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Solubility of Chlorine in Mixed Solutions of HCl and $CuCl_2$

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The solubility of chlorine in a mixed solution of HCl and $CuCl_2$ under various conditions of concentration, temperature, and partial pressure 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; its slope decreased with an increase in the concentration of cupric ions due to the salting-out effect.

The recovery of chlorine from waste HCl is an attractive prospect, but the design engineer in this field requires data on systems consisting of HCl and Cl_2. The present authors have previously reported on the solubility of Cl_2 in concentrated HCl.[1)]

The HCl cell with the oxygen-depolarized cathode developed by Hine *et al.*,[2)] the so-called "Kyoto Process," contains a mixture of HCl and $CuCl_2$ in order to increase the reaction rate at the cathode represented by:

$$4H^+ + O_2 + 4e = 2H_2O \qquad (1)$$

where the cupric ions form a chloride complex such as $CuCl_3^-$ in concentrated HCl.[3)] The solubility of chlorine is, therefore, affected by the concentration of cupric chloride in the solution.

Experimental

The apparatus for vapor-pressure measurements reported by Smith *et al.*[4)] was modified.[5)] The temperature was controlled within a range of ±0.1°C; it caused a minor variation in the vapor pressure, but this variation was less than 3 mmHg at 90°C, for example.

The equipment and the flow sheet used for solubility measurements were the same as have previously been described.[1)]

The chlorine gas diluted with nitrogen to be sent to the measurement cell was exactly analyzed, and its moisture and temperature were brought to equilibrium before measurement.

The chlorine dissolved in the solution was titrated by iodometry. Since cupric ions in the solution also reacted on KI, the balance, total amount of KI consumed minus the amount of KI for Cu^{2+}, was taken. The cupric ions were also examined by iodometry. The compositions of the solutions examined are listed in Table 1.

Results and Discussion

Since the pressure of water vapor was not negligible in comparison with the total pressure, it was determined as a function of the temperature and of the composition of the solution. The data obtained are listed in Table 2, while an example of Dühring diagram of a system consisting of HCl and $CuCl_2$ is shown in Fig. 1. The logarithm of the vapor pressure is linear to the reciprocal temperature, $1/T$, as is shown in Fig. 2; therefore, the latent heat seems to be independent of the tempera-

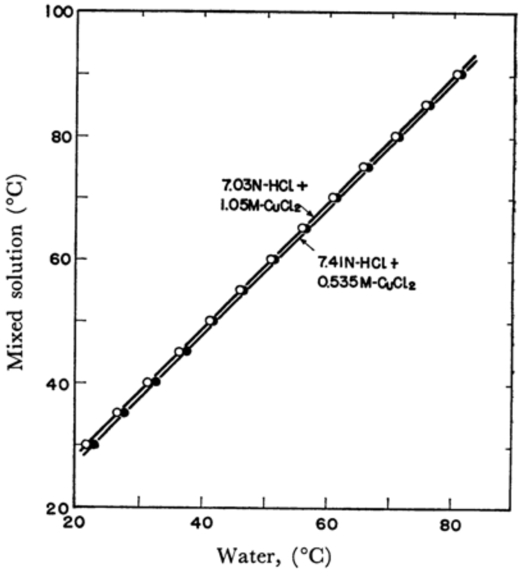

Fig. 1. The Dühring diagram of the mixed solution of HCl and $CuCl_2$ referred to water.

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1) F. Hine and S. Inuta, This Bulletin, **41**, 71 (1968).

2) F. Hine, S. Yoshizawa, K. Yamakawa and Y. Nakane, *Electrochem. Techn.*, **4**, 555 (1966).

3) F. Hine and K. Yamakawa, *Electrochim. Acta*, **13**, 2119 (1968).

4) A. Findlay and J. A. Kitchener, "Practical Physical Chemistry," Longmans, Green & Co., London (1955), p. 79.

5) F. Hine and S. Inuta, *Kenkyu Hokoku* (*Reports of the Training Institute for Engineering Teachers, Kyoto Univ.)*, No. 4, 19 (1968).

TABLE 1. ANALYSIS OF SAMPLE SOLUTIONS

	5 N HCl		6 N HCl		7 N HCl	
Concentration of Cu^{2+}	0.5 M	1.0 M	0.5 M	1.0 M	0.5 M	1.0 M
Concn. of HCl (N)	5.49	5.45	6.25	6.32	7.41	7.03
Concn. of Cu^{2+} (mol/l)	0.516	1.019	0.512	1.038	0.535	1.052

TABLE 2. VAPOR PRESSURE OF WATER OVER THE SAMPLE SOLUTION

t (°C)	$\frac{1000}{T}$ (1/°K)	5 N HCl				6 N HCl				7 N HCl			
		0.5 M $CuCl_2$		1 M $CuCl_2$		0.5 M $CuCl_2$		1 M $CuCl_2$		0.5 M $CuCl_2$		1 M $CuCl_2$	
		p	t_w	p	t_w	p	t_w	p	t_w	p	t_w	p	t_w
30.0	3.299	20.8	22.8	19.5	21.7	18.2	20.6	17.7	20.2	17.5	20.0	17.5	20.0
35.0	3.245	28.0	27.8	26.3	26.7	24.7	25.7	24.3	25.4	24.0	25.2	24.1	25.2
40.0	3.193	37.0	32.7	34.5	31.4	33.0	30.6	32.5	30.4	32.5	30.4	32.4	30.3
45.0	3.143	48.5	37.6	45.5	36.4	43.0	35.4	42.5	35.1	43.7	35.6	43.0	35.4
50.0	3.095	61.5	42.0	59.0	41.2	56.8	40.5	55.5	40.1	57.8	40.8	55.5	40.1
55.0	3.047	78.5	46.7	76.5	46.2	73.2	45.4	71.3	44.8	74.3	45.6	72.5	45.2
60.0	3.002	100.0	51.6	97.5	51.1	93.7	50.3	91.7	49.8	95.9	50.7	93.6	50.2
65.0	2.957	126.5	56.5	123.7	56.0	119.3	55.2	116.5	54.7	123.4	55.9	119.8	55.3
70.0	2.914	160.0	61.5	155.5	60.9	151.5	60.3	149.0	59.9	159.2	61.4	154.1	60.7
75.0	2.872	199.8	66.4	195.0	65.9	190.8	65.4	188.0	65.1	202.2	66.7	195.0	65.9
80.0	2.832	247.5	71.3	241.5	70.8	238.8	70.5	236.0	70.2	255.0	72.0	247.0	71.3
85.0	2.792	305.7	76.3	298.8	75.8	297.0	75.6	295.3	75.5	320.0	77.5	309.6	76.6
90.0	2.754	376.3	81.4	366.8	80.8	367.2	80.8	365.2	80.7	398.9	82.9	385.4	82.0

p: vapor pressure, in mmHg.
t_w: temperature of water at the vapor pressure p, in °C.

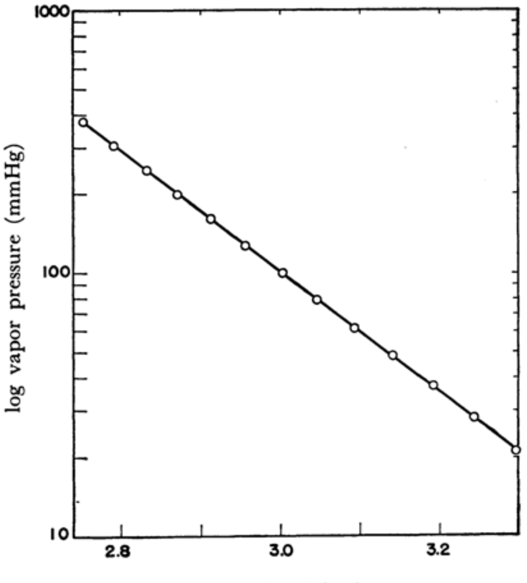

Fig. 2. The vapor pressure of the aqueous solution consisting of 5.49 N HCl and 0.516 M $CuCl_2$ as a function of temperature.

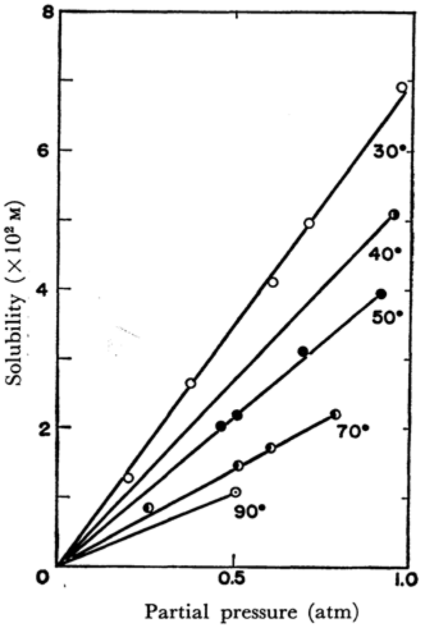

Fig. 3. The solubility of chlorine in 5.49 N HCl +0.516 M $CuCl_2$.

Table 3. Henry's coefficient ($\times 10^2$)

t (°C)	$\frac{1000}{T}$ (1/°K)	5 N HCl 0.5 M	5 N HCl 1.0 M	6 N HCl 0.5 M	6 N HCl 1.0 M	7 N HCl 0.5 M	7 N HCl 1.0 M
30	3.2987	6.99	6.57	7.82	6.81	8.07	7.23
40	3.1934	5.37	5.02	5.88	5.31	6.31	5.40
50	3.0945	4.28	3.78	4.60	4.50	4.92	4.12
70	2.9142	2.76	2.36	3.01	2.42	3.04	2.63
90	2.7537	2.15	2.08	2.16	2.40	2.41	2.18

ture between 30 and 90°C.

The solubilities of chlorine at various temperatures and concentrations were plotted against the partial pressure of chlorine. As the example in Fig. 3 shows, it is clear that the following Henry equation can be applied:

$$S_m = H_m \cdot p_{\mathrm{Cl}_2} \tag{2}$$

where: S_m: the solubility of chlorine in a mixed solution mol/l
H_m: Henry's coefficient mol/l·atm
p_{Cl_2}: the partial pressure of chlorine atm

The Henry coefficient decreases with an increase in the concentration of cupric ions as is listed in Table 3. However, the slope of the logarithm of the H_m *vs.* $1/T$ curve is independent of the cupric ions, as is shown in Fig. 4. Therefore, the enthalpy change upon the dissolution of chlorine in a mixture of HCl and $\mathrm{CuCl_2}$ is equal to that in a solution of HCl.[6]

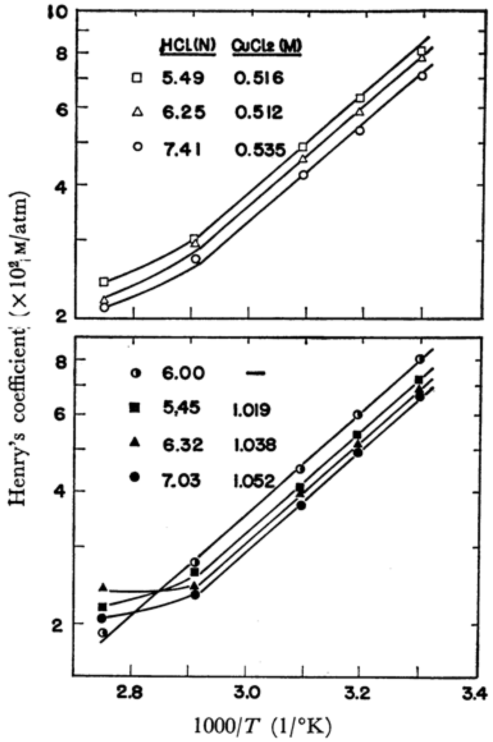

Fig. 4. Henry's coefficient at various conditions of temperature and concentration.

Let us discuss the single solution of HCl first. It is well known that a part of the chlorine forms trichloride complex ions, $\mathrm{Cl_3^-}$, in a chloride solution, and that the other part may dissolve as its molecule, $\mathrm{Cl_2}$.

The total amount of chlorine in HCl, as the sum of $\mathrm{Cl_3^-}$ and $\mathrm{Cl_2}$, is a linear function of the HCl concentration and of the partial pressure in the gas phase, as has been described in a previous report,[1] that is,

$$S = H \cdot p_{\mathrm{Cl}_2} = (\alpha x + \beta) p_{\mathrm{Cl}_2} \tag{3}$$

where: S: the solubility of chlorine mol/l
$H = \alpha x + \beta$: Henry's coefficient mol/l·atm
x: the concentration of $\mathrm{Cl^-}$ mol/l
p_{Cl2}: the partial pressure of $\mathrm{Cl_2}$ atm
α and β: coefficients

Because the system consisting of $\mathrm{Cl_2}$, $\mathrm{Cl^-}$, and $\mathrm{Cl_3^-}$ is in a state of equilibrium, the concentration of $\mathrm{Cl_3^-}$ is proportional to x as follows:

$$(\mathrm{Cl_3^-}) = K \cdot p_{\mathrm{Cl}_2} \cdot x \tag{4}$$

where K is the equilibrium constant and where ( ) shows the concentration. Therefore, the concentration of $\mathrm{Cl_2}$ can be represented by the balance of S minus $(\mathrm{Cl_3^-})$; it is also linear to the concentration of $\mathrm{Cl^-}$ as follows:

$$(\mathrm{Cl_2}) = [(\alpha - K)x + \beta] p_{\mathrm{Cl}_2} \tag{5}$$

The effects of the electrolyte on the solubility of gas as its molecule have been studied by many authors[7,8] as the "Salting-Out Effect." They reached the important conclusion that a linear relationship exists between the logarithm of the solubility and the concentration of electrolytes in a solution.

At relatively low concentrations of HCl and in water, the data obtained at 25°C by Sherrill *et al.*[9] agree with Eq. (6), as is shown in Fig. 5.

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6) See Eq. (12) in Ref. 1.

7) A. E.. Markham and K. A. Kobe, *Chem. Revs.*, **28**, 519 (1941).

8) H. Hikita, *Kagaku Kogaku (J. Chem. Eng. Japan)*, **23**, 537 (1959).

9) M. S. Sherrill and E. F. Izzard, *J. Am. Chem. Soc.*, **53**, 1667 (1931).

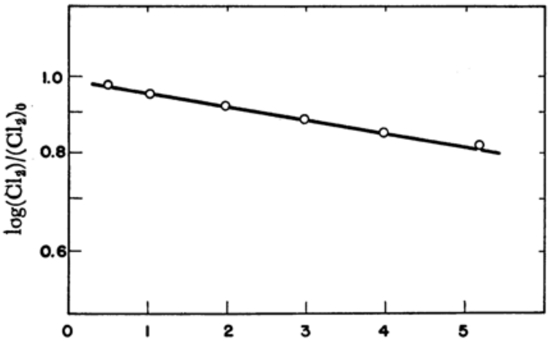

Fig. 5. Concentration of Cl_2 in HCl solution at 1 atm.

That is,

$$\log \frac{(Cl_2)}{(Cl_2)_0} = -kx \tag{6}$$

where $(Cl_2)_0$ is the solubility of Cl_2 in pure water and where k is a constant and is very small (about 0.0183). Accordingly, the first approximation;

$$(Cl_2) = (Cl_2)_0 \cdot (1 - 2.303kx) \tag{7}$$

is allowable with a variation of less than 2%. It is essentially the same as Eq. (5).

Zimmerman *et al.*[10] found the equilibrium constant, K, in Eq. (4) or (5) to be 0.01 at 25°C using the spectroscopic method; this value is in good agreement with that of Sherrill.[9] The relationship between K and T has been discussed in the previous report,[1] where the salting-out effect was not considered. Because the slope of the $\log K$ *vs.* $1/T$ curve is independent of the concentration of HCl, the value of K and, hence, that of $\alpha - K$ in Eq. (5) at various temperatures between 30 and 90°C can be predicted to be as listed in Table 4.

TABLE 4. K AND $(\alpha - K)$ (in mol/l·atm)

Temperature (°C)	$K \times 10^2$	$-(\alpha - K) \times 10^2$
30	0.845	0.215
40	0.620	0.186
50	0.462	0.158
70	0.273	0.093
90	0.172	0.067

With these values, the concentrations of Cl_2 and Cl_3^- shown in Fig. 6 are obtained. The solid line with open points shows the sum of chlorine dissolved at $p_{Cl_2} = 1$ atm; the data at 25°C, with the closed point, are quoted from the paper by Sherrill *et al.*[9] The thin line represents the concentration of Cl_2 predicted by Eq. (5) at a partial pressure of 1 atm. The closed points with the thin line are also based on Sherrill's data. Accordingly, the concentration of Cl_3^- can be evaluated as the balance of the two lines.

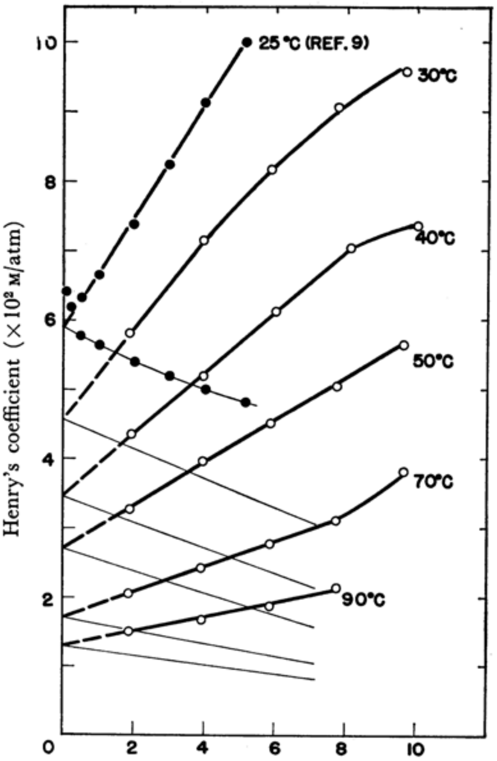

Fig. 6. Henry's coefficient as various conditions of temperature and HCl concentration.

The effect of cupric chloride on the solubility of chlorine in a mixture of HCl and $CuCl_2$ was also examined. The data obtained are shown in Fig. 7, where the ordinate is the Henry coefficient or the solubility at $p_{Cl_2} = 1$ atm and where the abscissa is the concentration of $CuCl_2$ in HCl. The concentrations of Cl_2 and Cl_3^- can be calculated by the procedure described above; the results are listed in Table 5, together with the Henry coefficients.

Now we may consider the mixed solution. It is well known that cupric ions form a chloride complex with HCl as follows:

$$CuCl_2 + Cl^- = CuCl_3^- \tag{8}$$

This is according to Hine *et al.*,[8] who obtained the coordination number of the complex ion by means of EMF measurements. Therefore, the concentration of Cl^- in the solution decreases with an increase in the cupric ions; that is,

$$(Cl^-) = x - y \tag{9}$$

where y is the concentration of cupric chloride in mol/l. By substituting this into Eq. (4), the next equation can be obtained:

$$(Cl_3^-) = K \cdot p_{Cl_2}(x - y) \tag{10}$$

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[10] G. Zimmerman and F. C. Strong, *ibid.*, **79**, 2063 (1957).

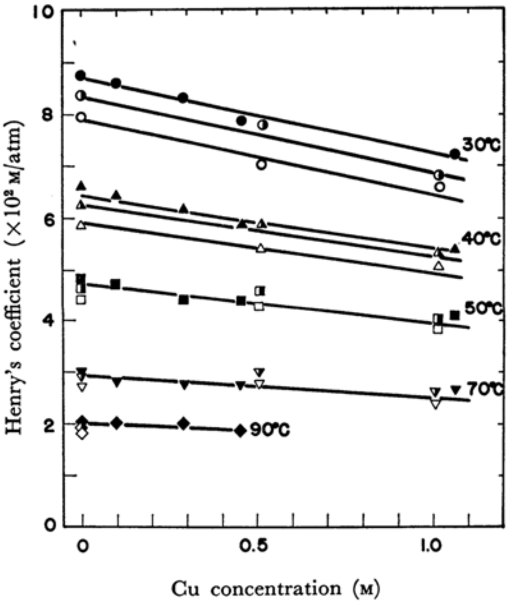

Fig. 7. Henry's coefficient at various conditions of temperature and concentrations of HCl and $\mathrm{CuCl_2}$.
Closed point (●): 7.23 N HCl
Semi-closed point (◑): 6.25 N HCl
Open point (○): 5.49 N HCl

TABLE 5. SOLUBILITY OF CHLORINE IN 7.23 N HCl AT $p_{\mathrm{Cl_2}}=1$ atm (mol/l)

Temperture (°C)	$\mathrm{H}\times 10^2$	$(\mathrm{Cl_2})\times 10^2$	$(\mathrm{Cl_3^-})\times 10^2$
30	8.80	3.03	5.77
40	6.65	2.13	4.52
50	4.87	1.57	3.30
70	3.02	1.05	1.97
90	2.06	0.81	1.25

We may assume that $(\mathrm{Cl_2})$ decreases with an increase in the concentration of cupric ions due to the salting-out effect, and that it can be represented by the following equation:

$$(\mathrm{Cl_2}) = (a - by)p_{\mathrm{Cl_2}} \tag{11}$$

where a and b are constants (a should be equal to $(\alpha-K)x+\beta$ because $(\mathrm{Cl_2})$ is represented by Eq. (5) at $y=0$). Accordingly, the solubility of chlorine as the sum of $\mathrm{Cl_2}$ and $\mathrm{Cl_3^-}$ can be formulated as follows:

$$S_m = (\mathrm{Cl_3^-})+(\mathrm{Cl_2}) = [(\alpha x+\beta)-(K+b)y]p_{\mathrm{Cl_2}} \tag{12}$$

From Eqs. (2), (3) and (12), we have:

$$b = \frac{H - H_m}{y} - K \tag{13}$$

Equation (13) represents the salting-out effect due to cupric chloride in the HCl solution on the solubility of chlorine; the data obtained are shown in Fig. 8. The logarithm of b is linear to $1/T$ with the slope of 2.

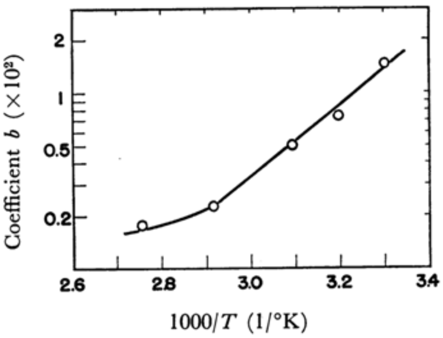

Fig. 8. The coefficient b as a function of temperature.

Equation (11) is an approximation of the next equation:

$$\log \frac{(\mathrm{Cl_2})}{(\mathrm{Cl_2})_0} = -k_m y \tag{14}$$

where k_m is a coefficient. As is shown in Fig. 7, k_m, and, hence, b in Eq. (11) are small and are functions of the temperature.

Summary

The vapor pressure of the aqueous solution consisting of HCl and $\mathrm{CuCl_2}$ was measured. The solubility of chlorine in the same solution at a partial pressure of chlorine lower than 1 atm and at 30—90°C was also determined. The enthalpy change upon the dissolution of chlorine in the mixed solution was equal to that in a solution of HCl alone. Henry's Law was found to hold good in this case as well as in pure HCl, while the Henry coefficient decreases with decrease in the HCl concentration and increase in the $\mathrm{CuCl_2}$ concentration because of the salting-out effect.