investigations of Stock and his co-workers have shown that when the mono-, di-, and trichloro derivatives of monosilane are treated with ammonia, the affinity of the silicon for hydrogen is such that it retains, in the first reaction, all of the hydrogen atoms that it possessed before treatment with the ammonia, the chlorine being removed as a negative ion.

Germanium, standing below silicon in the group, has weaker affinity for hydrogen, and, when caused to react with ammonia, the chlorinated derivatives of monogermane, GeH_2Cl and GeH_2Cl_2, lose all of the halogen, and a part or all of the hydrogen.

The study, not as yet completed, of the action of ammonia upon trichloromonogermane indicates that there is first formed a diammonate, $GeHCl_3 \cdot 2NH_3$, and that this, upon further treatment with ammonia, is converted to germanous imide, GeNH.[16]

Summary

1. The reaction between monochloromonogermane and an excess of liquid ammonia is, $3xGeH_3Cl + 3xNH_3 = 3xNH_4Cl + xGeH_4 + 2(GeH)_x$.

2. The reaction between dichloromonogermane and an excess of liquid ammonia is $GeH_2Cl_2 + 2NH_3 = Ge + 2NH_4Cl$.

3. The reaction between monochloromonogermane and an excess of water produces neither hydrogen nor the hypothetical compound $(GeH_3)_3O$.

[16] Johnson, Morey and Kott, THIS JOURNAL, 54, 4278 (1932).

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The Thermodynamic Constants of Iodine Monochloride, Iodine Monobromide and Bromine Monochloride in Carbon Tetrachloride Solutions

BY CHARLES M. BLAIR, JR., AND DON M. YOST

Introduction

The changes in free energy, heat content and entropy of most reactions have been determined for only a single environment. In order to facilitate future studies on the relations between reactions taking place both in the gas phase and in solutions the determination of the thermodynamic constants of iodine monochloride, iodine monobromide and bromine monochloride in carbon tetrachloride was undertaken. The solvent, carbon tetrachloride, was chosen so that the resulting solutions would be as nearly perfect as possible. The constants for iodine monochloride,[1] iodine mono-

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[1] McMorris and Yost, THIS JOURNAL, 54, 2247 (1932).

bromide,[2] and bromine monochloride[3] have been previously determined for the case in which all substances are present as gases.

In order to obtain the desired thermodynamic quantities, measurements were made on the partial vapor pressures of iodine monochloride and chlorine above their carbon tetrachloride solutions, on the heats of solution of iodine and bromine, and on the heats of formation of iodine monochloride, iodine monobromide and bromine monochloride when present in carbon tetrachloride solutions.

Experimental Method and Preparation of Materials

The vapor pressures of iodine monochloride and chlorine above their solutions in carbon tetrachloride were determined at 25° by a dynamic method, similar in most respects to that described by Bichowsky and Storch.[4] Dry nitrogen was forced from a rubber balloon through the solutions at a rate of about one liter per hour, and the volume delivered was determined by weighing the water used to deflate the balloon.[5] The iodine monochloride was absorbed in a sodium sulfite solution and the resulting iodide was determined by titration with standard permanganate solution according to the method described by Swift.[6] Preliminary experiments showed that no appreciable excess of either iodine or chlorine was present in the vapor. This was to be expected since iodine monochloride is only slightly dissociated (0.42%) at room temperature, and because a small excess (1%) of iodine was present in the solutions. In the experiments with chlorine the gas was absorbed in potassium iodide solution and the liberated iodine was titrated with standard thiosulfate.

The iodine monochloride solution was prepared by adding a small excess (1%) of iodine to a carbon tetrachloride solution of chlorine of known concentration. The small excess of iodine decreased the dissociation of the iodine monochloride without contributing appreciably to the total vapor pressure. All reagents were of the highest purity obtainable.

The calorimeter used consisted of a 1.5 liter Dewar flask equipped with an insulating cover, an electrically operated stirrer, a heating coil of platinum wire, and a Reichsanstalt Beckmann thermometer. The Dewar flask was surrounded by ample insulation and the whole enclosed in a wooden box.

In determining the heats of solution of iodine and bromine, weighed amounts of these substances were added to about one liter of carbon tetrachloride contained in the calorimeter. The halogens were contained in easily breakable glass bulbs attached to a glass rod passing through the cover. After the temperature rise of the calorimeter had become constant, the bulb was broken and the temperature change observed at regular intervals until the slow, steady rise resulting from the stirring again set in. In determining heats of reaction the carbon tetrachloride was replaced by a solution of chlorine or bromine in this solvent, and the concentrations were such that an excess was always present, thus making corrections for incomplete reaction unnecessary, except in the case of bromine monochloride. The heat capacity of the calorimeter was determined by passing a measured electric current through the heating coil for a known length of

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

[3] The results, obtained by P. Murdoch, Philip Brass and Don M. Yost, have not yet been published, but are presented in the theses of the two former investigators. At room temperature a light absorption method was used (P. M.) and at higher temperatures advantage was taken of the reversible dissociation of nitrosyl chloride (P. B.) and phosgene (D. M. Y.).

[4] Bichowsky and Storch, THIS JOURNAL, **37**, 2696 (1915).

[5] For further details see McMorris and Badger, *ibid.*, **55**, 1952 (1933).

[6] Swift, *ibid.*, **52**, 899 (1930).

time. The temperature changes accompanying solution or reaction varied from 0.120 to 0.300°.

Results of the Vapor Pressure Experiments.—In Table I are presented the results of the experiments on the partial vapor pressures at 25.0° of iodine monochloride above its solutions in carbon tetrachloride, together with the values for the constant of Henry's law $p_{\text{mm.}}/N_{\text{ICl}} = H_{\text{ICl}}$. The pressures, $p_{\text{mm.}}$, are given in millimeters and concentrations, N_{ICl}, in mole fractions.

TABLE I

PARTIAL PRESSURES OF IODINE MONOCHLORIDE ABOVE ITS CARBON TETRACHLORIDE SOLUTIONS AT 25.0°

Mole fraction of ICl, N_{ICl}	0.00159	0.00290	0.00496	0.00800	0.00933	0.0128	0.0203
Pressures of ICl in mm., $P_{\text{mm.}}$	.331	.594	1.05	1.70	1.94	2.68	4.16
$p_{\text{mm.}}/N_{\text{ICl}} = H_{\text{ICl}}$	208	209	212	212	209	209	205
H_{ICl} mean	209						

With the exception of the first two, all vapor pressures are the mean of several determinations. The concentrations cover a twelve-fold range while the values of H_{ICl} are practically constant with an average deviation from the mean of 1%. Henry's law is evidently obeyed quite closely. This was also found to be the case for iodine monobromide.[7]

Table II presents the partial pressures of chlorine above its carbon tetrachloride solutions at 25.0° together with the Henry's law constant, $p_{\text{mm.}}/N_{\text{Cl}_2} = H_{\text{Cl}_2}$.

TABLE II

PARTIAL PRESSURES OF CHLORINE ABOVE ITS CARBON TETRACHLORIDE SOLUTIONS AT 25.0°

Mole fraction of Cl_2, C_{Cl_2}	0.00394	0.00448	0.00609	0.00615	0.00690	0.00781	0.01245	0.01363	0.01391
Pressures of Cl_2 in mm., $p_{\text{mm.}}$	18.6	22.8	2.80	30.4	32.2	39.8	64.6	69.0	73.4
$p_{\text{mm.}}/N_{\text{Cl}_2} = H_{\text{Cl}_2}$	4730	5080	4600	4940	4670	5100	5180	5070	5280
H_{Cl_2} mean	4960								

The average deviation of the constants from the mean in this case is 4%, and is to be ascribed to the fact that the vapor pressures are high, thus making the attainment of equilibrium less certain. As will appear later, the free energy change attending the solution of chlorine as calculated from these results is in good agreement with that obtained from solubilities and distribution experiments.

With the aid of the above results, data obtained from the literature, and the well-known thermodynamic relation $\Delta F^\circ = -RT \ln K$, the free energy of formation of iodine monochloride in carbon tetrachloride solution may be calculated.

$$\tfrac{1}{2}I_2(g) + \tfrac{1}{2}Cl_2(g) = ICl(g) \qquad \Delta F^\circ_{298} = -3685 \text{ cal.}^{1,12} \qquad (1)$$

$$\tfrac{1}{2}I_2(\text{in } CCl_4) = \tfrac{1}{2}I_2(g) \qquad \Delta F^\circ_{298} = 985 \text{ cal.}^{8} \qquad (2)$$

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[7] Yost, Anderson and Skoog, THIS JOURNAL, **55**, 552 (1933).

[8] See Reference 2 and Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 522.

$$\tfrac{1}{2}\mathrm{Cl_2(in\ CCl_4)} = \tfrac{1}{2}\mathrm{Cl_2(g)} \qquad \Delta F^\circ_{298} = -555 \text{ cal.} \qquad (3)$$

$$\mathrm{ICl(g)} = \mathrm{ICl(in\ CCl_4)} \qquad \Delta F^\circ_{298} = -763 \text{ cal.} \qquad (4)$$

Hence

$$\tfrac{1}{2}\mathrm{I_2(in + CCl_4)} + \tfrac{1}{2}\mathrm{Cl_2(in\ CCl_4)} = \mathrm{ICl(in\ CCl_4)},\ \Delta F^\circ_{298} = -4018 \pm 50 \text{ cal.} \qquad (5)$$

It is seen that the standard free energy decrease attending reaction (5) is greater than that for reaction (1), although the difference is not large. In the case of iodine monobromide the free energy changes for the corresponding reactions differ by only 50 cal.[7]

The standard free energy change attending reaction (3), −555 cal., is very nearly that calculated from solubility measurements,[9] −546 cal., and does not deviate greatly from the value, −515 cal., obtained by Lewis and Randall (*loc. cit.*, p. 502) from the solubility of chlorine in water and distribution ratios.

The equilibrium constant for reaction (5) is 812 at 25.0°, and is independent of the units used to express the concentrations since there is no change in the number of molecules when the reaction takes place. The degree of dissociation of iodine monochloride in carbon tetrachloride solution at 25.0° is 0.25%, while in the gas phase it is 0.42%.[1]

Results of Thermochemical Measurements.—In Tables III, IV, V, VI and VII are presented representative results of the measurements on heats of solution and formation of iodine, bromine, iodine monochloride, iodine monobromide and bromine monochloride in carbon tetrachloride.

TABLE III

HEAT OF SOLUTION OF IODINE IN CARBON TETRACHLORIDE AT 25°

I_2(s) in g./liter CCl_4	4.270	5.060	5.275	5.277	5.366	5.519	5.618	5.645	5.748	6.246	6.661
Heat of soln. in cal./mole I_2	−5970	−6060	−5950	−5910	−5960	−6010	−6090	−5990	−5900	−6180	−5910
Mean	−5990 ± 60 cal.										

TABLE IV

HEAT OF SOLUTION OF BROMINE IN CARBON TETRACHLORIDE AT 25°

Br_2(l) in g./liter CCl_4	8.109	10.938	11.525	14.362	14.965
Heat of soln., cal./mole Br_2	−730	−698	−710	−705	−718
Mean	−712 ± 10 cal.				

These results show that the heats of solution of iodine and bromine, are within the limits of experimental error, independent of the final concentration attained, and hence the heats of dilution are small. This behavior is to be expected of solutions which are perfect or nearly perfect.

TABLE V

HEAT OF FORMATION OF IODINE MONOCHLORIDE IN CARBON TETRACHLORIDE SOLUTION

$\tfrac{1}{2}\mathrm{I_2(IN\ CCl_4)} + \tfrac{1}{2}\mathrm{Cl_2(IN\ CCl_4)} = \mathrm{ICl(IN\ CCl_4)}$

I_2(s) in g./liter CCl_4	5.563	5.741	6.013	6.230	7.269	8.722
Heat of formation, cal./mole ICl	3980	3960	3980	3960	3970	3990
Mean	3970 ± 30 cal.					

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[9] Taylor and Hildebrand, THIS JOURNAL, **45**, 682 (1923).

TABLE VI

HEAT OF FORMATION OF IODINE MONOBROMIDE IN CARBON TETRACHLORIDE SOLUTION

$\frac{1}{2}I_2(\text{in } CCl_4) + \frac{1}{2}Br(\text{in } CCl_4) = IBr(\text{in } CCl_4)$

I_2(s) in g./liter CCl_4	4.363	4.727	5.310	5.313	5.418	5.639	5.665
Heat of formation, cal./mole IBr	1630	1670	1600	1630	1610	1620	1630
Mean	1630 ± 30 cal.						

TABLE VII

HEAT OF FORMATION OF BROMINE MONOCHLORIDE IN CARBON TETRACHLORIDE SOLUTION. $\frac{1}{2}Br_2(\text{in } CCl_4) + \frac{1}{2}Cl_2(\text{in } CCl_4) = BrCl(\text{in } CCl_4)$

Br_2(l) in g./liter CCl_4	11.867	13.442	13.556	15.517	22.276
Heat of formation, cal./mole BrCl	363	374	391	392	372
Mean	378 ± 10 cal.				

Since the measurements on the heats of formation of iodine monochloride, iodine monobromide and bromine monochloride were carried out by adding solid iodine or liquid bromine to solutions of chlorine or bromine in carbon tetrachloride, it was necessary, in arriving at the values given in Tables V, VI and VII, to take into account the heat of solution of the iodine and bromine given in Tables III and IV. It was assumed, in accordance with the results of the experiments on heats of solution, that the heats of dilution involved are small. Moreover, since the halogens and interhalogen compounds are similar in nature, and since there is no change in the number of molecules accompanying the formation of the interhalogen compounds, the small heats of dilution in all probability cancel each other. The results given in Tables V, VI and VII may therefore be regarded as partial molal heats of reaction.

In Table VII the values for the heat of formation of bromine monochloride in carbon tetrachloride have been corrected for the degree of dissociation as calculated from the mean, 0.3, of the equilibrium constants found by Barratt and Stein[10] for the reaction $2BrCl(\text{in } CCl_4) = Br_2(\text{in } CCl_4) + Cl_2(\text{in } CCl_4)$.

In making the measurements of this heat of formation it was found that the reaction involved is a relatively slow one. After adding the bromine to the solution of chlorine in carbon tetrachloride, from ten to fifteen minutes was required for the temperature to reach a maximum, whereas for the analogous reactions to form iodine monochloride and iodine monobromide four to six minutes was required.

It is not convenient to determine directly the heat of solution of chlorine, and this quantity was calculated from the data of Taylor and Hildebrand[9] on the temperature variation of the solubility of the gas in carbon tetrachloride. This quantity, −3720 cal., is, of course, the partial molal heat of solution, but will not differ greatly from the total heat of solution since the solutions are nearly perfect. A similar calculation for the case of iodine gave a result which compared favorably with the values given in Table III.

[10] Barratt and Stein, *Proc. Roy. Soc.* (London), **A122**, 582 (1929).

The following chemical equations together with the corresponding changes in free energy, heat content, entropy and degree of dissociation α may be written

$$\tfrac{1}{2}I_2(\text{in } CCl_4) + \tfrac{1}{2}Cl_2(\text{in } CCl_4) = ICl(\text{in } CCl_4) \qquad (6)$$

$\Delta H^\circ_{298} = -3970$ cal. $\Delta F^\circ_{298} = -4018$ cal. $\Delta S^\circ_{298} = 0.16$ cal./deg. $\alpha = 0.25\%$

$$\tfrac{1}{2}I_2(\text{in } CCl_4) + \tfrac{1}{2}Br_2(\text{in } CCl_4) = IBr(\text{in } CCl_4) \qquad (7)$$

$\Delta H^\circ_{298} = -1630$ cal. $\Delta F^\circ_{298} = -1746$ cal. $\Delta S^\circ_{298} = 0.39$ cal./deg. $\alpha = 9.5\%$

$$\tfrac{1}{2}Br_2(\text{in } CCl_4) + \tfrac{1}{2}Cl_2(\text{in } CCl_4) = BrCl(\text{in } CCl_4) \qquad (8)$$

$\Delta H^\circ_{298} = -349$ cal. $\Delta F^\circ_{298} = -357$ cal. $\Delta S^\circ_{298} = 0.025$ cal./deg. $\alpha = 52.4\%$

In each case the entropy change is smaller than for the corresponding gas reaction, 1.36 cal./deg., 1.51 cal./deg. and 1.11 cal./deg., respectively.

Further, the following equations may be written

$ICl(g) = \tfrac{1}{2}I_2(g) + \tfrac{1}{2}Cl_2(g)$ $\Delta H^\circ_{298} = 3280$ cal.[1]
$\tfrac{1}{2}Cl_2(g) = \tfrac{1}{2}Cl_2(\text{in } CCl_4)$ $\Delta H^\circ_{298} = -1860$ cal.
$\tfrac{1}{2}I_2(g) = \tfrac{1}{2}I_2(s)$ $\Delta H^\circ_{298} = -7438$ cal.[1]
$\tfrac{1}{2}I_2(s) = \tfrac{1}{2}I_2(\text{in } CCl_4)$ $\Delta H^\circ_{298} = 2995$ cal.
$\tfrac{1}{2}I_2(\text{in } CCl_4) + \tfrac{1}{2}Cl_2(\text{in } CCl_4) = ICl(\text{in } CCl_4)$ $\Delta H^\circ_{298} = -3970$ cal.

Hence

$ICl(g) = ICl(\text{in } CCl_4)$ $\Delta H^\circ_{298} = -6993$ cal.

and since $\Delta F^\circ_{298} = -763$ cal., $\Delta S^\circ_{298} = -20.9$ cal./deg. If the value 59.2 cal./deg.[1] is used for the standard absolute entropy of gaseous iodine monochloride at 25.0° the absolute entropy of the compound in carbon tetrachloride solution becomes 38.3 cal./deg. This value refers to a hypothetical solution in which the mole fraction of iodine monochloride is unity. Similarly

$IBr(g) = \tfrac{1}{2}I_2(g) + \tfrac{1}{2}Br_2(g)$ $\Delta H^\circ_{298} = 1372$ cal.[11]
$\tfrac{1}{2}Br_2(l) = \tfrac{1}{2}Br_2(\text{in } CCl_4)$ $\Delta H^\circ_{298} = 356$ cal.
$\tfrac{1}{2}Br_2(g) = \tfrac{1}{2}Br_2(l)$ $\Delta H^\circ_{298} = -3795$ cal.[2]
$\tfrac{1}{2}I_2(g) = \tfrac{1}{2}I_2(s)$ $\Delta H^\circ_{298} = -7438$ cal.
$\tfrac{1}{2}I_2(s) = \tfrac{1}{2}I_2(\text{in } CCl_4)$ $\Delta H^\circ_{298} = 2995$ cal.
$\tfrac{1}{2}I_2(\text{in } CCl_4) + \tfrac{1}{2}Br_2(\text{in } CCl_4) = IBr(\text{in } CCl_4)$ $\Delta H^\circ_{298} = -1630$ cal.

Hence

$IBr(g) = IBr(\text{in } CCl_4)$ $\Delta H^\circ_{298} = -8140$ cal.

and since $\Delta F^\circ_{298} = -1124$ cal., $\Delta S^\circ_{298} = -23.5$. The standard absolute entropy of gaseous iodine monobromide[11] at 25° is 62.0 cal./deg., and the absolute entropy in carbon tetrachloride solution becomes 38.3 cal./deg. Here again the standard state is a solution in which the mole fraction of the compound is unity.

To obtain the entropy of bromine monochloride in carbon tetrachloride solution, we write the following equations

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[11] W. G. Brown, *Phys. Rev.*, **42**, 355 (1932), has found spectroscopically that for the reaction $\tfrac{1}{2}I_2(g) + \tfrac{1}{2}Br_2(g) = IBr(g)$, $\Delta H = -1372$ cal. This value, combined with the equilibrium data of McMorris and Yost,[2] leads to the free energy equation $\Delta F^\circ = -1372 - 1.51\,T$. It is believed that this spectroscopic value for ΔH is a bit more accurate than the one obtained from the variation of the equilibrium constant with temperature, −1270 cal. The entropy of IBr(g) now becomes 62.0 cal./deg. at 25° and one atmosphere.

$\frac{1}{2}\text{Br}_2(\text{in CCl}_4) + \frac{1}{2}\text{Cl}_2(\text{in CCl}_4) = \text{BrCl}(\text{in CCl}_4)$ $\Delta H^\circ_{298} = -378$ cal.
$\frac{1}{2}\text{Br}_2(\text{l}) = \frac{1}{2}\text{Br}_2(\text{in CCl}_4)$ $\Delta H^\circ_{298} = 356$ cal.
$\frac{1}{2}\text{Cl}_2(\text{g}) = \frac{1}{2}\text{Cl}_2(\text{in CCl}_4)$ $\Delta H^\circ_{298} = -1860$ cal.
$\frac{1}{2}\text{Br}_2(\text{g}) = \frac{1}{2}\text{Br}_2(\text{l})$ $\Delta H^\circ_{298} = -3795$ cal.[2]

Hence

$\frac{1}{2}\text{Br}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) = \text{BrCl}(\text{in CCl}_4)$ $\Delta H^\circ_{298} = -5677$ cal.

and since $\Delta F^\circ_{298} = 15$ cal.,[10] $\Delta S^\circ = -19.1$ cal./deg., and the absolute entropy of bromine monochloride in carbon tetrachloride solution becomes 36.9 cal./deg. when the standard absolute entropies of gaseous bromine[1] and chlorine[1] are taken as 58.63 cal./deg. and 53.31 cal./deg., respectively, at 25.0°.

The Thermodynamic Constants of the Halogens and Interhalogen Compounds in Carbon Tetrachloride Solution.—The results of the determinations and calculations made, together with the entropies of the gaseous halogens and interhalogen compounds, are presented in Tables VIII and IX in a conveniently usable form.

TABLE VIII

THERMODYNAMIC CONSTANTS OF THE GASEOUS HALOGENS AND INTERHALOGEN COMPOUNDS AT 25°

Substance	$\text{I}_2(\text{g})$	$\text{Br}_2(\text{g})$	$\text{Cl}_2(\text{g})$	$\text{ICl}(\text{g})$[12]	$\text{IBr}(\text{g})$	$\text{BrCl}(\text{g})$
Ref. subs.	$\text{I}_2(\text{s})$	$\text{Br}_2(\text{l})$	$\text{Cl}_2(\text{g})$	$\text{I}_2(\text{s})$ $\text{Cl}_2(\text{g})$	$\text{I}_2(\text{s})$ $\text{Br}_2(\text{l})$	$\text{Br}_2(\text{l})$ $\text{Cl}_2(\text{g})$
Free energy	4630	755	0	−1370	971	−251[13]
Heat content	14876	7590	0	4158	9861	(3495)[14]
Entropy[a]	62.29	58.63	53.31	59.15	62.0	(57.1)[14]

[a] These are the standard absolute entropies of the substances given in the first row of the table.

TABLE IX

THERMODYNAMIC CONSTANTS OF THE HALOGENS AND INTERHALOGEN COMPOUNDS IN CARBON TETRACHLORIDE SOLUTION AT 25°

Substance	$\text{I}_2(\text{in CCl}_4)$	$\text{Br}_2(\text{in CCl}_4)$	$\text{Cl}_2(\text{in CCl}_4)$	$\text{ICl}(\text{in CCl}_4)$	$\text{IBr}(\text{in CCl}_4)$	$\text{BrCl}(\text{in CCl}_4)$
Ref. subs.	$\text{I}_2(\text{s})$	$\text{Br}_2(\text{l})$	$\text{Cl}_2(\text{g})$	$\text{I}_2(\text{s})$ $\text{Cl}_2(\text{g})$	$\text{I}_2(\text{s})$ $\text{Br}_2(\text{l})$	$\text{Br}_2(\text{l})$ $\text{Cl}_2(\text{g})$
Free energy	2660	389	1110	−2133	−153	393
Heat content	5990	712	−3720	−2835	1721	−1882
Entropy[a]	39.1	36.8	37.1	38.3	38.5	36.9

[a] These are the standard absolute entropies of the substances given in the first row of the table.

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(12) In Table IV of the article by McMorris and Yost the values for the free energies and entropies of $\text{ICl}(\text{g})$, $\text{ICl}(\text{l})$ and $\text{ICl}(\text{s})$ in the last three columns are in error. The error arose from using twice the free energy value for the reaction $^1/_2\text{I}_2(\text{s}) = {}^1/_2\text{I}_2(\text{g})$ instead of the correct one of 4620 cal. The corrected values given in this paper were obtained by using the spectroscopically determined free energy equation $\Delta F^\circ = -3280 - 1.36\,T$ for the reaction $^1/_2\text{I}_2(\text{g}) + {}^1/_2\text{Cl}_2(\text{g}) = \text{ICl}(\text{g})$, since it is in essential agreement with that determined from equilibrium measurements and is probably less subject to error.

(13) The equilibrium constant obtained by Murdoch (Ref. 3) for the reaction $2\text{BrCl}(\text{g}) = \text{Br}_2(\text{g}) + \text{Cl}_2(\text{g})$ is 0.12, and this value was used to calculate the above free energy change.

(14) In the case of both iodine monochloride and iodine monobromide it was found that the heats of formation of the gaseous compound from the gaseous elements are about 20% less than those for the corresponding reactions with all substances in carbon tetrachloride; accordingly, the heat of the reaction $^1/_2\text{Br}_2(\text{g}) + {}^1/_2\text{Cl}_2(\text{g}) = \text{BrCl}(\text{g})$ was assumed to be 300 cal., and the above heat content and entropy calculated using this value.

It will be noted that the entropies of both the halogens and the interhalogen compounds in carbon tetrachloride solution do not differ greatly from each other; this is not the case for the gases.

Summary

The partial vapor pressures of iodine monochloride and chlorine above their carbon tetrachloride solutions have been measured and from the results, combined with those of other investigators, the free energy of formation of the monochloride in solution has been calculated.

Determinations of the heats of solution of iodine and bromine in carbon tetrachloride and the heats of formation of iodine monochloride, iodine monobromide and bromine monochloride in the same solvent have been made. These data were combined with the known free energy values to obtain the thermodynamic constants of the halogens and interhalogen compounds in their carbon tetrachloride solutions. The values are collected in Table IX, and in Table VIII are presented the corresponding data for the same substances in the gas phase.

It was found that the reaction between bromine and chlorine in carbon tetrachloride solution is appreciably slower than the corresponding reactions between iodine and chlorine and iodine and bromine.

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The Thermodynamics of Ionized Water in Potassium and Sodium Bromide Solutions

BY HERBERT S. HARNED AND WALTER J. HAMER

Recently considerable information regarding the behaviors of the ions of water in potassium and lithium chloride solutions from electromotive force measurements of cells without liquid junction has been obtained.[1] This study has now been extended to include similar data and calculations of related properties in potassium and sodium bromide solutions. To this end, measurements of the cells

$$H_2 \mid MOH(m_0),\ MBr\ (m) \mid AgBr \mid Ag, \quad \text{and} \tag{A}$$
$$H_2 \mid HBr\ (m_0),\ MBr\ (m) \mid AgBr \mid Ag \tag{B}$$

have been made throughout a temperature range of from 0 to 60°, where M represents potassium or sodium.

Much valuable information may be obtained from these data of which we have included (1) the ionization constant of water; (2) the normal potential, E_0, of the silver–silver bromide electrode; (3) the activity

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[1] (a) Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933); (b) Harned and Copson, *ibid.*, **55**, 2206 (1933).