[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

# The Hydrolysis of Chlorine and its Variation with Temperature

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The hydrolysis equilibrium constant of chlorine was measured from 0 to 45° using a conductivity method. The value at 25° of $(3.94 \pm 0.02) \times 10^{-4}$ is compared with previous results. In agreement with the observations of earlier investigators, the reaction was found to have a positive $\Delta\bar{H}^0$ which changes rapidly with temperature, corresponding to a value of $\Delta\bar{C}_p{}^0$ of approximately $-93$ cal. mole$^{-1}$ deg.$^{-1}$. It is argued that this value arises primarily from the properties of $Cl_2(aq)$ and the significance of the large heat capacity of this species is discussed in terms of plausible models. A picture based on a gas hydrate-like structure, which undergoes a progressive breakdown with increasing temperature, is contrasted with a model consisting of two species, one of which is more hydrated than the other. Evidence for the latter comes from spectral changes, while the former model is supported by the similarity in behavior of the partial molal heat capacity of other non-polar gases in water.

Liebhafsky[1] called attention to the remarkable variation of the heat of hydrolysis of chlorine with temperature. From Jakowkin's[2] measurements it appears that $\Delta\bar{H}$ changes from 8000 cal. per mole near 0° to 2900 cal. per mole near 50°. Liebhafsky interpreted these results as indicating the existence of hydrated chlorine in equilibrium with non-hydrated or less hydrated chlorine, with the equilibrium shifting with temperature. He pointed out that similar temperature effects are found in the aqueous solubility equilibrium of chlorine gas and the distribution of chlorine between water and carbon tetrachloride. Bromine and iodine show similar effects.

It was of interest to repeat Jakowkin's measurements of the hydrolysis constant in order to determine more accurately the variation of heat of hydrolysis and also to resolve the disagreement between the various values for the hydrolysis constant reported in the literature. Since Jakowkin did not interpret the change in conductance as it is now interpreted, his data have been recalculated by other investigators[3-7] with results ranging from $4.84$ to $3.90 \times 10^{-4}$ at 25°. Several additional investigators[4,6-10] have determined experimentally the hydrolysis constant, but their values at 25° vary from $2.09 \times 10^{-4}$ up to "values close to Jakowkin's."[9]

Various methods have been used to measure the hydrolysis: conductance,[2] distribution equilibrium between water and carbon tetrachloride,[2] solubility,[2] $p$H,[4] spectrophotometry,[7] kinetics[6] and freezing point lowering.[8] Conductance was chosen for the present work because it was believed to be the most accurate. In this method the hydrochloric acid formed by the hydrolysis

$$Cl_2 + H_2O = H^+ + Cl^- + HOCl \qquad (1)$$

is determined from the conductivity of the solution. The hypochlorous acid concentration is essentially equal to the hydrochloric acid concentration in water solutions of chlorine. The chlorine concentration is obtained by difference using the titer of the total chlorine present.

## Experimental

The conductivity cell illustrated in Fig. 1 permitted the measurement of the conductivity of a chlorine solution in (C), followed by the determination of the total concentration of chlorine. The apparatus was constructed so as to minimize the chlorine volatility error. The volume of flask (A) was 500 cc. and of bulb (B) about 30 cc. The electrodes were approximately 1 cm. in diameter and lightly platinized according to the procedure of Jones and Bollinger.[11] The distance between the two electrodes was chosen so that the resistance of all measurements could be read to about ±0.03%. The leads from the electrodes to the contact tubes were sealed in solid glass and were connected directly to the wire leads to the bridge, with no mercury being used for making the contacts. The Parker effect[12] was believed to be negligible.

The volume of the cell (*i.e.*, the volume between stopcocks $S_1$ and $S_2$) was determined to be 45.74 cc. at 25° by titration of hydrochloric acid with sodium hydroxide; this value was checked iodimetrically. The volume at other temperatures was calculated from the equation

$$V_t = V_{25}(1 + 1.11 \times 10^{-5}(t - 25))$$

where $t$ is the temperature in °C.

The cell and the chlorine generator were covered with black cloth or paper during the whole experiment in order to avoid any light induced decomposition of hypochlorous acid or attack of platinum by chlorine on exposure to light.[13]

The cell constant was determined at 25° with 0.1 demal potassium chloride solution both before and after the chlorine hydrolysis measurements at 25°. The value was 0.4324 cm.$^{-1}$ and no difference was found in the two sets of determinations. Values at other temperatures were calculated[14] using the coefficients of thermal expansion of Pyrex glass and platinum. The cell constant was also measured at 0°, and the result agreed with the value calculated from 25° by correction for temperature.

The conductance apparatus consisted of three vacuum tube oscillators (550, 900 and 2800 c.p.s.), in conjunction with a Leeds and Northrup conductivity bridge. The null point was detected by an oscilloscope. The resistance box was a six dial, shielded instrument supplying a total of 11,111.1 ohms.

Five temperatures, *i.e.*, 0, 15, 25, 35 and 45°, were used in measuring the hydrolysis constant. A thermostated transformer oil-bath constant to ±0.05° (±0.03° for 25°) was employed.

The equivalent conductances of pure HCl solutions with the concentrations in the region from 0.005 to 0.05 $M$ were examined at 0, 15 and 45°. The results agreed with those of Owen and Sweeton[15] within experimental error at 15 and 45°.

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[1] H. A. Liebhafsky, *Chem. Revs.*, **17**, 89 (1935).

[2] A. A. Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899).

[3] G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Company, New York, N. Y., 1923.

[4] H. Hagisawa, *Bull. Inst. Phys. and Chem. Research (Tokyo)*, **20**, 999 (1941).

[5] J. C. Morris, THIS JOURNAL, **68**, 1692 (1946).

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[8] W. A. Roth, *Z. physik. Chem.*, **145A**, 289 (1929).

[9] G. B. Kolhatkar and U. A. Sant, *J. Univ. Bombay*, **12A**, 57 (1943).

[10] E. A. Shilov and S. N. Solodushenkov, *Acta Physiochim. U.R.S.S.*, **20**, 667 (No. 5, 1945).

[11] G. Jones and D. M. Bollinger, THIS JOURNAL, **57**, 280 (1935).

[12] G. Jones and G. M. Bollinger, *ibid.*, **53**, 411 (1931).

[13] J. W. Mellor, *J. Chem. Soc.*, **81**, 1280 (1902).

[14] E. W. Washburn, THIS JOURNAL, **38**, 2431 (1916).

[15] B. B. Owen and F. H. Sweeton, *ibid.*, **63**, 2811 (1941).

**Reagents.**—Chlorine gas was prepared by adding 4 *M* hydrochloric acid to Baker and Adamson reagent grade manganese dioxide and heating the mixture. The evolved gas was passed through two bubblers successively filled with distilled water and conductivity water, in order to remove any hydrochloric acid. The gas was passed into another flask filled with conductivity water for collection.

Conductivity water was prepared by redistilling distilled water from alkaline permanganate solution in a tin still. The specific conductance was about $1.0 \times 10^{-6}$ $\text{ohm}^{-1}$ at 25°.

The 0.1 demal potassium chloride solution was prepared according to the procedure of Jones and Bradshaw.[16] Three independently prepared samples of Mallinckrodt Analytical Reagent KCl were used to measure the cell constant and no difference was found.

A stock solution of sodium thiosulfate was prepared from Mallinckrodt Analytical Reagent and was standardized against potassium iodate using starch as indicator.

The standard HCl solution used in checking the equivalent conductance of HCl was prepared by diluting Baker and Adamson C.P. HCl with conductivity water. The hydrochloric acid solution was titrated against standard sodium hydroxide and the latter was standardized against potassium acid phthalate.

**Procedure.**—The aqueous chlorine solution was poured into flask (A) and the apparatus was closed by inserting ground glass stoppers in the tops of (A) and (B). With both stopcocks open the solution was tilted back and forth thoroughly through the cell and flask (A), until the contents were homogeneously mixed. The stopcocks were then closed, after making sure that there were no bubbles in the cell. The black jacket around (A) was taken off and both (A) and (B) were washed with distilled water until the washings taken out from (E) and (F) were free of chlorine according to the potassium iodide test. This washing procedure was repeated four times more. Then both (E) and (F) were half filled with water. This distilled water was used for testing for chlorine with potassium iodide after the measurement of conductivity, in order to confirm that there were no leaks through the stopcocks which had been lubricated with Kel-F No. 90 grease or Dow Corning silicone lubricant. The cell then was put into the bath and left there about one hour so as to establish temperature equilibrium.

The resistance was measured at each frequency. The readings were taken every five minutes until three successive readings checked with each other. After the completion of the third frequency measurement (550 c.p.s.) the resistance reading at the first frequency measurement (2800 c.p.s.) was checked once more. No difference between the final resistance measurement and that of the initial measurement at 2800 c.p.s. ever was found.

After the measurement of the conductivity, the cell was taken out of the bath. Bulb (B) was filled with potassium iodide solution, and potassium iodide solution acidified with sulfuric acid was added to (A) to about level (D). The concentrations of iodide ion and hydrogen ion were both adjusted to 0.1 *M* for the titration.

As the stopcocks were opened in the order of $S_1$ and then $S_2$, the chlorine was pushed out by the potassium iodide solution in (B) and received by the potassium iodide solution in (A). The cell was washed twice more with potassium iodide passing through compartment (B). Finally the stopcocks were closed, and the triiodide solution was titrated with 0.1 normal standard sodium thiosulfate solution in compartment (A). The cell was washed once more with distilled water through compartment (B) and was again tilted back and forth near the end-point and before the starch indicator was added to make sure that all the chlorine was titrated.

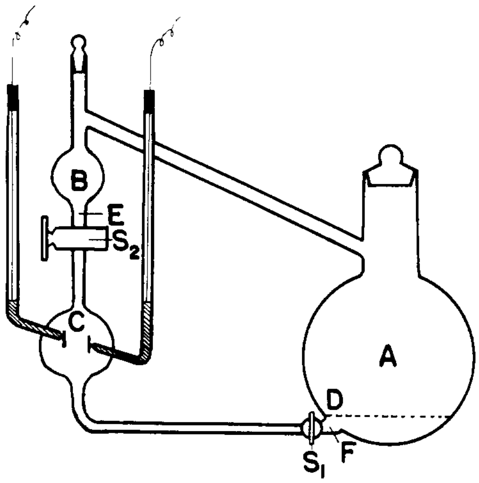

Fig. 1.—Conductivity cell.

### Results and Calculations

The data used in calculating the hydrolysis constant at 25° are presented in Table I. Similar measurements were made at 0, 15, 35 and 45°. The first column records the molarity (moles per liter of solution) of the chlorine solution at the temperature of the experiment, as obtained from the titration. The second column gives the specific conductance calculated from the conductance measurements by using $\kappa = c/R$ where $c$ equals the cell constant and $R$ is the resistance. For a given solution the resistances at the three frequencies were plotted *versus* the reciprocal of the square root of the frequency so that the data could be extrapolated to infinite frequency to eliminate polarization resistance. The plot was not a straight line as found by Jones and Christian.[17] The best smooth curve was drawn through the data and extrapolated. The cell constant was determined similarly. Hydrochloric acid solutions of known concentration gave equivalent conductances equal to those of Owen and Sweeton[15] within the accuracy of the titration when treated similarly.

In the third column of Table I is given the equivalent conductance of hydrochloric acid in the chlorine solution, interpolated from the data of reference 15, while in the fourth column is listed the fraction of the chlorine hydrolyzed. These latter two values depend on each other and had to be obtained by successive approximations. Although Owen and Sweeton[15] measured the equivalent conductance at 15, 25, 35 and 45°, their lowest temperature was 5°; therefore the equivalent conductances of three standardized HCl solutions in the concentration range 0.005 to 0.05 *M* were measured at 0°. The values agreed well with those extrapolated from Owen and Sweeton's data.

The $K'$ values in column 5 are defined as

$$K' = (H^+)(Cl^-)(HOCl)/(Cl_2) = M^2x^3/(1 - x)$$

where the parentheses represent concentrations in moles per liter. The activity coefficients of hydrochloric acid shown in the seventh column were obtained by interpolation of Harned and Owen's values.[18] The $K$ values in the last column represent the hydrolysis constant of chlorine at zero ionic strength

$$K = a_{H^+}a_{Cl^-}a_{HOCl}/a_{Cl_2}a_{H_2O} \cong K'\gamma^2_{\pm HCl}$$

where $a$ is the activity of the species designated. In calculating $K$ it was assumed that $\gamma_{Cl_2}\gamma_{H_2O}$ cancelled $\gamma_{HOCl}$ to a good approximation. The

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[16] G. Jones and B. C. Bradshaw, This Journal, **55**, 1780 (1933).

[17] G. Jones and S. M. Christian, *ibid.*, **57**, 272 (1935).

[18] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold Publ. Corp., New York, N. Y., 1958.

TABLE I

DATA FOR THE DETERMINATION OF THE HYDROLYSIS CONSTANT AT 25.00 ± 0.03°

Av. $K_{25} = (3.944 \pm 0.020) \times 10^{-4}$

| $M \times 10^2$ (mole l.$^{-1}$) | $\kappa \times 10^3$ (cm.$^{-1}$ ohm$^{-1}$) | $\lambda$ (ohm$^{-1}$ cm.$^2$ eq.$^{-1}$) | $x$ | $K' = M^2x^3/(1-x) \times 10^4$ | (H$^+$) $\times 10^2$, $M$ | $\gamma_{\pm \text{HCl}}$ | $K = K'\gamma^2_{\pm \text{HC}} \times 10^4$ |
|---|---|---|---|---|---|---|---|
| 1.307 | 4.362 | 411.6 | 0.8110 | 4.819 | 1.060 | 0.9031 | 3.931 |
| 2.025 | 5.863 | 409.6 | .7070 | 4.943 | 1.431 | .8922 | 3.934 |
| 2.667 | 6.943 | 408.4 | .6375 | 5.083 | 1.700 | .8843 | 3.974 |
| 3.733 | 8.355 | 407.0 | .5500 | 5.151 | 2.053 | .8747 | 3.941 |
| 4.398 | 9.080 | 406.3 | .5081 | 5.158 | 2.235 | .8720 | 3.922 |
| 5.360 | 10.03 | 405.5 | .4616 | 5.249 | 2.474 | .8684 | 3.958 |
| 6.442 | 10.92 | 404.8 | .4189 | 5.249 | 2.699 | .8650 | 3.927 |
| 7.397 | 11.67 | 404.3 | .3904 | 5.338 | 2.887 | .8622 | 3.968 |

TABLE II

THERMODYNAMIC QUANTITIES FOR THE HYDROLYSIS OF CHLORINE

| $T$, °K. | $K \times 10^4$ | $\Delta\bar{F}^0$, cal. mole$^{-1}$ | $\Delta\bar{H}^0$, kcal. mole$^{-1}$ | $\Delta\bar{S}^0$, cal. mole$^{-1}$ deg.$^{-1}$ |
|---|---|---|---|---|
| 273.16 ± 0.05 | 1.458 ± 0.011 | 4795 ± 4 | 7.32 ± 0.14 | 9.24 ± 0.51 |
| 288.16 ± .05 | 2.809 ± .015 | 4683 ± 3 | 5.97 ± .14 | 4.47 ± .49 |
| 298.16 ± .03 | 3.944 ± .020 | 4644 ± 3 | 5.06 ± .13 | 1.40 ± .44 |
| 308.16 ± .05 | 5.104 ± .021 | 4642 ± 3 | 4.09 ± .12 | −1.79 ± .39 |
| 318.16 ± .05 | 6.051 ± .027 | 4685 ± 3 | 3.12 ± .12 | −4.92 ± .38 |

uncertainty of the average value of the hydrolysis constant represents the standard deviation.

In Table II are listed the average values of $K$ obtained from the experiments at other temperatures, along with the standard deviation. Eight solutions were measured at each temperature. The logarithm of the average value of the hydrolysis constant was plotted against the reciprocal of the absolute temperature as shown in Fig. 2. From the slope of the curve, one obtains $\Delta\bar{H}^0$ as reported in the fourth column of Table II. The uncertainty of $\Delta\bar{H}^0$ given in column 4 was estimated by allowing the maximum range in the standard deviation of the equilibrium constants. The values of $\Delta\bar{S}^0$ were calculated from $\Delta\bar{F}^0$ and $\Delta\bar{H}^0$.

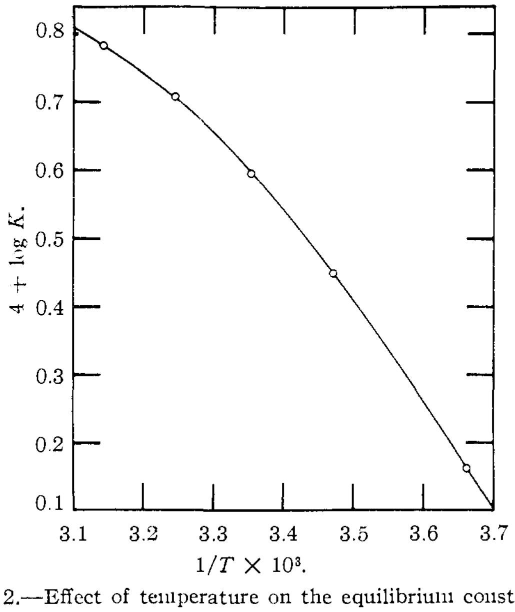

Fig. 2.—Effect of temperature on the equilibrium constant for the hydrolysis of chlorine.

From the slope of the plot of $\Delta\bar{H}^0_0$ *versus* temperature (Fig. 3) $\Delta\bar{C}^0_p$ was obtained. Because of the uncertainty in $\Delta\bar{H}^0_0$ (indicated by the vertical lines), $\Delta\bar{C}^0_p$ is relatively inaccurate, although it is clearly a large negative quantity. The value of $\Delta\bar{C}^0_p$ calculated from the slope of the straight line of Fig. 3 is −93 cal. deg.$^{-1}$ mole$^{-1}$ and it appears to be fairly constant over the temperature range studied.

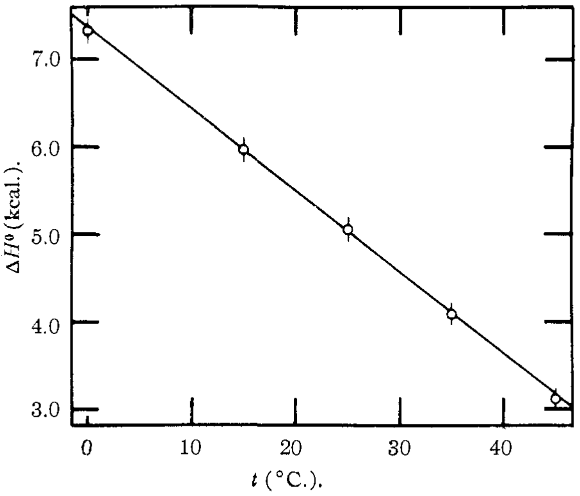

Fig. 3.—Variation of $\Delta\bar{H}^0$ of the hydrolysis of chlorine with temperature.

The formation of trichloride ion was taken into consideration as one of the possible sources of error. The equilibrium constant of the reaction

$$Cl_2 + Cl^- \overset{K_1}{\rightleftharpoons} Cl_3^- \qquad (2)$$

has been reported to be 0.18 at 25°.[19] The presence of $Cl_3^-$ introduces a small error because of the differing equivalent conductances of $Cl^-$ and $Cl_3^-$ and because it lowers the concentrations of $Cl_2$ and $Cl^-$. This correction vanishes at approximately equal concentrations of $Cl_2$ and $Cl^-$, the exact con-

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(19) M. S. Sherrill and E. F. Izard, THIS JOURNAL, **53**, 1667 (1931).

dition depending on the difference in equivalent conductances of the ions. At 25° the maximum error in $K$ was estimated to be 0.2%, which is less than the experimental accuracy. The variation in $K_1$ with temperature is estimated to be small so that the error arising from $Cl_3^-$ formation should lie well within the experimental accuracy over the whole temperature range covered.

In the preparation of chlorine the volatility of hypochlorous acid through the occurrence of the reaction

$$2HOCl(aq) = Cl_2O(g) + H_2O(l) \qquad (3)$$

was also a possible source of error. The value of $\Delta F^0_{298°K}$ of this reaction has been given as 3350 cal.[20] The vapor pressure of $Cl_2O$ in the washing bottle solution, which was supposed to be saturated with chlorine, was calculated in order to estimate the volume of chlorine gas which would be needed to carry sufficient $Cl_2O$ from the washing bottle to the collection flask to give 1% error in the concentration of hypochlorous acid in the collection flask. The result was of the order of magnitude of $10^3$ liters of chlorine gas per liter of solution. Therefore this source of error was thought to be negligible.

## Discussion

The present results are compared with those of other investigators in Table III. The variety of results obtained merely by recalculation of Jakowkin's data is interesting. Jakowkin used several methods of measurement and different authors have weighted the methods differently. Zimmerman and Strong's recalculation of Jakowkin's conductivity data yielded a $K$ in excellent agreement with our value. Of the more recent experimental determinations of $K$, that of Zimmerman and Strong[7] appears to be most carefully done. The discrepancy between their value and the present result at 25° lies well outside of the combined, estimated uncertainties. In correspondence with Professor Zimmerman we have been unable to identify with certainty a systematic error in either method which could produce the observed difference. In the conductivity method, the assumption that the equivalent conductances of $H^+$ and $Cl^-$ are unaffected by the presence of $Cl_2$ and HOCl, would probably result in too low values of $K$, since it would be expected that the mobility of the ions would be decreased by the replacement of water by foreign molecules. In the spectrophotometric method it was assumed that the molar absorptivities of $Cl_2$ were unchanged in going from an ionic strength of 1.0 to *ca.* 0.015 $M$, but it seems unlikely that the change could be large enough to account for the discrepancy. A few spectral measurements of chlorine dissolved in hydrochloric acid indicate that Zimmerman and Strong's use of too low a value for the molar absorptivity of $Cl_2$ at 3250 Å. might be the source of the difference.

TABLE III

SUMMARY OF THE VALUES OF THE HYDROLYSIS CONSTANT ($K \times 10^4$) AT DIFFERENT TEMPERATURES

| Ref. | 0° | 15° | 25° | 35° | 45° |
|---|---|---|---|---|---|
| 3[a] | 1.45 | 3.28 | 4.84 | 6.43 | 7.84 |
| 8 | 1.5 to 1.6 | ... | ... | ... | ... |
| 4[a] | ... | ... | 4.06 | ... | ... |
| 4 | ... | ... | 2.09 | ... | ... |
| 5[a] | 1.56 | 3.16 | 4.48 | ... | ... |
| 6[a] | 1.45 | (2.88)[b] | 4.47 | 5.68 | ... |
| 6 | 1.23 | ... | 3.4 | ... | ... |
| 7[a] | ... | ... | 3.90 | ... | ... |
| 7 | ... | ... | 3.35 | ... | ... |
| This investigation | 1.46 | 2.81 | 3.94 | 5.10 | 6.05 |

[a] Results recalculated from Jakowkin's data. [b] For 12.8° rather than 15°.

The most interesting feature of the hydrolysis of chlorine is the rapid change of $\Delta \bar{H}^0$ with temperature, arising from a large negative value of $\Delta \bar{C}_p{}^0$ for the hydrolysis. An attempt was made to confirm the magnitude of $\Delta \bar{C}_p{}^0$ from other measurements. The partial molal heat capacity of hypochlorous acid has not been measured, but it seemed likely that methyl alcohol would serve as a good analog. The data of Doroshevskii[21] yielded 32 cal. deg.$^{-1}$ mole$^{-1}$ for aqueous methanol which was averaged with 37 cal. deg.$^{-1}$ mole$^{-1}$ calculated by Glew[22] from the data of Bose. For the solution of chlorine gas in water Glew's[23] value of 84.30 cal. deg.$^{-1}$ mole$^{-1}$, calculated from the data of Winkler[24] without correction for hydrolysis, was corrected to give 70 cal. deg.$^{-1}$ mole$^{-1}$. Combination with the heat capacity of chlorine gas[25] yields 78 cal. deg.$^{-1}$ mole$^{-1}$ for the partial molal heat capacity of aqueous chlorine.

Using the above values and that for hydrochloric acid,[18] the value of $\Delta \bar{C}_p{}^0$ at 25° for the hydrolysis of chlorine is estimated to be $-90$ cal. deg.$^{-1}$ mole$^{-1}$. This value agrees fortuitously well with the value of $-93$ cal. deg.$^{-1}$ mole$^{-1}$ found experimentally in the present research.

It is apparent that the large negative value of $\Delta \bar{C}_p{}^0$ of hydrolysis arises primarily from the large positive value of the aqueous partial molal heat capacity of chlorine, *i.e.*, 78 cal. deg.$^{-1}$ mole$^{-1}$. Liebhafsky[1] had reached this conclusion from his study of equilibria involving aqueous chlorine and he hypothesized the existence of two hydrates whose relative concentrations varied with temperature. Frank and Evans[26] have proposed that nonpolar gases dissolved in water cause the formation of ordered arrangements of water around them—"icebergs"—whose "melting" with increasing temperature is the source of the large $\bar{C}_p{}^0$. Such configurations might correspond to partially formed gas-hydrate structures[27-30] for which it is known that the water molecules, while being hydrogen

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(20) C. H. Secoy and G. H. Cady, THIS JOURNAL, **63**, 2504 (1941).

(21) A. G. Doroshevskii, *C. A.*, **4**, 1404 (1910).

(22) D. N. Glew, *Disc. Faraday Soc.*, **15**, 267 (1953).

(23) D. N. Glew and E. A. Moelwyn-Hughes, *ibid.*, **15**, 150 (1953).

(24) L. W. Winkler, *Mathematikai ės Természettudományi Ertesitö*, **25**, 86 (1907), Budapest.

(25) "Selected Values of Chemical Thermodynamic Properties," Series III, National Bureau of Standards, 1954.

(26) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

(27) W. F. Claussen, *ibid.*, **19**, 1425 (1951).

(28) H. R. Müller and M. v. Stackelberg, *Naturwissenchaften*, **39**, 20 (1952).

(29) L. Pauling and R. E. Marsh, *Proc. Natl. Acad. Sci. U.S.*, **38**, 112 (1952).

(30) M. v. Stackelberg and H. R. Müller, *Z. Elektrochem.*, **58**, 25 (1954).

bonded to each other, leave holes for the gas molecules which presumably interact through London forces with the atoms on the inner surface of the holes. Recently Heidt and Johnson[31] have discussed the behavior of oxygen dissolved in water and suggested the existence of two definite hydrates having water molecules hydrogen bonded to oxygen.

In principle the variation of $\Delta\bar{C}_p^0$ with temperature could be used to distinguish between a two-hydrate model and a more complex "gas-hydrate like" or "iceberg" type of model. In practice no decision can be made for chlorine. The chlorine hydrolysis data can just barely be fitted by a two-hydrate model, assuming fixed heat capacities for the hydrates. Equally well $\Delta\bar{C}_p^0$ could be constant over the whole temperature range, corresponding to a continuous breakdown of a more complex structure. The oxygen solubility data, which cover a larger temperature interval, can be fitted by a two-hydrate model except near 100°, and of course can be fitted by more complex models.

The appreciable changes in the spectrum of $Cl_2$[7] and $O_2$[31] on dissolution in water might indicate a specific interaction with one (or a small number of) water molecule. The similarity in behavior of all inert gases, however, would argue for a more general "iceberg" or "gas-hydrate" type of interaction.

**Thermodynamic Functions.**—From the hydrolysis equilibrium it is possible to calculate a number of thermodynamic quantities which are not presently tabulated in the literature. These quantities are shown in Table IV. The $Cl_2(aq)$ data were obtained from the solubility[24] of chlorine in water (corrected for hydrolysis) and the temperature coefficient of solubility. The HOCl values were then obtained using the present hydrolysis data. A value of −29.7 kcal. for $\Delta\bar{H}_f^0$ of HOCl at 18° also was calculated and found to be in good agreement with the calorimetrically measured value of −29.8 kcal.[32]

TABLE IV

THERMODYNAMIC FUNCTIONS OF CHLORINE COMPOUNDS

Temperature, 298.16°K.

| | $\Delta\bar{F}_f^0$ (kcal./mole) | $\Delta\bar{H}_f^0$ (kcal./mole) | $\bar{S}^0$ (e.u.) |
|---|---|---|---|
| $Cl_2(aq)$ | 1.656 | −6.16 | 27.1 |
| HOCl | −19.040 | −29.39 | 32.0 |
| $ClO^-$ | −8.858 | −25.94 | 9.5 |

The $ClO^-$ data were calculated using Ingham and Morrison's value[33] for the ionization constant of HOCl at 18° and the value for the heat of ionization at 18°.[32] Both values were corrected to 25° using Pitzer's equations[34] for the effect of temperature on the ionization of oxygenated acids.

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BERKELEY, CALIF.

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[31] L. J. Heidt and A. M. Johnson, THIS JOURNAL, **79**, 5587 (1957).

[32] F. R. Bichowsky and F. D. Rossini, "Thermochemistry of the Chemical Substances," Reinhold Publ. Corp., New York, N. Y., 1936.

[33] J. W. Ingham and J. Morrison, *J. Chem. Soc.*, 1200 (1933).

[34] K. S. Pitzer, THIS JOURNAL, **59**, 2365 (1937).

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[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORIES, LOUISIANA STATE UNIVERSITY]

# The Stability of $FeCl^{++}$ in Perchlorate Solutions[1]

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The stability constants of the species $FeCl^{++}$, formed by complexing chloride ion with a large excess of iron(III), have been determined. This complex exhibits an absorption band around 350 mμ which was used for a spectrophotometric estimation of $K_1$, the stability constant of $FeCl^{++}$. $K_1$ was determined by measuring the concentration of the complex at the wave length of maximum absorption at various concentrations of iron(III) in perchloric acid media between 2.5 and 9 *M*. $K_1$ was found to increase with acidity from a value of 4.2 to 6100. Solutions of sodium and magnesium perchlorate in perchloric acid were also used as solvents in these studies. A plot of log $K_1$ *vs.* perchlorate ion concentration resulted in separate curves for the acid and the salt solutions. From the change of $K_1$ with temperature $\Delta H°$ and $\Delta S°$ were determined for solutions of 3.0 and 8.5 *M* perchloric acid. A qualitative explanation for the dependence of the stability of the chloro complex on the composition of the medium is given in terms of the dehydrating action of perchlorates. The formation of iron(III) perchlorate complexes appears to be unlikely.

## Introduction

During the development of a spectrophotometric procedure[3] for the quantitative determination of chloride ion by means of iron(III) perchlorate in perchloric acid, it was observed that the intensity of the absorption band of the iron(III) chloro complex, around 350 mμ, increased appreciably with acid concentration. A high excess of iron(III) with respect to chloride ion (about 100:1) was maintained in these experiments. Under these conditions, the exclusive formation of the lowest chloro complex, $FeCl^{++}$, can be assumed in view of previous studies on the stability of iron(III) chloro complexes.[4-6] The sharp increase of light absorption with perchloric acid concentration suggested a pronounced influence of the acid concentration on the stability of the complex $FeCl^{++}$. The primary purpose of our investigation was then

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[2] Request for reprints should be addressed to Philip W. West.

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