# 388. *The Dissociation Constants of Organic Acids. Part VII. Acetic Acid: A Correction. The Solvent Correction for Salts of Weak Monobasic Acids.*

By George H. Jeffery, Arthur I. Vogel, and (in part) Hugh V. Lowry.

The view that carbonic acid is the chief impurity in equilibrium water has long been held (compare Kendall, *J. Amer. Chem. Soc.*, 1916, **38**, 2460; 1917, **39**, 7) and supporting experimental evidence has been provided by the present authors' determinations of the conductivities of sodium and potassium hydroxides in such water (*Phil. Mag.*, 1933, **15**, 395). The solvent correction for these alkali hydroxides was applied on the basis that carbonic acid is the sole impurity, and the corrected results were in agreement above *ca.* 0·0005*N* with the similar measurements of Goworecka and Hlasko (*Rocz. Chem.*, 1932, **12**, 403; Jeffery and Vogel, *Phil. Mag.*, 1933, **16**, 64) with ultra-pure conductivity water ($\kappa$ about 0·1 gemmho). The importance of conductivity measurements of the alkali-metal acetates in the evaluation of the dissociation constant of acetic acid led us to investigate the influence of the specific conductivity of the water upon the results for the equivalent conductivity. Potassium acetate, being anhydrous, was chosen. With water of $\kappa = 0{\cdot}420$ gemmho it was found that the conductivities were appreciably higher, after application of the solvent and hydrolysis correction, than those obtained with equilibrium water. This suggested that the independent solvent and hydrolysis corrections in our previous determinations (Part VI; J., 1932, 2829) with equilibrium water were inadequate. New determinations were therefore carried out with equilibrium water to which sufficient of a dilute solution of barium hydroxide was added to react with all the carbonic acid, it being assumed that this was the only impurity present. In order to suppress the hydrolysis of the resultant barium carbonate in dilute solution, about 20% excess of barium hydroxide was actually employed (compare MacInnes and Shedlovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1432, who used excess of acetic acid in the parallel case of sodium acetate). The conductivity of the solvent after the addition of the barium hydroxide was subtracted from the total observed specific conductivity, and the hydrolysis correction applied as before (J., 1932, 2835). The corrected results were higher than those previously obtained and are regarded as more trustworthy.

The above method of correcting the observed results applies only to those weak acids for which the approximate expression $\alpha_h = \sqrt{K_w/C \, . \, K_{\text{class.}}}$ is valid, *i.e.*, where $\alpha_h$ is small: $C$ is the molecular concentration of the salt and $K_{\text{class.}}$ is the classical dissociation constant of the acid (compare J., 1932, 2835). A general correction, applicable to the alkali salts of all weak acids, may be deduced as follows. This derivation is for equilibrium water to which barium hydroxide solution has been added in 20—40% excess of that required completely to react with all the carbonic acid present. This will be termed the " baryta water " method. The presence of a small quantity of barium carbonate and hydroxide in solution is allowed for by subtracting its specific conductivity from the total observed conductivity, the resultant figure being regarded as the specific conductivity of the salt. Definite experimental evidence in support of this is provided by the results of another run for potassium acetate which was carried out with 40% excess of barium hydroxide. These are given in Table I; the third line contains the values of $\Lambda$ interpolated from the conductivity–concentration curve obtained with 20% excess of barium hydroxide. The agreement is excellent except at the lowest concentration. The values of $\kappa$ relate to the water after and before addition of baryta.

TABLE I.

Cell *S*. Series 7. $\kappa = 3{\cdot}61$ [0·776].

| | | | | | | |
|---|---|---|---|---|---|---|
| $C \times 10^4$ ............... | 1·511 | 3·520 | 5·743 | 12·79 | 21·79 | 33·63 |
| $\Lambda_{\text{obs.}}$ ..................... | 114·03 | 113·77 | 113·56 | 112·65 | 111·64 | 110·97 |
| $\Lambda_{\text{interp.}}$ .................. | 114·20 | 113·87 | 113·54 | 112·67 | 111·72 | 110·87 |

The following equilibria must be considered in the solution of a salt NaA in such water: $NaA \rightleftharpoons Na^{\cdot} + A'$; $H_2O \rightleftharpoons H^{\cdot} + OH'$; $A' + H^{\cdot} \rightleftharpoons HA$. Since the solution is electrically neutral,

$$[Na^{\cdot}] + [H^{\cdot}] = [A'] + [OH'] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Now

$$[H^{\cdot}][A']/(C - [A']) = K_a$$

or

$$[A'] = K_aC/([H^{\cdot}] + K_a).$$

Substitution in (1) with $[Na^{\cdot}] = C$, gives

$$C + [H^{\cdot}] = K_aC/([H^{\cdot}] + K_a) + K_w/[H^{\cdot}] \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The solution of this cubic equation for $[H^{\cdot}]$ is (see Appendix)

$$[H^{\cdot}]^2 = H_5^2 + H_5(K_w - H_5^2)/(K_a + C) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where

$$H_5^2 = K_wK_a/(K_a + C) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$[H^\cdot]$ being known, $[A']$ and $[OH']$ can be readily computed from the above relations. The correction $\Delta\kappa$ to be *added* to the observed specific conductivity is given by

$$\Delta\kappa = 10^{-3}\{\Lambda_{A'}(C - [A']) - \Lambda_{H^\cdot}[H^\cdot] - \Lambda_{OH'}[OH']\} \quad . \quad . \quad . \quad . \quad (5)$$

where $\Lambda_{A'}$, $\Lambda_{H^\cdot}$, $\Lambda_{OH'}$ are the limiting mobilities of the anion, hydrogen, and hydroxyl ions respectively.

This treatment may be applied with slight modifications to solutions made with equilibrium water, or with water of lower conductivity provided it be assumed that carbonic acid is the only conducting impurity present. The equilibrium, $H_2CO_3 \rightleftharpoons H^\cdot + HCO_3'$, must be considered in addition to the three detailed above. The concentration of carbonic acid is designated by $m$, its secondary dissociation may be assumed negligible, and the primary constant is represented by $K_c$.

Equation (2) now becomes

$$C + [H^\cdot] = K_aC/([H^\cdot] + K_a) + K_w/[H^\cdot] + K_cm/([H^\cdot] + K_c) \quad . \quad . \quad (6)$$

(Ives, this vol., p. 314; compare Davies, *Trans. Faraday Soc.*, 1932, **28**, 607).

The solution of this equation of the fourth degree for $[H^\cdot]$ (see Appendix) for values of $m > 1 \times 10^{-5}$, expressed in g.-mols./l., is

$$[H^\cdot] = H_1 + (s - H_1)/H_1(2pH_1 + q) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where

$$H_1 = \{\sqrt{(q^2 + 4pr)} - q\}/2p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and $p = K_c + K_a + C$, $q = K_cC + K_cK_a - K_cm - K_w$, $r = K_cK_am + K_wK_c + K_wK_a$, and $s = K_wK_cK_a$.

For values of $m < 1 \times 10^{-5}$, *i.e.*, with water of $\kappa < 0{\cdot}8$—$0{\cdot}9$ gemmho at 25°,

$$[H^\cdot] = H_3 + (H_3^4 + pH_3^3)/(2qH_3 - r) \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where

$$H_3 = \{\sqrt{(r^2 + 4qs)} + r\}/2q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The correction to be *added* to the measured specific conductivity is

$$\Delta\kappa = 10^{-3}\{\Lambda_A(C - [A']) - \Lambda_{H^\cdot}[H^\cdot] - \Lambda_{OH'}[OH'] - \Lambda_{HCO_3'}[HCO_3'] \quad . \quad (11)$$

We have applied equation (11) to our original measurements on potassium and sodium acetates (J., 1932, 2836) and also to the new determinations for potassium acetate with water of $\kappa = 0{\cdot}420$ gemmho. The results are in Table II.

TABLE II.

*Potassium Acetate at 25°.*

| Run 1. Cell V. $\kappa = 0{\cdot}730$. | | | Run 2. Cell S. $\kappa = 0{\cdot}819$. | | | Run 3. Cell S. $\kappa = 0{\cdot}420$. | | |
|---|---|---|---|---|---|---|---|---|
| $C \times 10^4$. | $[H^\cdot] \times 10^7$. | $\Lambda_{corr.}$. | $C \times 10^4$. | $[H^\cdot] \times 10^7$. | $\Lambda_{corr.}$. | $C \times 10^4$. | $[H^\cdot] \times 10^7$. | $\Lambda_{corr.}$. |
| 1·415 | 5·401 | 117·12 | 2·909 | 5·019 | 115·55 | 1·112 | 6·482 | 116·91 |
| 6·177 | 2·201 | 113·36 | 7·096 | 2·221 | 113·58 | 7·212 | 1·091 | 113·40 |
| 11·53 | 1·312 | 112·54 | 15·79 | 1·220 | 112·25 | 14·06 | 0·606 | 112·39 |
| 23·11 | 0·761 | 111·67 | 30·27 | 0·669 | 111·06 | 26·54 | 0·295 | 111·32 |
| 48·22 | 0·406 | 110·14 | 39·70 | 0·482 | 110·52 | 43·63 | 0·167 | 110·29 |
| 72·85 | 0·279 | 109·17 | 68·68 | 0·301 | 109·23 | 72·01 | 0·096 | 109·17 |
| 92·45 | 0·248 | 108·45 | | | | | | |
| 111·0 | 0·199 | 107·83 | | | | | | |

*Sodium Acetate at 25°.*

| Run 1. Cell V. $\kappa = 0{\cdot}811$. | | | | | | Run 2. Cell S. $\kappa = 0{\cdot}840$. | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $C \times 10^4$. | $[H^\cdot] \times 10^7$. | $\Lambda_{corr.}$. | $C \times 10^4$. | $[H^\cdot] \times 10^7$. | $\Lambda_{corr.}$. | $C \times 10^4$. | $[H^\cdot] \times 10^7$. | $\Lambda_{corr.}$. | $C \times 10^4$. | $[H^\cdot] \times 10^7$. | $\Lambda_{corr.}$. |
| 1·285 | 6·441 | 94·01 | 38·74 | 0·571 | 86·44 | 2·808 | 5·672 | 91·56 | 32·06 | 0·581 | 86·72 |
| 5·368 | 2·762 | 89·75 | 57·78 | 0·398 | 85·52 | 6·076 | 2·122 | 89·38 | 51·09 | 0·401 | 85·80 |
| 9·927 | 1·722 | 88·72 | 75·24 | 0·268 | 84·81 | 14·87 | 1·316 | 88·26 | 64·91 | 0·315 | 85·15 |
| 19·71 | 1·009 | 87·66 | 91·77 | 0·251 | 84·19 | 26·38 | 0·792 | 87·06 | 99·01 | 0·232 | 83·96 |

The values of the equivalent conductivities for both of these acetates determined by the baryta method are in good agreement with the above data at concentrations exceeding 0·0005*N* (see Experimental). Agreement below this concentration was not expected from the work on the alkali hydroxides (see Jeffery and Vogel, *Phil. Mag.*, 1933, **16**, 64); it appears that below *ca.* 0·0005*N* the influence of minute quantities of saline impurities, otherwise negligible, becomes appreciable. The determinations by the baryta-water method, when corrected by the authors' original method (J., 1932, 2835) or by the new general method as expressed by equation (5), give practically the same values for the equivalent conductivities (see Experimental).

In Part VI (*loc. cit.*; see also *Nature*, 1932, **130**, 435) we commented upon the discrepancies between our own measurements and those of MacInnes and Shedlovsky (*loc. cit.*) upon sodium acetate. As the solvent correction applied by us at that time was inadequate, it is now clear that the original comparison was not a legitimate one. A true comparison of the two sets of results at round concentrations shows that the results are in satisfactory accord with one another in spite of the differences in solvent correction and general manipulation.

The conductivity at infinite dilution of the final corrected results for both sodium and potassium acetate have been computed both by the " *n* " and by the square-root formula. The former method gives

$$\text{NaOAc}: \quad \Lambda_0^n = \Lambda_C + 139{\cdot}8\, C^{0{\cdot}664}, \quad \Lambda_0^n = 90{\cdot}27;$$
$$\text{KOAc}: \quad \Lambda_0^n = \Lambda_C + 210{\cdot}4\, C^{0{\cdot}735}, \quad \Lambda_0^n = 114{\cdot}17.$$

These lead to 40·47 and 40·77 respectively for the limiting mobility of the acetate ion; mean, 40·62. The square-root formula gives 41·45, which is less probable. The new value of $\Lambda_0$ for acetic acid is therefore 348·0 + 40·62 = 388·62 (cf. J., 1932, 2830), which differs appreciably from that (387·85) originally employed by us, but is less than that (390·59) of MacInnes and Shedlovsky (*loc. cit.*). The results of the three series of measurements described in Part VI have been recalculated with $\Lambda_0 = 388{\cdot}62$; $\Lambda_e$ was the mean value obtained from the relations

$$\Lambda_e\text{HOAc} = \Lambda_{C'}\text{HCl} - \Lambda_{C'}\text{KCl} + \Lambda_{C'}\text{KOAc}.$$
$$= \Lambda_{C'}\text{HCl} - \Lambda_{C'}\text{NaCl} + \Lambda_{C'}\text{NaOAc}.$$

The final figures for the three runs with acetic acid (J., 1932, 2837) are collected below, $K_{\text{therm.}}$ being the thermodynamic or true dissociation constant.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $C \times 10^4$ | 1·873 | 25·62 | 45·23 | 65·27 | 89·55 | 113·2 | | |
| $\Lambda_c$ | 102·5 | 31·59 | 24·05 | 20·06 | 16·99 | 15·42 | | |
| $K_{\text{class.}} \times 10^5$ | 1·780 | 1·843 | 1·847 | 1·843 | 1·790 | 1·865 | | |
| $K_{\text{therm.}} \times 10^5$ | 1·772 | 1·788 | 1·790 | 1·764 | 1·717 | 1·776 | | |
| $C \times 10^4$ | 1·772 | 9·400 | 24·78 | 38·86 | 56·74 | 80·23 | 92·16 | 106·3 |
| $\Lambda_c$ | 103·9 | 50·60 | 31·94 | 25·78 | 21·48 | 18·51 | 16·99 | 15·81 |
| $K_{\text{class.}} \times 10^5$ | 1·733 | 1·832 | 1·824 | 1·832 | 1·835 | 1·806 | 1·842 | 1·834 |
| $K_{\text{therm.}} \times 10^5$ | 1·708 | 1·792 | 1·770 | 1·771 | 1·768 | 1·732 | 1·766 | 1·748 |
| $C \times 10^4$ | 5·160 | 12·96 | 25·78 | 68·71 | 84·50 | 112·2 | | |
| $\Lambda_c$ | 65·95 | 43·50 | 31·43 | 19·58 | 17·74 | 15·41 | | |
| $K_{\text{class.}} \times 10^5$ | 1·790 | 1·826 | 1·835 | 1·837 | 1·843 | 1·837 | | |
| $K_{\text{therm.}} \times 10^5$ | 1·759 | 1·784 | 1·780 | 1·766 | 1·772 | 1·758 | | |

The mean values of the classical and the thermodynamic dissociation constant are $1{\cdot}824 \times 10^{-5}$ and $1{\cdot}764 \times 10^{-5}$ respectively. MacInnes and Shedlovsky (*loc. cit.*) found $1{\cdot}813 \times 10^{-5}$ and $1{\cdot}753 \times 10^{-5}$ respectively, the difference being due to their higher value of $\Lambda_0$.

## EXPERIMENTAL.

The technique employed in the conductivity measurements has been described in earlier papers of this series. The sodium and potassium acetates were the specimens utilised in Part VI (J., 1932, 2834). The water with $\kappa = 0{\cdot}420$ gemmho used in the run for potassium acetate (Table I) was prepared by charging the boiler with equilibrium water (J., 1930, 1201).

The runs by the baryta-water method were carried out by first measuring the specific conductivity of the equilibrium water used, calculating the corresponding concentration of carbonic acid by the method described by the present authors (*Phil. Mag.*, 1933, **15**, 402), and then adding from a carefully calibrated burette the necessary quantity of *ca.* 0·0002*N*-barium hydroxide solution,* prepared by dissolving A.R. material in equilibrium water and standardised by titration (phenolphthalein) against solid succinic acid (A.R.) weighed on a microbalance. Usually about a litre of the water was prepared in a stoppered Pyrex flask, the whole was well shaken after the addition of the baryta, and used after 24 hours. This was employed for the preparation of the stock solution and in the Hartley and Barrett cell.

The results are tabulated below; $\kappa$ is the specific conductivity of the water after the addition of the baryta solution (the initial value is shown in parentheses), $\Lambda_{\text{norm.}}$ is the equivalent conductivity at concentration $C$ (g.-equivs./l.), in which the conductivity of the solvent has been subtracted, $\Lambda_{\text{corr.}}$ (A) are the values corrected for hydrolysis by the method previously described (J., 1932, 2835), and $\Lambda_{\text{corr.}}$ (B) are the corresponding values corrected by equation (5). The values of all the necessary constants are to be found in the earlier papers of this series and in *Phil. Mag.*, 1933, **15**, 398. The mean values of $\Lambda_0{}^n$ evaluated from the equation $\Lambda_0{}^n = \Lambda_C + BC^n$, the values of the constants of which are given, are included at the head of the tables, together with the values of $\Lambda_0{}^s$ and $x$ deduced from the square-root formula $\Lambda_0{}^s = \Lambda_C + xC^{0{\cdot}5}$. The values of $x_{\text{calc.}}$ and $\Delta$ (J., 1931, 720) for sodium and potassium acetates are 80·6, − 4·2% and 86·0, − 25·2% respectively. Col. 5 gives the values of $\Lambda_0{}^n$ calculated by the "*n*" formula, col. 6 the values of $\Lambda_{\text{calc.}}$ computed from the given values of $\Lambda_0{}^s$ and $x$, and col. 7 is the difference between col. 3 and col. 6. *M* is the molecular weight.

*Sodium Acetate at* 25° ($M = 82{\cdot}04$).

$$\Lambda_0{}^n = \Lambda_C + 139{\cdot}8C^{0{\cdot}664};\ \Lambda_0{}^n = 90{\cdot}27. \quad \Lambda_0{}^s = \Lambda_C + 77{\cdot}3C^{0{\cdot}5};\ \Lambda_0{}^s = 91{\cdot}25.$$

| $C \times 10^4$ | $\Lambda_{\text{norm.}}$. | $\Lambda_{\text{corr.}}$ (A). | $\Lambda_{\text{corr.}}$ (B). | $\Lambda_0{}^n$. | $\Lambda_{C\text{calc.}}$. | Diff. |
|---|---|---|---|---|---|---|
| Pyrex Cell S. Series 3. $\kappa = 2{\cdot}97$ [0·665]. | | | | | | |
| 2·001 | 90·26 | 89·81 | 89·85 | 90·34 | 90·12 | − 0·31 |
| 6·134 | 89·42 | 89·23 | 89·23 | 90·26 | 89·24 | − 0·01 |
| 12·07 | 88·61 | 88·50 | 88·49 | 90·11 | 88·45 | − 0·05 |
| 28·82 | 86·96 | 86·91 | 86·92 | 90·25 | 86·95 | 0·05 |
| 47·13 | 85·87 | 85·84 | 85·82 | 90·31 | 87·77 | 0·07 |
| 69·26 | 84·92 | 84·92 | 84·94 | [90·59] | 84·01 | 0·91 |
| 81·99 | 84·46 | 84·46 | 84·46 | [90·92] | — | — |
| Pyrex Cell V. Series 4. $\kappa = 3{\cdot}04$ [0·671]. | | | | | | |
| 0·997 | 90·48 | 89·89 | 89·96 | 90·32 | 90·44 | − 0·55 |
| 3·236 | 89·92 | 89·61 | 89·62 | 90·28 | 89·84 | − 0·23 |
| 7·987 | 89·12 | 88·97 | 88·95 | 90·21 | 88·90 | 0·07 |
| 21·07 | 87·62 | 87·55 | 87·58 | 90·29 | 87·55 | 0·00 |
| 36·25 | 86·43 | 86·38 | 86·37 | 90·27 | 86·32 | 0·06 |
| 59·97 | 85·27 | 85·27 | 85·26 | [90·57] | 85·12 | 0·15 |

*Potassium Acetate at* 25° ($M = 98{\cdot}13$).

$$\Lambda_0{}^n = \Lambda_C + 210{\cdot}4C^{0{\cdot}735};\ \Lambda_0{}^n = 114{\cdot}17. \quad \Lambda_0{}^s = \Lambda_C + 65{\cdot}7C^{0{\cdot}5};\ \Lambda_0{}^s = 114{\cdot}84.$$

| $C \times 10^4$ | $\Lambda_{\text{norm.}}$. | $\Lambda_{\text{corr.}}$ (A). | $\Lambda_{\text{corr.}}$ (B). | $\Lambda_0{}^n$. | $\Lambda_{C\text{calc.}}$. | Diff. |
|---|---|---|---|---|---|---|
| Pyrex Cell V. Series 5. $\kappa = 3{\cdot}06$ [0·672]. | | | | | | |
| 1·301 | 114·24 | 113·76 | 113·78 | 114·07 | 114·07 | − 0·33 |
| 5·378 | 113·55 | 113·30 | 113·40 | 114·23 | 113·42 | − 0·12 |
| 11·14 | 112·93 | 112·78 | 112·84 | 114·26 | 112·91 | 0·13 |
| 18·25 | 112·12 | 112·00 | 112·01 | 114·26 | 111·95 | 0·05 |
| 28·26 | 111·25 | 111·20 | 111·18 | 114·10 | 111·08 | 0·12 |
| 37·29 | 110·64 | 110·59 | 110·52 | [114·64] | 110·38 | 0·19 |
| Pyrex Cell S. Series 6. $\kappa = 3{\cdot}12$ [0·673]. | | | | | | |
| 2·511 | 114·02 | 113·62 | 113·64 | 114·10 | 113·95 | − 0·32 |
| 9·023 | 113·08 | 112·92 | 112·95 | 114·17 | 112·98 | − 0·06 |
| 15·56 | 112·39 | 112·29 | 112·27 | 114·09 | 112·22 | 0·07 |
| 35·23 | 110·87 | 110·83 | 110·81 | 114·23 | 110·70 | 0·13 |
| 50·05 | 109·92 | 109·92 | 110·93 | 114·25 | 109·68 | 0·24 |
| 61·25 | 109·48 | 109·48 | 109·47 | [114·45] | — | — |
| 91·42 | 108·40 | 108·40 | 108·41 | [115·09] | — | — |

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* When these runs were carried out in 1932, Kendall's value of $3{\cdot}50 \times 10^{-7}$ for the primary dissociation constant of carbonic acid was employed in the calculations. With the new figure of $4{\cdot}54 \times 10^{-7}$ (MacInnes and Belcher, *J. Amer. Chem. Soc.*, 1933, **55**, 2630), published after this paper was submitted, recalculation shows that what was originally regarded as the calculated quantity of barium hydroxide solution was actually 20% excess. All the results have been recalculated with the new value.

*$\Lambda_C$ at Round Concentrations.*—The revised values for the equivalent conductivity at round concentrations for sodium and potassium acetates are given below. Interpolation was carried out on a $\Lambda_C$–$C$ graph drawn with a flexible spline.

| | | | | | | |
|---|---|---|---|---|---|---|
| $C \times 10^4$ ........................ | 2·0 | 5·0 | 10·0 | 20·0 | 30·0 | 40·0 |
| NaOAc ........................ | (89·98) | 89·39 | 88·73 | 87·67 | 86·82 | 86·17 |
| KOAc ........................ | (113·80) | 113·33 | 112·79 | 111·86 | 111·08 | 110·40 |
| $C \times 10^4$ ........................ | 50·0 | 60·0 | 70·0 | 80·0 | 90·0 | 100·0 |
| NaOAc ........................ | 85·68 | 85·25 | 84·90 | 84·53 | 84·19 | 83·86 |
| KOAc ........................ | 109·95 | 109·49 | 109·14 | 108·79 | 108·48 | 108·16 |

## APPENDIX (with H. V. LOWRY).

Equation (6) may be solved for $[\mathrm{H}^{\cdot}]$ as follows. Cleared of fractions, it becomes

$$[\mathrm{H}^{\cdot}]^4 + p[\mathrm{H}^{\cdot}]^3 + q[\mathrm{H}^{\cdot}]^2 - r[\mathrm{H}^{\cdot}] - s = 0 \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

where $p$, $q$, $r$, and $s$ are the expressions given on p. 1639. Equation (i) can be written

$$p[\mathrm{H}^{\cdot}]^3 + q[\mathrm{H}^{\cdot}]^2 - r[\mathrm{H}^{\cdot}] = s - [\mathrm{H}^{\cdot}]^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

and hence its roots are given by the points of intersection of the graphs of $y_1 = p[\mathrm{H}^{\cdot}]^3 + q[\mathrm{H}^{\cdot}]^2 - r[\mathrm{H}^{\cdot}]$, and $y_2 = s - [\mathrm{H}^{\cdot}]^4$. The graph of $y_1$ cuts the axis of $[\mathrm{H}^{\cdot}]$ at $[\mathrm{H}^{\cdot}] = 0$, and at a positive value $\mathrm{H}_1$ and a negative value $\mathrm{H}_1'$; $\mathrm{H}_1$ and $\mathrm{H}_1'$ are given by

$$\mathrm{H}_1 = \{\sqrt{(q^2 + 4pr)} - q\}/2\mathrm{p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iii)}$$

and

$$\mathrm{H}_1' = -\{\sqrt{(q^2 + 4pr)} + q\}/2p \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iv)}$$

The graph of $y_2$ cuts the axis of $[\mathrm{H}^{\cdot}]$ at $[\mathrm{H}^{\cdot}] = \pm s^{1\ 4}$. For values of the constants within the range under consideration, *i.e.*, for acetic acid, $\mathrm{H}_1$ is always less than $s^{1/4}$, and consequently the graphs intersect between $\mathrm{H}_1$ and $s^{1\ 4}$. Moreover, if the gradient of the graph of $y_1$ at $[\mathrm{H}^{\cdot}] = \mathrm{H}_1$ is sufficiently large, the graphs will intersect at $[\mathrm{H}^{\cdot}] = \mathrm{H}_1$. With this assumption one may take $\mathrm{H}_1$ as a first approximation to the required root. A closer approximation can then be found by writing (ii) in the form

$$p[\mathrm{H}^{\cdot}]([\mathrm{H}^{\cdot}] - \mathrm{H}_1)([\mathrm{H}^{\cdot}] - \mathrm{H}_1') = s - [\mathrm{H}^{\cdot}]^4,$$

and putting $[\mathrm{H}^{\cdot}] = \mathrm{H}_1$ in every term except $[\mathrm{H}^{\cdot}] - \mathrm{H}_1$. This gives

$$\mathrm{H}_2 = \mathrm{H}_1 + \frac{s - \mathrm{H}_1^4}{p\mathrm{H}_1[\mathrm{H}_1 - \mathrm{H}_1']} = \mathrm{H}_1 + \frac{s - \mathrm{H}_1^4}{\mathrm{H}_1[2p\mathrm{H}_1 + q]} \quad . \quad . \quad . \quad \text{(v)}$$

The approximation gives the root to within 1% for the values of the constants for acetic acid except for $m < 1 \times 10^{-5}$.*

*For values of* $\mathrm{m} < 1 \times 10^{-5}$, one proceeds as follows. Equation (i) can be written

$$q[\mathrm{H}^{\cdot}]^2 - r[\mathrm{H}^{\cdot}] - s = -([\mathrm{H}^{\cdot}]^4 + p[\mathrm{H}^{\cdot}]^3) \quad . \quad . \quad . \quad . \quad . \quad \text{(vi)}$$

and hence the required root is between the point of intersection of the graphs $y_3 = q[\mathrm{H}^{\cdot}]^2 - r[\mathrm{H}^{\cdot}] - s$, and $y_4 = -([\mathrm{H}^{\cdot}]^4 + p[\mathrm{H}^{\cdot}]^3)$. The graphs intersect to the left of the positive root, $\mathrm{H}_3$, of $q[\mathrm{H}^{\cdot}]^2 - r[\mathrm{H}^{\cdot}] - s = 0$, which is given by

$$\mathrm{H}_3 = \{\sqrt{(r^2 + 4qs)} + r\}/2q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(vii)}$$

and therefore the required root is less than $\mathrm{H}_3$. If one takes $\mathrm{H}_3$ as a first approximation and proceeds as before, one finds that a close approximation is

$$\mathrm{H}_4 = \mathrm{H}_3 - (\mathrm{H}_3^4 + p\mathrm{H}_3^3)/(2q\mathrm{H}_3 - r) \quad . \quad . \quad . \quad . \quad . \quad \text{(viii)}$$

In every case the required root lies between $\mathrm{H}_1$ and $\mathrm{H}_3$.

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* The corresponding values of the specific conductivity of the water at 25° and the total concentration of the carbonic acid $m$ are :

| | | | | | |
|---|---|---|---|---|---|
| $\kappa$ ............................. | 0·2 | 0·4 | 0·8 | 1·0 | 2·0 |
| $m \times 10^5$ ......................... | 0·057 | 0·228 | 0·910 | 1·424 | 5·698 |

*Solution of the "Baryta-water Method" Equation* (2).—This may be written

$$[\mathrm{H}^{\cdot}]^3 + [K_a + C][\mathrm{H}^{\cdot}]^2 - K_w[\mathrm{H}^{\cdot}] - K_wK_a = 0 \quad . \quad . \quad . \quad . \quad \text{(ix)}$$

In this equation $K_w$ is small compared with $K_a$, and graphical considerations show that the root must be less than $K_w$. Hence the second and fourth terms of (ix) are much the largest, and a first approximation to $[\mathrm{H}^{\cdot}]$ is given by

$$\mathrm{H}_5^2 = K_wK_a/(K_a + C) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(x)}$$

Substituting this value of $[\mathrm{H}^{\cdot}]$ in the other two terms, one finds that a closer approximation to $[\mathrm{H}^{\cdot}]$ is given by

$$\mathrm{H}_6^2 = \mathrm{H}_5^2 + \mathrm{H}_5[K_w - \mathrm{H}_5^2]/(K_a + C) \quad . \quad . \quad . \quad . \quad . \quad \text{(xi)}$$

For the acids which will be considered in this series of researches, $K_c = 4{\cdot}54 \times 10^{-7}$, and the ranges of the constants are $m = 0{\cdot}1$—$3{\cdot}0 \times 10^{-5}$, $C = 1 \times 10^{-4}$—$1 \times 10^{-2}$, and $K_a = 1 \times 10^{-5}$—$1 \times 10^{-2}$, and the approximations, which are in some cases of greater accuracy than are necessary, to the positive value of $[\mathrm{H}^{\cdot}]$ hold.

The applications of these corrections to salts of dibasic acids will be described in a later paper.

## SUMMARY.

(1) Full details are given of the water correction for solutions of salts of weak monobasic acids, valid above a concentration of *ca.* 0·0005*N*, made with equilibrium water, and the method has been applied to our measurements with sodium and potassium acetates (J., 1932, 2836).

(2) A new method is described for the accurate measurement of the conductivities of salts of weak acids. It involves the addition of 20—40% excess over the calculated quantity of barium hydroxide required to react with all the carbonic acid (assumed to be the only impurity) in the water used. When applied to sodium and potassium acetates at 25°, this method gives 40·62 for the limiting mobility of the acetate ion at 25°.

(3) Corrected values for the classical and the thermodynamic dissociation constant of acetic acid are $1{\cdot}824 \times 10^{-5}$ and $1{\cdot}764 \times 10^{-5}$ respectively.

The authors' thanks are due to the Chemical Society and the Royal Society and to Imperial Chemical Industries for grants.

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[*Received, July 6th,* 1933.]