# The Hydrolysis of Aluminium Salt Solutions.

By R. K. SCHOFIELD and A. WORMALD TAYLOR.

[Reprint Order No. 5632.]

The value of the equilibrium constant of the reaction $(Al,6H_2O)^{3+} + H_2O \rightleftharpoons (AlOH,5H_2O)^{2+} + H_3O^+$ has been determined by direct measurement of the pH values of a series of aluminium salt solutions, and a p*K* value of 4·98 at 25° C ($K = 1{\cdot}05 \times 10^{-5}$) has been obtained. The temperature coefficient of $-0{\cdot}03$ units/° C suggests that the mechanism of the reaction is similar to the dissociation of water. The results obtained are compared with those of a previous determination by Brønsted and Volqvartz (*Z. physikal. Chem.*, 1928, **97**, 134).

THE first stage in the hydrolysis of an aluminium salt solution is due to the reaction

$$(Al,6H_2O)^{3+} + H_2O \rightleftharpoons (AlOH,5H_2O)^{2+} + H_3O^+ \quad . \quad . \quad . \quad (1)$$

which has an equilibrium constant given by

$$K = [A(AlOH^{2+}) \times A(H^+)]/A(Al^{3+}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or

$$pK = pAlOH + pH - pAl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

where p*K*, pH, pAlOH, and pAl are the negative logarithms of the equilibrium constant and of the activities (*A*) of the ions concerned.

Previous determinations of this constant have been made by Bjerrum (*Z. physikal Chem.*, 1907, **59**, 350), by Brønsted and Volqvartz (*ibid.*, 1928, **97**, 134), by Lacroix (*Ann. Chim.*, 1949, **4**, 5), and by Faucherre (*Compt. rend.*, 1948, **227**, 1367). Of the values obtained, that of 4·95 (at 15° C) by Brønsted and Volqvartz is the most reliable, since it is the only one in which any correction for activity coefficient has been made. This value was based upon the study of the hydrogen-ion concentrations of a number of acidified aluminium perchlorate solutions, the hydrogen ion being measured by determination of the rate of hydrolysis of ethyl diazoacetate. The activity-coefficient correction was estimated by comparison with that found necessary in chromium salt solutions of similar concentration.

As a result of the work now reported a new value has been obtained based on the measurements of the pH values of dilute solutions of potassium alum and aluminium chloride, corrections for activity coefficients being applied on the basis of Debye and Hückel's theory of the behaviour of solutions of electrolytes.

## EXPERIMENTAL

The pH values quoted in the Table were measured directly on the solutions with a glass electrode saturated potassium chloride solution|calomel cell, a Marconi 717a pH meter being used. The cell was standardized with 0·05N-potassium hydrogen phthalate buffer at a pH of

4·00; this was considered to be independent of temperature over the range under investigation. Temperature control to within 0·5° was achieved by conducting the experiments in a constant-temperature room.

The aluminium chloride samples used were commercial laboratory reagents and were not specially purified; they may have contained a small quantity of iron. The potassium alum was of analytical grade and gave results in agreement with the chloride.

The solutions were made up by dilution of accurately prepared 0·1M-solution, freshly boiled distilled water being used. Water was considered unsatisfactory unless a 0·001M-solution of potassium chloride in it had pH between 6·1 and 6·3. 0·01M-Potassium chloride was also added to bring the final solution to 0·001M in that salt. The presence of this concentration of potassium chloride was found to be very desirable, particularly in the more dilute aluminium salt solutions, since much steadier pH readings are then obtained owing to the more reproducible nature of the liquid junction potential at the saturated potassium chloride bridge junction. The design of junction tube used was one in which saturated potassium chloride solution is allowed to diffuse slowly outwards through a sintered glass plug into the bulk of the solution.

The pH readings were made immediately after preparation of the solutions, the following procedure, being used :

The electrodes were washed free from buffer with distilled water, and then with about 30 ml. of the aluminium salt solution, which was rejected. The remainder (*ca.* 70 ml.) of the solution was halved and the pH of each half measured. The readings were not accepted unless they agreed to within 0·02 pH unit. The values quoted in the Table are all the mean of measurements made in at least three separate experiments.

pH *values of salt solutions.*

| Concentration | Aluminium chloride 15° | 20° | 25° | Alum 21·5° | Concentration | Aluminium chloride 15° | 20° | 25° | Alum 21·5° |
|---|---|---|---|---|---|---|---|---|---|
| $1 \times 10^{-2}$ | 3·81 | 3·76 | 3·68 | 3·67 | $2{\cdot}5 \times 10^{-4}$ | — | — | — | 4·48 |
| $5 \times 10^{-3}$ | 3·98 | 3·91 | 3·84 | 3·90 | $2 \times 10^{-4}$ | 4·59 | 4·52 | 4·46 | — |
| $1 \times 10^{-3}$ | 4·27 | 4·21 | 4·13 | 4·19 | $1 \times 10^{-4}$ | 4·74 | 4·68 | 4·61 | 4·65 |
| $7{\cdot}5 \times 10^{-4}$ | — | — | — | 4·26 | $5 \times 10^{-5}$ | 4·90 | 4·87 | 4·79 | — |
| $5 \times 10^{-4}$ | 4·40 | 4·36 | 4·26 | 4·33 | $2 \times 10^{-5}$ | 5·15 | 5·09 | 5·06 | — |

*Evaluation of* p*K'*. Over the range of concentrations used we may expect equation (3)

$$pK = \mathrm{pH} + \log\,[\mathrm{Al}^{3+}] - \log\,[\mathrm{AlOH}^{2+}] - \phi(I) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

to be a sufficiently close approximation, $\phi(I)$ being some function of the ionic strength $I$. Furthermore, Debye and Hückel's theory leads us to expect that the dependence of $\phi(I)$ on $(I)$ will be given with sufficient accuracy by the expression

$$\phi(I) = A(3^2 - 2^2)I^{\frac{1}{2}}/(1 + B'I^{\frac{1}{2}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

except perhaps at the highest concentrations. $A$ varies slightly with temperature; over the range 15—25° it differs very little from 0·5, and this value was used in all our calculations.

The " best " value for $B'$ can be found only by trial, but theory indicates that it should be close to unity. Consequently p$K'$, given by equation (4), may be expected to exceed p$K$ by an

$$pK' = \mathrm{pH} + \log\,[\mathrm{Al}^{3+}] - \log\,[\mathrm{AlOH}^{2+}] - 2{\cdot}5I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) \quad . \quad . \quad . \quad (4)$$

amount which approximates to $2{\cdot}5(B' - 1)I$ at the lower concentrations.

The concentration of hydrogen ions was obtained from equation (5) and if nothing more

$$-\log\,[\mathrm{H_3O^+}] = \mathrm{pH} - 0{\cdot}5I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

basic than $\mathrm{AlOH}^{2+}$ was formed in these experiments it follows that

$$[\mathrm{AlOH}^{2+}] = [\mathrm{H_3O^+}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

## RESULTS

Values of p$K'$ are plotted against $I^{\frac{1}{2}}$ in the Figure. It is evident from the falling away of p$K'$ at the higher ionic strengths that the " best " value for $B'$ is a little greater than unity. It is clear, however, that the use of a " better " value of $B'$ would not change the following values of p$K$ found by extrapolation to infinite dilution :

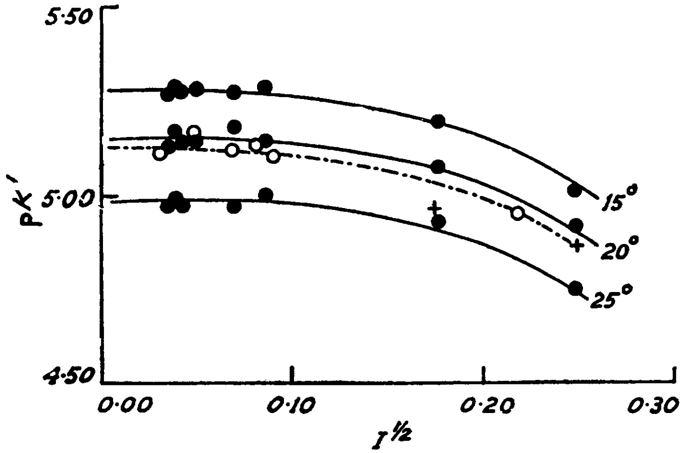
| | | | | | |
|---|---|---|---|---|---|
| p*K* | 5·28 | 5·15 | 5·13 | 4·98 | All ± 0·02 unit |
| *t*, °C | 15 | 20 | 21·5 | 25 | |

A linear relation being assumed between p$K$ and temperature over this range, these figures give a temperature coefficient of —0·03 unit/° c. The similarity of this to the temperature coefficient of the ionic product of water suggests that the aluminium salt hydrolysis has a similar mechanism to the ionisation of water, the reaction consisting of the transfer of a proton from one of the water molecules in the hydration sheath of the aluminium ion to one of the free solvent water molecules. This is the reaction represented by equation (1).

The method employed for the calculation of the p$K$ value rests on the assumption that no basic ion other than $\mathrm{AlOH^{2+}}$ is present in the solution. The next stage of hydrolysis will be the production of the second basic ion by the reaction

$$(\mathrm{Al,5H_2O,OH})^{2+} + \mathrm{H_2O} \rightleftharpoons [\mathrm{Al,4H_2O(OH)_2}]^{+} + \mathrm{H_3O^+}$$

The amount of this secondary hydrolysis will increase with the pH of the solution, but clearly it has no effect on the results even at the highest pH reached in these experiments.



p$K'$, *the negative logarithm of the approximate equilibrium constant of the reaction*

$$\mathrm{Al,6H_2O^{3+}} + \mathrm{H_2O} \rightleftharpoons \mathrm{Al,5H_2O{\cdot}OH^{2+}} + \mathrm{H_3O^+}$$

*plotted against* $I^{\frac{1}{2}}$, *the square root of the ionic strength in solutions of aluminium salts at different temperatures.* ● *Aluminium chloride ;* ○ *alum ;* + *aluminium perchlorate at* 15° (*Brønsted*).

It is considered that, owing to the high dilution used, any errors caused by impurity in the original material will be slight, and the effect of any ferric iron will be negligible at pH >4·0. The agreement between the results obtained with material from different sources shows that no serious errors have arisen from any of these causes.

In the original determination of the p$K$ by Brønsted, the activity-coefficient correction applied was purely empirical, being estimated from that found necessary to correct the value found for chromium ion in a solution of the same concentration. In this case Brønsted used a wide range of concentrations and extrapolated the experimental results to $I^{\frac{1}{2}} = 0$. With aluminium only three solutions were used and the value of the equilibrium constant at infinite dilution was calculated from the mean of these three results by applying a correction equal to that found necessary in the case of the chromium.

We have recalculated Brønsted's data at 15° for aluminium perchlorate solutions using equation (4). Even the most dilute solution used by him, 0·005M, is too concentrated for accurate calculation of activities, but the values obtained for the p$K$ are shown plotted against the ionic strengths of the solution in the Figure. It will be seen that the points obtained lie about 0·2—0·15 unit lower than those obtained by us for aluminium chloride solutions of similar concentration and temperature. This discrepancy appears to be a feature of the actual measurements and is probably due to the different standards of pH used.

The results obtained by Faucherre also refer to measurements made on rather more concentrated solutions than those used by us, and no activity coefficient corrections were applied at all. Correction of his figures on the basis of equation (5) give a value of p$K$ = 5·22 in a solution of $I = 0{\cdot}12$, which is in agreement with our data for 15°, but since no temperature details are given by Faucherre any critical comparison of the two sets of data is impossible.

ROTHAMSTED EXPERIMENTAL STATION,
HARPENDEN, HERTS.

[*Received, August 7th,* 1954.]