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The Thermodynamic Constants of Chlorine Monoxide

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Introduction

The determination of the free energy and entropy of such unstable substances as chlorine monoxide is best made indirectly since measurable decomposition equilibria can be attained only at inconveniently high temperatures. Moreover, the fact that chlorine monoxide is explosive and is decomposed by light would doubtless give rise to difficulties in specific heat measurements undertaken with the view of applying the third law. There do not exist at present sufficient spectroscopic data to make possible a direct calculation of the entropy and free energy, although such information would be desirable and should not be too difficult to obtain.

In the present investigation the following reversible reactions have been employed in evaluating the thermodynamic constants of chlorine monoxide: (1) the hydrolysis of chlorine to form hypochlorous and hydrochloric acid; (2) the dissociation of hypochlorous acid into water and chlorine monoxide in aqueous solution; (3) the distribution of the monoxide between water and carbon tetrachloride; and (4) the partial vapor pressure of the monoxide above its carbon tetrachloride solutions. Reliable data already exist for all of the reactions except the last, and the results of the necessary measurements on it are presented in this paper together with the calculations involving the other three.

Experimental

The vapor pressures of chlorine monoxide above its carbon tetrachloride solutions were determined by a dynamic method already described in a previous paper.[1]

Solutions of chlorine monoxide in carbon tetrachloride were prepared by treating a solution of chlorine in this solvent with finely divided mercuric oxide. The unattacked mercuric oxide and mercuric chloride settled rapidly and were removed by repeated decantations. The monoxide was determined by allowing its solutions or the gas to react with solutions of potassium iodide containing a known amount of hydrochloric acid. The liberated iodine was first titrated with standard thiosulfate, and then an excess of potassium iodate was added and the resulting iodine, equivalent to the amount of acid remaining, was again determined as before. The amount of acid consumed was regarded as the true measure of the chlorine monoxide present. Separate experiments established the absence of chlorine dioxide, and since the solutions were kept in the dark, the photochemical formation of this substance was avoided.[2] Fresh solutions were frequently prepared.

Results of the Vapor Pressure Measurements

The partial vapor pressures of chlorine monoxide above its carbon tetrachloride solutions were determined at 25.0 and at 0.0°. The results are presented in Table I, together with the constants of Henry's law $p_{\text{mm.}}/N = H$. All concentrations in the table are given in mole fractions and the pressures in millimeters of mercury.

TABLE I

THE PARTIAL VAPOR PRESSURES OF CHLORINE MONOXIDE ABOVE ITS CARBON TETRACHLORIDE SOLUTIONS

Mole fraction Cl_2O, N	Pressure of Cl_2O, $p_{\text{mm.}}$	$H = p_{\text{mm.}}/N$
Temperature 25.0°		
0.00670	12.16	1800
.00585	11.44	1960
.00545	9.62	1770
.00474	8.44	1780
.00421	7.31	1740
.00363	6.60	1820
.00324	5.81	1790
.00320	5.75	1800
.00301	5.67	1880
.00298	5.47	1840
.00283	5.16	1820
.00272	4.33	1590
0.00260	5.44	2090
.00236	4.75	2010
.00135	2.42	1790
	Mean	1830
Temperature 0.0°		
.00434	3.01	694
.00290	2.08	654
.00165	1.10	669
.00163	1.11	681
.00107	0.658	615
	Mean	662

As the results in the table show, Henry's law is obeyed over a rather wide range of concentrations.

To simplify the subsequent calculations it is convenient to change the standard state from unit mole fraction to unit concentration in moles per liter of carbon tetrachloride. By making use of the well-known relation $\Delta F^\circ = -RT \ln K$, and the results given in the table, after converting to the new units, the following equation may be derived

$$Cl_2O(g) = Cl_2O(\text{in } CCl_4),\ \Delta F^\circ_{298} = -864 \text{ cal.},\quad \Delta H^\circ = 6590 \text{ cal.} \qquad (1)$$

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[1] Blair and Yost, THIS JOURNAL, **55**, 4489 (1933).

[2] Dickinson and Jeffreys, *ibid.*, **52**, 4288 (1930).

The Free Energy and Entropy of Chlorine Monoxide Gas

Lewis and Randall[3] have recalculated the results of Jakowkin on the hydrolysis of chlorine and find the value 1.45×10^{-4} for the constant at 0.0°. Therefore

$$Cl_2(Aq) + H_2O(l) = H^+ + Cl^- + HClO \qquad \Delta F^\circ_{273} = 4797 \text{ cal.} \quad (2)$$

From the data given by the "International Critical Tables,"[4] and by Jakowkin, the free energies of formation of $H_2O(l)$, $HCl(Aq)$ and $Cl_2(Aq)$ at 0.0° were calculated to be −57,548 cal., −32,007 cal., and 1010 cal., respectively. These values, combined with equation (2), lead to the following result

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) + \tfrac{1}{2}O_2(g) = HClO(Aq) \qquad \Delta F^\circ_{273} = -19{,}730 \quad (3)$$

The dissociation of aqueous hypochlorous acid into water and chlorine monoxide was determined at 0.0° by Goldschmidt, and his results were subjected to a critical analysis by Roth.[5] We have chosen to use the results of Roth's calculations without modification

$$2HClO(Aq) = Cl_2O(Aq) + H_2O(l)$$

$$K = \frac{(Cl_2O(Aq))}{(HClO)^2} = \frac{1}{282} \quad (4)$$

$$Cl_2O(Aq) = Cl_2O(\text{in } CCl_4)$$

$$R = \frac{(Cl_2O(\text{in } CCl_4))}{(Cl_2O(Aq))} = 2.22 \quad (5)$$

By making a simple calculation and combining with equation (3) there results

$$Cl_2(g) + \tfrac{1}{2}O_2(g) = Cl_2O(\text{in } CCl_4) \qquad \Delta F^\circ_{273} = 20{,}712 \text{ cal.} \quad (6)$$

It has been assumed throughout that the activities of all solutes could be replaced by their concentrations. Due to the fact that only dilute solutions or non-ionizing solutes are involved the assumption appears to be justified. The free energy of reaction (6) is believed to be in error by less than 1000 cal.

The heat of formation of chlorine monoxide gas is given as −18,260 cal. in the "International Critical Tables."[6] When to this value is added the heat of solution, −6590 cal., of the monoxide in carbon tetrachloride, there is obtained 24,850 cal. for the change in heat content attending reaction (6). The final free energy and heat content equation for 25° becomes, then, as follows

$$Cl_2(g) + \tfrac{1}{2}O_2(g) = Cl_2O(g) \quad \Delta F^\circ_{298} = 21{,}207 \text{ cal.} \qquad \Delta H = 18{,}260 \text{ cal.} \quad (7)$$

If Giauque and Overstreet's[7] value for the standard entropy of chlorine, 53.31 cal./deg., and that of Johnston and Walker[8] for oxygen, 49.02 cal./deg., are assumed, the entropy of chlorine monoxide gas at 25° and one atmosphere becomes 67.9 cal./deg.

The heat of formation of chlorine monoxide has been redetermined recently by Günther and Wekua[9] by an explosion method, as −25,100 cal. If their value is used the standard entropy of chlorine monoxide gas becomes 93.0 cal./deg. at 25°. Inasmuch as the contribution of the energy of vibration is certainly small,[10] and since the assumption of very conservative moments of inertia leads to an entropy considerably lower than 93.0 cal./deg., it must be concluded that Günther and Wekua's value for the heat of formation is in error by being too large.

Summary

The partial vapor pressures of chlorine monoxide above its carbon tetrachloride solutions have been measured at 25.0 and at 0.0°, and the corresponding constants of Henry's law found to be $p_{\text{mm.}}/N = 1830$ and 662, respectively.

The results of the experiments when combined with those of other investigators lead to the free energy equation $Cl_2(g) + \tfrac{1}{2}O_2(g) = Cl_2O(g)$ $\Delta F^\circ_{298} = 21{,}210$ cal. If the heat of formation of chlorine monoxide given in the "International Critical Tables," −18,260 cal., is assumed to be correct, the entropy of chlorine monoxide gas at 25° and one atmosphere becomes 67.9 cal./deg.

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[3] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 508; Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899).

[4] "International Critical Tables," McGraw-Hill Book Co., New York, 1930, Vol. 7, pp. 232, 233; Vol. 5, p. 176.

[5] Roth, *Z. physik. Chem.*, **A145**, 289 (1929); S. Goldschmidt, *Ber.*, **52**, 753 (1919). For comments on hypochlorous acid in solution see also W. A. Noyes, THIS JOURNAL, **44**, 1630 (1922).

[6] "International Critical Tables," Vol. 5, p. 176.

[7] Giauque and Overstreet, THIS JOURNAL, **54**, 1731 (1932).

[8] H. L. Johnston and M. K. Walker, *ibid.*, **55**, 172 (1933).

[9] Günther and Wekua, *Z. physik. Chem.*, **A154**, 193 (1931).

[10] Bailey and Cassie, *Nature*, **129**, 652 (1932), give the fundamental frequencies of chlorine monoxide as 639,973 and 1245 cm.$^{-1}$.