## 106. *The Hydrolysis of Salts in Solution.*

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A brief summary of the authors' previous investigations of salt hydrolysis by means of the glass electrode is given, and it is emphasised that, although atmospheric contamination can be ignored for salts showing medium hydrolysis, it must be guarded against when the $p_H$ of the solution under examination is less than two units removed from 7. An apparatus is shown for the preparation of solutions and the measurement of their $p_H$ values without exposure to the atmosphere, and results for a number of salt solutions, most of which require protection against atmospheric contamination, are recorded along with the corresponding stoicheiometric " hydrolysis constants." A table of $p_H$ values obtained by interpolation at selected dilutions is given for 18 common salts in water.

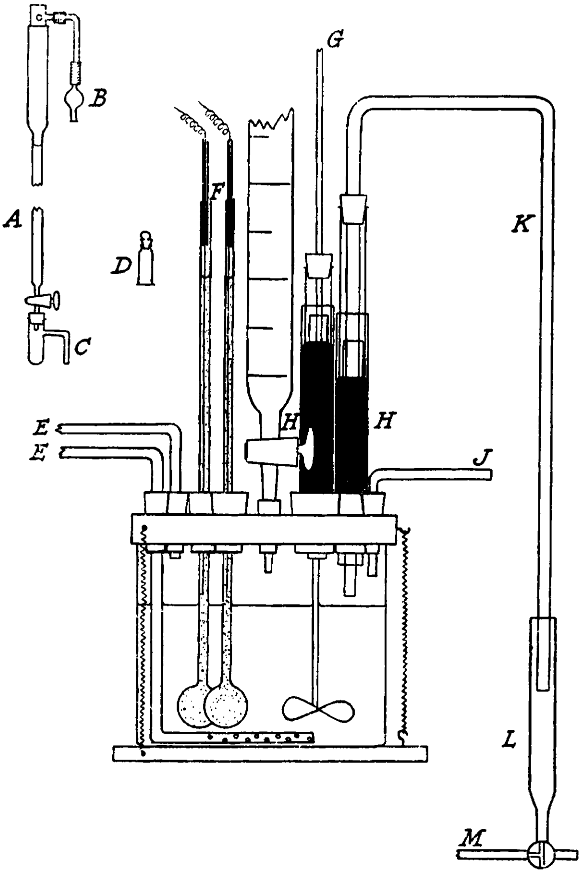
In a series of papers the authors have (i) discussed the reasons for the paucity of data on the hydrolysis of common inorganic salts, and the advantages of the use of the glass electrode for hydrolysis determination, and have shown the absence of neutral-salt effect with this electrode at the salt concentrations examined [*J. Roy. Tech. Coll.* (*Glasgow*), 1937, **4**, 46]; (ii) described how the final purification of salts may be effected by crystallisation from a solution containing about 100 times the concentration of acid or alkali estimated to be produced by hydrolysis (*loc. cit.*); and (iii) shown that consistent measurements of unbuffered solutions may be obtained by preparing carbon dioxide-free water, solutions of salts and dilutions of these, all without coming into contact with acid or alkaline impurities in the atmosphere (*Trans. Faraday Soc.*, 1937, **33**, 1455). Table V summarises the data on hydrolysis obtained by the authors.

In this paper the $p_H$ values and hydrolysis constants are recorded for a number of additional salts. For salts showing only slight hydrolysis, in which the $p_H$ is within two units of 7, pure neutral water must be used, not merely " conductivity water " which has, in general, a $p_H$ of about 5·7. Table I shows the $p_H$ of solutions of sodium acetate, zinc sulphate, and ammonium chloride prepared with distilled water from which carbon dioxide had been excluded until the last operation of transferring them to the glass-electrode vessel. Subsequently, this work was repeated with the apparatus shown in the figure, and a comparison of the results in Table I with those in Tables II, III, and IV shows how rigorously carbon dioxide must be excluded throughout with such slightly hydrolysed salts. For solutions having a $p_{\mathrm{H}}$ more than 2—3 units removed from 7 the error occasioned by atmospheric contamination becomes insignificant and conventional apparatus may be employed.

TABLE I.

*The* $p_{\mathrm{H}}$ *of three slightly hydrolysed salts in water containing dissolved carbon dioxide.*

| *v* (l./mol.). | 10. | 50. | 100. | 250. | 500. | 1000. |
|---|---|---|---|---|---|---|
| Sodium acetate | 7·96 | 7·34 | 7·13 | 6·86 | 6·71 | 6·53 |
| Zinc sulphate | 5·67 | 5·62 | 5·57 | 5·65 | 5·63 | 5·58 |
| Ammonium chloride | 5·34 | 5·49 | 5·55 | — | 5·59 | 5·63 |



A, *Burette assembly on reduced scale.* B, *Soda–lime tube.* C, *Pure-air inlet.* D, *Weighing bottle.* E, *Air from purifying train.* F, *Mercury contacts.* G, *Stirrer.* H, *Mercury seals.* J, *Air outlet to soda–lime tube.* K, *Agar*–KCl *bridge.* L, *Saturated* KCl. M, *To calomel electrode.*

## EXPERIMENTAL.

The electrode chain used was, apart from modifications to prevent atmospheric contamination, essentially the same as that previously used to examine salts hydrolysed to an appreciable extent (*J. Roy. Tech. Coll.*, **1937**, **4**, 32, 46). Dissolved carbon dioxide was removed from the distilled water (prepared in a Bousfield still), contained in the electrode chamber and burette shown in the figure, by the passage of carbon dioxide-free air purified as described elsewhere

(*Trans. Faraday Soc., loc. cit.*). The bridge of potassium chloride in agar-agar (Michaelis and Fuzita, *Biochem. Z.*, 1923, **142**, 398) was lowered only during measurements. A fairly concentrated solution of known strength was prepared in the burette by adding the salt rapidly from a weighing bottle, the passage of pure air through the burette preventing ingress of carbon dioxide. The hydrolytic equilibrium of a salt solution is, in general, disturbed by the passage of a gas, and so this supply was stopped immediately the burette stopper was replaced in position. The salt was dissolved by shaking the burette, which was then fitted to the lid of the electrode chamber. The passage of air through the water in the electrode chamber was now stopped, but a slow stream was passed over the surface to prevent atmospheric contamination. Solutions of known concentration were prepared in the electrode chamber by adding measured amounts from the burette.

The two glass electrodes used were calibrated before and after a set of measurements against two hydrogen electrodes which were fitted to the apparatus for the purpose, the buffer solutions employed being adjusted to the $p_H$ of the limiting values obtained with the salt solution under examination. Unless otherwise stated, the salts, which were of " AnalaR " quality, were recrystallised by the method described elsewhere (*J. Roy. Tech. Coll.*, 1937, **4**, 54).

The E.M.F.'s of the electrode chain for both glass and hydrogen electrodes were recorded on a McFarlane–Pye valve potentiometer reading to 0·1 mv.

*Sodium Acetate.*—Although calculated data for this salt are widely quoted in textbooks to illustrate the derivation of hydrolysis formulæ, there appeared to be no experimental figures available to test the formulæ. The results now obtained for the recrystallised salt are given in Table II, the value for $K_H$ used being the simplified expression $K^2_W . v/a^2_H$. The mean value obtained, *viz.*, $2{\cdot}18 \times 10^{-10}$, may be compared with that of $2{\cdot}8 \times 10^{-10}$ for $K_W/K_{\text{acetic acid}}$ at 16·5°.

TABLE II.

*The* $p_H$ *at* 16·5° *of carbon dioxide-free solutions of sodium acetate, and values for the hydrolysis constant.*

| $v$ (l./mol.). | $p_H$. | $K_H \times 10^{10}$. | $v$ (l./mol.). | $p_H$. | $K_H \times 10^{10}$. | $v$ (l./mol.). | $p_H$. | $K_H \times 10^{10}$. |
|---|---|---|---|---|---|---|---|---|
| 1451 | 8·02 | 4·38 | 159·1 | 8·34 | 2·09 | 33·2 | 8·61 | 1·52 |
| 735 | 8·09 | 3·20 | 123·8 | 8·39 | 2·05 | 23·6 | 8·66 | 1·36 |
| 459 | 8·17 | 2·76 | 91·0 | 8·44 | 1·89 | 19·2 | 8·70 | 1·32 |
| 291·5 | 8·22 | 2·21 | 68·4 | 8·49 | 1·79 | | Mean | 2·18 |
| 204·5 | 8·29 | 2·14 | 49·1 | 8·54 | 1·64 | | | |

*Zinc Sulphate.*—The hydrolysis of zinc sulphate, unlike that of most salts, has been studied by several workers. Denham and Marris (*Trans. Faraday Soc.*, 1928, **24**, 510), using a hydrogen electrode, obtained a series of $p_H$ values which decreased with dilution, owing, there seems little doubt in the light of the present work, to atmospheric contamination. Kolthoff and Kameda (*J. Amer. Chem. Soc.*, 1931, **53**, 832) used a bright platinum hydrogen electrode and obtained slightly more acid values than those given in Table III. Our results support their evidence that the first-stage hydrolysis predominates, *viz.*, $Zn^{\bullet\bullet} + H_2O \rightleftharpoons ZnOH^{\bullet} + H^{\bullet}$. Values for the simplified equilibrium constant $K_H = a^2_H . v$ corresponding to this reaction at 16·5° are given in Table III. The mean value obtained gives a dissociation constant of $1{\cdot}6 \times 10^{-4}$ for $ZnOH^{\bullet}$.

TABLE III.

*Zinc sulphate.*

| $v$ (l./mol.). | $p_H$. | $K_H \times 10^{11}$. | $v$ (l./mol.). | $p_H$. | $K_H \times 10^{11}$. | $v$ (l./mol.). | $p_H$. | $K_H \times 10^{11}$. |
|---|---|---|---|---|---|---|---|---|
| 1820 | 6·92 | 2·64 | 134·3 | 6·32 | 3·07 | 25·5 | 5·90 | 4·05 |
| 1052 | 6·80 | 2·65 | 97·3 | 6·25 | 3·08 | 21·5 | 5·86 | 4·10 |
| 528 | 6·65 | 2·65 | 73·2 | 6·16 | 3·51 | 18·1 | 5·82 | 4·10 |
| 356 | 6·55 | 2·93 | 48·5 | 6·06 | 3·68 | | Mean | 3·3 |
| 203·9 | 6·41 | 3·09 | 34·6 | 5·97 | 3·95 | | | |

*Sodium Oxalate.*—The $p_H$ values obtained for this salt at 16° (see table) indicate that the first-stage hydrolysis predominates, giving the simplified expression $K_H = K^2_W . v/a^2_H$.

*Sodium oxalate.*

| $v$ (l./mol.). | $p_H$. | $K_H \times 10^{10}$. | $v$ (l./mol.). | $p_H$. | $K_H \times 10^{10}$. | $v$ (l./mol.). | $p_H$. | $K_H \times 10^{10}$. |
|---|---|---|---|---|---|---|---|---|
| 482 | 8·25 | 3·81 | 144 | 8·52 | 3·96 | 67·7 | 8·72 | 4·64 |
| 248 | 8·40 | 3·92 | 93·5 | 8·63 | 4·25 | 27·8 | 8·92 | 4·83 |
| | | | | | | | Mean | 4·2 |

*Sodium Hydrogen Carbonate.*—Sodium hydrogen carbonate is not so poorly buffered as the salts already dealt with, and its solutions are thus less seriously affected by atmospheric contamination. Noyes (*Z. physikal. Chem.*, 1893, **11**, 495) has shown theoretically that the hydrogen-ion concentration of an acid salt of a weak acid and a strong base is constant at any dilution and equal to the square root of the product of the two dissociation constants of the weak acid. The $p_{\mathrm{H}}$ of sodium bicarbonate solutions should be 8·37 at 25° from this formula, which is based on purely stoicheiometric principles. The experimental figures obtained (see table) give a smooth curve of slightly increasing $p_{\mathrm{H}}$ value with increasing dilution up to $v = 200$, after which the constant value of 8·62 is maintained. Powney and Jordan (*J. Soc. Chem. Ind.*, 1937, **56**, 133) record rather similar results for this salt, their graph showing a maximum $p_{\mathrm{H}}$ of about 8·75 at $v = 100$, after which it falls slowly with increasing concentration to about 8·65 at $v = 11$.

*Potassium Chloride.*—The $p_{\mathrm{H}}$ of this salt of "double-sided strength" is especially sensitive to atmospheric or other contamination. Kolthoff and Kameda (*loc. cit.*, p. 821) obtained erratic results when using bright platinum hydrogen electrodes in solutions of potassium chloride. The salt used in the present work was twice crystallised from conductivity water and was not washed with organic solvents, as were salts recrystallised from slightly acid or alkaline solutions. With increasing salt concentration the $p_{\mathrm{H}}$ values fall gradually from neutrality at high dilutions to about 6·8 at $v = 100$. The smooth curve then falls rapidly to about $p_{\mathrm{H}}$ 6 at $v = 1$. Such a result, in the absence of unforeseen sources of contamination with this salt, must be due to the influence of the salt ions on the activity of the hydrogen ions present. Ellis and Kiehl (*J. Amer. Chem. Soc.*, 1935, **57**, 2139) obtained results approximately one unit lower than these by using a specially designed glass electrode to avoid contamination, which they state is rapid, from the alkali of the glass. However, we have not experienced a rapid drift to high $p_{\mathrm{H}}$ value with the seasoned-bulb type of glass electrodes used in this apparatus, although a rise was noted when an unbuffered solution remained motionless in contact with the electrode. Stirring caused the $p_{\mathrm{H}}$ to fall immediately to the original value, due undoubtedly, as Edwards and Evans (J., 1937, 1938), who experienced a similar phenomenon, have suggested, to dispersion through the bulk of the liquid of a minute quantity of dissolved alkali forming a layer around the electrode. Our results for this salt are in agreement with those of Edwards and Evans where the concentrations overlap, but for the most part we have worked over a range of higher concentration.

*Sodium hydrogen carbonate.*

| $v$ (l./mol.) | 955 | 463 | 252·5 | 175 | 116 | 73·0 | 53·0 | 34·2 | 21·6 | 13·98 | 7·95 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $p_{\mathrm{H}}$ at 18° | 8·62 | 8·62 | 8·62 | 8·60 | 8·59 | 8·56 | 8·54 | 8·51 | 8·46 | 8·43 | 8·37 |

*Potassium chloride.*

| $v$ (l./mol.) | 1149 | 468 | 96·1 | 62·8 | 38·0 | 15·5 | 10·5 | 6·45 | 4·61 | 3·26 |
|---|---|---|---|---|---|---|---|---|---|---|
| $p_{\mathrm{H}}$ at 18° | 7·05 | 6·96 | 6·81 | 6·74 | 6·69 | 6·55 | 6·47 | 6·37 | 6·31 | 6·20 |

*Potassium Chromate.*—This salt reacts alkaline as shown in the table, which relates to 16°. The "hydrolysis constant," calculated with the usual assumptions as $K^2_{\mathrm{W}}\,.\,v/a^2_{\mathrm{H}}$ (where $K_{\mathrm{W}} = 0{\cdot}5 \times 10^{-14}$) from the equation $CrO_4'' + H_2O \rightleftharpoons HCrO_4' + OH'$, is shown in col. 3, and decreases with increasing concentration. If the hydrolysis were to proceed according to the second-stage equation, $CrO_4'' + 2H_2O \rightleftharpoons H_2CrO_4 + 2OH'$, the quantity $v/a^3_{\mathrm{H}}$ should be constant. In fact, however, the power of $a_{\mathrm{H}}$ which gives the best constant is 2·5, and this affords evidence that the hydrolysis has gone somewhat beyond the first stage.

*Potassium Dichromate.*—The distinctly acid reaction of this salt permits the use of conductivity water containing dissolved carbon dioxide without significant error, and so solutions were prepared by dilution of a standard. Numerous workers (*e.g.*, Abegg and Cox, *Z. physikal. Chem.*, 1904, **48**, 725; Sand and Kaestle, *Z. anorg. Chem.*, 1907, **52**, 101; Sherrill, *J. Amer. Chem. Soc.*, 1907, **29**, 1614, 1675; Neuss and Rieman, *ibid.*, 1934, **56**, 2238) have proved the presence of $CrO_4''$ in solutions of this salt, and the acid reaction is most probably due to the equilibrium $Cr_2O_7'' + H_2O \rightleftharpoons 2HCrO_4' \rightleftharpoons 2H^{\bullet} + 2CrO_4''$.

A hydrolysis constant can be calculated from this equation only if, in addition to the usual assumptions, the relative concentrations of $Cr_2O_7''$ and $HCrO_4'$ are taken as constant. The quantity $a^4_{\mathrm{H}}\,.\,v$ should then be constant. Experiment shows (see table, col. 3) that $a^{2\cdot5}_{\mathrm{H}}\,.\,v$ is constant, and suggests that one or both of these ions are being hydrolysed as well, with the production of hydroxyl ions, *e.g.*, $Cr_2O_7'' + H_2O \rightleftharpoons HCr_2O_7' + OH'$. The data relate to 16°.

*Potassium chromate.*

| $v$ (l./mol.). | $p_H$. | $K_H \times 10^9$. | $v$ (l./mol.). | $p_H$. | $K_H \times 10^9$. | $v$ (l./mol.). | $p_H$. | $K_H \times 10^9$. |
|---|---|---|---|---|---|---|---|---|
| 1218 | 8·81 | 2·0 | 160·0 | 9·19 | 1·5 | 35·4 | 9·45 | 1·1 |
| 600 | 8·95 | 1·9 | 91·0 | 9·30 | 1·4 | 14·2 | 9·58 | 0·8 |
| 302·1 | 9·08 | 1·9 | 55·8 | 9·38 | 1·3 | 10·6 | 9·62 | 0·7 |

*Potassium dichromate.*

| $v$ (l./mol.). | $p_H$. | $a_H^{2\cdot5} . v \times 10^9$. | $v$ (l./mol.). | $p_H$. | $a . v_H^{2\cdot5} \times 10^9$. | $v$ (l./mol.). | $p_H$. | $a_H^{2\cdot5} . v \times 10^9$. |
|---|---|---|---|---|---|---|---|---|
| 10 | 3·86 | 2·2 | 100 | 4·22 | 2·8 | 500 | 4·50 | 2·8 |
| 50 | 4·10 | 2·8 | 250 | 4·37 | 3·0 | 1000 | 4·63 | 2·7 |

*Beryllium Sulphate.*—Precautions against atmospheric contamination were unnecessary for this salt also, as its solutions have a markedly acid solution. The $p_H$ values for 16·5° given in Table IV are for " pure " beryllium sulphate which had been recrystallised twice. The fall in $p_H$ with increase in concentration of the solution is too great to give a hydrolysis constant. In fact, our results show (Table IV, col. 3) that the degree of hydrolysis given by $a_H . v/2$ does not vary much over a wide range of concentration. The quantity $a_H^{4/3} . v$ was found to be constant (col. 4). Prytz (*Trans. Faraday Soc.*, 1928, **24**, 281), who obtained similar results with the hydrogen electrode over the range $v = 1$—23 l./mol., suggested that the anomalous behaviour of this salt might be due to an enhanced value of $a_H$ caused by the salt molecules present, but were this true, a knowledge of the activities of the reacting ions would be essential for the calculation of $K_H$. Neglect of this fact no doubt explains Prytz's failure to obtain a constant with the aid of certain results given by magnesium sulphate solutions, to which sufficient sulphuric acid was added to give the same $p_H$ value as the corresponding beryllium sulphate solutions, even if the necessary assumption that magnesium sulphate is not hydrolysed were true. We rather ascribe the anomaly to the marked tendency shown by beryllium salts to form basic complexes. The same phenomenon is observed with cadmium sulphate, the $p_H$ values of which are given in Table V, and chemical evidence again suggests a similar cause.

TABLE IV.

*Beryllium sulphate.*

| $v$ (l./mol.). | $p_H$. | $10^3a_H . v/2$. | $10^3a_H^{4/3} . v$. | $v$ (l./mol.). | $p_H$. | $10^3a_H . v/2$. | $10^3a_H^{4/3} . v$. |
|---|---|---|---|---|---|---|---|
| 10 | 2·92 | 6·0 | 1·3 | 250 | 3·96 | 13·7 | 1·3 |
| 50 | 3·46 | 8·7 | 1·2 | 500 | 4·17 | 16·9 | 1·3 |
| 100 | 3·68 | 10·5 | 1·2 | 1000 | 4·36 | 21·8 | 1·5 |

TABLE V.

$p_H$ *Values of salt solutions obtained by interpolation.*

(Salts examined in carbon dioxide-free solutions are marked with an asterisk.)

| $v$ (l./mol.). | $NaHSO_4$, 19°. | $BeSO_4$, 16·5°. | $Al_2(SO_4)_3$, 16°. | $K_2Cr_2O_7$, 16°. | $Pb(NO_3)_3$, 15°. | $CuSO_4$, 15°. | $CdSO_4$, 16°. | $NH_4Cl$,* 15°. | $NH_4NO_3$ * 15°. |
|---|---|---|---|---|---|---|---|---|---|
| 10 | 1·31 | 2·92 | 3·59 | 3·86 | 4·17 | 4·32 | 4·40 | 5·42 | 5·43 |
| 50 | 1·91 | 3·46 | 3·87 | 4·10 | 4·73 | 4·82 | 5·07 | 5·75 | 5·74 |
| 100 | 2·17 | 3·68 | 3·98 | 4·22 | 4·91 | 4·99 | 5·27 | 5·92 | 5·89 |
| 250 | 2·52 | 3·96 | 4·14 | 4·37 | 5·10 | 5·20 | 5·39 | 6·14 | 6·11 |
| 500 | 2·81 | 4·17 | — | 4·50 | 5·23 | 5·33 | — | 6·31 | 6·29 |
| 1000 | 3·07 | 4·36 | — | 4·63 | 5·35 | 5·45 | — | 6·51 | 6·45 |

| $v$ (l./mol.). | $(NH_4)_2SO_4$,* 15°. | $ZnSO_4$,* 16·5°. | KCl,* 18°. | $NH_4OAc$,* 15°. | $NaHCO_3$,* 18°. | NaOAc,* 16·5°. | $Na_2C_2O_4$,* 16°. | $K_2CrO_4$, 16°. | KCN, 15°. |
|---|---|---|---|---|---|---|---|---|---|
| 10 | 5·63 | 5·69 | 6·45 | 7·16 | 8·38 | 8·76 | 9·05 | 9·63 | 11·37 |
| 50 | 5·88 | 6·07 | 6·70 | 7·14 | 8·52 | 8·54 | 8·80 | 9·37 | 11·07 |
| 100 | 6·01 | 6·24 | 6·80 | 7·11 | 8·56 | 8·41 | 8·60 | 9·28 | 10·91 |
| 250 | 6·10 | 6·45 | 6·89 | 7·08 | 8·62 | 8·24 | 8·39 | 9·10 | 10·69 |
| 500 | 6·34 | 6·62 | 6·96 | 7·06 | 8·62 | 8·13 | 8·24 | 8·96 | 10·52 |
| 1000 | 6·55 | 6·77 | 7·02 | 7·04 | 8·62 | — | — | — | 10·35 |

*Copper Sulphate.*—This salt has been dealt with by the authors elsewhere (*J. Roy. Tech. Coll.*, 1937, **4**, 54). The solutions showed a slow increase in acidity for several days after their preparation, and other salts of sparingly soluble bases, *e.g.*, lead nitrate, behaved similarly. This phenomenon had been noted by others, O'Sullivan (*Trans. Faraday Soc.*, 1925, **21**, 319) attributing the change in $p_H$ to the slow coagulation of the colloidal hydroxide with consequent liberation of adsorbed acid, and Hughes (J., **1928**, 491) believing it to be due to the slowness of the hydrolytic reaction. The suggestion recently made by Friedman and Stokes (*J. Amer. Chem. Soc.*, 1939, **61**, 118) that either the slow oxidation of quinhydrone or the contamination of the solution by potassium chloride is responsible is untenable, for neither Hughes nor the present authors used quinhydrone, and in our case at any rate potassium chloride contamination with the set-up used for this salt was impossible. The authors prefer O'Sullivan's explanation.

The $p_H$'s for the salt solutions examined here and elsewhere are tabulated in Table V, the values shown being interpolated for convenience to the same dilutions for each salt.

The variations in the values obtained for the equilibrium " constants " in this work are due, apart from experimental error, to the use of the ordinary stoicheiometric expressions for $K_H$ in the absence of reliable data on the activities of the salt ions concerned, and possibly, in the case of multivalent ions, to the presence of side reactions.

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