[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AT THE UNIVERSITY OF WASHINGTON]

A Study of the Chromous–Chromic Iodide Equilibrium

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The reaction between chromium and iodine has been studied by several investigators, particularly Hein and Wintner-Holder[2] who attempted measurement of equilibrium pressures of iodine above a mixture of chromium iodides. Their results do not permit quantitative determination of the thermodynamic characteristics of the system. Others[3] have predicted that chromium triiodide would be unstable at room temperature. Preparation of the pure substance in the anhydrous state has not been reported previously. We have prepared CrI_3 in a state of high purity and find it to be very stable at room temperature. The equilibrium

$$CrI_3(s) = CrI_2(s) + {}^1/_2I_2(g)$$

has been investigated in the temperature interval between 309 and 373° by means of the Knudsen effusion technique.[4] A rather long extrapolation of the data to 25° leads to the approximate value of 10^{-21} atmospheres for the equilibrium dissociation pressure of iodine above solid chromium triiodide.

Experimental Part

(a) **Reaction of Chromium with Iodine.**—Chromium metal (Eimer and Amend, 98%) was heated at 500° in one atmosphere pressure of iodine vapor in a Pyrex tube which had been previously evacuated and sealed. The product was removed and separated from unreacted chromium by sublimation in a quartz vessel at 700° under high vacuum. CrI_2 was obtained as the result of this sublimation. CrI_2 was heated at 500° in one atmosphere pressure of iodine to convert it into CrI_3. Two samples were prepared independently for the equilibrium study.

CrI_3 forms black, shiny crystals. Like $CrCl_3$, it does not dissolve readily in water, but its solution is facilitated by chromous ion. CrI_3 containing a small amount of CrI_2 dissolves with ease. Whereas the dihalide is extremely hygroscopic, CrI_3 is reasonably stable in the presence of oxygen and moisture. At temperatures in the vicinity of 200° it reacts rapidly with oxygen to liberate iodine. Its melting point is > 600°. Chromium diiodide is reddish-brown, forming needle-like crystals. It dissolves readily in water with considerable evolution of heat.

(b) **Analysis.**—Because of the difficulty in dissolving CrI_3 in water, iodine was determined by igniting the product in air and assuming the weight loss to be caused by replacement of iodine by oxygen to form Cr_2O_3. To determine chromium the residue was fused with sodium peroxide, the product dissolved in water and the excess peroxide removed by boiling. The chromate formed was reduced with potassium iodide and the liberated iodine titrated with standard thiosulfate solution. Results:

Theoretical for CrI_3		Sample 1		Sample 2	
		I, %	Cr, %	I, %	Cr, %
Cr, %	12.02		11.66		
I, %	87.98	85.38	11.50	87.79	12.01
		85.56	11.71	87.59	12.06
			11.71	87.57	
			12.09		
Average		85.47	11.73	87.65	12.03

The results for sample 2 are observed to be very good. The total per cent. of Cr and I in sample 1 is 97.2. The reason for this has not been ascertained, although the presence of a non-volatile impurity is indicated (possibly SiO_2). It is observed, however, that the Cr/I ratio for this sample is very close to the theoretical value for CrI_3.

(c) **Equilibrium Measurements.**—The pressure of iodine above solid CrI_3 and CrI_2 was determined by observing the rate of effusion from a calibrated knife-edge orifice in a Pyrex capsule. Temperatures were maintained constant by means of an electric furnace controlled with a thermoregulator. The iodine was collected in a trap and the quantity evolved determined by titrating a potassium iodide solution with standard thiosulfate. A stopcock with large diameter bore, lubricated with a fluorocarbon grease, was placed between the capsule and the trap to permit isolation of the sample while the iodine was removed from the trap after a given run. The external vacuum in the system was maintained between 10^{-5} and 10^{-6} mm. during the effusion process.

We have assumed that the iodine pressures in the capsule represent equilibrium values. The time of the effusion runs varied from two to seventy-two hours, depending on the temperature. The average size of the iodine samples collected was approximately 0.03 g. It can be seen from this value, that the rate of decomposition required to maintain the equilibrium pressure is very low.[4a]

Results and Discussion.—The experimental results are given in Table I. Whereas measurements were made varying the temperature randomly, the data are tabulated in the order of ascending temperature. The two sets of values are entirely independent, with separate samples and different orifice diameters used in each series of measurements. The average deviation of the experimental pressures from the least squares equation fitted to all the results is found to be approximately 5%.

The values of P (apparent) given in Table I correspond to those which were calculated from Knudsen's equation[5] using the molecular weight of iodine as 254.

$$P = \frac{gW_1}{t}\sqrt{\frac{RT_1}{M}} + \frac{gW_2}{t}\sqrt{\frac{RT_2}{M}}$$

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[1] Standard Oil of California Fellow for 1947-1948.

[2] Fr. Hein and I. Wintner-Holder, *Z. anorg. allgem. Chem.*, **202**, 81 (1931).

[3] L. L. Quill, "The Chemistry and Metallurgy of Miscellaneous Materials—Thermodynamics," National Nuclear Energy Series IV-19B, McGraw-Hill Book Co., Inc., 1950, Paper 6.

[4] M. Knudsen, *Ann. Physik*, **29**, 179 (1909).

[4a] NOTE ADDED IN PROOF: Recent experiments performed at higher temperatures (using a quartz vessel with a diaphragm gage) yield data which indicate that log P_{atm} obtained by the effusion method may be lower than the equilibrium values by approximately 8%. However, the thermodynamic quantities obtained by both methods agree with those reported in this paper well within the estimated experimental error which we have given here.

[5] M. Knudsen, *Ann. Physik*, **28**, 1002 (1909).

TABLE I

IODINE PRESSURES ABOVE CrI_3 AND CrI_2

The number of measurements made at a given temperature (±0.5°) is given in parentheses. In these cases, an average value of P is given; actual values are shown in Fig. 1.

	Sample 1 Orifice diameter, 0.977 mm.				Sample 2 Orifice diameter, 1.087 mm.		
t, °C.	P mm. × 10^3 (apparent)	P mm. × 10^3 (actual)	P mm. × 10^3 I_2	t, °C.	P mm. × 10^3 (apparent)	P mm. × 10^3 (actual)	P mm. × 10^3 I_2
309	0.324	0.341	0.266	309	0.293	0.309	0.237
316 (2)	.496	.520	.412	313.7 (3)	.495	.518	.415
322	.787	.813	.655	315.5 (3)	.544	.569	.457
329	1.22	1.27	1.04	317 (2)	.599	.627	.504
332	1.53	1.59	1.31	330.7 (3)	1.35	1.40	1.14
339	1.98	2.06	1.69	332	1.46	1.52	4.24
346	3.07	3.19	2.65	347.5 (3)	3.13	3.25	2.68
354	4.27	4.44	3.69	357.5 (2)	5.57	5.77	4.84
358	4.88	5.08	4.18	365	7.84	8.12	6.81
361	6.77	7.02	5.91	372 (2)	10.3	10.7	8.97
367	8.34	8.62	7.26	373 (3)	10.6	11.0	9.29
374	13.0	13.4	11.4				

where

g = weight of gas leaving the orifice
t = time required for effusion of gas
R = gas constant
M = molecular weight
T_1 = temperature within the capsule
T_2 = temperature representing mean value of path to trap
$W_1 = \frac{1}{A}\sqrt{2\pi}$ where A is the area of the orifice

$$W_2 = \frac{3}{8}\sqrt{2\pi}\int_0^L \frac{o_1}{A_1^2}\,dL$$

where

o_1 = tube circumference
L = tube length
A_1 = tube cross section

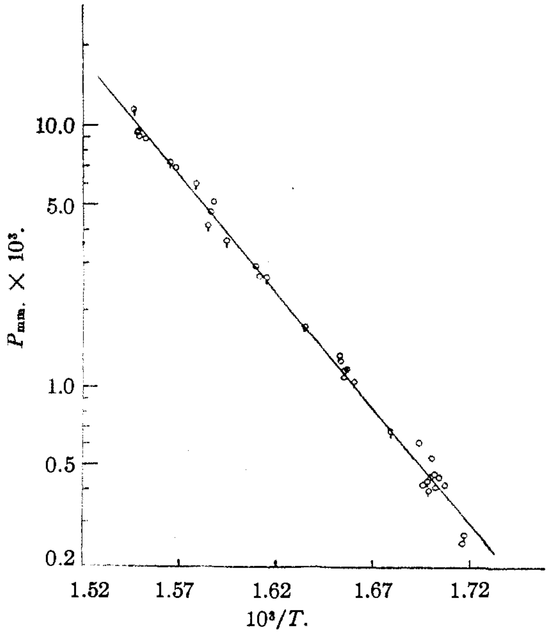

Fig. 1.—Equilibrium pressures of iodine above CrI_3 and CrI_2; ♀, Sample 1; O, Sample 2.

Since the apparatus was constructed of tubes of varying cross section, W_2 was taken as the sum of terms for the various segments and found to be 24 cm.$^{-2}$. W_1 = 335 cm.$^{-2}$ and 271 cm.$^{-2}$, respectively, for the two orifice diameters used. The effect of W_2 was verified by measuring the vapor pressure of iodine in the original apparatus and comparing the results with those obtained in a modified apparatus in which the iodine was collected on a cold finger trap placed immediately above the orifice (W_2 is essentially zero under these conditions). The absolute values for the vapor pressure of iodine which were measured in this calibration were in good agreement with those reported by Haber and Kerschbaum[6] and those of Naumann.[7] However, these data lie somewhat below those which are obtained by extrapolation of the transpiration data of Baxter, Hickey and Holmes.[8]

The effective molecular weight of iodine was calculated from the equation given by Lewis and Randall,[9] based on the data of Starck and Bodenstein,[10] for the equilibrium $I_2(g) = 2I(g)$. The effective molecular weight of iodine can be expressed by the relationship

$$M = 254\left[1 - \frac{(-K + \sqrt{K^2 + 4KP})}{4P}\right]$$

where $K = P_I^2/P_{I_2}$. It can be shown that

$$P_{(\text{actual})} = P_{(\text{apparent})}\left[0.414\left(\frac{254}{M}\right) + 0.586\right]$$

Since the degree of dissociation is a function of both temperature and pressure, a method of successive approximations was employed to determine the composition of the gas mixture and

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(6) F. Haber and F. Kerschbaum, *Z. Elektrochem.*, **20**, 296 (1914).

(7) Naumann, Dissertation, Berlin, 1907.

(8) G. Baxter, C. Hickey and W. Holmes, THIS JOURNAL, **29**, 127 (1907).

(9) G. N. Lewis and M. Randall, "Thermodynamics and Free Energies of Chemical Substances," McGraw-Hill Pub. Co., New York, N. Y., 1923.

(10) G. Starck and M. Bodenstein, *Z. Elektrochem.*, **16**, 961 (1910).

the actual total pressure corresponding to the experimental conditions. From this information the partial pressure of I_2 may be determined readily.

Whereas the corrections described above have a material influence on the absolute values of the pressures, it was observed that the experimental heat of reaction was not affected greatly. Figure 1 illustrates a plot of log P_{I_2} (mm.) against $1/T$ for the data from both samples as recorded in Table I. A least squares treatment led to the equation log Pmm. $= -8936/T + 11.832$.

In the absence of experimental heat capacities for the chromium iodides, a value of $\Delta C_p = -0.5$ for the process

$$CrI_3(s) = CrI_2(s) + {}^1/_2\, I_2(g)$$

was estimated by assuming classical behavior. This assumption seems reasonable in view of results found for the chloride system.[3,11] Following is a summary of the thermodynamic values calculated for the reaction as written above. The standard state for iodine has been taken as the gas at one atmosphere. The expressions for $\Delta H°$ and $\Delta F°$ are based on the least squares slope.

$$\Delta H° = 20{,}760 - 0.5\,T$$
$$\Delta F° = 20{,}760 + 1.15\,T\log T - 24.2\,T$$

Extrapolated values at 25°: $\Delta H° = 20.6$ kcal.; $\Delta F° = 14.4$ kcal.; $\Delta S° = 20.8$ e.u. The estimated uncertainty in ΔH indicated by the scatter of the data is ±1 kcal.

The heat of reaction may be compared with the value of 36.8 kcal. reported by Doerner[11] for the corresponding reaction for the chromium chlorides. The difference in entropy between CrI_3 and CrI_2 is calculated as 10.4 e.u. This is slightly lower than predicted from Latimer's rule,[12] but is much larger than found in the chloride system.

Bichowsky and Rossini[13] report a value of -63.7 kcal. for the heat of formation of CrI_2 (solid iodine as the standard state) based on the heat of solution measured by Recoura.[14] With our results this leads to a value of -76.8 kcal. for the heat of formation of solid CrI_3, or -99.2 kcal. using iodine gas as the standard state. This is a much larger negative value than one would expect by comparison with results for the chromium chlorides,[11] which supports the statement by Brewer, *et al.*,[3] to the effect that the heat of formation reported in Bichowsky and Rossini for CrI_2 appears to be too large.

A material balance record was kept for Sample 2 and the decomposition continued until the supply of CrI_3 was almost completely exhausted. In view of the consistency of the data throughout the run, it does not appear that this system is complicated by the formation of solid solutions or by formation of intermediate complexes between CrI_2 and CrI_3. The CrI_3 used in the measurements was initially in a macrocrystalline state. It is assumed that the CrI_2 formed as a result of the decomposition is in a finely divided state. Macrocrystalline size could not reasonably be achieved by sublimation since a temperature of the order of 700° is required to sublime CrI_2 at an appreciable rate in high vacuum. Similarly, CrI_3 is not appreciably volatile at these temperatures.

Summary

CrI_3 has been prepared in a high state of purity. Its physical appearance and chemical characteristics are discussed briefly.

The equilibrium $CrI_3(s) = CrI_2(s) + {}^1/_2I_2(g)$ has been investigated in the temperature interval between 309 and 373°, using the Knudsen effusion technique. The results may be summarized by the equation

$$\Delta F° = 20{,}760 + 1.15\,T\log T - 24.2\,T$$

in which ΔC_p has been estimated as -0.5. Iodine gas at one atmosphere has been taken as the standard state.

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[11] H. A. Doerner, Bureau of Mines Bulletin 577, U. S. Govt. Ptg. Office, 1937.

[12] W. M. Latimer, THIS JOURNAL, **43**, 331 (1921).

[13] F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

[14] Recoura, *Compt. rend.*, **110**, 1029 (1889).