I. THE THERMODYNAMIC CONSTANTS OF IODINE MONOCHLORIDE,
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I.

THE THERMODYNAMIC CONSTANTS OF IODINE MONOCHLORIDE,

IODINE MONOBROMIDE AND BROMINE MONOCHLORIDE IN

CARBON TETRACHLORIDE SOLUTIONS

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-

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

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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

(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 $p_{mm.}/N_{ICl} = H_{ICl}$. The pressures, $p_{mm.}$, 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., $P_{mm.}$	.331	.594	1.05	1.70	1.94	2.68	4.16
$p_{mm.}/N_{ICl} = H_{ICl}$	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, $p_{mm.}/N_{Cl_2} = H_{Cl_2}$.

TABLE II

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

Mole fraction of Cl₂, C_{Cl_2}	0.00394	0.00448	0.00609	0.00615	0.00690	0.00781	0.01245	0.01363	0.01391
Pressures of Cl₂ in mm., $p_{mm.}$	18.6	22.8	2.80	30.4	32.2	39.8	64.6	69.0	73.4
$p_{mm.}/N_{Cl_2} = H_{Cl_2}$	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 $\Delta F° = -RT \ln K$, the free energy of formation of iodine monochloride in carbon tetrachloride solution may be calculated.

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

$$\tfrac{1}{2}I_2(\text{in } CCl_4) = \tfrac{1}{2}I_2(g) \qquad \Delta F°_{298} = 985 \text{ cal.}^8 \qquad (2)$$
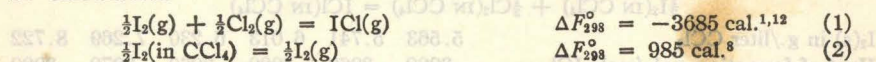
(7) Yost, Anderson and Skoog, THIS JOURNAL, **55**, 552 (1933).

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

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

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

Hence

$$\tfrac{1}{2}I_2(\text{in} + CCl_4) + \tfrac{1}{2}Cl_2(\text{in } CCl_4) = ICl(\text{in } CCl_4), \ \Delta F^\circ_{298} = -4018 \pm 50 \text{ cal.} \quad (5)$$
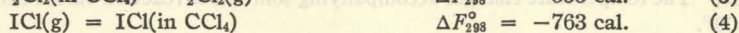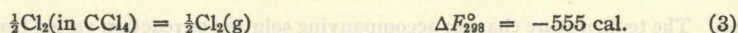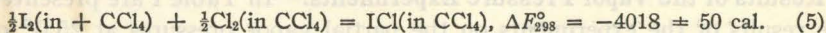
It is seen that the standard free energy decrease attending reaction (5) is greater than that for reaction (1), although the difference is not large. In the case of iodine monobromide the free energy changes for the corresponding reactions differ by only 50 cal.[7]

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

$$\tfrac{1}{2}I_2(\text{IN } CCl_4) + \tfrac{1}{2}Cl_2(\text{IN } CCl_4) = ICl(\text{IN } CCl_4)$$
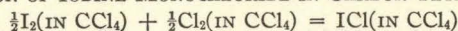
$I_2(s)$ in g./liter CCl_4	5.563	5.741	6.013	6.230	7.269	8.722
Heat of formation, cal./mole ICl	3980	3960	3980	3960	3970	3990
Mean	3970 ± 30 cal.					

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

TABLE VI

HEAT OF FORMATION OF IODINE MONOBROMIDE IN CARBON TETRACHLORIDE SOLUTION

$$\tfrac{1}{2}I_2(\text{IN } CCl_4) + \tfrac{1}{2}Br(\text{IN } CCl_4) = IBr(\text{IN } CCl_4)$$

$I_2(s)$ 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. $\tfrac{1}{2}Br_2(\text{IN } CCl_4) + \tfrac{1}{2}Cl_2(\text{IN } CCl_4) = BrCl(\text{IN } CCl_4)$

$Br_2(l)$ 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		878 ± 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).

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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. $\quad \Delta F^{\circ}_{298} = -4018$ cal. $\quad \Delta S^{\circ}_{298} = 0.16$ cal./deg. $\quad \alpha = 0.25\%$
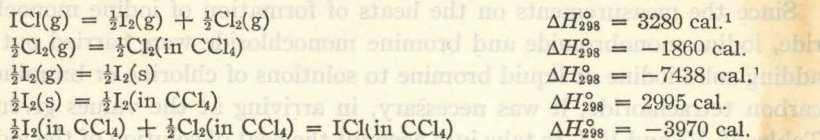
$$\tfrac{1}{2}I_2(\text{in } CCl_4) + \tfrac{1}{2}Br_2(\text{in } CCl_4) = IBr(\text{in } CCl_4) \qquad (7)$$

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

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

$\Delta H^{\circ}_{298} = -349$ cal. $\quad \Delta F^{\circ}_{298} = -357$ cal. $\quad \Delta S^{\circ}_{298} = 0.025$ cal./deg. $\quad \alpha = 52.4\%$
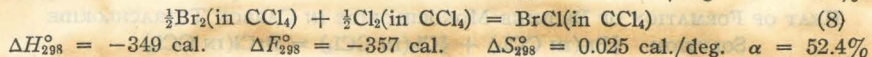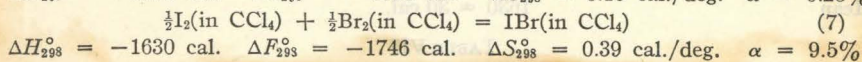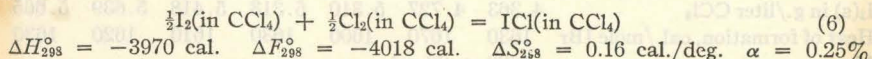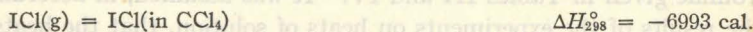
In each case the entropy change is smaller than for the corresponding gas reaction, 1.36 cal./deg., 1.51 cal./deg. and 1.11 cal./deg., respectively.
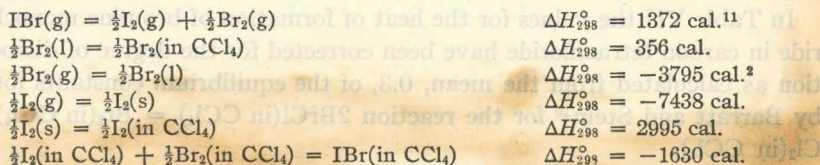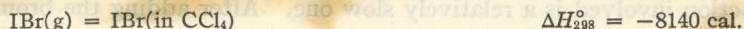
Further, the following equations may be written

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

Hence

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

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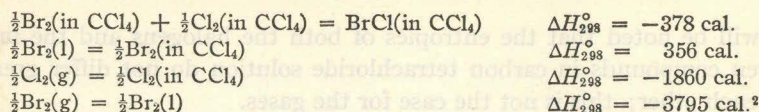
$$IBr(g) = \tfrac{1}{2}I_2(g) + \tfrac{1}{2}Br_2(g) \qquad\qquad \Delta H^{\circ}_{298} = 1372 \text{ cal.}[11]$$
$$\tfrac{1}{2}Br_2(l) = \tfrac{1}{2}Br_2(\text{in } CCl_4) \qquad\qquad \Delta H^{\circ}_{298} = 356 \text{ cal.}$$
$$\tfrac{1}{2}Br_2(g) = \tfrac{1}{2}Br_2(l) \qquad\qquad \Delta H^{\circ}_{298}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

Hence

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

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

(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.

$$\tfrac{1}{2}Br_2(\text{in } CCl_4) + \tfrac{1}{2}Cl_2(\text{in } CCl_4) = BrCl(\text{in } CCl_4) \qquad \Delta H^{\circ}_{298} = -378 \text{ cal.}$$
$$\tfrac{1}{2}Br_2(l) = \tfrac{1}{2}Br_2(\text{in } CCl_4) \qquad \Delta H^{\circ}_{298} = 356 \text{ cal.}$$
$$\tfrac{1}{2}Cl_2(g) = \tfrac{1}{2}Cl_2(\text{in } CCl_4) \qquad \Delta H^{\circ}_{298} = -1860 \text{ cal.}$$
$$\tfrac{1}{2}Br_2(g) = \tfrac{1}{2}Br_2(l) \qquad \Delta H^{\circ}_{298} = -3795 \text{ cal.}[2]$$

Hence

$$\tfrac{1}{2}Br_2(g) + \tfrac{1}{2}Cl_2(g) = BrCl(\text{in } CCl_4) \qquad \Delta H^{\circ}_{298} = -5677 \text{ cal.}$$

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	$I_2(g)$	$Br_2(g)$	$Cl_2(g)$	$ICl(g)$[12]	$IBr(g)$	$BrCl(g)$
Ref. subs.	$I_2(s)$	$Br_2(l)$	$Cl_2(g)$	$I_2(s)$	$I_2(s)$	$Br_2(l)$
				$Cl_2(g)$	$Br_2(l)$	$Cl_2(g)$
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	$I_2(\text{in } CCl_4)$	$Br_2(\text{in } CCl_4)$	$Cl_2(\text{in } CCl_4)$	$ICl(\text{in } CCl_4)$	$IBr(\text{in } CCl_4)$	$BrCl(\text{in } CCl_4)$
Ref. subs.	$I_2(s)$	$Br_2(l)$	$Cl_2(g)$	$I_2(s)$	$I_2(s)$	$Br_2(l)$
				$Cl_2(g)$	$Br_2(l)$	$Cl_2(g)$
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.

(12) In Table IV of the article by McMorris and Yost the values for the free energies and entropies of ICl(g), ICl(l) and ICl(s) in the last three columns are in error. The error arose from using twice the free energy value for the reaction $\tfrac{1}{2}I_2(s) = \tfrac{1}{2}I_2(g)$ 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 $\tfrac{1}{2}I_2(g) + \tfrac{1}{2}Cl_2(g) = ICl(g)$, 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 $2BrCl(g) = Br_2(g) + Cl_2(g)$ 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 $\tfrac{1}{2}Br_2(g) + \tfrac{1}{2}Cl_2(g) = BrCl(g)$ 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.

II.

THE EQUILIBRIUM BETWEEN NITRIC OXIDE, BROMINE AND NITROSYL BROMIDE

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 418]

The Equilibrium between Nitric Oxide, Bromine and Nitrosyl Bromide

BY CHARLES M. BLAIR, JR., PHILIP D. BRASS AND DON M. YOST

Introduction

The formation of nitrosyl bromide from nitric oxide and bromine is of considerable interest because, kinetically, the reaction is one of very few third order homogeneous gas reactions. Since the reaction is readily and measurably reversible, it would be possible to predict the rate of decomposition of nitrosyl bromide if the standard free energy change as a function of the temperature were known accurately. Moreover, the reaction may find application in the study of other reversible reactions involving bromine or nitric oxide.

Fig. 1.—Reaction cell and auxiliary apparatus (not to scale).

The equilibrium has been studied by Trautz and Dalal,[1] but due to the manometer system which they used the results are not very accurate. Moreover, they postulate the existence of nitrosyl dibromide, $NOBr_2$, and nitrosyl tribromide, $NOBr_3$, although Dixon's[2] results with nitrosyl chloride do not indicate the existence of the corresponding chlorine compounds, which would be expected to be more stable. The experiments described in this paper were undertaken to determine accurately the equilibria in the reaction between nitric oxide and bromine to form nitrosyl bromide.

(1) Trautz and Dalal, *Z. anorg. allgem. Chem.*, **110**, 1 (1920).

(2) Dixon, *Z. physik. Chem.*, Bodenstein Festband, 679 (1931).

Preparation of Materials and Experimental Method

The bromine was prepared by treating a saturated solution of twice recrystallized potassium bromate and potassium bromide with C. P. concentrated sulfuric acid. The bromine was distilled from this mixture and then dried over specially purified anhydrous calcium bromide. The material was finally twice distilled from fresh portions of anhydrous calcium bromide, the middle fraction of the last distillation being that used in the experiments. At no time did the bromine come in contact with rubber or other organic matter, since an all-glass distilling system was used.

The nitric oxide used was prepared by a slight modification of the method described by Johnston and Giauque,[3] and was of high purity.

A preliminary series of equilibrium measurements was made using a reaction vessel of about 300 cc. capacity heated in an electric furnace, but the apparatus described below was finally adopted in order to decrease the errors due to external volume and temperature gradient.

The apparatus is shown diagrammatically in Fig. 1. V is a Pyrex reaction vessel of 1054.7 cc. capacity at 22°. G is a thermostat containing either water or molten hydrogenated cottonseed oil. The reaction vessel was connected to a Pyrex glass click-gage F and to the side-arm B by means of capillary tubing. A weighed amount of bromine to be used in a run was held in a tube C having an easily breakable tip. E is a glass enclosed iron hammer, and D a solenoid for operating it.

Several equilibrium measurements were made at different temperatures with each filling of the reaction vessel. In carrying out such a series of measurements the reaction vessel was first heated and evacuated for several hours. A convenient pressure of nitric oxide was then admitted at H and the system sealed off at A. The pressure of nitric oxide in the reaction vessel was determined by use of the click-gage and manometer M. By means of liquid air the nitric oxide was condensed in the tube J; the bromine bulb was then broken with the magnetic hammer and the bromine also allowed to condense in J. The side-arm was then sealed off at A and its volume (about 3 cc.) was determined. The pressure of nitric oxide in the reaction vessel was corrected for the small change in volume. After mixing the nitric oxide and bromine by alternately freezing and evaporating them several times, the thermostat was put in place, adjusted to some definite temperature, and pressure readings were taken until the system reached equilibrium. The thermostat was then readjusted to other temperatures and a number of measurements of equilibrium pressures at various temperatures were made, equilibrium being approached from both the low and high temperature sides. From these pressures and the known amounts of nitric oxide and bromine originally present in the reaction vessel the equilibrium con-
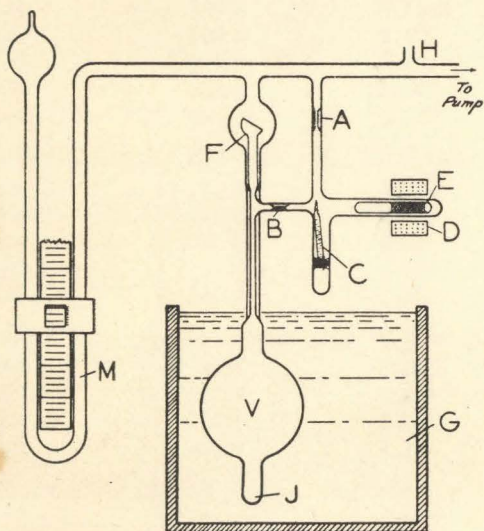
(3) Johnston and Giauque, THIS JOURNAL, **51**, 3194 (1929).

stants for the reaction $2NO(g) + Br_2(g) = 2NOBr(g)$ were calculated for each temperature.

The temperature of the thermostat varied not over $\pm 0.1°$ at temperatures up to about 200° and not over $\pm 0.2°$ above that. The temperature was measured by means of calibrated mercury thermometers kept totally immersed. The mercury manometer used was 12 mm. in diameter and by means of a vernier the pressure readings were made to within ± 0.1 mm.

Five separate fillings of the reaction vessel were made, three with an excess of nitric oxide and two with an excess of bromine. In Table I are presented representative results of these runs. Only every third measurement is given in the table. The equilibrium constant for the

TABLE I

REPRESENTATIVE RESULTS OF THE EQUILIBRIUM MEASUREMENTS[a]

T, °K.	p, mm.	$\log_{10} K_{mm}$
At 299.4°K.:	p_{NO}^0 99.3 mm.	$p_{Br_2}^0$ 41.6 mm.
296.9	110.5	0.7452
386.5	168.6	2.779
412.1	184.2	3.272
436.7	197.4	3.545
497.1	230.2	4.575
At 298.1°K.:	p_{NO}^0 98.6 mm.	$p_{Br_2}^0$ 116.8 mm.
296.8	175.7	0.7721
392.2	264.9	2.980
433.6	298.7	3.443
473.9	332.7	4.051
492.5	346.3	4.129
At 299.9°K.:	p_{NO}^0 173.8 mm.	$p_{Br_2}^0$ 73.2 mm.
299.9	192.7	0.8333
376.3	277.6	2.535
442.2	346.1	3.556
503.4	402.6	4.188
At 297.0°K.:	p_{NO}^0 181.0 mm.	$p_{Br_2}^0$ 77.3 mm.
273.1	175.9	0.0730
290.1	193.0	.5914
320.6	206.8	.9555
323.7	231.2	1.492
349.7	262.2	2.078
373.4	290.6	2.541
409.6	332.2	3.191
441.6	365.9	3.631
476.9	401.3	4.066
497.7	421.3	4.303
At 296.3°K.:	p_{NO}^0 101.4 mm.	$p_{Br_2}^0$ 150.4 mm.
290.6	205.0	0.5555
294.8	209.3	.7378
302.1	216.0	.9050
330.2	244.8	1.651
367.4	284.9	2.431
406.9	326.2	3.110
446.4	365.8	3.688
479.5	397.3	4.123
502.9	419.0	4.421

[a] All pressure measurements are given in millimeters of mercury at 22°.

reaction $2NO(g) + Br_2(g) = 2NOBr(g)$ is given by the expression

$$K_{mm.} = \frac{4\,\Delta p^2}{(p_{NO}^0 - 2\,\Delta p)^2(p_{Br_2}^0 - \Delta p)}$$

where p_{NO}^0 is the pressure of nitric oxide which would exist at the temperature in question if no reaction had taken place, $p_{Br_2}^0$ the corresponding pressure of bromine and Δp the difference between $p_{NO}^0 + p_{Br_2}^0$ and p, the observed pressure.

The results are shown graphically in Fig. 2, where the logarithm of the equilibrium constant is plotted against the reciprocal of the absolute temperature. The shape of the curve gives no evidence for the existence of nitrosyl dibromide or nitrosyl tribromide in the gas phase at temperatures as low as 12°, even in the presence of a large excess of bromine.

Fig. 2.

The error in the pressure measurements was ± 0.1 mm., but since pressure differences are involved in the expression for the equilibrium constant, the error in this quantity may be $\pm 4\%$, corresponding to an error of about 2% in $\log K$ at room temperature and less above that temperature. Because of the number of experiments made, the probable error in any equilibrium constant must be below $\pm 2\%$, corresponding to an error in the heat content change accompanying the reaction of $\pm 0.5\%$. The error in the free energy change calculated from the equilibrium constant at 25° is $\pm 1\%$.

All of the results obtained with the large capacity equilibrium apparatus are presented in Table III.[*]

Table III

At $299.4°K$, $\quad p^o_{NO}$ 99.3 mm. $\quad p^o_{Br_2}$ 41.6 mm.

T °K	p mm.	$-\log_{10}K_{mm}$
296.9	110.5	0.7452
368.7	157.2	2.437
368.9	157.9	2.490
386.5	168.6	2.779
391.0	171.6	2.884
400.0	177.3	3.082
412.1	184.2	3.272
418.7	188.0	3.368
433.0	195.5	3.519
436.7	197.4	3.545
463.0	211.9	3.948
485.6	224.4	4.412
497.1	230.2	4.575
519.2	241.7	5.046
297.4	112.0	0.8969

At $298.1°K$, $\quad p^o_{NO}$ 98.6 mm. $\quad p^o_{Br_2}$ 116.8 mm.

T °K	p mm.	$-\log_{10}K_{mm}$
296.8	175.7	0.7721
297.9	177.4	0.8861
390.0	263.1	2.950
392.2	264.9	2.980
408.9	279.2	3.210
412.5	284.1	3.392
433.6	298.7	3.443
445.4	305.1	3.310
451.9	314.8	3.770
473.9	332.7	4.051
466.3	326.5	3.949
492.5	346.3	4.129

At $299.9°K$, $\quad p^o_{NO}$ 173.8 mm. $\quad p^o_{Br_2}$ 73.2 mm.

T °K	p mm.	$-\log_{10}K_{mm}$
299.9	192.7	0.8333
343.8	241.4	1.922
365.1	265.5	2.351
376.3	277.6	2.535
412.4	316.9	3.161
437.7	341.4	3.471
442.2	346.1	3.556
461.6	364.5	3.778
503.4	402.6	4.188

At $297.0°K$, $\quad p^o_{NO}$ 181.0 mm. $\quad p^o_{Br_2}$ 77.3 mm.

T °K	p mm.	$-\log_{10}K_{mm}$
273.1	175.9	0.0730
280.3	182.9	0.2967
284.8	187.5	0.4334
290.1	193.0	0.5914
293.9	197.2	0.7117
296.8	200.7	0.8080
302.6	206.8	0.9555
308.7	213.2	1.094
318.0	224.5	1.361
323.7	231.2	1.492
330.1	239.0	1.657
337.1	247.7	1.829
349.7	262.2	2.078
354.3	267.7	2.161
365.8	281.8	2.410
373.4	290.6	2.541
383.8	303.0	2.745
403.9	325.3	3.056

[*] For a complete table of results obtained with the 300 cc. capacity reaction vessel see P. D. Brass, Dissertation, The California Institute of Technology, 1932.

Table III (continued)

At 297.0^{O}K (continued)

T ^{O}K	p mm.	$-\log_{10}K_{mm}$
409.6	332.2	3.191
422.8	346.6	3.370
434.2	357.7	3.488
441.6	365.9	3.631
451.3	376.3	3.779
462.8	387.6	3.926
476.9	401.3	4.066
485.0	409.0	4.162
497.7	421.3	4.303

At 296.3^{O}K, p_{NO}^{O} 101.4 mm.

               $p_{Br_2}^{O}$ 150.4 mm.

T ^{O}K	p mm.	$-\log_{10}K_{mm}$
290.6	205.0	0.5555
291.8	205.9	0.5665
291.5	205.6	0.5681
294.8	209.3	0.7378
297.1	211.6	0.8022

At 296.3^{O}K (continued)

T ^{O}K	p mm.	$-\log_{10}K_{mm}$
299.8	213.8	0.8462
302.1	216.0	0.9050
311.2	225.0	1.167
321.0	235.5	1.454
330.2	244.8	1.651
336.7	252.0	1.813
349.3	265.4	2.071
367.4	284.9	2.431
386.6	305.5	2.779
399.3	318.8	3.002
406.9	326.2	3.110
419.2	339.8	3.356
428.0	347.3	3.409
446.4	365.8	3.688
458.8	378.0	3.866
468.1	386.8	3.997
479.5	397.3	4.123
486.1	403.8	4.240
502.9	419.0	4.421

No correction was made for the small volume of the click-gage and capillary tubing which were out of the thermostat and at approximately room temperature. This volume was about one cubic centimeter and the correction due to this dead space would make a negligible difference in $\log K$ below 450°K. but may be as much as -1% at temperatures around 500°K.

When the results of the experiments are combined with specific heat data, the following expression for the standard change in heat content and free energy accompanying the reaction $2NO (g) + Br_2(g) = 2NOBr(g)$ are obtained

$$NO(g),[4] \quad C_p = 7.922 - 0.00441\,T + 6.30 \times 10^{-6}T^2$$
$$Br_2(g),[5] \quad C_p = 7.710 + 0.00415\,T - 3.7 \times 10^{-6}T^2$$
$$NOBr(g),[6]\ C_p = 5.07 + 0.0163\,T - 12.9 \times 10^{-6}T^2$$

Whence

$$\Delta C_p = -13.41 + 0.0372\,T - 34.7 \times 10^{-6}T^2$$
$$\Delta H^0 = -8780 - 13.14\,T + 0.0186T^2 - 11.6 \times 10^{-6}T^3$$
$$\Delta F^0 = -8780 + 30.88\,T \log_{10}T - 51.26T$$
$$\qquad\qquad - 0.0186T^2 + 5.8 \times 10^{-6}T^3$$

These expressions are valid in the temperature range 250–600°K.

Directly from the experimental curve and independent of specific heat data, we obtain

(4) Constructed from the data of Johnston and Chapman, THIS JOURNAL, **55**, 153 (1933).

(5) Constructed from the data of Gordon and Barnes, *J. Chem. Phys.*, **1**, 694 (1933).

(6) In the absence of experimental data for nitrosyl bromide the equation given by Eastman, Bureau of Mines, Technical Paper, 1929, for the specific heat of sulfur dioxide was used.

$$\Delta H^0_{298.1} = -11,430 \pm 60 \text{ cal.}$$
$$\Delta F^0_{298.1} = -2790 \pm 30 \text{ cal.}$$
$$\Delta S^0_{298.1} = -29.0 \pm 0.3 \text{ cal./deg.}$$

This last value, combined with the known entropies of bromine[7] and nitric oxide,[4] gives for the standard virtual entropy of NOBr, $S^0_{298.1} = 65.2 \pm 0.3$ cal./deg. When the free energy change for the reaction studied is combined with that for the formation of nitric oxide, 20,650 cal.,[8] the standard free energy of formation of nitrosyl bromide gas from the elements in their standard states at 25° becomes 19,260 cal.

Summary

The equilibrium in the reaction $2NO(g) + Br_2(g) = NOBr(g)$ has been measured in the temperature range from 273.1 to 520°K. From the results of the measurements the following thermodynamic equations have been derived for the reaction

$$\Delta H^0 = -8780 - 13.41\,T + 0.0186\,T^2 - 11.6 \times 10^{-6}T^3$$
$$\Delta F^0 = -8780 + 30.88\,T \log_{10}T - 51.26\,T$$
$$\qquad\qquad - 0.0186\,T^2 + 5.8 \times 10^{-6}T^3$$

At 25° the free energy of formation of NOBr(g) from the elements is 19,260 cal. The virtual entropy of NOBr(g) at 25° and one atmosphere is 65.2 ± 0.3 cal./deg.

(7) Brown, *Phys. Rev.*, **42**, 355 (1932).

(8) Giauque and Clayton, THIS JOURNAL, **55**, 4875 (1933).

For the equilibrium $2NO + Br_2 = 2NOBr$ we have the relations:

$$-d(Br_2)/dt = k_f(NO)^2(Br_2)$$

$$-d(NOBr)/dt = k_d(NOBr)^2$$

At equilibrium

$$2d(Br_2)/dt = d(NOBr)/dt$$

therefore, $\qquad 2k_f = k_d \dfrac{(NOBr)^2}{(NO)^2(Br_2)} = k_d K$

or, $\qquad k_d = 2k_f/K$

where k_f is the specific reaction rate constant for the formation of NOBr, k_d the specific reaction rate constant for the decomposition of NOBr and K the equilibrium constant for the above written reaction. Trautz[1] has measured the rate of formation of NOBr at three different temperatures; using his values of k_f and values of K obtained from Fig. 2 (the units of K must be changed to cc. per mole) we may calculate three values of k_d and two values of $d\ln k_d/dT$. The results of these calculations are shown in Table IV.

TABLE IV

T	k_f (Trautz)	logK	k_d	$\dfrac{d \log k_d}{dT}$
265	3.0×10^9	7.18	398	
				0.030
273	3.0×10^9	6.94	692	
				0.060
279	4.8×10^9	6.78	1590	

Applying the simple Arrhenius equation to these
results we may obtain a rough value for the heat of acti-
vation of the decomposition reaction.

$$d \ln k_d/dT = q/RT^2 \qquad \text{(Arrhenius)}$$

Taking the mean of the $d \log k_d/dT$ values of Table IV
and assuming the same value at T 300°K, we find

$$q = 19,000 \text{ cal.} \pm 6,000 \text{ cal.},$$

an approximate value for the heat of activation involved
in the decomposition of nitrosyl bromide.

III.

THE INFRA-RED EMISSION SPECTRUM OF THE

BUNSEN TYPE FLAME

THE INFRA-RED EMISSION SPECTRUM OF THE BUNSEN TYPE FLAME

INTRODUCTION

In many cases it has been found difficult or impossible to obtain desired absorption spectra in the photographic infra-red without employing impracticably long absorption paths. The present work was undertaken with the object of determining whether or not, in some instances, it might be possible to obtain the desired spectra in emission. It was thought that by making long exposures, and thus utilizing the integrating effect of the photographic plate, that even very weak emission spectra might be recorded.

Since the absorption spectrum of water vapor has been well studied, it seemed desirable to study the emission spectrum of this molecule in particular since the results would afford a good comparison of the methods. The Bunsen flame seemed a likely source in which to find the rotation-vibration spectrum of water and, perhaps also, OH molecules. It was hoped that, in addition to the information got in regard to the relative value of absorption and emission methods of obtaining spectra, a more accurate determination of the molecular constants and energy levels of these molecules might be made.

Numerous studies of the light emitted by the Bunsen flame have been made[1], but previous investigations have been concerned almost entirely in the analysis of the bands found in the visible and ultraviolet regions of the spectrum. These investigations have shown that the banded emission in these regions is due to OH, C_2, CH and perhaps CH_2 molecules in the flame. The spectra of the CO_2 and H_2O molecules have been found in the far infra-red $(1 - 7\mu)$ emission spectrum.[2] The photographs taken during the present investigation cover the relatively unexplored region of the spectrum extending from λ6500A. to λ10,200A.

EXPERIMENTAL

The source used in the present experiments was a bank of eight "Fisher" burners mounted in a line and fed with natural gas. The air inlets were adjusted to give a hot, non-luminous flame with a short, blue inner cone. Most of the photographs were taken using a Bausch and Lomb spectrograph, Littrow type, with a glass prism, and having a dispersion of about 40 Angstrom units per millimeter in the region around λ9500A. This spectrograph was not designed for use in the region of the spectrum beyond λ6800A, and so required special adjustments of the angle and distance between the prism face and plate holder to bring the region investigated into focus on the plate. The Barium spectrum, obtained from an arc between hollow carbon rods packed with $BaCl_2$, was used as a comparison spectrum on all plates taken with the prism

spectrograph. For high dispersion work the first order of a
6 meter focal length, concave grating having 15,000 lines to
the inch and a dispersion of approximately 2.4 A. per mm.
was used. In this case the second and third order iron arc
spectra were used for comparison. Photographs were taken
on Eastman Infra-Red spectroscopic plates supersensitized
in 4% ammonia solution. With the prism spectrograph, expo-
sure times varied from 2 to 12 hours. With the grating
spectrograph from 36 to 48 hours were required for a satis-
factory photograph.

RESULTS I

Photographs taken with the prism spectrograph showed
several strong bands in the region between $\lambda 7000$A. and 1.02μ.
Intense heads with bands extending away on the red side were
observed at $\lambda 7112$A., $\lambda 8919.2$A. and $\lambda 9280.5$A., and in addi-
tion several moderately intense bands with predominantly
strong Q branches were observed in the region between $\lambda 8000$A.
and $\lambda 8700$A. The bands at $\lambda 7112$A. and $\lambda 9280.5$A. were very
similar in appearance and more intense than the others.
Their rotational structure showed regularly spaced lines,
suggesting that a diatomic molecule was the emitter (see
Plate I). After measurement, however, they were identified
with bands appearing in the absorption spectrum of water vapor,
with centers at $\lambda 7228$A. and $\lambda 9420$A., respectively. The
regularity in the rotational structure is due to the pre-

dominant intensity of the close doublets arising from the

transitions $\begin{Bmatrix} (j+1)_{-(j+1)} \rightleftharpoons j_{-j} \\ (j+1)_{-j} \rightleftharpoons j_{-(j-1)} \end{Bmatrix}$, using asymmetrical top notation. (3)

The bands at λ8229A. and λ8919A. also were identi-
fied with known water vapor absorption bands. Mecke's
analysis of the absorption spectrum(4) shows bands with
centers at λ8227A. and λ9062A., and it is to these two
that the above mentioned bands correspond. In the present
case, since the bands are observed in emission and from
a relatively high temperature source, their general appear-
ance is quite different from the appearance of the same
bands observed in absorption. Transitions between
levels of high rotational energy occur, the band heads
appear and the centers of gravity of the bands have been
moved toward the red. The rotational structure of each
band extends over a region of the spectrum about three
times as great as that so far observed in absorption.

The bands near and including the one at λ8227A. are
of particular interest since some of them have been iden-
tified as arising from transitions not involving the
ground level. Table I gives the wave length, frequencies
and intensities of the main lines observed in this region.
In column four of Table I are given the assignments only
for the Q branches. Many of the other lines have been
identified with lines appearing in the absorption spec-
trum of the λ8227A. band.

Most of the frequencies given are the mean of measurements made on three different plates and have a probable error of about one wave number. Plate II shows the appearance of these bands as photographed with the prism spectrograph.

TABLE I

Summary of Main Lines Appearing on Low Dispersion Photographs Taken in the Region λ8000A. to λ8700A.

λ (A)	Estimated Intensity	ν (vac. cm.⁻¹)	Assignment
8043.2	1	12429	
8057.3	1	12408	
8072.1	4	12385	
8094.0	4	12351	
8109.7	4	12327	
8132.6	8	12293	
8196.9	4	12196	
8229.6	10	12148	121→000 (Q Branch)
8262.4	3	12100	
8293.0	7	12055	122→001 (Q Branch)
8319.3	1	12018	
8336.8	2	11992	
8358.5	5	11961	123→002 (Q Branch)
8385.4	1	11922	
8399.7	2	11902	
8419.2	2	11874	
8467.5	2	11807	
8485.5	2	11782	
8535.6	3	11712	
8550.6	2	11692	
8609.3	1	11612	
8631.5	2	11582	

Mecke's analysis of the 000→121 absorption band (see Mecke's paper[4] for the notation used in connection with the vibrational quantum numbers) shows several strong lines forming an intense Q branch at λ8227A. The strong

line at $\lambda 8229$ (see Table I) is consequently assigned to the
Q branch of the $121 \rightarrow 000$ emission band. The relatively
strong lines at $\lambda 8293A.$ and $\lambda 8358.5A.$ do not correspond
to lines observed in absorption spectra; since these lines
form, with the line at $\lambda 8229$, a series of three almost
equally spaced lines of regularly diminishing intensity
it is believed that they belong to the Q branches of bands
arising from transitions involving the same change in
quantum numbers (121) as the $\lambda 8229$ band but having differ-
ent initial and final states. The assignments made, as
shown in Table I, are to the transitions $122 \rightarrow 001$ and
$123 \rightarrow 002$.

From the wave length of these lines forming the
sequence $121 \rightarrow 000$, $122 \rightarrow 001$ and $123 \rightarrow 002$ we may obtain a
quantity involving three of the interaction constants
appearing in the energy equation for water.[5] This
equation is of the form

$$W(V_1 V_2 V_3) = X_0 + X_1 V_1 + X_2 V_2 + X_3 V_3 + X_{11} V_1^2 + X_{22} V_2^2$$
$$+ X_{33} V_3^2 + X_{12} V_1 V_2 + X_{13} V_1 V_3 + X_{23} V_2 V_3 \qquad (1)$$

where the X's are constants and the V's are the vibration
quantum numbers. From (1) we find

$$W(122 \rightarrow 001) - W(121 \rightarrow 000) = 2X_{33} + X_{13} + 2X_{23}$$

or, generally,

$$W\left[(V_1+1)(V_2+2)(V_3+2) \rightarrow V_1 V_2 (V_3+1)\right] - W\left[(V_1+1)(V_2+2)(V_3+1) \right.$$
$$\left. \rightarrow V_1 V_2 V_3\right]$$

$$= 2X_{33} + X_{13} + 2X_{23}$$

From Table I we obtain

$$W(123 \rightarrow 002) - W(122 \rightarrow 001) = 94 \text{ cm.}^{-1}$$

$$W(122 - 001) - W(121 - 000) = 93 \text{ cm.}^{-1}$$

$$\text{Mean} = 93.5 \text{ cm.}^{-1}$$

Whence, $2X_{33} + X_{13} + 2X_{23} = 93.5 \text{ cm.}^{-1}$

From a theoretical treatment of the vibrational spectrum of water, Bonner[5] obtains values of the interaction constants which yield for the same sum the value 97.8 cm.$^{-1}$. While the difference in these two values is greater than corresponds to the experimental error in the measurement of wave lengths, it is still small enough to be absorbed by changes of the order of 5% in each of the three constants involved. The near agreement of the sums seems to confirm the assignments given, and in addition would appear to indicate the general correctness of Bonner's treatment and to show with what accuracy the positions of bands arising from transitions between higher vibrational levels may be estimated by the use of his energy equation.

RESULTS II

Because of the large amount of rotational structure appearing in the emission spectrum it seemed of some interest to study one of the bands under high dispersion.

Consequently, the most intense, $\lambda 9420A.$, band was photo-
graphed in the first order of the 6 meter grating. The
photographs obtained are shown in Plates III and IV.
The figures below the strong lines are the values of j
for the final state in the transitions $\begin{cases} (j+1)_{-(j+1)} \rightleftharpoons j_{-j} \\ (j+1)_{-j} \rightleftharpoons j_{-(j-1)} \end{cases}$,

which give rise to these prominant lines. The wave lengths,
frequencies and estimated relative intensities of some
of the lines appearing in the band are given in Table II.
In column four of Table II are given the rotational quantum
number assignments for the strong lines. These assignments
were made by use of the approximate expression for the
notational energy of the nearly coincident pair of energy
levels, j_{-j} and $j_{-(j-1)}$,[6] taking for $z_0^{\prime}$ the value given
by Mecke.[4] Except for low j values, the frequencies cal-
culated by the approximate equation did not correspond to
the observed frequencies; the discrepancy was found to be
approximately proportional to j^2 (for the upper state),
so very little difficulty was had in making the assignments.
For lines with j less than 8, assignments have been made
by Mecke.

From the intensities of the close doublets arising
from the transitions $\begin{cases} (j+1)_{-(j+1)} \rightleftharpoons j_{-j} \\ (j+1)_{-j} \rightleftharpoons j_{-(j-1)} \end{cases}$, we may calculate the
effective "rotational" temperature of the excited water
molecules in the flame. The transitions correspond to the

TABLE II

Some Lines from the λ9420A. Water Vapor Band (Plate III)

λ (A)	Intensity	ν (vac. cm.$^{-1}$)	j_j -- j_k
9815.15	5	10185.54	$15_{-15,-14}$ - $16_{-16,-15}$
9814.20	3	10186.52	
9783.53	7	10218.46	$14_{-14,-13}$ - $15_{-15,-14}$
9781.26	2	10220.79	
9775.18	3	10227.12	
9775.13	4	10228.22	
9756.60	3	10246.66	
9753.16	6	10250.28	$13_{-13,-12}$ - $14_{-14,-13}$
9752.91	6	10258.48	
9728.95	2	10275.78	
9727.27	2	10277.56	
9723.77	6	10281.26	$12_{-12,-11}$ - $13_{-13,-12}$
9723.32	7	10281.74	
9719.20	3	10286.09	
9715.79	3	10289.70	
9709.57	3	10295.87	
9698.32	4	10308.24	
9697.39	3	10309.23	
9695.03	8	10311.74	$11_{-11,-10}$ - $12_{-12,-11}$
9694.79	8	10311.99	
9692.10	7	10314.85	
9687.36	6	10319.90	
9681.23	6	10326.44	
9671.40	5	10336.93	
9667.46	8	10345.91	$10_{-10,-9}$ - $11_{-11,-10}$
9665.98	3	10342.73	
9664.16	6	10344.68	
9656.46	3	10352.92	
9652.17	5	10357.53	
9649.73	6	10360.14	
9642.36	4	10368.06	
9640.83	9	10369.71	
9639.84	6	10370.26	
9636.05	7	10374.85	
9629.14	7	10382.30	
9624.70	4	10387.09	
9618.18	4	10394.13	
9616.47	6	10394.98	
9615.60	6	10296.92	
9615.18	6	10397.38	$8_{-8,-7}$ - $9_{-9,-8}$
9614.24	2	10398.39	
9610.21	5	10402.75	
9609.44	2	10403.58	
9604.70	8	10408.71	

TABLE II (Continued)

λ (A)	Intensity	ν (vac. cm.$^{-1}$)	$j_j\text{--}j_k$
9601.63	5	10412.04	
9595.42	5	10418.78	
9594.36	2	10419.93	
9591.42	6	10423.13	
9590.42	5	10424.21	$7_{7,-6} - 8_{-8,-7}$
9589.28	7	10425.45	
9581.29	4	10434.15	
9569.51	4	10446.99	
9468.88	5	10447.68	
9566.78	7	10449.97	$6_{-6,-5} - 7_{-7,-6}$
9564.22	4	10452.77	
9562.44	5	10454.72	
9556.47	5	10460.15	
9556.28	6	10461.46	
9553.47	6	10464.53	
9551.15	7	10467.07	
9544.11	6	10474.80	$5_{-5,-4} - 6_{-6,-5}$
9536.20	2	10483.48	
9533.94	2	10485.97	
9522.51	5	10498.56	$4_{-4,-3} - 5_{-5,-4}$
9507.91	7	10514.68	
9403.46	2	10519.60	
9500.62	6	10522.74	$3_{-2} - 4_{-3}$
9494.19	8	10529.87	
9487.47	2	10537.32	
9481.86	2	10543.56	$2_{-2} - 3_{-3}$
9480.58	6	10544.99	$2_{-1} - 3_{-2}$
9476.96	3	10549.02	
9474.70	7	10549.02	
9465.64	2	10561.63	
9461.43	6	10566.33	$1_{-1} - 2_{-2}$
9456.38	6	10571.97	
9454.25	2	10574.36	
9443.48	3	10586.42	
9442.59	4	10588.85	$0 - 1_{-1}$
9441.31	4	10587.41	
9430.72	1	10600.74	
9428.45	1	10603.29	
9427.11	1	10604.80	
9403.27	1	10631.68	
9390.12	1	10646.57	
9376.82	1	10661.67	
9374.86	1	10663.90	
9365.64	1	10674.40	
9360.80	2	10679.92	
9358.82	2	10682.18	
9354.46	2	10687.16	$4_{-4} - 3_{-3}$
9352.25	2	10689.68	
9351.36	2	10690.70	

TABLE II (continued)

λ (A)	Intensity	ν (vac. cm.$^{-1}$)	$j_j - j_k$
9350.55	2	10691.63	
9349.52	3	10693.56	
9348.56	2	10693.90	
9346.22	4	10696.58	
9345.69	4	10697.19	
9344.48	3	10698.57	
9343.75	2	10699.41	$5_{-5} - 4_{-4}$
9342.76	4	10700.54	
9341.16	4	10702.38	
9340.38	2	10703.27	
9339.56	2	10704.21	
9336.30	2	10707.95	
9335.80	3	10708.52	
9334.52	4	10709.99	
9333.75	4	10710.87	$6_{-6} - 5_{-5}$
9329.96	3	10715.22	

Some Lines from λ9420A. Water Vapor Band (Plate IV)

λ (A)	Intensity	ν (vac. cm.$^{-1}$)	$j_j - j_k$
9334.43	2	10710.09	
9333.76	5	10710.86	$6_{-6} - 5_{-5}$
9329.97	2	10715.21	
9322.72	3	10723.54	
9320.90	5	10725.64	
9317.02	5	10730.10	
9316.40	4	10630.82	
9315.34	5	10732.04	$8_{-8} - 7_{-7}$
9309.66	5	10738.59	
9308.27	8	10740.19	
9304.02	6	10745.10	
9301.22	6	10748.33	
9300.60	5	10749.05	
9295.24	7	10755.25	
9293.35	7	10757.43	
9291.66	5	10759.39	
9290.04	7	10761.27	
9289.15	4	10762.30	
9285.82	8	10766.16	
9285.16	5	10766.92	
9284.44	6	10767.76	
9282.44	7	10770.08	
9281.95	5	10770.65	
9279.99	6	10772.92	
9278.50	5	10774.65	
9277.82	6	10775.44	
9276.45	4	10777.03	
9269.30	2	10785.35	
9272.37	1	10781.77	
9266.47	2	10788.64	
9264.97	2	10790.39	
9253.89	2	10803.31	
9249.40	1	10808.55	

single transition $(j-1)_{(j-1)} \rightleftharpoons j_j$ in the symmetric top;
and since the doublets are unresolved for all but quite
low j values, it is assumed that the symmetric top intensity
formulas may be applied without serious error. Dennison[3]
gives the following formula for the intensity of an
emission line in the spectrum of a symmetric rotator:

$$I_{j'',\kappa''}^{j',\kappa'} = Rg_{j'\kappa'} \exp\left[-W_{j'\kappa'}/kT\right] (A_{j'',\kappa''}^{j',\kappa'})^2$$

Primes indicate quantities belonging to the upper state,
double-primes, quantities belonging to the lower state.
R is, to a first approximation, a constant for a given
band, $g_{j'\kappa'}$ is the quantum weight of the initial level,
$W_{j'\kappa'}$ is the energy of the rotator in the initial state and
$(A_{j'',\kappa''}^{j',\kappa'})^2$ is the probability of the transition in question.

$$g_{j\kappa} = (2j+1) \qquad \kappa = 0$$
$$g_{j\kappa} = 2(2j+1) \qquad \kappa \neq 0$$
$$(A_{j,j}^{j-1,j-1})^2 = (2j-1)/8(2j\,1)$$

For the P branch, the intensity of a line is given by

$$I_{j,j}^{j-1,j-1} = \frac{R(2j-1)^2}{4(2j+1)} \exp\left[-\sigma j(j-1) - \sigma\beta (j-1)^2\right] \qquad (1)$$

where, $\quad \sigma = \dfrac{hc(A\ B)}{2kT}$

$$\beta = \frac{2C}{(A\ B)} - 1$$

$$A = \frac{h}{8\pi^2 cI_A}; \qquad B = \frac{h}{8\pi^2 cI_B}; \qquad C = \frac{h}{8\pi^2 cI_C}$$

Where I_A , I_B and I_C are the three principal moments of inertia ($I_A < I_B < I_C$). In the above equations the quantity A, which appears in the symmetric rotator energy formula, has been replaced by the quantity $\frac{1}{2}(A+B)$ to which it corresponds in the asymmetric rotator.

Differentiating equation (1) with respect to j and solving for the temperature in terms of j_m, where j_m is the final j value for the line of maximum intensity, we obtain

$$\frac{dI_{j,j}^{j-1,j-1}}{dj} = \frac{R}{4}\left[\frac{(2j+1)4(2j-1) - 2(2j-1)^2}{(2j+1)^2}\right] \exp\left[-\sigma j(j-1) - \sigma(j-1)^2\beta\right]$$
$$- \frac{RC(2j-1)^2(j-1)}{(2j+1)(A+B)}\exp\left[-\sigma j(j-1)-\sigma\beta(j-1)^2\right] = 0$$

whence,
$$T = \frac{(2j_m-1)^2(j_m-1)(2j_m+1)}{4j_m(j_m+1) - 3}\cdot\frac{hcC}{k} \qquad (2)$$

The photometer record of the P branch shows the line of maximum intensity to be at $j = 10$. Substituting this value of j_m in equation (2) we obtain for the effective rotational temperature of the water molecule in the flame the value $T = 1990^{\circ}K$.

Since this value is in good agreement with values for the temperature of the Bunsen flame,[7] it is concluded that the water vapor is practically in thermal equilibrium with the flame.

As regards the relative value of absorption and emission methods of obtaining spectra in the photographic infra-red it is concluded that little real advantage over an absorption spectrum is got by obtaining the same spectrum in emission. With the best photographic plates obtainable at the present time, the general fog developed during the long periods of exposure required practically offsets any advantage gained in intensity of the bands themselves. However, due to their high temperature source, emission spectra do show transitions between higher vibrational levels in addition to large amounts of rotational fine structure involving high j values which are not readily obtained in absorption. For this reason emission spectra may offer particular advantages, especially for the study of the effect of high vibrational and rotational energy on the shape, size and bond force constants of molecules.

SUMMARY

The emission spectrum of the Bunsen flame has been investigated with low dispersion in the region $\lambda 6500A$. to $\lambda 10,200A$. Six bands have been observed in this region. Four of the bands have been identified with bands appearing in the absorption spectrum of water vapor. The bands at $\lambda 8293A$. and $\lambda 8359A$. previously have not been observed. They are also believed to be water vapor bands and are thought to arise from transitions not involving the ground

level. With data obtained from the positions of these
two bands and a third one at λ8229A., a calculation is
made of a quantity involving three of the interaction
constants appearing in the energy equation for water.
The value obtained differs by about 5% from the value got
using the interaction constants calculated by Bonner.

The band at λ9420A. has been photographed with
high dispersion. From the distribution of intensities
in the band, an estimate of the "rotational" temperature
of the water molecules in the flame is made. The temper-
ature obtained, $1990^{\circ}K$, leads to the conclusion that the
water is effectively in thermal equilibrium with the
flame.

Finally, it is concluded that in general emission
spectra in the photographic infra-red show little improve-
ment over the same spectra obtained in absorption. However,
since emission spectra show transitions between high
vibrational and rotational levels, they may find parti-
cular use in the study of the effect of vibrational and
rotational energy on the physical constants of molecules.

PLATE I
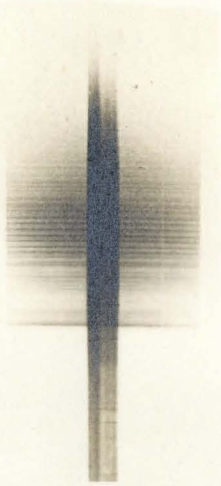λ9420A. Water Vapor Band
Low Dispersion

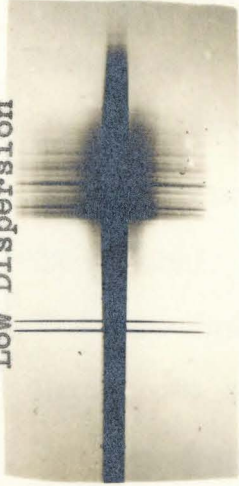PLATE II
Bands Near λ8300A.
Low Dispersion

PLATE III
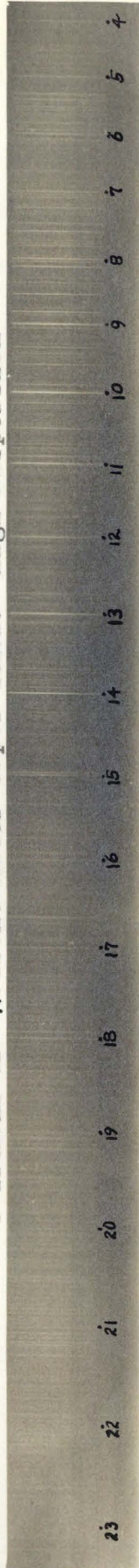P Branch of λ9420A. Water Vapor Band. High Dispersion

PLATE IV
λ9420A. Water Vapor Band. High Dispersion

REFERENCES

1. Bonhoeffer and Hale; Z. Phy. Chem., **A** <u>137</u>, 263 (1928); Grenat, Compt. Rendus, <u>192</u>, 1553 (1931); Rassweiler and Withrow, Jour. Ind. and Eng. Chem., <u>23</u>, 539, 769 (1931); <u>24</u>, 528 (1932).

2. Bailey, Trans Faraday Soc., <u>25</u>, 29 (1929); <u>25</u>, 32 (1929).

3. See Dennison, Rev. Mod. Phy., <u>3</u>, 280 (1931).

4. Mecke, et al, Zeit. Phy., <u>81</u>, 313, 445, 465 (1933).

5. Bonner, Phys. Rev., <u>46</u>, 458 (1934).

6. Mecke, Ref. 4, and Cross, Phys. Rev. <u>47</u>, 7 (1935).

7. Griffiths and Awbery, Proc. Roy. Soc., **A** <u>123</u>, 401 (1929). These investigators have made an extensive study of Bunsen flame temperatures. Using several different methods of measurement they find maximum flame temperatures ranging from 2003 to 2106°K.

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