

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

The Effect of Temperature and Pressure on the Solubility of Chlorine Monoxide in Water

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Chlorine monoxide dissolves in water to form hypochlorous acid according to the equation $\text{Cl}_2\text{O}(\text{g}) + \text{H}_2\text{O} = 2\text{HOCl}(\text{aq.})$. Since this equilibrium is involved in a process which is being used commercially to prepare hypochlorous acid, it is desirable that the solubility of chlorine monoxide be known.

Data of this type now in the literature are those of Ourisson and Kastner,² who used a dynamic method to measure the partial pressure of chlorine monoxide over dilute hypochlorous acid at 10 and 20°. Due to the fact that their determinations are of limited extent the work described in this paper is presented. Ourisson and Kastner believe that their experiments indicate the presence of molecules of both hypochlorous acid and chlorine monoxide in the gaseous phase. This point of view is difficult to maintain, however, in view of the fact that even solid hypochlorous acid cannot be prepared at low temperatures.³ Instead, one obtains liquid chlorine monoxide and

either solid $\text{HOCl}\cdot 2\text{H}_2\text{O}$ or a concentrated aqueous solution of the acid. Probably in a gas of low chlorine monoxide content, substantially no hypochlorous acid could be present. In this paper the authors assume hypochlorous acid and all hydrates of chlorine monoxide to be absent from the vapor phase.

Experimental

An apparatus was used in which equilibrium could be established between the solution of hypochlorous acid and the gas phase above it at a constant temperature. A measured volume of the gas was then removed for analysis, and the composition of the solution was determined. The apparatus devised for this purpose is shown diagrammatically in Fig. 1. It consisted of two Pyrex glass bulbs, B_1 and B_2 , connected by 6-mm. glass tubing as shown. The bulbs were of about 300 ml. and 250 ml. capacity, respectively, and the volume of B_2 between stopcocks S_2 and S_3 was accurately known as a result of careful calibration. Outlet A was equipped with a sealed cap. Tubes C and D were of 10 mm. inside diameter and C was closed with a ground glass plug. The apparatus was mounted on a bakelite panel equipped so that the entire assembly could be rotated in a thermostat.

Hypochlorous acid was introduced through C. Outlet tubes were then closed, and the apparatus was placed in the thermostat regulated to the desired temperature. The volume of acid used varied only between narrow limits. Enough was needed to fill completely bulb B_2 but not B_1 . Tube D was tightly closed with a stopper while equilibrium was being attained. During this time stopcock S_4 was open and stopcock S_2 was turned so that the solution and gas could flow from one bulb to the other, but tube D was closed at each end. The apparatus was rotated in the thermostat and was raised occasionally to permit the release of pressure by opening outlet A. In this manner the solution and gas flowed from one bulb to the other and were shaken together until equilibrium was established, usually within twenty to ninety minutes, the solutions of high concentration and temperature requiring the longest time. Rotation of the apparatus was continued for from ten to fifteen minutes after the system had apparently reached equilibrium, as evidenced by the failure of gas to escape upon opening tube A. At the highest concentrations used, however, a little gas always escaped even after rotating the apparatus for a long time. This effect was probably due to decomposition of the acid.

To permit removal of the gas sample for analysis, the apparatus was turned so that the liquid drained from bulb B_2 into B_1 . The apparatus was then shifted to a new position such that the liquid from bulb B_1 just reached stopcock S_3 . This stopcock and S_2 were then closed, the apparatus was placed in an upright position and raised in

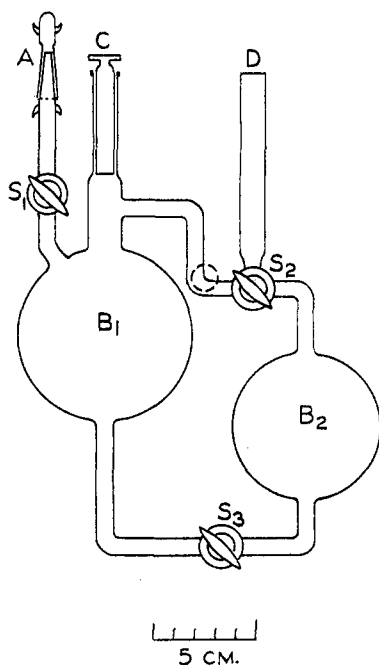


Fig. 1.—The vapor pressure apparatus.

- (1) Present address: University of Oregon, Eugene, Oregon.
- (2) Ourisson and Kastner, *Bull. Soc. Chim. Memoirs*, **6**, 1307 (1939).
- (3) Secoy and Cady, *THIS JOURNAL*, **62**, 1036 (1940).

the thermostat until the three outlet tubes were above the surface of the water. Tube D was then wiped dry and the absorption train was placed in the proper position for sampling. The absorption train consisted of two 250-cc. Erlenmeyer flasks connected in series with rubber stoppers and glass tubing. The outlet from the second flask was connected to an aspirator so that air could be drawn through solutions of potassium iodide held in the flasks. As a sample was collected the 6-mm. glass tube from the absorption train was inserted far into tube D but not to the bottom. These tubes fitted loosely so that a slow stream of air could be drawn from the outside into D and then back through the train without reducing the pressure on the gas sample escaping from the bulb. With the absorption train in place, cap A was removed, and stopcocks were opened in the order, S_1 , S_2 (from B to D), S_3 . The liquid entering B_2 from B, forced the gas up into D from which it was removed by the air stream into the absorption flasks. When the level of the liquid rose to S_2 , this stopcock was closed and the train was removed. The amount of chlorine monoxide present in the gas sample of known volume was then determined by titration of the iodine liberated in the flasks. Very little was set free in the second flask.

A 1-to-2-g. sample of the liquid was removed by means of a pipet through tube C and added to water in a weighed 50-ml. volumetric flask. By reweighing the flask the weight of the sample taken was determined. The flask was then filled with water to the mark and an aliquot part was taken for analysis.

Temperatures below 15° were maintained by placing a small wire basket or metal box containing ice in one corner of the thermostat. Higher temperatures could be maintained by properly adjusting the flow of water into and from the thermostat. All of the temperatures were carefully checked by means of the thermocouple described elsewhere by the authors.³

The inside of tube D was kept dry, for a drop of the solution at this point would release enough chlorine monoxide during the taking of the gas sample to alter the results materially. The film of solution which clung to the walls of bulb B_2 had no such effect since the gas sample was pushed from the bulb by the inflowing solution and not swept out. The rate of flow of air through the absorption flasks was rapid enough to avoid the loss of any of the sample but slow enough to prevent a harmful reduction of the pressure in bulb B_2 .

The method of analysis used for the gas samples was essentially the same as that described by Spinks⁴ for the determination of both free chlorine and chlorine monoxide. This method is based upon the fact that chlorine liberates iodine from potassium iodide with no change in the hydrogen ion concentration while chlorine monoxide and hypochlorous acid use up hydrogen ion as iodine is liberated. When determining chlorine monoxide of high concentration, an aliquot part of the solution from the absorption train was taken for analysis and 0.1 *N* solutions were used for the titrations. Dilute samples of the gas contained only a little chlorine monoxide but a moderate amount of chlorine; therefore, the entire solution from the absorption train was titrated. A measured quantity of 0.01 *N* hydrochloric acid was added, then 0.1 *N* sodium thiosulfate was

run in until nearly all of the iodine had been reduced. The final end-point was reached using 0.01 *N* sodium thiosulfate and the same reagent was used to determine the excess hydrogen ion. This procedure in effect determined the chlorine with 0.1 *N* and the chlorine monoxide with 0.01 *N* reagents.

The method of analysis of the liquid samples was the same except that an aliquot part was used in each case and 0.1 *N* solutions were always employed. Another portion was used for the determination of chloric acid, a strong acid which, if present, would furnish part of the hydrogen ion used by hypochlorous acid in oxidizing the iodide ion to free iodine. An excess of standard arsenious acid was added to the sample and the unused reducing agent was titrated hot with standard potassium bromate using the bleaching of methyl orange as an indication that the end-point had been reached. Arsenious acid reduces chlorine, hypochlorous acid, and chloric acid. Since the amount of chlorine and hypochlorous acid combined was known from the previous titration, the oxidizing equivalents of chloric acid present could be calculated and the proper correction made for the acid equivalents of chloric acid in the calculation of the hypochlorous acid content.

Little or no chloric acid was found in solutions which had been freshly prepared; however, solutions which had been used for several determinations at the higher temperatures contained appreciable amounts.

Results

The partial pressures of the chlorine monoxide

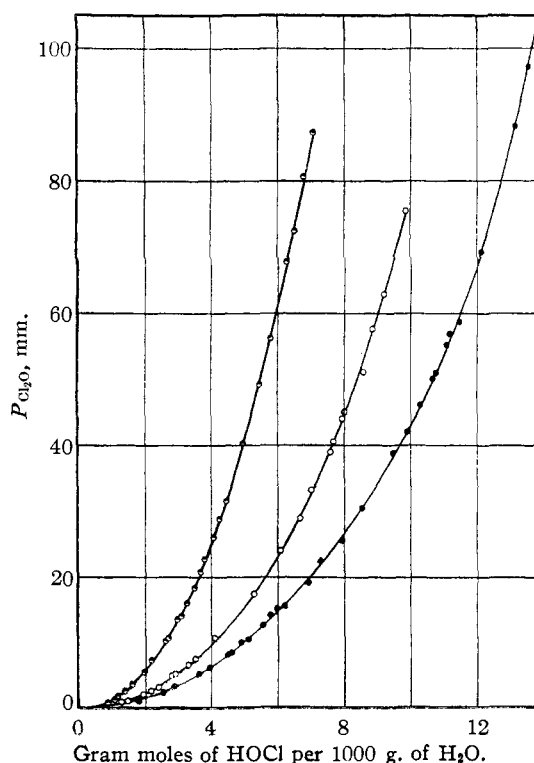


Fig. 2.—Vapor pressure curves for chlorine monoxide: ●, represents points at 3.46° ; ○, at 9.92° ; and ◐, at 19.98° .

(4) Spinks, *THIS JOURNAL*, **53**, 3015 (1931).

were calculated from the analyses by use of the ideal gas equation. The data are tabulated in Table I, and the relationship of pressure to concentration is shown graphically in Fig. 2.

TABLE I
PARTIAL PRESSURES OF CHLORINE MONOXIDE

m , g. moles HOCl per 1000 g. H ₂ O	$P_{\text{Cl}_2\text{O}}$, mm.	K'	m , g. moles HOCl per 1000 g. H ₂ O	$P_{\text{Cl}_2\text{O}}$, mm.	K'
At 3.46°					
1.76	1.27	0.411	3.48	7.58	0.626
2.49	2.54	.409	4.16	10.88	.629
2.84	3.40	.422	5.25	17.53	.636
3.60	5.31	.410	6.04	24.04	.659
3.89	6.31	.417	6.64	29.10	.660
4.48	8.27	.412	6.99	33.27	.681
4.57	8.46	.405	7.53	39.12	.690
4.88	10.10	.424	7.64	40.92	.701
5.07	10.62	.413	7.89	44.20	.710
5.51	12.87	.424	8.00	45.12	.705
5.76	14.47	.436	8.42	51.33	.724
5.97	15.36	.431	8.81	57.83	.745
6.18	15.81	.414	9.14	62.99	.754
6.90	19.33	.406	9.84	75.62	.781
7.25	22.86	.435	At 16.00°		
7.91	25.78	.412	5.50	33.66	1.112
8.50	30.71	.425	5.41	32.48	1.111
9.48	39.00	.434	5.40	32.38	1.109
9.89	42.26	.432	At 19.98°		
10.28	46.29	.438	0.861	1.11	1.49
10.65	50.02	.441	1.02	1.55	1.49
10.75	51.10	.443	1.13	1.92	1.50
11.08	55.37	.451	1.35	2.72	1.50
11.11	57.02	.462	1.57	3.73	1.51
11.49	58.88	.446	1.92	5.61	1.52
12.13	69.16	.470	2.16	7.13	1.53
13.14	88.40	.512	2.58	10.29	1.55
13.56	97.27	.529	2.64	10.78	1.55
14.95	126.1	.564	2.98	13.83	1.56
17.64	178.0	.572	3.03	14.41	1.57
19.95	247.6	.622	3.22	16.35	1.57
At 6.00°					
5.61	15.70	0.498	3.42	18.60	1.59
5.54	15.17	.494	3.61	20.93	1.61
5.52	15.22	.499	3.77	22.82	1.60
At 9.92°					
1.22	0.918	0.617	4.01	26.18	1.62
1.44	1.37	.661	4.22	29.00	1.63
1.89	2.24	.627	4.42	31.67	1.62
2.12	2.84	.633	4.92	40.61	1.68
2.38	3.46	.611	5.40	49.48	1.70
2.76	5.09	.668	5.74	56.31	1.71
2.88	5.29	.638	6.23	67.88	1.75
3.26	6.71	.631	6.49	72.58	1.73
			6.80	80.82	1.75
			7.01	87.49	1.78

The experimental values of Table I have been used to estimate the solubility of chlorine monoxide at 0, 10 and 20° to be as indicated in Table II.

TABLE II
SOLUBILITY OF CHLORINE MONOXIDE, G. Cl₂O/100 G. H₂O

$P_{\text{Cl}_2\text{O}}$, mm.	t , °C.		
	0°	10°	20°
1	7.6	5.2	3.5
5	16.7	12.3	8.0
10	23.7	17.4	11.1
20	33.6	24.2	15.4
30	40.7	29.2	18.7
40	46.9	33.0	21.3
50	52.4	36.2	23.7
60	56.7	39.0	25.8
70	60.2	41.4	27.7
75	61.6	42.5	28.6

Discussion

From the equilibrium $2\text{HOCl}(\text{aq}) = \text{Cl}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{l})$, the equilibrium constant may be expressed by the equation

$$K = P_{\text{Cl}_2\text{O}} \times a_{\text{H}_2\text{O}} / (a_{\text{HOCl}})^2$$

If the activity of the water is neglected and the molal concentration of the hypochlorous acid, m , is used instead of its activity, we have, $K' = P_{\text{Cl}_2\text{O}}/m^2$. The calculated values of K' given in the tables do not remain constant for any one temperature but, when plotted against the molality, lie on a smooth curve which, when extrapolated to infinite dilution, gives the value of the true equilibrium constant, K . These curves and their extrapolations are shown in Fig. 3, and the values of K are given in Table III.

TABLE III
VALUES OF THE EQUILIBRIUM CONSTANT, K

Temp., °C.	K
3.46	0.41 ± 0.01
6.00	.48 ± .01
9.92	.62 ± .01
16.00	1.01 ± .01
19.98	1.47 ± .01

The data of this research are in good agreement with those of Ourisson and Kastner² at their higher concentrations. Their measurements were made at 10 and 20° using solutions ranging in concentration from 0.15 to about 2.5 gram moles of hypochlorous acid per 1000 g. of water. At concentrations below about 0.75 molal their data for the equilibrium pressures of chlorine monoxide are erratic, and values of K' as calculated in this paper increase rapidly as the concentration decreases. Since K' should approach a constant value at infinite dilution, this behavior makes it appear that their pressures are too high at the lower concentrations.

If the densities of solutions of hypochlorous

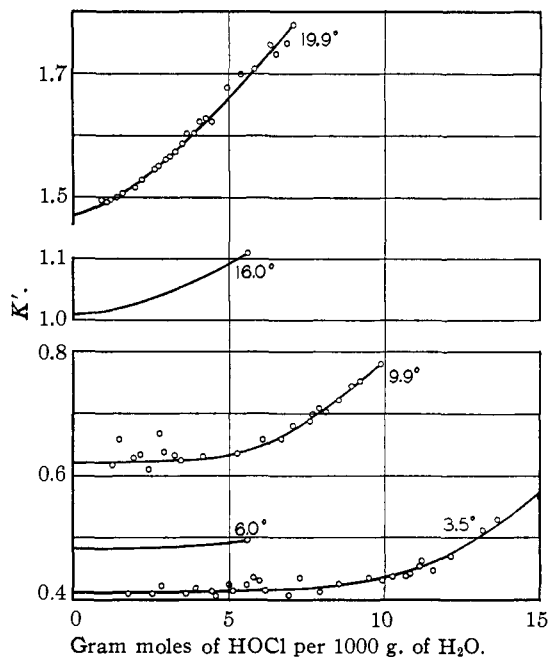
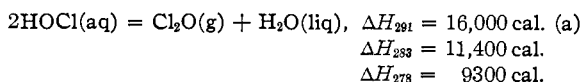


Fig. 3.—Graph of K' against molality, m , for the evaluation of the true equilibrium constant, K .

acid were known, it would be possible to compare the values in the 0° column of Table II with solubilities which might be estimated by combining the data of Goldschmidt^{5a} with those of Yost and Felt.^{5b} The former determined the distribution of chlorine monoxide between water and carbon tetrachloride at 0° , his concentrations being expressed in gram moles per liter, while the latter authors determined the solubility of gaseous chlorine monoxide, expressed as mole fraction, in carbon tetrachloride at 0 and at 25° . If one assumes that one liter of hypochlorous acid contains 1000 g. of water and that one liter of the carbon tetrachloride solution contains 1632 g. of the solvent, he finds that the value of K at 0° is about 0.48. The fact that this is not in harmony with the data of Table III is at least in part due to errors in the above assumptions.

Using the equation, $R \, d \ln K / d(1/T) = -\Delta H$, the heat of the reaction can be calculated from the slope of the curve in Fig. 4.



The "International Critical Tables"⁶ give the

(5) (a) Goldschmidt, *Ber.*, **52B**, 753 (1919); (b) Yost and Felt, *This Journal*, **56**, 68 (1934).

(6) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., Vol. V, 1928, p. 176; J. Thomsen, "Systematisk gennemførte termokemiske undersøgelseres numeriske og teoretiske resultater," (1882-1886).

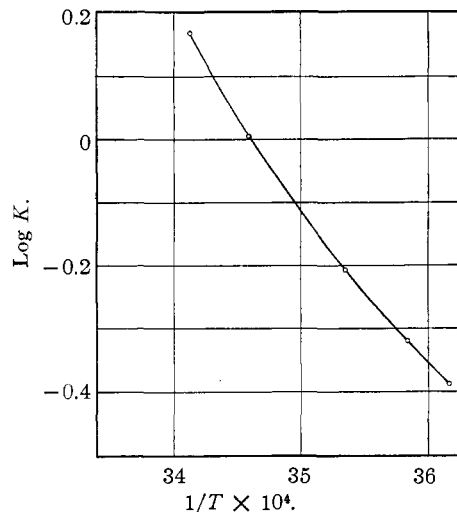


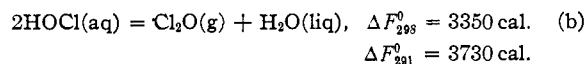
Fig. 4.—The variation of $\log K$ with the reciprocal of the temperature.

value 9439 cal. for the heat of solution of chlorine monoxide at 18° , while Neumann and Müller⁷ obtained 8737 cal., by a calorimetric method. In the latter case the temperature was not specified. The large increase in ΔH with temperature, indicated by the present research, causes one to doubt the accuracy of both the calculated pressures of chlorine monoxide and the equilibrium constants. In spite of the fact that the experimental work was performed carefully and the results obtained were reproducible, it is possible that the pressures as given in the tables are incorrect. Perhaps the assumptions involved in the calculations were not all justified. It seems more probable, however, that the mistake, if one actually was made, was a systematic error in the determination of the concentration of gaseous chlorine monoxide. The titrations may have failed to indicate the correct values, particularly at low pressures of the gas. Under the circumstances, it appears that the question should be settled by making accurate calorimetric determinations of the heat of solution of chlorine monoxide at several different temperatures. Such data together with a value of unquestionable accuracy for the heat of formation of chlorine monoxide would remove uncertainties regarding a number of thermodynamic constants for hypochlorous acid and chlorine monoxide. The present unsatisfactory state of affairs is indicated by the discussion which follows. It is evident that the calorimetric data and those resulting from equilibrium measurements can be reconciled only by further research.

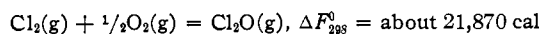
(7) Neumann and Müller, *Z. anorg. Chem.*, **182**, 245 (1929).

The commonly accepted value for the heat of formation of liquid water at 18° is $\Delta H = -68,387$ cal.⁶ Perhaps the best data regarding the heat of formation of HOCl(aq) are those of Neumann and Müller,⁷ who report that, presumably at room temperature, ΔH is $-30,439$ cal. By combining these quantities with ΔH_{291} for equation (a) one finds that for the formation of one mole of gaseous Cl₂O, ΔH is about 23,500 cal. Among the other values for this quantity which have resulted from calculations using the heats of several reactions are 18,260 cal.,⁶ 16,239 cal.,⁷ 18,000 cal.,⁸ 15,800 cal.⁹ Each of these determinations involves the use of a value for the heat of solution of chlorine monoxide in the neighborhood of 9000 cal. By measuring the amount of heat liberated as chlorine monoxide explodes, ΔH has been found to be $20,050 \pm 1000$ cal.,¹⁰ $21,735 \pm 560$ cal.,¹¹ or $25,100 \pm 100$ cal.⁷

By making use of the equation, $\Delta F^0 = -RT \ln K$, ΔF^0 may be evaluated by obtaining K from the graph in Fig. 4. In order that the materials in the reaction may each be in their standard state at one atmosphere pressure, K must first be divided by 760. The following free energy equation is obtained



Values given by Lewis and Randall¹² for the free energy of formation of HOCl(aq) and H₂O(liq) at 25° are $-19,018$ cal. and $-56,560$ cal., respectively. By combining these values with equation (b) one obtains



Yost and Felt^{5b} obtained 21,207 cal. Their value is probably in error, for it requires that K (see Table III) at 25° be 8.2.

Yost and Felt used the value of Giaque and

(8) J. Thomsen, "Thermochemistry," 1908.

(9) Berthelot, "Thermochem. Messungen," Leipzig, 1893.

(10) H. Mayer, Dissertation, Hannover, 1924.

(11) Wallace and Goodeve, *Trans. Faraday Soc.*, **27**, 648 (1931)

(12) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, pp. 485, 508.

Overstreet¹³ for the standard entropy of chlorine, 53.31 cal. per degree, and that of Johnston and Walker¹⁴ for oxygen, 49.02 cal. per degree, to calculate the entropy of chlorine monoxide gas at 25° and one atmosphere to be 67.9 cal. per degree. If the values $\Delta F_{298}^0 = 21,870$ cal., and $\Delta H = 23,500$ cal., are employed in place of their data, the entropy of chlorine monoxide gas is found to be 83.3 cal. per degree. This discrepancy is due, for the most part, to the difference in the ΔH values employed. The establishment of the correct value apparently must wait for more accurate determinations of the heats of formation of chlorine monoxide and hypochlorous acid. In private correspondence Yost has pointed out that molecular data indicate approximately 73 cal./degree as the maximum magnitude of S_{298}^0 .

Summary

The solubility of gaseous chlorine monoxide in water has been measured over a range of pressures and at temperatures of 3.46 to 19.98°. Since the pressure of the gas was determined by an indirect and complicated method, it is possible that the data, particularly the low pressures, may be erroneous in a systematic way. Values of the equilibrium constant for the reaction $2\text{HOCl(aq)} = \text{Cl}_2\text{O(g)} + \text{H}_2\text{O(liq)}$ have been estimated. A plot of $\log K$ against $1/T$ indicates that the heat of solution of chlorine monoxide increases rapidly with the temperature passing from 9300 cal. at 5°, to 16,000 cal. at 18°. This change is difficult to believe, and it makes one feel that the heat of the reaction should be determined calorimetrically at several temperatures.

Using heats of solution estimated from the curve, together with various data already in the literature, several thermodynamic constants of chlorine monoxide and hypochlorous acid have been calculated. The values should not be regarded as final.

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(13) Giaque and Overstreet, *THIS JOURNAL*, **54**, 1731 (1932).

(14) Johnston and Walker, *ibid.*, **55**, 172 (1933).