Dissociation Pressures of Uranium Hydride and Uranium Tritide

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The measured dissociation pressures of UH_3 over the temperature interval 300 to 420°C and of four UH_3 - UT_3 mixtures over the temperature interval 320 to 390°C are reported. The dissociation pressures of UH_3 are accurately represented by the equation

$$\log P_{\text{mm}} = \frac{-6270.1}{T} - 6.0146 \log T + 28.9235 \quad (1)$$

and are in satisfactory agreement with those reported by Spedding et al. [Nucleonics 4, 10 (1949)].

For the mixtures, an ionization chamber built into the apparatus was used to determine the T/H ratio in the gas; from this analysis, the composition of the solid phase was determined by difference. The logarithms of the partial pressures of H_2 and T_2 molecules, calculated from the data and the equilibrium constant for the reaction $\text{H}_2 + \text{T}_2 = 2\text{HT}$, are linear functions of the mole fractions of the respective components in the solid, at constant temperature. By extrapolating to mole fraction equal one, the dissociation pressures of pure UH_3 and pure UT_3 are obtained. The dissociation pressures for UH_3 so obtained are in good agreement with those calculated from equation (1); the dissociation pressures for UT_3 are represented by the equation

$$\log P_{\text{mm}} = \frac{-4471}{T} + 9.461 \quad (2)$$

The dissociation pressure is one atmosphere at 430°C for UH_3 and at 406°C for UT_3 . The heats of dissociation at these temperatures are 20.3 kcal./mole H_2 and 20.5 kcal./mole T_2 .

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INTRODUCTION

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The dissociation pressures of UH_3 and UD_3 have been previously reported.⁽¹⁾ A limited study has also been made of UH_3 - UD_3 mixtures.⁽²⁾ These investigations are inadequate to determine the relation between the mole fractions of hydrogen and deuterium in the solid and the dissociation pressures, since no analysis was made of the solid or gas phase. It was thought desirable to study this relation by measuring the dissociation pressures of UH_3 - UT_3 mixtures and analyzing the gas by means of an ionization chamber. At the same time the dissociation pressures of UT_3 were determined by an extrapolation. A more accurate determination of the dissociation pressures of UH_3 was also made.

APPARATUS

About 0.5 g. of pure uranium was placed in a specially designed quartz tube. The tube was constructed so that thermal diffusion effects were minimized and so that the volume of the heated zone was small and accurately known. An ionization chamber and a constant volume mercury manometer completed the system.

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1. Spedding, et al., Nucleonics 4, 10 (1949).
  2. Johnson, O., "Plutonium Project Report," CC-1063 (Nov., 1943).

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The quartz tube was surrounded by a well insulated resistance furnace. The temperature of the furnace was electronically controlled to $\pm 0.2^{\circ}\text{C}$. A platinum-platinum-10% rhodium thermocouple which was calibrated at the freezing points of the National Bureau of Standards lead, tin, and zinc was used to determine the temperature of the uranium.

The ionization chamber was constructed in the form of two concentric cylinders. The outer high voltage electrode was a Kovar tube $3/4$ inch in diameter and four inches long; an 0.080 in. tungsten wire served as a center collecting electrode. The entire chamber was enclosed in pyrex. Ionization currents are obtained by measuring the voltage drop across a standard 0.25 megohm resistor with a Leeds and Northrup type K potentiometer. The ionization chamber was calibrated against gas density determinations of tritium-hydrogen gas mixtures.

All pressures were read with a cathetometer to ± 0.1 mm. The volume of the quartz tube, the ionization chamber, the mercury manometer, and connecting tubing was determined to an accuracy of ± 0.1 cc.

A similar apparatus was used for the uranium-hydrogen system, except that the ionization chamber was omitted.

EXPERIMENTAL PROCEDURE

The system was degassed with the furnace at 450°C and then cooled to 250°C . An excess of pure H_2 was pumped into the system and allowed to react with the uranium metal. After all the uranium reacted to form UH_3 the furnace was cooled to room temperature and

the excess H_2 was pumped out. The UH_3 was decomposed at $420^\circ C$ and the volume of H_2 evolved was measured. From this determination the mass of uranium was calculated, and an amount of gas was taken for dissociation pressure runs such that 20 to 80% of the uranium reacted to form hydride at equilibrium.

Tritium-hydrogen gas mixtures were purified prior to use by passing the gas through a palladium thimble at $400^\circ C$. The gas was then analyzed for T/H ratio with the ionization chamber.

A measured volume of gas was then pumped into the system and allowed to react with the uranium. The furnace temperature was then raised to the desired value and the pressure and ionization current were followed with time. The pressure reached 95% of the equilibrium value in the first few hours but took ten to fourteen days to reach equilibrium. A similar situation exists when equilibrium is approached from the formation side, except that the approach to equilibrium is slower. After the pressure and ionization currents remained constant for twenty-four hours, equilibrium was considered to be established. The procedure for determination of the dissociation pressures of UH_3 was the same except that no isotopic analyses were necessary.

RESULTS AND CALCULATIONS

Besides pure H_2 , four different tritium-hydrogen starting mixtures were used; they ranged from 19 to 95 atom percent tritium. The dissociation pressures for UH_3 are summarized in Table I and for UH_3 - UT_3 mixtures in Table II.

Table I

Observed and Calculated Dissociation Pressures of UH_3

T ($^{\circ}\text{K}$)	Observed Pressure (mm Hg)	Calculated Pressure (mm Hg)
573.2	24.9	24.8
594.3	48.4	49.6
612.9	85.0	84.8
633.2	148.1	148.3
653.3	247.7	247.8
673.2	398.2	397.6
693.4	621.3	621.6

Table II
Dissociation Pressures of $\text{UH}_3\text{-UT}_3$ Mixtures

T (°K)	Dissociation Pressure (mm Hg)	$N_T(\text{gas})$	$N_T(\text{solid})$	Partial Pressure T_2 (mm Hg)	Partial Pressure H_2 (mm Hg)
592.2	54.2	0.234	0.183	3.3	32.1
	54.5	0.412	0.332	9.8	19.3
	60.5	0.707	0.614	30.6	5.6
	78.0	0.977	0.955	74.6	0.2
623.1	125.8	0.222	0.170	6.7	76.6
	125.8	0.398	0.317	21.0	46.7
	152.0	0.699	0.604	75.2	14.7
	183.3	0.978	0.946	175.2	0
648.2	240.0	0.228	0.173	13.4	144.0
	241.7	0.370	0.299	34.6	97.4
	293.6	0.688	0.586	140.6	30.2
	337.3	0.946	0.911	301.9	1.0
663.5	345.0	0.219	0.160	17.6	211.5
	346.0	0.367	0.285	48.8	140.8
	419.1	0.669	0.574	189.9	48.2
	499.6	0.939	0.903	440.6	2.0

The last column in Table I gives pressures calculated from the equation

$$\log P_{\text{mm}} = - \frac{6270.1}{T} - 6.0146 \log T + 28.9235 \quad (1)$$

which are in satisfactory agreement with those previously reported. At 430°C the dissociation pressure of UH_3 is one atmosphere and the heat of dissociation is calculated to be 20.3 kcal/mole H_2 .

In Table II, $N_T(\text{gas})$ is the mole fraction of tritium in the gas phase as determined by ionization chamber analysis. $N_T(\text{solid})$ is the ~~mole~~ ^{atom} fraction of tritium in the solid; this was determined by difference in a mass balance calculation. The partial pressures of T_2 and H_2 molecules respectively were calculated from the isotopic gas analysis and the equilibrium constant⁽³⁾ for the reaction

Using the data in Table II, the logarithms of the partial pressure of T_2 plotted against the logarithms of the mole fraction of tritium in the solid at constant temperature resulted in straight lines with an average slope of 1.9. Similar plots for hydrogen resulted in straight lines with an average slope of 2.2. By extrapolating to mole fraction equal one, the dissociation pressures of pure UT_3 or UH_3 were obtained. Table III gives the extrapolated values together with the dissociation pressure of pure UH_3 as calculated from equation (1).

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3. Jones, W. M., J. Chem. Phys. 17, 1062 (1949).

Table III

Dissociation Pressures of UT_3 and UH_3 by Extrapolation

T (°K)	P_{T_2} (Extrapolated)	P_{H_2} (Extrapolated)	P_{H_2} (Equation (1))
592.2	81.5	49.0	46.0
623.1	196	115	113
648.2	359	220	219
663.5	535	316	317

It can be seen that the extrapolated values for UH_3 agree with those from equation (1) fairly well, although not as well as the directly measured ones.

The dissociation pressures for pure UT_3 as given in Table III are represented within experimental error by the equation

$$\log P_{\text{mm}} = - \frac{4471}{T} + 9.461. \quad (2)$$

UT_3 has a dissociation pressure of one atmosphere at 406°C and a calculated heat of dissociation at this temperature of 20.5 kcal/mole T_2 .

DISCUSSION

Both UH_3 and UD_3 are known to have the same structure with a slightly different lattice constant.⁽⁴⁾ The UH_3 - UT_3 mixture is believed to have the UH_3 structure with tritium and protium

4. Rundle, R. E., J. Am Chem. Soc. 69, 1719-23 (1947).

distributed randomly in the H positions in the lattice. If the solid mixture is assumed to be ideal, then

$$(P_{T_2})^{\frac{1}{2}} = K_1 a_T(\text{solid}) = K_2 N_T(\text{solid})$$

and

$$\log P_{T_2} = 2 \log N_T(\text{solid}) + \text{constant}$$

P_{T_2} is the partial pressure of T_2 molecules in the gas phase, K_1 and K_2 are constants, $a_T(\text{solid})$ is the activity of tritium in the solid, and $N_T(\text{solid})$ is the mole fraction of tritium in the solid.

It follows that a plot of $\log P_{T_2}$ versus $\log N_T(\text{solid})$ would be linear with a slope of two. The deviation of the experimental slopes from two may be explained by a systematic error of 2 to 3% in the isotopic analyses, although possibly it is due to deviations of the solid mixture from ideality.

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