[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

A Comparison of the Colorimetric, Electrometric and Catalytic Methods for Determining Hydrogen-Ion Concentration[1]

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Hydrogen-ion concentrations determined catalytically by the use of the rate of hydrolysis of diethyl acetal, and electrometrically with the quinhydrone electrode, have been found to yield concordant results for benzoic acid–benzoate buffer systems in potassium chloride solution up to a concentration of two molar. At higher concentrations the results by the two methods are not in agreement. The assumptions involved in each method have been discussed.[3]

In an attempt to clear up this discrepancy further experiments with benzoate buffers have been carried out.[4] To discover whether this difference existed in the case of other buffer systems, and to test more thoroughly the assumptions of the two methods, a set of independent determinations was made on acetic acid–acetate buffers. At the same time the hydrogen-ion concentration of the buffer solutions was measured colorimetrically using brom phenol blue. The technique of the colorimetric method has already been given, and the necessary dissociation constant of brom phenol blue determined.[5] The results are summarized in Table I.

TABLE I

THE COLORIMETRIC, CATALYTIC AND ELECTROMETRIC DETERMINATION OF HYDROGEN-ION CONCENTRATION

Temperature, 25°

	Moles per liter			$c_{H_3O^+} \times 10^4$		
μ	CH_3-COOH	CH_3-COONa	KCl	Colorimetric	Catalytic	Electrometric
0.10	0.0941	0.0100	0.09	2.68	2.72	2.64
.10	.1462	.0100	.09	3.89	4.05	4.03
.10	.1982	.0100	.09	4.88	5.35	5.22
.50	.0941	.0100	.49	2.84	2.87	2.83
1.0	.0941	.0100	.99		2.59	2.73
1.0	.0959	.0100	.99	2.71	2.63	
1.0	.0421	.0100	.99	1.22	1.20	1.15
1.5	.0421	.0100	1.49	1.03	1.01	1.04
2.0	.0421	.0100	1.99	0.850	0.821	0.844
2.5	.0421	.0100	2.49	.687	.681	.680
3.0	.0421	.0100	2.99	.504	.525	.540

From Table I it is evident that all three methods yield hydrogen-ion concentrations agreeing within the experimental error of the measurements, *i. e.*, about 5% in the case of the colorimetric measurements and one-half that for the other two methods. The agreement extends out to the buffers three molar in salt concentration. From these measurements the conclusion is drawn that the discrepancy in the case of the benzoic acid–benzoate buffer solutions at high salt concentrations is not due to the invalidity of the assumptions involved, but is peculiar to the benzoate buffer.

In Table II are given the values of the dissociation constant of acetic acid as determined by the three methods.

TABLE II

THE DISSOCIATION CONSTANT OF ACETIC ACID IN POTASSIUM CHLORIDE SOLUTIONS AT 25°

	$K_c \times 10^5$, determined		
μ	Colorimetrically, with brom phenol blue	Catalytically, with the acetal reaction	Electrometrically, with the quinhydrone electrode
0.1	2.75	2.90	2.84
.5	3.11	3.14	3.11
1.0	2.94	2.85	2.83
1.5	2.49	2.49	2.50
2.0	2.04	1.97	2.03
2.5	1.65	1.63	1.64
3.0	1.21	1.26	1.30

To determine the dissociation constant of acetic acid at low ionic strengths the following experiment was carried out. An acetic acid–acetate buffer solution with an acid–base ratio of 3/1 was prepared, and the c_{I^-}/c_{HI^-} ratio for brom phenol blue measured in this buffer. The original buffer solution was then diluted with an equal volume of water and the c_{I^-}/c_{HI} ratio again measured. This was repeated for eight successive dilutions. The indicator concentration was always 2×10^{-5} *M*. Table III summarizes the results. The values of the dissociation constant of brom phenol blue, given in the fifth column, were obtained from Table III of the preceding paper, values for intermediate ionic strengths being read from a graph.

By plotting the logarithm of the ratio of the dissociation constant of acetic acid to that of brom phenol blue against the square root of the ionic strength, and extrapolating to zero-ion con-

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(1) Paper presented at the Florida meeting of the American Chemical Society, March, 1934.

(2) George Lieb Harrison Fellow at the University of Pennsylvania.

(3) Kilpatrick and Chase, THIS JOURNAL, 53, 1732 (1931).

(4) Riesch and Kilpatrick, unpublished work.

(5) Kilpatrick, THIS JOURNAL, 56, 2048 (1934).

TABLE III

THE DISSOCIATION CONSTANT OF ACETIC ACID AT LOW IONIC STRENGTHS[a]

CH_3COONa, mole/liter	c_{HAc}/c_{Ac^-}	$c_{HI^-}/c_{I^=}$	Kc_{HAc}/Kc_{BPB}	$Kc_{BPB} \times 10^5$	$Kc_{HAc} \times 10^5$
0.2516	3.00	0.587	0.196	17.8	3.48
.1259	2.99	.595	.199	15.4	3.06
.0630	2.99	.605	.202	12.6	2.55
.03152	2.99	.676	.226	10.5	2.38
.01580	2.98	.717	.240	9.2	2.21
.00793	2.96	.733	.248	8.2	2.03
.00399	2.94	.751	.256	7.6	1.95
.00203	2.94	.778	.270	7.1	1.91
.00099	2.92	.792	.272	6.85	1.86

[a] These experiments were carried out in this Laboratory by C. E. Gulezian in 1930.

centration, a value of the thermodynamic dissociation constant can be calculated. The extrapolation gives for the ratio 0.295, and using the value of K_a for brom phenol blue from the preceding paper, 6.0×10^{-5}, the thermodynamic dissociation constant of acetic acid is found to be 1.8×10^{-5}.

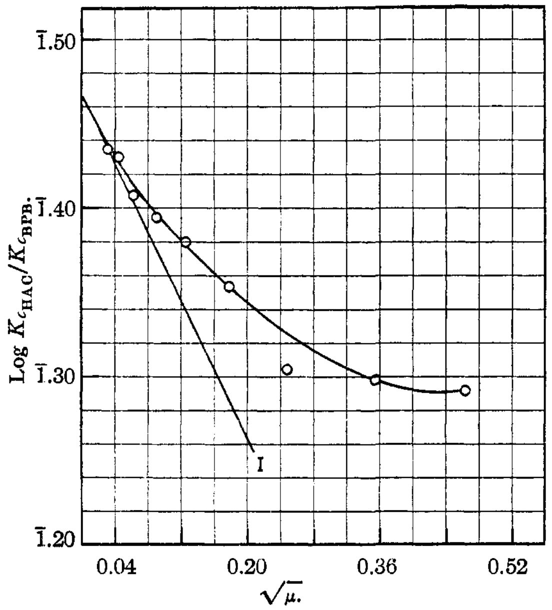

Fig. 1.—The ratio of the dissociation constants: I, Slope = 1.0.

It should be pointed out that the values obtained for the dissociation constant of acetic acid involve the assumption that the dissociation constant of brom phenol blue is the same in the sodium acetate–acetic acid solution as in potassium chloride solution of the same ionic strength. This is probably true only for concentrations of acetic acid and acetate below 0.1 *M*. Consequently no great weight should be attached to the first three values in the sixth column of Table III.

The Effect of Temperature upon the Dissociation Constant of Acetic Acid in Salt Solutions.—The catalytic method offers a convenient means of determining the effect of temperature upon the dissociation constant of an acid in salt solutions. The method involves the determination of the velocity constant of the reaction at two temperatures, using the same solution.[3]

TABLE IV

THE TEMPERATURE COEFFICIENT k_{35}/k_{25} FOR THE HYDROLYSIS OF ACETAL

Moles per liter			
CH_3COOH	CH_3COONa	KCl	k_{35}/k_{25}
0.04279	0.01000	0.49	3.398
.02379	.01000	.99	3.457
.01534	.01000	1.99	3.415
.01112	.01000	2.99	3.494

The results in Table IV indicate that there is little effect of added salt upon the temperature coefficient, the average value of k_{35}/k_{25} being 3.441 ± 0.035. Similar experiments with dilute hydrochloric acid gave for k_{35}/k_{25} an average value of 3.395 ± 0.069. The difference must be caused by a change in the hydrogen-ion concentration of the buffer solution due to change in the dissociation constant of acetic acid with temperature. From the data it appears that the classical dissociation constant of acetic acid increases slightly with temperature. Harned and Ehlers[6] found a slightly lower value of the thermodynamic dissociation constant at 35° than at 25°.

The dissociation constants in potassium chloride solution are in agreement with the corresponding values calculated from the paper of Harned and Murphy[7] and with those determined by Larsson and Adell[8] at 18°, but they are not in agreement with the results of Dawson and Key,[9] obtained catalytically by means of the acetone–iodine reaction.

Summary

1. The hydrogen-ion concentration of a series of acetic acid–acetate buffer solutions has been determined by colorimetric, catalytic and electrometric measurements.

2. The three methods give results in agreement with one another.

3. The values of the dissociation constant of acetic acid calculated from these measurements

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[6] Harned and Ehlers, THIS JOURNAL, **54**, 1350 (1932); **55**, 652 (1933).

[7] Harned and Murphy, *ibid.*, **53**, 8 (1931).

[8] Larsson and Adell, *Z. physik. Chem.*, **156**, 352 (1931).

[9] Dawson and Key, *J. Chem. Soc.*, 1239 (1928).

are in agreement with the results of Harned and Murphy, and Larsson and Adell.

4. The classical dissociation constant of acetic acid is found to increase slightly between 25 and 35°.

PHILADELPHIA, PA. RECEIVED AUGUST 14, 1934

NOTES

A Quantitative Addition Tube

BY JOSEPH GREENSPAN

It is often necessary to add quantitatively a definite weighed amount of solid through a narrow opening, *e. g.*, the neck of a volumetric flask, bottle or separatory funnel in a brief interval of time. We have found the glass tube illustrated in the figure useful for this purpose. The required amount of material is weighed out directly in the tube, and the latter, held by the central rod, is set in position through the opening. Upon depressing the rod, the stopper opens and the major portion of the solid drops into the lower container. Any solid clinging to the walls is then washed down with a solvent, at the same time inclining either addition tube or receiver to prevent splashing or dusting.

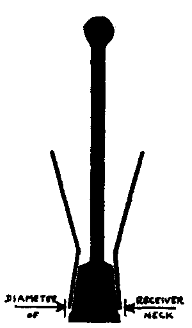

Fig. 1.

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RECEIVED JUNE 19, 1934

The "Dead-Space" Correction in Gas Reaction Rate Measurements

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In the course of some kinetic studies on the decomposition of acetaldehyde–azomethane mixtures, a formula was derived for the effect on the measured pressure of the "dead-space," or part of the reaction system external to the high temperature bath which surrounds the main portion of reactant. Later this formula was found not to be needed in this particular research; its applicability, however, is fairly general, so it may be worth separate presentation.

In many gas reactions the pressure increases as the reaction occurs, so that gas will be continually expanding from the hot part of the system into the "dead-space;" an accurate correction must take account of this effect, as well as of the initial distribution of reactant between the two zones. The problem is to determine for any reaction the actual partial pressure of reactant in the reaction as a function of the measured pressure, and also the ratio of the pressure measured at the end of the reaction to the initial pressure. It is assumed that no back-diffusion occurs from the dead space; this must be true as long as the reaction is proceeding at any appreciable rate.

Let N be the total number of moles in the hot part of the system, R of these being moles of reactant. Let the ratio of the number of moles produced by the reaction to the number consumed be q. Now let dx moles react. The total increase in the number of moles is $(q-1)\mathrm{d}x$. This increase distributes itself between the hot and cold parts of the system in accordance with the gas laws; the amount dN remaining in the hot part is obviously

$$(q-1)\mathrm{d}x\,\frac{V_h}{V_h + \frac{T_h}{T_c}V_c} = (q-1)\mathrm{d}x\,\frac{1}{a}$$

where the subscripts refer to the hot and cold parts of the system, and T and V are, respectively, absolute temperature and volume. We thus have

$$\mathrm{d}x = a\mathrm{d}N/(q-1) \qquad (1)$$

This expansion of the gas causes a loss of reactant from the hot part, given by $R/N[(q-1)\mathrm{d}x - \mathrm{d}N]$. Thus the total change in number of moles of reactant in the hot part is

$$\mathrm{d}R = -\mathrm{d}x - \frac{R}{N}\left[(q-1)\mathrm{d}x - \mathrm{d}N\right] \qquad (2)$$

Substituting for dx from (1), we find

$$\frac{\mathrm{d}R}{\mathrm{d}N} + \frac{(a-1)}{N}R = -\frac{a}{q-1} \qquad (3)$$

This differential equation is readily solved, the constant of integration being obtained from the condition that at the start of the reaction $N = R = N_0$. We find

$$R = \frac{q}{q-1}\,\frac{N_0^a}{N^{a-1}} - \frac{N}{q-1} \qquad (4)$$

For the ratio between final and initial pressure, we set $R = 0$ in (4) and find

$$N_{\text{final}}/N_0 = q^{1/a} \qquad (5)$$

Neglecting the dead-space effect is equivalent to setting $a = 1$ in the above formulas; this may