tration increased. It was decided, therefore, to test Robinson and Brown's conclusions in relatively concentrated mixtures of HCl and $CoCl_2$.

The optical densities were measured by means of a Beckman DU spectrophotometer at 30° employing 1-cm. corex cells whose optical thickness had been decreased to 0.1 cm. by silica spacers. Because of the high optical densities involved, only a portion of the 4.84 *m* series of solutions could be studied. Following Robinson and Brown, the optical densities at wave lengths characteristic of the blue complex (λ *630, 660, 690* mμ) were assumed to be proportional to the activity of the complex. It was also assumed that the quantity of the complex corresponded to but a small fraction of the total $CoCl_2$ in solution. The latter assumption was supported by the constancy of the apparent extinction coefficients at wave lengths characteristic of the rose species (λ 480 mμ).

The results showed that the optical densities $(O.D.)_\lambda$ of the blue colored solutions were proportional to the activities of $CoCl_2$ except at the higher Cl/Co ratios where appreciable deviations of the apparent extinction coefficients from constancy at 480 mμ were observed. These results, therefore, provide evidence for the association reaction

$$Co^{++}(aq.) + 2Cl^-(aq.) \rightleftarrows CoCl_2(aq.)$$

rather than for the formation of higher chlorocomplexes. Table IV presents the values of the constant *k* defined by

$$k = a(CoCl_2)/(O.D.)_\lambda$$

TABLE IV

CONSTANTS FOR THE ASSOCIATION OF Co^{++} AND Cl^- IN 4.84 *m* HCl

$CoCl_2$, *m*	O.D. (λ = 630 mμ)	$k \times 10^{-2}$
0.5	1.95	1.38
0.6	2.82	1.49
0.7	4.03	1.66
0.8	5.37	1.63
0.9	7.08	1.86
1.0	9.33	1.68
1.1	*12.3*	*1.66*
1.2	15.1	1.54
1.3	19.1	1.51
1.4	21.9	1.56
1.5	24.7	1.66
1.6	28.5	1.75

Although both investigations indicate the presence of an undissociated complex, the results obtained here differ from those of Robinson and Brown, who found that the optical densities of the blue solutions were proportional not only to the assumed activities of $CoCl_2$ but also to the 4th power of the water activities. Although the experimental data of these authors do not support the mechanisms given by the equations on page 8 of their paper, their results can be accounted for on the basis of the reaction

$$Co^{++}(aq.) + 4H_2O + 2Cl^-(aq.) \longrightarrow Co(H_2O)_4Cl_2$$

It is possible that the cause for the differences in these two studies may arise from the differences in the systems under investigation or from the assumptions underlying the approximation to the $CoCl_2$ activities made by Robinson and Brown.

STILLWATER, OKLAHOMA

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Vaporization of TiN and ZrN[1]

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The vaporization of TiN and ZrN has been studied by the Knudsen effusion method between 1987–2241 and 2236–2466° K., respectively. Whereas TiN vaporizes to gaseous Ti and N_2, the heat of reaction being $\Delta H_0^0 = 191.20$ kcal., ZrN decomposes to solid Zr and N_2 with $\Delta H_0^0 = 79.53$ kcal./mole. From these data, the standard heat of formation for TiN is $\Delta H_{298}^0 = 79.4$ kcal./mole; and for ZrN, $\Delta H_{298}^0 = 80.43$ kcal./mole.

Introduction

No experimental data are available on the vaporization of TiN and ZrN. Kelley[2] calculated an equation for the free energy of formation of these two compounds by using the heats of formation obtained by Neumann, Kröger and Kunz[3] and estimated entropies.

In the present investigation the Knudsen effusion method was used to determine the vapor pressure above TiN and ZrN.

Materials.—The TiN was obtained from Metal Hydrides, Inc., Beverly, Mass. The composition, as given by the manufacturer, was Ti 77.5%, N 18.0%, corresponding to a Ti:N ratio of 1:0.794, impurities being mostly Ca, Mg, Si, 4.5%. During degassing, at 1750°, for 2.5 hr., a 500-mg. sample lost 25 mg., which corresponds approximately to the weight of the impurities present.

The ZrN was prepared by heating ZrH_2, obtained from Charles Hardy, Inc., N. Y., in a stream of nitrogen for 21 hr. at 1050°. From the weight gain, the ratio Zr:N was calculated to be 1:0.979. On degassing at 1500°, a 500-mg. sample lost 6 mg. No other purification was carried out on either material.

Apparatus and Experimental Procedure.—The same vacuum apparatus and identical Knudsen effusion cells made of tantalum were used as described previously.[4]

Experimental Results

Both nitrides could vaporize according to the following patterns: (1) undissociated, as TiN and ZrN, (2) dissociated, into gaseous metal and nitrogen or (3) dissociated, into solid metal and nitrogen.

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[1] This work was supported in part by the Office of Naval Research under contract with The Ohio State Univerity Research Foundation.

[2] K. K. Kelley, "Contribution to the Data on Theoretical Metallurgy, VIII," U. S. Bureau of Mines, Bull. No. 407 (1937).

[3] B. Neumann, C. Kröger and H. Kunz, *Z. anorg. allgem. Chem.*, **218**, 379 (1934).

[4] M. Hoch and H. L. Johnston, THIS JOURNAL, **76**, 4833 (1954).

TABLE I

PRESSURE ABOVE TiN

Temp., °K.	Effective time, sec.	Area of orifice, cm.^{2}	Wt. loss, g.	Total evaporation rate, g./cm.^{2}/sec. × 10^5	Evaporation rate Ti, g./cm.^{2}/sec. × 10^5	Evaporation rate N_2, g./cm.^{2}/sec. × 10^5	P_{Ti}, atm. × 10^6	P_{N_2}, atm. × 10^6	$-\log P_{Ti}$	$-\log p_{N_2}$	$-\log K_p$
1987	14400	0.02042	0.0044	1.510	1.168	0.342	1.697	0.650	5.770	6.187	8.864
2017	14400	.02042	.0058	1.972	1.526	.446	2.234	0.854	5.651	6.069	8.685
2050	14400	.02042	.0092	3.129	2.421	.708	3.573	1.366	5.447	5.865	8.379
2058	14400	.02042	.0099	3.360	2.600	.760	3.845	1.469	5.415	5.833	8.332
2155[a]	10800	.00837	.0144	15.963	12.351	3.612	18.685	7.146	4.729	5.146	7.302
2157[a]	7200	.00837	.0124	20.510	15.869	4.642	24.016	9.187	4.620	5.037	7.138
2212[a]	7200	.00837	.0200	33.254	25.728	7.525	39.435	15.081	4.404	4.822	6.816
2241[a]	7200	.00837	.0425	70.555	54.589	15.767	84.221	32.211	4.076	4.492	6.322

[a] A different effusion cell was used for these runs.

TABLE II

PRESSURE ABOVE ZrN

Temp., °K.	Effective time, sec.	Area of orifice, cm.^{2}	Wt. loss, g.	Total evaporation rate, g./cm.^{2}/sec. × 10^6	p_{Zr}, atm. × 10^6	Evaporation rate Zr, g./cm.^{2}/sec. × 10^5	Evaporation rate N_2, g./cm.^{2}/sec. × 10^5	p_{N_2}, atm. × 10^6	$-\log K_p = -{}^1/_2 \log p_{N_2}$
2236[a]	14400	0.02042	0.0016	0.534	0.080	0.072	0.462	0.915	3.019
2259	14400	.02042	.0038	1.299	.105	.094	1.205	2.397	2.810
2318[a]	14400	.02042	.0088	2.979	.236	.208	2.771	5.583	2.627
2333	14400	.02042	.0080	2.714	.286	.251	2.463	4.977	2.652
2344	14400	.02042	.0089	3.020	.327	.287	2.733	5.536	2.628
2451	14400	.02042	.0441	14.981	1.170	1.001	13.980	28.956	2.269
2466	14400	.02042	.0474	16.127	1.388	1.184	14.943	31.044	2.254

[a] A different effusion cell was used for these runs.

The material condensing on the collector plates in both cases was amorphous. Both nitrides are thermodynamically stable in the solid phase. If condensed from the gas, the material should be crystalline. This seems to exclude the possibility of undissociated vaporization. Much more material condensed on the collector plates when TiN was vaporized than when ZrN was investigated. Approximately the same weight loss was registered in both cases. Thus, ZrN loses more non-condensable material than TiN.

The measured rates of evaporation from TiN are about one-fourth as much as the rates of evaporation for Ti, as determined in this Laboratory.[5] The rates of evaporation from ZrN are ten times larger than the corresponding values for Zr.[6]

From the above mentioned facts, it follows that TiN vaporizes to gaseous Ti and N_2; ZrN decomposes to solid Zr and N_2. The two reactions occurring are

$$TiN(s) \longrightarrow Ti(g) + {}^1/_2N_2 \tag{1}$$

with the equilibrium constant

$$K_p = p_{Ti} \times p_{N_2}{}^{1/2} \tag{2}$$

and

$$ZrN(s) \longrightarrow Zr(s) + {}^1/_2N_2 \tag{3}$$

The equilibrium constant is expressed here by

$$K_p = p_{N_2}{}^{1/2} \tag{4}$$

The data obtained for TiN are presented in Table I. The measured rates of evaporation were divided according to the ratio of the atomic weights (47.90: 14.01), and the partial pressure of Ti and N_2 calculated by the equation

$$p = m\sqrt{\frac{2\pi RT}{M}} \tag{5}$$

In this equation, p is the pressure in atmospheres, R is the molar gas constant, T is the absolute temperature, m is the rate of effusion in g./sq. cm./sec., and M is the molecular weight of the vapor (47.90 for titanium, 28.02 for nitrogen). The equilibrium constant was obtained by using equation 2.

The data obtained for ZrN are presented in Table II. The rate of evaporation of Zr was calculated from the vapor pressure equation.[6] The difference between the rates of evaporation of ZrN and Zr is the rate of evaporation of N_2. From this value the pressure and equilibrium constant were calculated according to equations 4 and 5.

Thermodynamic Calculations

For both reactions 1 and 2 the heat of reaction ΔH_0° was calculated by using the formula

$$\frac{\Delta H_0^\circ}{T} = -\frac{1}{2}\left(\frac{F^\circ - H_0^\circ}{T}\right)_{N_2} - \left(\frac{F^\circ - H_0^\circ}{T}\right)_{\text{Metal}} + \left(\frac{F^\circ - H_0^\circ}{T}\right)_{\text{Nitride}} - R\ln K_p \tag{6}$$

for each pressure given in Tables I and II. The free energy functions of nitrogen were taken from Johnston and Davis[7]; the values of Ti and TiN were taken from Skinner, Johnston and Beckett.[8] Free energy functions of Zr and ZrN were calcu-

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(5) J. W. Edwards, H. L. Johnston and W. E. Ditmars, THIS JOURNAL, **75**, 2467 (1953).

(6) G. B. Skinner, J. W. Edwards and H. L. Johnston, *ibid.*, **73**, 174 (1951).

(7) H. L. Johnston and C. O. Davis, *ibid.*, **56**, 271 (1934).

(8) G. B. Skinner, H. L. Johnston and C. W. Beckett, "Titanium and Its Compounds," Herrick L. Johnston Enterprises, Columbus, Ohio, 1954, pp. 95–119.

lated from the heat capacity data of Todd,[9] and Coughlin and King.[10] As the experimental data for TiN, Zr and ZrN go up only to 1700°K., the free energy functions had to be extrapolated. This introduces a constant error in our calculations.

The numerical values are given in Tables III and IV, the standard deviations being 1.28 kcal. for TiN and 0.53 kcal. for ZrN.

Equations for the equilibrium constants have been obtained by inserting the mean value of ΔH_0° into equation 6 and expanding the term $\Delta(F^0 - H_0^\circ/T)$ as a linear function of the temperature. By using equations 2 and 4, the partial pressures of Ti and N_2 above TiN, and the pressure of N_2 above ZrN are obtained. (The pressure of Zr over ZrN is the same as over pure Zr.)

TABLE III

HEAT OF REACTION FOR TiN

Temp., °K.	$-R \ln K_p = -\left(\frac{\Delta F^0}{T}\right)_{TiN}$	$-\left(\frac{F^0 - H_0^\circ}{T}\right)_{TiN}$	$-\left(\frac{F^0 - H_0^\circ}{T}\right)_{1/2N_2}$	$-\left(\frac{F^0 - H_0^\circ}{T}\right)_{Ti_{gas}}$	$\left(\frac{\Delta H^0}{T}\right)_{TiN}$	ΔH_0°, kcal./mole
1987	40.54	18.46	26.21	47 74	96.03	190.81
2017	39.73	18.62	26.27	47.82	95.18	191.98
2050	38.33	18.78	26.33	47.91	93.79	192.27
2058	38.11	18.82	26.35	47.93	93.57	192.57
2155	33.40	19.28	26.53	48.18	88.83	191.43
2157	32.65	19.29	26.53	48.19	88.08	189.99
2212	31.18	19.54	26.63	48.33	86.60	191.56
2241	28.91	19.66	26.68	48.40	84.33	188.98
					Av.	191.20 ± 0.96

TABLE IV

HEAT OF REACTION OF ZrN

Temp., °K.	$-R \ln K_p = -\left(\frac{\Delta F^0}{T}\right)_{ZrN}$	$-\left(\frac{F^0 - H_0^\circ}{T}\right)_{ZrN}$	$-\left(\frac{F^0 - H_0^\circ}{T}\right)_{1/2N_2}$	$-\left(\frac{F^0 - H_0^\circ}{T}\right)_{Zr_{solid}}$	$\left(\frac{\Delta H^0}{T}\right)_{ZrN}$	ΔH_0°, kcal./mole
2236	13.82	23.57	26.67	18.87	35.79	80.03
2259	12.86	23.69	26.71	18.95	34.83	78.68
2318	12.02	23.97	26.81	18.17	34.03	78.88
2333	12.13	24.04	26.84	19.23	34.16	79.70
2344	12.03	24.09	26.86	19.27	34.07	79.86
2451	10.38	24.56	27.04	19.64	32.50	79.66
2466	10.31	24.62	27.06	19.66	32.41	79.92
					Av.	79.53 ± 0.43

Thus

$$\text{TiN: } \log K_p = -\frac{41789}{T} - 0.60 \times 10^{-4}\,T + 12.245$$

$$\log p_{Ti} = -\frac{27859}{T} - 0.40 \times 10^{-4}\,T + 8.263$$

$$\log p_{N_2} = -\frac{27859}{T} - 0.40 \times 10^{-4}\,T + 7.963$$

and for

$$\text{ZrN: } \log K_p = -\frac{17408}{T} + 1.48 \times 10^{-4}\,T + 4.467$$

$$\log p_{N_2} = -\frac{34816}{T} + 2.96 \times 10^{-4}\,T + 8.934$$

If the heat of vaporization of Ti,[5] $\Delta H_0^\circ = 112.7$ is subtracted from the heat of reaction of equation 1, we obtain the heat of formation of TiN, ΔH_0° = 78.5 kcal./mole. For the heat of formation of ZrN, we measured ΔH_0° = 79.53 kcal./mole. From these data, we calculate the standard heat of formation at 25°: TiN ΔH_{298}^0 = 79.4 kcal./mole and for ZrN ΔH_{298}^0 = 80.53 kcal./mole.

Discussion of Results

Thermodynamic calculations were carried out with the assumption that in the solid there is a two-phase system: β-form of the metal and metal nitride, which are practically insoluble in each other.

The fact that ΔH_0° does not vary with the composition of the solid (though in the case of ZrN, the amount of nitride present decreased by a factor of 10) supports this assumption.

In the case of ZrO_2,[11] this assumption was proved to be correct, as the pressure above pure ZrO_2 and a mixture of ZrO_2 and β-Zr was equal.

For TiN, Neumann, Kröger and Kunz[3] measured $\Delta H_{25^\circ}^0$ = 80.3 kcal./mole; for ZrN, $\Delta H_{25^\circ}^0$ = 82.2 kcal. Humphrey[12] obtained $\Delta H_{25^\circ}^0$ = 80.47 kcal./mole for TiN.

The difference between our values and the calorimetric values for ZrN is estimated by calculating how much any one of the functions in Table IV has to be changed in order to obtain the same heat of formation as Neumann, Kröger and Kunz. On the average, $\Delta H_0^\circ/T$ has to be changed by 1.8%. To obtain this change, any one of the free energy functions in Table IV has to be changed by the following amounts: 3.3% for Zr, 1.2% for N_2 or 2.7% for ZrN. These are very small amounts, in view of the fact that the free energy functions for Zr and ZrN had to be extrapolated over a temperature range varying from 400–900°, showing an excellent agreement between our data and data obtained by combustion calorimetry.

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[9] S. S. Todd, THIS JOURNAL, **72**, 2914 (1950).

[10] J. P. Coughlin and E. G. King, *ibid.*, **72**, 2262 (1950).

[11] M. Hoch, M. Nakata and H. L. Johnston, *ibid.*, **76**, 2651 (1954).

[12] G. L. Humphrey, *ibid.*, **73**, 2261 (1951).