[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BRYN MAWR COLLEGE]

Equilibria and Spectra of Aqueous Chlorine Solutions

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The thermodynamic equilibrium constants for the reactions: $Cl_2(aq) + H_2O = HOCl(aq) + H^+(aq) + Cl^-(aq)$, $Cl_2(aq) + Cl^-(aq) = Cl_3^-(aq)$, have been determined by a spectrophotometric method which involved accurate determinations of the absorption spectra of aqueous Cl_2, HOCl and Cl_3^- from 2000 to 3900 Å. The second, shorter wave length absorption bands observed for aqueous Cl_2 and Cl_3^- (in the former case, absent in the gas spectrum) can be interpreted as excitation to an "ionic" excited state, or, less likely, as a "charge transfer to solvent" spectrum.

We have determined spectrophotometrically the equilibrium constants for the reactions

$$Cl_2(aq.) + H_2O(l) \overset{K_1}{=} HOCl(aq.) + Cl^-(aq.) + H^+(aq.) \quad (1)$$

$$Cl_2(aq.) + Cl^-(aq.) \overset{K_2}{=} Cl_3^-(aq.) \quad (2)$$

and have obtained precise absorption spectra for HOCl(aq.), Cl_2(aq.) and Cl_3^-(aq.). The work was undertaken partly because of interest in the nature of the absorption spectra and partly to verify the presently accepted values of the two equilibrium constants, namely, $K_1 = 3.90 \times 10^{-4}$,[2] and $K_2 = 0.176$.[3] Several other recorded values of K_1 [(4.75×10^{-4}),[4] (2.09×10^{-4})[5] at 25° and (1.55×10^{-4})[6] at 0°] show only fair agreement. Our results ($K_1 = 3.35 \times 10^{-4}$, $K_2 = 0.191$) support Jakowkin's value for K_1 and are consistent (*vide infra*) with Sherrill and Izard's value for K_2. The absorption spectra for Cl_2(aq.) and Cl_3^-(aq.) have not been separated properly hitherto; in pure water and even in concentrated H_2SO_4 there is a considerable contribution to the net absorption spectrum of chlorine by Cl_3^-, especially at short wave lengths (<2800 Å.).

TABLE I

ABSORPTIVITIES

Wave length, Å.	a_{HOCl}	a_{Cl_2}	$a_{Cl_3^-}$
2537	59.0 ± 0.4	5.0 ± 0.5	3311 ± 78
2885	27.0 ± .2	26.3 ± .2	180.4 ± 1.7
3250	11.0 ± .2	75.3 ± .3	192.9 ± 5.0

Experimental

Absorbancies[7] were measured with a Beckman D.U. spectrophotometer for solutions of HOCl, OCl^- and Cl_2 in pure water and for solutions of Cl_2 in $HCl-HClO_4$ solutions of constant ionic strength ($\mu = 1.000$) and varying HCl concentration. In order to prevent loss of Cl_2 during absorption measurements and analysis, two techniques giving identical results were used. In one case, a hypodermic syringe was connected, through a stopcock and ground joints, to a standard, Beckman, 1 cm. path quartz absorption cell; in the other case, a cell was designed to trap (below a ground joint) an exactly known volume of solution in the absorption cell and, subsequent to absorption measurements, to release the solution under the surface of a KI solution. In both cases liberated I_2 was titrated with carefully standardized thiosulfate solution. In this way highly reproducible (0.5% average deviation) values were obtained for A/bc[7] (c = total chlorine concentration in moles per liter of solution at 25°). During absorption measurements, solutions were held at 25.0 ± 0.1° in a thermostated cell holder. Pure commercially available HCl (Baker Analyzed), $HClO_4$ (G. F. Smith, triple distilled) and Cl_2 (Ohio Chemical Co.) were used; all chlorine solutions were made up immediately before using, and never kept for more than 1 or 2 hours. No detectable decomposition of the chlorine solutions was found, however, over considerably longer periods of time in strong artificial light. Pure HOCl solutions were prepared[8] by adding the stoichiometrically correct amount of NaOH solution to an aqueous chlorine solution, vacuum distilling on to Ag_2SO_4, and redistilling. The spectrum of this solution agreed with that of the original half-neutralized solution. As an additional check, the spectrum of OCl^- (prepared by adding the correct amount of chlorine to pure, carbonate-free NaOH solution) was determined carefully and compared with the spectra of $HOCl-OCl^-$ mixtures. The longer wave length, weaker band in the HOCl spectrum definitely belongs to HOCl

TABLE II

EQUILIBRIUM CONSTANTS FROM ABSORPTION OF AQUEOUS CHLORINE SOLUTIONS

c	A_{3250}	A_{2537}	(HOCl)	(Cl_2)	(Cl_3^-) × 10^5	$K_1 \times 10^4$	K_2
0.01971	0.604	0.893	0.01372	0.00598	1.569	3.44 ± 0.11	0.191 ± 0.016
.02301	.774	1.006	.01496	.00803	2.439	3.29	.203
.02631	.942	1.115	.01622	.01006	3.147	3.32	.193
.02964	1.122	1.223	.01734	.01226	4.054	3.31	.191
.03290	1.294	1.322	.01849	.01436	4.651	3.40	.175
					Av.	3.35 ± 0.11	0.191 ± 0.016

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[1] Taken from a dissertation submitted by F. C. Strong to the Graduate School of Bryn Mawr College in partial fulfillment of the requirements for the Ph.D. degree, June, 1954. This work was supported by funds from the Plan for the Coördination of the Sciences of Bryn Mawr College and was presented at the first Delaware Valley Regional meeting of the American Chemical Society, Feb. 1956.

[2] A. A. Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899). This value was obtained by recalculating Jakowkin's original conductance data, using recent values for the activity coefficient of HCl taken from "Electrochemical Data" by B. E. Conway, Elsevier Publishing Co., Amsterdam, 1952. The above value is substantially lower than the one usually tabulated; for example, see "Oxidation Potentials," by W. M. Latimer, 2nd edition, Prentice-Hall, New York, N. Y., 1952.

[3] M. S. Sherrill and E. F. Izard, THIS JOURNAL, **53**, 1667 (1931). This value was recalculated from Sherrill and Izard's data to apply to reaction 1 as written here.

[4] S. N. Shilov and E. A. Solodushenkov, *Compt. rend. acad. sci. U.R.S.S.*, **3**, 17 (No. 1, 1936); *Acta Physicochim. U.R.S.S.*, **20**, 667 (No. 5, 1945).

[5] H. Hagisawa, *Bulletin Inst. Phys. Chem. Res. (Tokyo)*, **20**, 899 (1941).

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

[7] The terms and symbols used here are those recommended by the Joint Committee on Nomenclature on Applied Spectroscopy in *Anal. Chem.*, **24**, 1349 (1952); A = absorbance, b = thickness of absorbing layer in cm.; a = absorptivity.

[8] W. C. Fergusson, L. Slotin and D. W. G. Style, *Trans. Faraday Soc.*, **32**, 956 (1936).

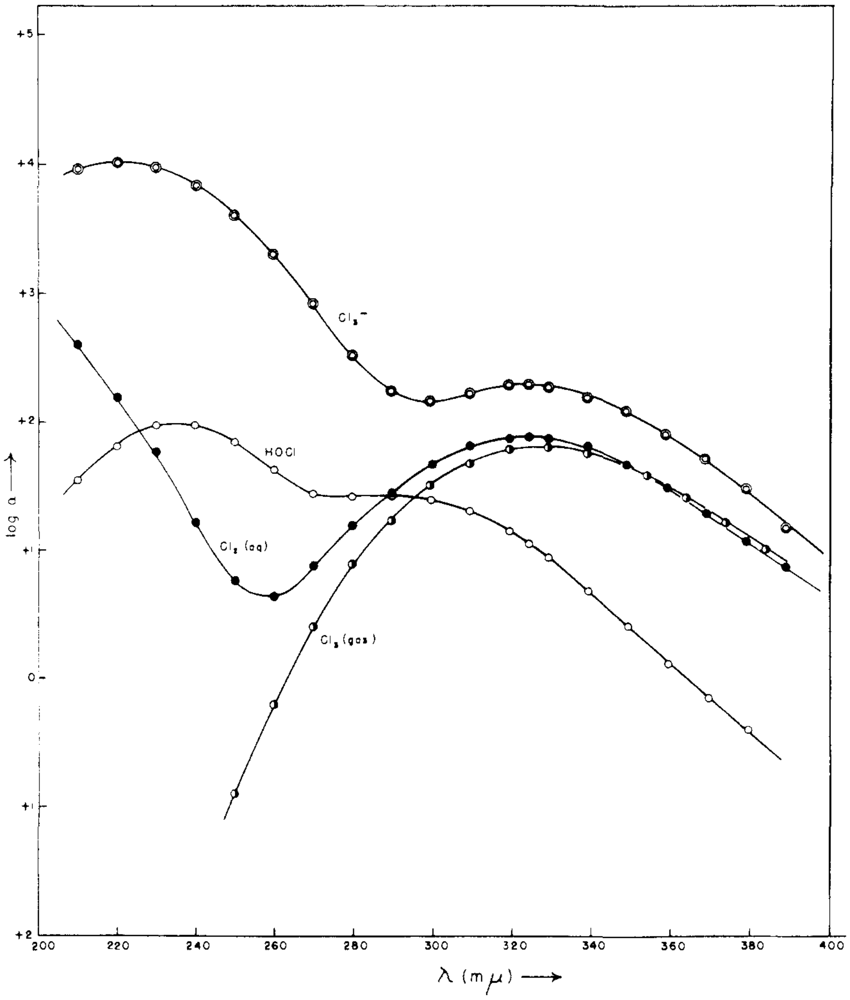

Fig. 1.—Absorption spectra.

and not to OCl^-, which happens to have a maximum absorption at the same wave length.

Results

The absorption spectrum of HOCl(aq.) shown in Fig. 1) (precise data for several wave lengths are given in Table I) is essentially the same as previously obtained[8,9,10] and was repeated mainly in order to obtain more precise values of the absorption coefficients. For solutions of chlorine in HCl–$HClO_4$ mixtures of ionic strength unity and with the initial concentration of HCl (U_0) larger than 0.02 molar, the concentration of HOCl becomes negligibly small and assuming Beer's law to hold for the two species, Cl_2(aq.) and Cl_3^-(aq.), it can be shown easily that (to better than 0.1%) the relation holds

$$A/bc = a_{Cl_2} + K_2(a_{Cl_3^-} - a_{Cl_2})\frac{U_0}{1 + K_2'(U_0 + c)}$$

where the a's are molar absorptivities[7] and $K_2' = (Cl_3^-)/(Cl_2)(Cl^-)$ for $\mu = 1.000$; parenthesis ( ) indicate molar concentrations. Figure 2 shows some typical plots of A/bc against $U_0/[1 + K_2' \cdot (U_0 + c)]$ for three wave lengths, and Table I gives the values and probable errors for a_{Cl_2} and $a_{Cl_3^-}$ obtained from least square calculations. All of the points for the corresponding spectra in Fig. 1 were obtained in the same way. For these calculations the value of 0.176 for K_2' from Sherrill and Izard's work[3] was used as representing the best value of K_2' for an ionic strength of 1.000.

Absorbances of solutions of Cl_2 in pure water are given in Fig. 3 and Table II. From the former there appears to be an isosbestic point at 2885 Å. ($A/bc = 27.02$) for $0.015 < c < 0.034$ mole/liter. It is not a true isosbestic point since all three species, HOCl, Cl_2 and Cl_3^- contribute significantly to the absorption (see Table I). However for the above limited range of c values and with no added electrolytes, A/bc for this "isosbestic" wave length is constant to within the limits of experimental accuracy and can be used conveniently to determine c from absorption measurements. In order to determine K_1 and K_2 from the data in Table II the three equations

$$A/bc = a_{HOCl}(HOCl) + a_{Cl_2}(Cl_2) + a_{Cl_3^-}(Cl_3^-) \text{ for the 2 wave lengths 2537 and 3250 Å.}$$

$$c = (HOCl) + (Cl_2) + (Cl_3^-)^{11}$$

were solved for the three concentrations, and the K's calculated using accurate values for the activ-

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(9) H. L. Friedman, *J. Chem. Phys.*, **21**, 319 (1953).

(10) K. Schaefer, *Z. physik. Chem.*, **93**, 312 (1919).

(11) c was usually determined from a measurement of A/bc at the "isosbestic wave length."

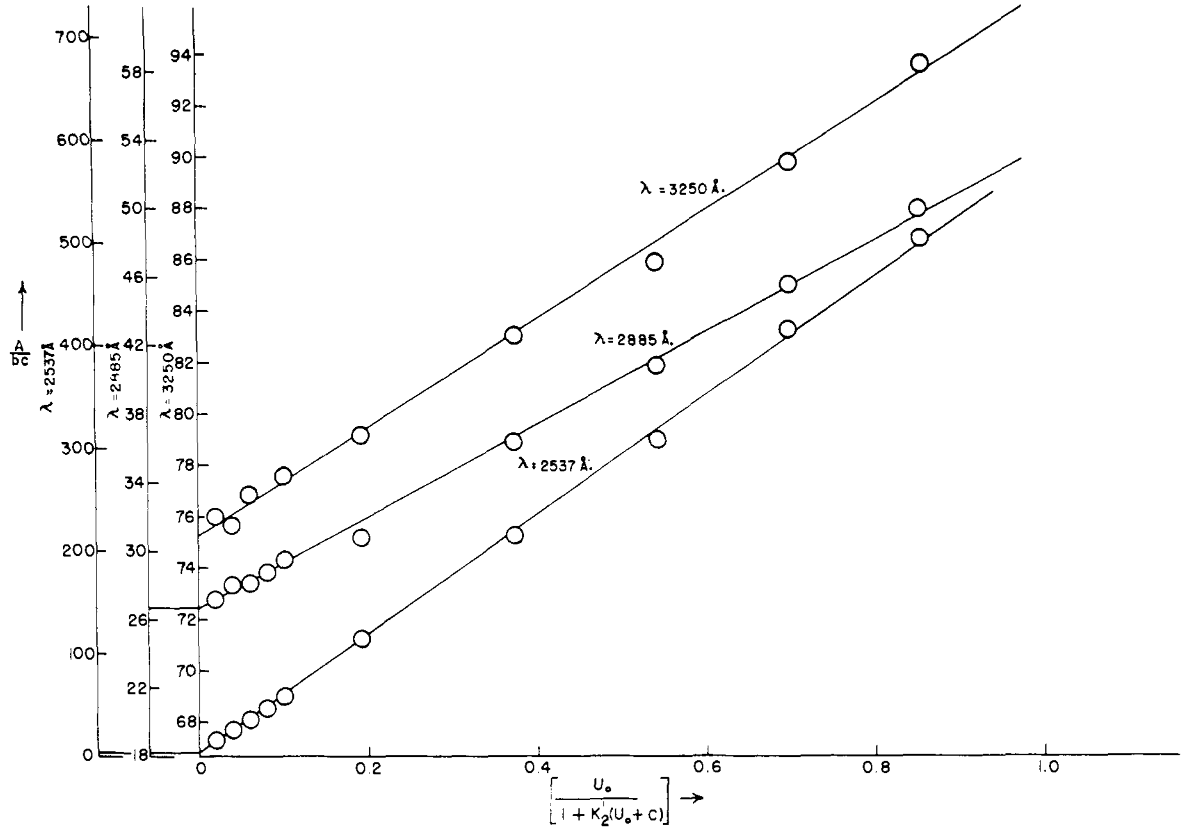

Fig. 2.—Absorption of chlorine in HCl–HClO$_4$ solutions.

ity coefficient of aqueous HCl[2] and making all other activity coefficients unity. The uncertainties (probable errors) in the individual K's in Table II are all essentially the same and result mainly from the uncertainties in the a's in Table I; the uncertainties in the a's also mainly determine the uncertainty in the average K's.

Aqueous Chlorine and Trichloride Ion Spectra.—In the Cl$_2$(aq.) absorption spectrum (see Fig. 1) the longer wave length band clearly corresponds to the similar known $^1\Pi_{Lu} \leftarrow {}^1\Sigma_g^+$ band for the gas[12,13]; the band which begins to appear at shorter wave lengths and which must involve fairly strong solvent-excited state interaction (since it differs greatly from the gas spectrum) probably represents either a transition to an "ionic" excited state of Cl$_2$[14–16] or to an excited state involving neighboring solvent molecules roughly similar to the case of aqueous halide and certain other ions.[17–19] This latter sort of excitation has been referred to frequently as "electron transfer" to solvent molecules. A semiquantitative explanation can be based on the first assumption. Thus Fig. 4 shows the various possible levels for the separated nuclei and potential curves for (a) the ground ($^1\Sigma_g^+$) state, (b) the $^1\Pi_{lu}$

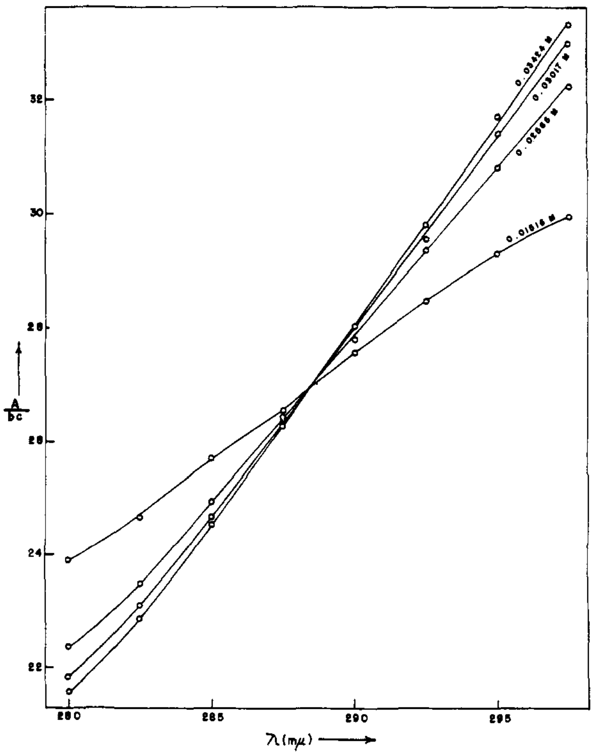

Fig. 3.—Absorption in aqueous chlorine solutions.

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(12) Gerhard Herzberg, "Molecular Spectra and Molecular Structure," Vol. 1, Second Ed., D. Van Nostrand Co., New York, N. Y., pp. 390–394.

(13) G. E. Gibson and N. S. Bayliss, *Phys. Rev.*, **44**, 191 (1938).

(14) R. S. Mulliken, *J. Chem. Phys.*, **7**, 14, 20 (1939).

(15) R. S. Mulliken, *ibid.*, **8**, 234, 382 (1940).

(16) See also the discussion for I$_2$ by L. Mathieson and A. L. G. Rees, *ibid.*, **25**, 753 (1956).

(17) E. Rabinowich, *Rev. Mod. Phys.*, **14**, 112 (1942).

(18) L. E. Orgel, *Quart. Rev.*, **8**, 422 (1954).

(19) R. Platzman and J. Franck, "L. Farkas Memorial Volume," Research Council of Israel. Special Publication No. 1, 1952.

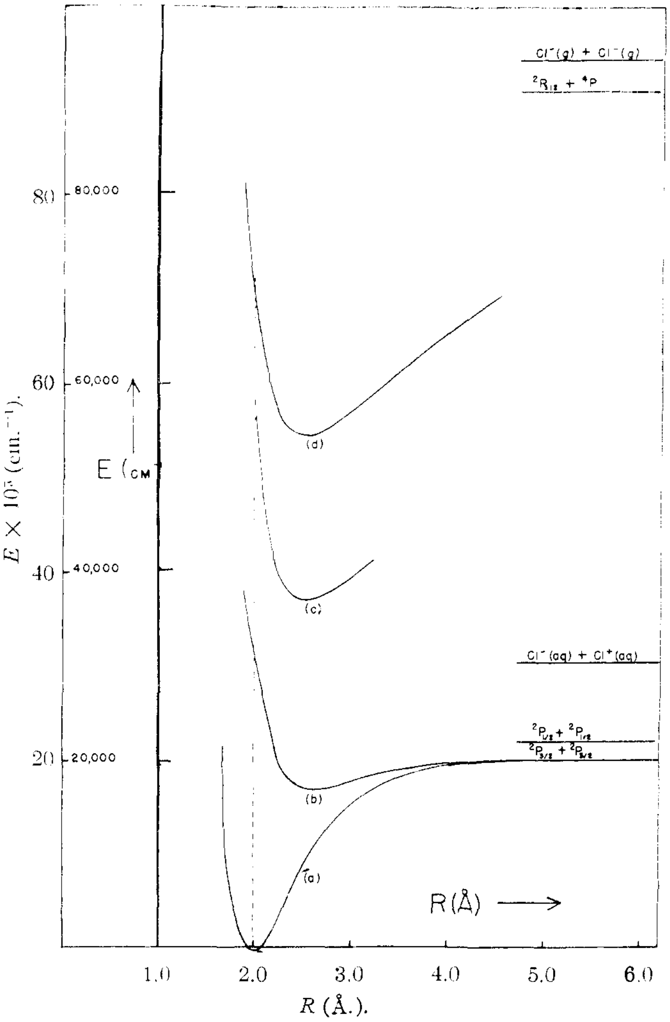

Fig. 4.—Potential energy curves for Cl_2.

state presumably giving rise to the longer wave length band,[12,13] (d) the state[20] formed from gaseous Cl^- and Cl^+ ions. The last curve was calculated assuming that Cl^+ behaves approximately as does Na^+ with respect to ion-pair formation and hydration energy. Curve (c) is obtained from a rough estimate of the hydration energy of the gaseous Cl^+Cl^- ion pair, assuming a dipole moment equal to that of NaCl(g) and a continuous dielectric medium; the dipole–solvent interaction would presumably also increase slightly the equilibrium internuclear separation. This estimate predicts an absorption maximum at 1700–1800 Å. and a long wave length limit of about 2700 Å. This admittedly very rough estimate is at least consistent with the observations, and it is hard to find any other excited state of the Cl_2 molecule which would both lie as low in energy and show a large solvent interaction. The interpretation suggests the possibility of dissociation into ions in solution by the absorption of the shorter wave lengths. In Cl_3^- the interaction of the Cl_2 and Cl^- is so weak (about 2 kcal.)[21] that one can think of the spectrum as that of Cl_2 perturbed by a close Cl^- neighbor. Thus absorption within the longer wave length band would lead to dissociation into $Cl_2 + Cl^-$ as suggested by existing photochemical evidence,[22,23] while in the lower band the upper state would be an ion triplet, $Cl^-Cl^+Cl^-$, the additional ion–dipole interaction shifting the maximum further toward the red. It would be interesting to see whether the photochemical behavior of Cl_2(aq.) for wave lengths less than about 2200 Å. would contribute to the present picture.

We wish to acknowledge the advice and suggestions of the late Professor J. L. Crenshaw under whose direction the work was begun.

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[20] From the lowest states of the ions $Cl^-(^1S)$, $Cl^+(^3P)$ one would expect a triplet state of the molecule and hence a low intensity of absorption. It is hard to draw definite conclusions from the present data concerning the intensity; more knowledge could prove to be a serious objection to the above suggested explanation.

[21] Obtained from the known equilibrium constant and a semi-empirical estimate of the entropy of Cl_3^- (aq.).

[22] A. C. Rutenberg and H. Taube, THIS JOURNAL, **72**, 5561 (1950)

[23] A. C. Rutenberg and H. Taube, *ibid.*, **73**, 4426 (1951).