495. *The Effect of Perchlorate Association on the Hydrolysis of Ferric Ion.*

By K. W. Sykes.

The variation of the hydrolysis of ferric ion with perchlorate ion concentration at constant ionic strength is interpreted in terms of ferric–perchlorate association. The association constant at 25° is estimated to be 6·7 ± 0·7 and 3·7 ± 0·7 l. mole^{-1} at ionic strengths of 0·0236 and 0·0437 respectively. Specific interactions of this magnitude can be explained by Bjerrum's theory if the ferric and perchlorate ions, at their closest approach, are assumed to be separated by two water molecules.

Olson and Simonson [1] showed spectrophotometrically that the extent of the hydrolysis of ferric ion increases as the perchlorate-ion concentration decreases at constant ionic strength in solutions of sodium, barium, and lanthanum perchlorates. It has been stated without proof that the changes can be explained by ferric–perchlorate association.[2] Since the extent to which deviations from the principle of constant ionic strength can be attributed to association is a question of general interest, details of an improved analysis of Olson and Simonson's results are now presented.

Calculation of Ferric–Perchlorate Association Constant.—Perchlorate ion is assumed to associate with Fe^{3+} but not with $FeOH^{2+}$, so the equilibria to be considered are:

$$Fe^{3+} + H_2O = FeOH^{2+} + H^+ \qquad K_1 \qquad . \; . \; . \; . \; . \quad (1)$$

$$Fe^{3+} + ClO_4^- = FeClO_4^{2+} \qquad K_2 \qquad . \; . \; . \; . \; . \quad (2)$$

The dimeric hydrolysed species $Fe_2(OH)_2^{4+}$ is neglected at this stage, since Milburn's data [3] indicate that its concentration is only about 2% of that of the total iron under the conditions specified below. Calculations are therefore made to find out whether given values of K_1 and K_2, assumed constant at a given ionic strength, adequately represent the experimental results.

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[1] Olson and Simonson, *J. Chem. Phys.*, 1949, **17**, 1322.
[2] Sykes, *Chem. Soc. Spec. Publ.*, 1954, No. 1, p. 64.
[3] Milburn, *J. Amer. Chem. Soc.*, 1957, **79**, 537.

If c_0 denotes the total iron concentration ($4{\cdot}7 \times 10^{-4}$M), $c_1{}^0$ the concentration of added perchloric acid ($1{\cdot}485 \times 10^{-3}$M), and c_2 the free perchlorate-ion concentration, those of the other species are as follows:

$$Fe^{3+},\ c_0c_1/\beta;\ FeOH^{2+},\ K_1c_0/\beta;\ FeClO_4{}^{2+},\ K_2c_0c_1c_2/\beta;\ \text{where } \beta = c_1 + K_1 + K_2c_1c_2,$$

and

$$[H^+] = c_1 = c_1{}^0 + \left(\frac{{}^*K_1 + c_1{}^0}{2}\right)\left[\left\{1 + \frac{4{}^*K_1c_0}{({}^*K_1 + c_1{}^0)^2}\right\}^{\frac{1}{2}} - 1\right] \quad . \quad . \quad (3)$$

where

$${}^*K_1 = K_1/(1 + K_2c_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

${}^*K_1$ is also equal to $[FeOH^{2+}][H^+]/([Fe^{3+}] + [FeClO_4{}^{2+}])$ and is thus the conventional hydrolysis constant obtained when perchlorate association is ignored. The extinction coefficients, ε_0 for Fe^{3+} and $FeClO_4{}^{2+}$ and ε_1 for $FeOH^{2+}$, are assumed to be independent of perchlorate-ion concentration at constant ionic strength on the basis of the following observations on perchlorate media. There is very little change in the conventional ε_0 for free and associated ferric ions at 260—360 mμ between ionic strengths of 0·047 and 4·7,[1] and ε_1 at 340 mμ does not vary appreciably over the ionic strength range 0·0147—1·07.[4] The mean molar extinction coefficient of the ferric ion, ε, thus becomes

$$\varepsilon = \frac{\varepsilon_0\{[Fe^{3+}] + [FeClO_4{}^{2+}]\} + \varepsilon_1[FeOH^{2+}]}{c_0} = \frac{\varepsilon_0 + \varepsilon_1({}^*K_1/c_1)}{1 + ({}^*K_1/c_1)} \quad . \quad . \quad (5)$$

Application of eqns. (4) and (5) to two solutions, denoted by (*a*) and (*b*), of different perchlorate concentration but of the same ionic strength gives the following expression for the calculation of K_2, since both K_1 and K_2, though not ${}^*K_1$, may be regarded as constant under these conditions:

$$\frac{1 + K_2c_2(a)}{1 + K_2c_2(b)} = \left\{\frac{\varepsilon(b) - \varepsilon_0}{\varepsilon(a) - \varepsilon_0}\right\}\left\{\frac{\varepsilon_1 - \varepsilon(a)}{\varepsilon_1 - \varepsilon(b)}\right\}\frac{c_1(b)}{c_1(a)} \quad . \quad . \quad . \quad . \quad (6)$$

The hydrogen-ion concentrations $c_1(a)$ and $c_1(b)$ differ slightly on account of the change in the degree of hydrolysis of the iron, but can be estimated for each solution from the observed optical density by means of the relation:

$$c_1 = c_1{}^0 + c_0(\varepsilon - \varepsilon_0)/(\varepsilon_1 - \varepsilon_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

As the observed differences in optical density do not exceed 0·023, significant results can only be obtained under the most favourable conditions. Analysis is therefore confined to the wavelengths 290—310 mμ, where $FeOH^{2+}$ has its maximum absorption, and to the two more concentrated solutions where ΔI, the contribution of the added sodium, barium, or lanthanum perchlorate to the ionic strength, is 0·02 and 0·04. Table 1, except for the columns " La corr." which refer to other calculations described below, gives the concentrations for use in eqn. (6). The values assumed for the extinction coefficients are those determined by Olson and Simonson [1] at the same total iron concentration and at an ionic strength of 0·0474, and are obtained as follows by photographic enlargement of their Fig. 1: ε_0 372 at 290 mμ, 172 at 300 mμ, 79 at 310 mμ; ε_1 1910 at 290 mμ, 1950 at 300 mμ, 1820 at 310 mμ.

TABLE 1. *Concentrations and ionic strengths* (*mole l.*$^{-1}$).

	$\Delta I = 0{\cdot}02$				$\Delta I = 0{\cdot}04$			
	Na	Ba	La	La corr.	Na	Ba	La	La corr.
10^3c_1	1·786	1·789	1·793	1·793	1·773	1·777	1·781	1·781
10^3c_2	22·90	16·23	12·90	12·63	42·90	29·56	22·90	22·37
10^3I	23·63	23·65	23·65	22·84	43·65	43·67	43·67	42·09

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[4] Milburn and Vosburgh, *J. Amer. Chem. Soc.*, 1955, **77**, 1352.

No significant differences are found in the hydrogen-ion concentrations given by eqn. (7) for the wavelength range 290—310 mμ, so only the average is listed. Decreases in the perchlorate concentration due to association do not exceed 0·1% and are neglected. The ionic strengths are those computed subsequently, taking account of all equilibria; they are not appreciably altered by changes in either hydrolysis or association.

Table 2 shows the calculated values of K_2, errors in which arise chiefly from the experimental errors in $\varepsilon(a)$ and $\varepsilon(b)$. If the latter are σ_a and σ_b, the standard deviation σ of the extinction coefficient term on the right-hand side of equation (6) is given by

$$\sigma = \frac{(\varepsilon_1 - \varepsilon_0)}{\{\varepsilon(a) - \varepsilon_0\}\{\varepsilon_1 - \varepsilon(b)\}}\left[\left\{\frac{\varepsilon(b) - \varepsilon_0}{\varepsilon(a) - \varepsilon_0}\right\}^2 \sigma_a{}^2 + \left\{\frac{\varepsilon_1 - \varepsilon(a)}{\varepsilon_1 - \varepsilon(b)}\right\}^2 \sigma_b{}^2\right]^{\frac{1}{2}} \quad . \quad (8)$$

TABLE 2. *Values of* K_2 *(mole*$^{-1}$ *l.).*

	$\Delta I = 0{\cdot}02$			$\Delta I = 0{\cdot}04$		
	Ba	La	La corr.	Ba	La	La corr.
290 mμ	5·4 ± 1·5	6·5 ± 1·1	6·0 ± 1·0	3·1 ± 0·8	5·1 ± 0·5	4·7 ± 0·5
300 mμ	6·5 ± 1·4	9·0 ± 0·9	8·4 ± 0·9	3·7 ± 0·7	4·3 ± 0·5	4·0 ± 0·4
310 mμ	6·7 ± 1·4	7·8 ± 0·9	7·3 ± 0·9	2·7 ± 0·7	4·1 ± 0·5	3·8 ± 0·4
Average over mμ	6·2 ± 0·7	7·8 ± 1·3	7·2 ± 1·2	3·2 ± 0·5	4·5 ± 0·5	4·2 ± 0·5
Average over Ba & La ...	—	7·0 ± 1·1	6·7 ± 0·7	—	3·8 ± 0·9	3·7 ± 0·7

The errors in the first three rows of Table 2 are calculated in this way, assuming that σ_a and σ_b correspond to an uncertainty of ±0·001 in the optical density, which is the accuracy to which Olson and Simonson reported their data. These predicted errors cover adequately the standard deviation of the average of the K_2 values for the various wavelengths as listed in the fourth row, so the analysis is independent of wavelength over the range considered. At each ionic strength, however, K_2 is higher for the lanthanum than for the barium solution, though the differences are comparable with the predicted errors. Differences in this sense are to be expected if the lanthanum associates with perchlorate, so it is necessary to estimate the possible effect of such association.

As La^{3+} has the same charge as Fe^{3+} and the small difference (0·55 Å) in crystal radius [5] is unlikely to be important because the ions are highly hydrated, the lanthanum–perchlorate association constant is assumed equal to the ferric value as given by the average of the barium and lanthanum results in the fifth row of Table 2. The ionic strengths of the lanthanum solutions are now decreased as in the " La corr." columns of Table 1, and neither K_1 nor K_2 can strictly be considered constant. Equation (6) must be replaced by:

$$\frac{1 + K_2(a) \,.\, c_2(a)}{1 + K_2(b) \,.\, c_2(a)} = \left\{\frac{\varepsilon(b) - \varepsilon_0}{\varepsilon(a) - \varepsilon_0}\right\}\left\{\frac{\varepsilon_1 - \varepsilon(a)}{\varepsilon_1 - \varepsilon(b)}\right\}\frac{c_1(b) \,.\, K_1(a)}{c_1(a) \,.\, K_1(b)} \quad . \quad . \quad . \quad (9)$$

and the changes in K_1 and K_2 estimated as follows:

$$\frac{K_1(a)}{K_1(b)} = \frac{{}^*K_1(a)}{{}^*K_1(b)}\left\{\frac{1 + K_2(a) \,.\, I(a)}{1 + K_2(b) \,.\, I(b)}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\frac{{}^*K_1(a)}{{}^*K_1(b)} = \frac{4A\{I^{\frac{1}{2}}(a) - I^{\frac{1}{2}}(b)\}}{\{1 + 2{\cdot}40I^{\frac{1}{2}}(a)\}\{1 + 2{\cdot}40I^{\frac{1}{2}}(b)\}} \quad . \quad . \quad . \quad . \quad (11)$$

$$\frac{K_2(a)}{K_2(b)} = \frac{6A\{I^{\frac{1}{2}}(a) - I^{\frac{1}{2}}(b)\}}{\{1 + 3{\cdot}52I^{\frac{1}{2}}(a)\}\{1 + 3{\cdot}52I^{\frac{1}{2}}(b)\}} \quad . \quad . \quad . \quad . \quad (12)$$

Eqn. (10) follows from eqn. (4) and the fact that $^*K_1$ is conventionally measured in sodium perchlorate solution of perchlorate-ion concentration closely approximating to the ionic strength. Eqn. (11) expresses the variation of $^*K_1$ with ionic strength as determined experimentally by Milburn [3]; A. is the Debye–Hückel constant equal to 0·509 at 25°. Eqn. (12) describes the variation of K_2 with ionic strength on the assumption that the

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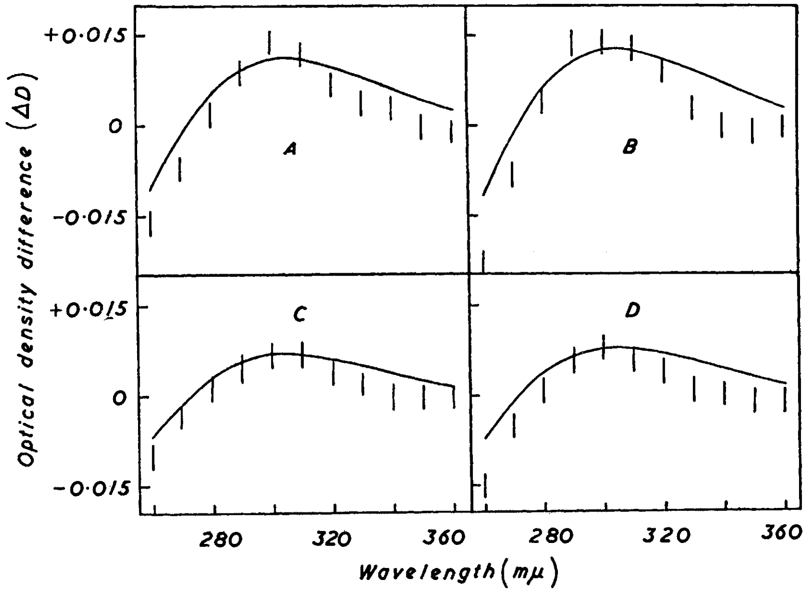
[5] Pauling, The Nature of the Chemical Bond," Cornell University Press, New York, 1940, p. 346, 350.

closest approach of the free ions is the Bjerrum distance q of 10·7 Å for a 3 : 1 electrolyte.[6] Although this procedure cannot strictly be justified for mixed electrolytes, the error cannot be large since the differences between $K_2(a)$ and $K_2(b)$ are estimated to be less than 1%. The values of K_2 calculated in this way are shown in the " La corr." columns of Table 2; no great error is made by neglecting the lanthanum association, but the new values approach the barium ones more closely and their averages with the latter are the best estimates which can be derived from the present data.

FIG. 1. *Comparison of observed optical-density differences*[1] *with curves calculated from* $K_2 = 6{\cdot}7$ *for* $\Delta I = 0{\cdot}02$ and 3·7 for $\Delta I = 0{\cdot}04$.



A: La; $\Delta I = 0{\cdot}02$. *B*: La; $\Delta I = 0{\cdot}04$. *C*: Ba; $\Delta I = 0{\cdot}02$. *D*: Ba; $\Delta I = 0{\cdot}04$.

Calculation of Optical-density Differences.—To calculate the differences in optical density over the whole range 260—360 mμ from the final values of K_2, $^*K_1(a)$ for the sodium solutions is found from

$$^*K_1(a) = \left\{\frac{\varepsilon(a) - \varepsilon_0}{\varepsilon_1 - \varepsilon(a)}\right\} c_1(a) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Data for 290—310 mμ give 3·17 and $2{\cdot}80 \times 10^{-3}$ mole l.^{-1} for the lower and higher ionic strengths. Since K_2 is known, $^*K_1(b)$ is obtained from

$$^*K_1(b) = {}^*K_1(a) \left\{\frac{1 + K_2(b) \,.\, c_2(b)}{1 + K_2(a) \,.\, c_2(a)}\right\} \frac{K_1(b)}{K_1(a)} \quad . \quad . \quad . \quad . \quad (14)$$

For the barium solutions $K_1(a) = K_1(b)$ and $K_2(a) = K_2(b)$. For the lanthanum solutions the ratios $K_1(a)/K_1(b)$ and $K_2(a)/K_2(b)$ are estimated by eqns. (10)—(12) from the change in ionic strength due to lanthanum–perchlorate association. As c_1 must be obtained from eqn. (3), the optical density differences ΔD for 1 cm. cells are conveniently found from

$$\Delta D = (\varepsilon_1 - \varepsilon_0)\{c_1(b) - c_1(a)\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Fig. 1 shows the calculated values as curves and the observed differences as vertical lines of ±0·002 corresponding to the uncertainty of ±0·001 in the individual measurements.

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[6] Bjerrum, *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.*, 1926, **7**, No. 9.

The general form of the results is well reproduced, but there are appreciable deviations at 260—270 mμ and 330—350 mμ. Failure of the simple analysis in these regions is also indicated by the optical densities of the sodium solutions. At 290—310 mμ they are within 0·001 of the values calculated from Olson and Simonson's extinction coefficients and the hydrolysis constants given above, but differ by up to 0·017 at 260 mμ and 0·008 at 340 mμ. Presumably another species, such as $Fe_2(OH)_2^{4+}$, which has its maximum absorption at 340 mμ,[4] contributes. On account of its higher charge, the dimer should associate more strongly with perchlorate than $FeOH^{2+}$ does, and so be more stable in the sodium than in the barium or lanthanum solutions. The maximum possible decrease in optical density, $\Delta D'$, which would occur if there was no dimer in the lanthanum solution, is equal to $c_d\{\varepsilon_d - 2\varepsilon(a)\}/(1 - 2c_d/c_0)$, where c_d is the dimer concentration (0·99 and $1{\cdot}12 \times 10^{-5}$M at the lower and higher ionic strengths according to Milburn's constants [3]) and ε_d its extinction coefficient (3000 at 340 mμ [4]). The corresponding values of $\Delta D'$ are 0·019 and 0·022, whereas the observed optical-density differences ΔD at 340 mμ are less than those calculated from the simple analysis by 0·004 and 0·007 respectively; changes of 20—30% in the dimer concentration would thus account for the discrepancies. The value of ε_d is not known at other wavelengths, but as it decreases from its maximum and approaches $2\varepsilon(a)$, the correction should become negligible. Dimer is clearly a possible interfering species, but further experiments would be needed to establish its rôle with certainty.

Comparison with Bjerrum's Theory and Interatomic Distances.—Since the association constant K_2 describes the experimental results satisfactorily, its theoretical significance must be considered. In the absence of an adequate fundamental theory of activity coefficients in mixed electrolytes of finite concentration, it is not possible to calculate accurately the distance at which the ionic interactions cease to depend specifically on the perchlorate concentration and become a function of the ionic strength in general. However, an intuitive approximation, which is compatible with the known properties of the ions, is to regard the Bjerrum distance q for ferric perchlorate as the critical radius.

As Brown and Prue [7] have emphasised, the same distance of closest approach of the free ions (d) must be used for extrapolation to zero ionic strength as for the upper limit of integration in Bjerrum's theory. The previous use [2] of the Davies activity coefficient function is therefore replaced by extrapolation according to eqn. (12) which makes d equal to 10·7 Å. Extrapolation of the limits assigned to K_2 at the lower and higher ionic strengths gives 12·1—14·9 and 7·0—11·3 l. mole^{-1}. According to Bjerrum's theory [6] and Guggenheim's table of integrals,[8] the corresponding distances of closest approach of the associated ions (a) are 8·2—9·5 Å. If $FeOH^{2+}$ and ClO_4^- are similarly separated, the absence of association assumed above is understandable, since q for a 2 : 1 electrolyte is only 7·1 Å. The size of a implies considerable hydration of the ions, as might be expected from the formula of the normal hydrate, $Fe(ClO_4)_3,9H_2O$, the hygroscopic nature of $Fe(ClO_4)_3,6H_2O$, and the absence of lower hydrates.[9] The structures of these hydrates are unknown, but $LiClO_4,3H_2O$, which has been studied by West,[10] is a useful model since Li^+ and Fe^{3+} have the same crystal radius of 0·6 Å.[5] Fig. 2(a) is a projection of the metal atom surrounded octahedrally by six water molecules, two of which are hydrogen-bonded to a perchlorate ion. The M–Cl distance should be approximately the distance apart in solution of ferric and perchlorate ions separated by one water molecule; it is not listed by West,[10] but is equal to $\sqrt{[(a_0/\sqrt{3})^2 + (c_0/4)^2]}$, which is 4·65 Å with the unit-cell dimensions $a_0 = 7{\cdot}71$ Å and $c_0 = 5{\cdot}42$ Å. Fig. 2(b) shows the probable configuration with two water molecules between the ions; the separation is increased by 2·76 Å, the O–O distance in ice,[11] to 7·41 Å. Addition of ionic and molecular radii, 2·8 Å being assumed for the diameter of a water

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[7] Brown and Prue, *Proc. Roy. Soc.*, 1955, *A*, **232**, 320.

[8] Guggenheim, *Discuss. Faraday Soc.*, 1957, **24**, 53.

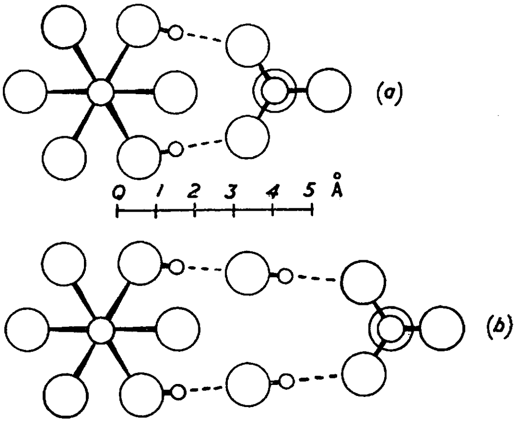
[9] Gmelin's Handbuch der anorganischen Chemie, **59**, Fe(B), 321.

[10] West, *Z. Krist.*, 1934, **88**, 198.

[11] Barnes, *Proc. Roy. Soc.*, 1929, *A*, **125**, 670.

molecule[11] or the radius of a perchlorate ion,[12] gives 6·2 Å for the insertion of one water molecule and 9·0 Å for two. The distance of 8·2—9·5 Å estimated from the equilibrium constant thus leaves room for two, but not three, water molecules between the ions.

FIG. 2. *Configuration of* Fe^{3+} *and* ClO_4^- *separated by* (*a*) *one and* (*b*) *two molecules of water.*



These conclusions are consistent with the only other data on tervalent perchlorates which appear to be available for comparison. Spedding and Jaffe[13] estimate, from the electrophoretic term of the conductivity equation, a minimum ionic separation of about 7 Å for a number of rare-earth perchlorates. The conductivities of these salts approach the limiting-law values without any marked indication of association, which also implies that *a* must be close to *q*.

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[12] Bragg, " The Crystalline State," Bell, London, 1939, Vol. I, p. 129.
[13] Spedding and Jaffe, *J. Amer. Chem. Soc.*, 1954, **76**, 884.