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THE SOLUBILITY OF CHLORINE IN AQUEOUS SOLUTIONS OF CHLORIDES AND THE FREE ENERGY OF TRICHLORIDE ION

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Introduction

Previous investigations¹ show that the solubility of chlorine in water is decreased by small additions of hydrogen chloride, but is increased by larger additions. The initial decrease in solubility is readily explained by the depression of the hydrolysis of the dissolved chlorine by the added acid. At the higher concentrations of added acid, however, where the percentage hydrolysis is reduced to an extremely small value, a further decrease in solubility might be expected to arise from the salting-out effect of the hydrogen chloride. Actually an increase in solubility has been observed which indicates the formation of a complex ion, probably the trichloride ion, in sufficient amount to more than compensate the salting-out effect.

In contrast to hydrogen chloride, additions of sodium chloride to water continue to decrease the solubility of chlorine, even at the higher concentrations. This indicates that the salting-out effect predominates over the complex ion formation in determining the total solubility. This view is confirmed by the fact that the salting-out effect of the metallic chlorides is in general considerably greater than that of hydrochloric acid.²

In order to test these views more quantitatively, a systematic study was made of the solubility of chlorine at a pressure of one atmosphere and 25° in solutions of sulfuric acid, hydrogen chloride and a series of other chlorides. The results were compared with existing values of the solubility of oxygen in the presence of the same series of electrolytes. The solubility data relating to oxygen were taken from the compilation of Randall and Failey² and from an investigation by McArthur.³ The theoretical considerations involved in the interpretation of the results of the solubility determinations are briefly as follows.

The dissolved chlorine exists in the saturated solutions partly in the form of free chlorine (Cl_2), partly in its hydrolyzed form (HClO), and the remainder in the form of the complex ion (Cl_3^-). In the case of the sulfuric acid solutions saturated with chlorine the complex-ion formation is inappreciable, and the small hydrolysis can be computed, so that the salting-out effect of the electrolyte on the chlorine as such can be estimated and compared with the corresponding effect on the dissolved oxygen in its

¹ Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899).

² Scatchard, *Chem. Reviews*, **3**, 398 (1927); Randall and Failey, *ibid.*, **4**, 271 (1927).

³ McArthur, *J. Phys. Chem.*, **20**, 495 (1916).

saturated solution. This is conveniently done by computing the ratio s_0/s of the saturation concentration of chlorine (Cl_2 as such) in pure water to its value in the presence of the electrolyte, and comparing it with the corresponding value for oxygen. This ratio represents the activity coefficient of the chlorine, or of the oxygen, in the presence of the different electrolytes.

Debye and McAuley⁴ have shown, with the aid of the ion attraction theory, how the activity coefficient of a non-electrolyte in the presence of electrolyte varies, for a given solvent, with the nature and concentrations of the non-electrolyte and electrolyte. Though the derivation of this theoretical relation is complicated, the final result may be expressed for this special case of gas solubility by the relatively simple equation

$$\text{Log } \frac{s_0}{s} = \kappa \left(\frac{\partial D}{\partial s} \right) \frac{1}{r} \sum (C_i z_i)^2$$

In this equation κ is a constant characteristic of the solvent at a temperature T , the ratio $\partial D/\partial s$ is the rate of change of the dielectric constant of the solution (containing only non-electrolyte) with the concentration s of the non-electrolyte, r is a mean of the radii of the ions present, and c_i is the concentration and z_i the charge of any ion of kind i (hence $1/2 \sum (c_i z_i)^2$ is the ionic strength). The ratio $\partial D/\partial s$ may be assumed to be independent of the concentration s , and therefore regarded as a constant characteristic of the non-electrolyte.

It follows from this theory that the saturation concentrations of chlorine and oxygen in different electrolytes of the same ionic strength must bear the definite relation to each other expressed by the equation

$$\frac{\text{Log } (s_0/s)_{\text{Cl}_2}}{\text{Log } (s_0/s)_{\text{O}_2}} = \text{Const.}$$

That is, the theory requires that at small concentrations this logarithmic ratio be independent of the particular ionic strength at which the solubilities of the two gases are compared, and also of the nature of the ions which make up that ionic strength.

Direct comparison of the solubility of chlorine with that of oxygen in solutions of sulfuric acid up to a concentration 1 formal (the concentration range covered by the compilation of Randall and Failey²) showed the activity coefficients of these two gases to be nearly the same, and correspondingly the logarithmic ratio to be approximately equal to unity. Thus, in 1.036 formal sulfuric acid the activity coefficients of the chlorine and oxygen in their saturated solutions were 1.170 and 1.185, respectively, and the corresponding logarithmic ratio was 0.925.

In the interpretation of results this value for the logarithmic ratio was assumed to hold at all ionic strengths, and accordingly the concentration of free chlorine (Cl_2) in the various chlorine saturated solutions of chlorides

⁴ Debye and McAuley, *Physik. Z.*, 26, 22 (1925).

was computed from the known values of the solubility of oxygen in the same solutions with the aid of the equation

$$\text{Log } (s_0/s)_{\text{Cl}_2} = 0.925 \text{ log } (s_0/s)_{\text{O}_2} \quad (1)$$

The hydrolyzed portion (HClO) of the dissolved chlorine was calculated, as indicated below, with the aid of the mass action law, and the remainder of the dissolved chlorine was assumed to be trichloride ion (Cl_3^-).

The equilibrium conditions of the reaction $\text{Cl}_2 + \text{H}_2\text{O} = \text{H}^+ + \text{Cl}^- + \text{HClO}$, are represented by the equation

$$\frac{[\text{H}^+][\text{Cl}^-][\text{HClO}]}{[\text{Cl}_2][\text{H}_2\text{O}]} = \frac{\alpha^2(\text{H}^+)(\text{Cl}^-)(\text{HClO})}{(\text{Cl}_2)(p/p_0)} = K \quad (2)$$

in which the activities of the substances are indicated by brackets and the concentrations (expressed in moles per 1000 g. of water) by parentheses. The symbol α is the mean activity coefficient of the H^+ and Cl^- ions; and p/p_0 is the ratio of the vapor pressure of water in the solution to that of pure water. The value for the equilibrium constant K of the hydrolysis reaction was taken from Lewis and Randall⁵ to be 4.84×10^{-4} . The mass action expression for the hydrolyzed part of the dissolved chlorine varies with the type of added electrolyte. The equations employed in computing the concentration of the hypochlorous acid (HClO) in c formal solution of the various substances were as follows

$$(\text{HClO})^2 = K \frac{(p/p_0)[\Sigma(\text{Cl}_2) - (\text{HClO})]}{2c\alpha^2} \text{ for } \text{H}_2\text{SO}_4 \quad (3)$$

$$(\text{HClO}) = K \frac{(p/p_0)s}{c^2\alpha^2} \text{ for } \text{HCl} \quad (4)$$

$$(\text{HClO})^2 = K \frac{(p/p_0)s}{c\alpha^2} \text{ for } \text{NaCl or KCl} \quad (5)$$

$$(\text{HClO})^2 = K \frac{(p/p_0)s}{2c\alpha^2} \text{ for } \text{BaCl}_2 \quad (6)$$

In applying Equation 3, the mean activity coefficient of the H^+ and Cl^- ions was placed equal to that found by Livingston⁶ at the same ionic strength for H^+ and Br^- in mixtures of sulfuric acid and potassium bromide. The equation was derived under the assumption that H_2SO_4 is completely ionized into 2H^+ and SO_4^- , since Livingston had made this assumption in evaluating the mean activity coefficients of hydrogen and bromide ions.

The values for the activity coefficient α substituted in Equation 4 were taken from Lewis and Randall;⁷ in Equation 5 from Harned;⁸ and in Equation 6 from Harned and Brumbaugh.⁹

⁵ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 508.

⁶ Livingston, THIS JOURNAL, 48, 45 (1926).

⁷ Ref. 5, p. 336.

⁸ Harned, THIS JOURNAL, 48, 326 (1926).

⁹ Harned and Brumbaugh, *ibid.*, 44, 2729 (1922).

Experimental Procedure

The solutions of the various electrolytes which were to be saturated with chlorine were prepared of known strength, and the conditions of saturation, described below, were so regulated that no change in concentration could result from the absorption of the chlorine. In consequence it was only necessary to analyze the saturated solutions for the total amount of dissolved chlorine. The solutions of sulfuric and hydrochloric acid were prepared by adding a weighed amount of distilled water to a weighed amount of a stock solution whose composition by weight had been carefully determined. The sodium, potassium and barium chloride solutions were prepared by adding weighed amounts of distilled water to weighed amounts of the carefully purified and dried salts.

The chlorine was prepared by the action of hydrochloric acid on chromic acid, and bubbled through the solution under investigation in an absorption train. As a precaution the absorption train was painted black to prevent the decomposition of chlorine by light. A brief description of the apparatus and method of saturating the solution with chlorine follows.

Two hundred cubic centimeters of 6.0 normal hydrochloric acid (the constant boiling mixture of hydrochloric acid and water) was added to a one-liter round-bottomed flask provided with a water-cooled return condenser. Into this flask were sealed two side tubes connecting with large funnels, and so arranged that concentrated hydrochloric acid could be delivered through one of these tubes beneath the surface of the liquid in the flask, and a saturated solution of chromic acid introduced through the other. The flask was heated by means of a ring burner, and the rate of influx of the two acids was regulated so as to keep the concentration of the hydrochloric acid in the flask nearly equal to that of the constant boiling mixture. The moist chlorine on leaving the condenser was bubbled through the solution under investigation in two washing bottles placed in series, and finally through a third portion of the solution in a bubble-tube, shown in the figure, which was especially designed to insure complete saturation and easy removal of a sample for analysis without loss of chlorine. The preliminary washing of the chlorine served to prevent loss by evaporation in this final absorption tube. When all air had been displaced from this train of apparatus and the solution approximately saturated at atmospheric pressure and room temperature with chlorine, the stopcock J was closed to supersaturate the solution by building up a somewhat larger pressure. After a few minutes stopcock H

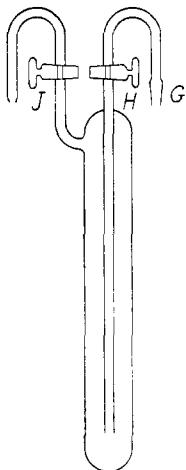


Fig. 1.

was closed, and the tube disconnected at the ground glass joint G. The tube was then placed in a rocking device in a thermostat at $25 \pm 0.01^\circ$, and slowly rocked under these conditions for a short time. Finally stopcock J was opened and the agitation continued for three or four hours to ensure the solution being saturated with chlorine at the barometric pressure. In removing a sample for analysis the tube was placed in a vertical position in a rack in the thermostat. By applying pressure at J with both stopcocks open, the sample of solution was forced out through H directly into a weighing bottle containing a solution of potassium iodide. The iodine liberated in this weighed sample was determined by titration with sodium thiosulfate using starch as an indicator.

Tabulation and Discussion of Results

The results of the determination of the solubility of chlorine at 25° and one atmosphere in pure water, and in the presence of the various electro-

lytes are recorded in the following tables. In computing the solubilities from the experimental data the partial pressure of chlorine above the solution was found by deducting from the observed barometric pressure the vapor pressure of water in the respective solutions. Then the solubility corresponding to a saturation pressure of chlorine equal to one atmosphere was calculated by applying Henry's law, which is valid over the small range of pressure involved. The values for the vapor pressure of water, shown in the third column, were obtained for the solutions of sulfuric acid from Brönsted¹⁰ and from Grollman and Frazer,¹¹ of hydrochloric acid from Dobson and Masson,¹² of sodium chloride from Negus,¹³ of potassium chloride from Lovelace, Frazer and Sease¹⁴ (calculated over from 20° to 25°), and of barium chloride, where no data were available, under the assumption that the vapor pressures of these solutions were equal to those of potassium chloride of the same formality.

The equilibrium concentrations recorded in the tables were calculated from the total solubility by the equations considered in the introduction. The value (0.0592 molal) given in Table I for the molality s_0 of Cl_2 in pure water saturated with chlorine at 25° and 1 atmosphere was obtained by extrapolation of the values for s , the molality of Cl_2 in the different sulfuric acid solutions saturated with chlorine, to zero concentration of sulfuric acid. This value for the solubility constant of chlorine in water was confirmed by making a similar extrapolation of the concentrations of the unhydrolyzed portion of the dissolved chlorine in solutions of hydrochloric acid saturated with chlorine. Since hydrochloric acid has a much larger effect in depressing the hydrolysis of chlorine than does sulfuric acid, and since the trichloride formation in the diluter solutions of hydrochloric acid is inappreciable, this latter method of extrapolation is attended with much less error.

A comparison of the values (in Table I) for the activity coefficient (s_0/s) of chlorine in the sulfuric acid solutions with the corresponding values for oxygen given by Randall and Failey² led to the adoption of equation (1) for the converse calculation of the values (in Table II) for the activity coefficient of chlorine in the chloride solutions. For these calculations reference was made to the solubility data for oxygen given by Randall and Failey,² and by McArthur.³

The equilibrium constant of the reaction $\text{Cl}_2(\text{g}) + \text{Cl}^- = \text{Cl}_3^-$ may be expressed in either of the following forms

$$K = \frac{\alpha_{\text{Cl}_3^-} (\text{Cl}_3^-)}{\alpha_{\text{Cl}^-} (\text{Cl}^-) p_{\text{Cl}_2}} \text{ or } K = \frac{\alpha_{\text{Cl}_3^-} (\text{Cl}_3^-)}{\alpha_{\text{Cl}^-} \alpha_{\text{Cl}_2} (\text{Cl}^-)(\text{Cl}_2)} \cdot s_0$$

¹⁰ Brönsted, *Z. physik. Chem.*, **68**, 693 (1910).

¹¹ Grollman and Frazer, *THIS JOURNAL*, **47**, 712 (1925).

¹² Dobson and Masson, *J. Chem. Soc.*, **125**, 668 (1924).

¹³ Negus, "Dissertation," Johns Hopkins University.

¹⁴ Lovelace, Frazer and Sease, *THIS JOURNAL*, **43**, 102 (1921).

The values for this complex constant recorded in the tenth column of Table II were calculated by the first of these expressions under the assumption that the activity coefficients ($\alpha_{\text{Cl}_2^-}$ and α_{Cl^-}) of the ions were equal; and those in the eleventh column by the second under the assumption that the activity coefficient ($\alpha_{\text{Cl}_2^-}$) of the complex ion is equal to the product ($\alpha_{\text{Cl}^-}\alpha_{\text{Cl}_2}$) of the activity coefficients of the chloride ion and of the

TABLE I

SOLUTIONS OF SULFURIC ACID SATURATED WITH CHLORINE AT 1 ATM.						
Formality of H_2SO_4 , C	Total solubility, $\Sigma(\text{Cl}_2)$	Vap. press. of water, $p_{\text{H}_2\text{O}}$	Act. coeff. of HCl, α	Equilibrium concentrations (HClO) ($\text{Cl}_2 = s$)		Act. coeff. of Cl_2 , $\alpha_{\text{Cl}_2} = s_0/s$
4.9901	0.04066	16.7 mm.	..	0	0.04066	1.45
3.9934	.04278	18.3	..	0	.04278	1.39
3.0090	.04550	19.9	1.186	0.0014	.04410	1.34
1.9686	.04977	21.7	0.719	.00318	.04659	1.270
1.0240	.05617	22.8	.634	.00535	.05082	1.165
0.4995	.06272	23.3	.579	.00874	.05398	1.097
0.0000	.0923	23.8	..	(.0331)	(.0592)	1.000

TABLE II

SOLUTIONS OF VARIOUS CHLORIDES SATURATED WITH CHLORINE AT 1 ATM.

Formality of electrolyte, C	Total solubility, $\Sigma(\text{Cl}_2)$	Vap. press. of water, $p_{\text{H}_2\text{O}}$	Act. coeff. of HCl, α	Act. coeff. of Cl_2 , s_0/s	Equilibrium Concentrations				Complex constant	
					$s = (\text{Cl}_2)$	(HClO)	(Cl_2^-)	(Cl^-)	$(\text{Cl}_2^-)/(\text{Cl}^-)$	$\frac{(\text{Cl}_2^-)(0.0592)}{(\text{Cl}_2)(\text{Cl}^-)}$
Hydrochloric Acid										
5.180	0.1004	17.2	...	1.228	0.04821	0.000	0.0522	5.128	0.0100	0.0123
3.987	.0914	19.0	...	1.180	.05017	.000	.0412	3.946	.0104	.0123
2.990	.0824	20.4	...	1.138	.05200	.000	.0304	2.960	.0103	.0117
1.991	.0737	21.7	...	1.095	.05404	.000	.0197	1.971	.0100	.0110
1.019	.0665	22.8	...	1.052	.05630	.000	.0102	1.009	.0101	.0106
0.496	.0630	23.3	0.762	1.027	.05766	.0001	.0052	0.4908	.0106	.0109
.200	.0619
.100	.06394
.010	.08264
Sodium Chloride										
4.989	0.03087	19.2	1.995	4.076	0.01452	0.00017	0.01618	4.973	0.00325	0.0132
3.989	.03601	20.2	1.336	3.075	.01925	.001054	.01571	3.974	.00395	.0121
2.991	.04161	21.2	1.083	2.318	.02554	.001772	.01430	2.978	.00480	.0112
0.998	.05795	23.0	0.766	1.319	.04488	.005987	.00708	0.997	.00710	.0094
0.501	.06575	23.3	0.731	1.151	.05144	.00954	.00477	0.5058	.00943	.0108
Potassium Chloride										
3.913	0.04724	20.7	1.028	2.36	0.02509	0.00160	0.02055	3.984	0.00528	0.0128
3.014	.04865	21.4	0.866	1.96	.03014	.00241	.01610	3.003	.00536	.0105
2.013	.05388	22.3	.783	1.58	.03737	.00370	.01281	2.004	.00639	.0101
1.000	.06109	23.0	.711	1.26	.04694	.00659	.00756	0.9990	.00757	.0097
0.500	.06610	23.4	.706	1.12	.05266	.01003	.00341	0.5066	.00673	.0075
Barium Chloride										
1.333	0.04468	22.5	1.011	2.046	0.02894	0.00220	0.01354	2.655	0.00508	0.0106
1.000	.04924	23.0	0.884	1.696	.03491	.00323	.01110	1.992	.00557	.0095
0.667	.05494	23.3	.784	1.406	.04210	.00493	.00791	1.331	.00593	.0085
0.330	.06216	23.5	.731	1.173	.05046	.00822	.00348	0.6713	.00521	.0061

dissolved chlorine. Each series of values thus computed should, on extrapolation to zero concentration of the added chloride, give the true value for the complex constant.

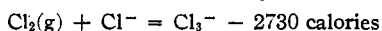
The best agreement of the complex constants among themselves was obtained in the case of the hydrogen chloride solutions. Furthermore, both expressions for computing the complex constant lead to substantially the same value, namely, nearly equal to 0.01.

This good agreement is accounted for by the fact that in the hydrogen chloride solutions an increase in solubility of chlorine due directly to the formation of the complex ion is the predominating effect, and hence the calculation of the concentration of the trichloride ion from the total solubility is attended with slight error. On the contrary, in the case of the other chloride solutions the increase in solubility due to complex ion formation becomes of minor influence, and is more than compensated by the very large decrease in solubility due to salting-out effect. The effect of hydrolysis also enters as a small but appreciable factor.

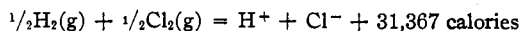
For example, in the 3.987 formal solution of hydrochloric acid the increase in solubility of chlorine (referred to 0.0592 *m*) due to hydrolysis is negligible, the decrease due to the salting-out effect is 15.3% whereas the increase due to complex-ion formation is 69.6%. In contrast, in the 3.989 formal solution of sodium chloride, the increase in solubility due to hydrolysis is 1.8%, the decrease due to the salting-out effect is 67.5%, and the increase due to complex-ion formation is 26.5%.

In the case of the solutions of sodium, potassium and barium chlorides the agreement of the values computed for the complex constants with each other, and with those obtained from the investigation of the hydrogen chloride, is very satisfactory when there is taken into consideration the fact that the large salting-out effect of these chlorides on chlorine was indirectly estimated by comparison with their salting-out effects on oxygen. Thus, for the sodium chloride and potassium chloride solutions, the complex constants recorded in the last column agree well among themselves, and yield an average value approximately equal to 0.01, the value found for solutions of hydrogen chloride. The values in the tenth column show greater variation among themselves and are all less than 0.01, but there appears to be a trend toward this value as the concentration of the added electrolyte approaches zero. The least satisfactory agreement was found in the case of the barium chloride solutions, due probably to the additional approximate assumptions involved in the calculations.

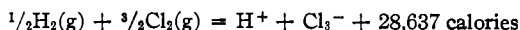
If 0.01 be adopted as the value for the complex constant of the trichloride ion, the free-energy decrease attending its formation out of chlorine gas and chloride ion may be computed by the familiar expression $-\Delta F = RT \ln K$. The result is shown by the free-energy equation



According to Lewis and Randall at 25°



By addition of these two free-energy equations there results



That is, $\Delta F_{298} = -28,637$ calories for Cl_3^- (or for one formula weight of aqueous HCl_3).

Summary

The solubility of chlorine was determined at 25° and 1 atmosphere in solutions of sulfuric acid, of hydrogen chloride, of sodium chloride, of potassium chloride and of barium chloride, and compared with the corresponding solubilities of oxygen. By means of such a comparison the salting-out effect of these electrolytes on the dissolved chlorine was estimated. This made it possible to compute from the total solubility of chlorine the extent of trichloride formation in the chloride solutions, and the corresponding value for the equilibrium constant of the reaction $\text{Cl}_2(\text{g}) + \text{Cl}^- = \text{Cl}_3^-$. The value for this constant was found to be 0.01, the corresponding free energy of formation of trichloride ion, in the system of Lewis and Randall being $-28,637$ calories.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

THE COMPARISON OF CERTAIN COMMERCIAL GETTERS

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For many years certain materials have been used in lamps and vacuum tubes for the removal of traces of gases so as to improve the vacuum. These materials may be divided into two classes: (1) those acting as adsorbents by virtue of their finely divided condition or activation, that is, those having tremendous surfaces upon which gases can be strongly held by adsorption, and (2) those which possess high chemical activity. To the first class belong active charcoal, copper oxide powder, powdered thoria, etc. The second class includes the alkali metals, alkaline earth metals, and probably phosphorus—the material so much used in incandescent lamps. All of these materials are called "getters" in the technical slang of the day.

The work reported here is confined to a comparison of the efficacy of the common getters of class two. We have tested calcium, barium, magnesium, sodium and phosphorus for the degree of vacuum produced under given conditions and the speed with which this vacuum is reached. These getters are all used as thin coatings on the walls of bulbs or tubes. They