[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY IN THE LABORATORIES OF PHYSIOLOGY, HARVARD MEDICAL SCHOOL]

THE DISSOCIATION CONSTANT OF ACETIC ACID AND THE ACTIVITY COEFFICIENTS OF THE IONS IN CERTAIN ACETATE SOLUTIONS[1]

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The characterization of weak and of strong electrolytes has involved quite different conceptions and methods. The concept of partial dissociation and the method of conductivity yielded the Ostwald dilution law, and accurate constants in terms of which the dissociation of weak acids could be defined. The dissociation constant of acetic acid has been very accurately determined by this method to be 1.85×10^{-5} by Kendall.[3] Recently MacInnes[4] has shown that a slightly lower value for this constant is obtained "provided (a) that the degrees of ionization are computed in a manner which allows for inter-ionic attraction, and (b) that the resulting ion concentrations are multiplied by the appropriate activity coefficients." His values for the dissociation constant of acetic acid vary from 1.743 to 1.784×10^{-5}.

The partial neutralization of a weak acid by a strong base may also be described by the mass law. The salt of the weak acid formed by the neutralization must be considered a strong electrolyte leading to interionic forces. None the less the mass law must hold provided the quantities involved are expressed as activities. When the neutralization is followed by electromotive force measurements with the hydrogen electrode the activity of the hydrogen ion is determined. The activity of the acid anion may be expressed by multiplying its stoichiometric concentration by its activity coefficient. If the activity coefficient of the acetate ion is defined by the Debye-Hückel equation, a general expression is obtained[5] which may be written in the following logarithmic form for acetic acid

$$P_{\mathrm{H}^+} - \log\left[(\mathrm{CH_3COO^-})/(\mathrm{CH_3COOH})\right] = P_K - 0.5\sqrt{\mu}/(1+\kappa b) + Ks\mu = P_{K'} \quad (1)$$

In this equation P_{H^+} and P_K are the negative logarithms respectively of the hydrogen ion activity and of the dissociation constant of the acid; μ is the ionic strength; and b and Ks and κ are the usual terms in the Debye-Hückel equation, the latter having the value of $0.33 \times 10^8\sqrt{\mu}$. The assumption made by MacInnes that the activity coefficient of the undissociated acetic acid is equal to unity has been tentatively adopted. As

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[1] A preliminary account of this investigation was communicated to the Twelfth International Physiological Congress, Stockholm, 1926, *Skandinav. Archiv*, 49 (1926).

[2] Fellow in Medicine of the National Research Council.

[3] Kendall, *J. Chem. Soc.*, 101, 1275 (1912).

[4] MacInnes, THIS JOURNAL, 48, 2068 (1926).

[5] Cohn, *ibid.*, 49, 173 (1927).

a result Ks is attributed entirely to the acetate anion, although it includes the effect on acetic acid. This simplification influences neither the value of the apparent nor of the true dissociation constant of acetic acid.

The Dissociation Constant of Acetic Acid

The left side of Equation (1) yields the negative logarithm of the apparent dissociation constant of the acid, sometimes expressed by the symbol $P_{K'}$. At low values of the ionic strength the activity coefficient of the acetate ion approaches one and $P_{K'}$ approaches the negative logarithm of the true dissociation constant, P_K. If $P_{K'}$ is plotted as ordinate, and the square root of the ionic strength as abscissa, a graphical method of determining the true dissociation constant of the acid is obtained, for at low values of ionic strength the terms containing b and Ks become vanishingly small and linear extrapolation possible.

In the study of buffer solutions,[6,7] the useful approximation has generally been made that the concentration of the acid anion, (CH_3COO^-), could be put equal to the concentration of sodium acetate. This approximation breaks down in precisely those solutions with which we are concerned here, namely, those that are both very dilute and appreciably acid. Under these circumstances the assumption is no longer justified that the amount of the anion derived from the dissociation of the acid is negligible in comparison with that derived from the dissociation of the salt. The amount derived from the salt may be put equal to the concentration of sodium ions, and that derived from the acid to the stoichiometric concentration of hydrogen ions. The sum of these concentrations yields the concentration of the anion

$$(Na^+) + (H^+) = (CH_3COO^-) \tag{2}$$

Electromotive force measurements do not yield the stoichiometric concentration but the activity of the hydrogen ion, a_{H^+}. This quantity divided by the activity coefficient of the hydrogen ion, γ_{H^+}, yields the concentration of hydrogen ions and may be substituted in the above equation. Lewis and Randall,[8] Scatchard,[9] and Sherrill and Noyes[10] have estimated the activity coefficient of the hydrogen ion. Their results over the range employed do not differ by more than one per cent. The values employed in these calculations have been taken from a curve drawn through their values relating the activity coefficient of the hydrogen ion to the ionic strength of the solution. Taking into account the acetate

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[6] Henderson, *Am. J. Physiol.*, **15,** 257 (1906); **21,** 173 (1908); THIS JOURNAL, **30,** 954 (1908).

[7] Washburn, *ibid.*, **30,** 31 (1908).

[8] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923.**

[9] Scatchard, THIS JOURNAL, **47,** 696 (1925).

[10] Sherrill and Noyes, *ibid.*, **48,** 1861 (1926).

anion derived from the dissociation of acetic acid, the complete equation for the apparent dissociation constant, $P_{K'}$, in mixtures of acetic acid and sodium acetate becomes

$$P_{H^+} - \log \frac{(Na^+) + (a_{H^+}/\gamma_{H^+})}{(CH_3COOH)} = P_K - 0.5\sqrt{\mu}/(1 + \kappa b) + K_S\mu = P_{K'} \qquad (3)$$

The concentration of acetic acid, (CH_3COOH), has been substituted for its activity and has been estimated by subtracting the concentration of the anion from the total acetate in the system.

Accurate electromotive force measurements upon dilute equimolecular mixtures of acetic acid and sodium acetate were made by Walpole[11] in 1914, and Brönsted[12] attempted certain calculations with these data in 1921. Walpole's result at very low molecular concentrations do not fall upon a straight line, probably because of the difficulty of making measurements in such dilute solutions. No attempt has been made to make measurements at these low concentrations, but from 0.02 to 0.2 *M* it has been possible to confirm the general trend of Walpole's data.

The determination of P_K by extrapolation becomes more accurate the lower the ionic strength of the solution. On the other hand, the usual experimental errors are encountered in measurements upon solutions of low molecular concentration. In the case of buffer mixtures this difficulty has been overcome by studying mixtures containing relatively large amounts of the weak acid but small amounts of the salt. Under these

Table I

Electromotive Force Measurements upon Dilute Acetate Solutions

Calculated by means of the Sørensen value of the 0.1 *N* calomel electrode

Total acetate *M*	Mole fraction of total acetate as CH_3COONa			Total acetate *M*	Mole fraction of total acetate as CH_3COONa		
	0.1	0.2	0.5		0.1	0.2	0.5
	Hydrogen potentials of acetate solutions				Hydrogen potentials of acetate solutions		
0.02	3.793	4.110	4.686	0.08	3.747	4.069	4.647
	3.790	4.115	4.683		3.744	4.073	4.650
	3.788	4.116	4.686		...	4.074	4.643
	3.793	4.110	4.690		...	4.070	4.646
	3.794	4.115	4.691		...	4.070	4.650
	3.787	4.119	4.692		...	...	4.644
	3.791	4.114	4.688		3.746	4.071	4.647
0.04	3.770	4.091	4.666	0.20	3.708	4.037	4.623
	3.770	4.091	4.662		3.710	4.039	4.622
	...	4.090	4.665		3.717	4.036	4.623
	...	4.088	4.672		3.712	4.041	4.618
	...	4.092	4.672		3.708	4.043	4.623
	...	4.093	4.676		3.706	4.044	4.621
	3.770	4.091	4.669		3.710	4.040	4.621

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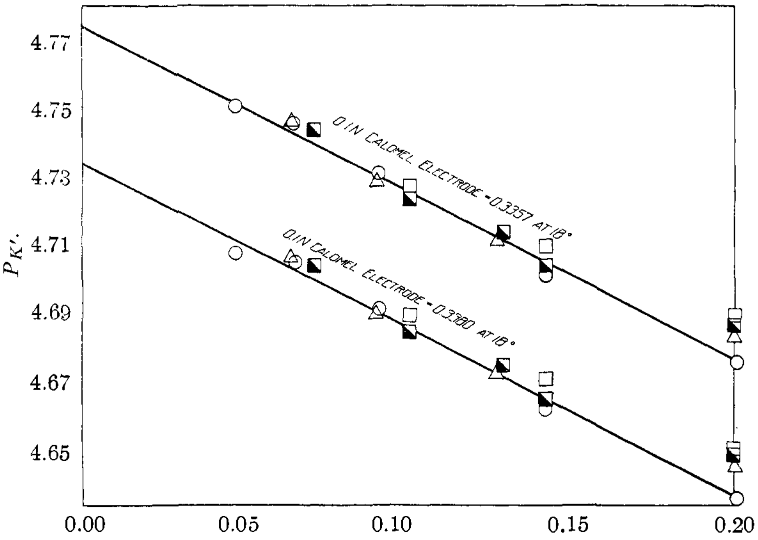
[11] Walpole, *J. Chem. Soc.*, **105**, 2501, 2521 (1914).

[12] Brönsted, *ibid.*, **119**, 574 (1921).

circumstances the molecular concentration may be retained at a relatively high level and the ionic strength allowed to reach a much lower value. Measurements have now been made upon solutions containing four and nine times as much acetic acid as sodium acetate. A 0.02 molecular solution of acetic acid of which only 0.1 has been transformed into sodium acetate has an ionic strength of 0.00217. None the less this solution is well buffered and readily studied by means of the hydrogen electrode. Measurements upon such solutions are recorded in Table I and, together with Walpole's measurements, graphically represented in Fig. 1.



Mole fractions of CH_3COONa: ○, 0.1; △, 0.2; ▫, 0.5; ◪, Walpole, 0.5.

Fig. 1.

Measurements upon dilute acetic acid solutions have been reported by Loomis and Acree[13] and Walpole. Their results are not in entire agreement, and the empirical dilution law deduced by Walpole from his data is at variance with the theoretical equation under consideration. These data upon dilute solutions of acetic acid, like those upon extremely dilute buffer solutions, show an apparent change in $P_{K'}$ upon dilution far greater than should be expected. For the present it seemed desirable to restrict the investigation to buffered solutions whose concentrations were not lower than 0.01 molar.

The electromotive force measurements that have been made have been calculated as hydrogen potentials by means of Sørensen's[14] value for the 0.1 N calomel electrode in order to render them comparable to Walpole's

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[13] Loomis and Acree, *Am. Chem. J.*, **46**, 585 (1911).

[14] Sørensen, *Compt. rend. trav. lab. Carlsberg*, **8**, 1 (1909).

measurements upon standard acetate solutions. Walpole states that his measurements were constant and reproducible to 0.1 millivolt. He attempted to correct for diffusion potentials by the Bjerrum extrapolation method but reported no diffusion potential as great as 0.1 millivolt for the solutions considered in Table I. He noted the extremely small diffusion potentials of all of the acetate solutions that he studied. In our measurements the saturated potassium chloride salt bridge was employed and no correction for diffusion potentials attempted.

The mean values of the hydrogen potentials recorded in Table I have been employed in Table II for the calculation of the apparent dissociation constant of acetic acid by means of Equation (3). The measurements upon equimolecular mixtures of acetic acid and sodium acetate of Walpole and of Michaelis and his collaborators[15] are included in Table II. Our results and those of Walpole upon solutions with ionic strengths less than 0.05 (excepting those of Walpole upon the most dilute solutions, which are given in parentheses) are graphically represented in Fig. 1, in which $P_{K'}$ is the ordinate and the square root of the ionic strength the abscissa.

In dilute solutions, which alone are considered in Fig. 1, the change in $P_{K'}$ is nearly proportional to the square root of the ionic strength. Under these circumstances the values of the apparent dissociation constant, calculated in Table II, may be employed in estimating the true dissociation constant of acetic acid. This was attempted by the graphical extrapolation in Fig. 1. A straight line originating at P_K 4.733 (where $\sqrt{\mu} = 0$) has been drawn with the theoretical slope of 0.5 demanded by the Debye equation. This line passes between the lower set of experimental points, but the specific ion effects, which are known to occur from the study of more concentrated solutions, and are evident in the figure when $\sqrt{\mu}$ is greater than 0.1, exert a slight influence even in more dilute solution. Were these effects considered, a slightly lower value of P_K would have to be adopted, approximately equal to 4.73. The value of P_K, 4.733, equal to $Ka = 1.85 \times 10^{-5}$, is identical with Kendall's estimate of the dissociation constant of acetic acid derived from conductivity measurements. The uncertainty in obtaining a value of P_K from the extrapolation of the electromotive force measurements in Fig. 1 is not greater than ± 0.005. The results of Kendall's conductivity measurements and these electromotive force measurements are thus entirely consistent with each other, provided Sørensen's value of the 0.1 normal calomel electrode is employed.

The Value of the 0.1 *N* Calomel Electrode

The value of the 0.1 *N* calomel electrode has long been in doubt by over 2 millivolts. As a result the entire scale upon which so much chemical and

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[15] Michaelis and Krüger, *Biochem. Z.*, **119**, 307 (1921); Michaelis and Kakinuma, *ibid.*, **141**, 394 (1923).

TABLE II

THE APPARENT DISSOCIATION CONSTANT OF ACETIC ACID IN DILUTE ACETATE SOLUTIONS

Calculated by means of the Sørensen value of the 0.1 N calomel electrode

Total acetate	P_{H^+}	(Na^+)	(H^+)	(CH_3COOH^-)	$\sqrt{\mu}$	$\log \frac{(CH_3COOH)}{(CH_3COO^-)}$	P_K'
Mole fraction of total acetate as CH_3COONa = 0.1							
0.020	3.791	0.002	0.000170	0.002170	0.0466	0.915	4.706
.040	3.770	.004	.000181	.004181	.0647	.933	4.703
.080	3.746	.008	.000194	.008194	.0905	.943	4.689
.200	3.710	.020	.000220	.020220	.142	.949	4.659
.400	3.681	.040	.000239	.040239	.201	.951	4.632
1.000	3.641	.100	.000272	.100272	.317	.953	4.594
Mole fraction of total acetate as CH_3COONa = 0.2							
0.020	4.114	0.004	0.000082	0.004082	0.0639	0.591	4.705
.040	4.091	.008	.000087	.008087	.0899	.597	4.688
.080	4.071	.016	.000094	.016094	.1269	.599	4.670
.200	4.040	.040	.000105	.040105	.2003	.601	4.641
.400	4.020	.080	.000113	.080113	.283	.601	4.621
Mole fraction of total acetate as CH_3COONa = 0.5							
0.020	4.688	0.010	0.000023	0.010023	0.100	$\bar{1}.998$	4.686
.040	4.669	.020	.000023	.020023	.142	$\bar{1}.999$	4.668
.080	4.647	.040	.000026	.040026	.200	.000	4.647
.200	4.621	.100	.000029	.100029	.317	.000	4.621
Walpole's measurements							
0.002	4.758	0.001	0.000017	0.001017	0.0319	$\bar{1}.985$	(4.743)
.004	4.736	.002	.000019	.002019	.0449	$\bar{1}.992$	(4.728)
.010	4.706	.005	.000021	.005021	.0709	$\bar{1}.996$	4.702
.020	4.684	.010	.000023	.010023	.100	$\bar{1}.998$	4.682
.032	4.673	.016	.000023	.016023	.129	$\bar{1}.999$	4.672
.040	4.663	.020	.000025	.020025	.142	$\bar{1}.999$	4.662
.080	4.645	.040	.000026	.040026	.200	.000	4.645
.200	4.623	.100	.000029	.100029	.317	.000	4.623
.400	4.606	.200	.000030	.200030	.447	.000	4.606
Michaelis and Krüger's measurements							
0.200	4.616	0.100	0.000029	0.100029	0.317	0.000	4.616
Michaelis and Kakinuma's measurements[16]							
0.010	4.695	0.005	0.000021	0.005021	0.0709	$\bar{1}.996$	4.691
.200	4.607	.100	.000029	.100029	.317	.000	4.607

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[16] Dr. Michaelis has made the following personal communication to me regarding the P_H of standard acetate as calculated by Michaelis and Kakinuma: "The activity coefficients of HCl had been calculated by Lewis and Randall from the mean activity of HCl. In order to obtain the activity coefficient of the hydrogen ion one had to apply the hypothesis that $\gamma_{H^+} = \gamma_{Cl^-} = \sqrt{\gamma_{HCl}}$. Such an assumption, which is certainly justified for molecules such as KCl, is not true for HCl. It seemed to me better to take γ_{H^+} in $N/500$ HCl = 1. Upon this assumption the value P_H 4.607 was obtained. In the meantime, γ_{H^+} has been determined more carefully by Scatchard, and we should take γ_{H^+} for 0.002 HCl = 0.956. In this case the value 4.607 must be changed to 4.627, which is in agreement with Walpole's original value, my own earlier values, and Cohn's new measurements."

biochemical work depends is in doubt. Sørensen's value for the 0.1 N calomel electrode at 18° was 0.3380, and Clark[17] has calculated a value for this half cell of 0.3360 from Lewis, Brighton and Sebastian's[18] measurements upon the normal calomel electrode at 25°. Although he has pointed out this discrepancy, Clark has suggested that the Sørensen value for the 0.1 N calomel electrode be retained, since so much work already published depends upon it.

In certain incidental measurements of the activity coefficients of the hydrogen ion in dilute hydrochloric acid solutions, we were forced to the use of the Lewis, Brighton and Sebastian value for the 0.1 N calomel electrode.[19] The Sørensen value rendered the accumulated data uninterpretable. Sørensen's measurements were made in 1909, and his value depended upon estimates of dissociation derived from conductivity data. He has recently pointed out, in collaboration with Linderstrøm-Lang,[20] that the value 0.3357 is obtained provided the activity of the hydrogen ion is referred to. They have suggested retaining both the old and the new value, the one referring to the concentration, the other to the activity of hydrogen ions. Scatchard[9] has also recalculated Sørensen's old value "using 0.0801 instead of 0.0917 for the mean activity of the ions of 0.1 M hydrochloric acid." "Taking 0.0762 for the activity of the chloride ion in 0.1 M potassium chloride" Scatchard obtains 0.3353 for the half cell at 25°. The same temperature coefficient as has been previously employed renders Scatchard's estimate identical with Sørensen's own revision of this electrode potential, 0.3357 at 18°. Lewis and Randall in recalculating the result of Lewis, Brighton and Sebastian estimate "the activity of chloride ion in 0.1 M KCl . . . . to be 0.0794, whence for the deci-normal electrode . . . . $E = -0.3351$" at 25°. Their value for the half cell thus becomes 0.3355 at 18°.

These various estimates of the 0.1 N calomel electrode based upon the activity of hydrogen ions in 0.1 N solution thus vary from 0.3355 to 0.3360 at 18°. If the electromotive force measurements reported are calculated by means of these values of the 0.1 N calomel electrode, the value of P_K becomes greater than that estimated by means of Sørensen's original value. The upper set of points in Fig. 1 has been calculated on the basis of the value 0.3357 for the 0.1 N calomel electrode at 18°. Besides increasing all the values of $P_{K'}$ by approximately 0.04, this effects a relatively greater change in $P_{K'}$ the more acid the reaction. For this reason measurements made upon mixtures containing but a small proportion of sodium acetate are raised in $P_{K'}$ more than are equimolecular mixtures by the assumption

[17] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Company, Baltimore, Md., 1922.

[18] Lewis, Brighton and Sebastian, THIS JOURNAL, **39**, 2245 (1917).

[19] Cohn and Berggren, *J. Gen. Physiol.*, **7**, 45 (1924).

[20] Sørensen and Linderstrøm-Lang, *Compt. rend. trav. lab. Carlsberg*, **15**, 1 (1924).

of a lower value for the calomel electrode. The points representing the measurements upon the most dilute acid solutions appear to fall more nearly on a straight line when calculated by means of the lower value for the calomel electrode.

A far greater uncertainty is introduced in the interpretation of these measurements by the value ascribed to the calomel electrode than by the measurements themselves. The uncertainty regarding the calomel electrode depends upon the activity coefficient of the hydrogen ion in cells containing strong electrolytes in concentrations as great as 0.1 molal. The inter-ionic forces in such solutions are appreciable. Electromotive force measurements by means of the hydrogen electrode can, however, be carried on upon mixtures of a weak acid and its salt in solutions of relatively high molecular concentration, but of such low ionic strength that specific ion effects can practically be neglected. It is therefore suggested that electromotive force measurements upon mixtures of a weak acid and its salt might be used in the standardization of calomel electrodes (see also the papers of Michaelis and his collaborators[15]) since the dissociation constants obtained by the extrapolation of such data may be compared with the very accurate constants of the weak acids yielded by means of the Ostwald dilution law and conductivity measurements.

In the recalculation of the dissociation constants of weak acids recently reported by MacInnes, "the only case in which there is a definite trend in the value of the constant K is that of acetic acid in which there is a change of 2.2% from 0.07 to 0.002 N. This is probably due to the fact that the conductance data for the acid and its sodium salt were obtained by different workers." This is unfortunate and renders it desirable either that new conductance work be done on acetates, or that electromotive force measurements be made upon the other weak acids studied by MacInnes and by Sherrill and Noyes. The values calculated by MacInnes range in P_K from 4.749 to 4.759. The difference of 0.01 in P_K or P_{H^+} is greater than the probable error in the measurements reported, but only one-fourth as large as the difference introduced by the use of the new and the old values of the 0.1 N calomel electrode. If MacInnes' calculations are assumed to yield the correct value of P_K, the value of the 0.1 N calomel electrode should lie between 0.3364 and 0.3370.

It is not possible, at this time to do more than indicate the interdependence of estimates of the dissociation constant of a weak acid derived from conductivity measurements, with those derived from electromotive force measurements and with the value of the calomel electrode. A redetermination of any of these quantities will yield more accurate values of all the others. The values of the negative logarithm of the dissociation constant of acetic acid, P_K, derived from the reported electromotive force measurements upon acetate solutions, and the various values of the 0.1 N

calomel electrode are reported in Table III, and compared with the values of P_K derived from conductivity measurements by Kendall and MacInnes.

TABLE III

THE RELATION BETWEEN THE VALUES OF THE DISSOCIATION CONSTANT OF ACETIC ACID AND OF THE 0.1 N CALOMEL ELECTRODE

	Values of the 0.1 N calomel electrode at 18°	Values of P_K derived from electromotive force measurements	Values of P_K derived from conductivity measurements	
Sørensen[14]	0.3380	4.730	Kendall[3]	4.733
Clark[17] from Lewis, Brighton and Sebastian's measurements	.3360	4.765		...
Sørensen and Linderstrøm-Lang[20]	.3357	4.770	MacInnes[4]	4.749 to 4.759
Scatchard[9] from Sørensen's measurements	.3357	4.770		
Lewis and Randall[8]	.3355	4.773		...

The Activity Coefficients of the Ions in Certain Acetate Solutions

The activity coefficients of the acetate anion that may be derived from electromotive force measurements are independent of the value ascribed to the calomel electrode. The difference between $P_{K'}$ in any given solution and P_K yields the negative logarithm of the activity coefficient of the anion in that solution, provided both are calculated by means of the same value for the reference electrode. In Fig. 1 values of $P_{K'}$, derived from hydrogen electrode measurements upon dilute mixtures of acetic acid and sodium acetate, were plotted against $\sqrt{\mu}$, and graphical extrapolation yielded a value of P_K equal to 4.733, with an uncertainty not greater than 0.005. A slightly lower value of P_K, perhaps 4.730, would have resulted had not linear extrapolation been entirely relied upon, for the effect of the size of the ions, which becomes so significant a factor in more concentrated solutions, cannot be entirely neglected in these dilute solutions.

Taking the round value 4.73 for P_K the values of the constants in Equation (3) have been estimated from measurements of the P_H of systems containing known amounts of acetic acid and sodium acetate, and therefore having known ionic strengths. The ionic strength per liter of solution rather than per thousand g. of water is always given. Measurements of the P_H of the same mixture of acetic acid and sodium acetate, at various dilutions, may be employed, and values of b and Ks deduced from them by means of Equation (3). If, on the other hand, values of b and Ks, derived from such calculations, be assumed, the equations can be solved for P_K. In this way the experimental results can be considered from the point of view of the additional information that they yield regarding the dissociation constant of acetic acid.

The stock solutions employed in preparing the acetate mixtures consisted of 4 *M* sodium hydroxide and of 4 *M* and 8 *M* acetic acid. The acetic acid solutions were regularly standardized against the sodium hydroxide and these in turn were standardized against 0.1 *M* oxalic acid. The stock solutions were always diluted approximately to 0.1 *M* for standardization.

The solutions to be measured were prepared by placing a given amount of acetate as acetic acid in a volumetric flask and transforming the desired amount into sodium acetate by the addition of sodium hydroxide. Boiled distilled water was then added to bring the solution to volume. At least two, and sometimes three, mixtures of each mole fraction, at each concentration, were measured by means of three different electrodes. The electromotive force measurements upon dilute acid solutions are reported in Table I and have already been considered with respect to certain of the implications to be derived from them. These solutions varied in molecular

TABLE IV

ELECTROMOTIVE FORCE MEASUREMENTS UPON CONCENTRATED ACETATE SOLUTIONS

Calculated by means of the Sørensen value of the 0.1 *N* calomel electrode

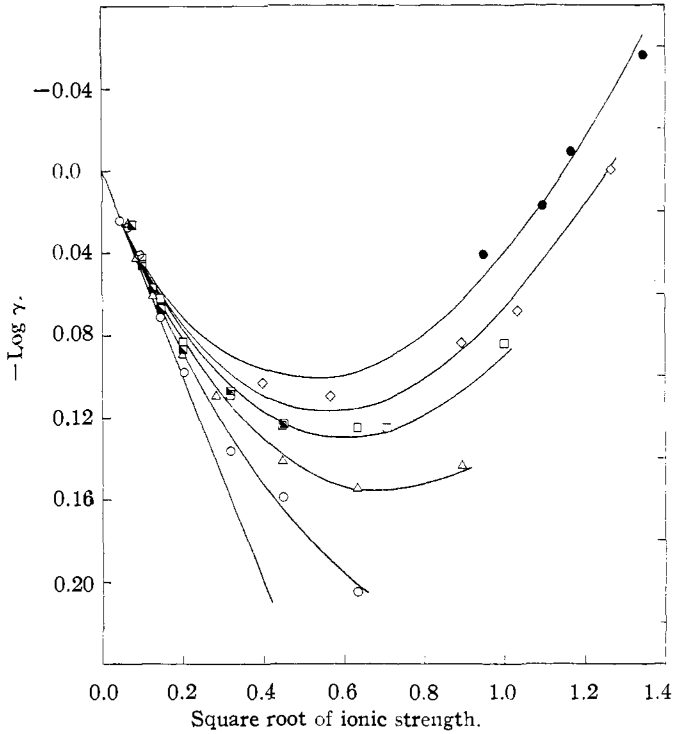
Total acetate	Mole fraction of total acetate as CH_3COONa				
	0.1	0.2	0.5	0.8	0.9
M	Hydrogen potentials of acetate solutions				
	(Walpole's Measurements)				
0.20	3.723	4.047	4.626	5.227	5.574
	(New Measurements)				
0.40	3.686	4.019	4.616	5.219	...
	3.691	4.016	4.609	5.220	...
	3.680	4.021	4.608	5.220	...
	3.677	4.021	4.605	5.226	...
	3.676	4.025	4.611	5.233	...
	3.677	...	4.605	5.217	...
	3.681	4.020	4.609	5.222	...
0.80	...	...	4.607	...	...
	...	...	4.605	...	...
	...	...	4.604	...	...
	...	...	4.605	...	...
1.00	3.643	3.986	4.608	5.251	5.645
	3.646	3.983	4.610	5.243	5.642
	3.642	3.981	4.602	5.248	5.644
	3.636	3.991	4.602	5.253	5.643
	3.641	3.991	4.605	5.251	5.638
	3.637	3.989	4.602	6.245	5.646
	3.641	3.987	4.605	5.248	5.643
1.33	...	...	...	5.265	5.663
	...	...	...	5.262	5.666
	...	...	...	...	5.671
	...	...	...	5.263	5.667
1.50	...	...	...	...	5.697
	...	...	...	...	5.694
	...	...	...	...	5.696
	...	...	...	...	5.682
	...	...	...	...	5.694
	...	...	...	...	5.693
2.00	3.621	3.973	4.642	5.329	5.736
	3.622	3.972	4.648	5.334	5.728
	3.611	3.973	4.650	5.328	5.742
	3.617	3.975	4.643	5.340	5.749
	3.617	3.977	4.647	5.338	5.738
	3.615	...	4.647	5.326	5.745
	3.617	3.974	4.646	5.332	5.740
4.00	3.572	3.985	...	...	...
	3.572	3.981	...	...	...
	3.569	3.980	...	...	...
	...	3.988	...	...	...
	...	3.990	...	...	...
	3.571	3.985	...	...	...

concentration from 0.02 to 0.2, and in ionic strength from 0.00216 to 0.1. This range is extended by the data in Table IV, in which are reported measurements upon solutions more concentrated than those studied by Walpole. The concentrations varied from 0.2 to 4.0 molecular, and the mole fraction of total acetate as CH_3COONa from 0.1 to 0.9. The ionic strengths in Table IV thus vary from 0.02016 to 1.80. If all of the measurements be considered they range in ionic strength from 0.00216 to 1.80.

The averages are taken in Table IV of the different electromotive force measurements made upon these different acetate solutions. With a few exceptions each solution was prepared several times, from different stock solutions, and studied by more than one of us. In Table V, $P_{K'}$ has been calculated from the average P_H measurements by means of Equation (3). In the accompanying figure $-\log \gamma$ has been plotted as ordinate and the square root of the ionic strength as abscissa. The straight line which represents the limiting slope for a univalent ion originates at $P_K = 4.73$, and the values of $-\log \gamma$, given as ordinates, are calculated on this basis. The curves which pass through the experimental points have been constructed on the basis of the values of b given in Table V. The term Ks has been retained constant at 0.16 throughout these preliminary calculations. It is probable that certain of the measurements could have been more accurately represented by varying not only b but Ks as well. This was certainly the case with the most alkaline series studied. However, it was not believed that this was warranted by the experimental accuracy that has been achieved, and the simplification in calculation that results renders it desirable to consider Ks constant.

The description of these measurements upon diverse mixtures by means of a constant value for the salting-out constant is noteworthy. In the study of the activity coefficients of the ions in certain phosphate solutions, it was found possible to describe the data on the basis of a constant value for b, but a variable value for Ks. It was pointed out that this approximation could be justified only in so far as the Debye-Hückel equation was being employed as an empirical interpolation formula. Though the same reservation must be made in connection with the present investigation, it should be pointed out that in this case we are not dealing with the univalent and bivalent salts of a weak acid but with the weak acid itself and its univalent salt. Under these circumstances not only is the change of the activity coefficient with concentration very much less—the limiting slope being 0.5 instead of 1.5—but in all save the most dilute acid solutions the ionic strength is proportional to the sodium ion. Whether or not this simple proportionality results in the apparent constancy of Ks must await further experimentation. It may well be a real rather than an apparent phenomenon, to be expected in other comparable mixtures of weak univalent acids and their salts.

Another method of considering these data is presented in Table V. The values of *b* and *Ks* employed in the construction of the curves in Fig. 2 have been used in the calculation of the values of $-\log \gamma$ given in the table. These values of the negative logarithm of the activity coefficient of the acetate anion, added to the negative logarithm of the apparent dissociation constant $P_{K'}$, yield in the last column calculated estimates of the negative logarithm of the true dissociation constant, P_K. Errors either in the theoretical calculation of the activity coefficient or in the experimental determination of the *P*H appear as deviations from the theoretical value of this constant. The method of calculation has the further advantage that these deviations are proportional to their value as errors in *P*H. It will be noted that in all of the calculated values of P_K, made from measurements of the *P*H of solutions varying in mole fraction of sodium acetate from 0.1 to 0.9 and in ionic strength from 0.00217 to 1.80, none is higher than 4.741 and none lower than 4.721. Within the range that has been considered, no error in estimating the *P*H of a solution greater than 0.02



Mole fraction of CH_3COONa: ⊙, 0.1; △, 0.2; □, 0.5; ◇, 0.8; ●, 0.9; ◪, Walpole, 0.5.

Fig. 2.

TABLE V

A COMPARISON OF THE CALCULATION AND THE MEASUREMENT OF THE ACTIVITY COEFFICIENTS OF MIXTURES OF CH_3COOH AND CH_3COONa

Mole fraction of total acetate as CH_3COONa	Total acetate concentration M	Ionic strength μ	$P_{K'}$, obs.[a]	$-\log \gamma$, obs. $4.73 - P_{K'}$	$-\log \gamma$,[b] calcd.	P_{K_1} calcd.[a] $P_{K'} + \log \gamma$[b]
0.1	0.02	0.00217	4.706	0.024	0.023	4.729
	.04	.00418	4.703	.027	.030	4.733
	.08	.00819	4.689	.041	.043	4.732
	.20	.02022	4.666	.064	.065	4.731
	.40	.04024	4.632	.098	.089	4.721
	1.00	.10027	4.594	.136	.129	4.723
	2.00	.20000	4.571	.159	.165	4.736
	4.00	.40000	4.525	.205	.201	4.726
0.2	0.02	0.0041	4.705	0.025	0.029	4.734
	.04	.0081	4.688	.042	.041	4.729
	.08	.0161	4.670	.060	.055	4.725
	.20	.0401	4.645	.085	.081	4.726
	.40	.0801	4.621	.109	.105	4.726
	1.00	.2000	4.589	.141	.138	4.727
	2.00	.4000	4.576	.154	.155	4.731
	4.00	.8000	4.587	.143	.147	4.734
0.5	0.02	0.010	4.686	0.044	0.044	4.730
	.04	.020	4.668	.062	.059	4.727
	.08	.040	4.647	.083	.077	4.724
	.20	.100	4.624	.106	.104	4.728
	.40	.200	4.609	.121	.123	4.732
	.80	.400	4.605	.125	.130	4.735
	1.00	.500	4.605	.125	.127	4.732
	2.00	1.000	4.646	.084	.090	4.736
0.8	0.20	0.160	4.625	0.105	0.109	4.734
	.40	.320	4.620	.110	.117	4.737
	1.00	.800	4.646	.084	.088	4.734
	1.33	1.067	4.661	.069	.060	4.721
	2.00	1.600	4.730	.000	− .005	4.725
0.9	0.20	0.18	4.620	0.110	0.101	4.721
	1.00	.90	4.689	.041	.052	4.741
	1.33	1.20	4.713	.017	.015	4.728
	1.50	1.35	4.739	− .009	− .004	4.735
	2.00	1.80	4.786	− .056	− .065	4.721
					Average	4.729

[a] Calculated on the basis of the value 0.3380 for the 0.1 *N* calomel electrode at 18°. The values at 0.2 *M* are the averages of those obtained by Walpole and by us.

[b] The values of $-\log \gamma$ have been calculated by means of the equation

$$\left(\frac{0.5\sqrt{\mu}}{1+\kappa b} - 0.16\mu\right)$$

The following values of $0.33 \times 10^8 b$ were employed for the mole fractions of total acetate as the sodium salt from 0.1 to 0.9: 0.3, 0.7, 1.0, 1.2, 1.5.

should therefore be expected in employing the values for b and Ks that have been deduced from these data.

Moreover, the average of all of these calculated values of P_K is 4.729, which is in excellent agreement with the value obtained by graphical extrapolation in Fig. 1. In so far as the Sørensen value is accepted for the 0.1 N calomel electrode, it therefore appears that 4.73 may be employed as the negative logarithm of the dissociation constant of acetic acid; $Ka = 1.86 \times 10^{-5}$. This result, as we have seen, is in excellent agreement with Kendall's value of 1.85×10^{-5}, an estimate based upon conductivity data uncorrected for inter-ionic forces. Recalculation of the data in Table V by means of the value 0.3357 for the 0.1 N calomel electrode yields a value of P_K higher by approximately 0.04. The activity coefficients of the acetate anion that have been estimated appear to be calculable, regardless of any assumption regarding the calomel electrode, by means of the Debye-Hückel equation and the appropriate constants.

The acetate solutions that have generally been used as standard buffers are those studied by Walpole and by Michaelis and his collaborators. Their measurements were, for the most part, upon solutions whose total acetate concentration was 0.2 M. These solutions are sufficiently dilute and all but the most acid are of so nearly the same ionic strength that the apparent dissociation constants calculated from the P_H measurements only vary from 4.615 to 4.689. This constancy unquestionably demonstrates why it was possible to apply the mass law to the titration of univalent weak acids by strong bases without considering the activity coefficients of the anions.[6,15,17] Indeed, in the most diverse solutions that have now been studied $P_{K'}$ varies only from 4.52 to 4.79. As a first approximation there can be no doubt, therefore, that the dilution of acetate buffer solutions does not greatly affect their acidity.

The electromotive force measurements made by Walpole upon the titration of 0.2 M acetic acid by means of sodium hydroxide have been employed in Table VI in the calculation of $P_{K'}$ on the basis of both the old and the new values of the 0.1 N calomel electrode. The former have been subtracted from 4.73, and the latter from 4.77 to yield estimates of $-\log \gamma$, given in the fourth and fifth columns.

The complete Debye-Hückel equation that has been employed in the more concentrated acetate mixtures that have now been studied is not necessary for the characterization of the dilute acetate mixtures studied by Walpole and previous investigators. As has previously been pointed out,[1] the changes in the apparent dissociation constant of such solutions can be satisfactorily calculated by omitting the salting-out term in the Debye-Hückel equation and employing instead so high a value for b as 5.4×10^{-8} cm. Values of $-\log \gamma$, calculated by this approximation, are compared with those previously deduced for concentrated solutions in the

TABLE VI

RECALCULATION OF WALPOLE'S ELECTROMOTIVE FORCE MEASUREMENTS UPON THE NEUTRALIZATION OF 0.2 MOLAL ACETIC ACID BY SODIUM HYDROXIDE AT 18°

Mole fraction of total acetate as CH_3COONa	$P_{K'}$ 0.1 *N* electrode = 0.3380[a]	$P_{K''}$, 0.1 *N* electrode = 0.3357[a]	$-\text{Log}\ \gamma$, $4.73-P_{K'}$	$-\text{Log}\ \gamma$, $4.77-P_{K''}$	$-\text{Log}\ \gamma$, calcd., $\left(\frac{0.5\sqrt{\mu}}{1+1.8\sqrt{\mu}}\right)$	$-\text{Log}\ \gamma$, calcd., $\left(\frac{0.5\sqrt{\mu}}{1+\kappa b}-0.16\mu\right)$
0.000	4.665	4.744	0.065	0.026	0.021	...
.005	4.676	4.743	.054	.027	.023	...
.010	4.689	4.744	.041	.026	.026	...
.015	4.676	4.729	.054	.041	.029	...
.020	4.683	4.729	.047	.041	.031	...
.025	4.675	4.720	.055	.050	.033	...
.030	4.664	4.709	.066	.061	.036	...
.040	4.667	4.709	.063	.061	.040	...
.050	4.676	4.718	.054	.052	.043	...
.075	4.674	4.716	.056	.054	.051	...
.100	4.672	4.713	.058	.057	.057	0.065
.200	4.648	4.688	.082	.082	.074	.082
.300	4.637	4.677	.093	.093	.085	.092
.400	4.630	4.670	.100	.100	.094	.099
.500	4.626	4.666	.104	.104	.101	.105
.600	4.626	4.666	.104	.104	.107	.108
.700	4.623	4.663	.107	.107	.112	.109
.750	4.615	4.655	.115	.115	.114	.110
.800	4.625	4.665	.105	.105	.116	.109
.850	4.620	4.660	.110	.110	.118	.105
.900	4.619	4.659	.111	.111	.120	.101
.950	4.615	4.655	.115	.115	.122	...
.962	4.615	4.655	.115	.115	.123	...
.975	4.619	4.659	.111	.111	.123	...
.987	4.622	4.662	.108	.108	.123	...

[a] Walpole's results were calculated by means of the value 0.0577 for *RT*/*F* at 18°. We have recalculated his results with the same value though the other measurements in this paper have been calculated with the value 0.05772.

final columns of Table VI. Until 0.8 of the acetic acid has been transformed into the sodium salt, the two equations yield results which agree within 0.01 *P*H. In more alkaline solutions the approximation equation yields too high results since the salting-out phenomenon is encountered there. The agreement with the values of the activity coefficients calculated from Walpole's data by means of the old value of the 0.1 *N* calomel electrode, and the value 4.73 for P_K, is adequately represented by either of the interpolation equations from mole fraction 0.1 to 0.9. These successive approximations render it possible to estimate the activity coefficients and therefore the *P*H of these solutions with an error not greater than 0.01 in *P*H. The general relations that have been deduced thus include and are capable of characterizing the solutions studied by Walpole.

In the more acid solutions studied by Walpole the values of $-\log\gamma$ calculated by means of the value 0.3380 for the 0.1 *N* calomel electrode diverge widely from what should be expected from the Debye equation. Indeed the values of $-\log \gamma$ calculated in Table VI show no significant drift from acetic acid to the mixture containing 0.1 mole fraction sodium acetate, although $\sqrt{\mu}$ varies from 0.046 to 0.142 and the calculated values of $-\log \gamma$ from 0.021 to 0.057. If, however, the value 0.3357 is employed for the 0.1 *N* calomel electrode and 4.77 for the negative logarithm of the dissociation constant of

TABLE VII

INTERPOLATED VALUES OF THE ACTIVITY COEFFICIENTS OF MIXTURES OF CH_3COOH AND CH_3COONa

Concn. of total acetate, *M*	Mole fraction of total acetate as CH_3COONa								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
	$-\text{Log}\ \gamma = 0.5\sqrt{\mu}/(1 + \kappa b) - 0.16\mu$								
0.05	0.034	0.045	0.053	0.060	0.064	0.069	0.071	0.075	0.073
.10	.047	.062	.071	.078	.084	.088	.091	.093	.089
.20	.065	.082	.092	.099	.105	.108	.109	.109	.101
.40	.088	.106	.115	.119	.123	.123	.120	.118	.100
.60	.105	.120	.127	.130	.129	.125	.119	.112	.089
.80	.118	.130	.136	.134	.130	.123	.112	.102	.072
1.00	.129	.139	.140	.134	.127	.117	.102	.088	.052
1.20	.138	.144	.141	.133	.123	.109	.090	.071	.030
1.40	.146	.148	.143	.130	.116	.099	.075	.054	.007
1.60	.153	.152	.142	.126	.108	.086	.061	.035	− .016
1.80	.159	.153	.142	.121	.100	.075	.044	.016	− .040
2.00	.166	.155	.139	.115	.090	.061	.028	− .005	− .065

TABLE VIII

INTERPOLATED VALUES OF THE ACTIVITY COEFFICIENTS OF MIXTURES OF CH_3COOH AND CH_3COONa

Ionic strength of acetate soln., μ	Mole fraction of total acetate as CH_3COONa								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
	$-\text{Log}\ \gamma = 0.5\sqrt{\mu}/(1 + \kappa b) - 0.16\mu$								
0.02	0.065	.0061	0.061	0.060	0.059	0.059	0.058	0.058	0.056
.04	.088	.082	.080	.078	.077	.077	.075	.075	.071
.06	.105	.095	.092	.090	.089	.088	.086	.085	.080
.08	.118	.106	.102	.099	.098	.096	.094	.093	.087
.10	.129	.114	.110	.106	.105	.103	.101	.099	.092
.12	.138	.120	.115	.112	.110	.108	.105	.103	.095
.14	.146	.126	.120	.116	.114	.112	.109	.107	.098
.16	.153	.130	.124	.119	.117	.114	.111	.109	.099
.18	.159	.134	.127	.123	.120	.117	.114	.111	.101
.20	.166	.139	.131	.126	.123	.120	.116	.114	.102
.40	.202	.155	.142	.134	.130	.125	.120	.116	.098
.60	...	.155	.139	.128	.123	.117	.110	.105	.083
.80	...	.147	.127	.115	.108	.101	.093	.088	.063
1.00	...	...	...	...	.090	.083	.074	.067	.040
1.20	...	...	...	...	...	...	...	.045	.015
1.40	...	...	...	...	...	...	...	.021	− .011
1.60	...	...	...	...	...	...	...	− .005	− .038
1.80	...	...	...	...	...	...	...	...	− .065

acetic acid this discrepancy is largely removed. Walpole's results and those that are now reported are rendered more consistent by the use of what must now be considered, upon other grounds, a more probable value for the 0.1 N calomel electrode.

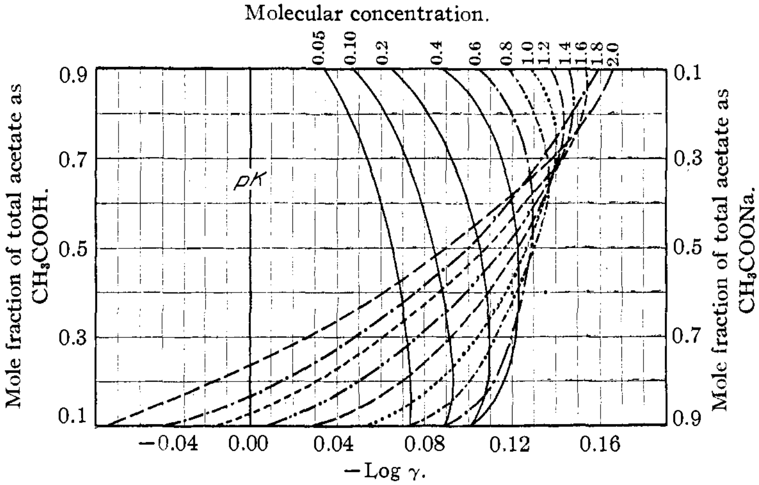


Fig. 3.

It has become a matter of convenience in a great deal of chemical and biochemical work to prepare solutions of known P_H and ionic strength, and the present paper is a contribution to this end. It therefore seemed desirable to construct interpolation tables so as to facilitate the preparation of any desired solution of known P_H and ionic strength.

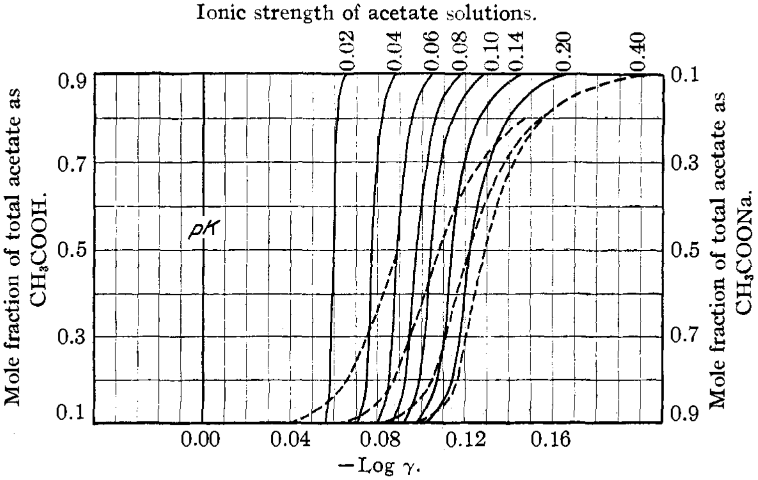


Fig. 4.

This has been done by calculating values of $-\log \gamma$ for different mixtures of acetic acid and sodium acetate for even values of the total acetate concentration (Table VII), and for even values of the ionic strength (Table VIII). These interpolated values are graphically represented in Figures III and IV, in which $-\log \gamma$ is given as abscissa and the mole fraction of total acetate as the sodium salt as ordinate. In the one chart the contour lines represent the molecular concentration, in the other the ionic strength of the acetate solution whose P_{H} is to be calculated.

Summary

1. The dissociation of acetic acid has been studied in the presence of its sodium salt. Inter-ionic forces have been considered by combining the mass law expression for the dissociation of a weak acid with the Debye-Hückel equation for the activity coefficient of an ion. This yields for acetic acid

$$P_{\mathrm{H}^+} - \log\,[(\mathrm{CH_3COO^-})/(\mathrm{CH_3COOH})] = P_K - 0.5\sqrt{\mu}/(1 + \kappa b) + Ks\mu = P_{K'}$$

2. Precise measurements can be made with the hydrogen electrode upon buffer solutions of relatively high molecular concentration but such low ionic strength that specific ion effects are nearly eliminated. Under such circumstances the dissociation constant of the acid can be accurately determined by extrapolation.

3. If 0.3380 is taken as the value of the 0.1 *N* calomel electrode, these data yield for acetic acid $P_K = 4.73$; $Ka = 1.86 \times 10^{-5}$. The dissociation constant of acetic acid derived from electromotive force measurements, and this value for the 0.1 *N* calomel electrode, thus agree with Kendall's estimate from conductivity measurements of 1.85×10^{-5}.

4. The electromotive force measurements that have been made determine the dissociation constant of acetic acid with an error of less than 0.6 millivolts. The value assumed for the 0.1 *N* calomel electrode thus becomes the controlling factor in determining the dissociation constant of acetic acid by this method.

5. If 0.3357 is taken as the value of the 0.1 *N* calomel electrode, these data yield $P_K = 4.77$; $Ka = 1.7 \times 10^{-5}$. Certain of the results are more consistent when calculated by means of this value of the 0.1 *N* calomel electrode.

6. It is urged that the accumulating data render it desirable both from theoretical and practical considerations to employ a value for the 0.1 *N* calomel electrode other than 0.3380, and therefore to increase the entire P_{H} scale. It is suggested that the comparison of electromotive force measurements of the kind here presented, with conductivity measurements upon the same weak acid and its salt, corrected for inter-ionic forces, could form the basis for standardization.

7. The activity coefficients estimated for the acetate anion are inde-

pendent of any assumption regarding the 0.1 N calomel electrode. Values of the salting-out constant, Ks, and of b, have been estimated for solutions varying in molecular concentration from 0.02 to 4 M, and in the mole fraction as CH_3COONa from 0.1 to 0.9.

8. Interpolation tables and graphs are given to facilitate the preparation of buffer solutions of the same ionic strength and varying *P*H, or of the same *P*H and varying ionic strength.

9. These measurements upon acetate mixtures together with those already published upon phosphate mixtures render it possible to prepare buffer solutions of known ionic strength at any reaction between *P*H 3.6 and 7.6.

BOSTON, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

THE DECOMPOSITION OF AZO-ISOPROPANE. A HOMOGENEOUS UNIMOLECULAR REACTION

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The decomposition of azomethane was found to be first order at high pressures[2] but at lower pressures a reduction in the rate constant was found.[3] This result has been accounted for on one of the theories (Theory II)[4] of unimolecular gas reactions developed by Rice and Ramsperger.[5] It was to be expected that other azo compounds would also decompose in unimolecular manner and that the higher, more complex azo compounds would maintain the same rate constant to lower pressures than does azomethane. In this research the rate of reaction of azo·*iso*propane has been determined at initial pressures from 4.60 cm. to 0.025 cm. and at temperatures from 250 to 290°.

Reaction Products

Azomethane reacted principally according to the equation $CH_3NNCH_3 = N_2 + C_2H_6$. A small amount of side reaction could be attributed to either of the following reactions.

$$2CH_3NNCH_3 = 2N_2 + C_2H_4 + 2CH_4$$
$$CH_3NNCH_3 = N_2 + C_2H_4 + H_2$$

The final pressure was 2.04 times the initial pressure instead of exactly 2 times, due to one or both of these side reactions. The complete decomposition of azo·*iso*propane at constant temperature and constant

[1] National Research Fellow in Chemistry.

[2] Ramsperger, THIS JOURNAL, 49, 912 (1927).

[3] Ramsperger, *ibid.*, 49, 1495 (1927).

[4] Rice and Ramsperger, *ibid.*, 49, 1617 (1927).

[5] Rice and Ramsperger, *ibid.*, 50, 617 (1928).