

cient do not differ much from those calculated by the method used here. If their slope were exactly  $1/2$  throughout the entire range, then the curves of our figures would have been horizontal lines; however, because the curves are not horizontal it is a curious coincidence, when the experimental points in certain concentration ranges were used, that the  $\log j$  against  $\log m$  curves were found to give approximately straight lines with slopes other than  $1/2$ , and that the values of the activity coefficients so calculated were not seriously in error.

### Summary

1. The freezing-point apparatus of Randall and Vanselow has been improved. Measurements of the freezing points of dilute aqueous solutions of barium nitrate, sodium sulfate and sulfuric acid have been made.

2. The activity coefficients of these electrolytes have been calculated from the above measurements.

3. From the form of the  $j/m^{1/2}$  plots we conclude that sodium sulfate is a typical strong electrolyte, that barium nitrate is very slightly weak, and that sulfuric acid must be considered as only a moderately strong electrolyte.

BERKELEY, CALIFORNIA

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]  
**THE THERMAL DISSOCIATION OF IODINE AND BROMINE**

BY THOMAS DEVRIES<sup>1</sup> WITH WORTH H. RODEBUSH

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Starck and Bodenstein<sup>2</sup> determined the constant for the reaction  $I_2 \rightarrow 2I$  by measuring the pressure produced by a known amount of iodine sealed in a quartz bulb of known capacity in the presence of an inert gas. They worked in the temperature range 800–1200° and summarized their results by an equation for  $\log K_p$ . Braune and Ramstetter<sup>3</sup> repeated their work with somewhat different results.

The dissociation of bromine has been determined by the same method by Perman and Atkinson,<sup>4</sup> and Bodenstein and Cramer.<sup>5</sup>

Lewis and Randall<sup>6</sup> have commented on the fact that the results of Starck and Bodenstein are not in agreement with the values required by

<sup>1</sup> This communication is an abstract of a thesis submitted by Thomas DeVries in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

<sup>2</sup> Starck and Bodenstein, *Z. Elektrochem.*, **16**, 961 (1910).

<sup>3</sup> Braune and Ramstetter, *Z. physik. Chem.*, **102**, 480 (1922).

<sup>4</sup> Perman and Atkinson, *ibid.*, **33**, 215 (1900).

<sup>5</sup> Bodenstein and Cramer, *Z. Elektrochem.*, **22**, 327 (1916).

<sup>6</sup> Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p.523.

the Sackur-Tetrode relation for the entropy of monatomic gases. Thus, the entropy of monatomic iodine at 298°K. and 1 atmosphere as calculated from the data of Starck and Bodenstein is 42.6, while the predicted value is 40.4. A still greater discrepancy results if the data of Braune and Ramstetter are used and similar discrepancies are found when the entropy of monatomic bromine is calculated. The data on bromine are probably not very accurate because of the high temperatures involved, but results of Starck and Bodenstein on iodine are beautifully self-consistent and their method appears free from objection except for the possible errors in assuming the perfect gas law for the substances involved. However, it has been shown that an element whose atoms possess a magnetic moment in the vapor state, may be expected to have an entropy higher than the value predicted by the Tetrode equation. This effect has apparently been confirmed in the case of sodium and potassium. It seemed desirable, therefore, to develop an alternative method for the measurement of the dissociation of the halogens with the hope of establishing more certainly the values of the thermal quantities involved.

The method developed was an adaptation of the method of Knudsen<sup>7</sup> for the determination of vapor pressure by the measurement of the rate of diffusion through an orifice. At low pressures the amount of gas diffusing through a small opening with thin edges is given accurately by the expression

$$W = pat \sqrt{M/2\pi RT} \quad (1)$$

where  $W$  is the weight in grams,  $p$  the pressure in dynes,  $a$  the area of the opening in centimeters,  $t$  the time in seconds,  $M$  the molecular weight of the gas,  $R = 8.31 \times 10^7$  and  $T$  is the absolute temperature.

It remains to modify this expression for the case of a partially dissociated gas. Let  $100\alpha$  be the percentage dissociation of a diatomic gas under a total pressure  $p$ . The partial pressure of the undissociated molecules will be  $[(1-\alpha)/(1+\alpha)]p$  and the partial pressure of the atoms  $[(2\alpha)/(1+\alpha)]p$ . Equation 1 then becomes

$$W = pat \frac{1}{\sqrt{2\pi RT}} \left( \frac{1-\alpha}{1+\alpha} \sqrt{M} + \frac{2\alpha}{1+\alpha} \sqrt{\frac{M}{2}} \right) \quad (2)$$

while at a lower temperature  $T$  where no dissociation occurs, Equation 1 is still valid. If we designate by  $\bar{w}$  the weight of iodine diffusing per hour at any temperature and divide Equation 2 by Equation 1 we have for the same orifice

$$\bar{w} \sqrt{T} p_0 / \bar{w}_0 \sqrt{T_0} p = (1 + 0.414\alpha)/(1 + \alpha) \quad (3)$$

Here the subscript zero is used to designate the quantities measured at room temperatures.

<sup>7</sup> Knudsen, *Ann. Physik*, **29**, 179 (1909). Egerton, *Phil. Mag.*, **33**, 33 (1917); *Proc. Roy. Soc.*, **103A**, 469 (1923). Rodebush and DeVries, *THIS JOURNAL*, **47**, 2488 (1925).

The percentage of dissociation is thus seen to depend upon the ratio of the term  $\bar{w} \sqrt{T}/p$  at the temperature in question to the same product at a temperature low enough so that the dissociation is negligible. If no dissociation takes place, it is seen from Equation 1 that the term  $\bar{w} \sqrt{T}/p$  should be independent of the temperature. The ratio of  $\bar{w} \sqrt{T}/p$  at high temperatures where dissociation is complete ( $\alpha = 1$ ) to the same quantity at temperatures low enough for no dissociation, should have the value 0.7071. If we solve Equation 3 for  $\alpha$  we obtain

$$\alpha = \frac{1 - \bar{w} \sqrt{T} p_0 / \bar{w}_0 \sqrt{T_0} p}{(\bar{w} \sqrt{T} p_0 / \bar{w}_0 \sqrt{T_0} p) - 0.414} \quad (4)$$

The most serious difficulty in the application of Equation 4 is the determination of the ratio  $p/p_0$ . In our apparatus the vapor was supplied by a considerable amount of solid material which was kept at constant temperature. The cold part of the apparatus was thus filled with vapor at a pressure equal to the vapor pressure of the solid at the temperature of the bath, and the pressure at the orifice when the latter is at 25° ( $p_0$  in Equation 4) is not sensibly different. However, when the orifice is several hundred degrees hotter than the bath, the pressure at the orifice can no longer be assumed to be the same as in the cold part of the apparatus on account of thermal transpiration. The theory of thermal transpiration has been discussed by Knudsen and others<sup>8</sup> and an equation developed which has been verified for certain limiting conditions but which is inapplicable under the conditions of our work. It was necessary to determine the ratio  $p/p_0$  experimentally. This was done by measuring the rates of diffusion of the vapor at various temperatures low enough so that no appreciable dissociation takes place, and again at temperatures so high that the dissociation is practically complete. By reference to Equation 1-4 it will be seen that the ratio  $p/p_0$  is given for the one case by the equation

$$p/p_0 = \bar{w} \sqrt{T} / \bar{w}_0 \sqrt{T_0} \quad (5)$$

and for the other case by the equation

$$p/p_0 = 1.414 w \sqrt{T} / \bar{w}_0 \sqrt{T_0} \quad (5a)$$

### Experimental Part

**Iodine.**—The apparatus consisted (see Fig. 1) essentially of a quartz tube T, 66 cm. long and 2.4 cm. in diameter, with a small opening O in a diaphragm, 20 cm. from one end. The opening had an approximate diameter of 0.7 mm. This tube was externally heated by a Hoskins tube furnace, 33 cm. long. The tube was sealed with de Khotinsky cement A to the iodine reservoir I<sub>2</sub> at one end and the vacuum line and liquid-air cooled receiver R at the other end.

The iodine reservoir consisted of a 300cc. Erlenmeyer flask to give a

<sup>8</sup> Knudsen, *Ann. Physik*, **21**, 205, 633 (1910); **33**, 1435 (1910). West, *Proc. Phys. Soc.*, **31**, 278 (1919).

large evaporating surface. The iodine was also fused in the flask for good thermal contact. The iodine, a Mallinckrodt Reagent quality, was re-sublimed once from the same grade of potassium iodide and kept in a desiccator over concd. sulfuric acid for several days. The iodine was kept at  $0^{\circ}$  in a vacuum for about a day after the iodine had been melted in the flask. The vapor pressure decreased during this time, very likely due to a "digesting" of the smaller crystals onto the larger ones. After about ten hours in a vacuum, the vapor pressure remained constant at 0.030 mm.

It was also necessary to keep an intimate ice water mixture around the flask containing the iodine. A few hundredths of a degree variation would change the vapor pressure sufficiently to make a determination worthless. Finally, the apparatus was built so that the radiation from the furnace could not strike the iodine surface and increase the vapor pressure. The iodine reservoir was also connected through a stopcock S to the vacuum

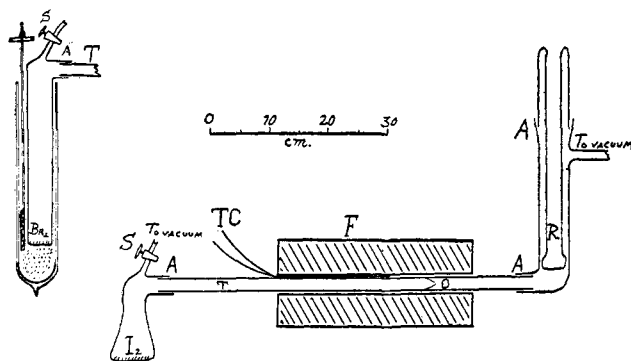


Fig. 1.—Apparatus.

line in order to obtain better evacuation between determinations. The stopcock is, of course, closed during a determination.

The temperature of the furnace was measured at its center by means of a platinum-platinrhodium thermocouple which was frequently calibrated against steam, boiling sulfur and the melting point of potassium chloride ( $770.3^{\circ}$ ). The microvoltages were read with a White potentiometer, reading to one microvolt. The furnace temperature was hand-regulated and it was comparatively easy to keep the temperature constant to  $\pm 1^{\circ}$  with no larger variation than  $2^{\circ}$  at short intervals.

The iodine was collected on a glass surface R, cooled by means of liquid air. No appreciable amount of iodine escaped since, even after a two-hour determination, no iodine was visible more than a few centimeters from the end, whereas two seconds was sufficient time to give a visible deposit on the bottom of R. At the end of a determination air was admitted into the apparatus to stop the diffusion, the receiver was disconnected at the joint and while still cold with liquid air, the iodine receiver was immersed in

warm (40°) potassium iodide solution (about 5%). The iodine was then titrated with 0.01 *N* sodium thiosulfate solution from weight burets with starch as an indicator. The 0.01 *N* solution was prepared fresh each week from a 0.1 *N* stock solution, kept in an opaque bottle and which had been prepared nine months before from water free from carbon dioxide. On several occasions the 0.1 *N* solution was titrated against a standard iodine solution but no changes greater than 0.2% were ever noticed. The iodine solution was standardized against sodium thiosulfate crystals at the same time. It was not necessary to know the absolute standardization of the thiosulfate since the final calculation depends only on a ratio of amounts used. However, it was used for calculating the vapor pressure of the iodine in a different apparatus.

The vacuum was produced by a mercury-vapor pump and measured with a McLeod gage. The pump was separated from the apparatus by a liquid-air trap.

The procedure in beginning a run was as follows. The furnace was brought to constant temperature and a vacuum of  $10^{-5}$  mm. of mercury obtained in the upper part of the apparatus. The stopcock S was closed and liquid air poured into the receiver R. The time was recorded at the same instant. A run usually lasted from one to three hours. The run was stopped by admitting air to the apparatus.

**Bromine.**—The same quartz tube was used for bromine as for iodine. Instead of the Erlenmeyer flask, a tube 4 cm. in diameter and 30 cm. long was used to contain the bromine (Fig. 2) and was cooled in a thermostatic bath which will be described in greater detail below.

The bromine was prepared from recrystallized Kahlbaum grade potassium bromate and recrystallized Baker's Analyzed potassium bromide and Baker and Adams' sulfuric acid (c. p.). The calculated amounts of potassium bromide and dil. sulfuric acid were mixed together with a 10% excess of potassium bromate and the bromine was washed twice with distilled water in the reaction flask. It was distilled from this into water and then from concd. sulfuric acid into a dry, glass-stoppered Erlenmeyer flask. All-Pyrex apparatus was used.

For the thermostatic bath, a heavy mush was made of carbon dioxide snow and acetone which was stirred very rapidly (500–750 r.p.m.). Carbon dioxide gas is bubbled into this for about 20 minutes or until the mixture becomes rather limpid, and to a constant temperature of  $-79.10^\circ$ , which may fall to  $-79.2^\circ$  or even  $-79.3^\circ$  if the carbon dioxide has not been bubbled through long enough. If this is done, however, the temperature will remain constant at  $-79.10^\circ$  for two to four hours (for about 300 cc. of mixture), after which it will slide up to between  $-79.03^\circ$  and  $-78.96^\circ$  and remain constant at that temperature for some four hours longer. After the thermocouple registered  $-78.96^\circ$ , the temperature increased

rather rapidly (about  $0.4^\circ$  per hour). The copper-constantan thermocouple, used to measure these temperatures, was calibrated against the boiling points of water and naphthalene and the melting point of mercury ( $-38.88^\circ$ ). The temperatures may be in error by  $0.05^\circ$ .

After the bromine was frozen, it was necessary to keep it in a vacuum for a day before the vapor pressure was constant. A determination was started and ended in the same manner as for iodine. The bromine was condensed on the receiver R by cooling it with liquid air. It was dissolved in warm potassium iodide solution and the equivalent amount of iodine set free was titrated with  $0.01 N$  sodium thiosulfate solution. The furnace temperatures were read with the same thermocouple as for the iodine. For the very high temperatures the de Khotinsky seals were kept cool by blowing air against a piece of wet towel which covered them.

### Discussion of Results

The data for iodine are given in Table I. In Col. 4 is given the important quantity  $\bar{w} \sqrt{T}$ , where  $w$  is the weight of iodine diffused per hour and  $T$  the absolute temperature. The values for the ratio  $p/p_0$  are given in Col. 5.

TABLE I

DATA FOR IODINE				
Temp., °K.	Time, min.	Iodine diffused, g.	$\bar{w} \sqrt{T}$	$p/p_0$
No Dissociation				
298	120	0.03673	0.3170	1.00
300	90	.02755	.3180	1.00
300	90	.02749	.3174	1.00
341	90	.02570	.3164	0.997
468	90	.02161	.3115	.982
479	90	.02123	.3096	.975
588	90	.01903	.3077	.969
588	105	.02226	.3084	.971
Complete Dissociation				
1019	180	0.02222	0.2364	1.050
1125	150	.01787	.2397	1.068
1220	150	.01749	.2443	1.088
1328	150	.01698	.2475	1.102
Partial Dissociation				
732	90	0.01608	0.2900	1.002
732	150	.02680	.2900	1.002
794	120	.01926	.2709	1.012
794	120	.01926	.2709	1.012
823	120	.01810	.2595	1.017
848	75	.01084	.2525	1.021
873	120	.01662	.2455	1.025
898	120	.01615	.2419	1.030
898	90	.01211	.2420	1.030

} interpolated

In the range of partial dissociation these values are obtained by interpolation. Fortunately in the case of iodine  $p/p_0$  is so nearly a linear function of the temperature in this range that the interpolation can be made with considerable confidence.

The percentage dissociation,  $100\alpha$ , is calculated by Equation 4, the term  $\bar{w} \sqrt{T}/p$  being the value at the temperature in question and  $\bar{w}_0 \sqrt{T_0}/p_0$  the value at 298°K. By a series of runs with an orifice of measured area the vapor pressure of iodine at 0°C. was determined to be 0.030 mm. and the pressure at the orifice at 25°C. ( $p_0$ ) may be taken as the same figure without appreciable error. From the value for the dissociation constant,  $K_p$  is calculated by the relation  $4\alpha^2 p/(1-\alpha^2) = K_p$ . Here, as is customary in the calculation of equilibrium constants,  $p$  is expressed in atmospheres.

To illustrate the foregoing calculation, suppose the value of  $\alpha$  and  $\log K_p$  are to be calculated at 823°K. The value of  $\bar{w} \sqrt{T}$  is 0.2595 while the average value of  $\bar{w} \sqrt{T}$  at 298°K. is 0.3175. In order to calculate  $\alpha$  by Equation 4 it is necessary to know in addition  $p/p_0$ , the ratio of the pressure at the orifice at 823°K. to the pressure at 298°K. This is obtained by interpolation. For instance, at 1328°K. where  $\alpha$  may be assumed to be 100%, the value of  $\bar{w} \sqrt{T}$  is 0.2475. By Equation 5a,  $p/p_0 = 1.414 \times (0.2475/0.3175) = 1.102$ . Other determinations in the region of complete dissociation and between 298°K. and 588°K. indicate that  $p/p_0$  is a linear function of the temperature between 700°K. and 1328°K., having a value of 1.00 at or about 700°K. In this conclusion rather more weight was given to the determinations at high temperatures where the dissociation is complete because the values for  $p/p_0$  between 468° and 588°K. are believed to be affected by a slight dissociation which could not be estimated with accuracy. Interpolating at 794°K., we find  $p/p_0 = 1.017$ . We then have

$$\alpha = \frac{1 - (0.2595/0.3175 \times 1.017)}{(0.2595/0.3175 \times 1.017) - 0.414} = 0.504 \quad (6)$$

$K_p$  is calculated by Equation 6. Here again the pressure is  $0.03 \times (p/p_0)$  and must be expressed in atmospheres

$$K_p = \frac{(0.504)^2 \times 4 \times 0.03 \times 1.017/760}{1 - (0.504)^2} = 5.47 \times 10^{-5}$$

$$\log_{10} K_p = -4.262$$

In Table II are given the values of  $100\alpha$  and  $\log K_p$  for the dissociation as derived from the experimental data. Col. 4 of Table II gives the values of  $\log K_p$  calculated by the empirical relation<sup>9</sup>

$$\log_{10} K_{p(atm.)} = -6840/T + \log_{10} T + 1.121 \quad (7)$$

<sup>9</sup> The  $\log T$  term of Equation 7 arises from  $\Delta C_p$  for the dissociation, which is assumed to be 2 cal. per mole. Were accurate experimental data available it would be necessary to correct the apparent heat capacity for dissociation.

TABLE II

## IODINE

Temp., °K.	Dissociation, %	Log $K_p(\text{atm.})$ , obs.	Log $K_p$ , calcd.	Difference
732	17.8	-5.286	-5.360	-0.074
794	36.1	-4.625	-4.595	+ .030
823	50.4	-4.262	-4.275	- .013
848	60.5	-4.031	-4.017	+ .014
873	72.1	-3.756	-3.753	+ .003
898	80.0	-3.539	-3.543	- .004

The agreement of Equation 7 with the experimental data is seen to be good except at the lowest temperature, where the experimental errors are presumably largest.

From the data for dissociation we may readily calculate the heat of dissociation and the entropy of monatomic iodine at 298°K. and 1 atmosphere. The entropy of solid iodine ( $1/2\text{I}_2$ ) at 298°K. is 13.95. The vapor-pressure measurements of Baxter, Hickey and Holmes,<sup>10</sup> and Baxter and Grose<sup>11</sup> agree with our measurement at 273.1°K. and are fitted by the equation<sup>12</sup>

$$\log_{10} p_{\text{mm.}} = -3272.5/T + 10.4643 \quad (8)$$

The entropy of vaporization to one atmosphere and 298°K. is given by the thermodynamic equation  $\Delta S_v = \Delta H_v/T + R \log \ln p(\text{atm.})$ , and from Equation 8 is calculated to be 17.35 cal. per 0.5 mole. The entropy of dissociation to one atmosphere at 298°K. is obtained from the equation

$$\Delta S = (\Delta H - \Delta F)/T \quad (9)$$

The values of  $\Delta H$  and  $\Delta F$  are obtained from Equation 7,  $\Delta H$  being equal to  $RT^2 d \ln K/dT$  and  $\Delta F = -RT \ln K$ . On substituting these values in Equation 9 we obtain

$$\begin{aligned} \Delta S &= 4.575 \log_{10} T + 1.99 + 4.575 \times 1.121 \\ &= 18.4 \\ &= 9.25 \text{ per } 0.5 \text{ mole} \end{aligned} \quad (10)$$

This gives 40.5 as the entropy of monatomic iodine at 298°K. and 1 atmosphere. The value predicted by the Tetrode equation is 40.4. This extremely close agreement is probably fortuitous. If the iodine atom does not possess a magnetic moment then this agreement must be taken as an indication that our values for the percentage and heat of dissociation are correct. On the other hand, spectroscopic data indicate that the iodine atom should have a magnetic moment and a higher entropy in consequence. In that case, the results of Starck and Bodenstein may give a better agreement with the theory. The principal uncertainty in our calculation appears to be in the interpolation of the values of  $p/p_0$ . It is possible to

<sup>10</sup> Baxter, Hickey and Holmes, *THIS JOURNAL*, 29, 127 (1907).

<sup>11</sup> Baxter and Grose, *ibid.*, 37, 1061 (1915).

<sup>12</sup> The use of a simple linear vapor equation is entirely justifiable if no extrapolation is attempted.



choose these values so that our results approach those of Starck and Bodenstein, but this choice can only be justified by the assumption of considerable error in the determinations. We may infer that the true values for the entropy and heat of dissociation of iodine must lie somewhere between our results and those of Starck and Bodenstein. The heat of dissociation per mole of iodine vapor at 298°K. is calculated to be 31,600 cal. as compared with the value, 35,000 cal., of Starck and Bodenstein and 34,100 of Braune and Ramstetter.

### Bromine

The results on bromine are by no means as satisfactory as in the case of iodine. In the first place, as has been indicated, the bath of carbon dioxide snow and acetone could not be kept at exactly the same temperature for each run although it could generally be kept constant for the period of a run. Accordingly, it is necessary to include the temperature of the bath with the data for each run. This is done in Col. 5 of Table III, where the data on bromine are given. The temperature is indicated in microvolts, 2480 microvolts corresponding to  $-78.96^{\circ}\text{C}$ . It is estimated that a change in temperature of 1 microvolt would change the vapor pressure of bromine in this range by 0.4%. Accordingly, in Col. 6 the values of  $w\sqrt{T}$  are corrected to correspond to a temperature of  $-78.96^{\circ}$ . The vapor pressure of bromine at this temperature ( $p_0$ ) was found by the Knudsen method to be 0.032 mm.

Still greater difficulty was found in determining the ratio of  $p/p_0$  in the range of partial dissociation. The temperature of complete dissociation

TABLE III  
BROMINE

Temp., °K.	Time, min.	Bromine diffused, g.	$\bar{w}\sqrt{T}$	Bath temp. (microvolts)	$\bar{w}\sqrt{T}$ (corr.)	$p/p_0$
No Dissociation						
302	60	0.01523	0.2646	2483	0.2675	1.00
299	90	.02340	.2695	2482	.2720	
298	60	.01515	.2615	2486	.2680	
300	60	.01552	.2688	2481	.2698	
	120	.03112	.2695	2481	.2704	
	90	.02328	.2688	2483	.2720	
					Av. 0.2700	
823	90	.01404	.2688	2480	.2688	0.982
	90	.01385	.2648	2483	.2680	
	90	.01400	.2678	2482	.2695	
					Av. 0.2648	
Complete Dissociation						
1315	90	0.00962	0.2326	2479	0.2316	1.212
1381	90	.00925	.2293	2482	.2314	1.212
	90	.00935	.2318	2482	.2336	1.223

TABLE III (Concluded)

Temp., °K.	Time, min.	Bromine diffused, g.	$\bar{w} \sqrt{T}$	Bath temp. (microvolts)	$\bar{w} \sqrt{T}$ (corr.)	$p/p_0$
Partial Dissociation						
923	90	0.01335	0.2706	2480	0.2706	1.04
	90	.01320	.2672	2481	.2692	
	60	.00866	.2630	2484	.2674	
					Av. 0.2691	
1000	90	.01264	.2662	2481	.2670	1.08
	60	.00824	.2606	2485	.2658	
1051	90	.01212	.2618	2481	.2630	1.10
	90	.81246	.2695	2476	.2652	
	60	.00787	.2562	2484	.2603	
	60	.00804	.2608	2484	.2650	
					Av. 0.2634	
1130	90	.01090	.2442	2482	.2460	1.13
	90	.01112	.2490	2480	.2490	
	90	.01142	.2556	2476	.2514	
	60	.00739	.2480	2483	.2518	
					Av. 0.2495	
1169	90	0.01087	0.2470	2478	0.2458	1.15
1173	89	.01030	.2378	2482	.2398	
	90	.01052	.2400	2480	.2400	
	60	.00712	.2440	2480	.2440	
	90	.01050	.2400	2483	.2430	
					Av. 0.2425	

tion is so high and the range of partial dissociation so great that a linear interpolation from the rather meager data for  $p/p_0$  introduces uncertainties of several per cent. The results for  $w \sqrt{T}$  are sufficiently concordant but an error of 1% in the ratio  $p/p_0$  will in some cases introduce an error of several times that amount in the value for  $\alpha$ . It will be noted that while in the case of iodine the maximum value used for  $p/p_0$  was 1.03 so that the uncertainty is small, in the case of bromine  $p/p_0$  reaches the value 1.15 with corresponding chances for error.

TABLE IV  
BROMINE

Temp., °K.	Dissociation, %	Log $K_p$ (atm.), obs.	Log $K_p$ , calcd.	Difference
923	7.7	-5.983	-6.055	-0.072
1000	17.0	-5.267	-5.305	-.038
1051	23.9	-4.944	-4.868	+.076
1130	45.8	-4.296	-4.269	+.027
1173	59.3	-3.982	-3.977	+.005

In Table IV are given the values of  $\log K_p$  and the value calculated from a simple empirical equation

$$\log K_p = -9000/T + 3.695 \quad (11)$$

This equation fits the data fairly well. The value for the heat of dissociation is 41,200 cal. The entropy of  $\frac{1}{2}\text{Br}_2$  (liquid) at 298°K. is found by Latimer and Hoenshel<sup>14</sup> to be 18.4. Lewis and Randall<sup>15</sup> find the entropy of vaporization of  $\frac{1}{2}\text{Br}_2$  to be 11.3. From Equations 9 and 11 we calculate the entropy of dissociation to be 8.5. This gives as the entropy of monatomic bromine at 298°K. and 1 atmosphere 38.2. The Tetrode equation predicts 39.0. No significance can be attributed to the close agreement with the predicted value since we have neglected terms for  $\Delta C_p$  in our equation for  $\log K_p$ .

### Summary

A new method has been developed for the measurement of the thermal dissociation of diatomic gases.

Satisfactory values have been obtained for iodine, and the entropy of monatomic iodine appears to agree with the value predicted by the Tetrode equation.

Results have been obtained for bromine which, while not entirely satisfactory, are believed to be better than any previous data.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 121]

## AN X-RAY STUDY OF THE ALLOYS OF LEAD AND THALLIUM

BY EDWIN MCMILLAN AND LINUS PAULING<sup>1</sup>

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### Review of Previous Work

The system lead-thallium gives, on investigation by the methods of thermal analysis, an unusual type of phase diagram, whose interpretation has raised some interesting questions. Four significant reports of previous work on this system exist. Lewkonja<sup>2</sup> and Kurnakow and Puschin<sup>3</sup> investigated it by the method of thermal analysis, while Kurnakow and Zemczuzny<sup>4</sup> and Guertler and Schulze<sup>5</sup> used the method of electrical conductivity.

The phase diagram of the system is shown in Fig. 1. The upper part (above 300°) was taken from the work of Kurnakow and Puschin, and the lower part from that of Guertler and Schulze. Lewkonja deter-

<sup>14</sup> Latimer and Hoenshel, *THIS JOURNAL*, **48**, 19 (1926).

<sup>15</sup> Ref. 6, p. 513.

<sup>1</sup> National Research Fellow in Chemistry.

<sup>2</sup> Lewkonja, *Z. anorg. Chem.*, **52**, 452 (1907).

<sup>3</sup> Kurnakow and Puschin, *ibid.*, **52**, 430 (1907).

<sup>4</sup> Kurnakow and Zemczuzny, *ibid.*, **64**, 149 (1909).

<sup>5</sup> Guertler and Schulze, *Z. physik. Chem.*, **104**, 269 (1923).