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**THERMODYNAMIC DATA
FOR URANIUM FLUORIDES**

J. M. Leitnaker

**Materials and Chemistry Technology
Process Support**

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Process Support

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SUMMARY

Self-consistent thermodynamic data have been tabulated for uranium fluorides between UF_4 and UF_6 , including UF_4 (solid and gas), U_4F_{17} (solid), U_2F_9 (solid), UF_5 (solid and gas), U_2F_{10} (gas), and UF_6 (solid, liquid, and gas). Included are thermal functions -- the heat capacity, enthalpy, and free energy function, heats of formation, and vaporization behavior.

INTRODUCTION

The purpose of this document is to tabulate self-consistent thermodynamic data for uranium fluorides. In addition to selecting data from the literature, a number of enthalpies of formation as well as entropies have been derived, notably of the intermediate fluorides and the UF_5 and U_2F_{10} gases. This tabulation has the advantage that a consistent set of thermal functions and heats of formation data are collected in one document. Much of the thermal function data for the intermediate fluorides are estimated, but, when used with the calculated enthalpies of formation for the compounds, they yield values consistent with the known thermodynamic data.

Consistency is an important consideration in the choice of thermodynamic data. For example, we have used the value of 45.3 e.u.* for the entropy of $\alpha\text{-UF}_5$. A recent publication by the National Bureau of Standards¹ uses the value of 47.7 e.u. for this same quantity which results in a difference of 2.4 e.u. for the entropy of vaporization. For UF_5 pressure calculations at 1400 K, a difference of a factor of 3.3 results, which would raise the calculated pressure of UF_5 from less than an atmosphere to nearly three atmospheres--not a trivial difference.

THERMODYNAMIC FUNCTIONS OF URANIUM FLUORIDES

In this section the thermodynamic functions C_p/R , $(H^\circ_T - H^\circ_{298})/R$, S°_T/R , and $(G^\circ_T - H^\circ_{298})/RT$ are tabulated for those uranium fluorides for which we can either obtain data or can reasonably estimate the quantities involved. We choose to tabulate dimensionless quantities, except for $(H^\circ_T - H^\circ_{298})/R$, for which the unit is Kelvin. The functions are tabulated in Tables 1 through 10 at the end of this section.

Thermal functions for the elements, condensed uranium² and gaseous fluorine,³ are readily available and not in doubt. They have been tabulated here for completeness and convenience of a user of the tables. While thermal functions of UF_6 in both the condensed and the gaseous phases are well established, they have not been conveniently tabulated. Brickwedde et al.⁴ reported the heat capacity of the condensed hexafluoride from 14 to 350 K. Weinstock et al.⁵ thoroughly reevaluated the vapor pressure data of UF_6 , as well as spectroscopic constants of the gas and its equation of state. The agreement among those sets of data bearing

*See Appendix for explanation of terms.

on the thermodynamic properties of UF_6 is excellent. It is interesting that in order to bring the structural information on gaseous UF_6 into agreement with thermodynamic data the theory on electron diffraction had to be modified.⁶ The interesting sequence of events is not directly recorded but can be appreciated by following the references back from Weinstock et al.⁵

For solid UF_4 the thermal data are in reasonable accord. The low temperature data have been carefully obtained by Burns et al.⁷ Dworkin's⁸ high temperature measurements reaffirm those of King and Christensen⁹. Although there are differences between the two measurements of about 1% in the measured heat content, the differences are probably within the inherent errors in this type of preparation and measurement.

The vaporization behavior of UF_4 has recently been reexamined,¹⁰ and it is clear that the data are in accord with vaporization to the UF_4 monomer. There is general agreement among the various experimenters on the vapor pressure over the solid. However, the derived entropy for the gas did not agree with the entropy calculated for a tetrahedral molecule. Lau and Hildenbrand¹¹ have recently pointed out that essentially all of the discrepancy can be removed by using a less symmetrical model for UF_4 (C_{2v}) and a reestimation of vibrational and electronic energy levels. Nevertheless, the thermal functions for gaseous UF_4 are not tabulated here.

Solid fluorides between UF_4 and UF_6 have been largely ignored by the thermochemical community. However, enough data have been obtained to allow reasonable estimates of the thermal functions to be made. The validity of the estimates can be judged by their use to correctly yield independent thermodynamic quantities by appropriate combinations. One example of such substantiation will be shown below.

The thermal functions of solids can be considered as coming from two sources, generally: a lattice contribution and an electronic contribution. In this view, the atoms are perceived to vibrate about their equilibrium lattice sites, contributing to the heat capacity as (nearly) harmonic oscillators, dependent only on a force constant and the atomic weight. This is a reasonably consistent view of solid UF_6 . On the other hand, an additional term must be included to explain the heat capacity of solid UF_4 , which may be viewed as arising from an electronic contribution by the uranium atom to the heat capacity of the solid. It is reasonable to suppose that the heat capacity of the fluorides intermediate to UF_4 and UF_6 would have intermediate heat capacities and, consequently, intermediate thermal functions.

The real situation is not so simple if the fine details are considered. For example, the uranium atom in UF_4 would be expected to have two electrons not used in bonding. If the electrons are unpaired, the electronic entropy expected would be $R \ln 3$ or 2.18 e.u. The entropy of UF_4 at room temperature is just 2.29 e.u. greater than ThF_4 , which would not be expected to have any electrons unused in bonding. The electronic entropy of UF_4 does not arise in a simple randomization process, however.

A Schottky anomaly occurs in UF_4 below about 20 K, but the contribution to the entropy is only about 0.3 e.u.¹²

Other fine details are troublesome. The uranium atoms are not all equivalent in UF_4 as they are in UF_6 , UF_5 , and U_2F_9 . Even so, one can "get" to U_4F_{17} by adding F atoms in appropriate holes, and then to U_2F_9 by a similar addition. In the alpha form of UF_5 all uranium atoms are bonded to six fluorine atoms; however, all the fluorine atoms are not precisely equivalent. In UF_6 the uranium atoms are equivalent, as are the fluorine atoms.

The regularities suggest that a simple interpolation for the thermal functions may be satisfactory, despite the difficulties of explaining the entropy of UF_4 . If one averages the entropy of UF_4 and UF_6 at 298 K, one obtains very nearly the entropy for UF_5 reported by Katz and Rabinowitch.¹³ Thus, for S°_{298}/R of UF_5 , one estimates $(18.24 + 27.40)/2$ or 22.82, as compared to 22.65 reported for a sample of UF_5 thought to be of the alpha form. The composition of the material was only about 83% UF_5 , the remainder being UF_4 and UO_2F_2 . According to the original National Bureau of Standards report cited by Katz and Rabinowitch,¹³ correction for the UO_2F_2 was made by assuming that it had the same heat capacity as UF_4 . If a correction is made based on more recent data, the value of S°_{298}/R derived is 22.79 rather than 22.65. At any rate, little error results in averaging the entropies of UF_4 and UF_6 to get the entropy of UF_5 . The further interpolation to get those for U_2F_9 and U_4F_{17} should be just as valid.

The same interpolation between UF_4 and UF_6 cannot be made for the heat capacity. At 298 K, C_p/R of UF_4 is 13.956, C_p/R of UF_6 is 20.06, and a linear interpolation yields 17.01, while the reported value for UF_5 is 15.92. Since the hexafluoride melts at 64.2 °C and a pressure of 1,150 torr, one might expect to see a premelting increase in the heat capacity of UF_6 , accounting for the discrepancy of slightly more than 1.0 in the linear interpolation versus the measured value of UF_5 . It seems more appropriate to accept the reported value of the heat capacity of UF_5 at 298 K, and use this and the heat capacity of UF_4 as a basis for calculating thermal functions of UF_5 , U_2F_9 , and U_4F_{17} . No corrections were made for UO_2F_2 in the $\alpha\text{-UF}_5$ which would have increased the heat capacity by a negligible amount.

The heat capacity for UF_4 from Dworkin's⁸ data is:

$$C_p/R = 14.86 + 1.157 \times 10^{-3}T - 1.112 \times 10^{-5}T^{-2}. \quad (1)$$

To obtain the heat capacity of UF_5 as a function of temperature, each term in equation (1) is multiplied by 1.1407, and other functions are obtained by integration in the usual way. For $\text{UF}_{4.5}$ the factor 1.0704 was used, and for $\text{UF}_{4.25}$ the factor 1.0352 was used.

It should be emphasized that there are two forms of UF_5 : alpha, stable above about 125°C, and beta, stable at lower temperature.¹⁴ Thus, the

low temperature heat capacity has been determined from near zero to above 298 K for a substance which is not stable below ~ 370 K. Measurement of heat capacities of unstable substances, and calculation of the third law entropy therefrom, is not unheard of. An example would be those data for diamond, a form of carbon. Perhaps somewhat more unusual is the fact that these data are not available for the stable, beta form of UF_5 .

While the material for which the low temperature heat capacity was measured was stated by Katz and Rabinowitch¹³ to be the alpha form, some doubt was cast by the source document which had only "presumed" the fluoride to be the alpha form. Nevertheless, it is entirely reasonable to suppose that the material was indeed the alpha form, since it was manufactured in a way recommended to give the high temperature form.

It is customary to choose the most stable condensed phase as the reference state for thermodynamic calculations at the temperature of interest, but it is not necessary to do so. In the present case it seems desirable to use $\alpha\text{-UF}_5$ as the reference state at all temperatures. This has been the basis for estimates of heat capacities of U_2F_9 ($\text{UF}_{4.5}$) and U_4F_{17} ($\text{UF}_{4.25}$), as explained above.

Without loss of generality, one can still calculate thermodynamic quantities for $\alpha\text{-UF}_5$ relative to the other phases in the system. There is good reason to suppose that the beta form is stable at low temperatures, below 125°C . An entropy for $\beta\text{-UF}_5$ lower than that for alpha is a necessary consequence. It is also necessary to suppose, because of phase rule considerations, that the composition of the alpha and beta phases differ, if only slightly. A difference in composition has not been detected and it is assumed to be negligibly small.

If a temperature of 125°C is accepted as the transition point of UF_5 , data are available to calculate the difference in entropy. O'Hare et al.¹⁵ have measured the enthalpy of solution of both forms, from which the enthalpy of transition can be derived: 7.5 kJ mol^{-1} at 298 K. This value should be relatively independent of temperature, and the value of $\Delta S^\circ_{298}/R$ is thus calculated to be 2.27, with the beta form having the lower entropy.

The entropy values at every temperature for $\beta\text{-UF}_5$ can be computed by subtracting 2.27 from those tabulated in Table 5. Likewise, the free energy function, $-(G^\circ_T - H^\circ_{298})/RT$, can be computed for $\beta\text{-UF}_5$ by adding 2.27.

The reader may well wonder why one chooses to estimate the entropies--and, indeed, all the thermal functions--of U_2F_9 and U_4F_{17} from consideration of a compound which is not stable at the temperature at which the primary argument is made. The reasons can be summarized as follows. First, data are available for the alpha form of UF_5 and not for the beta form. Second, the interpolation between UF_4 and UF_6 was consistent for the entropy of UF_5 in its alpha form. Third, consistency in recalculating values of interest is even more important than accuracy for many calculations. And, finally, it will be seen in the next paragraph that

the estimation results in consistency with other existing independent values.

Thermal functions for gaseous UF_5 can be calculated from spectroscopic data by Jones and Ekberg¹⁶ whose observations are in accord with calculations by Krohn et al.¹⁷ The structure of the molecule seems to be C_{4v} . The U-F distance is 1.995 Å, and the angle beta is 101° . One must add $\frac{1}{2}$ to account for one unpaired electron on uranium. Calculation of the entropy of gaseous UF_5 can be checked by an alternative calculation, much as for UF_4 , and agreement is obtained. The entropy of $\text{UF}_5(\text{s})$ has been measured, as mentioned above. Wolf et al.¹⁸ have measured the transport of UF_5 in a UF_6 atmosphere. Kleinschmidt and Hildenbrand¹⁹ determined the proportion of UF_5 and U_2F_{10} in the vapor, and an earlier publication by Leitnaker²⁰ corrected the data of Wolf et al.¹⁸ for an effect by UF_6 on the amount of UF_5 transported. From these data the entropy of vaporization of UF_5 , $\Delta S^\circ_{298}/R$, is calculated to be 22.6. Adding the entropy of solid UF_5 , one obtains for gaseous UF_5 an entropy, S°_{298}/R , of 45.42. By use of spectroscopic data, the value for the entropy is calculated to be 45.21, in excellent agreement. In addition, the enthalpy of vaporization via the second and third law calculations can be compared by virtue of having free energy functions for both the solid and gas. Using the second law one calculates, for UF_5 , a value of the enthalpy $\Delta H^\circ_{298}/R$, of 18,978 K. Using the third law one obtains 18,855 K. The agreement is excellent.

Thermal functions for gaseous U_2F_{10} cannot be calculated directly, for the data do not exist. Nevertheless, a very good approximation to the desired functions can be obtained. The high temperature heat capacity of $\text{U}_2\text{F}_{10}(\text{g})$ should be approachable through $\text{UF}_5(\text{g})$. In the previous paragraph, we have calculated the thermal function of $\text{UF}_5(\text{g})$ from spectroscopic data and found that the calculated entropy of the gas agreed with that obtained by adding the entropy of vaporization to the entropy of the solid. The fact that the calculations agree tends to substantiate both numbers. Moreover, the agreement suggests that there are no important low lying electronic levels not accounted for in the calculation. Classically, the value of C_p/R for $\text{UF}_5(\text{g})$ should be 16. In Table 7 the value at 298 K is seen to be 13.286, rising to 15.917 at 2000 K. If it is assumed that $\text{U}_2\text{F}_{10}(\text{g})$ would behave in a similar way, the value of C_p/R for $\text{U}_2\text{F}_{10}(\text{g})$ at any temperature, T , can be estimated by multiplying the heat capacity of $\text{UF}_5(\text{g})$ at T by $34/16$, where 34 is the classical value for U_2F_{10} and 16 is the classical value for UF_5 . Then, $(H^\circ_T - H^\circ_{298})/R$ can be obtained by integration, as can $(S^\circ_T - S^\circ_{298})/R$. To get S°_{298}/R one can use the data of Wolf et al.¹⁸ on the transport, suitably corrected as described subsequently for $\text{UF}_5(\text{g})$. All the functions for $\text{U}_2\text{F}_{10}(\text{g})$ are tabulated in Table 8.

Table 1

THERMODYNAMIC FUNCTIONS FOR CONDENSED URANIUM^(a)

T, K	C_p/R	$(H^\circ_T - H^\circ_{298})/R, K$	S°_T/R	$-(G^\circ_T - H^\circ_{298})/RT$
298.15	3.33	0	6.04	6.04
300	3.33	6	6.06	6.04
400	3.57	352	7.05	6.17
500	3.85	722	7.88	6.43
600	4.18	1122	8.61	6.73
700	4.57	1560	9.28	7.05
800	5.03	2038	9.92	7.37
900	5.55	2566	10.54	7.68
941(α)	5.77	2798	10.79	7.82
941(β)	5.16	3135	11.15	7.82
1000	5.16	3442	11.46	8.02
1048(β)	5.16	3689	11.70	8.19
1048(α)	4.60	4257	12.25	8.19
1100	4.60	4499	12.47	8.38
1200	4.60	4957	12.87	8.74
1300	4.60	5420	13.24	9.07
1400	4.60	5878	13.58	9.38
1405(α)	4.60	5903	13.60	9.40
1405(ℓ)	(4.60)	(7458)	(14.70)	9.40
1500	(4.60)	(7896)	(15.01)	9.74
2000	(4.60)	(10200)	(16.33)	11.23

^(a)Calculated from data of Hultgren et al.²

Table 2

THERMODYNAMIC FUNCTIONS FOR UF_4 (SOLID) (a)

$T, \text{ K}$	C_p/R	$(H^\circ_T - H^\circ_{298})/R, \text{ K}$	S°_T/R	$-(G^\circ_T - H^\circ_{298})/RT$
298.15	13.956	0	18.240	18.240
300	13.973	26	18.326	18.241
400	14.629	1460	22.447	18.798
500	14.995	2942	25.754	19.869
600	15.247	4455	28.511	21.086
700	15.445	5990	30.877	22.320
800	15.614	7543	32.951	23.522
900	15.766	9112	34.799	24.674
1000	15.908	10696	36.467	25.771
1100	16.043	12294	37.990	26.814
1200	16.173	13904	39.391	27.804
1300	16.301	15528	40.691	28.746

(a) Calculated from data of Burns, et al.⁷ and Dworkin⁸

Table 3

THERMODYNAMIC FUNCTIONS FOR $\text{UF}_{4.25}$ (SOLID) (a)

$T, \text{ K}$	C_p/R	$(H^\circ_T - H^\circ_{298})/R, \text{ K}$	S°_T/R	$-(G^\circ_T - H^\circ_{298})/R$
298.15	14.447	0	19.390	19.390
300	14.465	27	19.479	19.391
400	15.144	1511	23.745	19.968
500	15.523	3046	27.169	21.077
600	15.784	4612	30.023	22.336
700	15.989	6201	32.472	23.614
800	16.163	7809	34.619	24.858
900	16.321	9433	36.532	26.051
1000	16.468	11073	38.259	27.186

(a) Interpolated as described in text.

Table 4

THERMODYNAMIC FUNCTIONS FOR $\text{UF}_{4.5}$ (SOLID) (a)

T, K	C_p/R	$(H^\circ_T - H^\circ_{298})/R, K$	S°_T/R	$-(G^\circ_T - H^\circ_{298})/RT$
298.15	14.938	0	20.530	20.530
300	14.957	28	20.622	20.531
400	15.659	1563	25.033	21.127
500	16.051	3150	28.573	22.274
600	16.321	4769	31.525	23.577
700	16.532	6412	34.057	24.897
800	16.713	8074	36.276	26.184
900	16.876	9754	38.255	27.417
1000	17.028	11449	40.041	28.591

(a) Interpolated as described in the text.

Table 5

THERMODYNAMIC FUNCTIONS FOR UF_5 (ALPHA) (a)

T, K	C_p/R	$(H^\circ_T - H^\circ_{298})R, K$	S°_T/R	$-(G^\circ_T - H^\circ_{298})/RT$
298.15	15.919	0	22.820	22.820
300	15.939	29	22.919	22.821
400	16.688	1665	27.619	23.456
500	17.105	3356	31.391	24.679
600	17.392	5082	34.537	26.067
700	17.618	6833	37.235	27.474
800	17.811	8604	39.601	28.845
900	17.984	10394	41.709	30.159
1000	18.146	12201	43.612	31.411

(a) Calculated as described in the text for the alpha form.

Table 6

THERMODYNAMIC FUNCTIONS FOR UF_6 (SOLID AND LIQUID)^(a)

$T, \text{ K}$	C_p/R	$(H^\circ_T - H^\circ_{298})/R, \text{ K}$	S°_T/R	$-(G^\circ_T - H^\circ_{298})/RT$
298	20.06	0	27.40	27.40
300	20.13	37	27.53	27.40
310	20.57	241	28.20	27.42
320	21.04	449	28.86	27.46
330	21.53	662	29.51	27.51
337.212(s)	21.89	819	29.98	27.55
337.212(l)	22.95	3128	36.83	27.55
340	22.99	3192	37.02	27.63
350	23.16	3424	37.69	27.91
360	23.32	3657	38.34	28.18
370	23.46	3892	38.98	28.46

^(a) Calculated from data by Brickwedde, et al.⁴

Table 7

THERMODYNAMIC FUNCTIONS FOR UF_5 (GAS) (a)

$T, \text{ K}$	C_p/R	$(H^\circ_T - H^\circ_{298})/R, \text{ K}$	S°_T/R	$-(G^\circ_T - H^\circ_{298})/RT$
298.15	13.286	0	45.214	45.214
300	13.319	25	45.297	45.214
400	14.278	1409	49.272	45.750
500	14.824	2867	52.522	46.790
600	15.153	4367	55.257	47.979
700	15.363	5893	57.609	49.191
800	15.505	7437	59.671	50.375
900	15.605	8993	61.503	51.511
1000	15.678	10557	63.151	52.594
1100	15.732	12128	64.648	53.623
1200	15.774	13703	66.019	54.600
1300	15.807	15283	67.283	55.528
1400	15.833	16865	68.455	56.410
1500	15.854	18449	69.548	57.250
1600	15.872	20035	70.572	58.051
1700	15.886	21623	71.535	58.816
1800	15.898	23212	72.443	59.548
1900	15.909	24803	73.303	60.250
2000	15.917	26394	74.119	60.923

(a) Calculated from vibrational data by Jones and Ekberg¹⁶

Table 8

THERMODYNAMIC FUNCTIONS FOR U_2F_{10} (GAS) (a)

T, K	C_p/R	$(H^\circ_T - H^\circ_{298})/R, \text{K}$	S°_T/R	$-(G^\circ_T - H^\circ_{298})/RT$
298.15	28.233	0	69.464	69.464
300	28.284	52	69.639	69.466
400	30.341	2984	78.072	70.612
500	31.501	6076	84.971	72.819
600	32.200	9261	90.778	75.343
700	32.646	12503	95.776	77.915
800	32.948	15783	100.156	80.427
900	33.161	19088	140.049	82.840
1000	33.316	22412	107.551	85.139
1100	33.431	25749	110.732	87.324
1200	33.520	29097	113.645	89.398
1300	33.590	32452	116.330	91.367
1400	33.645	35814	118.822	93.241
1500	33.690	39181	121.145	95.024
1600	33.728	42552	123.320	96.725
1700	33.758	45926	125.366	98.351
1800	33.783	49303	127.296	99.905
1900	33.807	52683	129.123	01.395
2000	33.824	56064	130.858	02.826

(a) Calculated as described in the text.

Table 9

THERMODYNAMIC FUNCTIONS FOR UF_6 (GAS) (a)

$T, \text{ K}$	C_p/R	$(H^\circ_T - H^\circ_{298})/R, \text{ K}$	S°_T/R	$-(G^\circ_T - H^\circ_{298})/RT$
298.15	15.593	0	45.401	45.401
300	15.623	29	45.498	45.402
400	16.826	1657	50.174	46.031
500	17.511	3377	54.009	47.255
600	17.925	5150	57.241	48.657
700	18.191	6957	60.026	50.087
800	18.371	8786	62.467	51.485
900	18.497	10629	64.639	52.828
1000	18.590	12484	66.593	54.108
1100	18.659	14347	68.368	55.325
1200	18.712	16215	69.994	56.481
1300	18.754	18089	71.493	57.578
1400	18.787	19966	72.884	58.623
1500	18.814	21846	74.181	59.617
1600	18.836	23729	75.396	60.566
1700	18.855	25613	76.539	61.472
1800	18.870	27499	77.617	62.339
1900	18.884	29387	78.638	63.170
2000	18.895	31276	79.607	63.968

(a) Calculated from data of Weinstock, et al.⁵

Table 10

THERMODYNAMIC FUNCTIONS FOR F_2 (GAS) ^(a)

T, K	C_p/R	$(H^\circ_T - H^\circ_{298})/R, K$	S°_T/R	$-(G^\circ_T - H^\circ_{298})/RT$
298.15	3.77	0	24.38	24.38
300	3.77	7	24.40	24.38
400	3.97	394	25.52	24.54
500	4.12	799	26.42	24.83
600	4.23	1217	27.18	25.15
700	4.31	1645	27.84	25.50
800	4.37	2079	28.42	25.82
900	4.41	2518	28.94	26.14
1000	4.45	2960	29.41	26.45
1100	4.48	3408	29.83	26.73
1200	4.50	3857	30.22	27.01
1300	4.52	4308	30.58	27.27
1400	4.54	4761	30.92	27.52
1500	4.56	5216	31.23	27.76
1600	4.57	5671	31.52	27.98
1700	4.58	6130	31.81	28.20
1800	4.59	6589	32.07	28.41
1900	4.60	7050	32.32	28.61
2000	4.62	7511	32.55	28.80

(a) Recalculated from the data of Stull and Sinke³.

TRANSPORT OF URANIUM PENTAFLUORIDE

Data of Wolf et al.¹⁸

The vapor pressure of uranium pentafluoride cannot be determined, for example, by means of a Knudsen cell measurement, because the pentafluoride loses $\text{UF}_6(\text{g})$ preferentially on heating. However, by using UF_6 as a transporting gas one can prevent the disproportionation and determine the vapor transport of UF_5 . Wolf¹⁸ and co-workers performed this measurement a number of years ago.

From the measurement of the transport the pressure of the pentafluoride could be calculated by the formula

$$P_{\text{UF}_5} = N_{\text{UF}_5} \times P_{\text{UF}_6} / N_{\text{UF}_6} \quad (2)$$

where P_{UF_5} and P_{UF_6} are the vapor pressures of the pentafluoride and hexafluoride and the N's represent the number of moles of the two materials transported.

Enhanced Transport by Uranium Hexafluoride

Reevaluation of the data reported by Wolf et al.¹⁸ indicated that the UF_6 was providing a mechanism of transporting the UF_5 .²⁰ When the data were tested against the equation

$$\ln "P_{\text{UF}_5}" = a_0 + a_1 (1/T) + a_2 P_{\text{UF}_6} \quad (3)$$

the constant a_2 was shown to be statistically significant, especially when the UF_5 was solid.

The reason for the enhanced transport is not now clear. A first conjecture was that the process

or possibly

produced the enhanced transport. (The U_2F_{11} simply represents the simplest combination of solid UF_5 and gaseous UF_6 to produce a gaseous molecule--and $\text{UF}_5 \cdot (\text{UF}_6)_x$ represents the general possibility.) The existence of such a molecule is certainly not outside the realm of possibility. The ion-molecule $\text{U}_2\text{F}_{11}^+$ has been observed in the mass spectrometer,¹⁹ although it is not clear whether it formed in a reaction, such as between an ion and a molecule, or if it was present as a parent ion. The presence of such a molecule would explain the observed enhancement. Notice that as the pressure of UF_6 increases the pressure of the gaseous adduct also would increase.

However, the explanation above is not the only way in which additional transport could be produced by an increased pressure of UF_6 . Such a process could occur via the reaction

It is extremely difficult to prevent small traces of moisture from contaminating the system, particularly during assembly and disassembly, and this could provide the required UO_2F_2 via the reaction

Very little is known about the thermodynamics of UOF_4 and nothing about the gaseous state. Only fragmentary references to the gas are found in the literature.

Gaseous Polymers of Uranium Pentafluoride

A recent mass spectrometric examination of the vaporization behavior of a UF_x solid, somewhat richer in fluorine than UF_4 but of unknown exact composition, by Kleinschmidt and Hildenbrand,¹⁹ revealed that the most important species in the gas over UF_5 --other than UF_6 --was U_2F_{10} rather than the monomeric UF_5 . No other polymers were seen, although in the Mo-F system polymers have been seen of the formula $(\text{MoF}_5)_n$ with n from 1 to 5 inclusive.²¹ In the W-F system the pentafluoride polymers seen include the tetramer but not the pentamer.²²

The presence of polymeric UF_5 in the vapor phase necessitates correction of the vapor pressures measured by Wolf et al.¹⁸ not only for the enhancement of transport by the UF_6 but also for the dimerization. It is for this reason that quotation marks were put around P_{UF_5} in Equation (3). Note particularly in Equation (2) that the N_{UF_5} requires a molecular weight to calculate its value from the mass of UF_5 transported.

Vapor Pressure Equations for Pentafluoride

There is still uncertainty about the cause of the additional transport seen, via UF_6 , for the pentafluoride. Nevertheless, the data available can be usefully described with equations. The raw transport data of Wolf et al.¹⁸ for solid UF_5 have been fitted by use of Equation (3), obtaining

$$\ln "P_{\text{UF}_5}" = -16.93 (\pm 0.41) \times 10^3/T + 22.47 (\pm 0.76) + 0.416 (\pm 0.065) P_{\text{UF}_6} \quad (8)$$

where the unit of pressure is atmospheres and T is in kelvin.

The quotation marks around P_{UF_5} emphasize this is not really a pressure but an effective pressure calculated assuming all the transported UF_5 was present as a monomer in the gas phase.

If P_{UF_6} is set equal to zero, one obtains

$$\ln "P_{UF_5}" = -16,930/T + 22.47, \quad (9)$$

which represents the transport of UF_5 unaided by UF_6 .

To obtain pressure equations, one must draw on the data of Kleinschmidt and Hildenbrand⁸ which related the equilibria of

as

$$\ln [P_{U_2F_{10}}/(P_{UF_5})^2] = \ln K = 19,625/T - 20.15. \quad (11)$$

Recall that

$$\begin{aligned} \text{wt } UF_5 \text{ (measured)} &= \text{wt } UF_5 \text{ (transported)} + \\ &\quad \text{wt } U_2F_{10} \text{ (transported)}. \end{aligned} \quad (12)$$

From the gas law

$$\begin{aligned} "P_{UF_5}" \cdot M_{UF_5} \cdot (V/RT) &= P_{UF_5} \cdot M_{UF_5} \cdot (V/RT) + \\ P_{U_2F_{10}} \cdot M_{U_2F_{10}} \cdot (V/RT) \end{aligned}$$

A simple substitution and cancellation yields

$$"P_{UF_5}" = P_{UF_5} + 2P_{U_2F_{10}} \quad (14)$$

Combination of Equations (9), (11), and (14) yield the equations

$$\ln P_{U_2F_{10}} = -16,900/T + 21.704 \quad (15)$$

and

$$\ln P_{UF_5} = -18,263/T + 20.926 \quad (16)$$

These last two equations represent the best present estimation of the pressures of the two known pentafluoride species over solid UF_5 in the range of the measurements.

There is an interesting historical note related to these pressures. Brewer et al. estimated the pressure of the pentafluoride in the early 40s in connection with the Manhattan Project. In Figure 1 the relationship among the various pressures referred to is shown. The highest pressures are those reported by Wolf et al.¹⁸ which, as mentioned previously, are really transport values. The next lower line represents these transport values corrected for the effect of UF_6 on the measurements. The next line represents the pressure of U_2F_{10} computed from a combination of the data of Kleinschmidt and Hildenbrand¹⁹ and of Wolf et al.¹⁸. The lowest line represents the pressure of UF_5 estimated by Brewer and superimposed on the line is a point representing the calculated pressure of the gaseous monomer of UF_5 at its melting point, indicating

Figure 1

PRESSURE-TEMPERATURE RELATIONSHIPS OF " UF_5 " SPECIES

Brewer was nearly correct in his estimation of the pressure of the monomer. It was several years later that the importance of polymeric gaseous halides was recognized.

ENTHALPIES OF FORMATION OF URANIUM FLUORIDES

The Heat of Formation of UF₆ and UF₄

Johnson²³ has recently redetermined the heat of formation of uranium hexafluoride, obtaining $-2197.7 \pm 1.8 \text{ kJ mol}^{-1}$ and $-2148.1 \pm 1.8 \text{ kJ mol}^{-1}$ for UF₆ (c) and UF₆ (g), respectively, at 298.15 K. This value was consistent with a previous finding by Johnson and O'Hare²⁴ that the enthalpy of UO₃, as determined by calorimetry, would be consistent with other thermodynamic measurements if the value for the enthalpy of formation of the hexafluoride were in error by about 11 kJ mol⁻¹. The UO₃ work was solution calorimetry and the UF₆ investigation consisted of combustion in a bomb calorimeter.

Previous measurements, which differed from the results of Johnson given above, had also been consistent, however, and the consistency of the latest results is no guarantee of accuracy. Nevertheless, we have adopted these more recent values. Additional calculations lend strength to the new values, albeit indirectly.

Another quantity determined by Johnson²⁵ bears importantly on that which follows this section. Johnson determined calorimetrically the enthalpy of formation of UF₄. His value was $-1910.4 \pm 2.1 \text{ kJ mol}^{-1}$ for the enthalpy of formation at 298.15 K. These values can be used to recalculate the results of Agron² which is done in the next section.

Recalculation of Thermodynamic Data from Equilibrium Pressures of UF₆ (g) over Intermediate Fluorides

All four fluorides of uranium between UF₆ and UF₄ lose UF₆ preferentially on heating in a vacuum. The stepwise reactions are:

and

Equilibrium pressures of UF₆ for Reactions (17)-(20) were measured a number of years ago by Agron.¹⁴ In this section, the data obtained by Agron are re-examined by both the second and third law methods.

Results of vaporization studies, almost always performed as a function of temperature, are customarily tabulated by considering the logarithm of the measured pressure as an inverse function of the absolute temperature, via the well-known Clausius-Clapeyron equation. This treatment is frequently known as the "second law" method; one obtains the enthalpy of the reaction from the slope of the line and the entropy from the intercept with the ordinate, extrapolated to $(1/T)$ equals zero. The method is useful, but has the disadvantage that, if the range of measurements is short, small errors, particularly temperature-dependent ones, are magnified and large errors often much greater than the observed statistical precision, can be obtained in both the enthalpy and the entropy.

A somewhat more sophisticated method, when the heat capacity change, ΔC_p , for the reactions studied is known, is available. One uses the equation

$$\Sigma = \left[-\ln K + \frac{\Delta C_p}{R} (-\ln T + \Theta/T) \right] = \frac{\Delta H^\circ_\Theta}{R} (1/T) + I \quad (21)$$

to obtain ΔH°_Θ at some fixed temperature, Θ , where K is the equilibrium constant for the reaction studied and R is the gas constant. I is a constant of integration and is related to the entropy for the process via

$$\Delta S^\circ_\Theta/R = (\Delta C_p/R)(1 + \ln \Theta) - I. \quad (22)$$

The fixed temperature, Θ , is usually chosen near the temperature of measurement so that treating ΔC_p as a constant is a good approximation. While this treatment was employed, it offers little advantage over the "second law" method described above for the relatively small temperature ranges studied by Agron.

A better method of treating vapor pressure data, when thermal data are available, is the so-called "third law" method. Here the change in standard free energy for the process is calculated for each point and the thermal data are used to normalize the answers to some standard temperature by calculation of the enthalpy, usually ΔH°_{298} . An equation normally used is

$$\Delta H^\circ_{298} = \Delta G^\circ_T - T[\Delta(G^\circ_T - H^\circ_{298})/T] \quad (23)$$

where

$$\Delta G^\circ_T = -RT \ln K \quad (24)$$

for the process and $\Delta(G^\circ_T - H^\circ_{298})/T$ is the change in the free energy function for the process under consideration. The free energy functions change slowly with temperature, interpolation is easy, and the process is almost always both more accurate and more precise than the "second law"

calculation. A disadvantage is that the entropy for the process must be known, either by measurement or reliable estimation, rather than being calculated from the measurements as for the second law process.

The free energy functions, usually tabulated as the negative because the function itself is negative, are more readily visualized when re-arranged. Note that

$$\frac{G^\circ_T - H^\circ_{298}}{T} = \frac{H^\circ_T - TS^\circ_T - H^\circ_{298}}{T} \quad (24)$$

$$= \frac{H^\circ_T - H^\circ_{298}}{T} - S^\circ_T, \quad (25)$$

and if no transitions occur,

$$\frac{\int_{298}^T C_p dT}{T} - \int_{298}^T \frac{C_p}{T} dT - S^\circ_{298} \quad (26)$$

The function is controlled numerically, to an important degree, by S°_{298} . This is true because the other two terms of equation (26) are of opposite sign and tend to cancel. It is for this reason that the function changes so slowly with temperature and hence is so powerful a tool in examining trends. Notice that if a phase change occurs at a temperature, θ ,

$$\frac{\Delta H_{\text{transition}}}{\theta} = \Delta S_{\text{transition}}. \quad (27)$$

Consequently, the two terms cancel in Equation (25), and

$$(G^\circ_T - H^\circ_{298}/T)_\alpha = (G^\circ_T - H^\circ_{298}/T)_\beta \quad (28)$$

at $T = \theta$

Equations (27) and (28) would have been appropriate if the usual procedure for treating a substance with a transition temperature had been used. They were not used in this treatment for UF_5 as explained above. It is important that this caveat be repeated, since the treatment used here has been non-standard.

The recalculation of Agron's¹⁴ data (Table 11) reveals good agreement of the second law calculation with that given by Agron, except for reaction (19). The other differences are slight and arise almost entirely from the fact that Agron assumed ΔC_p of all the reactions was negligible. Agron's calculation of reaction (19) resulted from a weighting of data which we did not use.

There are significant differences between values calculated for reactions (17) through (20) using the second and third law methods. Note that the $\Delta S^\circ_{298}/R$ third law values are essentially the same, except for reaction (18). The reason is the method of estimation, since each reaction is written as a vaporization of one mole of gaseous UF_6 . The small differences that exist are the result of propagation of rounding errors.

There is clearly a difference between the entropy calculated via the second law and that estimated for the third law calculation. In each reaction the change in entropy may be viewed as that for the change of one mole of solid UF_6 to one mole of gaseous UF_6 . There seems to be no reason why $\Delta S^\circ_{298}/R$ for these reactions should vary from a low of 11.69 to a high of 23.67, as the second law calculations indicate. There are two principal reasons why second law values could be at variance with those calculated via the third law. The first is that small errors in the temperature, particularly if the errors are temperature-dependent, are magnified in determining a slope and intercept. A second problem is that the compositions of the solid phases involved in the reactions are assumed to be constant. A changing composition of one or both phases involved would obviously vary the pressure relative to that expected at a constant temperature. In any case, one should expect a smoothly varying entropy among the three reactions (17), (19), and (20). The variation in the calculated second law entropy between Reactions (17) and (20) is inexplicable on chemical grounds. For these reasons, the third law estimated entropies are preferred over the entropies calculated using the second law. As a consequence of this acceptance, the enthalpies calculated using the third law are also preferred over those calculated using the second law.

From data discussed in the previous section, one can now calculate the enthalpies of formation of the intermediate fluorides U_4F_{17} , U_2F_9 , and UF_5 . One needs the enthalpy of formation of UF_6 (g), $(-258.38 \pm 0.25) \times 10^3$ K for $\Delta H^\circ_{f,298}/R$ (from Johnson²³) and the enthalpy of formation of UF_4 (s), $(-229.77) \pm 0.25 \times 10^3$ K (also from Johnson²⁵). Results of the calculation are given in Table 12 based on the second and third law calculations from Table 11.

One sees in Table 12 that the enthalpy values calculated are relatively insensitive to variations in values employed in the calculation for reactions (17)-(20). Notice the rather small difference per gram atom of uranium in the enthalpy values for the different compounds relative to the absolute size of the number. This means that the difference between the heats of formation of these compounds is more significant in some cases than the absolute value and emphasizes the necessity for using consistent values.

O'Hare et al.¹⁵ have recently determined, by solution calorimetry, the enthalpies of formation of both $\beta\text{-UF}_5$ and $\alpha\text{-UF}_5$. The values for $\Delta H^\circ_{298}/R$ were $(-250.53 \pm 0.77) \times 10^3$ K and $(-249.63 \pm 0.81) \times 10^3$ K, respectively. The agreement with the values calculated in Table 12 is

Table 11

RECALCULATED ENTHALPIES AND ENTROPIES OF DECOMPOSITION OF
INTERMEDIATE FLUORIDES

Equation	Second Law		Third Law		Agron	
	$\Delta H^\circ_{298/R}$ K	$\Delta S^\circ_{298/R}$	$\Delta H^\circ_{298/R}$ K	$\Delta S^\circ_{298/R}$	$\Delta H^\circ_{298/R}$ K	$\Delta S^\circ_{298/R}$
(17)	7038	11.69	9766	18.01	6774	10.92
(18)	9977	19.07	12452	24.64	9592	18.02
(19)	15785	23.28	12860	18.03	16844	24.86
(20)	16785	23.67	13457	17.96	16447	22.75

Table 12

ENTHALPIES OF FORMATION OF INTERMEDIATE URANIUM FLUORIDES (a)

<u>Compound</u>	<u>$-\Delta H^\circ_f, 298/R, 10^3K$</u>	
	<u>From 3rd Law</u>	<u>From 2nd Law</u>
UF _{4.25}	235.0	235.5
UF _{4.5}	240.2	241.0
α -UF ₅	249.5	249.1
β -UF ₅	250.4 ^(b)	250.1

(a) Calculations were made for reactions (17)-(20) using -258,384 and -229,770 for $\Delta H^\circ_{298/R}$ of UF₆ and UF₄, respectively.

(b) This value is derived from the value for α -UF₅ and the difference in enthalpies of the two forms of UF₅ observed by O'Hare, et al.¹⁵ It is not an independent result.

excellent. One must consider the extremely close agreement as, at least in part, fortuitous, since the absolute errors are considerably greater. Note that it is only the agreement between the two determinations of the alpha form of UF_5 that is being discussed, for the difference found by O'Hare between alpha and beta was arbitrarily put into this calculation. Another way of stating the finding is that O'Hare's value for $\alpha\text{-UF}_5$ is confirmed if you choose Johnson's²⁵ value for the enthalpy of formation of UF_4 and Johnson's²³ value for the enthalpy of formation of UF_6 (g).

The second law results of Agron, Table 11, can be used to check the differences between the enthalpies of formation of the two forms of UF_5 . Subtraction of reaction (18) from reaction (17) gives three times the enthalpy (and entropy) for the transformation of alpha to beta. For the enthalpy difference one obtains 0.98×10^3 K and for the entropy difference, 2.26; these may be compared to the values of 0.90×10^3 K and 2.21 (calculated) from O'Hare.

The agreement is good, but, as indicated above, must be regarded in part as fortuitous. Errors, (if they existed) in Agron's temperatures and variations in composition of U_2F_9 , if present, would tend to cancel in the subtraction performed above.

The enthalpies of formation and entropies selected for all the uranium fluorine compounds are tabulated in Table 13.

VAPORIZATION BEHAVIOR OF THE URANIUM - FLUORIDE SYSTEM

The Pressure-Composition Diagram

In a previous section the pressure of UF_6 over the various intermediate fluorides was described in quantitative terms based on the work of Agron.⁹ The pressure-composition diagram more clearly relates the various compounds and the composition of the gas phase over the solids. The diagram is shown in Figure 2 and explained in the following paragraphs.

Few scientists are familiar with the diagram shown in Figure 2. Actually, the general features are quite simple and are relatable to the more familiar temperature-composition diagram, appearing only to be turned upside down. Note that the compositions of the condensed phases are shown along the abscissa as line compounds and are at the "ideal" composition, cloaking our ignorance somewhat. The ordinate is pressure on a logarithmic scale and begins at one atmosphere. Because of the scale and to show some of the important features, there are two "breaks" in the diagram; between $\ln P$ of -38 and -102 and between a mole fraction of fluorine of 0.75 and 0.80. No essential information is thereby lost.

The more specific details show the tie lines of the phases of interest at a fixed temperature of 298 K. Consider some of the two phase regions: In the region between U_2F_9 and UF_5 but above $\ln P$ of about

Figure 2
PRESSURE-COMPOSITION RELATIONSHIPS IN THE
URANIUM-FLUORINE SYSTEM

Table 13

THERMODYNAMIC QUANTITIES FOR URANIUM-FLUORINE COMPOUNDS^(a)

Compound and State	$-\Delta H^\circ_f, 298/R$ (K) $\times 10^3$	$S^\circ_{298/R}$
UF ₄ (s)	229.8	18.24
UF ₄ (g)	191.0	44.94
UF _{4.25} (s)	235.0	19.39
UF _{4.5} (s)	240.2	20.53
UF ₅ (α)	249.5	22.82
UF ₅ (β)	250.4	20.55
UF ₅ (g)	230.6	45.21
U ₂ F ₁₀ (g)	481.0	69.46
UF ₆ (s)	264.4	27.40
UF ₆ (g)	258.4	45.40

(a) The quantities selected are consistent with the free energy functions in the text. The source and derivation are described therein.

-11.7 one has only two solid phases and no gaseous phase at all. But if the system pressure is lowered, say by easing off on an imaginary piston, when one reaches a $\ln P$ of -11.78 a gaseous phase appears, UF_6 primarily. At equilibrium, then one can no longer lower the pressure, that is until all the UF_5 is consumed in the reaction

Notice that once the UF_5 is consumed the system then moves, on lowering the pressure, into the two-phase region of $U_2F_9 (s)$ plus a gas which is largely UF_6 . One can then lower the pressure until the next three-phase tie-line is reached: U_4F_{17} - U_2F_9 -gas.

Notice that this process continues until $UF_4 (s)$ is reached as a solid residue. At this point the system will no longer allow the equilibrium pressure to be lowered until all the UF_4 is evaporated: the UF_4 evaporates congruently (without change of composition of the condensed phase). The U-F system is unusual, among inorganic systems, in that it has two congruently evaporating intermediate phases, the UF_4 phase and also UF_6 .

Some explanations are necessary concerning the curve giving the composition of the gas phase. Both UF_4 and UF_6 are congruently vaporizing phases, but it is difficult to see this is true from the drawing. It is not clear, for example, that UF_5 , solid UF_6 , and a gas consisting of mostly UF_6 but lying in composition between UF_5 and UF_6 , are all three at equilibrium. Nor is it clear that a similar situation exists near UF_4 . Both problems arise because the compositions of the intermediate gas phases lie so close to the solid compounds. The curvature of the line giving the composition of the gas phase may be somewhat exaggerated. In any case, the direction from the UF_6 -gas- UF_5 equilibria is monotonously toward UF_4 as the pressure decreases. Pressures relevant to the diagram are tabulated in Table 14.

Table 14

EQUILIBRIUM PRESSURES OVER SOLID PHASES IN THE U-F SYSTEM AT 298 K

Equilibria	Pressure (atm)	$\ln P$
UF ₆ (g) over UF ₆ (s)	0.15	-1.90
UF ₆ (g) over UF ₅ (s), U ₂ F ₉ (s)	7.7×10^{-6}	-11.78
F ₂ (g) over UF ₅ (s), UF ₆ (s)	8×10^{-44}	-99.23
UF ₅ (g) over UF ₅ (s)	3.1×10^{-17}	-38.00
U ₂ F ₁₀ (g) over UF ₅ (s)	6.3×10^{-16}	-35.01
UF ₆ (g) over U ₂ F ₉ (s), U ₄ F ₁₇ (s)	1.8×10^{-14}	-31.62
UF ₆ (g) over U ₄ F ₁₇ (s), UF ₄ (s)	8.2×10^{-15}	-32.44
UF ₄ (g) over UF ₄ (s)	1.4×10^{-45}	-103.3
U (g) over U (s)	4.5×10^{-86}	-196.5

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APPENDIX

Thermodynamic symbols and usage in this report conforms to most present day usage. Some explanations may aid the casual reader.

The heat capacity at constant pressure is C_p , the heat required to raise a gram-mole of material one degree. More rigidly it is defined as

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (1)$$

where T is the absolute temperature in kelvin.

Enthalpy, sometimes referred to as "heat content," is H. Rigidly, it is defined for a substance as

$$H = E + PV \quad (2)$$

where E is the internal energy, P is the pressure on the system and V is the volume of the system. It is customary to refer only to changes in enthalpy, since absolute values of enthalpy cannot be measured. Enthalpy of formation, for example, is customarily given at a specific reference temperature, indicated by a subscripted value of temperature. The usual reference temperature is 298.15K, and the decimal point with the two following digits are there only by implication. One usually also indicates that enthalpy values apply under conditions agreed on customarily with respect to pressure and form of material by use of a superscript degree sign. An enthalpy of formation would thus appear as $\Delta H^\circ_{298,f}$.

Entropy has a more subtle meaning, which sometimes seems mysterious. The symbol, S, can also be subscripted and superscripted as can enthalpy. The absolute value of entropy can be taken for a material as

$$S^\circ_T = \int_0^T \frac{C_p}{T} dT \quad (3)$$

if no phase changes occur. The entropy change at a phase transformation (e.g., melting) is $\Delta H/T$ at constant pressure.

For any process, the change in Gibbs free energy, G, is given by

$$\Delta G = \Delta H - T\Delta S. \quad (4)$$

Like enthalpy and entropy, the Gibbs free energy can be subscripted by temperature and superscripted for "standard conditions."

The gas constant, R, has been used in this document to obviate the need for choosing appropriate units for entropy, heat capacity, and Gibbs free energy. Each of these quantities has a unit of quantity (e.g., mole), a unit of temperature (e.g., kelvin), and a unit of heat (e.g., calorie). Since the gas constant has the same units, division of C_p or

S by R makes the quantity dimensionless. If H or G is divided by R, the resulting unit is temperature--and, in this report, is always kelvin.

In some cases in this report values of quantities are given in the units chosen by other authors. Most of these will be self evident as, for example, joules-mole⁻¹. The conversion via the latest internationally accepted standards will also be self evident. An exception may be the entropy unit, abbreviated e.u.. The units of e.u. are customarily calories-mole⁻¹ -degree⁻¹.

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