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THE THERMODYNAMIC CONSTANTS OF IODINE MONOBROMIDE

BY JOHN McMORRIS AND DON M. YOST

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Introduction

The properties of the diatomic interhalogen compounds are, in general, intermediate between those of the elements from which they are formed, and it is therefore of interest to determine whether or not their thermodynamic constants are also intermediate between those of the elementary substances. Moreover, these compounds lend themselves readily to spectroscopic investigations, and it is desirable to have thermodynamic data to confirm the interpretations of such investigations. For these reasons the present research upon one of these compounds, iodine monobromide, was undertaken.

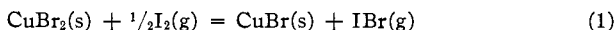
A determination of the extent to which combination takes place when two diatomic halogen molecules react to form two other diatomic molecules cannot, of course, be made by direct-pressure measurements; but if a substance can be found which is in equilibrium with one of the halogens and does not react with the other, then the extent of combination can be determined either by pressure measurements or by analysis of the vapor phase. In the present case cupric bromide was chosen for this purpose, since the careful work of Jackson¹ has shown that over the temperature range 100–200° convenient partial pressures of bromine vapor were to be expected without any complications arising from indeterminate solid phases. His measurements were made between 281 and 166°; and the log P –(1/ T) graph is a straight line. Jackson also found that the solid phases consist of cuprous bromide and cupric bromide. Furthermore, iodine will not replace the more electronegative bromine in either of these bromides.

Experimental Method

A number of experiments were carried out in which a weighed amount of pure iodine and a large excess of cupric bromide were placed in a 200-cc. Pyrex bulb equipped with a click gage. After carefully evacuating and baking out at about 150°, the bulb was sealed off and completely submerged in an oil thermostat. By means of a barometer the pressures were determined at various temperatures. Although this method gave results reproducible in order of magnitude when approaching equilibrium from either direction, the variation of the click constant with temperature

¹ Jackson, *J. Chem. Soc.*, 99, 1066 (1911).

and the possible presence of adsorbed gases or water rendered the method unreliable. Indeed, the presence of only one milligram of water at 127° gives rise to a pressure of 7 mm., which is unallowably large where the total pressure is less than 100 mm. These experiments did show, however, that the reaction



takes place reversibly and at a reasonable rate.

In the experiments whose results are here presented, the composition of the gaseous equilibrium mixture was determined by chemical analysis instead of by pressure measurements. The experiments were carried out in Pyrex bulbs of known volume, each being equipped with a narrow side-arm into which the vapors could be condensed by means of liquid air. Another side-arm was used for the introduction of the cupric bromide and iodine, the latter being contained in an easily breakable evacuated glass capsule. After charging, the bulbs were carefully evacuated and baked out until about one-third of the cupric bromide had been converted to cuprous bromide. The bulbs were sealed off, the tips of the iodine capsules were broken by moderate shaking, and the bulbs then immersed in an electrically heated oil thermostat whose temperature was maintained constant to within 0.1°.

After equilibrium had been reached a bulb was quickly removed from the bath, and the side-arm was plunged into liquid air and then sealed off from the bulb. This whole process required only twenty seconds, of which only a few seconds were necessary for the condensation of the vapor. Blank experiments carried out with cupric bromide alone yielded quantities of bromine which were in very good agreement with those corresponding to the pressures calculated by equation (4) given below. It follows therefore that the evolution of bromine from the cupric bromide is not rapid enough to introduce any serious errors.

That all of the vapors had condensed into the side-arm was shown by the fact that the bulb after again heating contained no iodine.

The side-arm containing the condensed vapor was broken under an acidified solution of potassium iodide, and the liberated iodine was titrated with standard thiosulfate, thus affording a measure of the total number of moles of iodine, bromine and iodine bromide, since they are all diatomic molecules.

The thermometer used was compared with one from the Bureau of Standards.

Preparation of the Materials

Iodine.—A high quality product, purchased on the market, was used. The quality was confirmed by analysis.

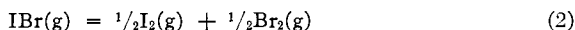
Cupric Bromide.—The best quality of material obtainable was dissolved in distilled water, filtered and then recrystallized and dried in a vacuum over phosphorus pentoxide

at room temperature.² Only cupric bromide which contained initially no acetic acid or acetates was used.

Standard Solutions.—The chemicals used were of the best quality obtainable. The thiosulfate was standardized by the method of Bray and Miller.³

Results of the Experiments

The reaction whose equilibrium constant is to be found is



The corresponding mass action expression is

$$\frac{(\text{I}_2)^{1/2} (\text{Br}_2)^{1/2}}{(\text{IBr})} = K \quad (3)$$

The partial pressure of the bromine at a given temperature is fixed, since it is in equilibrium with the cupric-cuprous bromide mixture. The value of this pressure was calculated from the following formula, which was constructed from Jackson's data

$$\log_{10} p_{\text{mm.}} = -\frac{4921.2}{T} + 11.6682 \quad (4)$$

In an equilibrium mixture the total iodine is known since a weighed amount is introduced initially. The titration of the material condensed out by the liquid air gives the total number of moles of halogen present. If, then, x is the total number of moles of halogen determined by titration, y the moles of iodine weighed out, and z the moles of free bromine calculated from its pressure and the volume of the bulb, then

$$2(x - y - z) = \text{moles of IBr} \quad (5)$$

$$2y - x + z = \text{moles of I}_2 \quad (6)$$

The equilibrium constants were calculated by substituting these derived quantities directly into mass-action equation (3) since the constant K is, in this case, independent of the units in which the quantities on the left-hand side of equation (3) are expressed. In Table I are presented the results of experiments made at three different temperatures.

That equilibrium was attained is shown by the fact that the equilibrium constants are independent of the time, as may be seen from the table and further, that first heating the bulbs to a higher temperature before making the measurements at a lower temperature did not affect their values. Also, in the click-gage experiments, the reaction showed itself to be readily reversible. It is to be noted that the partial pressure of bromine varied fifty-fold over the range of temperatures investigated.

The values for the constants at any given temperature are seen to agree very satisfactorily among themselves. They show a maximum deviation from the mean of 5%, and an average deviation of less than 2%.

² Mellor, "Comprehensive Treatise on Inorganic and Physical Chemistry," Longmans, Green and Co., London, Vol. III, p. 192.

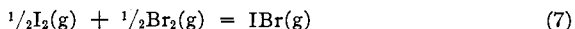
³ Bray and Miller, THIS JOURNAL, 46, 2204 (1924).

TABLE I
RESULTS OF THE EQUILIBRIUM MEASUREMENTS

Expt. no.....	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Temperature, °C.....	115	115	115	115	115	150.5	151.2	151.2	151.2	151.2	176	176	176	176
Volume of bulb, cc.....	221.5	115.5	115.5	423	430	116	119	116	114.5	117.5	116	118	118	111
Time in hours.....	16.5	6	16.5	24	24	6	6	7.5	5.5	6	2	6	5	12
Initial moles of I ₂ × 10 ⁴ ...	7.57	3.85	3.62	12.64	12.74	10.69	10.80	10.75	10.80	7.86	10.57	11.15	11.30	11.20
Total moles of halogen × 10 ⁴	9.10	4.60	4.33	15.25	15.37	13.98	14.34	14.19	14.24	10.71	15.99	16.90	17.07	16.90
Moles of free Br ₂ × 10 ⁶	0.891	0.465	0.465	1.70	1.73	4.94	5.29	5.16	5.09	5.23	21.27	21.64	21.64	20.35
Moles of free I ₂ × 10 ⁴	6.05	3.10	2.91	10.05	10.13	7.45	7.31	7.36	7.41	5.06	5.36	5.62	5.75	5.70
Moles of IBr × 10 ⁴	3.04	1.49	1.41	5.14	5.22	6.48	6.98	6.78	6.78	5.60	10.42	11.06	11.10	11.00
<i>K</i> × 10 ²	7.63	8.06	8.25	8.05	8.02	9.36	8.91	9.09	9.09	9.18	10.24	9.97	10.05	9.80
<i>K</i> × 10 ² , average.....	8.00 (115.0°)					9.20 (151.2°)					10.01 (176.0°)			
<i>K</i> × 10 ² calcd. by eq. (8).	8.00					9.14					10.00			

Thermodynamical Calculations

The free energy equation which represents the results to within the experimental error was found for the reaction



to be

$$\Delta F^\circ = -1270 - 1.7449 T \quad (8)$$

The assumption is made that ΔC_p is negligible, which for a reaction of this type is no doubt justifiable. The error in the heat content term has been estimated to be fifty calories, that is, $\Delta H = -1270 \pm 50$ cal. This value is in good agreement with the recently determined spectroscopic one, -1220 cal.¹¹

It is of interest to compare the values of the equilibrium constants found by Müller⁴ at 304.8° and by Bodenstein and Schmidt⁵ at 1222° with those calculated by Equation 8. Müller's value depends on his interpretation of the rate of the reaction between hydrogen and bromine in the presence of iodine whereas the value at the higher temperature was determined from vapor density measurements, as it is a region in which considerable dissociation of iodine into the monatomic gas occurs. At 304.8°, Equation 8 gives for K the value 0.137, for the reverse of reaction (7), while the average of Müller's results is 0.114, with a variation of $\pm 15\%$ from this value. The agreement is satisfactory and increases our confidence in his interpretation.

For 1222°, Equation 8 gives for K the value 0.271, as compared with Bodenstein and Schmidt's value of 0.305, which was the average from two experiments whose values differ by 8%. Taking into account the long extrapolation and the fact that deviations from the perfect gas laws at the higher temperatures may be considerable, the results are in very good accord.

The thermodynamic constants for iodine monobromide may be calculated from the present results by combining them with the following data. We use for the free energies and entropies of iodine and bromine vapors the values given by Giaque^{6a} and by Lewis and Randall.^{6b} For the heats of sublimation and of vaporization of one-half mole of solid iodine^{6a} and liquid bromine^{6b} we take 7438 cal. and 3795 cal., respectively; and we use Berthelot's⁷ value of 2470 cal. for the heat of formation of solid iodine monobromide from the elements in their standard states. The heats of dissociation of iodine and bromine⁸ into the monatomic gases were taken as

⁴ Müller, *Z. physik. Chem.*, **123**, 1 (1926).

⁵ Bodenstein and Schmidt, *ibid.*, **123**, 28 (1926).

⁶ (a) Giaque, *THIS JOURNAL*, **53**, 507 (1931); (b) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, pp. 464, 512, 522.

⁷ Cf. Mellor, "Comprehensive Treatise on Inorganic and Physical Chemistry," Longmans, Green and Co., London, 1922, Vol. II, p. 123.

⁸ R. Mecke, "Bandenspektren und ihre Bedeutung für die Chemie," Gebrüder Borntraeger, Berlin, 1929, p. 61; J. Franck, *Z. Electrochem.*, **36**, 581 (1930).

35,400 cal. and 45,200 cal., respectively. The entropy values used for monatomic iodine and bromine were 40.15 and 38.77 entropy units,^{6b} respectively.

Table II gives the so-calculated thermodynamic constants (expressed in calories) for one mole of the substance given in the first column. The standard states for the elements are indicated in each case.

TABLE II
THERMODYNAMIC CONSTANTS OF IODINE MONOBROMIDE AT 25°

Substance	Reference substances	Free energy	Heat content	Entropy	Heat of sublimation
IBr(g)	I ₂ (g), Br ₂ (g)	-1790	-1270	60.6	
IBr(g)	I ₂ (s), Br ₂ (l)	903	9,963		
IBr(s)	I ₂ (s), Br ₂ (l)	(-1830)	-2470	(31.8)	12433
I ₂ (g)	I(g)	-30,030	-35,400	62.29	
IBr(g)	I(g), Br(g)	-36,105	-41,570	60.6	
Br ₂ (g)	Br(g)	-38,600	-45,200	55.4	

The values in brackets for IBr(s) were calculated on the assumption that the vapor pressure of solid iodine monobromide is 7.6 mm. Its vapor pressure is certainly greater than that of iodine⁹ (0.305 mm.), and less than that of iodine monochloride¹⁰ (30 mm.), and doubtless lies closer to the former than to the latter value. If the estimate is in error by two-fold, an error of about 410 cal. will have been made in the free energy, and the value of the entropy will differ by 1.37 entropy units from the one given. The bracketed values are probably not in error by more than these amounts.

Discussion

The entropy of gaseous iodine monobromide (60.6) lies between the value 62.29 for iodine and the value 55.4 for bromine. However, it does not lie midway between them.

The free energy and heat content changes of the monobromide with respect to the monatomic elements in the gaseous form likewise lie between the corresponding values for iodine and bromine. These intermediate characteristics extend to the energy differences between the lowest vibrational levels of the molecules.¹¹ The entropy of another interhalogen compound, bromine monochloride gas, also lies between those of the gaseous diatomic elements of which it is composed as may be seen from an easy computation of the recent results of Jost.¹² In order to make a similar statement for the case of iodine monochloride it would be necessary to have further experimental data, although the results of Gibson and Ramsperger¹³ indicate that such is indeed the case. Whether or not one

⁹ Baxter, Hickey and Holmes, *THIS JOURNAL*, **29**, 127 (1907).

¹⁰ Recently determined by one of us [D. M. Y.].

¹¹ Badger and Yost, *Phys. Rev.*, **37**, 1548 (1931); also *cf.* Ref. 9, p. 24.

¹² Jost, *Z. physik. Chem.*, [A] **153**, 143 (1931).

¹³ Gibson and Ramsperger, *Phys. Rev.*, **30**, 598 (1927).

would be justified in generalizing the statement to cover all diatomic interhalogen compounds is not certain, but if one may judge by physical properties alone it would seem that even chlorine monofluoride¹⁴ might not prove an exception. The present results show, however, that the entropies of the compounds are not in general the average of those of the elements from which they are formed.¹⁵

Summary

The equilibrium between solid cupric and cuprous bromides and gaseous iodine and iodine monobromide has been measured. From the results, the free energy equation for the reaction $\frac{1}{2}\text{I}_2(\text{g}) + \frac{1}{2}\text{Br}_2(\text{g}) = \text{IBr}(\text{g})$ has been found to be $\Delta F^\circ = -1270 - 1.7449 T$. The increases in free energy, heat content and the entropy for this reaction at 25° were found to be $(\Delta F_{298}^\circ) - 1790$ cal., $(\Delta H_{298}) - 1270$ cal., and $(\Delta S_{298}) 1.75$ cal./degree, respectively. The degree of dissociation of the gaseous monobromide, at this temperature, into gaseous iodine and bromine has the value 8.9%.

With iodine and bromine in their standard states of solid and liquid, respectively, the free energy of formation of IBr(g) is $\Delta F_{298}^\circ = 903$ cal. The heat of sublimation of the solid monobromide has been calculated to be 12,545 cal.

The entropy of iodine monobromide gas is 60.6 and lies between that of gaseous iodine, 62.29, and bromine, 55.4, but is not the average of these. The increase in free energy and heat content at 25° attending the formation of the gaseous monobromide from monatomic iodine and bromine have values which lie between those for the formation of diatomic iodine and bromine from the monatomic elements. From the data for iodine and bromine monochlorides the same was found to be true; and it was suggested that this might be generally the case for diatomic interhalogen compounds in the vapor state.

PASADENA, CALIFORNIA

¹⁴ Ruff and Laass, *Z. anorg. allgem. Chem.*, **183**, 214 (1929).

¹⁵ Using recently published spectroscopic data [Curtis and Patkowski, *Nature*, **127**, 707 (1931); Gale and Monk, *Astrophys. J.*, **69**, 77 (1929)], the entropies of gaseous iodine monochloride and fluorine were calculated. These values, together with those already known or cited above, for the gases at 25° and one atmosphere, are: I₂, 62.29; IBr, 60.6; ICl, 59.2; Br₂, 55.4; BrCl, 54.1; Cl₂, 53.3; ClF, ?; F₂, 48.0. The order is that suggested above. Some of these values, but probably not the order, are subject to revision.