THE UOBr_2 DISPROPORTIONATION EQUILIBRIUM

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UOBr_2 has been prepared by reaction of UBr_4 gas on UO_2 solid in the neighborhood of 500°C (1). The equilibrium

is shifted to the left under conditions used in the preparation which employ UBr_4 pressures equal to the vapor pressure of the solid at the reaction temperatures. In high vacuum, however, disproportionation of the oxybromide occurs at appreciable rates at temperatures above 475°C . The equilibrium pressure of UBr_4 above the solid has been determined at various temperatures using the effusion method, following a procedure similar to that employed in the study of the analogous chloride system (1). *finish*

Experimental:

The equilibrium pressures of UBr_4 were established at various temperatures by the effusion method. A diagram of the apparatus is shown in Figure 1. The diameter of the orifice of the effusion capsule was determined with a measuring microscope and was found to be 0.843 mm, corresponding to an area of $5.582 \times 10^{-3} \text{ cm}^2$. Approximately one half of the volume of the capsule was filled with charge material. The UOBr_2 had been prepared previously (1), the sample having a composition corresponding to 94% UOBr_2 and 6% UO_2 .

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After the charge had been placed in the capsule, the top was screwed tightly into place and the bottle placed in the copper block shown in Figure I. The apparatus was assembled in the dry box, using a calrod heater to seal the ground glass joint with sealing wax. The stopcock was closed and the tube removed from the dry box and connected to the vacuum line and the apparatus completely outgassed. The temperature was raised to 500°C and the system maintained at high vacuum for twenty-four hours. The furnace was then cooled and the stopcock closed. The apparatus was then placed in the dry box and CO₂ admitted. The sealing wax joint was opened with the calrod heater and the capsule removed. A small steel ball bearing was placed over the orifice and the capsule and ball weighed. The assembly and disassembly procedure is repeated in this manner in each determination after the effusion has been allowed to take place for the length of time shown in Table I. All weighings were made with the effusion capsule filled with CO₂. From the weight loss observed, calculated as UBr₄, the Knudsen equation may be used to calculate the equilibrium pressure inside the capsule at each temperature. The theoretical aspects of the Knudsen equation

$$P_{\text{dynes/cm}^2} = \frac{G}{A t} \sqrt{\frac{2 \pi R T}{M}}$$

(where G = the weight of material sublimed; A, the area of the orifice; t = time in seconds; T, the absolute temperature; and M, the molecular weight of the sublimed material) have been reviewed in detail by Mueller⁽²⁾ and the expression found to apply with reliance in the pressure range below 10⁻² mm.

The temperature of the charge was determined using a chromel-alumel thermocouple in conjunction with a Rubicon semi-precision type thermocouple potentiometer. The temperature of the furnace was regulated with a Foxboro

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controller. With the arrangement shown in Figure I, the slight variation of the temperature of the furnace inherent in the regulation was not reflected in the temperature of the charge since the metal equalizing block is not in direct contact with the furnace. The temperature of the block remained very constant during the heating periods. The charge was brought to temperature and cooled after the run very quickly so that no appreciable correction was made for the heating and cooling periods.

Results:

The data in Table I were tabulated from experiments involving three different samples from the same preparation. The value at 478°C is felt to be the least reliable since the weight loss was very small for this run.

Table I

t°C	T°K	1/T	time(sec.)	weight loss	K _{mm} P _U Br ₄
478	751	1.332	2.754 x 10 ⁵	0.0450	5.93 x 10 ⁻⁴
504	777	1.287	1.710 x 10 ⁵	0.0703	1.49 x 10 ⁻³
514	787	1.270	1.566 x 10 ⁵	0.0917	2.14 x 10 ⁻³
520	793	1.261	8.640 x 10 ⁴	0.0705	2.99 x 10 ⁻³
525	798	1.253	1.512 x 10 ⁵	0.1515	3.67 x 10 ⁻³
541	814	1.229	7.020 x 10 ⁴	0.1219	6.44 x 10 ⁻³

Discussion of Results

The data given in Table I have been plotted as a function of 1/T as illustrated in Figure II. The slope calculated from the straight line drawn through the points gives a ΔH of 49.7 K cal/mol for the reaction.

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If we combine this information for reaction (1) with the heat of sublimation obtained from the vapor pressure data on $\text{UBr}_4(\text{s})$ (3) (this heat was determined in the same temperature range) we obtain the following:

Hence for the theoretical reaction (3), a heat of 6.0 K cal/mol may be obtained from experimental measurements at an average temperature of 773°K .

Using the heats of formation of the components of reaction (3) as determined by Barkelew⁽⁴⁾ at 273°K , the value of ΔH_{273} is found to be 12.4 K cal/mol. Hence ΔC_p for reaction (3) is calculated to be -12.8 cal/mol/deg.

Thus

$$\Delta H = \Delta H_0 - 12.8 T$$

and

$$\Delta H_0 = 15894 \text{ cal/mol}$$

therefore we have

$$\Delta H = 15894 - 12.8 T$$

Combining the equilibrium constants for reactions (1) and (2) to obtain experimental values for reaction (3) and using the ΔC_p value obtained above, the values in Table II were calculated.

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TABLE II

T	1/T	- R ln K ₃	$\Delta C_p \ln T$	$\Delta H_o/T$	I
751	1.332	15.108	-84.773	21.171	-90.836
777	1.287	15.244	-85.209	20.456	-90.421
787	1.270	15.286	-85.374	20.185	-90.273
793	1.261	14.996	-85.471	20.042	-90.517
798	1.253	14.939	-85.551	19.915	-90.527
814	1.229	14.871	-85.804	19.534	-90.467
				Mean	-90.507
				Excluding first value	-90.441

From these results, we may write

$$\Delta F = 15894 + 29.48 T \log T - 90.441 T$$

and using the expression

$$\Delta S = \Delta C_p (1 + \ln T) - I$$

we find that

$$\Delta S = 4.7 \quad (\text{reaction (3)}).$$

Using the standard entropies of $\text{UO}_2(\text{s})^{(5)}$ and of $\text{UBr}_4(\text{s})^{(6)}$, we calculate the entropy of $\text{UOBr}_2(\text{s})$ at 298.1°K to be 37.3 e.u.. This value for the entropy appears to be quite reasonable and about what one would expect in comparison with the value obtained for $\text{UOCl}_2(\text{s})^{(31.5)^{(6)}}$.

In consideration of the hydrogen reduction equilibrium data for $\text{UOBr}_2(\text{s})^{(6,7)}$, the heat capacities of $\text{UOBr}_2(\text{s})$ and $\text{UOBr}(\text{s})$ were estimated. If we use these estimates in conjunction with the present equilibrium data to calculate the entropy we obtain an answer in good agreement with that based on the experimental data alone. The calculation is demonstrated below.

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$$\text{UO}_2(\text{s}) \quad C_p = 18.45 + 2.431 \times 10^{-3} T - \frac{2.272 \times 10^5}{T^2}$$

$$\text{UBr}_4(\text{s}) \quad C_p = 32.00 + 8.18 \times 10^{-3} T$$

$$\text{UOBr}_2(\text{s}) - 2C_p = -56.18 - 16.08 \times 10^{-3} T$$

$$\Delta C_p = -5.73 - 5.47 \times 10^{-3} T - \frac{2.272 \times 10^5}{T^2}$$

Using this estimate for ΔC_p , an average value of -10.3 was calculated for the temperature range in which the equilibrium was studied. From the data calculated in Table III, a Σ plot was made and the value of ΔH_0 obtained as 14560 cal/mol. This yields values of I as tabulated in the following table.

TABLE III

T	1/T	- R ln K ₃	$-\Delta C_p \ln T$	$-\Sigma$	$\Delta H_0/T$	- I
751	1.332	15.108	68.209	53.101	19.394	72.495
777	1.287	15.244	68.560	53.316	18.768	72.084
787	1.270	15.268	68.693	53.425	18.491	71.916
793	1.261	14.996	68.771	53.775	18.360	72.135
798	1.253	14.939	68.835	53.896	18.244	72.140
814	1.229	14.871	69.039	54.168	17.894	72.062
					Mean	72.139
				Excluding first value		72.067

Hence we may write

$$\Delta F = 14560 + 23.72 T \log T - 72.067 T$$

and the value of ΔS from this expression is found to be 3.1 e.u. at 298.1°K. This gives a value of S_{298} for $\text{UOBr}_2(\text{s})$ of 38.1 e.u..

Comparison of these two entropy values indicates that the estimated heat capacity chosen for $\text{UOBr}_2(\text{s})$ is in agreement with the disproportionation equilibrium data. The value of the entropy is somewhat lower than that estimated earlier for UOBr_2 in the consideration of the hydrogen reduction equilibrium studies (6) (7). If we use the free energy equation which was derived for the reduction reaction

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from the experimental data and estimated heat capacity equations, we may recalculate the entropy of UOBr using the experimentally determined value for UOBr₂. For reaction (4)

$$\Delta H = \Delta H_0 - 15 T - 3.3 \times 10^{-3} T^2$$

$$\text{and } \Delta F = \Delta H_0 + 34.55 T \log T + 3.3 \times 10^{-3} T^2 - 126.78 T$$

$$\text{hence } \Delta S = -15.0 - 34.55 \log T - 6.6 \times 10^{-3} T + 126.78$$

$$= 24.3 \quad \text{at } 298^\circ\text{K.}$$

Therefore,

$$\Delta S = 24.3 = S_{\text{UOBr}} + S_{\text{HBr}} - S_{\frac{1}{2}\text{H}_2} - S_{\text{UOBr}_2}$$

$$S_{\text{UOBr}} + 47.48 - \frac{31.23}{2} = 38.1$$

and for UOBr(s)

$$S_{298^\circ\text{K}} = 30.5 \text{ cal/mol/deg}$$

SUMMARY

The equilibrium pressures of UBr₄ vapor over UO₂(s) have been established in the temperature range from 475°C to 540°C by effusion studies. In general the ratio of the pressure of UBr₄ over UO₂ to the vapor pressure of UBr₄ at the same temperature is approximately 5×10^{-4} . The heat of the disproportionation reaction is slightly above the heat of sublimation. The heat capacities assumed for UOBr₂(s) and UBr₄(s) in the consideration of thermodynamic data for other uranium compounds were found to be compatible with the results of this investigation and the heats of formation as determined at 0°C. The entropy of UOBr₂(s) was found to be 38.1 e.u. at 298°K. Using this value and the results from hydrogen reduction studies on UOBr₂, the entropy of UOBr(s) was recalculated to be 30.5 e.u. at 298°K. The heats of formation of these compounds have been reported previously.

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FIGURE 1 - Schematic Diagram (cross-section) of Apparatus Used in Studying the Disproportionation of UO_2

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FIGURE II

Equilibrium pressures of $\text{UBr}_4(\text{g})$ over $\text{UO}_2(\text{s})$

$\Delta H = 49.7 \text{ Kcal/mol}$

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