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Solubility of Chlorine in Hydrochloric Acid*[1]

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The solubility of chlorine in a concentrated HCl solution at various conditions of concentration, partial pressure, and temperature was determined. The concentration of chlorine in a solution as the sum of Cl_2 and Cl_3^- was found to be proportional to the partial pressure of chlorine in the gas phase, and its slope was a function of the HCl concentration and the temperature. Empirical equations representing these relations and the solubility of chlorine were obtained. It was confirmed that the results agreed with the experimental data in the 2—10 N HCl concentration range at partial pressures of chlorine lower than 1 atm and at 30—90°C. Such physicochemical properties as the Gibbs free-energy change were considered by using the data of solubility, and the behavior of the system consisting of Cl^-, Cl_2, and Cl_3^- was discussed.

The solubility of chlorine in water or in an aqueous solution of sodium chloride under various conditions has been studied by several authors previously,[1-3] but only a few results in an HCl solution at room temperature have been obtained.[4,5]

Today, many chlorine engineers are concerned with the recovery of chlorine from by-products or waste HCl, and they require more information and data on such properties of chlorine in an HCl solution as solubility.[6]

Experimental work was carried out at various conditions of temperature, concentrations and partial pressure, then some characteristic values, such as the Henry coefficient and the free energy, were evaluated from the solubility data thus obtained.

Experimental Procedure

The apparatus employed was essentially the same as that of Whitney and his collaborator,[2] who determined the solubility of chlorine in water with well-designed equipment, though we made some modifications for our own convenience.

The flow diagram is shown in Fig. 1. The absorption chamber and the gas pre-treatment system were set in a water bath so as to keep it at a constant temperature of ±0.1°C during the experiment.

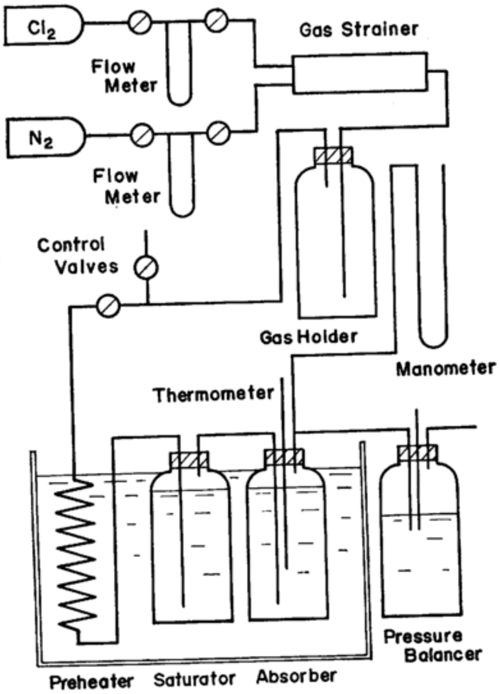

Fig. 1. Apparatus for experiment.

Chlorine and nitrogen from the cylinders were delivered to the gas strainer, which was packed with glass wool in order to mix the two gases thoroughly. The flow rate of chlorine and nitrogen was separately measured with a capillary-type flow meter.

The moisture and temperature of the gas were brought to equilibrium before it was introduced into the absorption chamber. The partial pressure of chlorine was maintained by mixing it with nitrogen, and was determined by chemical analysis. The total pressure of gas in the absorption chamber was assumed to be

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*[1] This paper was presented at the Spring Meeting of the Electrochemical Society of Japan, Tokyo, April, 1967.

1) F. W. Adams and R. G. Edmonds, *Ind. Eng. Chem.*, **29**, 447 (1937).

2) R. P. Whitney and J. E. Vivian, *ibid.*, **33**, 741 (1941).

3) N. Yokota, *Kagaku Kogaku (Chem. Eng., Japan)*, **22**, 476 (1958).

4) M. S. Sherrill and E. F. Izard, *J. Am. Chem. Soc.*, **50**, 1670 (1928).

5) M. S. Sherrill and E. F. Izard, *ibid.*, **53**, 1667 (1931).

6) F. Hine, S. Yoshizawa, K. Yamakawa and Y. Nakane, *Electrochem. Techn.*, **4**, 556 (1966).

the sum of the partial pressures of chlorine, nitrogen, hydrogen chloride, and water vapor, and was determined by means of a manometer. The partial pressure of water vapor was mostly obtained from Reference 7, though some data were confirmed empirically.

The sample gas was passed through the absorption chamber for an hour in order to gain an equilibrium state prior to measurement.

A certain amount of the solution at the equilibrium was pipetted out quickly, added to a 10% solution of potassium iodide, and diluted with water until its pH reached about 1. Its solution was then titrated by iodometry to measure the chlorine dissolved.

Results and Discussion

Sherrill and Izard⁵⁾ and Jokowkin⁸⁾ have studied the effects of HCl on the solubility of chlorine in water. They concluded that while the solubility of chlorine decreased upon the addition of a small amount of HCl, it increased in relatively concentrated HCl solutions because of the formation of tri-chloride ions by the combination of Cl_2 and Cl^- as follows:

$$Cl_2 + Cl^- = Cl_3^- \tag{1}$$

Furthermore, HClO may form in a weak acid solution when the pH of the solution is larger than 2. However, no such formation occurs in the present experiment because the concentration of hydrochloric acid is as high as 2—10 N. The results of titration show the sum of chlorine dissolved physically, or "free chlorine," and tri-chloride ions, it also shows the solubility of chlorine in a solution, that is:

$$S = (Cl_2) + (Cl_3^-) \tag{2}$$

where S is the solubility of chlorine, and where (Cl_2) and (Cl_3^-) are the concentrations of free chlorine and tri-chloride ions, respectively.

Experiment was carried out in a 2—12 N HCl solution at 30—90°C. The solubility obtained was plotted as a function of the partial pressure of chlorine under given conditions of HCl concentration and temperature, and the straight lines shown in Figs. 2—6 were thus obtained. The solubility of chlorine in HCl, then, follows Henry's Law; that is,

$$S = Hp \tag{3}$$

where p is the partial pressure of chlorine, and H is Henry's coefficient, which is a function of the temperature and HCl concentration.

Figure 7 shows the relationship between H and the HCl concentration at various temperatures.

Henry's coefficient is a function of the concentration as follows:

$$H = \alpha C + \beta \tag{4}$$

where C is the concentration of HCl, and where

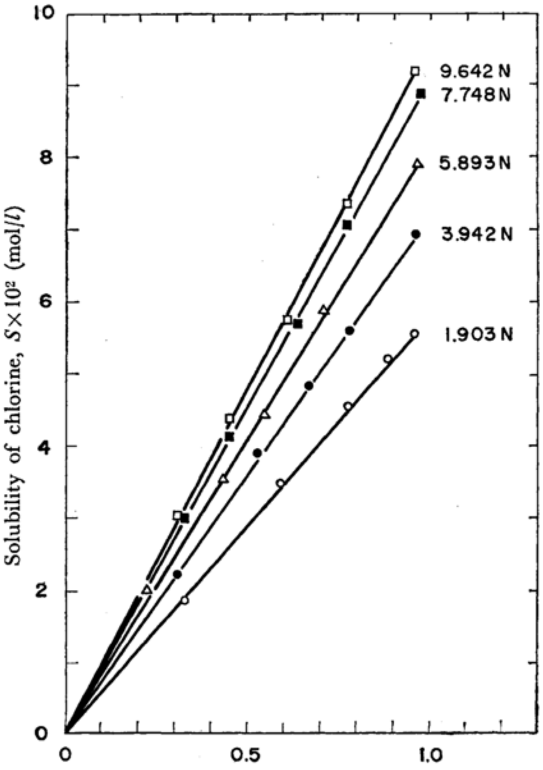

Fig. 2. Solubility of chlorine as a function of its partial pressure of chlorine at 30°C.

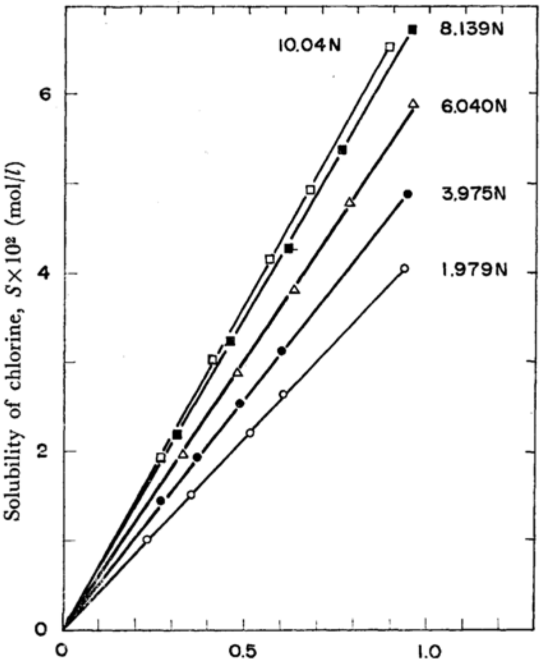

Fig. 3. Solubility of chlorine as a function of its partial pressure at 40°C.

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7) J. H. Perry, "Chemical Engineers' Handbook," 4th Ed., **3**-60 (1963).

8) A. A. Jakowkin, *Z. Physik. Chem.*, **29**, 613 (1899).

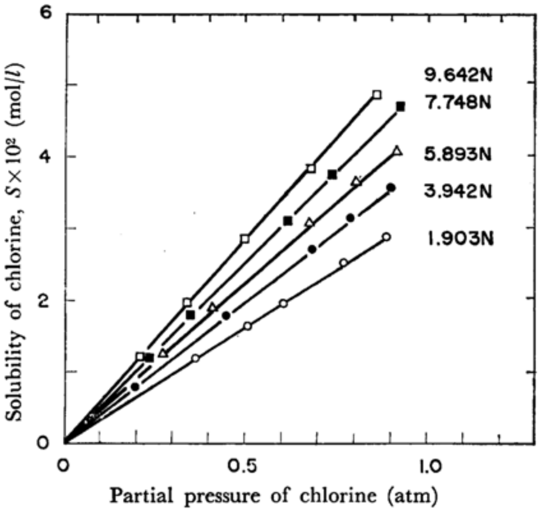

Fig. 4. Solubility of chlorine as a function of its partial pressure at 50°C.

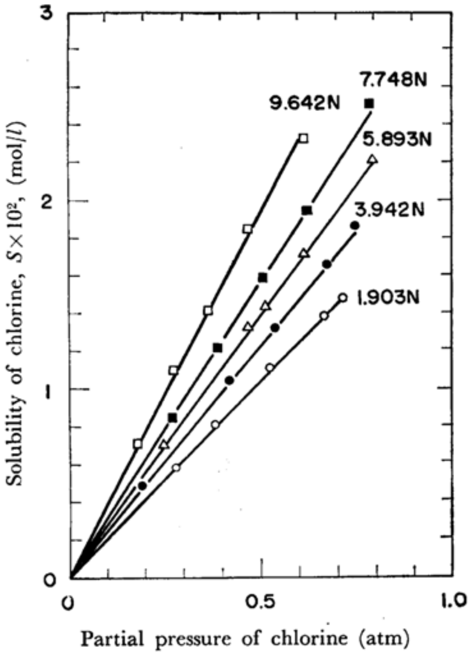

Fig. 5. Solubility of chlorine as a function of its partial pressure at 70°C.

α and β are constants. The substitution of H into Eq. (3) gives the following expression:

$$S=(\alpha C+\beta)p \qquad (5)$$

While the concentration of chlorine and HCl are represented in "molality" in these figures, relations similar to those above, also expressed in "grams per liter," were obtained.

As shown in Fig. 7, Henry's coefficient, and hence both α and β, could easily be derived as functions of the temperature. Figure 8 shows the relationship between α and the temperature: the logarithm of α is proportional to t°C. On the other hand, the logarithm of β *vs.* the logarithm of the temperature is linear, as shown in Fig. 9. Therefore, the empirical equations for α and β be written as follows:

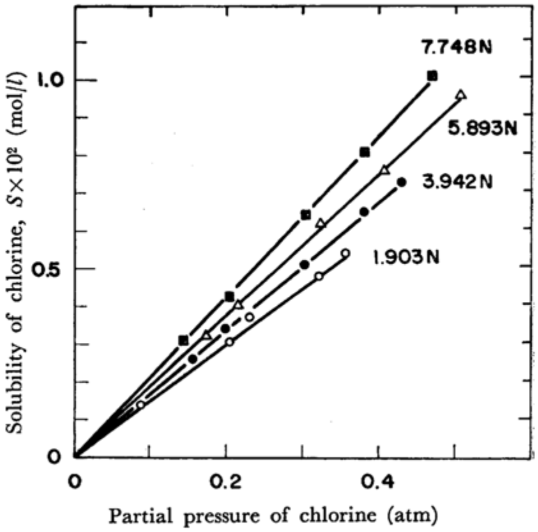

Fig. 6. Solubility of chlorine as a function of its partial pressure at 90°C.

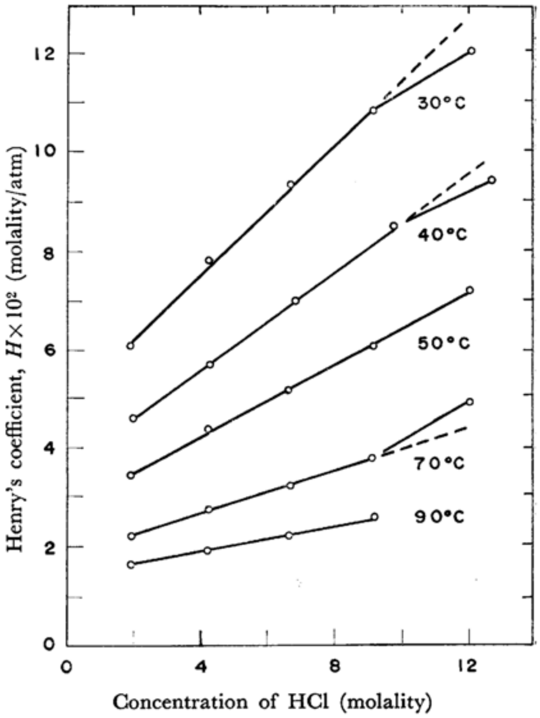

Fig. 7. Henry's coefficient at various temperatures as a function of HCl concentration.

$$\log\alpha=-1.21\times10^{-2}t-1.603 \qquad (6)$$

and:

$$\beta=2.14\times10^{2}t^{-1.21} \qquad (7)$$

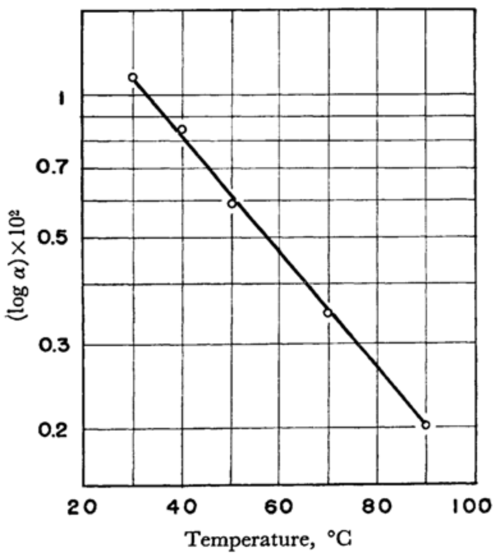

Fig. 8. Logarithm of α *vs.* temperature curve.

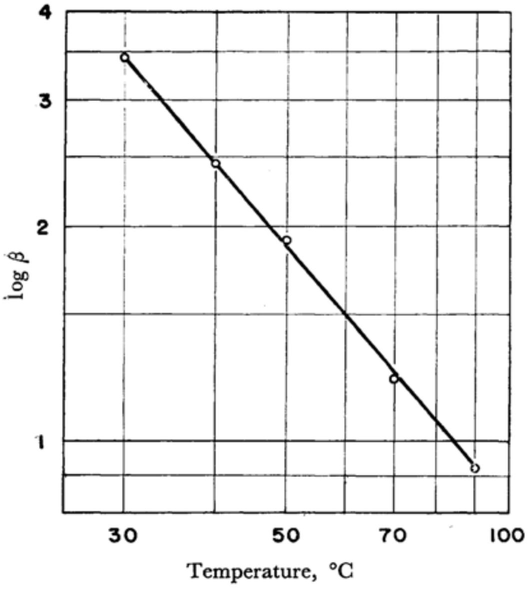

Fig. 9. Logarithm of β *vs.* logarithm of temperature.

where α and β are expressed in grams per liter-chlorine/grams per liter-HCl·atm and grams per liter-chlorine/atm respectively, and the temperature, in degrees centigrade.

Figure 10 shows the values calculated by Eqs. (5), (6), and (7) in comparison with the observed values. A good agreement was obtained between them at 30—90°C in HCl solutions of concentrations less than 10 N under partial pressures of chlorine lower than 1 atm.

It is well known that the equilibrium constant, K, for the reaction (1) may be represented as follows:

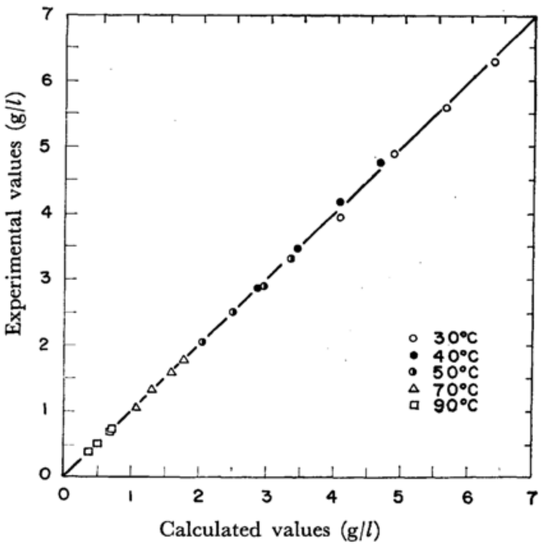

Fig. 10. Solubility of chlorine calculated by the empirical equation in comparison with the data determined.

$$K=\frac{a_{Cl_3^-}}{p\cdot a_{Cl^-}}=\frac{\gamma_{Cl_3^-}\cdot(Cl_3^-)}{p\cdot\gamma_{Cl^-}\cdot(Cl^-)} \tag{8}$$

where:

$a_{Cl_3^-}$	Activity of Cl_3^-	mol/l
a_{Cl^-}	Activity of Cl^-	mol/l
$\gamma_{Cl_3^-}$	Activity coefficient of Cl_3^-	
γ_{Cl^-}	Activity coefficient of Cl^-	

The unit of concentration of chlorine and trichloride ions, (Cl^-) and (Cl_3^-), is mol/l in this case.

Although the activity coefficient of Cl^- in aqueous solutions has been determined,⁶⁾ meagre data are available on the activity of Cl_3^-. Assuming that $\gamma_{Cl_3^-}=\gamma_{Cl^-}$, as Sherrill and Izard did,⁵⁾ the following equation was obtained:

$$K=\frac{(Cl_3^-)}{p\cdot(Cl^-)}=\frac{(Cl_3^-)}{p\cdot C} \tag{9}$$

where C is the concentration of Cl^- in mol/l.

On the other hand, we may assume that the concentration of chlorine dissolved, or "free chlorine," in a solution, is proportional to the partial pressure of chlorine in the gas phase, such as,

$$(Cl_2)=hp \tag{10}$$

where h is a constant.

By substituting Eqs. (9) and (10) into Eq. (3), we obtain the equation:

$$S=(KC+h)p \tag{11}$$

Therefore, it is evident that K and h should correspond to the two constants, α and β, in Eq. (4) or (5) respectively, if the same units of concentration, pressure, and temperature are used. Table 1 shows these values obtained at various temperatures: the values of α and β using conventional

TABLE 1. THE COEFFICIENTS, α and β, IN HENRY'S EQUATION (5)

Temperature		α		β	
°C	1/(°K)	mol/mol·atm	gpl/gpl·atm	mol/atm	gpl/atm
30	3.300×10^{-3}	6.57×10^{-3}	1.08×10^{-2}	4.85×10^{-2}	3.42
40	3.195	5.11	0.844	3.49	2.46
50	3.096	3.65	0.592	2.72	1.92
70	2.915	2.20	0.350	1.76	1.22
90	2.755	1.38	0.204	1.32	0.916

units are also listed in the table.

According to the van't Hoff Law, we may obtain the following equation:

$$\frac{d(\ln K)}{d(1/T)} = -\frac{\Delta H^\circ}{\boldsymbol{R}} \qquad (12)$$

where T is the temperature in °K; $\boldsymbol{R}$, the gas constant, and ΔH°, the standard enthalpy change for Reaction (1). The logarithm of K was plotted as a function of the reciprocal temperature, $1/T$, as shown in Fig. 11. That is, ΔH° is independent of the temperature. The enthalpy change, ΔH°, was calculated, from the slope of this curve, to be -5.77 kcal/mol.

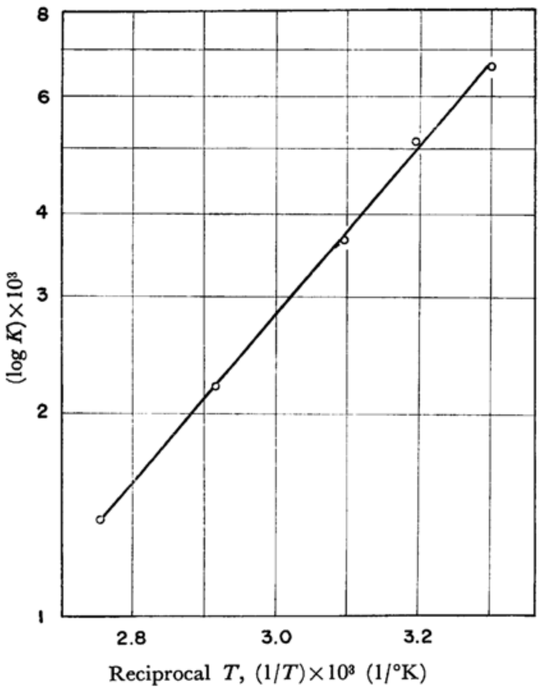

Fig. 11. Logarithm of K *vs.* reciprocal temperature curve.

The Gibbs free energy change, ΔG°, has the following relations with K:

$$\Delta G^\circ = -\boldsymbol{R}T\ln K \qquad (13)$$

and:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (14)$$

where ΔS° is the entropy change. The free energy change, ΔG°, was plotted against the temperature; it was completely linear, as shown in Fig. 12. The empirical equation for ΔG° is as follows:

$$\Delta G^\circ = 2.147 + 0.0290t \quad \text{(kcal/mol)} \qquad (15)$$

The entropy change, ΔS°, was then evaluated to be 29.0 cal/mol·°K, which was independent of the temperature.

The equation for K is as follows:

$$\log K = \frac{1.26\times10^3}{T} - 6.34 \qquad (16)$$

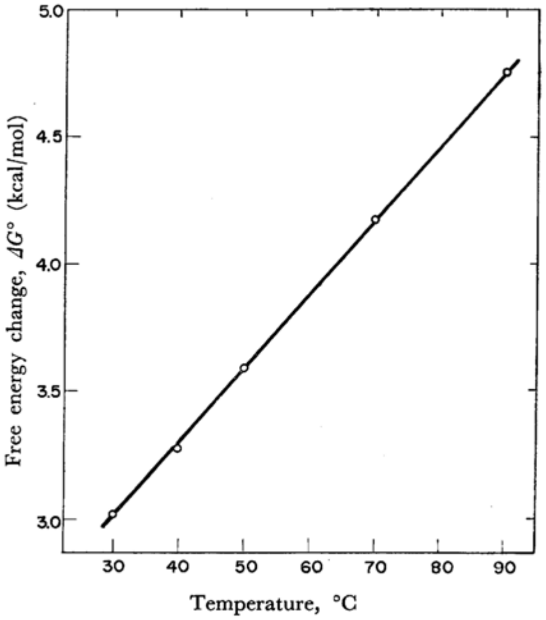

Fig. 12. Free energy change *vs.* temperature.

Summary

The solubility of chlorine in hydrochloric acid solutions of 2—12 N at partial pressures of chlorine lower than 1 atm and at 30—90°C was determined. Henry's Law was found to hold good in this range. Some thermodynamic characteristics of the system consisting of Cl_2, Cl^-, and Cl_3^- were also discussed.