[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 325]

The Free Energy of Formation of Iodine Monobromide in Carbon Tetrachloride Solution

BY DON M. YOST, THOMAS F. ANDERSON AND FOLKE SKOOG

Introduction

Inasmuch as the extent of dissociation of gaseous iodine monobromide into gaseous iodine and bromine is known,[1] it was considered of interest to determine the corresponding dissociation when all substances are present in a nearly ideal solvent, such as carbon tetrachloride. From such data the corresponding dissociation in aqueous solution can also be obtained when distribution experiments are made.

In this paper are presented the results of measurements on the vapor pressures of iodine monobromide above its carbon tetrachloride solutions, together with the thermodynamic quantities calculated by combining the results with other known data.

Experimental Method and Preparation of the Materials

The vapor pressure of iodine monobromide above its solutions in carbon tetrachloride was measured by passing dry nitrogen at constant pressure at the rate of about one liter per hour through a series of bulbs containing the monobromide solution at 25.0°. All-glass connections were used throughout. The total amount of halogens removed by the nitrogen was small compared with the amounts present in the solutions, and hence the concentrations were not appreciably changed.

It was necessary in all experiments to analyze for both the total halogen and the iodine in order to establish the composition of the vapor. This was accomplished by the analyses of two separate samples. In one sample the halogens were absorbed in potassium iodide solution and the liberated iodine titrated with standard thiosulfate, this procedure serving for the determination of the total halogen. In a second sample the halogens were absorbed by an excess of sodium sulfite solution, 0.5 *N* hydrochloric acid was added, and the iodide present was titrated with standard permanganate, the end-point being determined electrometrically.[2] In this latter determination a sudden increase in the e. m. f. takes place when all of the sulfite has been oxidized, and a second increase is observed when all of the iodide has been converted to iodine. For the oxidation of all but a trace of the sulfite a more concentrated permanganate solution was used. It was found that this procedure could be used for quantities of iodine as small as 0.1 milliequivalent with an accuracy of 1.0%, the accuracy increasing with an increase in the amount determined.

The iodine used was a product of high quality, the purity of 99.97% indicated by the manufacturer having been confirmed in this Laboratory. Bromine marked C. P. was twice distilled from very pure potassium bromide and then from phosphorus pentoxide, and the middle fraction from the last distillation was used in the experiments. The resulting material was sealed in glass tubes of known weight and the tubes with their contents weighed. The solutions of iodine monobromide were prepared by dissolving

---

[1] McMorris and Yost, THIS JOURNAL, **53**, 2625 (1931).

[2] Gorbatscheff and Kassatkina, *Z. anorg. allgem. Chem.*, **191**, 104 (1930); Hahn, *ibid.*, **195**, 75 (1930–1931).

exactly equivalent amounts of iodine and bromine in measured volumes of carbon tetrachloride.

To obtain pure carbon tetrachloride the C. P. material was saturated with chlorine and the chlorine removed by boiling. The residue was then redistilled and the middle fraction collected and used in the experiments.

Results of Experiments

In Table I are presented the results of the experiments made to determine the partial pressures of iodine monobromide over solutions of it in carbon tetrachloride. Each pressure is the average for several determinations in which the average deviation from the mean was 2%.

TABLE I

PARTIAL PRESSURES OF IODINE MONOBROMIDE ABOVE ITS CARBON TETRACHLORIDE SOLUTIONS

Mole fraction $IBr + I_2 + Br_2$	Pressure $IBr + 2I_2$	Pressure $IBr + Br_2 + I_2$	Mole fraction N of IBr	Pressure p of IBr	Ratio $k = p/N$
0.00179	0.202 mm.	0.229 mm.	0.00165	0.198 mm.	120[a]
.00390	.413	.476	.00355	.405	114
.00805	.860	.990	.00735	.842	115
.0108	1.17	1.32	.0100	1.15	115
.0224	2.36	2.68	.0207	2.32	112
				Mean	114

[a] This value was not included in estimating the mean.

That Henry's law, p/N = constant, is obeyed over a considerable range of concentration, is evident from the values of the constant given in the last column of the table.

In all experiments the vapor contained an excess of bromine, this excess being due to the presence in the solutions of free bromine, which results from the dissociation of the iodine monobromide. Under the assumption that the free bromine in the vapor is, to a first approximation, equal to the excess found, and by using for the Henry's law constant p_{Br}/N_{Br} for bromine in carbon tetrachloride solution the value[3] 409, expressed in millimeters, an approximate value for the mole fraction of free bromine in solution was calculated. Since iodine and bromine were present in equivalent amounts in solution the mole fraction of free iodine was equal to that of the bromine. The partial pressure of iodine, calculated by employing the value[4] 26.9 for the constant of Henry's law, was used to correct the partial pressure of free bromine. A second approximation was found unnecessary.

It is also possible to estimate the composition of the vapor by applying the known value for the dissociation constant of iodine monobromide to the results of the analyses. The two methods of calculation lead to the same result within the limits of experimental errors. The method used

(3) Lewis and Storch, THIS JOURNAL, **39**, 2544 (1917).

(4) This value was calculated from known values for the solubility of iodine in carbon tetrachloride and the vapor pressure of the solid at 25.0°. Jakowkin, *Z. physik. Chem.*, **18**, 588 (1885); Baxter Hickey and Holmes, THIS JOURNAL, **29**, 127 (1907).

above makes possible an independent evaluation of the extent of dissociation of the monobromide both in solution and in the gaseous state, and it was for this reason that it was chosen. It must be noted, however, that small differences between large quantities are involved and consequently the dissociations so calculated are subject to much greater errors than those given below.

The free energy changes accompanying the following changes in state were obtained directly from the literature[5] or by an application of the relation

$$\Delta F^\circ_{298} = -RT \ln K$$

to the known values K, of vapor pressures, solubilities and constants of Henry's law. The Henry's law constant p/N for the iodine monobromide is 114/760, the numerator being the mean value given in Table I.

$\frac{1}{2}I_2$ (s) + $\frac{1}{2}Br_2$ (l) = IBr (g) ΔF°_{298} = 903 cal.[1] (1)
$\frac{1}{2}I_2$ (in CCl_4) = $\frac{1}{2}I_2$ (s) ΔF°_{298} = −1330 cal.[6] (2)
$\frac{1}{2}Br_2$ (in CCl_4) = $\frac{1}{2}Br_2$ (l) ΔF = −195 cal.[5] (3)
IBr (g) = IBr (in CCl_4) ΔF°_{298} = −1124 cal. (4)
Hence, $\frac{1}{2}I_2$ (in CCl_4) + $\frac{1}{2}Br_2$ (in CCl_4)
= IBr(in CCl_4) ΔF°_{298} = −1746 cal. (5)

The final value, −1746 cal., for the free energy change accompanying reaction (5) is nearly equal to the value, −1790 cal., for the corresponding reaction where all substances are in the gaseous state. Both values are subject to an error of ±50 cal. The approximate equality of the free energies of the monobromide under these radically different conditions is of considerable interest because it indicates that the effect of the solvent on the three substances involved is much the same.

It is to be noted that the concentration units used above are mole fractions but since the equilibrium constant for reaction (5) is independent of the units used, the same constant may be employed in calculations in which the concentrations are expressed in moles per liter or moles per thousand grams of solvent. The value for the equilibrium constant for reaction (5) at 25° is 19.0 and the degree of dissociation of the iodine monobromide is 9.5%.

From the data given in Table I it is possible to determine independently, but not with great accuracy, the degree of dissociation of the iodine monobromide both in solution and in the gaseous state. The degrees of dissociation so calculated are 8 and 7% for the solution and gas, respectively, and agree satisfactorily with the corresponding more accurate values of 9.50 and 8.9%, respectively.

In Table II are presented the thermodynamic constants of iodine monobromide. The standard reference states are indicated in each case.

---

(5) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 516.

(6) Calculated from solubility data, Jakowkin, *Z. physik. Chem.*, **18**, 588 (1895).

TABLE II

THERMODYNAMIC CONSTANTS OF IODINE MONOBROMIDE AT 25°

Substance	Reference substances	Free energy, cal.
IBr (g)	I_2 (s), Br_2 (l)	903
IBr (g)	I_2 (g), Br_2 (g)	−1790
IBr (in CCl_4)	I_2 (in CCl_4), Br_2 (in CCl_4)	−1746
IBr (in CCl_4)	I_2 (s), Br_2 (l)	− 221
I_2 (in CCl_4)	I_2 (g)	−1970
IBr (in CCl_4)	IBr (g)	−1124
Br_2 (in CCl_4)	Br_2 (g)	− 366

The Stability of the Iodine Dibromide Ion, IBr_2^-

A large number of distribution experiments were made in which the solvents were carbon tetrachloride and aqueous solutions of hydrobromic and perchloric acids in order to determine the stability of the iodine dibromide ion, IBr_2^-. That there is a fairly strong tendency for the formation of this complex ion was shown by the fact that the monobromide dissolved much more freely in the hydrobromic acid than in the perchloric acid solutions. The results of experiments in which perchloric acid solutions were used showed that the reaction

$$I_2 + 5Br_2 + 6H_2O = 12H^+ + 2IO_3^- + 10Br^-$$

took place, and the bromide ion formed led to the formation of IBr_2^-. This complication rendered the values obtained for the distribution ratio of free iodine monobromide between the acid and carbon tetrachloride of doubtful significance. It is therefore impossible, at this time, to make more than a qualitative statement regarding the stability of the iodine dibromide complex. Its stability is shown roughly by the rather consistent value $300 = (IBr_2^-)/(IBr)(Br^-)$, for the equilibrium constant.

Summary

The partial pressures of iodine monobromide above its carbon tetrachloride solutions have been measured at 25.0° and the constant of Henry's law, $k = p_{IBr}/N_{IBr}$, found to have the value 114 where the pressures are in millimeters.

From this result combined with known thermodynamic data it was found that the standard free energy change for the reaction $\frac{1}{2}I_2$ (in CCl_4) + $\frac{1}{2}Br_2$ (in CCl_4) = IBr (in CCl_4) is −1746 cal. at 25°. This value is nearly the same as that for the reaction $\frac{1}{2}I_2(g) + \frac{1}{2}Br_2(g) = IBr(g)$, namely, −1790 cal. The degree of dissociation of iodine monobromide in carbon tetrachloride solution is 9.5%. The standard free energy change for the reaction $\frac{1}{2}I_2(s) + \frac{1}{2}Br_2(l) = IBr$ (in CCl_4) at 25° is −221 cal.

PASADENA, CALIFORNIA

RECEIVED AUGUST 8, 1932
PUBLISHED FEBRUARY 9, 1933