ ) was used to calculate the vapor pressure of liquid  $\text{UF}_6$  and the derivative of the vapor pressure with respect to temperature at integral values of the temperature. Some of the results are given in Table 43, although a more nearly complete tabulation of the results can be obtained directly from the primary literature source.

Grisard and Oliver compared the vapor pressures of normal  $\text{UF}_6$  and  $\text{UF}_6$  enriched to 92.93 weight percent  $\text{U}^{235}$ , in the temperature range 64° to 92°C. They found by a differential boiling point method that the average ratio of the vapor pressure of normal material to that of the enriched material was  $1.000072 \pm 0.000018$ .

Kigoshi<sup>90</sup> measured the vapor pressure of solid  $\text{UF}_6$  which had been purified by a sublimation process. The measurements were made by a static method at the temperature interval 0° to 34.6°C. The results, listed in column 6 of Table 39, are expressed by the following equation:

Solid, Vapor; 0° to 34.6°C.

$$\text{Log}_{10}P(\text{mm.}) = 10.023 - (2486/T) + 0.0012T \quad (85)$$

where T is the absolute temperature.

Amphlett, Mullinger, and Thomas<sup>9</sup> measured the vapor pressure of solid  $\text{UF}_6$  from 12° to 50°C. by a null method, the deflection produced in a quartz spiral manometer being

Table 43  
VAPOR PRESSURE OF THE LIQUID AND ITS DERIVATIVE  
WITH RESPECT TO TEMPERATURE\*

Temperature (°C.)	Pressure (mm. Hg)	(Reference 27)	Derivative dp/dt (mm. Hg /deg.)
65	1174.3		36.896
70	1370.5		41.686
80	1839.3		52.323
90	2422.6		64.534
100	3135.1		78.422
110	3997.0		94.192
120	5025.9		111.89
130	6240.8		131.55
140	7663.7		153.25
150	9313.5		177.01
160	11,210.0		202.86
170	13,379.0		231.06
180	15,840.0		261.84
190	18,626.0		295.78
200	21,768.0		333.56
210	25,313.0		376.26
220	29,314.0		425.24

\*For a more nearly complete listing see Ref. 27.

balanced by the admission of dry air and the balancing pressure being read on a mercury manometer. The data, listed in column 5 of Table 39, are represented by the equation:

Solid, Vapor; 12° to 50°C.

$$\text{Log}_{10} P(\text{mm.}) = 10.74. - 2592/T \quad (86)$$

Weinstock and Crist<sup>142</sup> also used a null method to measure the vapor pressure of UF<sub>6</sub> from 0 to 85°C. Their results compare favorably with those of Amphlett and his co-workers<sup>9</sup>. The apparatus used to make the measurements consisted of an all-metal system which contained a brass sylphon bellows and a multiple-type mercury-dibutylphthalate manometer. Temperatures are reported to the nearest 0.1°C., which the authors state introduces an error in the pressure of about 3 mm. at 60°C. and 5 mm. at 85°C. The data, listed in Tables 39 and 41, are represented by the following equations:

Solid, Vapor; 0° to 64°C.

$$\log_{10} P(\text{mm.}) = -3.77962 \log_{10} T - (3023.479/T) + 21.87103 \quad (87)$$

Liquid, Vapor; 64° to 85°C.

$$\log_{10} P(\text{mm.}) = -3.72662 \log_{10} T - (2065.679/T) + 18.60033 \quad (88)$$

The constants of Equations 87 and 88 were adjusted to include the values for the heat of fusion ( $\Delta H_f = 4588 \text{ cal./mole}$ ) and the triple point temperature which was obtained by Brickwedde, Hoge, and Scott.<sup>24</sup>

Masi<sup>113</sup> reconciled his measured heats of vaporization with the vapor pressure data of Weinstock and Crist by using an equation of state of the form  $PV = RT + BT$  where the virial coefficient is expressed as  $B_{cc.} = 1082 - (1.81 \times 10^8)T^{-2} \text{ cc.}$  The reported vapor pressure equations are:

Solid, Vapor

$$\log_{10} P(\text{mm.}) = -(2858.2/T) + 16.3619 - 1.9116 \log_{10} T \quad (89)$$

Liquid, Vapor

$$\log_{10} P(\text{mm.}) = -(2466.0/T) + 26.1868 - 6.2582 \log_{10} T \quad (90)$$

These equations were made to reproduce the heat of fusion (4588 cal./mole) and the vapor pressure data of Weinstock and Crist.

Llewellyn<sup>107</sup> reported vapor pressure data for temperatures from -15° to 100°C. The vapor pressure data for the 0° to -15°C. range are given in Table 40 and those for 0° to 100°C. are given in Tables 39 and 41. These data are represented by the equations:

Solid, Vapor

$$\log_{10} P(\text{mm.}) = -2751/T - 75.0e^{-2560/T} - 1.01 \log_{10} T + 13.797 \quad (91)$$

Liquid, Vapor

$$\log_{10} P(\text{mm.}) = -1946/T - 0.00492T + 0.934 \log_{10} T + 8.123 \quad (92)$$

Equations 91 and 92 have an estimated accuracy to 0.5 percent in the measured range.

Some of the earlier vapor pressure-temperature data, which appeared for the most part in early progress reports, were first summarized by Kirshenbaum<sup>93</sup> and later reported by Katz and Rabinowitch<sup>88</sup>, by Murphy<sup>115</sup>, and by others. From the pressure-temperature data available to Kirshenbaum, he derived Equations 93 and 94 as being the best representation of all the then available experimental data.

Solid, Vapor

$$\log_{10} P(\text{mm.}) = -57.7043 - 149,610/T^2 + 307.18/T + 26.436 \log T - 0.016796T \quad (93)$$

Liquid, Vapor

$$\log_{10} P(\text{mm.}) = -10.7098 - 107,969/T^2 - 540.8/T + 7.2876 \log T - 0.006241T \quad (94)$$

Equation 93 is reported by Kirshenbaum to represent the experimental data to  $\pm 0.5$  percent and Equation 94 to represent the data in the temperature range 65° to 90°C. to  $\pm 0.4$  percent.

Vapor pressure values of solid UF<sub>6</sub> at very low temperatures (between -200° and 0°C.) have been calculated by using Equation 91. These and other experimental and calculated vapor pressure data for low temperatures are presented in Table 40.

To complete as nearly as possible the record of literature findings on the vapor pressure-temperature relationships, a summary of some of the earlier data, consisting mostly of preliminary relationships, is shown in Table 42.

### SUBLIMATION POINT

Since  $UF_6$  has a triple point pressure in excess of one atmosphere, it cannot be melted at atmospheric pressure nor can it have a normal boiling point. However, a sublimation point, the temperature at which the solid vapor pressure attains 760 mm. Hg, has often been referred to in the literature as the "boiling point."

The sublimation point at 760 mm. Hg reported by Oliver and his co-workers<sup>119</sup> compares favorably with the value reported by Crist and Weinstock<sup>142</sup>. These values, presented in Table 44, are in agreement with the other reported values also listed.

Table 44

#### SUBLIMATION TEMPERATURE AT ONE ATMOSPHERE

Temperature (°C.)	Reference
56. 54	119
56. 5	142
56. 7 *	9
56. 76	11
56. 2	71

\* Calculated from vapor pressure Equation 86.

### TRIPLE POINT

Brickwedde, Hoge, and Scott<sup>24</sup> determined the melting point of  $UF_6$  containing 0.02 mole percent impurities. Oliver, Milton, and Grisard<sup>119</sup> determined a value which is in agreement with that of Brickwedde and his co-workers for material of similar purity. They stated that although the uncertainty of the melting point determination is  $\pm 0.05^\circ C.$ , close agreement could be reached if a correction for the partial pressure of helium over the  $UF_6$  were applied to the results of Brickwedde and his co-workers. However, Weinstock and his co-workers<sup>144</sup> report that solution of vapor pressure equations of Oliver and his co-workers gives  $64.05^\circ C.$  which is in agreement with the directly determined value of Brickwedde and his co-workers. These results, along with the pressure values at the triple point and the results of some of the earlier determinations, are presented in Table 45.

### CRITICAL CONSTANTS

Considerable discrepancy exists between some of the earlier reported values of critical temperature, critical pressure, critical density, and molar volume. Some of these reported values were obtained experimentally while others were calculated from related physical properties. However, values of the critical constants determined more recently compare favorably with those calculated from the refined values of related physical

Table 45  
TRIPLE POINT TEMPERATURE AND PRESSURE

Temperature (°C.)	Pressure (mm. Hg)	Impurity	Reference
64. 02 ± 0. 05	1137. 47	0. 015 (mole %)	119
64. 052	1142	0. 02 (mole %)	24
	1133 ± 7		142
65. 0 ± 0. 25	1161		55, 107
64. 8 ± 0. 4		150 ppm.	48
64. 5 ± 0. 3			
64. 45	1148. 0		11

properties. Comparisons indicate that the following values of the critical constants should be regarded as the most reliable: temperature ( $T_C$ ) = 230.2°C.; pressure ( $P_C$ ) = 45.5 atmospheres; density ( $\rho_C$ ) = 1.375 grams per cubic centimeter; and molar volume ( $V_C$ ) = 0.256 liters. These and other experimental and calculated values of the critical constants are presented in Table 46.

Probably the most reliable of the critical temperature and pressure values found in literature are those of Oliver and his co-workers<sup>119</sup> and those of workers in the U.S. liquid thermal diffusion project which are in agreement. Oliver and his associates started their vapor pressure system in an equilibrium state at temperature and pressure below the critical points. While they kept the heat input nearly constant, they increased the pressure until the critical pressure was exceeded. Plotting the pressure-temperature data as they were obtained, they estimated the critical values of the temperature and pressure at the point at which the slope,  $dp/dt$ , approached infinity. They estimated the critical temperature to be 230.2°C. and the critical pressure to be 45.5 atmospheres from the break in the curve.

Whybrew, Tayman, and Kokulis<sup>147</sup> determined the critical temperature visually by observing the disappearance of the liquid-gas meniscus as the liquid approached the critical temperature. The liquid-gas mixture was contained in a copper tube; disappearance of the meniscus was observed with the aid of an x-ray apparatus and a fluorescent screen. The meniscus was faint at 232.4°C. and disappeared entirely at 232.8°C. Therefore, the authors reported that the critical temperature fell between 232.4° and 232.8°C. From the amount and volume of  $UF_6$  contained in the tube, it was estimated that the critical density was close to 1.47 grams per cubic centimeter.

Brokaw<sup>26</sup> used the Cailletet-Mathias method (Law of Rectilinear Diameter) to determine the critical temperature and the critical density. In this method, the critical temperature, density, and molar volume are defined by the point of intersection of the straight line which represents the average of the liquid and vapor densities and the curve plotted from temperature against orthobaric density. As can be seen in Table 46, these values compare favorably with those determined by Oliver and his co-workers. It is also interesting to

Table 46  
CRITICAL CONSTANTS

Critical Temperature (°C.)	Critical Pressure (atm.)	Critical Density (g./cc.)	Critical Volume (l.)	Source
230.2 ± 0.2	45.5 ± 0.5	1.373 † 1.641 ‡	0.256* 0.215*	Ref. 119
232.6	-	1.47 (Preliminary Value)	-	Ref. 147
232.5	(45.6) §	1.41	0.250	Ref. 26
217	44	1.392	-	Ref. 141
228.5	-	1.378	0.256	Calculated using Hakala's method
232	47.6	-	-	Ref. 93
218	-	-	-	Ref. 132
245	63	1.91	-	Ref. 13
245 ± 5 (235 ± 20) //	-	-	-	Ref. 107

\*Calculated value.

†Calculated from Equation 108.

‡Calculated from Equation 106.

§Calculated from  $\frac{P_c V_c}{R T_c} = 0.275$

//Calculated from the Ramsay - Shields equation and measured values of surface tension.

note that if these critical values are substituted into the van der Waals relation,  $P_c V_c / R T_c = 0.275$ , we find that  $P_c = 45.6$  atmospheres, a value which is also in agreement with the value obtained by Oliver and his co-workers.

Hoge and Wechsler<sup>141</sup> used the Cailletet-Mathias method to check the critical values proposed by Cohen<sup>93</sup>. Cohen had predicted a critical temperature of 232°C. and a critical pressure of 700 pounds per square inch. Hoge and Wechsler employed the critical pressure value of 700 pounds per square inch in the vapor pressure equation proposed by Meyers\* to determine the vapor densities. They found that the average density of the liquid and vapor approximated a linear function represented by the equation:

$$\rho_{av} = 2.784 - 2.84 \times 10^{-3} T \quad (106)$$

They were able to estimate the critical temperature by using the empirical equation of Cragoe and Myers<sup>141</sup>:

$$\rho_{av}/\rho_c = 1 + m (1 - T/T_c) \quad (107)$$

Based on previous observations concerning other substances, they assumed  $m = 1$  and found that  $T_c = 490^{\circ}\text{K}$ . and  $\rho_c = 1.392$  grams per cubic centimeter. Using these critical

\*Myers, C. H. J. Research Natl. Bur. Standards 11, 691-701(1933).

values and the van der Waals relationship,  $P_c V_c / RT_c = 0.275$ , they obtained a critical pressure of 44 atmospheres. The authors did not place very much confidence in these values, since they were aware of the unusual behavior of  $UF_6$  in relation to other empirical correlations. Nevertheless, they did express the belief that the critical values fell below rather than above the values which were predicted by Cohen.

Llewellyn<sup>1</sup> also determined the critical temperature of  $UF_6$  by slowly heating a sealed tube containing  $UF_6$  as both the liquid and as the vapor until the meniscus between the two phases just disappeared. The temperature of disappearance and reappearance ( $245 \pm 5^\circ C.$ ), which was measured a number of times, was reported as the critical temperature. The critical temperature was also calculated from surface tension and viscosity data. From the Ramsay-Shields equation and measured values of the surface tension, a critical temperature value of  $235 \pm 20^\circ C.$  was obtained. This value was also arrived at on the basis of the viscosity data. However, Llewellyn placed little confidence in the latter critical value because of the large extrapolation necessary for the determination.

Since more accurate information was available for the determination of the vapor densities, although only for a limited temperature range, it seems advisable to make new estimates of the critical constants. Therefore, an orthobaric density chart (Figure 21) was constructed for this report, and the Cailletet-Mathias method was employed for the determination of the critical density. In addition, a method recently proposed by Hakala\* for the determination of critical density and critical temperature was utilized. Vapor density values needed for the methods mentioned above were computed by use of the Magnuson equation of state for  $UF_6$  at temperatures between  $50^\circ$  and  $140^\circ C.$ . Liquid density values used in the calculations were those obtained by Hoge and Wechsler<sup>141</sup>.

For the orthobaric density plots (Figure 21), the liquid density - vapor density averages were fitted to a linear function of temperature by the method of least squares. The following equation represents the relationship:

$$\rho_{av} (\text{g./cc.}) = 1.999 - 2.719 \times 10^{-3} t (\text{ }^\circ \text{C.}) \quad (108)$$

Comparisons of the average densities,  $\rho_{av}$ , which were calculated at various temperatures with those obtained from Equation 108 are shown in Table 47. If in Equation 108 the temperature is equal to the critical temperature, the averaged density becomes the critical density. At the experimental critical temperatures,  $230.2^\circ C.$  and  $232.5^\circ C.$ , the critical densities calculated from Equation 108 are 1.373 and 1.367 grams per cubic centimeter, respectively. These values are close to that estimated by Brokaw (1.41 grams per cubic centimeter) and that calculated by Hakala's method.

In the method proposed by Hakala, the liquid density,  $\rho_l$ , and the vapor density,  $\rho_v$ , values were substituted in the following equation:

$$(\rho_l + \rho_v) = 2\rho_c - a(\rho_l - \rho_v)^{10/3} \quad (109)$$

where  $\rho_c$  is the critical density and  $a$  is the characteristic constant. If the quantity  $(\rho_l + \rho_v)$  is plotted against  $(\rho_l - \rho_v)^{10/3}$ , a straight line is obtained, the intercept of which defines the critical density. Equation 109 was derived by simultaneously solving the Kathyama-Eotvos, the Macleod, and the Cailletet-Mathias equations and, according to Hakala, can be used to extrapolate a straight line to the critical point even when low temperature data were used.

\*Hakala, R. W. Chem. Eng. News 37, 43-4 (1959) March 16.

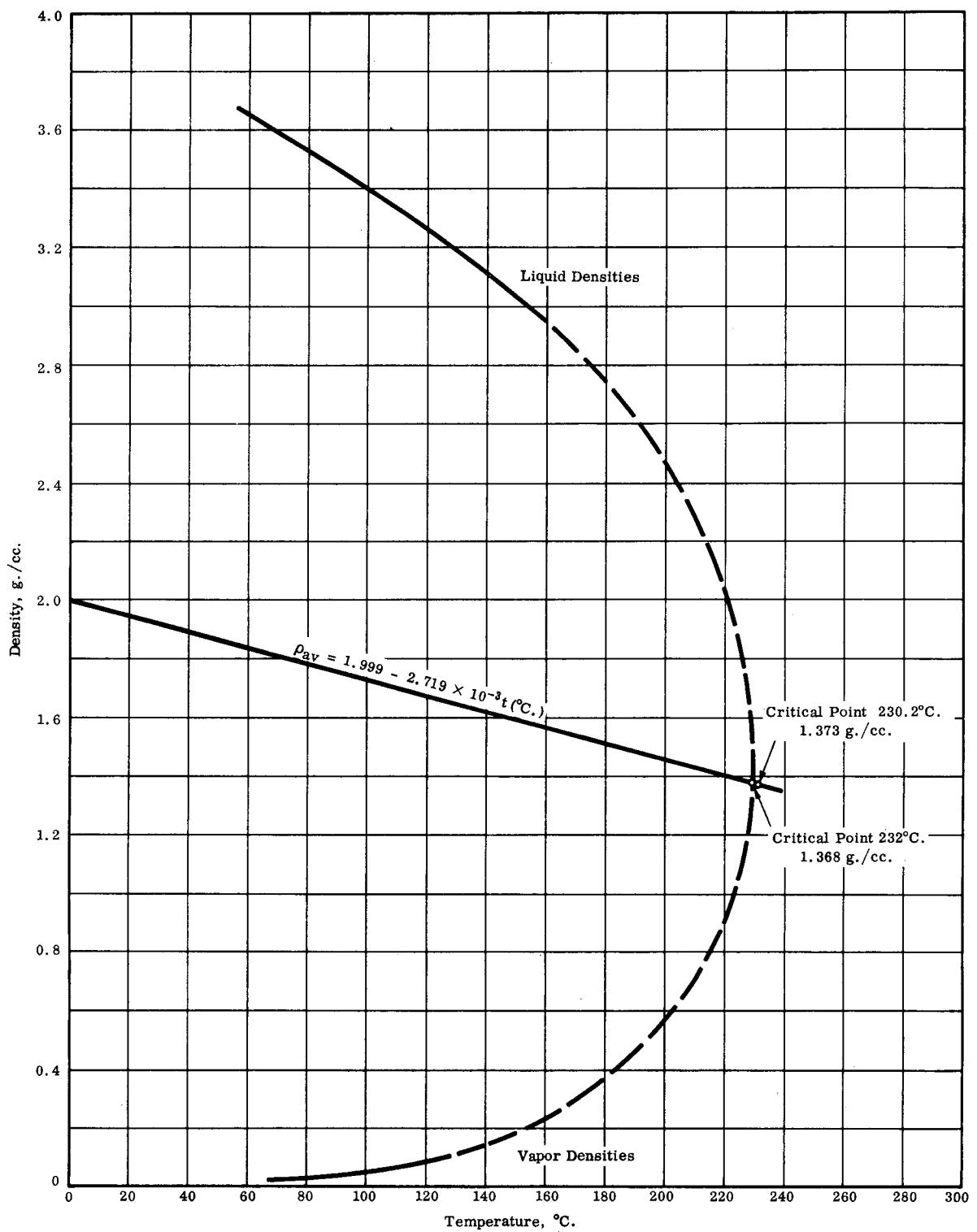


FIG. 21. ORTHOBARIC DENSITY CHART

Table 47

CALCULATED VAPOR DENSITIES, AVERAGE OF VAPOR AND LIQUID DENSITIES,  
AND DEVIATIONS OF THE LATTER FROM EQUATION 108

Temperature (°C.)	Density (g./ cc.)				Difference $\rho(\text{av.}) - \rho(\text{av.})(\text{Eq. 108})$
	$\rho(l)$	$\rho(v)$	$\rho(\text{av.})$	$\rho(\text{av.})(\text{Eq. 108})$	
65	3.624	0.0206	1.822	1.822	0.000
70	3.595	0.0238	1.809	1.809	0.000
80	3.532	0.0313	1.782	1.781	-0.001
90	3.470	0.0407	1.756	1.754	-0.002
100	3.404	0.0521	1.728	1.727	-0.001
110	3.332	0.0657	1.699	1.700	+0.001
120	3.263	0.0818	1.673	1.673	0.000
130	3.192	0.1009	1.647	1.646	-0.001

The critical temperature can be obtained in a similar manner from an equation which has the same geometry as the one used to determine the critical densities:

$$t = t_c - k (\rho_l - \rho_v)^{10/3} \quad (110)$$

Hakala refers to this equation as the Sugden-Verschaffelt equation. The values of  $(\rho_l + \rho_v)$  and  $(\rho_l - \rho_v)^{10/3}$  which are listed in Table 48 are plotted in Figure 22 for the determination of the critical density and in Figure 23 for the critical temperature. The critical density value, 1.378 grams per cubic centimeter, compares very well with those determined by use of the Law of Rectilinear Diameter. The critical temperature, 228.5°C., is also in agreement with some of the experimental results.

Table 48  
VALUES OF THE QUANTITIES  
 $(\rho_l + \rho_v)$  AND  $(\rho_l - \rho_v)^{10/3}$

Temperature (°C.)	$(\rho_l + \rho_v)$	$(\rho_l - \rho_v)^{10/3}$
80	3.563	65.15
90	3.511	60.80
100	3.456	56.36
110	3.401	51.84
120	3.345	47.33
130	3.289	42.83
140	3.234	38.84
160	3.127	29.81

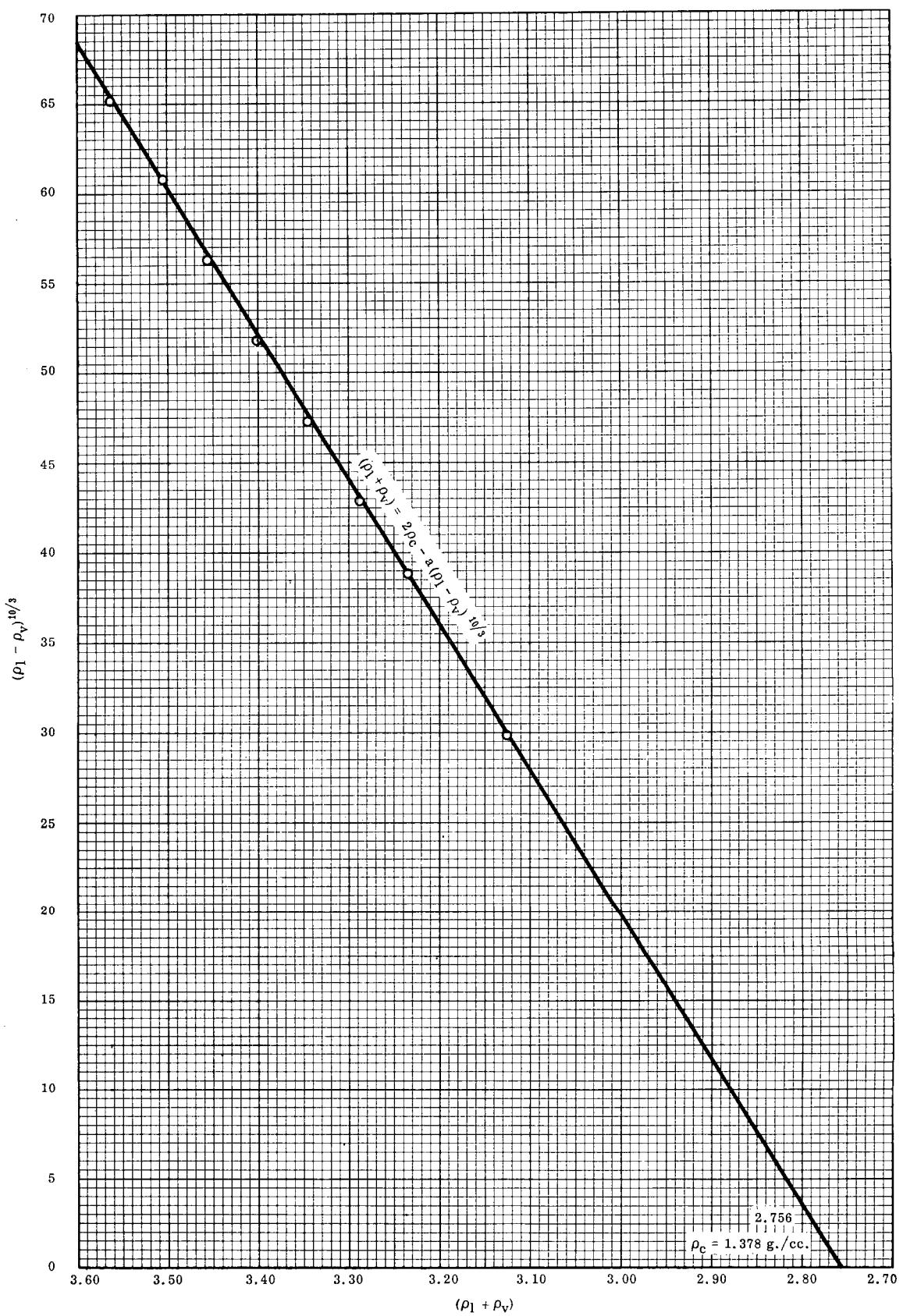


FIG. 22. GRAPHIC DETERMINATION OF CRITICAL DENSITY

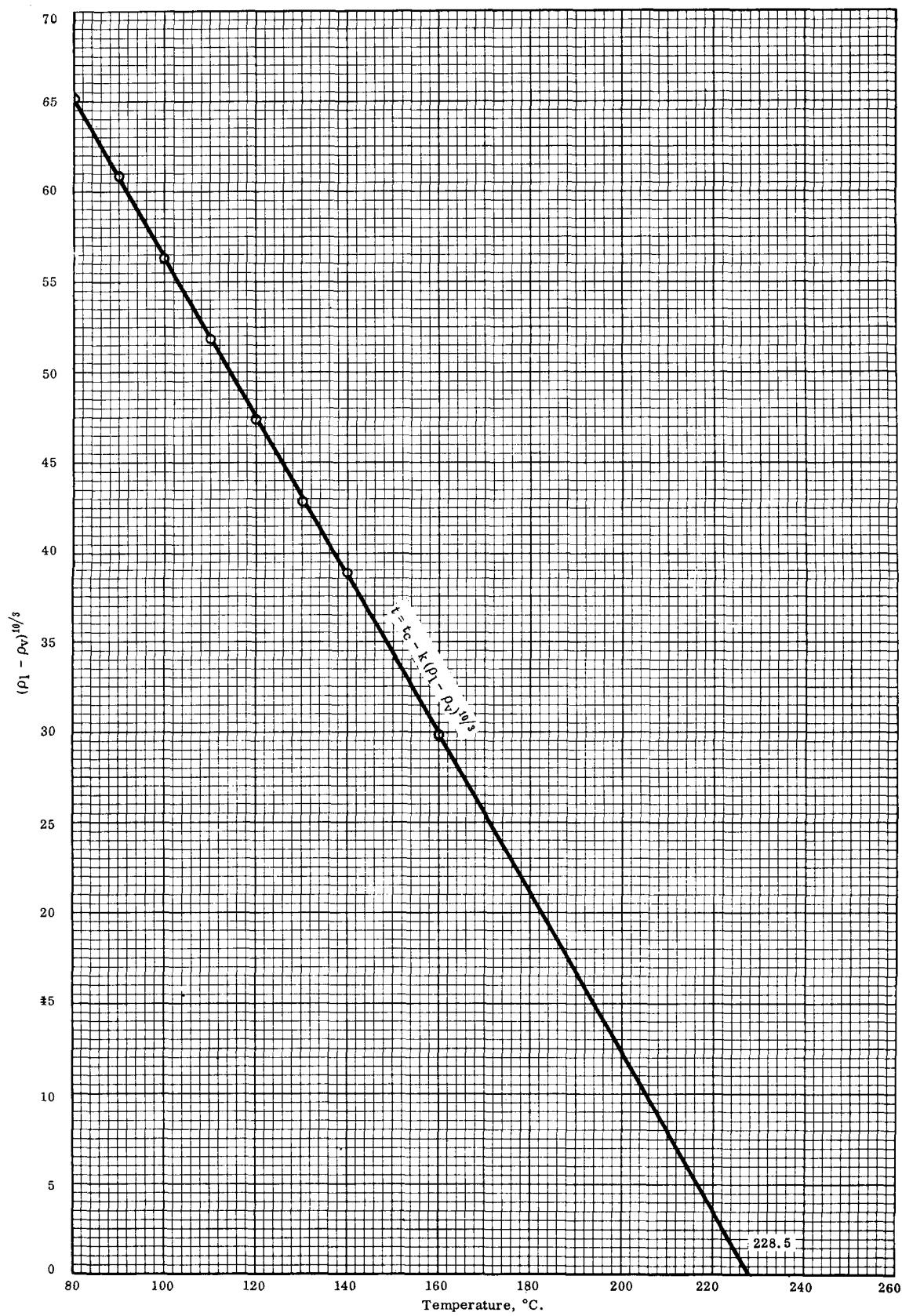


FIG. 23. GRAPHIC DETERMINATION OF CRITICAL TEMPERATURE

## EQUATIONS OF STATE

Early investigations of such things as the vapor density variations with pressure and temperature indicated that, within experimental error, the behavior of  $\text{UF}_6$  vapor does not deviate appreciably from that predicted by the simple gas laws. However, the more accurate pressure-volume-temperature experiments which were conducted somewhat later revealed deviations from ideality of as much as 3 percent at 60°C. and atmospheric pressure. These findings were verified by the experimental dielectric constant studies and later by studies of the variations between the thermodynamic properties of  $\text{UF}_6$  as calculated from heat capacity and vapor pressure data with those calculated from the vibrational frequencies. Values of the non-ideality parameters which were computed from the thermodynamic data compare favorably with those deduced from the dielectric constant studies. Comparisons of these non-ideality parameters with those obtained from the Berthelot and the van der Waals equations of state can be made from the data presented in Table 49 and Figure 24.

Table 49  
NON-IDEALITY PARAMETERS

Temperature (°C.)	A (atm. <sup>-1</sup> )							Weinstock et al. (Ref. 144) (1 + $\alpha$ ) <sup>*</sup>
	Magnuson (Ref. 110)		Ackley and Magnuson (Ref. 2)	Weinstock et al. (Ref. 144) Empirical <sup>†</sup>	Others (Ref. 3)	Berthelot	van der Waals	
	Experimental	Empirical						
0.0								0.9987
44.0			0.027					
25.0								0.9936
50.0		0.0365		0.0408		0.0326	0.0182	0.9764
53.2	0.0337 ± .003							
60.0		0.0333	0.032	0.0372	0.0239 <sup>‡</sup> 0.030 <sup>§</sup>	0.0297	0.0170	
61.1	0.0351 ± .0029							
70.0		0.0305						
71.0	0.0335 ± .0009 0.0313 ± .0013							
75.0								0.9441
78.4	0.0292 ± .0008							
78.5	0.0294 ± .0009							
79.3	0.0280 ± .0013							
80.0	0.0279 ± .0013 0.0288 ± .0015 0.0286 ± .0013	0.0279		0.0313		0.0246	0.0149	
90.0		0.0257						
94.0			0.021					
95.5	0.0251 ± .0006 0.0251 ± .0012							
100.0		0.0237		0.0265		0.0207	0.0131	
110.0		0.0219						
113.0	0.0200 ± .0007							
114.2	0.0197 ± .0005 0.0197 ± .0007 0.0187 ± .0008							
120.0		0.0203		0.0227		0.0176	0.0117	
130.0		0.0188						
132.4	0.0183 ± .0009							
132.5	0.0192 ± .0009							
140.0		0.0175		0.0195		0.0149	0.0104	

\*Ratio actual volume to ideal volume.

<sup>†</sup>Calculated on basis of non-ideality equation proposed by Weinstock et al., in which  $b = -3.6 \times 10^3 \text{ cal./mole (mm. Hg)}$

<sup>‡</sup>Calculated from Beattie-Bridgman equation of state.

<sup>§</sup>Calculated from the method of Brewer and Searcy.

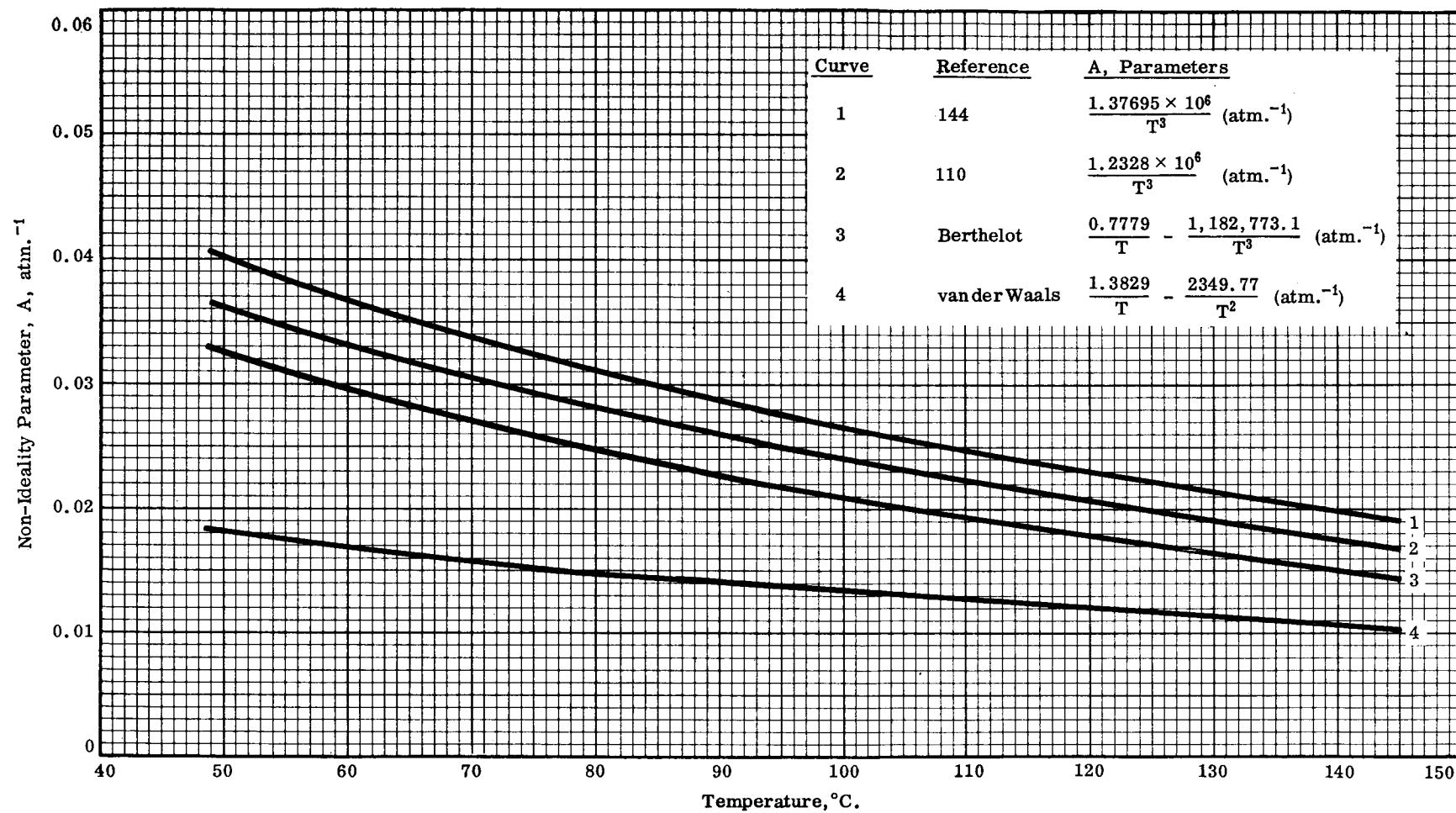


FIG. 24. NON-IDEALITY PARAMETERS

Ackley and Magnuson<sup>2</sup>, in their attempts to explain the behavior of certain  $\text{UF}_6$  adsorption isotherms, showed that  $\text{UF}_6$  vapor at pressures of the order of one atmosphere exhibited non-ideality. Their equation of state for  $\text{UF}_6$  vapor,  $P(1 + AP)V = NRT$ , contains a non-ideality parameter, A, which is only a function of temperature. Ackley evaluated A at 44°, 60° and 94°C. by measuring the pressures of a quantity of gas corresponding to two different known volumes under approximately isothermal conditions. Magnuson confirmed the results at 61.1°C. by utilizing microwave dielectric constant measurements. Other dielectric constant measurements<sup>108, 109</sup> of  $\text{UF}_6$  vapor at 9400 megacycles per second did not show non-ideality effects, but these observations were accounted for by the low  $\text{UF}_6$  vapor pressures that were used (less than 40 cm. Hg).

Magnuson used a form of the Debye equation, which results when the dipole moment is considered zero:

$$P_m = \frac{\epsilon-1}{\epsilon+2} M/P = \frac{4\pi\alpha}{3} N_0 \quad (111)$$

The equation of state was put into the form representing the quantity  $M/\rho$  and combined with Equation 111 to obtain Equation 112 from which dielectric constant measurements taken at various pressures could be used to obtain the non-ideality parameter, A, and the molar polarization,  $P_m$ , at a particular temperature:

$$\left[ \frac{\epsilon-1}{\epsilon+2} \right] \left[ \frac{1}{P} \right] \left[ \frac{P_0 V_0 T}{T_0} \right] = P_m (1 + AP) \quad (112)$$

From the plot of the quantity  $[(\epsilon-1)/(\epsilon+2)] [1/P]$  against  $P$  at a constant temperature Magnuson obtained a straight line, the slope of which defined the parameter A and the intercept of which defined the molar polarization  $P_m$  at the given temperature. The slope and intercept were obtained by the least squares method and the limit of error is said to be at the 95 percent confidence level. Using an improved dielectric constant apparatus, Magnuson<sup>110</sup> evaluated the non-ideality parameter A over the 53° to 132.5°C. range and expressed the results as a function of temperature by means of the equation:

$$A(\text{atm.}^{-1}) = 1.2328 \times 10^6 T^{-3} (\text{°K.}) \quad (113)$$

The equation of state for  $\text{UF}_6$  over the stated temperature range is then:

$$PV/RT = 1/[1 + (1.2328 \times 10^6 T^{-3}) (P)] \quad (114)$$

The van der Waals and Berthelot equations of state were put into the form  $PV/RT = 1 + AP$  to compare the A quantities with those calculated from Equation 111, where  $A_v$  and  $A_b$  are represented by Equations 115 and 116, respectively:

$$A_v = T_c/8P_c T - \frac{24}{64} \frac{T_c^2}{P_c T^2} \quad (\text{van der Waals}) \quad (115)$$

$$A_b = 9T_c/128P_c T - \frac{54}{128} \frac{T_c^3}{T^3 P_c} \quad (\text{Berthelot}) \quad (116)$$

The critical constants,  $T_c = 503.4^\circ\text{K.}$  and  $P_c = 45.5$  atmospheres, obtained by Oliver and his co-workers<sup>119</sup> were used in the above expressions for A. When  $A_v$  and  $A_b$  are compared to the empirical values of A, which are shown in Figure 24, they are found to be somewhat lower in value, the Berthelot non-ideality parameter  $A_b$  being more nearly representative of the empirical A values.

In addition to calculating the Berthelot  $A_b$  value at 60°C., Ackley and Barber<sup>3</sup>, determined an A value of 0.0239 atmosphere<sup>-1</sup> by using the Beattie-Bridgman equation. Using the

method of Brewer and Searcy\*, they determined an A value of  $0.030 \text{ atmosphere}^{-1}$ . Here again the observation was made that A values calculated from the various equations of state were found to be slightly lower than the experimentally determined values. Other remarks concerning values of A can be found in a number of other reports <sup>31, 98, 99</sup>.

Weinstock and his co-workers<sup>144</sup> used a modified form of the Berthelot equation of state,  $PV = RT + bP/T^2$ , to express the behavior of the vapor. By using a modification of the procedure given by Busey and Giauque<sup>†</sup> to determine the virial coefficient, b, from the heats of vaporization and sublimation, they obtained a value of  $b = -3.6 \times 10^3 \text{ cal. deg.}^2 \text{ mm.}^{-1} \text{ mole}^{-1}$ . Previously, Weinstock and Malm<sup>143</sup> had determined the virial coefficient as  $b = -5.1 \times 10^3 \text{ cal. deg.}^2 \text{ mm.}^{-1} \text{ mole}^{-1}$  using the same method. Putting the proposed equation of state into the form  $PV/RT = 1 + AP$ , where  $A_w = 1.3769 \times 10^6/T^3$ , the values of  $A_w$  can be compared with other proposed non-ideality parameters which are presented in Table 49 and in Figure 24. The final value of A proposed by Weinstock and co-workers compares favorably with that proposed by Magnuson.

Weinstock and Crist<sup>142</sup> had previously calculated the deviation from ideality by using the Berthelot equation and represented this deviation in terms of  $(1 + \alpha)$ , the ratio of the actual volume to the ideal volume. The values of the critical constants used for substitution in the Berthelot equation were those listed by Kirshenbaum<sup>93</sup>; that is,  $T_c = 518^\circ\text{K.}$ ,  $P_c = 36,000 \text{ mm. Hg.}$

Oliver and his co-workers<sup>119</sup> also expressed the deviation of  $\text{UF}_6$  from the ideal gas law by using the experimentally determined critical constants and the Berthelot equation. They reported deviations in AP of 0.0062 at  $25^\circ\text{C.}$ , 0.031 at  $56.54^\circ\text{C.}$ , and 0.043 at  $64.02^\circ\text{C.}$  At room temperature and pressures of the order of 100 mm. Hg, they found that  $\text{UF}_6$  vapor is essentially ideal.

An early attempt at establishing the behavior of  $\text{UF}_6$  vapor was made by Awbery<sup>12</sup>. He found that his data fit the Beattie and Bridgman equation of state:

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} \quad (117)$$

where the virial coefficients, B, C, and D, are only functions of temperature. After determining B, C, and D from tentative critical constants ( $T_c = 518^\circ\text{K.}$ ;  $\rho_c = 1.910 \text{ g./cc.}$ ) and correlating vapor pressure data with specific heats and other thermodynamic data, he obtained the following equation of state:

$$\begin{aligned} \frac{PV}{RT} = 1 + \frac{1}{V} \left[ 109.32 - \frac{1.4870 \times 10^5}{T} - \frac{6.2599 \times 10^9}{T^3} \right] \\ + \frac{1}{V^2} \left[ -6.479396 \times 10^7 + \frac{2.5386441 \times 10^{10}}{T} - \frac{6.84332 \times 10^{11}}{T^3} \right] \\ + \frac{1}{V^3} \left[ \frac{4.05603576 \times 10^{17}}{T^3} \right] \end{aligned} \quad (118)$$

Since the constants of the above equation were determined on the basis of preliminary data or data of unknown reliability, they can be considered approximations only.

Another early attempt at establishing the behavior of the vapor was made by Amphlett, Mullinger, and Thomas<sup>9</sup>. They found, within the limits of experimental error of vapor

\*Brewer, L. and Searcy, A. W. J. Chem. Ed. 548-52(1949).

†Busey, R. H. and Giauque, W. F. J. Am. Chem. Soc. 75, 806-9(1953).

density measurements (1 percent), that the molecular weight of  $\text{UF}_6$  was not systematically dependent upon temperature. They also found that the observed variation of the vapor density with pressure,  $(\partial\rho/\partial p)_t$ , at  $49.2^\circ\text{C}$ . is approximately that predicted by the kinetic theory for an ideal gas:

#### Experimental

$$(\partial\rho/\partial p)_{49.2^\circ\text{C.}} = 1.32 \pm 0.01 \times 10^{-8} \text{ sec.}^2/\text{cm.}^2 \quad (119)$$

#### Theoretical

$$(\partial\rho/\partial p)_{49.2^\circ\text{C.}} = 1.314 \times 10^{-8} \text{ sec.}^2/\text{cm.}^2 \quad (120)$$

They therefore concluded that  $\text{UF}_6$  vapor, at ordinary temperatures, consists of single "undissociated"  $\text{UF}_6$  molecules and that the vapor pressure nearly obeys the simple gas laws. Results of the investigation reported by Llewellyn<sup>107</sup> are the same.

#### PHASE DIAGRAM

The conditions of equilibrium between the three phases of  $\text{UF}_6$  are presented in Figure 25. The liquid-vapor equilibrium and the solid-vapor equilibrium utilized to construct the phase diagram were reported by Oliver and his co-workers<sup>119</sup>. The liquid-solid equilibrium (the change in melting point with change in pressure) was calculated from the Clausius-Clapeyron equation:

$$\frac{dT_m}{dP} = \frac{T(V_l - V_s)}{\Delta H_f} = 0.0439 \text{ deg.}/\text{atm.} \quad (121)$$

where  $\Delta H_f = 4588 \text{ cal.}/\text{mole}$  and the volumes,  $V_l$  and  $V_s$ , of the liquid and solid were obtained from density values given in this report.

#### $\text{UF}_6$ BINARY EQUILIBRIUM SYSTEMS

The solid-liquid and liquid-vapor equilibria of various  $\text{UF}_6$ -fluorocarbon systems have been experimentally evaluated. Many of the earlier data have been summarized in other publications<sup>62, 101</sup>.

Most of the experimental equilibrium data have been compared to the equilibrium data predicted by Raoult's law. However, in most of the recent investigations, the experimental data also have been compared to equilibrium data calculated by the activity coefficient technique of Hildebrand, Wood, Scatchard, Flory, and Higgins. This technique, which is discussed in detail by Barber and his co-workers<sup>14, 145</sup> utilizes the basic physical and thermodynamic properties of the pure components. From data relative to vapor pressure, heats of vaporization, molecular weights, and densities of the pure components, the activity coefficients and the phase composition of the system can be computed. In the case of  $\text{UF}_6$ -fluorocarbon equilibrium, the experimental data compare better with the data predicted by the activity coefficient method than they do with data predicted by Raoult's law. The results calculated using Raoult's law are referred to as "ideal" while those calculated by the activity coefficient technique are referred to as "theoretical."

#### SOLID AND LIQUID URANIUM HEXAFLUORIDE IN PERFECT SOLUTIONS

Libby<sup>100</sup> determined the solubility of vaporous and solid  $\text{UF}_6$  in perfect solutions using the vapor pressure data of Crist and Weinstock<sup>142</sup> and the equation:

$$Z = \frac{N}{(1-N)} \times \frac{35,200}{Y} \quad (122)$$

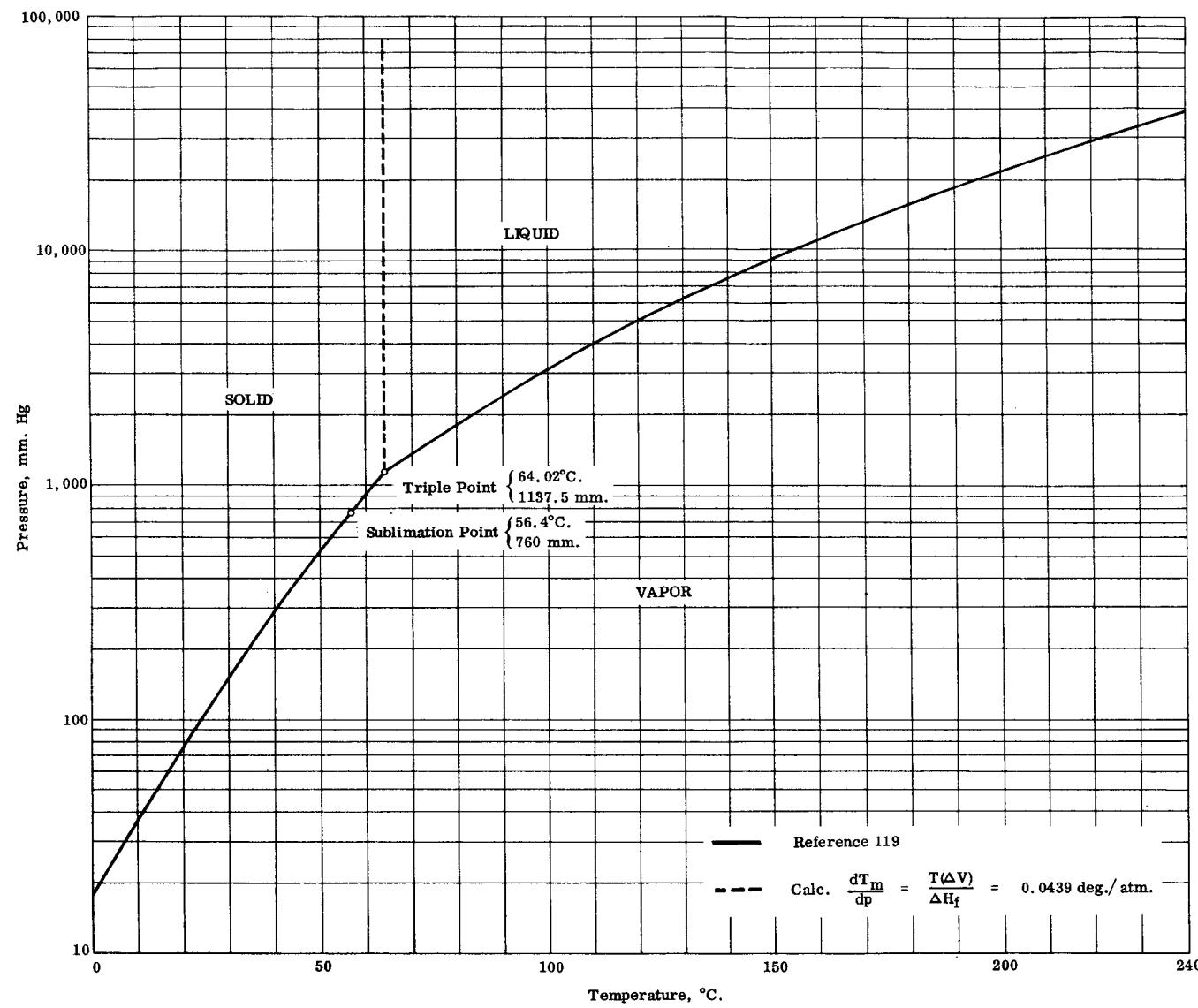


FIG. 25. PHASE DIAGRAM

where  $Z$  is the solubility in grams per 100 grams of solvent of molecular weight  $Y$ , and where  $N$ , which is the mole fraction of  $UF_6$  at 100 mm. Hg pressure in the saturated solution, can be calculated from the equation:

$$N = 10 (1486/T - 4.44)/11.70. \quad (123)$$

The solubilities of vaporous  $UF_6$  per 100 grams of solvent having a molecular weight  $Y$  at 100 mm. Hg pressure are given in the first part of Table 50 while those for solid  $UF_6$  are given in the second part.

#### URANIUM HEXAFLUORIDE IN FLUOROCARBONS GD-727c AND GD-727h

Kirshenbaum<sup>91</sup> determined the solubility of  $UF_6$  in the fluorocarbons GD-727c and GD-727h (Dupont samples). Lubricating oil fraction GD-727c was cut from 147° to 157°C./10 mm. Hg and was found to have an F/C ratio of 1.73/1, indicating a molecular weight of 900. Fraction GD-727h was cut from 197° to 207° C./10 mm. Hg. The experimental solubility values of  $UF_6$  in GD-727c and in GD-727h at various temperatures and pressures are presented in Table 51. These results agree with the calculated results obtained using Libby's formulae (Equations 122 and 123), although a better comparison (0 to 10 percent lower than ideal) can be obtained using a value of 1000 for the molecular weight of the oil.

Table 50  
SOLUBILITY IN PERFECT SOLUTIONS \*

(Reference 100)

Y	Solubility of the vapor per 100 grams of solvent of Y molecular weight								
	20°	30°	40°	50°	60°	70°	80°	90°	100°
100	236	129.3	80.9	54.6	37.3	27.0	19.8	14.8	11.5
200	118.0	64.65	40.45	27.30	18.65	13.5	9.90	7.40	5.75
300	78.7	43.1	26.9	18.2	12.42	8.99	6.60	4.94	5.83
400	59.0	32.3	20.2	13.6	9.33	6.75	4.95	3.70	2.87
500	47.2	25.86	16.18	10.92	7.46	5.40	3.96	2.96	2.30
600	39.3	21.6	13.50	9.10	6.21	4.50	3.30	2.47	1.92
700	33.7	18.5	11.52	7.80	5.33	3.86	2.83	2.11	1.64
800	29.5	16.2	10.12	6.84	4.66	3.38	2.47	1.85	1.44
900	26.2	14.4	8.99	6.07	4.15	3.00	2.20	1.65	1.28
1000	23.6	12.93	8.09	5.46	3.73	2.70	1.98	1.48	1.15

Solubility of the solid per 100 grams of solvent of Y molecular weight

Y	20°	30°	40°	50°	60°
100	177.2	280	462	919	3600
200	88.6	140	231	459.5	1800
300	59.07	93.3	154	306.3	1200
400	44.3	70.0	113	229.8	900
500	35.4	56.0	92.4	183.8	720
600	29.5	46.6	77.0	153.0	600
700	25.3	40.0	66.0	131.2	515
800	22.1	35.0	57.7	114.8	450
900	19.7	31.1	51.3	102.0	400
1000	17.7	28.0	46.2	91.9	360

\*Temperature is in degrees Centigrade.

Table 51  
SOLUBILITY IN THE HYDROCARBONS  
(Reference 91)

Temperature (°C.)	Pressure (mm. Hg)	Grams UF <sub>6</sub> /100 g. Oil	Temperature (°C.)	Pressure (mm. Hg)	Grams UF <sub>6</sub> /100 g. Oil
<u>In GD-727c</u>					
26	53	4.65	71	73	1.90
	41	4.28		48	1.03
	38	3.90		32	0.74
	34	3.36		19	0.57
	28	2.96		16	0.42
	24	2.50		12	0.33
	17	1.86		9	0.24
	97	4.62		5	0.12
51	77	3.67	80	101	1.91
	58	2.61		69	1.43
	39	1.90		51	0.98
	22	1.12		35	0.68
	14	0.64		24	0.49
				14	0.26
			100	98	0.91
				74	0.76
				42	0.44
				25	0.23
<u>In GD-727h</u>					
76	80	1.09	106	53	0.63
	45	0.68		48	0.53
	26	0.39		30	0.36
	15	0.23		16	0.25
				13	0.16

URANIUM HEXAFLUORIDE IN FLUOROCARBONS MFL (CHLOROTRIFLUORETHYLENE LIQUID POLYMER) AND C-2144

The solubilities of UF<sub>6</sub> in MFL (chlorotrifluoroethylene liquid polymer) lubrication oil, having the formula (CF<sub>2</sub> = CFCI)<sub>n</sub> and a molecular weight of 770, and in C-2144, having the formula CF<sub>3</sub>(CF<sub>2</sub>)<sub>19</sub>CF<sub>3</sub>, were experimentally determined<sup>149</sup>. The results are listed in Tables 52 and 53. It was found in the case of both solvents that the ratio of the measured solubility to the calculated solubility is less than one at low temperatures, but that it increases to a value of one at temperatures of 180°F. and higher. It was pointed out<sup>149</sup> that the deviation of the solubility from that predicted by Raoult's law at the lower temperatures was probably due to association and, hence, to a higher average effective molecular weight. At the higher temperature the solutions appear to be ideal.

Gabbard and McHenry<sup>64</sup> studied the vapor pressure relationship to the viscosity, density, and composition of a UF<sub>6</sub>-chlorotrifluoroethylene liquid polymer solution. The vapor pressure measurements were made at 60°C. from 0 to 650 mm. Hg pressure. The solution was found to deviate from Raoult's law. The composition and vapor pressure

Table 52  
SOLUBILITY IN MFL\*  
(Reference 149)

Temperature of Oil (°F.)	UF <sub>6</sub> Partial Pressure (psia.)	Solubility (lb. /gal.)		Ratio Measured/Calculated
		Measured	Calculated	
100	1.43	1.30	1.52	0.86
	1.44	1.18	1.52	0.78
	1.40	1.12	1.46	0.77
	1.44	1.23	1.52	0.81
	1.48	1.25	1.59	0.79
	1.53	1.29	1.65	0.78
	1.56	1.30	1.65	0.79
	1.56	1.29	1.65	0.78
	2.94	2.84	3.8	0.75
	2.94	3.16	3.8	0.83 Av. 0.79 ± 0.08
	1.59	0.54	0.71	0.76
	1.63	0.56	0.72	0.78
140	2.06	0.94	0.92	1.02
	2.69	1.22	1.21	1.01
	2.90	1.26	1.32	0.95 Av. 0.90 ± 0.11
	1.62	0.43	0.35	1.23
	1.62	0.35	0.35	1.00
	1.62	0.36	0.35	1.03
	1.62	0.37	0.35	1.06
	1.62	0.41	0.35	1.17
	1.43	0.41	0.31	1.32
	1.47	0.37	0.33	1.12
180	1.93	0.41	0.42	0.98
	2.17	0.50	0.45	1.11
	2.22	0.45	0.49	0.92
	2.40	0.49	0.53	0.92
	2.51	0.61	0.54	1.13
	2.85	0.61	0.62	0.98 Av. 1.07 ± 0.10
	2.29	0.20	0.28	0.71
	2.85	0.41	0.35	1.17
	2.90	0.44	0.36	1.22 Av. 1.03 ± 0.22
	1.62	0.18	0.20	0.90
	1.62	0.18	0.20	0.90
	2.41	0.34	0.30	1.13
220	2.95	0.39	0.37	1.05 Av. 1.00 ± 0.10

\*Molecular weight of MFL (790 ± 30) estimated from boiling point elevation.  
A value of 750 was used in calculations.

Table 53  
SOLUBILITY IN C-2144\*  
(Reference (149))

Temperature of Oil (°F.)	UF <sub>6</sub> Partial Pressure (psia.)	Solubility (lb./gal.)		Ratio Measured/Calculated
		Measured	Calculated	
140	1.02	0.30	0.34	0.88
	1.22	0.33	0.41	0.81
	1.85	0.41	0.60	0.63
	2.04	0.48	0.67	0.73 Av. 0.78 ± 0.07
180	2.16	0.39	0.35	1.11
212	1.62	0.14	0.15	0.94
	2.54	0.28	0.23	1.20
	2.85	0.26	0.26	0.97
	2.91	0.27	0.27	1.01 Av. 1.03 ± 0.08

\*Molecular weight (970 ± 50) estimated by boiling point elevation of C-716. A value of 1018 was used for calculations.

were related by the Margule's equation. The results are listed in Table 54 and Figure 26.

Johnson also reports vapor pressure values for UF<sub>6</sub> above a UF<sub>6</sub>-C<sub>21</sub>F<sub>44</sub> system.<sup>85</sup>

#### URANIUM HEXAFLUORIDE IN DICHLOROTETRAFLUOROETHANE

The solubility of UF<sub>6</sub> in dichlorotetrafluoroethane (Freon-114) from 22° to 64°C. was experimentally determined by Barber, Posey, and Judkins<sup>14</sup>. They also determined a liquid-vapor isobar at 40 psia. The experimental results are shown in Figure 27 in which the solid, liquid, and vapor compositions are shown as functions of temperature. Both the liquid-solid and the liquid-vapor equilibria were calculated for the system over the 0° to 100°C. range.

In addition to calculating an ideal phase relationship using Raoult's law, Barber and his co-workers also calculated phase relationships using a theoretical method based on the work of Hildebrand\* and others.<sup>14, 145</sup> This method requires that vapor pressures, heats of vaporization, molecular weights, and densities of the pure components be known for calculation of the activity coefficients from which the equilibrium data can be determined. The calculated activity coefficients are plotted as a function of composition in Figure 28. The experimental, theoretical, and ideal solubilities are shown in Figure 29. The experimental and calculated liquid-vapor equilibria at 40 psia. are shown in Figure 30. In this figure the experimental concentration of the more volatile component (Freon-114) in the vapor is plotted as a function of the experimental concentration of the more volatile component in the liquid.

\*Hildebrand, J. H. and Wood, S. E. J. Chem. Phys. 1, 817(1933).

Table 54  
VAPOR PRESSURE, COMPOSITION, AND DENSITY OF CHLOROTRIFLUOROETHYLENE  
LIQUID POLYMER AND URANIUM HEXAFLUORIDE SOLUTIONS AT 60°C.

(Reference 64)

Vapor Pressure (mm. Hg)	Composition (mole percent UF <sub>6</sub> )	Density (g./cc.)
46	4.9	1.920
52	6.3	
84	9.9	1.925
136		1.921
160		1.940
174		1.932
223	24.2	1.935
225		1.944
244	27.8	
260		1.949
278	31.4	
278	31.1	
283		1.941
325		1.983
330	36.1	1.975
347		1.991
351	38.7	
351	38.0	
351	37.9	
351	37.4	
367	38.9	1.987
375	39.8	
375	40.7	
375	41.0	
375	41.5	
402	42.9	2.033
410		2.053
410		2.078
452	44.6	
484	49.2	2.097
507		2.136
532		2.130
547		2.163
558		2.196
565	53.2	2.187
581	55.9	2.188
605		2.222
630		2.246
638		2.249
638		2.241
638		2.260
649		2.262

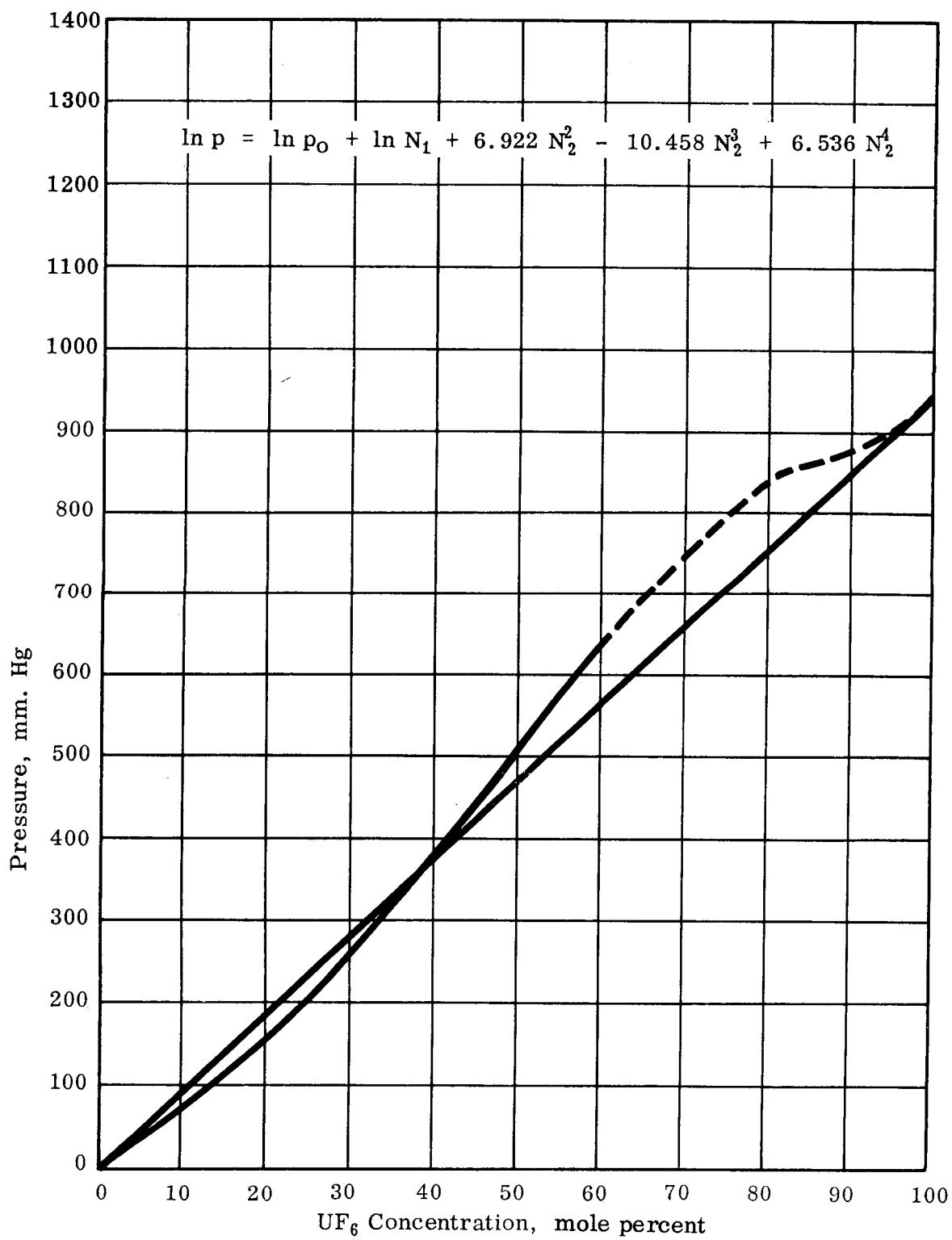


FIG. 26. COMPOSITION OF URANIUM HEXAFLUORIDE AND CHLOROTRIFLUOROETHYLENE POLYMER SOLUTIONS AS A FUNCTION OF THE EQUILIBRIUM PRESSURE OF URANIUM HEXAFLUORIDE AT 60°C.

(Reference 125)

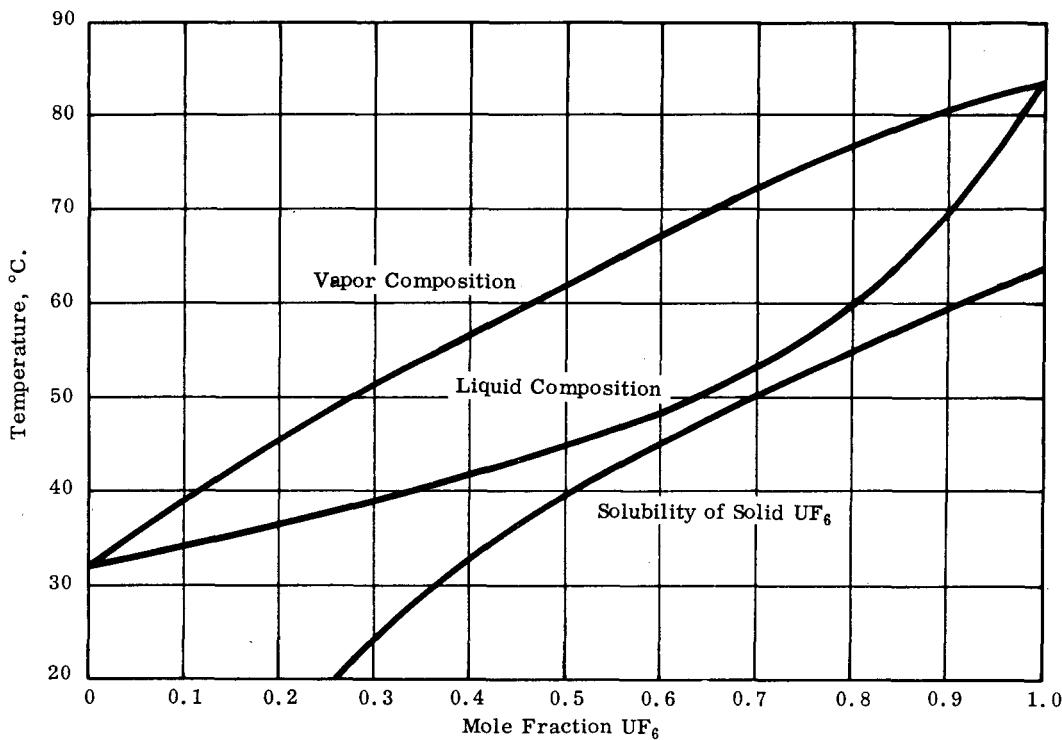


FIG. 27. VAPOR-LIQUID AND SOLID-LIQUID EQUILIBRIUM COMPOSITION OF THE URANIUM HEXAFLUORIDE-FREON-114 SYSTEM UNDER 40 PSIA. PRESSURE (Reference 14)

#### URANIUM HEXAFLUORIDE IN PERFLUOROTRIBUTYLAMINE

Jordon, Posey, and Rutledge<sup>86</sup> determined the solid-liquid and liquid-vapor equilibria of the  $\text{UF}_6$ -perfluorotributylamine system. The studies were conducted at 40 psia. and at temperatures ranging from 64° to 220°C. In addition, the solubility of  $\text{UF}_6$  in perfluorotributylamine was also determined at temperatures from 1° to 64°C. by slowly cooling solutions of known concentration until precipitation occurred. The experimental results were found to deviate from the results calculated from Raoult's law. However, there was less deviation from the results calculated by use of the activity coefficient technique. The experimental and calculated equilibria data are presented in Table 55

Table 55  
SOLUBILITY IN PERFLUOROTRIBUTYLAMINE  
(Reference 86)

Temperature (°C.)	Formula Percent $\text{UF}_6$	Temperature, (°C.)	Formula Percent $\text{UF}_6$
0.94	13.28	48.47	61.74
11.31	20.08	53.85	74.10
19.87	25.93	58.17	84.89
30.90	37.65	59.50	88.77
38.24	47.55	64.02	100.00

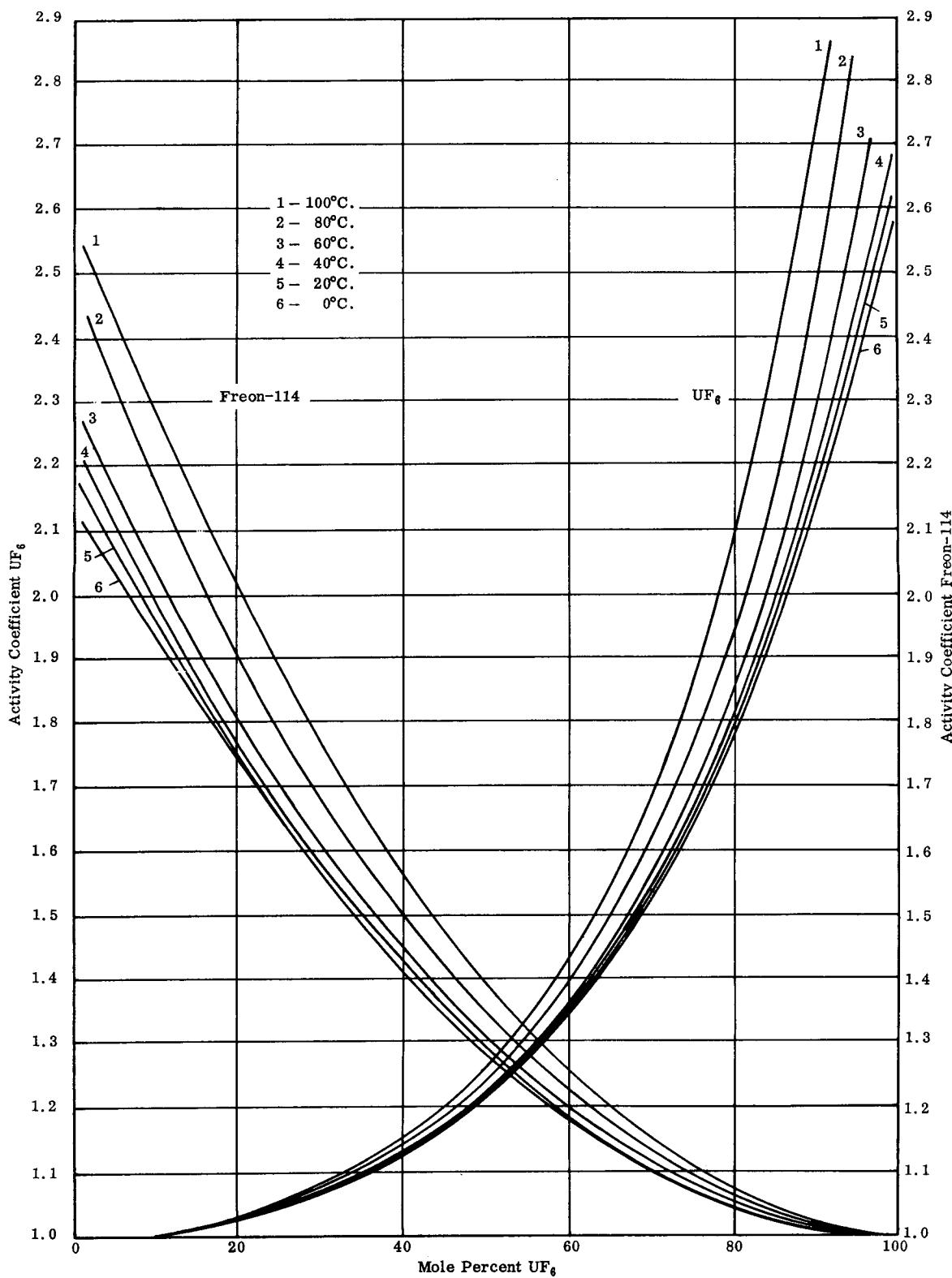


FIG. 28. ACTIVITY COEFFICIENT OF URANIUM HEXAFLUORIDE IN FREON-114 AS A FUNCTION OF COMPOSITION AT VARIOUS TEMPERATURES (Reference 14)

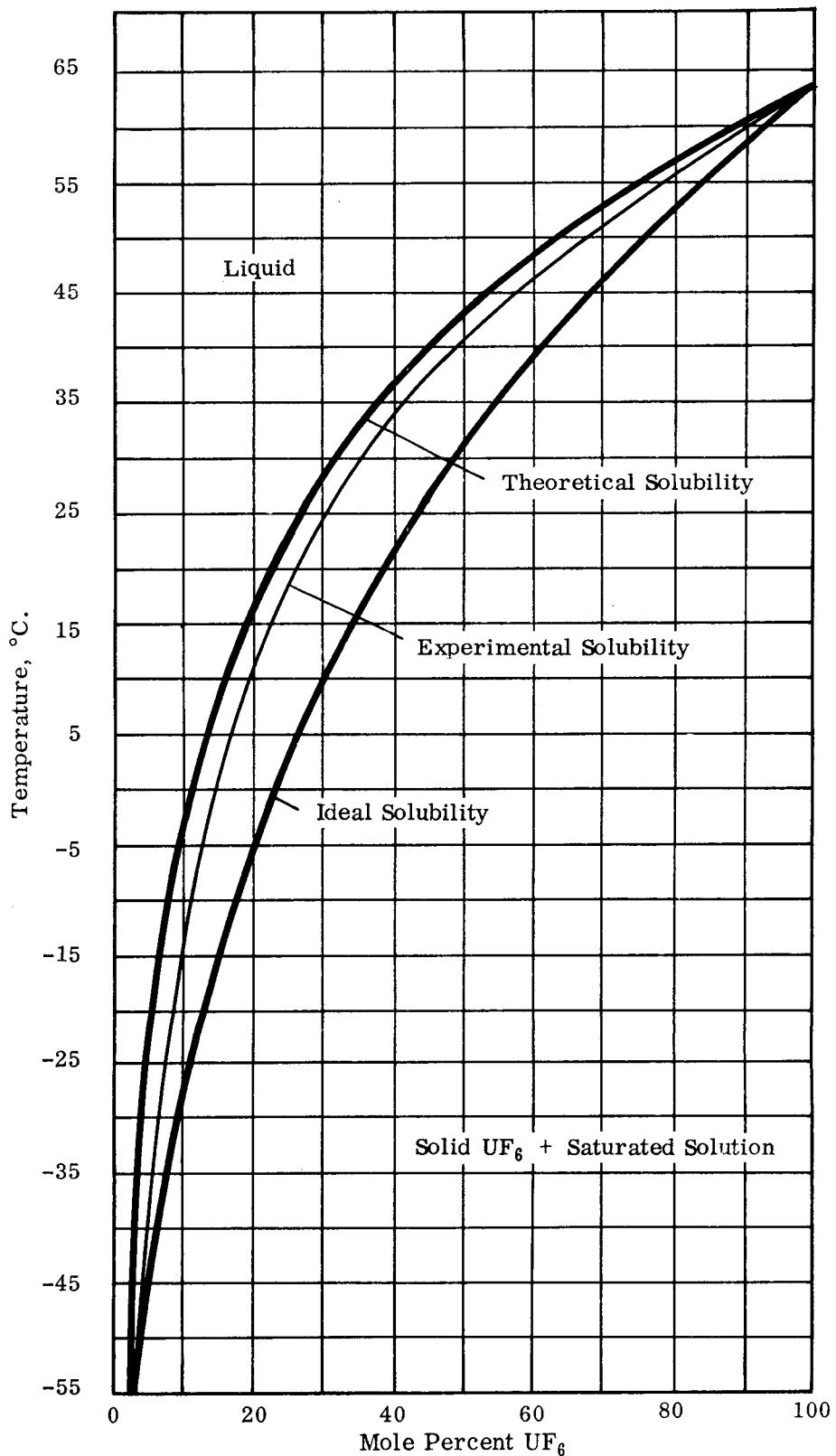


FIG. 29. SOLID - LIQUID EQUILIBRIUM OF THE URANIUM HEXAFLUORIDE - FREON-114 SYSTEM  
(Reference 14)

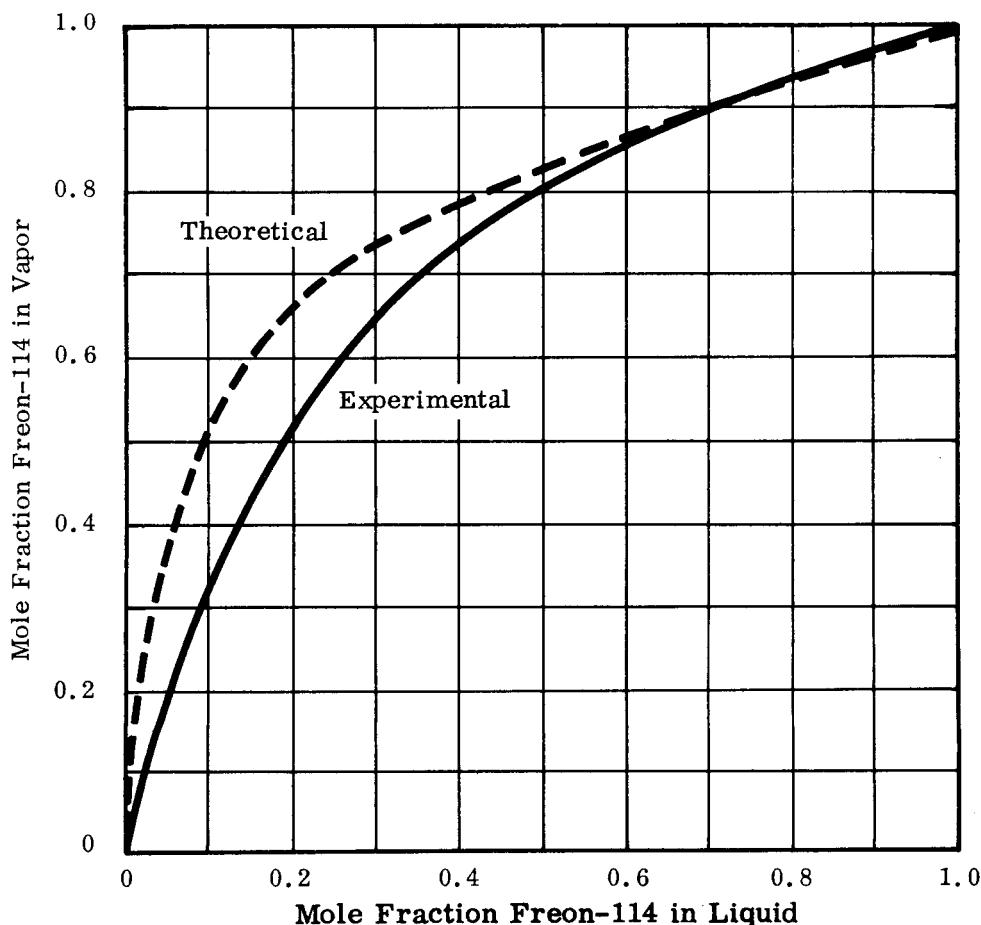


FIG. 30. LIQUID-VAPOR EQUILIBRIUM OF THE URANIUM HEXAFLUORIDE AND FREON-114 SYSTEM AT 40 PSIA. PRESSURE  
(Reference 14)

and in Figure 31. A comparison of the calculated and experimental coefficients is given in Table 56. The experimental liquid-vapor equilibria at 40 psia. are presented in Table 57 and a comparison of the experimental data with the calculated data is presented in Figure 32.

#### URANIUM HEXAFLUORIDE IN PERFLUOROISOPROPYL ETHER

Kirshenbaum<sup>62</sup> (see also References 115 and 116) investigated the equilibria of the  $\text{UF}_6$ -perfluoroisopropyl ether system. The results of the solubility studies of  $\text{UF}_6$  vapor in perfluoroisopropyl ether are presented in Table 58, while the results with solid  $\text{UF}_6$  in the same compound appear in Table 59.

#### URANIUM HEXAFLUORIDE IN PERFLUORO-*n*-PENTANE AND IN 1,2-DICHLOROHEXAFLUOROPROPANE

Posey and Barber<sup>126</sup> calculated the liquid-vapor equilibria of the  $\text{UF}_6$ -perfluoro-*n*-pentane and  $\text{UF}_6$ -1,2-dichlorohexafluoropropane systems by using the activity coefficient technique. The calculated activity coefficient, phase compositions, and total pressures for the  $\text{UF}_6$ -perfluoro-*n*-pentane system at 60°, 70°, 80°, and 90°C. are listed in Table 60 while those for the  $\text{UF}_6$ -1,2-dichlorohexafluoropropane system are given in Table 61.

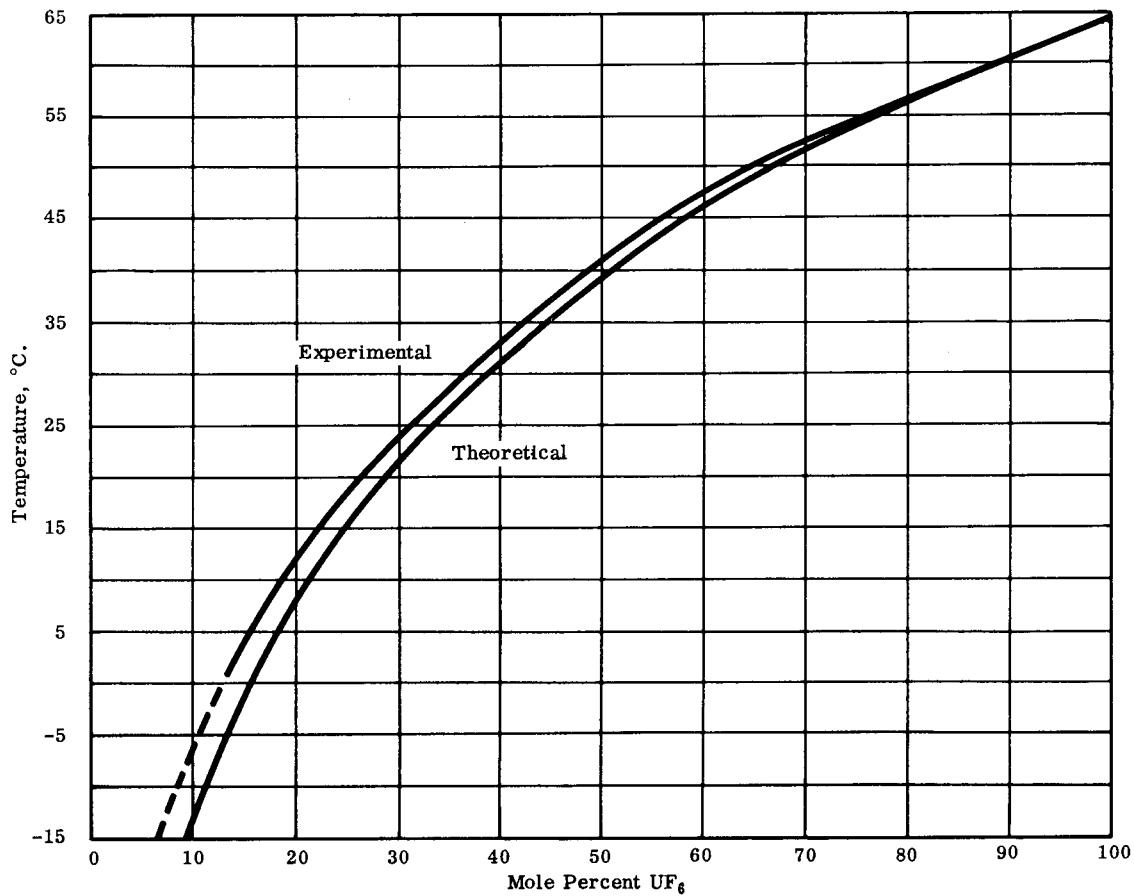


FIG. 31. SOLID - LIQUID EQUILIBRIUM OF THE URANIUM HEXAFLUORIDE - PERFLUOROTRIBUTYLAMINE SYSTEM  
(Reference 86)

Table 56  
ACTIVITY COEFFICIENTS IN PERFLUOROTRIBUTYLAMINE  
(Reference 86)

Temperature (°C.)	Experimental*	Theoretical†
-20	2.400	1.513
0	1.650	1.346
20	1.380	1.236
40	1.200	1.154
60	1.020	1.031
64	1.000	1.000

\*Calculated by using "smoothed" data.

†Calculated by using the activity coefficient method.

Table 57  
 LIQUID-VAPOR EQUILIBRIUM OF THE URANIUM HEXAFLUORIDE-  
 PERFLUOROTRIBUTYLAMINE SYSTEM  
 (Reference 86)

Pressure (psia.)	Boiling Temperature (°C.)	Composition (mole percent $UF_6$ )		Corrected Boiling Point at 40 psia.
		Liquid	Vapor	
39.9	84.0	89.1	99.3	84.1
40.9	90.0	55.0	96.9	89.2
42.6	93.2	46.4	98.6	90.8
39.7	95.4	29.1	98.9	95.7
39.9	109.5	15.3	96.5	109.6
39.9	119.6	13.2	94.5	119.7
40.5	139.9	16.3	92.2	139.4
40.4	182.9	9.87	69.3	182.5
40.0	200.6	4.35	47.8	200.6
39.9	209.2	0.88	15.1	209.3
39.9	219.6	0.00	0.0	219.7

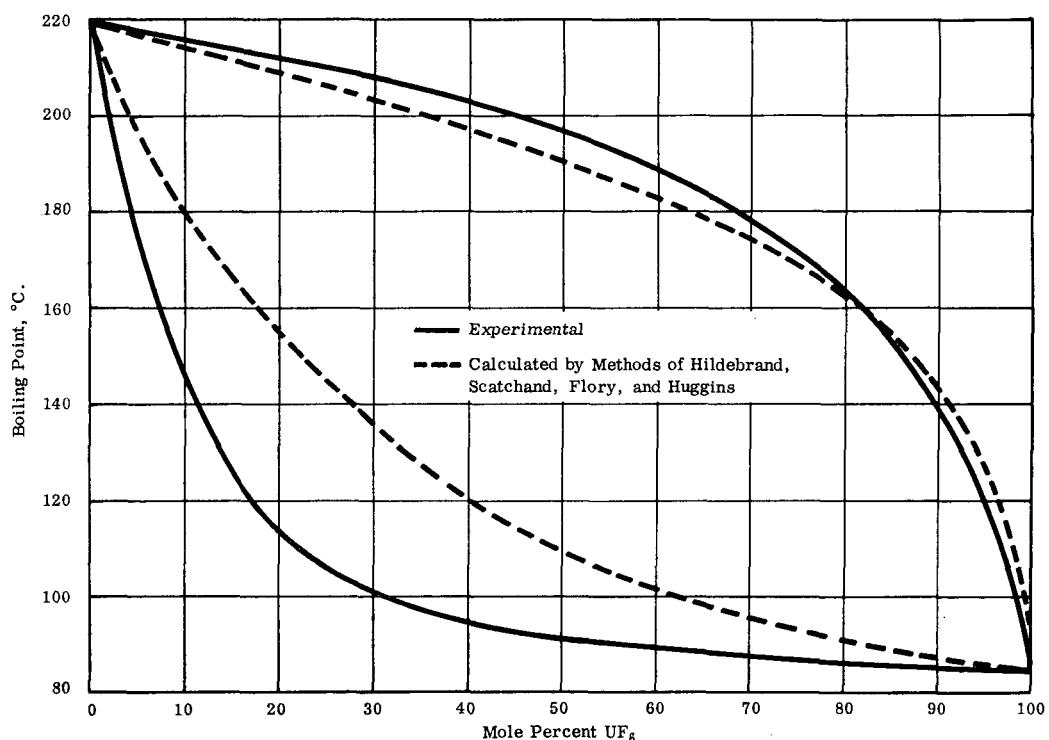


FIG. 32. LIQUID-VAPOR EQUILIBRIUM OF THE URANIUM HEXAFLUORIDE AND PERFLUOROTRIBUTYLAMINE SYSTEM AT 40 PSIA. PRESSURE  
 (Reference 86)

Table 58  
SOLUBILITY OF THE VAPOR IN PERFLUOROISOPROPYL ETHER  
(Reference 62)

Temperature (°C.)	Total Pressure (mm. Hg)	Pressure of $UF_6^*$ (mm. Hg)	Grams $UF_6$ / 100 g. Solvent	Mole Fraction $UF_6$	Raoult's Mole Fraction $UF_6$	$\gamma UF_6$
0.0	110.1	10.1	6.9	0.065	0.122	1.88
10.0	175.5	24.5	11.7	0.105	0.188	1.79
20.0	271.0	57.0	19.7	0.165	0.262	1.59
30.0	406.7	96.7	21.2	0.176	0.292	1.65
30.0	423.5	139.0	33.0	0.249	0.524	2.10
40.0	594.4	149.0	21.2	0.176	0.269	1.53
40.0	626.5	243.0	41.3	0.293	0.487	1.66
50.0	848.5	221.0	21.2	0.176	0.314	1.78
50.0	904.8	367.0	41.3	0.293	0.520	1.78

\*Assuming  $\gamma$  ether = 1.

Table 59  
SOLUBILITY OF THE SOLID IN PERFLUOROISOPROPYL ETHER  
(Reference 62)

Temperature (°C.)	Mole Fraction $UF_6$	Raoult's Mole Fraction $UF_6$	$\gamma UF_6$
0	0.0645	0.21	3.26
10	0.102	0.31	3.04
20	0.159	0.37	2.33
30	0.246	0.46	1.87
40	0.356	0.58	1.63
50	0.514	0.76	1.48

Table 60  
 LIQUID-VAPOR EQUILIBRIUM OF THE URANIUM HEXAFLUORIDE -  
 PERFLUORO-*n*-PENTANE SYSTEM

(Reference 126)

Mole Fraction UF <sub>6</sub> in Liquid	Activity Coefficient of UF <sub>6</sub>				Mole Fraction UF <sub>6</sub> in Vapor				Total Pressure (mm. Hg)			
	60°C.	70°C.	80°C.	90°C.	60°C.	70°C.	80°C.	90°C.	60°C.	70°C.	80°C.	90°C.
0.00	--	--	--	--	0.00	0.00	0.00	0.00	2084	2767	3606	4622
0.01	2.508	2.445	2.332	2.163	0.012	0.012	0.012	--	2088	2773	3613	4657
0.05	2.420	2.365	2.259	2.082	0.058	0.058	0.057	0.017	2103	2794	3637	4681
0.10	2.313	2.264	2.169	1.922	0.109	0.110	0.109	0.108	2116	2812	3659	4697
0.20	2.103	2.066	1.990	1.611	0.198	0.200	0.199	0.198	2124	2827	3674	4614
0.40	1.712	1.692	1.650	1.330	0.328	0.334	0.336	0.338	2084	2779	3612	4414
0.60	1.373	1.366	1.347	1.105	0.413	0.421	0.430	0.438	1994	2662	3457	4086
0.80	1.116	1.114	1.110	1.031	0.480	0.492	0.509	0.524	1861	2482	3210	3702
0.90	1.034	1.033	1.032	1.008	0.552	0.566	0.587	0.607	1685	2250	2908	3277
0.95	1.009	1.009	1.009	1.000	0.653	0.667	0.689	0.708	1467	1969	2560	2648
1.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	999*	1370	1840	2422

\*Extrapolated from the vapor pressure curve for UF<sub>6</sub>.

Table 61  
 PRESSURE - COMPOSITION EQUILIBRIUM OF THE URANIUM HEXAFLUORIDE -  
 1, 2 -DICHLOROHEXAFLUOROPROPANE SYSTEM  
 (Reference 126)

Mole Fraction $UF_6$		Total Pressure (mm. Hg)	Activity Coefficient $UF_6$ in Liquid
Liquid	Vapor		
0	0	456.6	-----
0.10	0.084	458	1.777
0.20	0.158	446	1.631
0.40	0.284	422	1.380
0.60	0.384	379	1.119
0.80	0.544	336	1.052
0.90	0.669	296	1.014
1.00	1.000	217	1.000

The phase compositions of the  $UF_6$ -perfluoro-*n*-pentane system at 60°, 70°, 80° and 90°C. are presented in Figure 33. The authors pointed out that an azeotrope formation is indicated by the calculated results.

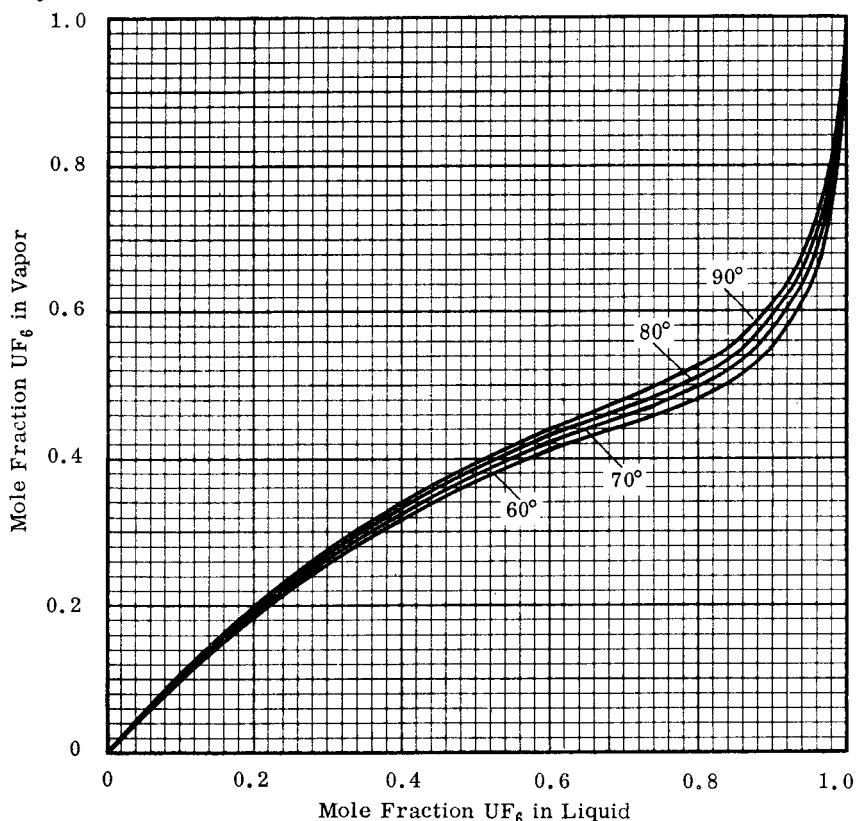


FIG. 33. LIQUID - VAPOR EQUILIBRIUM OF THE URANIUM  
 HEXAFLUORIDE-PERFLUORO-*n*-PENTANE SYSTEM

URANIUM HEXAFLUORIDE IN PERFLUOROHEPTANE

Haendler and Barber<sup>72</sup> investigated the liquid-vapor equilibrium of the  $\text{UF}_6$ -perfluoroheptane system at 1520 mm. Hg. The results are listed in Table 62. It was noted that the experimental difficulties encountered in the measurement of this system were such that extreme accuracy could not be claimed. A temperature-composition diagram of the system is presented in Figure 34.

Table 62  
EQUILIBRIUM DATA OF THE URANIUM HEXAFLUORIDE -  
PERFLUOROHEPTANE SYSTEM  
(Reference 72)

Temperature (°C.)	Mole Percent $\text{UF}_6$		Activity Coefficient of $\text{UF}_6$
	Liquid	Vapor	
105.3	0	0	-
103.8	1.50	6.85	2.28
101.8	3.95	13.4	1.76
101.0	4.89	16.3	1.74
99.1	7.47	23.2	1.68
98.7	7.59	24.1	1.72
82.8	44.9	70.9	1.24
80.8	56.1	76.5	1.14
78.9	65.6	82.1	1.06
78.0	72.4	85.2	1.02
77.2	75.7	87.8	1.04
76.4	80.0	90.9	1.04
75.8	84.0	92.4	1.03
75.2	91.5	93.1	0.97
73.8	97.8	99.2	1.01
73.6	100.0	100.0	1.00

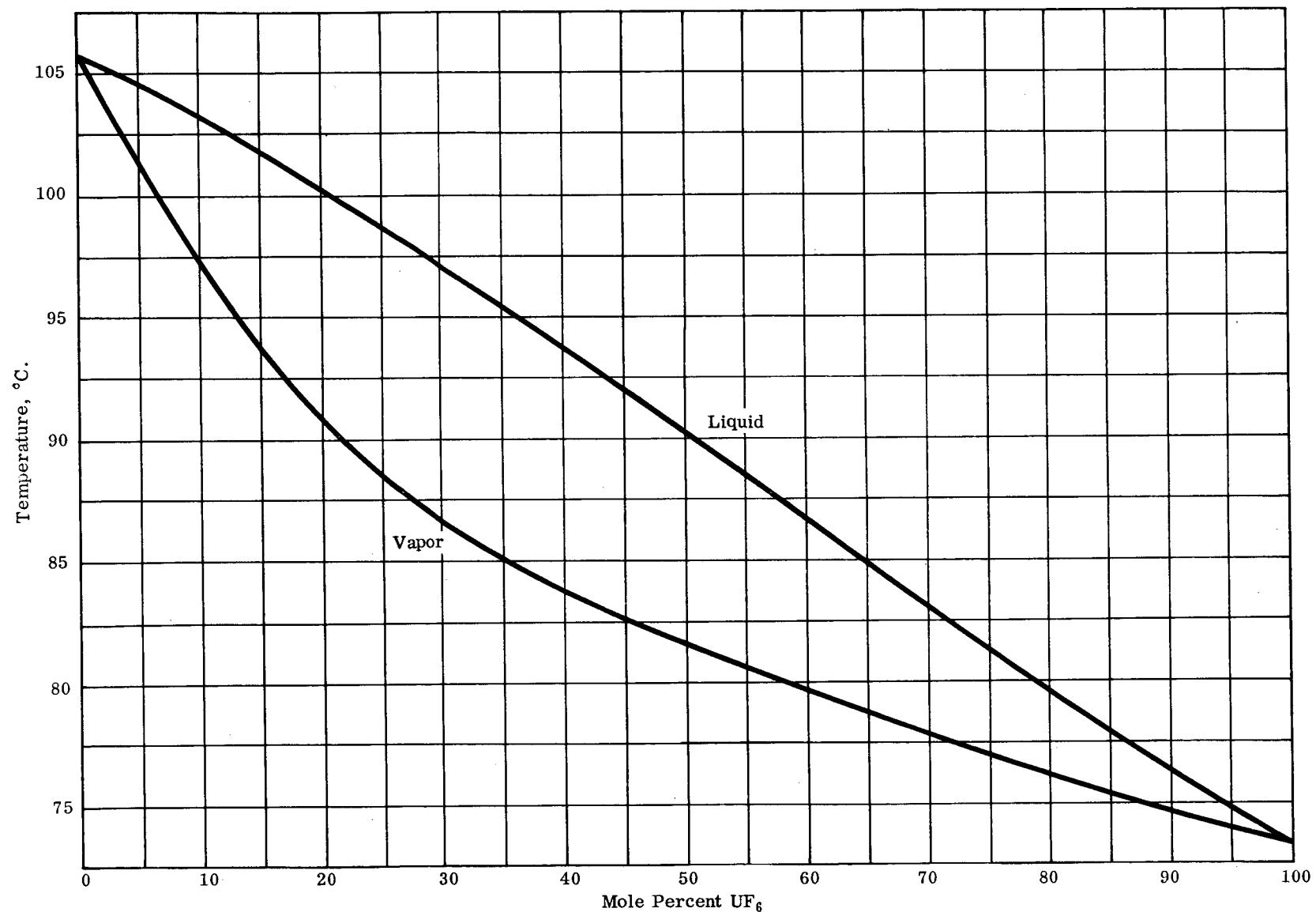


FIG. 34. LIQUID - VAPOR EQUILIBRIUM OF THE URANIUM HEXAFLUORIDE-  
PERFLUOROHEPTANE SYSTEM (Reference 72)

### URANIUM HEXAFLUORIDE IN 2, 2, 3-TRICHLOROHEPTAFLUOROBUTANE

Kuykendall, Jones, Rapp, and Barber<sup>95</sup> experimentally determined the solid-liquid equilibrium for temperatures ranging from 32° to 64°C. for the  $\text{UF}_6$ -2, 2, 3-trichloroheptafluorobutane system. In addition, the liquid-vapor equilibria were calculated at 30 to 40 psia. using the activity coefficient method.

The results of the solubility studies are presented in Table 63 and Figure 35. The agreement between the experimental and theoretical values are reported as being good. The theoretical values were calculated using the activity coefficient technique. The calculated liquid-vapor equilibrium data are presented in Table 64. The composition-temperature diagrams for 30 and 40 psia. are presented in Figures 36 and 37, respectively.

The solution densities of the  $\text{UF}_6$ -2, 2, 3-trichloroheptafluorobutane system were determined experimentally and the values fitted to the expression:

$$\ln \rho = \alpha(m) + \beta(m)X \text{ g./cc.} \quad (124)$$

where  $\rho$  is the solution density,  $m$  is the concentration of  $\text{UF}_6$  in mole percent,  $X$  is  $10^3/T^\circ\text{K.}$  and  $\alpha(m)$  and  $\beta(m)$  are expressed by the following equations:

$$\alpha(m) = 0.12698 + 3.73352 \times 10^{-3}m + 1.95458 \times 10^{-5}m^2 \quad (125)$$

$$\beta(m) = 0.12603 + 7.40421 \times 10^{-4}m \quad (126)$$

A comparison of the experimental and calculated densities is given in Table 65.

### URANIUM HEXAFLUORIDE IN C-816 (PERFLUORODIMETHYLCYCLOHEXANE)

Hodgson<sup>79</sup> found that at temperatures below -30°C., a mixture of 8.5 mole percent  $\text{C}_8\text{F}_{16}$  and 91.5 mole percent  $\text{UF}_6$  was a "free-flowing solid," while at temperatures above -30°C., the mixture tended to cake. At room temperature the solid resembled damp salt. Vapor composition data are consistent with complete miscibility above the melting point of the mixture (58.3°C.) and immiscibility below the melting point.

Gabbard, Bernstein, and Amis<sup>63</sup> studied the vapor-liquid equilibrium of the  $\text{UF}_6$ - $\text{C}_8\text{F}_{16}$  system at approximately 40 psia. A summary of the results is shown in Table 66. A comparison of the experimental data with calculated results (based on Raoult's law) appears in Figure 38. Data for a temperature-composition diagram (Figure 39) were obtained from the smooth curve of Figure 38. These data were found to compare favorably with the experimental data. The activity coefficients of  $\text{UF}_6$  and  $\text{C}_8\text{F}_{16}$  were calculated using the modification of Margule's method and are presented in Figure 40 which also contains the experimental values. The values used in the activity coefficient calculations were taken from the smooth curve in Figure 38.

Johnson<sup>85</sup> utilized the vapor pressure data of  $\text{UF}_6$  above its solutions in  $\text{C}_8\text{F}_{16}$  and  $\text{C}_{22}\text{F}_{44}$  (see also Reference 115) to make an extrapolation of the partial pressure of  $\text{UF}_6$  above these solutions through Raoult's and Henry's laws.

### URANIUM HEXAFLUORIDE IN HYDROGEN FLUORIDE

The solid-liquid, liquid-liquid, and liquid-vapor equilibria of the  $\text{UF}_6$ -HF system have been experimentally determined. Rutledge, Jarry, and Davis<sup>39, 133</sup> investigated the solid-liquid and liquid-liquid portions of the equilibria over the -85° to 105°C. range while Jarry, Rosen, Hale, and Davis<sup>40, 83</sup> investigated the liquid-vapor equilibria over the 40° to 105°C. range. Since the variation of the molecular weight of hydrogen

Table 63  
SOLUBILITY IN 2,2,3-TRICHLOROHEPTAFLUOROBUTANE  
(Reference 95)

Temperature (°C.)	Solubility (mole percent UF <sub>6</sub> )		
	Experimental	Theoretical	Ideal
32.4	42.3	44.5	49.5
37.5	48.6	51.0	55.9
38.4	50.2	52.3	57.0
44.3	59.5	61.5	65.3
45.9	62.0	64.0	67.8
54.1	80.1	80.0	81.3
55.9	82.4	83.5	84.5
64.0	100.0	100.0	100.0

Table 64  
CALCULATED LIQUID-VAPOR EQUILIBRIUM AT PRESSURES OF 30 AND  
40 PSIA. FOR THE URANIUM HEXAFLUORIDE-2,2,3-  
TRICHLOROHEPTAFLUOROBUTANE SYSTEM

(Reference 95)

Mole Percent UF <sub>6</sub> in Liquid	Temperature of Boiling (°C.)		Mole Percent UF <sub>6</sub> in Vapor	
	30 psia.	40 psia.	30 psia.	40 psia.
0.0	123.0	134.2	0.0	0.0
10.0	113.8	125.2	29.6	28.8
20.0	105.8	117.1	49.2	48.2
30.0	99.4	110.5	62.9	61.7
40.0	93.7	104.9	72.8	71.7
50.0	89.0	99.9	80.1	79.3
60.0	85.5	96.1	85.7	85.2
70.0	82.0	92.5	90.0	89.7
80.0	79.2	89.5	93.6	93.4
90.0	76.4	86.5	97.0	96.8
100.0	74.3	84.1	100.0	100.0

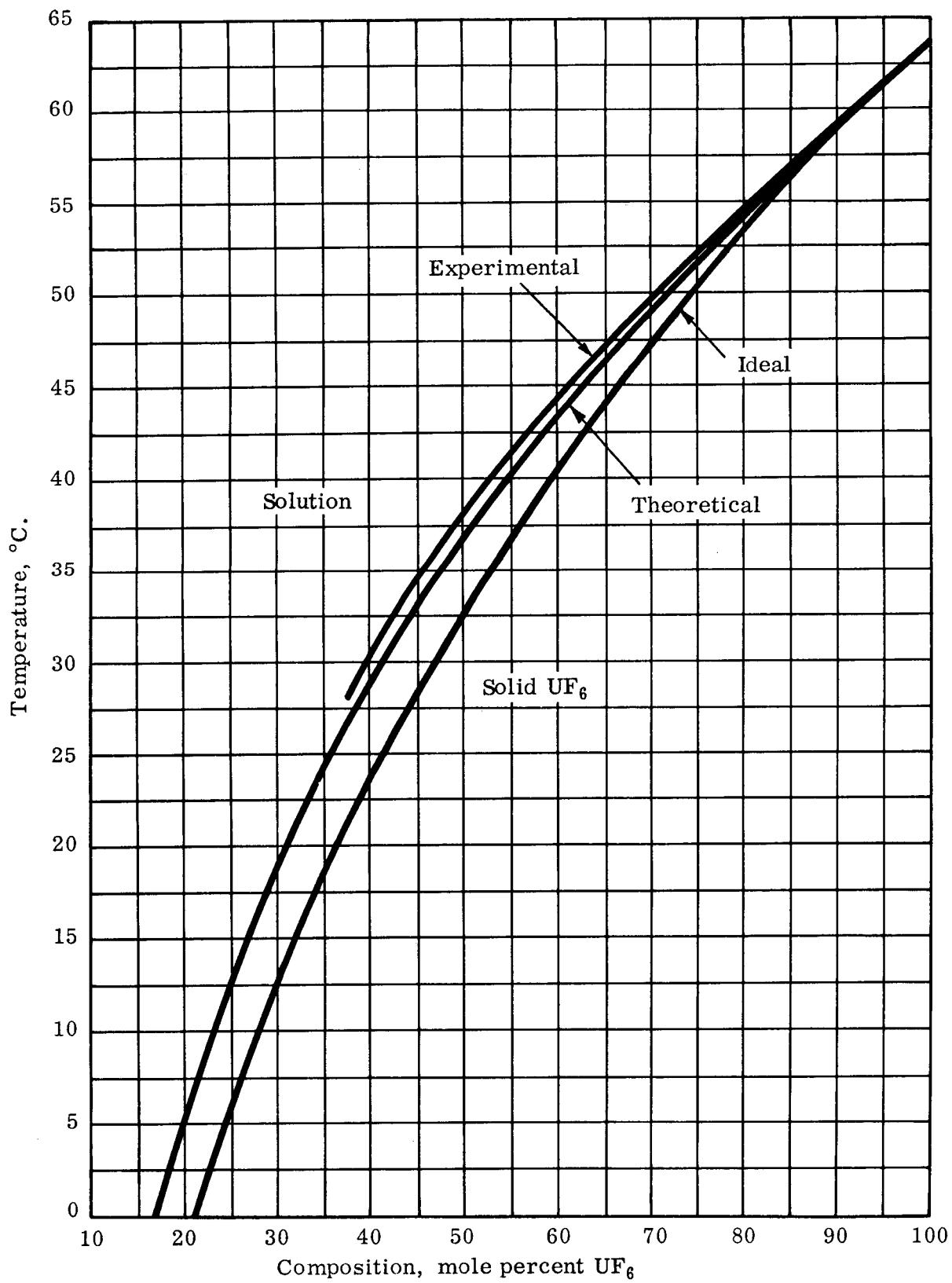


FIG. 35. SOLID - LIQUID EQUILIBRIUM OF THE URANIUM HEXAFLUORIDE-  
2,2,3-TRICHLOROHEPTAFLUOROBUTANE SYSTEM  
(Reference 95)

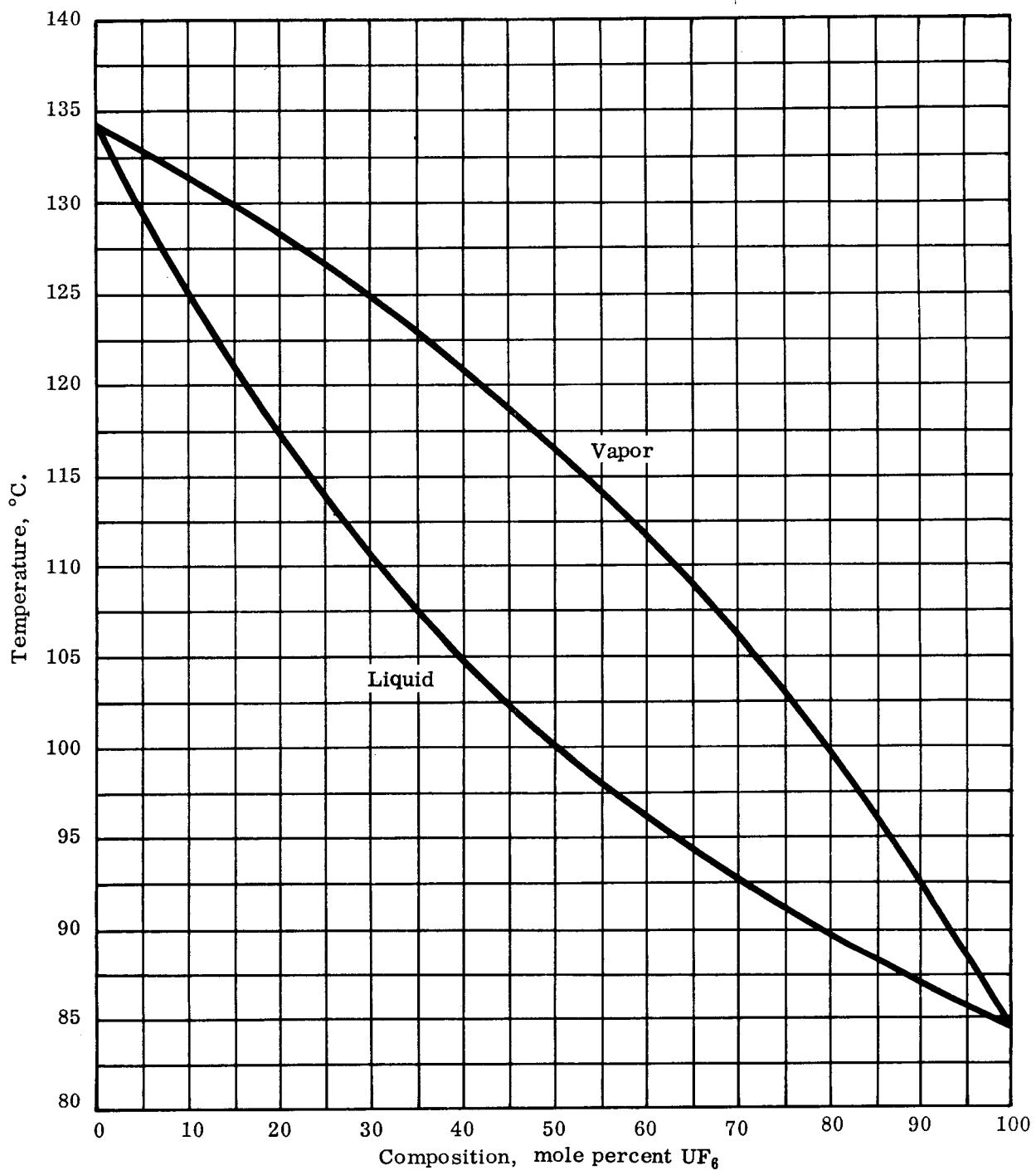


FIG. 36. VAPOR - LIQUID EQUILIBRIUM OF THE URANIUM HEXAFLUORIDE -  
2, 2, 3-TRICHLOROHEPTAFLUOROBUTANE SYSTEM AT 30 PSIA.  
PRESSURE  
(Reference 95)

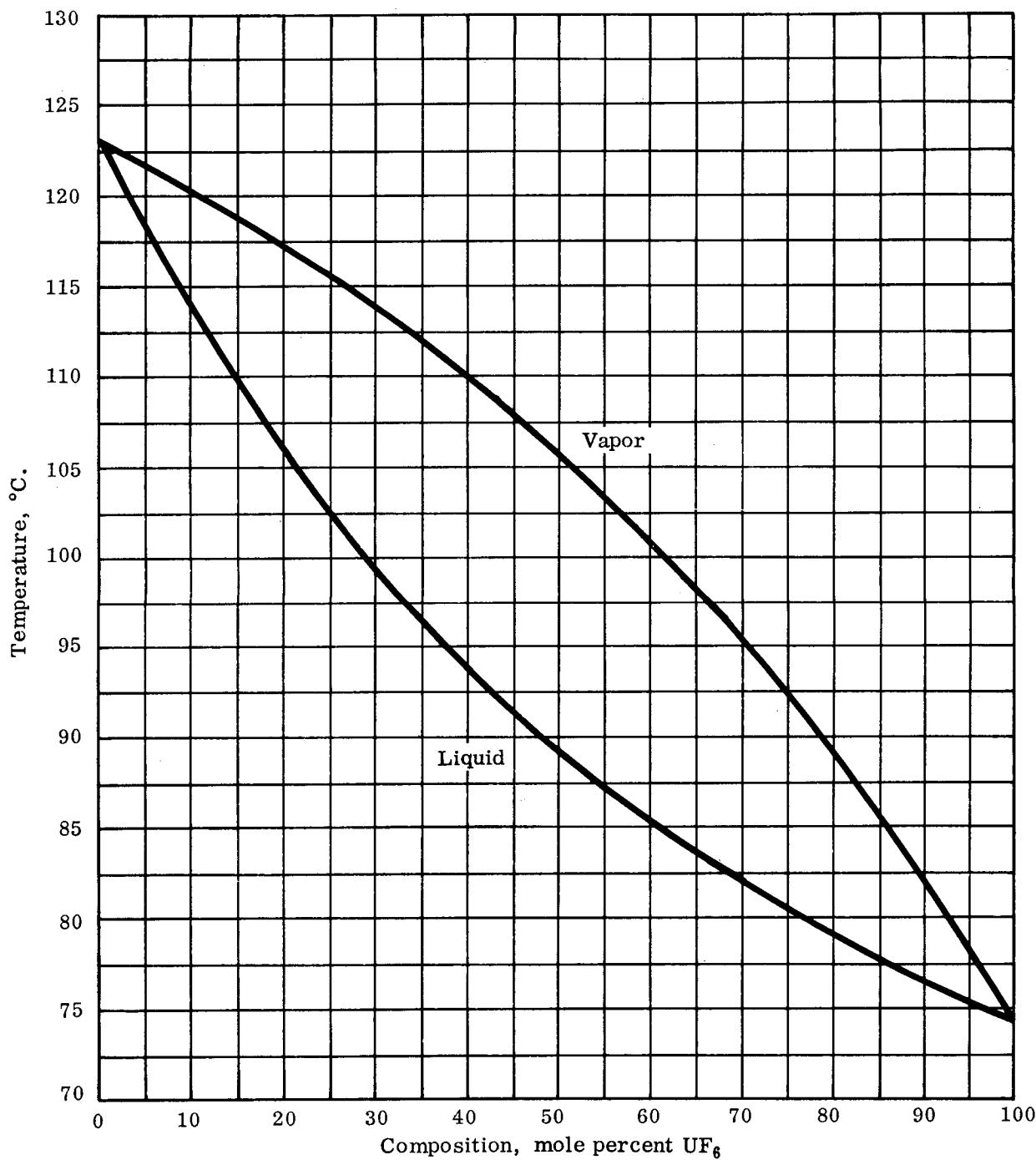


FIG. 37. VAPOR - LIQUID EQUILIBRIUM OF THE URANIUM HEXAFLUORIDE-  
2, 2, 3-TRICHLOROHEPTAFLUOROBUTANE SYSTEM AT 40 PSIA.  
PRESSURE  
(Reference 95)

Table 65  
 SOLUTION DENSITY OF THE  
 URANIUM HEXAFLUORIDE-2, 2, 3-TRICHLOROHEPTAFLUOROBUTANE SYSTEM,  
 EXPERIMENTAL AND CALCULATED RESULTS

(Reference 95)

Temperature (°C.)	Composition (mole percent UF <sub>6</sub> )	Experimental Density (g./cc.)	Calculated Density (g./cc.)	Deviation
25.2	16.97	1.944	1.936	- 0.008
35.0	16.97	1.916	1.907	- 0.009
45.0	16.97	1.888	1.880	- 0.008
50.2	16.97	1.874	1.867	- 0.007
35.0	28.32	2.065	2.066	+ 0.001
45.0	28.32	2.036	2.035	- 0.001
49.8	28.32	2.025	2.021	- 0.004
55.0	28.32	2.008	2.006	- 0.002
44.0	37.60	2.181	2.188	+ 0.007
52.0	37.60	2.156	2.162	+ 0.006
58.0	37.60	2.137	2.143	+ 0.006
64.0	37.60	2.119	2.126	+ 0.007
52.0	45.45	2.297	2.289	- 0.008
56.0	45.45	2.282	2.275	- 0.007
60.0	45.45	2.269	2.262	- 0.007
64.0	45.45	2.256	2.249	- 0.007
56.0	60.49	2.567	2.568	+ 0.001
58.0	60.49	2.558	2.560	+ 0.002
60.0	60.49	2.551	2.552	+ 0.001
62.0	60.49	2.542	2.544	+ 0.002
64.0	60.49	2.535	2.537	+ 0.002
66.0	60.49	2.528	2.529	- 0.001
58.0	72.21	2.822	2.830	+ 0.008
60.0	72.21	2.813	2.821	+ 0.008
62.0	72.21	2.804	2.811	+ 0.007
64.0	72.21	2.795	2.804	+ 0.009
59.0	86.24	3.196	3.209	+ 0.013
60.0	86.24	3.190	3.203	+ 0.013
62.0	86.24	3.179	3.192	+ 0.013
64.0	86.24	3.169	3.182	+ 0.013
66.0	86.24	3.158	3.171	+ 0.013

Table 66  
 SUMMARY OF VAPOR-LIQUID EQUILIBRIUM DATA FOR THE SYSTEM  
 URANIUM HEXAFLUORIDE-PERFLUORODIMETHYLCYCLOHEXANE\*  
 (Reference 79)

Average Pressure (psia.)	Average Composition (mole percent UF <sub>6</sub> )		Average Temperature (°C.)		
	Liquid	Vapor	Liquid	Vapor	Condensing Vapor
39.8	99.7	100.1	84.8	85.1	84.9
40.3	96.4	98.5	85.5	85.8	85.3
40.5	91.7	96.0	86.3	86.6	85.7
40.0	82.0	93.4	86.9	86.9	85.3
39.8	75.0	90.4	87.8	87.8	85.1
39.9	72.7	90.6	88.6	88.3	84.7
40.3	58.3	84.9	93.3	92.9	85.0
40.2	55.2	84.1	93.9	93.5	85.7
40.0	48.1	79.0	97.4	97.3	86.3
40.2	47.7	79.6	97.3	97.3	86.3
40.1	37.2	73.9	100.8	100.8	86.0
40.3	29.3	67.5	106.8	106.8	86.0
39.8	19.5	62.3	113.8	113.7	85.5
40.4	12.3	51.1	122.0	122.0	89.7
40.2	7.8	32.3	126.9	126.8	88.2
40.4	5.2	24.7	128.9	129.7	91.8
39.1	1.9	9.7	134.3	134.8	119.0
39.4	0.0	0.0	138.5	140.0	136.5
36.9	96.1	97.6			
40.6	65.4	88.5			
39.2	55.7	85.7			
40.3	50.3	83.4			
38.0	43.2	78.9			
38.2	33.8	72.9			
40.7	17.6	57.1			
39.3	11.5	46.0			
39.6	8.6	35.2			
39.8	0.0	0.0			

\*Each value represents an average of from 6 to 10 samples.

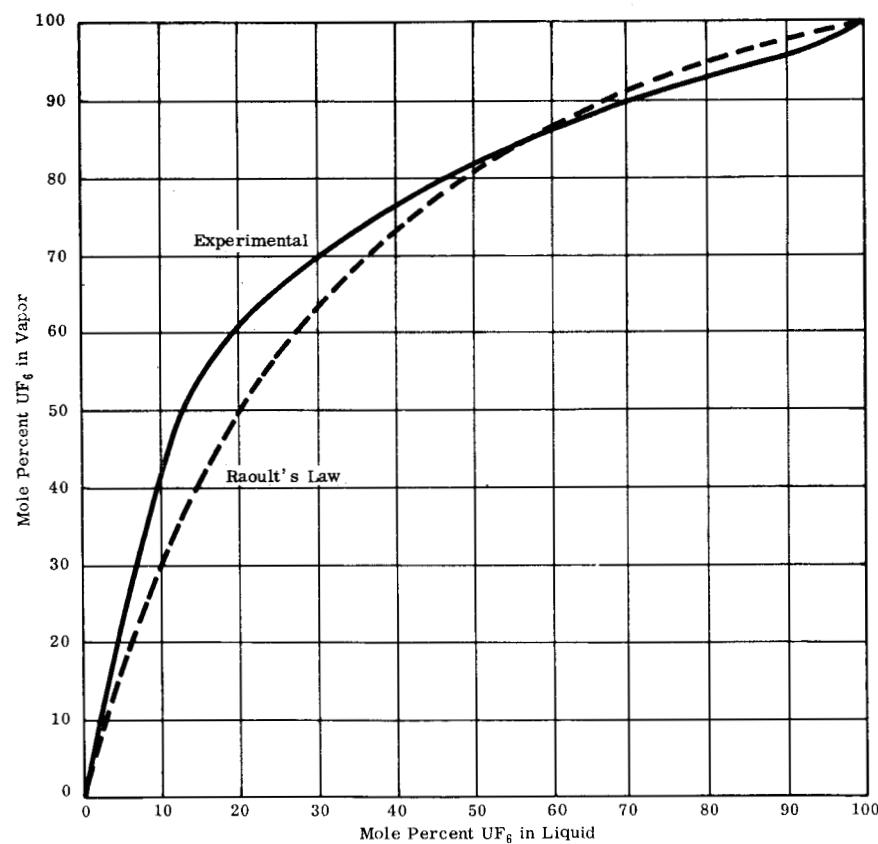


FIG. 38. VAPOR - LIQUID EQUILIBRIUM OF THE URANIUM HEXAFLUORIDE-  
PERFLUORODIMETHYLCYCLOHEXANE SYSTEM AT  
 $40 \pm 1$  PSIA. PRESSURE (Reference 63)

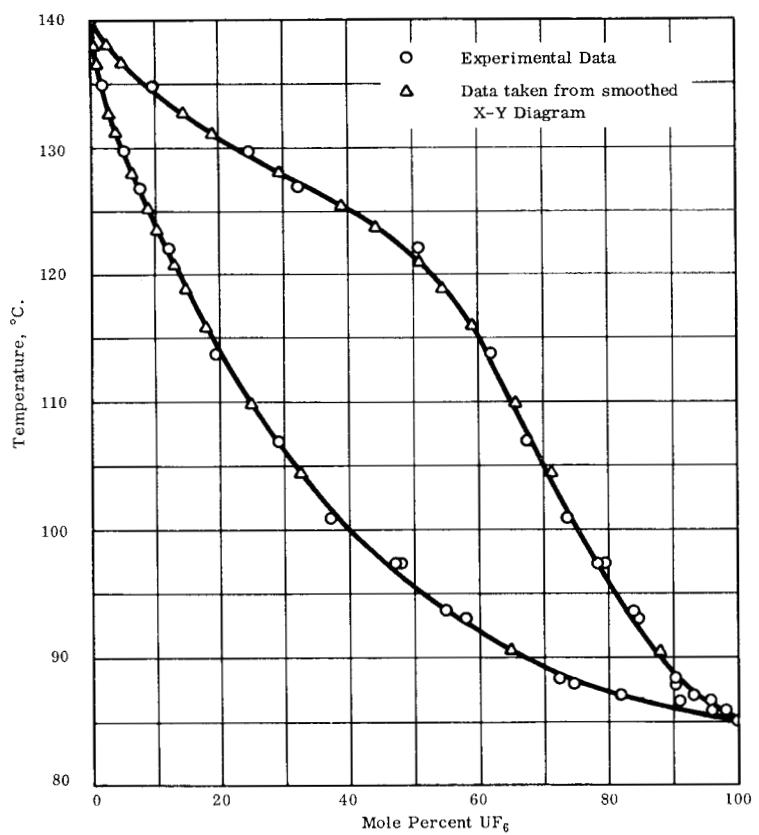


FIG. 39. TEMPERATURE - COMPOSITION DIAGRAM OF THE URANIUM  
HEXAFLUORIDE - PERFLUORODIMETHYLCYCLOHEXANE  
SYSTEM AT  $40 \pm 1$  PSIA. PRESSURE (Reference 63)

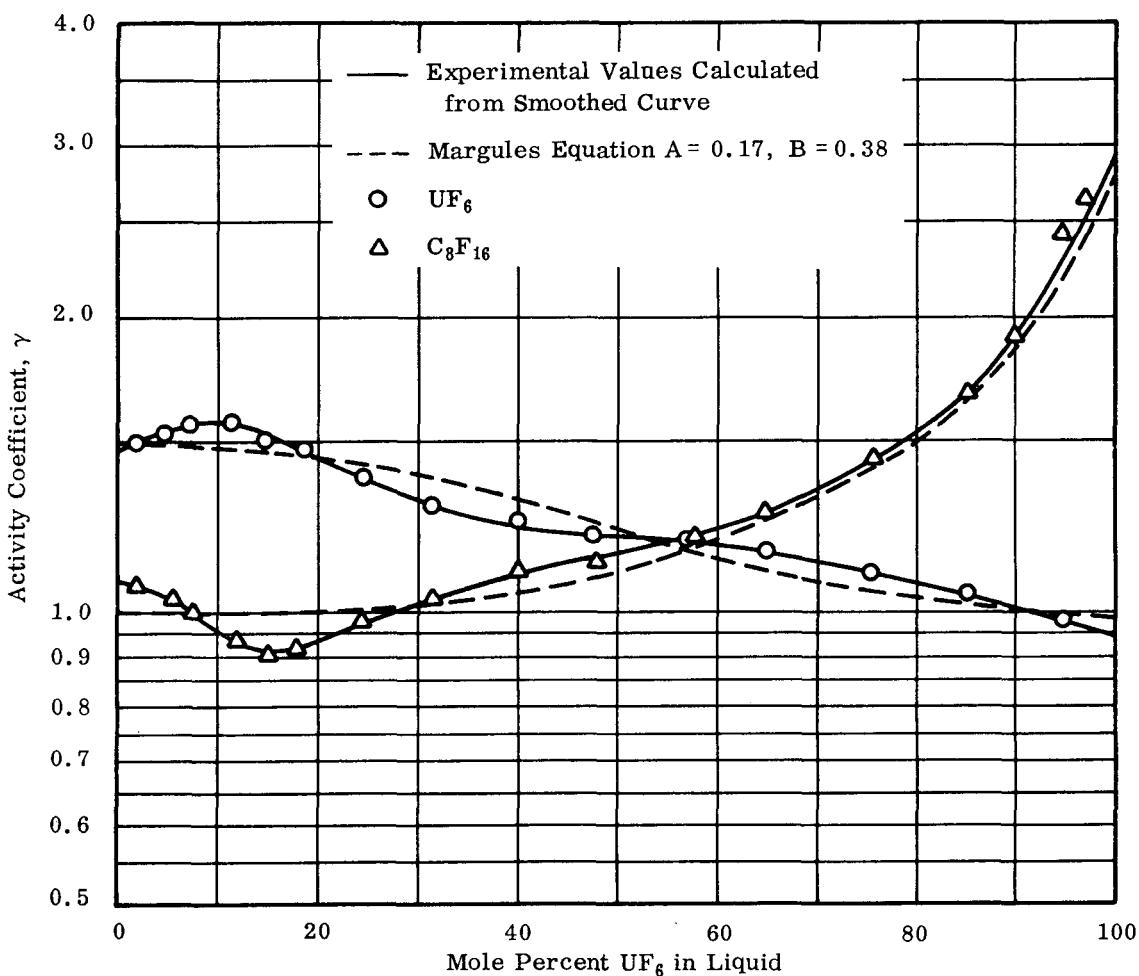


FIG. 40. COMPARISON OF EXPERIMENTAL AND CALCULATED ACTIVITY COEFFICIENTS AS A FUNCTION OF MOLE PERCENT URANIUM HEXAFLUORIDE  
(Reference 63)

fluoride with temperature, pressure, and concentration was not determined, all the equilibria of this system were expressed in terms of formula percent. The solid-liquid-and liquid-liquid data are presented in Table 67 and Figure 41, while the liquid-vapor data are given in Table 68 and Figure 42.

A cryoscopic constant of  $0.0820^{\circ}$  per 0.01 formula percent hydrogen fluoride was calculated by Rutledge and his co-workers from the vapor pressure data of  $\text{UF}_6$  obtained by Oliver and his co-workers<sup>119</sup>. In Figure 41 it is readily seen that hydrogen fluoride is very soluble in  $\text{UF}_6$ . At  $61.2^{\circ}\text{C}$ . hydrogen fluoride dissolves to the extent of about 20 formula percent at one end of the miscibility gap, or 90 formula percent at the other. As the solution temperature is increased to  $101^{\circ}\text{C}$ ., there is complete miscibility. The results obtained in the region of the miscibility gap by Rutledge and his co-workers are in agreement with those obtained by Jarry and his group. Both investigations revealed extensive deviations from ideal solution theory. This is indicated by the calculated activity coefficients shown in Table 68.

Table 67  
FREEZING POINTS AND LIQUID-LIQUID SOLUBILITIES OF THE  
URANIUM HEXAFLUORIDE-HYDROGEN FLUORIDE SYSTEM

Formula Percent UF <sub>6</sub>	Eutectic Temperature (°C.)	Freezing Temperature (°C.)	Miscibility Gap Temperature (°C.)
0.00		-83.6	
0.16		-5.0	
0.24		-5.1	
0.27		-5.0	
0.32		-5.2	
0.41		-5.0	
0.45		0.0	
0.48		-0.1	
0.781		5.0	
0.98		25.0	
1.593		26.5	
3.04		44.3	
3.93		50	
4.20		52	
5.39		55	
6.24		55	
6.67		59.12	
6.90	-84.18		
7.95		58	
8.32		60.25	
8.51		59	
9.45		60.55	
10.28			69
10.38			69
11.92		60.96	
12.20			78
16.29			83
19.85			87.9
23.39			90.3
24.52		61.16	
28.58			97.2
29.13			93.2
39.38			98.8+
49.97			100.5
53.14			99.9
53.53	-85.13		
55.02		61.14	
55.40			95.7
56.77		61.25	
57.09			95
58.45			98
61.35			90.5
62.03			93.5
64.49			87.5
65.21	-85.06		
66.70			83

Table 67 (Continued)

## FREEZING POINTS AND LIQUID-LIQUID SOLUBILITIES OF THE URANIUM HEXAFLUORIDE-HYDROGEN FLUORIDE SYSTEM

(Reference 133)

Formula Percent $\text{UF}_6$	Eutectic Temperature (°C.)	Freezing Temperature (°C.)	Miscibility Gap Temperature (°C.)
67.13			84.0
69.35			79.5
70.44		61.18	
72.54		61.25	
72.96			76
81.56		61.32	
82.03	-85.10		
83.06	-84.99		
87.73		61.56	
90.46		61.95	
91.09		62.3	
94.15		62.45	
95.06	-85.10		
95.77		62.51	
96.47		62.39	
96.47		62.53	
98.45		63.09	
99.63		63.76	
100.00		64.02	

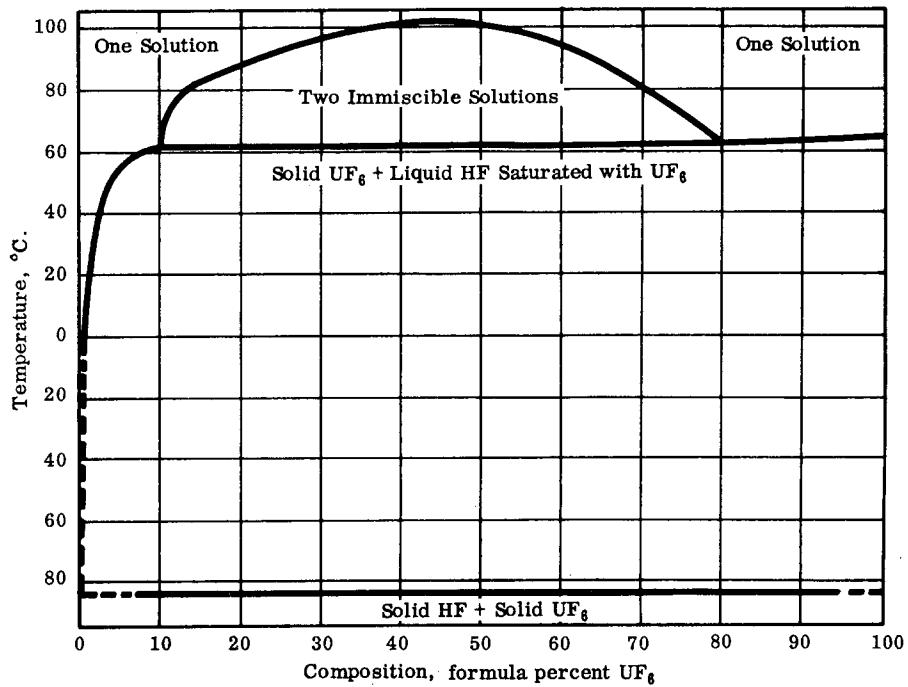


FIG. 41. PHASE DIAGRAM OF THE URANIUM HEXAFLUORIDE-HYDROGEN FLUORIDE SYSTEM (Reference 133)

Table 68  
 LIQUID-VAPOR EQUILIBRIUM DATA FOR THE URANIUM HEXAFLUORIDE -  
 HYDROGEN FLUORIDE SYSTEM  
 (Reference 133)

Temperature (°C.)	Pressure (cm.)	Composition*		Separation Factor $(HF)_V / (UF_6)_V$ $(HF)_1 / (UF_6)_1$	Activity Coefficient in Solution	
		Liquid	Vapor		$\gamma_{UF_6}$	$\gamma_{HF}$
40.89	156.0	0.00	0.00	--	--	1.000
40.89	179.6	2.74	6.85	0.383	8.76	1.103
40.89	51.3	100.00	100.00	--	1.00	--
50.90	214.0	0.00	0.00	--	--	1.000
50.90	244.7	2.47	7.45	0.315	10.03	1.085
50.90	258.3	3.81	9.09	0.396	8.37	1.141
50.90	73.6	100.00	100.00	--	1.00	--
59.66	275.0	0.00	0.00	--	--	1.000
59.56	314.4	1.64	7.54	0.205	14.62	1.075
59.75	343.8	5.78	11.59	0.468	6.97	1.173
59.66	98.9	100.00	100.00	--	1.00	--
66.87	340.0	0.00	0.00	--	--	1.000
66.99	382.7	1.89	7.17	0.249	11.66	1.065
67.01	412.7	4.07	12.48	0.298	10.16	1.107
66.92	429.6	7.40	14.01	0.491	6.53	1.173
66.97	431.1	--	13.99	--	--	--
66.79	424.5	7.42	13.96	0.494	6.41	1.160
66.97	430.5	7.67	15.14	0.466	6.82	1.164
66.83	428.3	8.27	14.40	0.536	5.99	1.176
66.87	423.1	77.72	15.33	19.27	0.670	4.73
66.85	422.6	78.86	14.96	21.21	0.643	5.00
66.74	360.8	91.45	24.70	32.61	0.782	9.35
66.81	360.1	92.53	25.10	36.96	0.784	10.62
--	--	91.93	--	33.99	0.789	9.83
66.92	262.0	98.50	46.73	74.86	0.998	27.4
66.87	124.5	100.00	100.00	--	1.000	--
72.47	396.0	0.00	0.00	--	--	1.000
72.48	442.5	1.83	7.38	0.234	12.82	1.054
72.28	442.8	2.55	8.00	0.301	9.41	1.056
72.50	482.6	4.26	13.13	0.294	10.07	1.106
72.48	498.4	7.44	15.04	0.454	6.82	1.155
72.48	503.6	10.84	16.15	0.629	5.19	1.191
72.48	499.8	73.48	16.40	14.12	0.755	3.98
72.62	494.7	77.62	16.93	17.02	0.731	4.64
72.28	409.1	93.57	28.40	36.69	0.841	11.50
72.62	286.7	98.43	51.15	59.88	1.009	22.5
72.47	147.7	100.00	100.00	--	1.000	--

\*Compositions calculated on the basis of association of HF in samples equivalent to a molecular weight of 20.35.

Table 68 (Continued)

LIQUID-VAPOR EQUILIBRIUM DATA FOR THE URANIUM HEXAFLUORIDE -  
HYDROGEN FLUORIDE SYSTEM

(Reference 133)

Temperature (°C.)	Pressure (cm.)	Composition*		Separation Factor $(HF)_V / (UF_6)_V$	Activity Coefficient in Solution	
		Liquid	Vapor		$(HF)_1 / (UF_6)_1$	$\gamma_{UF_6}$
84.46	538.0	0.00	0.00	--	--	1.000
84.45	597.3	1.55	6.07	0.244	11.21	1.059
84.49	652.1	3.60	11.60	0.285	10.08	1.112
84.40	681.9	7.36	16.00	0.417	7.11	1.149
84.47	688.2	11.05	17.75	0.517	5.30	1.183
84.38	688.6	11.32	17.81	0.589	5.20	1.186
84.38	686.6	65.78	17.80	8.88	0.892	3.07
84.55	678.4	73.12	17.56	12.77	0.782	3.87
84.53	543.5	93.74	33.33	29.95	0.927	10.8
84.53	364.7	98.96	58.75	66.81	1.039	26.9
84.46	208.5	100.00	100.00	--	1.000	--
92.30	656.0	0.00	0.00	--	--	1.000
92.28	718.8	1.50	6.15	0.232	11.45	1.044
92.28	789.2	3.50	11.22	0.287	9.83	1.111
92.30	830.5	6.91	16.95	0.364	7.91	1.129
92.30	840.6	11.24	18.51	0.558	5.38	1.176
92.30	837.9	61.67	18.70	6.99	0.987	2.71
92.37	821.8	71.17	19.19	10.40	0.861	3.51
92.30	637.6	93.94	35.45	28.23	0.935	10.4
92.28	421.1	99.53	62.43	127.4	1.026	51.3
92.30	257.5	100.00	100.00	--	1.000	--
104.74	886.0	0.00	0.00	--	--	1.000
104.77	962.4	1.18	5.24	0.216	12.13	1.042
104.73	1,051.3	3.22	10.73	0.277	9.93	1.095
104.60	804.6	94.92	40.85	27.06	0.983	10.6
104.87	524.8	99.56	66.44	114.3	0.993	45.2
104.74	352.5	100.00	100.00	--	1.000	--

\*Compositions calculated on the basis of association of HF in samples equivalent to a molecular weight of 20.35.

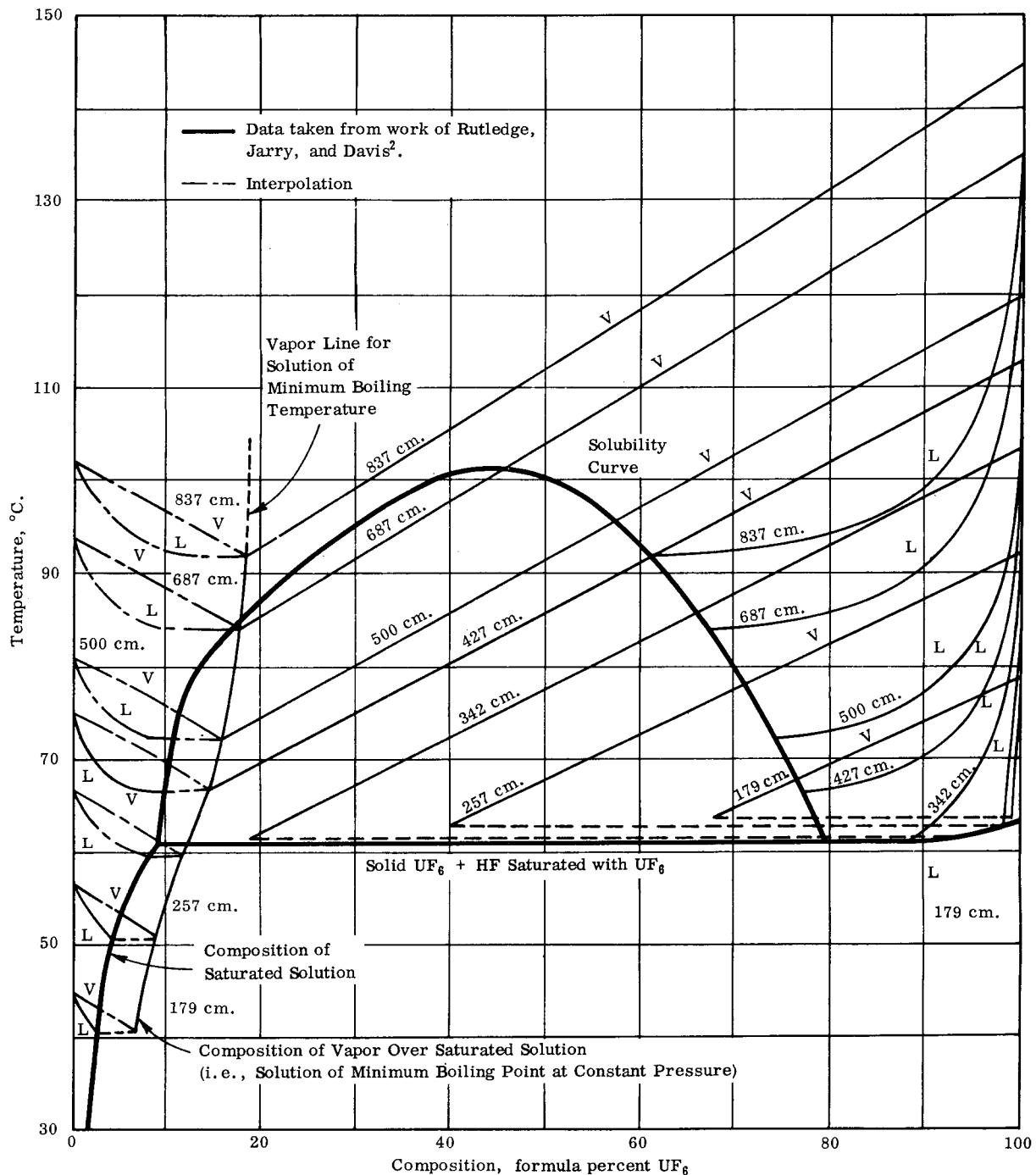


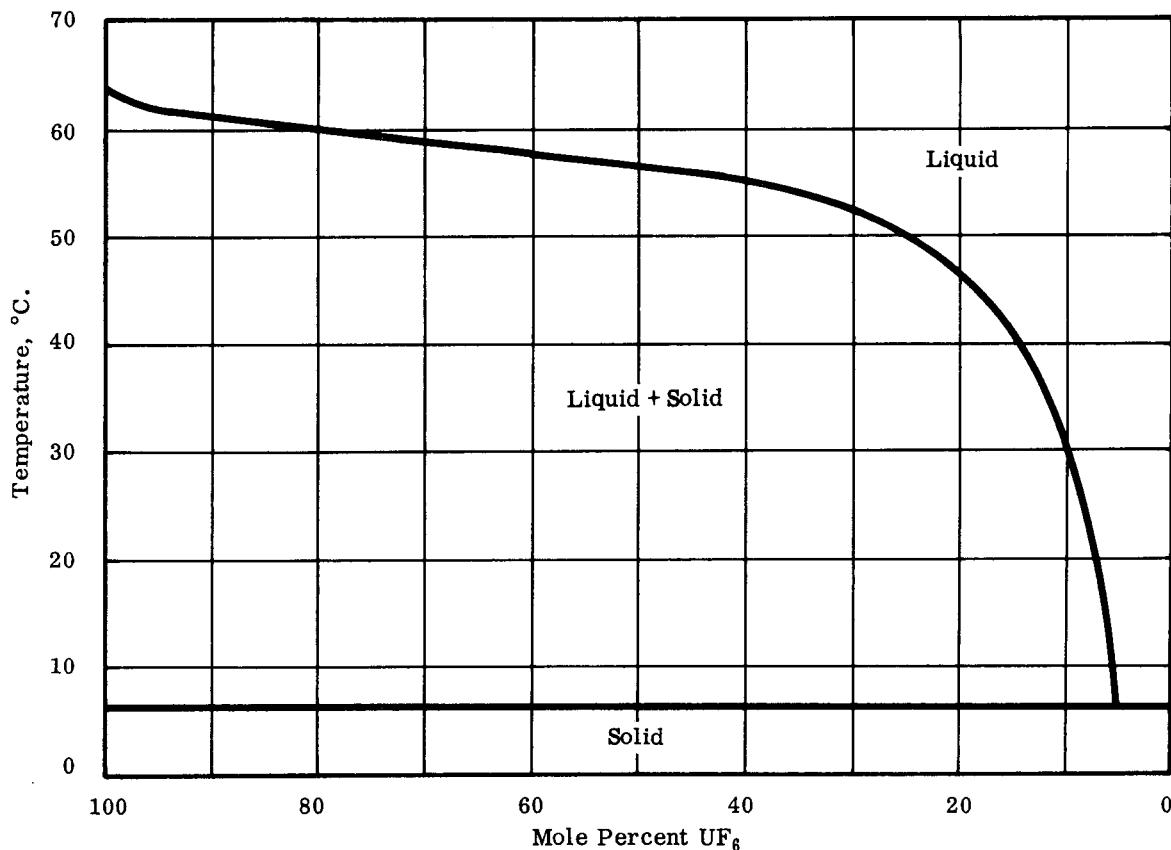
FIG. 42. SUMMARY OF LIQUID-VAPOR EQUILIBRIUM IN THE URANIUM HEXAFLUORIDE - HYDROGEN FLUORIDE SYSTEM  
(Reference 133)

**URANIUM HEXAFLUORIDE IN BROMINE FLUORIDES ( $\text{BrF}_3$  AND  $\text{BrF}_5$ )**

Fischer and Vogel<sup>60, 138</sup> reported that the solid-liquid equilibria at temperatures ranging from 0° to 64°C. of the  $\text{UF}_6$ - $\text{BrF}_3$  and  $\text{UF}_6$ - $\text{BrF}_5$  systems are of simple eutectic types. Data for solid-liquid equilibria of the  $\text{UF}_6$ - $\text{BrF}_3$  system are shown in Table 69 and in Figure 43. Table 70 presents a comparison of the experimental activity coefficient values with those theoretically obtained using the method described by Barber and Wendolkowski<sup>145</sup>. The  $\text{UF}_6$ - $\text{BrF}_3$  system exhibits positive deviation from ideality. Data for the  $\text{UF}_6$ - $\text{BrF}_5$  system are presented in Table 71 and in Figure 44. It was found that these data (solid curve of Figure 44) show little deviation from ideality (dotted curve) as calculated by Barber and Wendolkowski.

A preliminary investigation of the  $\text{UF}_6$ - $\text{BrF}_3$  system was made by Kirshenbaum<sup>94</sup> at -125°C. He observed only that  $\text{UF}_6$  is sparingly soluble in liquid  $\text{BrF}_3$ .

The liquid-vapor equilibrium of the  $\text{UF}_6$ - $\text{BrF}_5$  system has also been investigated by Ellis and Johnson<sup>58</sup> and re-investigated by Liimatainen<sup>102</sup>. The results of these two investigations are in conflict. Ellis and Johnson found that the system exhibits complete miscibility over the 68° to 80°C. range and has a single maximum vapor pressure azeotrope at a composition corresponding to a mole fraction of 0.1  $\text{UF}_6$ . The results are presented in Figure 45. Liimatainen found that when a 10 mm. Hg partial pressure of elemental fluorine is introduced to the system, the binary liquid-vapor equilibrium shows positive deviations from ideality and that the system does not have an azeotrope. Data calculated using the theory of regular solutions (activity coefficient technique) also indicate that



**FIG. 43. SOLID - LIQUID EQUILIBRIUM OF THE URANIUM HEXAFLUORIDE-BROMINE TRIFLUORIDE SYSTEM**  
(Reference 60)

Table 69  
 SOLID-LIQUID EQUILIBRIUM OF THE URANIUM HEXAFLUORIDE-  
 BROMINE TRIFLUORIDE SYSTEM  
 (Reference 60)

Mole Percent $\text{UF}_6$	Univariant Point		Invariant Point		Solid Phase
	Cooling Curve	Thaw Curve	Cooling Curve	Thaw Curve	
100	--	--	$64.0 \pm 0.1$	--	$\text{UF}_6$
96.4	62.3	62.8	--	--	$\text{UF}_6$
93.4	61.7	61.6	--	--	$\text{UF}_6$
90.4	61.4	--	--	--	$\text{UF}_6$
88.8	$61.0 \pm 0.2$	60.7	--	--	$\text{UF}_6$
85.7	60.0	--	--	--	$\text{UF}_6$
83.1	$60.4 \pm 0.2$	60.6	--	--	$\text{UF}_6$
81.8	60.0	60.2	--	--	$\text{UF}_6$
81.0	$60.0 \pm 0.1$	--	--	--	$\text{UF}_6$
80.2	60.0	--	--	5.6	$\text{UF}_6$
76.8	$59.6 \pm 0.3$	59.6	--	--	$\text{UF}_6$
72.9	59.1	59.3	--	6.0	$\text{UF}_6$
69.5	58.6	--	--	--	$\text{UF}_6$
67.0	58.4	58.4	--	--	$\text{UF}_6$
63.1	57.9	58.0	--	6.2	$\text{UF}_6$
58.8	57.7	--	6.4	6.5	$\text{UF}_6$
56.3	$57.3 \pm 0.2$	--	--	--	$\text{UF}_6$
53.9	56.9	--	6.3	--	$\text{UF}_6$
51.9	$56.7 \pm 0.1$	--	--	--	$\text{UF}_6$
48.7	$56.5 \pm 0.1$	--	--	--	$\text{UF}_6$
45.4	55.9	--	6.1	--	$\text{UF}_6$
41.1	55.1	--	6.3	--	$\text{UF}_6$
38.2	--	55.0	--	--	$\text{UF}_6$
35.6	53.3	--	6.1	--	$\text{UF}_6$
30.2	$51.8 \pm 0.4$	51.9	--	--	$\text{UF}_6$
29.1	--	52.2	--	--	$\text{UF}_6$
24.8	48.9	48.8	--	--	$\text{UF}_6$
19.5	--	46.5	--	--	$\text{UF}_6$
19.3	46.5	45.4	--	--	$\text{UF}_6$
14.7	--	--	6.3	--	$\text{UF}_6$
13.4	--	38.9	--	--	$\text{UF}_6$
9.9	--	--	6.5	--	$\text{UF}_6$
8.5	--	27.1	--	--	$\text{UF}_6$
8.4	--	--	6.5	--	$\text{UF}_6$
7.6	--	--	6.4	--	$\text{UF}_6$
6.0	--	16.3	--	--	$\text{UF}_6$
5.1	--	--	6.4	--	$\text{UF}_6$
2.6	--	7.1	6.7	6.3	$\text{BrF}_3$
0	$8.7 \pm 0.1$	--	--	--	$\text{BrF}_3$

Table 70  
ACTIVITY COEFFICIENTS IN BROMINE TRIFLUORIDE  
(Reference 60)

Temperature (°C.)	Experimental		Hildebrand Theoretical	
	Mole Fraction UF <sub>6</sub>	Activity Coefficient UF <sub>6</sub>	Mole Fraction UF <sub>6</sub>	Activity Coefficient UF <sub>6</sub>
64	1.00	1.0	1.0	1.00
63	0.980	1.0	0.978	1.00
62	0.946	1.01	0.955	1.00
61	0.877	1.07	0.912	1.02
60	0.795	1.16	0.855	1.08
58	0.630	1.40	0.665	1.33
56	0.465	1.80	0.411	2.05
52	0.290	2.67	0.153	5.05
50	0.250	2.96	0.108	6.83
40	0.140	4.22	0.028	21.2
30	0.094	4.98	0.011	41.8
20	0.065	5.64	0.005	74.0
10	0.050	5.66	0.003	106.0

Table 71  
SOLID-LIQUID EQUILIBRIUM OF THE URANIUM HEXAFLUORIDE –  
BROMINE PENTAFLUORIDE SYSTEM  
(Reference 60)

Mole Percent UF <sub>6</sub>	Univariant Point		Invariant Point		Solid Phase
	Freezing Curve	Thaw Curve	Freezing Curve	Thaw Curve	
100.0	--	--	63.9	--	UF <sub>6</sub>
92.32	58.8	59.4	--	--	UF <sub>6</sub>
89.52	57.3	--	--	--	UF <sub>6</sub>
84.67	54.6	54.2	--	-66.7	UF <sub>6</sub>
81.23	53.2	53.5	--	--	UF <sub>6</sub>
66.40	45.6	--	--	-66.1	UF <sub>6</sub>
56.81	39.0	--	--	-65.8	UF <sub>6</sub>
50.07	34.0	34.1	--	-63.5	UF <sub>6</sub>
41.68	26.7	--	--	--	UF <sub>6</sub>
34.35	18.5	--	--	-63.5	UF <sub>6</sub>
25.18	7.7	--	--	-63.8	UF <sub>6</sub>
18.81	-3.1	-2.9	--	-63.2	UF <sub>6</sub>
13.32	-18.3	--	--	--	UF <sub>6</sub>
10.53	-28.7	--	--	-63.2	UF <sub>6</sub>
7.51	-40.1	--	--	-63.2	UF <sub>6</sub>
5.78	-49.5	--	--	-63.5	UF <sub>6</sub>
4.81	--	--	--	-63.5	UF <sub>6</sub>
2.43	--	--	--	-63.5	BrF <sub>5</sub>
0.00	--	--	-61.3	-61.3	BrF <sub>5</sub>

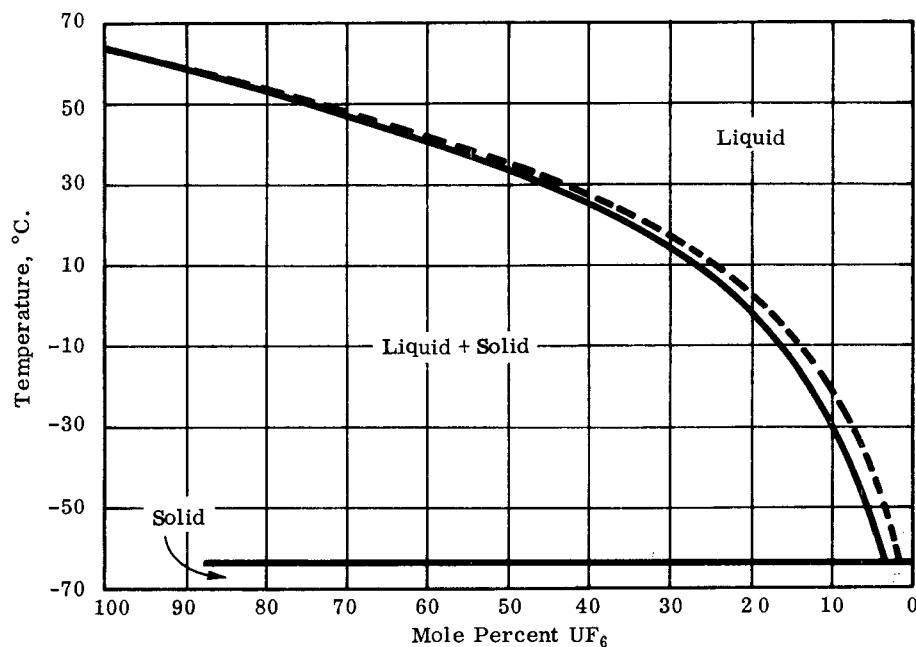


FIG. 44. SOLID - LIQUID EQUILIBRIUM OF THE URANIUM HEXAFLUORIDE - BROMINE PENTAFLUORIDE SYSTEM  
(Reference 60)

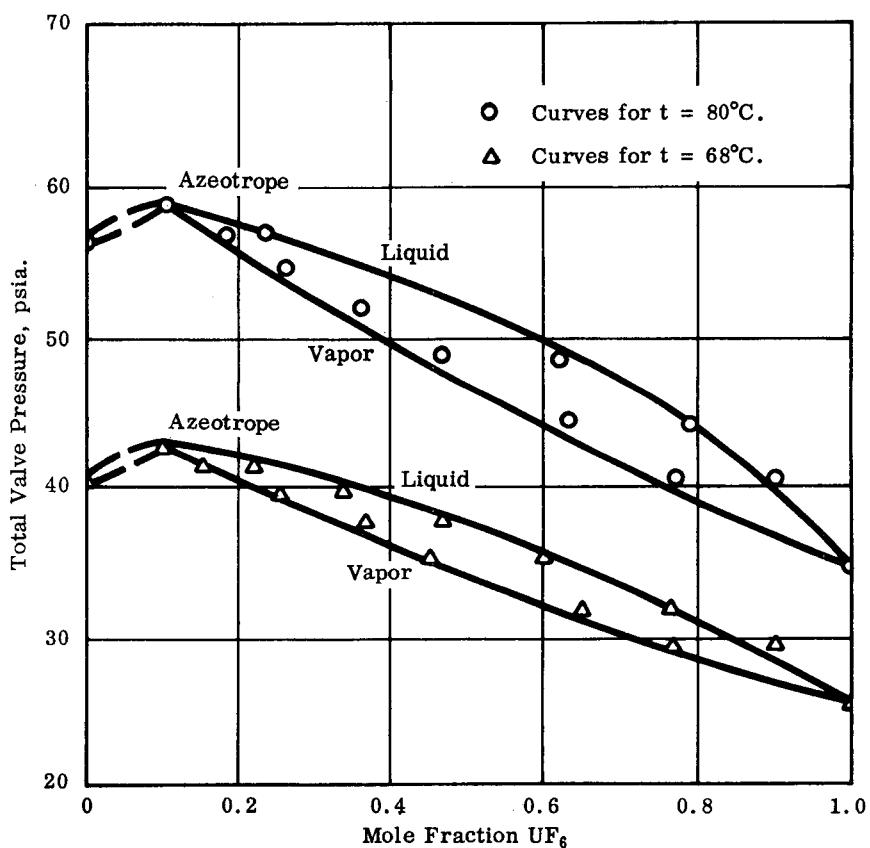


FIG. 45. PRESSURE - COMPOSITION DIAGRAM OF THE URANIUM HEXAFLUORIDE - BROMINE PENTAFLUORIDE SYSTEM  
(Reference 58)

the liquid-vapor equilibrium in the  $\text{UF}_6\text{-BrF}_5$  system shows small positive deviations from ideality with no azeotrope. The experimental liquid-vapor equilibrium data for the  $\text{UF}_6\text{-BrF}_5$  system at the 70°C. isotherm are presented in Table 72 and Figure 46 while those at the 90°C. isotherm are presented in Table 73 and in Figure 47.

Table 72

VAPOR-LIQUID EQUILIBRIUM DATA FOR THE URANIUM HEXAFLUORIDE –  
BROMINE PENTAFLUORIDE SYSTEM

70°C. Isotherm

(Reference 102)

Mole Percent $\text{BrF}_5$		Temperature (°C.)	Pressure (mm. Hg)	Relative Volatility	Activity Coefficient	
Liquid	Vapor				$\text{BrF}_5$	$\text{UF}_6$
2.1	4.2	69.4	1380	2.04	1.44	1.00
9.3	14.8	69.3	1429	1.68	1.19	1.00
19.4	28.0	69.9	1564	1.62	1.17	1.02
22.5	32.0	69.7	1582	1.62	1.17	1.03
23.1	30.7	69.6	1569	1.47	1.08	1.05
40.0	50.2	69.4	1683	1.51	1.11	1.03
40.6	50.4	69.7	1708	1.49	1.10	1.05
46.1	55.9	69.6	1731	1.49	1.09	1.05
57.2	63.8	69.5	1778	1.32	1.03	1.12
67.5	72.2	69.7	1836	1.25	1.02	1.16
76.7	79.4	69.6	1854	1.17	1.00	1.21
78.2	82.8	69.5	1870	1.34	1.03	1.09
80.1	83.3	69.6	1887	1.24	1.02	1.18
88.0	88.4	69.4	1890	1.04	1.00	1.36
88.0	89.1	69.4	1885	1.11	1.00	1.28
92.4	93.0	69.5	1909	1.09	1.00	1.30
92.8	93.3	69.1	1880	1.08	1.00	1.31
93.2	93.7	69.3	1888	1.09	1.00	1.30
93.4	94.9	69.5	1896	1.31	0.97	1.09
93.8	94.3	69.3	1904	1.10	1.01	1.30
94.2	94.3	69.3	1902	1.03	1.00	1.37
96.2	96.8	69.4	1913	1.21	1.01	1.20
98.5	98.6	69.6	1915	1.06	1.00	1.35

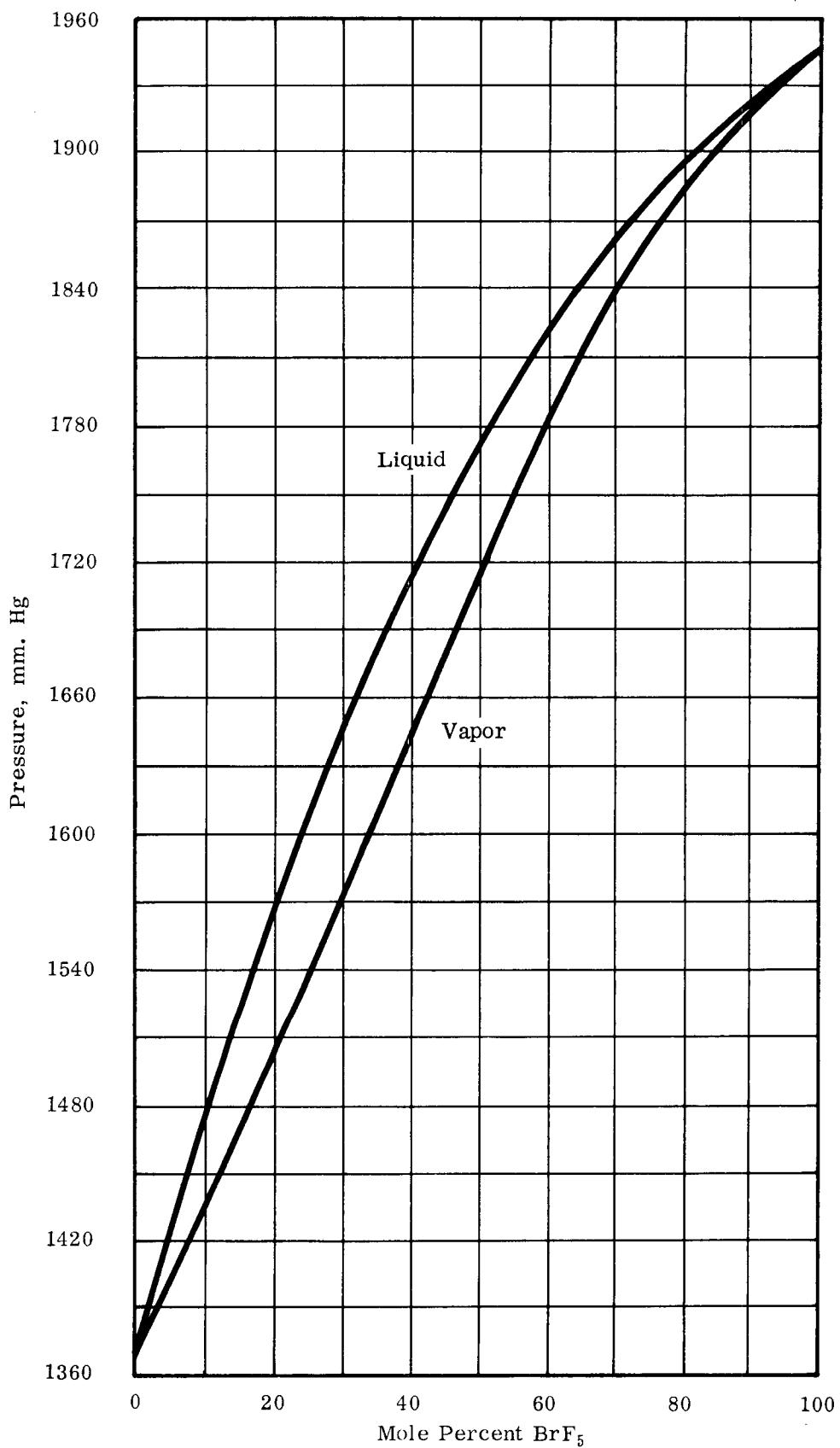
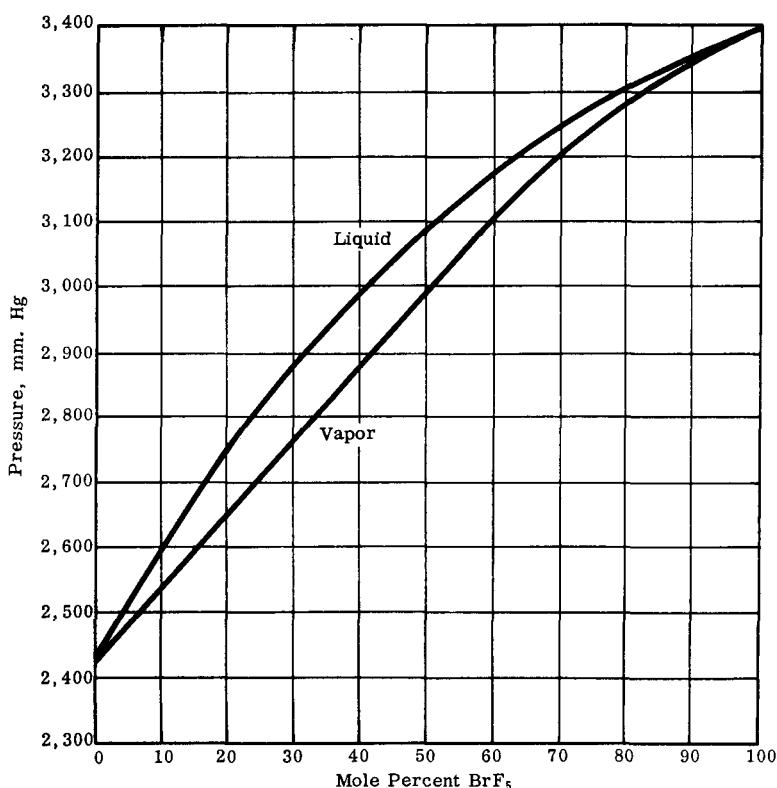


FIG. 46. PRESSURE - COMPOSITION DIAGRAM FOR THE URANIUM HEXAFLUORIDE - BROMINE PENTAFLUORIDE SYSTEM AT 70°C. (Reference 102)

Table 73

VAPOR-LIQUID EQUILIBRIUM DATA FOR THE URANIUM HEXAFLUORIDE -  
BROMINE PENTAFLUORIDE SYSTEM90°C. Isotherm  
(Reference 102)

Mole Percent $\text{BrF}_5$	Temperature (°C.)					Activity Coefficients	
	Liquid	Vapor	2472	2558	2790	$\text{BrF}_5$	$\text{UF}_6$
2.1	4.6	89.8	2472	2558	2790	1.64	1.00
8.9	13.8	89.5				1.18	1.01
25.6	35.2	89.7				1.14	1.01
41.0	47.8	88.6				1.04	1.10
42.6	48.8	89.4				1.02	1.11
47.5	55.0	89.1				1.05	1.08
50.7	57.3	89.2				1.03	1.20
70.6	75.0	89.6				1.01	1.13
79.8	81.8	89.7				1.00	1.23
81.4	81.8	89.1				0.97	1.34
88.2	88.6	89.2				0.99	1.31
92.8	93.3	89.3				1.00	1.33
93.6	94.0	89.3				1.00	1.30

FIG. 47. PRESSURE - COMPOSITION DIAGRAM FOR THE URANIUM  
HEXAFLUORIDE - BROMINE PENTAFLUORIDE SYSTEM  
AT 90°C. (Reference 102)

### URANIUM HEXAFLUORIDE IN CHLORINE TRIFLUORIDE ( $\text{ClF}_3$ )

Wendolkowski and Barber<sup>145</sup> investigated the solid-liquid equilibria of the  $\text{UF}_6$ - $\text{ClF}_3$  system over the entire composition range. The results of this investigation are presented in Figure 48. The data used in the plots of Figure 48 are average values which were obtained from a family of cooling and warming curves. At  $-77.4^\circ\text{C}$ . and 0.4 mole percent  $\text{UF}_6$ , the  $\text{UF}_6$  and chlorine trifluoride form a binary eutectic, and at  $-83.1^\circ\text{C}$ . the chlorine trifluoride exhibits enantiotropy. The actual solubility was found to be less than ideal and shows positive deviation from Raoult's law. The experimental solubilities, the ideal solubilities, and the theoretical activity coefficients of  $\text{UF}_6$  calculated using the activity coefficient method appear in Table 74.

The liquid-vapor equilibrium of the  $\text{UF}_6$ - $\text{ClF}_3$  system was investigated by Ellis,<sup>56, 57</sup> by McGill and Barber,<sup>15</sup> and by Kuykendall<sup>96</sup>. A discrepancy exists between the conclusions of Ellis and those of the other investigators. Ellis found that the phase diagrams for the liquid-vapor equilibria in the  $\text{UF}_6$ - $\text{ClF}_3$  system show that no azeotropic mixture exists. At  $67^\circ\text{C}$ . the components are completely miscible, but at  $75^\circ\text{C}$ . a partial miscibility region appears between the composition range from 0.3 to 0.5 mole fraction  $\text{UF}_6$ . On the other hand, Kuykendall found that the system displayed complete miscibility. This is in agreement with the data obtained by McGill and Barber.

Table 74  
SOLUBILITY AND ACTIVITY COEFFICIENTS IN CHLORINE TRIFLUORIDE SOLUTION  
(Reference 145)

Temperature ( $^\circ\text{C}.$ )	Composition of Saturated Solution (mole percent $\text{UF}_6$ )			Activity Coefficient	
	Experimental	Ideal	Theoretical	Experimental	Theoretical
64	100.0	100.0	100.0	1.00	1.00
60	90.0	92.0	92.0	1.02	1.00
50	67.7	74.3	73.5	1.10	1.01
40	48.2	59.3	57.6	1.23	1.03
30	33.0	46.7	44.2	1.42	1.06
20	22.3	36.3	33.0	1.63	1.10
10	15.6	27.8	24.6	1.78	1.13
0	10.5	21.0	18.1	2.00	1.16
-10	6.8	15.8	13.2	2.32	1.20
-20	4.4	12.4	10.2	2.81	1.22
-30	2.9	9.1	7.3	3.14	1.25

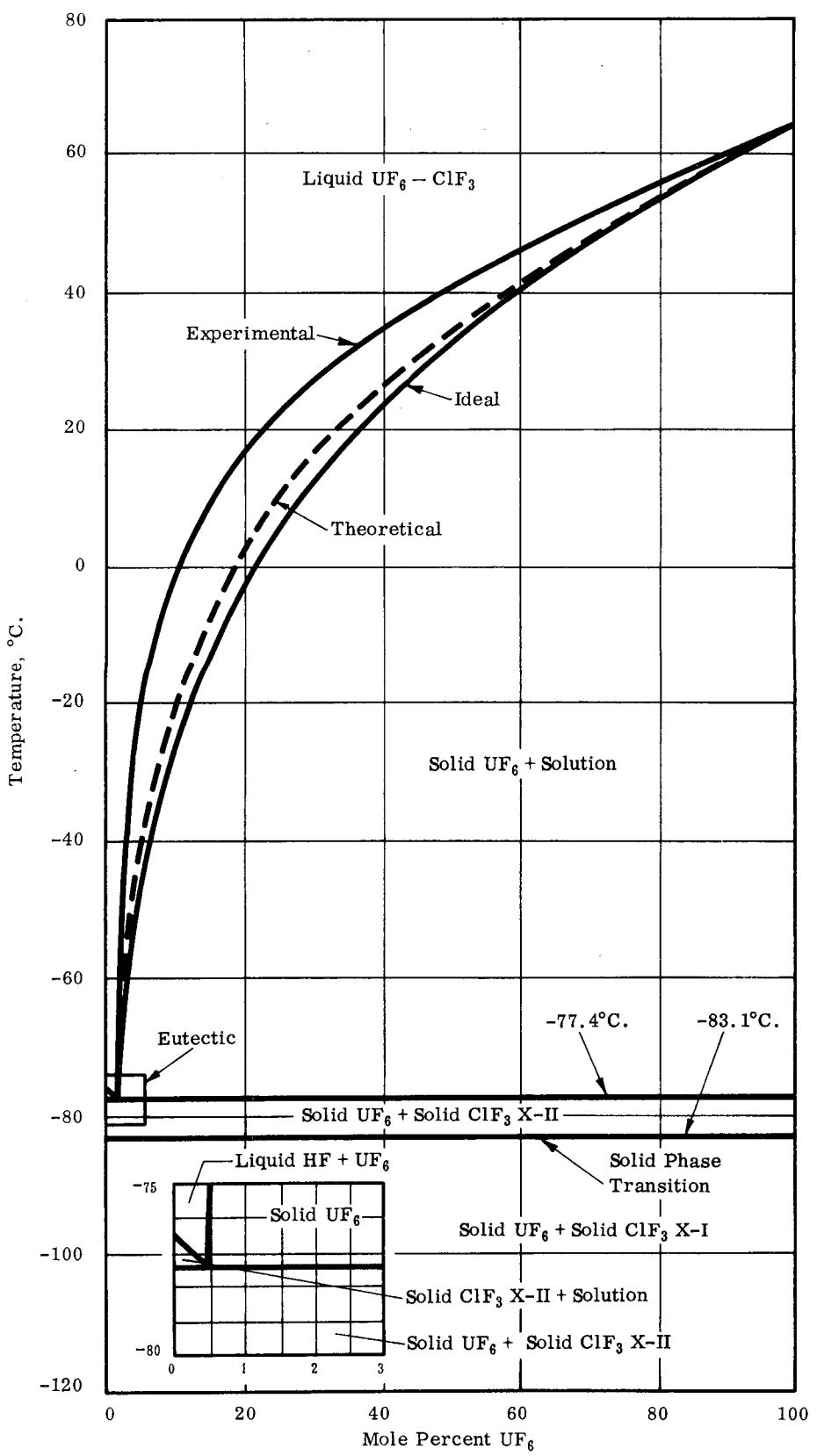


FIG. 48. SOLID - LIQUID EQUILIBRIUM OF THE URANIUM HEXAFLUORIDE-CHLORINE TRIFLUORIDE SYSTEM  
(Reference 145)

McGill and Barber<sup>15</sup> investigated the liquid-vapor equilibrium of the  $\text{UF}_6\text{-ClF}_3$  system at total pressures of 1.5, 2.0, 2.5 and 3.0 atmospheres (absolute) by means of a nickel Othmer-type equilibrium still. They found that the system is a simple azeotropic one, but at pressures of 2.5 atmospheres or less the liquid curves intersect the solubility curve for the system. The results obtained by McGill and Barber on the  $\text{UF}_6\text{-ClF}_3$  system are summarized in Table 75. The composition diagram for the system is given in Figure 49. The activity coefficients of  $\text{UF}_6$  in  $\text{ClF}_3$  calculated from the use of Raoult's laws are listed at various concentration in Table 76. The results obtained by Ellis are presented in Table 77 and Figure 50.

Recently, Kuykendall<sup>96</sup> obtained data which are in direct conflict with the conclusions of Ellis and which are consistent with the data obtained by McGill and Barber. Kuykendall obtained the vapor pressures for the  $\text{UF}_6\text{-ClF}_3$  system at approximately 76°, 83°, and 92°C. over the entire composition range. The results obtained by Kuykendall are presented in Table 78. Figure 51 shows the discrepancy between the results of Kuykendall and those of Ellis.

Table 75

LIQUID-VAPOR EQUILIBRIUM DATA ON THE URANIUM HEXAFLUORIDE –  
CHLORINE TRIFLUORIDE SYSTEM

(Reference 15)

Total Pressure* (mm. Hg)	Temperature (°C.)	Equilibrium Compositions (mole percent $\text{ClF}_3$ )	
		Liquid	Vapor
1144	25.0	86.0	93.5
1145	24.9	85.7	93.1
1533	32.9	82.7	92.5
1530	37.7	56.1	77.0
1908	38.9	80.9	90.7
1910	46.0		68.7
1913	51.9		60.1
2275	79.5	1.0	10.0
2274	70.0	6.9	
2280	61.5		44.6
2276	64.3	15.5	40.8
2275	58.6	21.4	57.5
2288	48.6	47.4	82.7
2285	47.3	58.3	84.6
2280	45.5	69.3	86.5
2297	50.4	41.0	

\* Pressures corrected for atmospheric pressure and temperature.

Table 76  
 ACTIVITY COEFFICIENTS  
 IN CHLORINE TRIFLUORIDE SOLUTION  
 (Reference 15)

Concentration (mole percent $UF_6$ )	Activity Coefficient
10	2.17
20	1.63
30	1.55
40	1.37
50	1.26
60	1.27
70	1.32
80	1.37
90	1.32

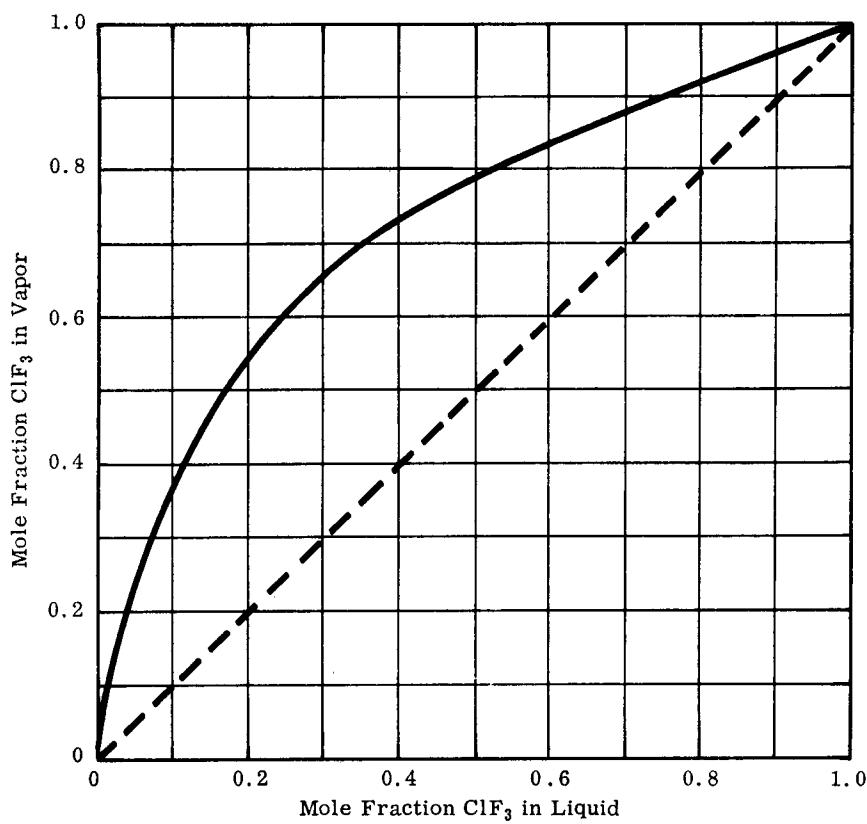


FIG. 49. DIAGRAM OF THE URANIUM HEXAFLUORIDE-CHLORINE TRIFLUORIDE SYSTEM  
 (Reference 15)

Table 77

LIQUID-VAPOR EQUILIBRIUM IN THE URANIUM HEXAFLUORIDE -  
CHLORINE TRIFLUORIDE SYSTEM

(Reference 56)

Gross Composition (mass estimate as mole fraction $UF_6$ )	Composition of Liquid Phase (as mole fraction $UF_6$ )	Vapor Composition (as mole fraction $UF_6$ )	Total Vapor Pressure (psia.)
0.000	0.000	0.000	132.7
0.192	0.188	0.075	121.2
0.296	0.298	0.132	109.7
0.42	0.512	0.138	109.7
0.49	0.505	0.139	109.7
0.583	0.603	0.150	105.7
0.686	0.675	0.220	93.2
0.79	0.790	0.455	69.7
0.87	0.875	0.595	56.7
0.93	0.945	0.725	44.7
1.0	1.0	1.0	30.6

MISCELLANEOUS BINARY URANIUM HEXAFLUORIDE PHASE RELATIONSHIPS

Bernhardt and his co-workers<sup>18</sup> determined the solubility of fluorine, oxygen, and nitrogen in solid and liquid  $UF_6$ . The determinations were made at temperatures between 30° and 90°C. It was found that, at a 95 percent confidence level, the average mole percent of fluorine which dissolves in solid  $UF_6$  in the range from 50°C. to the melting point is  $0.058 \pm 0.020$ . The mole percentages of nitrogen and oxygen dissolved in solid  $UF_6$  over the same temperature range are  $0.055 \pm 0.025$  and  $0.068 \pm 0.050$ , respectively, while the corresponding percentages in liquid  $UF_6$  are  $0.093 \pm 0.103$  and  $0.165 \pm 0.031$ . These solubilities correspond to calculated activity coefficients for fluorine, nitrogen and oxygen of  $0.24 \pm 0.08$ ,  $0.47 \pm 0.88$ , and  $0.25 \pm 0.07$ , respectively.

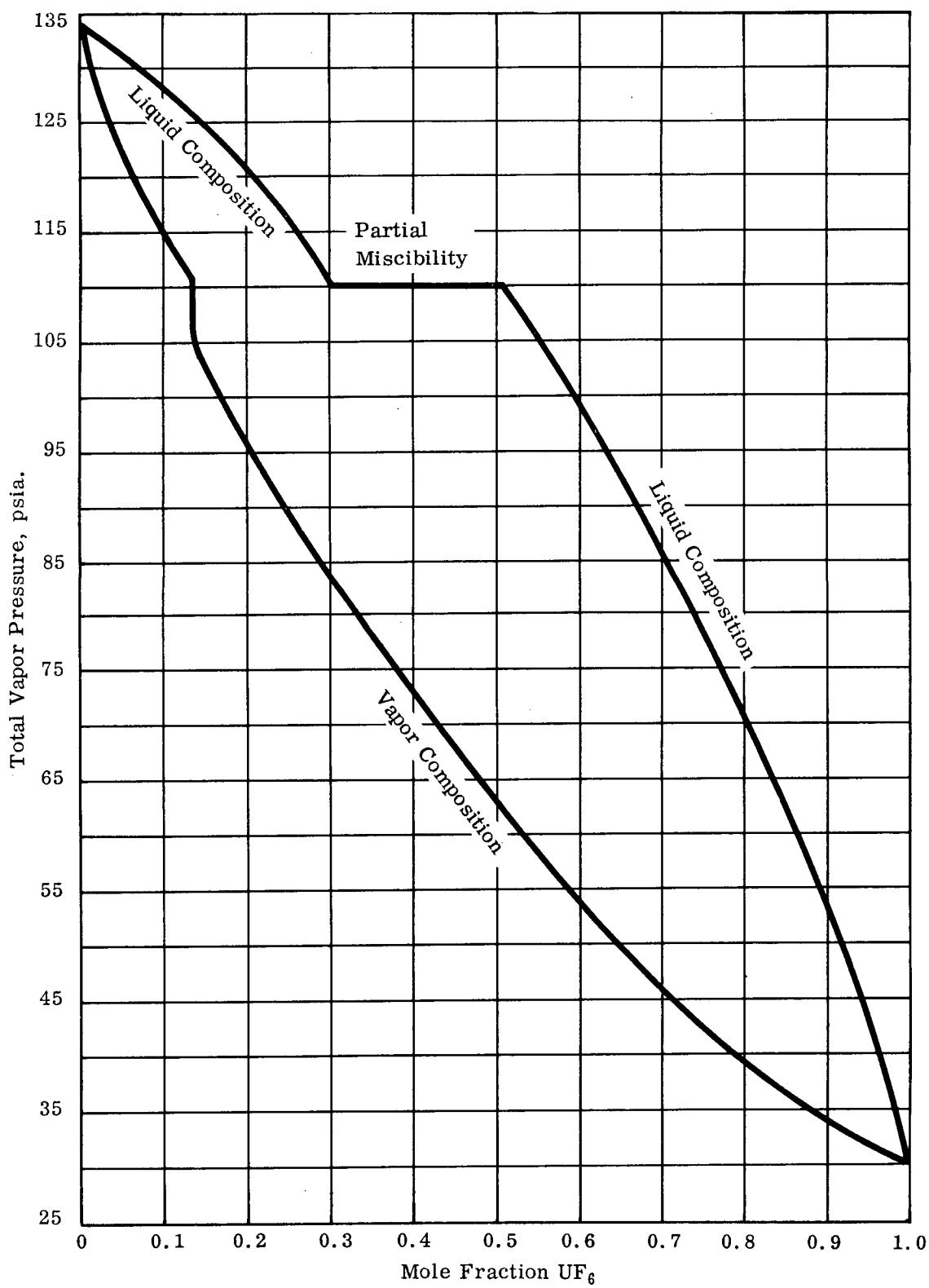


FIG. 50. LIQUID - VAPOR EQUILIBRIUM IN THE URANIUM HEXAFLUORIDE-CHLORINE TRIFLUORIDE SYSTEM AT 75°C.  
(Reference 56)

Table 78  
 VAPOR PRESSURE DATA FOR THE URANIUM HEXAFLUORIDE-  
 CHLORINE TRIFLUORIDE SYSTEM  
 (Reference 96)

Total Pressure (psia.)	Temperature (°C.)	Gross Composition (mole fraction UF <sub>6</sub> )
35	77.0	1.0000
44	84.0	1.0000
54	92.6	1.0000
91	76.5	0.5749
107	83.2	0.5749
130	92.0	0.5749
98	76.5	0.4681
115	83.2	0.4681
143	92.0	0.4681
108	76.5	0.3791
127	83.2	0.3791
154	92.0	0.3791
117	76.5	0.3456
137	83.2	0.3456
164	92.0	0.3456
124	76.5	0.2394
137	80.0	0.2394
146	83.2	0.2394
122	76.5	0.1970
141	83.2	0.1970
167	90.6	0.1970
105	67.8	0.0000
129	75.0	0.0000
134	76.5	0.0000
96	65.0	0.0000
111	70.0	0.0000
127	75.0	0.0000

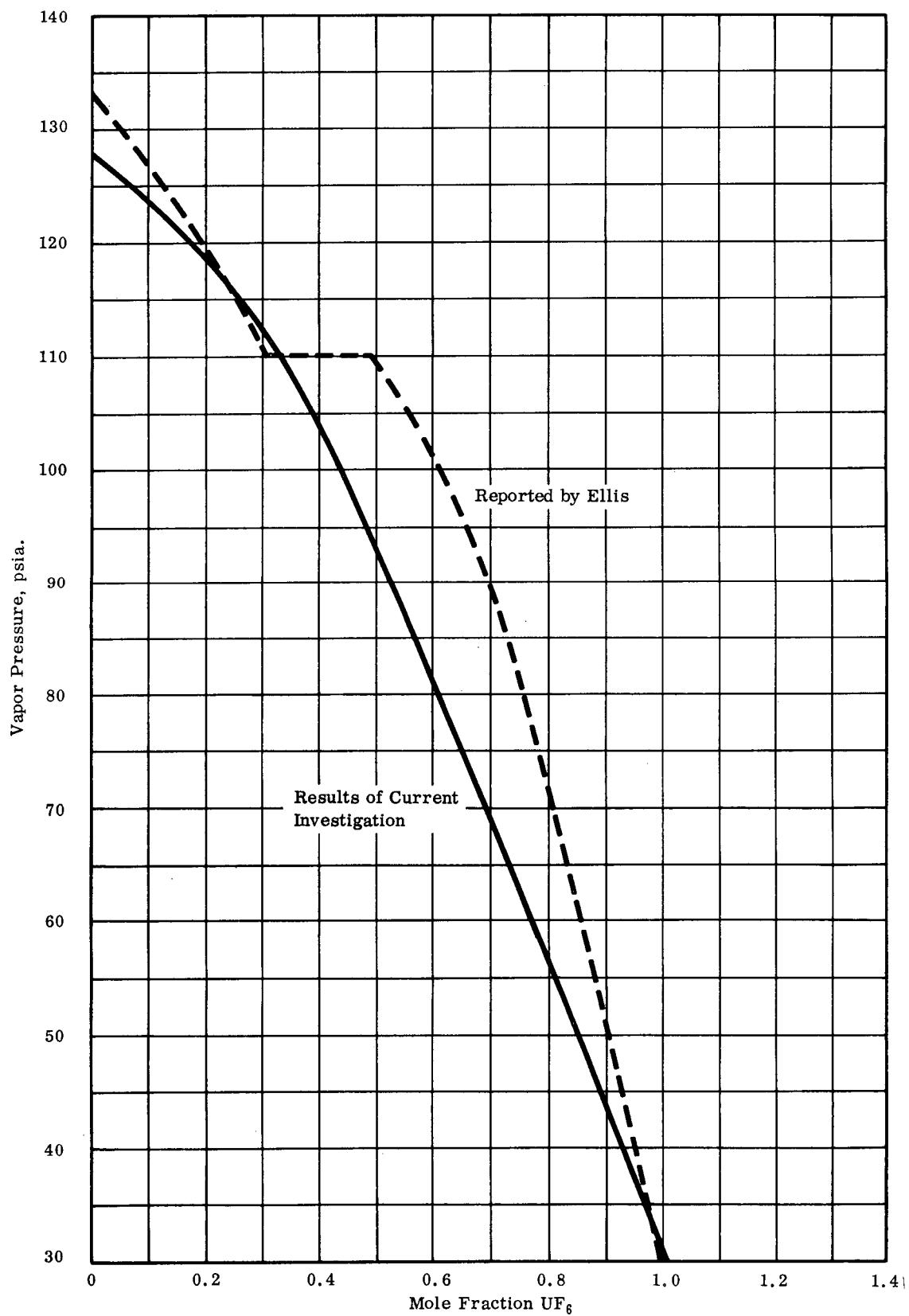


FIG. 51. VAPOR PRESSURE - COMPOSITION DIAGRAM FOR THE URANIUM  
HEXAFLUORIDE - CHLORINE TRIFLUORIDE SYSTEM  
(Reference 96)

## UF<sub>6</sub> TERNARY EQUILIBRIUM SYSTEMS

### URANIUM HEXAFLUORIDE - CHLORINE TRIFLUORIDE - HYDROGEN FLUORIDE

Rutledge and Davis<sup>134</sup> constructed the solid-liquid and the liquid-liquid equilibria of the ternary system UF<sub>6</sub>-ClF<sub>3</sub>-HF from the experimental data on the binary systems of these three components. A ternary eutectic was found at -91°C. and a composition of 0.0 to 0.2 formula percent UF<sub>6</sub>, 19.5 formula percent ClF<sub>3</sub>, and 80.5 formula percent HF. At a composition of 49 formula percent UF<sub>6</sub>, 13 mole percent ClF<sub>3</sub>, and 38 formula percent HF at a temperature of 53°C., a miscibility gap begins in which two liquids are saturated with solid UF<sub>6</sub>. This miscibility gap exists up to about 101°C.

Rowlinson<sup>130</sup> calculated the liquid-vapor equilibria for the ternary system UF<sub>6</sub>-ClF<sub>3</sub>-HF from a knowledge of the three binary systems using the statistical theory of solutions. The binary equilibria data which were used by Rowlinson are the same as those used by Rutledge and Davis.

### URANIUM HEXAFLUORIDE - 2, 2, 3-TRICHLOROHEPTAFLUOROBUTANE - PERFLUORODIMETHYLCYCLOHEXANE

Capps and Burke<sup>33</sup> obtained some preliminary data concerning the liquid-vapor equilibrium for the UF<sub>6</sub> - 2, 2, 3-trichloroheptafluorobutane - perfluorodimethylcyclohexane ternary system. Samples of the liquid and the condensed vapor which were withdrawn from a modified Othmer-type equilibrium still were analyzed by infrared spectroscopy. The results are listed in Table 79. The authors point out that the ratio of perfluorodimethylcyclohexane to 2, 2, 3-trichloroheptafluorobutane tends to approach the azeotropic composition ratio in going from the liquid to the vapor phase.

Table 79

LIQUID-VAPOR EQUILIBRIUM OF THE URANIUM HEXAFLUORIDE-  
 TRICHLOROHEPTAFLUOROBUTANE-PERFLUORODIMETHYLCYCLOHEXANE SYSTEM  
 (Reference 33)

Liquid-Vapor Sample Pair	Mole Percent					
	Trichloroheptafluorobutane		Perfluorodimethylcyclohexane		Uranium Hexafluoride	
	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor
1	44.7	30.8	42.0	23.0	13.2	48.4
2	51.2	33.4	29.3	19.2	19.5	47.4
3	45.0	23.5	26.7	13.4	28.2	63.0
4	37.8	19.4	37.3	15.7	25.0	64.9
5	32.8	17.6	52.9	20.7	14.3	61.7
6	26.9	19.7	57.8	27.5	15.3	52.8
7	25.0	6.6	50.8	9.6	24.2	83.8
8	36.5	14.6	40.1	13.0	23.3	72.4
9	35.9	13.3	38.8	12.4	22.9	74.4
10	25.9	9.6	27.3	9.7	46.8	80.8
11	22.6	5.5	25.0	6.6	52.4	87.8

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## LIST OF SYMBOLS

a	Empirical constant
A	Non-ideality parameter, $1/T^3$
$A_v$	First virial coefficient, atm. liters/mole
B	Empirical constant
B	Virial coefficient, liters
$B_v$	Second virial coefficient, atm. liters <sup>2</sup> /mole
$\bar{c}$	Mean velocity, cm./sec.
C	Empirical constant
C	Virial coefficient, liters <sup>2</sup>
$C_p$	Heat capacity at constant pressure, cal./mole deg.
$\Delta C_p$	Heat capacity at constant pressure at the triple point, cal./mole
$C_{sat}$	Heat capacity of condensed phase in equilibrium with saturated vapor, cal./mole deg.
$C_v$	Heat capacity at constant volume, cal./mole deg.
$C_v$	Third virial coefficient, atm. liters <sup>3</sup> /mole
D	Self-diffusion coefficient, cm. <sup>2</sup> /sec.
D	Virial coefficient, liters <sup>3</sup>
E	Energy content, cal./mole deg.
$E^{\circ}_0$	Energy content at absolute zero (zero-point energy), cal./mole
F	Free energy, cal./mole deg.
$F^{\circ}$	Free energy of a perfect gas, cal./mole deg.
h	Planck's constant, erg sec.
H	Enthalpy, cal./mole deg.
$H_o$	Enthalpy at standard state, cal./mole
$\Delta H_f$	Heat of fusion, cal./mole
$\Delta H_s$	Heat of sublimation, cal./mole
$\Delta H_v$	Heat of vaporization, cal./mole
k	Boltzmann constant, erg/deg.
k	Empirical constant
$k_x; k_{x,y}$	Force constants, $10^5$ dynes/cm.
K	Thermal conductivity, cal./cm. sec. °C.
l	Mean free path, cm.
m	Empirical constant
m	Mass of the molecule, grams

M	Molecular weight, grams
n	Empirical constant
n	Refractive index
n	Number of molecules per unit volume
N	Avogadro number
p	Pressure, mm.
P	Pressure, atm.
$P_m$	Molar polarization, cc.
r	Distance between atoms or molecules, cm.
R	Gas constant, atm. liter/mole °K.
$R_o$	Empirical constant (Lennard-Jones 6-12 parameter)
S	Sutherland's constant
S	Entropy, cal./mole deg.
$S^\circ$	Entropy of perfect gas, cal./mole deg.
$S_o$	Entropy at standard state, cal./mole
t	Temperature, degrees centigrade
$t_c$	Critical temperature, degrees centigrade
$t_f$	Triple point temperature, degrees centigrade
T	Temperature, degrees Kelvin
$T_c$	Critical temperature, degrees Kelvin
V	Volume, liters
$V_c$	Critical volume, liters
$V_c$	Volume of condensed phase, liters
$V_g$	Volume of vapor phase, liters
$V_f$	Volume of vapor at triple point, liters
X	Mole fraction
X	Repulsion force constant, g./sec. <sup>2</sup>
$\epsilon$	Empirical constant (Lennard-Jones Model 6-12)
$\epsilon$	Dielectric constant
$\eta$	Viscosity, poise or g./cm. sec.
$\lambda$	Force constant
$\mu$	Empirical constant

$\nu$	Fundamental vibrational frequency, $\text{cm.}^{-1}$
$\nu$	Rigidity of the molecule
$\nu_0$	Density of the molecule, grams/cc.
$\rho$ or $\rho_v$	Density of the vapor, grams/cc.
$\rho_l$	Density of the liquid, grams/cc.
$\rho_c$	Critical density, grams/cc.
$\sigma$	Molecular diameter, angstroms, $\text{\AA}$

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