

164. *The Determination of the Thermodynamic Dissociation Constants of Dibasic Acids.*

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Two difficulties have to be overcome in determining the thermodynamic dissociation constants of a dibasic acid from experiments on cells embodying liquid-liquid junctions: first, that of the standardisation of the p_H scale; and secondly, that of correcting for the activity effects of the ions. A procedure for overcoming these difficulties is suggested. Previous general formulæ are modified so as to lead to a linear equation, which enables first and second dissociation constants to be obtained very simply, and the use of which is very convenient in smoothing experimental data and leads to no appreciable errors in dilute solutions. The method has been tested by experiments on oxalic, succinic, glutaric, and adipic acids, and found to be satisfactory.

FOR determining the thermodynamic dissociation constants of polybasic acids the potentiometric method possesses the great advantage, amongst others, of giving strictly comparable values of successive constants. In work of the highest accuracy, cells without liquid-liquid junctions must be used (cf. Harned and Ehlers, *J. Amer. Chem. Soc.*, 1932, **54**, 1350; Nims, *ibid.*, 1933, **55**, 1946); but the method requires an elaborate series of experiments, followed by extrapolation to zero ionic strength. With a dibasic acid the extrapolation may become difficult, and especially when the acid is relatively highly dissociated (see p. 858). Methods based on cells with liquid junctions require less experimental work, and, provided two general difficulties can be adequately overcome, are capable of yielding results of considerable accuracy, as will be shown.

The first difficulty is concerned with the standardisation of the p_H scale (cf. Clark, "The Determination of Hydrogen Ions," 1928, Ch. XXIII), and is essentially one aspect of

the dilemma (not yet resolved) met in any attempt to measure either the activity of a single ionic species or the potential at a liquid-liquid junction. Hitchcock and Taylor (*J. Amer. Chem. Soc.*, 1937, **59**, 1812; 1938, **60**, 2710) have proposed an arbitrary standardisation designed to lead to correct thermodynamic dissociation constants, and have embodied it in a table of the p_H values to be attributed to various convenient buffer solutions. Any form of hydrogen electrode including a liquid junction with saturated potassium chloride can be calibrated accordingly, with the implied assumption that the junction potential is constant. Errors arising from this first difficulty are not likely to be large, and should in any case affect both dissociation constants of a dibasic acid similarly.

The second difficulty is more serious, and is due to the fact that activities, not concentrations, must be used in calculating the constants. Failure to allow for this may lead to particularly large errors in the second dissociation constant. General equations involving the necessary activity coefficients have been derived (*e.g.*, by Morton, *Trans. Faraday Soc.*, 1928, **24**, 14; Maxwell and Partington, *ibid.*, 1935, **31**, 922), but they are not very convenient to use with experimental data. Some workers have therefore resorted to the evaluation (*e.g.*, by a formula based on the work of Auerbach and Smolczyk, *Z. physikal. Chem.*, 1924, **110**, 65) of classical or "incomplete" dissociation constants, followed by an extrapolation, or some other equivalent correction, to zero ionic strength (*e.g.*, Kolthoff and Bosch, *Rec. Trav. chim.*, 1928, **47**, 861; Bjerrum and Unmack, *Kgl. Danske Videnskab. Selskab.*, 1929, **9**, 11; Gane and Ingold, *J.*, 1931, 2158; German, Jeffery, and Vogel, *J.*, 1935, 1624), a procedure less accurate, but little less laborious, than the use of cells free from liquid junctions. In the present paper a convenient method for evaluating thermodynamic dissociation constants is described.

The thermodynamic dissociation constants of a dibasic acid, H_2A , may be defined by the equations:

$$K_1 = \{H'\}[HA']/[H_2A]f_0 \quad \text{and} \quad K_2 = \{H'\}[A'']/[HA']f_1$$

where $\{H'\}$ signifies the *activity* of hydrogen ions, and f_0 , f_1 , and f_2 are the activity coefficients of the species H_2A , HA' , and A'' respectively. In a solution of total acid concentration a (molar)

$$a = [H_2A] + [HA'] + [A'']$$

and when a strong monoacid base, which may be taken as completely dissociated, has been added to give a molar concentration b , electrical neutrality requires that

$$b + [H'] = [HA'] + 2[A''] + [OH']$$

If we define L , M , and N by the equations

$$\begin{aligned} L &= b + [H'] - [OH'] && (= [HA'] + 2[A'']) \\ M &= a - b - [H'] + [OH'] && (= [H_2A] - [A'']) \\ N &= 2a - b - [H'] + [OH'] && (= 2[H_2A] + [HA']) \end{aligned}$$

then it can easily be shown that

$$\{H'\}^2 L f_2 / N f_0 = K_1 (\{H'\} M f_2 / N f_1) + K_1 K_2 \quad \dots \quad (1)$$

which may be written shortly

$$X = K_1 Y + K_1 K_2$$

When therefore X and Y can be evaluated from experimental data, the plot of one against the other should give rise to a straight line, the slope of which equals K_1 , and the intercept on the X -axis $K_1 K_2$. A linear relationship is very convenient, in that by drawing the most suitable straight line amongst the experimentally determined points an average based on all the measurements is simply obtained.

Equation (1) is rigorous; and, although in evaluating X and Y approximations have to be made, they are not such as seriously to affect its accuracy when the solutions used are dilute. In the first place the success of the system of p_H standardisation depends on the validity of putting $-\log\{H'\}$ equal to p_H .* As $[H']$ normally makes only a small

* In accordance with general usage, p_H is defined as above in terms of the hydrogen-ion *activity*, and not as $-\log [H']$.

contribution to L , M , and N , no sensible error is introduced if $\{H^*\}$ is used in its place: in the exceptional cases when $[H^*]$ is relatively more important, the quantity may be estimated with sufficient exactness by dividing $\{H^*\}$ by f_1 ; $[OH^*]$ is negligible on the acid side of p_H 7. Salting-out data for neutral molecules show that f_0 is unlikely to differ appreciably from unity when the ionic-strength (I) is less than 0.01. f_1 and f_2 are in general not known; in very dilute solutions, however, they will not be much less than unity, and they may then be estimated with sufficient accuracy by the Debye-Hückel limiting law (*viz.*, $\log f_1 = -0.5\sqrt{I}$; $\log f_2 = -2.0\sqrt{I}$; $\log f_2/f_1 = -1.5\sqrt{I}$). I can be estimated by successive approximations if necessary; but in the very dilute solutions (generally less than 0.001M) used in the present work I may without serious error be taken as $(b + \{H^*\})$ when $b < a$, and as $(2b - a)$ when $b > a$. The use of such dilute solutions does not give rise to serious errors in the experimental work, provided carbon dioxide is excluded.

For a monobasic acid equation (1) assumes the well-known form $K = \{H^*\}L f_1 / M f_0$. For acids of basicity higher than two, a simple general treatment is not possible, but equation (1), or some modification of it, would be applicable over any range of p_H where only two successive dissociations were in effective operation, as, *e.g.*, with orthophosphoric acid up to p_H 7.

EXPERIMENTAL.

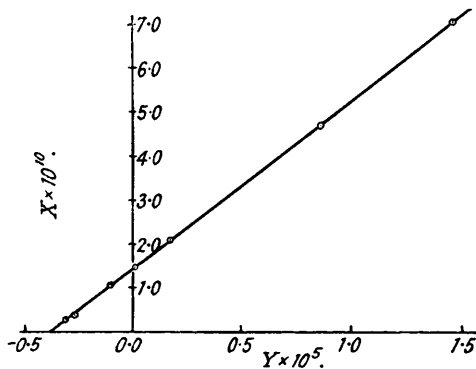
The procedure described was tested with measurements made on oxalic, succinic, glutaric, and adipic acids, these being chosen partly because they show a range of strengths, and partly for comparison with measurements being made on certain of their derivatives. The oxalic acid was of "AnalaR" quality. The other acids were pure specimens, and were further purified by recrystallisations from ethyl acetate and water.

p_H Values were measured by means of the glass electrode, embodied in the complete cell:

Ag|AgCl, HCl (0.02M)|Glass|Solution under investigation|Saturated KCl|HCl (0.02M), AgCl|Ag.

It was important to avoid appreciable contamination of the working solution by potassium chloride from the salt bridge. The siphon-tube dipping into the working solution was therefore drawn out into a fine capillary, which was then bent into several "waves."

The system was standardised before and after each potentiometric titration by use of some of the buffer solutions recommended by Hitchcock and Taylor (*loc. cit.*), particularly the three following: 0.01M-HCl + 0.09M-KCl, 0.015M-HOAc + 0.015M-NaOAc, 0.025M-KH₂PO₄ + 0.025M-Na₂HPO₄. These authors give p_H values at 25° and 35°. The present work was carried out at 20° ($\pm 0.2^\circ$), and the solutions were taken to have p_H 's of 2.08, 4.72, and 6.86 respectively. The glass electrodes had resistances of 5—8 megohms, and efficiencies (*cf.* Morton, J., 1934, 256) of 99.0—99.5%. A thermionic valve voltmeter was used to measure the potentials of the cell. Placing a 0.001 μ farad condenser in parallel with the cell cut down electrical interference sufficiently to render elaborate screening of the apparatus unnecessary. The standardisation of the electrode was apt to drift slightly during an experiment; p_H values are reliable to within 0.03 unit over the whole period, though neighbouring readings are accurately comparable to within 0.01.



Solutions were made in carbon dioxide-free distilled water, and titrations were carried out with sodium hydroxide free from carbonate and in an atmosphere free from carbon dioxide. In order to avoid considerable alterations in the total volume of solution, the alkali used was much more concentrated than the acid, and was run from a calibrated 5 c.c. microburette. p_H Values were observed at several stages between 25% and 75% neutralisation, and finally in the neighbourhood of complete neutralisation in order to check the acid concentration. A typical experiment is recorded in Table I, some details of the computation being also shown. The slight increase in total volume can be neglected. The plot of X against Y is shown in the figure, the points lying very close to the straight line. From this line $K_1 K_2$ is found to be 1.43×10^{-10} , and K_1 and K_2 to be $3.8_0 \times 10^{-5}$ and $3.7_6 \times 10^{-6}$ respectively.

TABLE I.

Titration of adipic acid ($a = 0.000793$; total vol. = 40 c.c.) with 0.0194M-NaOH at 20°.

NaOH, c.c.	p_H .	$\{H^+\} \times 10^5$.	$b \times 10^6$.	$I \times 10^5$.	f_2/f_1 .	f_2 .	$X \times 10^{10}$.	$Y \times 10^5$.
0.726	4.32	4.79	352	40	0.93	0.91	7.04	1.47
0.944	4.47	3.39	458	49	0.92 ₅	0.90 ₅	4.68	0.862
1.397	4.76	1.74	678	70	0.91 ₅	0.88 ₅	2.09	0.175
1.582	4.88	1.32	767	78	0.91	0.88	1.48	0.019
1.769	4.99	1.023	858	93	0.90	0.87	1.10	-0.096
2.281	5.35	0.447	1106	143	0.88	0.84	0.39	-0.262
2.462	5.48	0.331	1194	160	0.87	0.83	0.28	-0.299

In Table II the results of a number of determinations are collected. Dissociation constants are expressed as $p_K (= -\log K)$, since this preserves a more direct relationship with the p_H values upon which they depend. For each acid the results agree to within experimental error (± 0.03). For any acid the value of Δp_K is more reliable than are those of the individual p_K 's. Any desired change in the scale of p_H can be made by adding the necessary correction to p_K .

TABLE II.

Thermodynamic dissociation constants at 20°.

$a \times 10^5$.	p_{K_1} .	p_{K_2} .	Δp_K .	$a \times 10^5$.	p_{K_1} .	p_{K_2} .	Δp_K .
	Oxalic acid.				Glutaric acid.		
543	1.25	4.19	2.94	105.0	4.36	5.47	1.11
270	(1.21)	4.25	(2.95)	55.6	4.39	5.51	1.12
81.5	—	4.24	—	28.0	4.41	5.52	1.11
Means	1.25	4.23	2.94	Means	4.39	5.50	1.11
	Succinic acid.				Adipic acid.		
76.6	4.21	5.68	1.47	79.3	4.42	5.42	1.00
62.1	4.19	5.64	1.45	56.4	4.40	5.42	1.02
37.3	4.24	5.68	1.44	40.6	4.45	5.42	0.97
18.8	4.21	5.70	1.49	Means	4.43	5.42	0.99
Means	4.22	5.67	1.45				

DISCUSSION.

Oxalic acid is difficult to deal with because its first dissociation constant is so high (cf. Parton and Gibbons, *Trans. Faraday Soc.*, 1939, **61**, 542). In very dilute solutions the first stage of dissociation is almost complete; the calculation of L , M , and N is therefore very uncertain in the early part of the titration, and it is possible to determine only the second constant. At concentrations of about 0.0025M it begins to be possible to estimate K_1 , though with considerable uncertainty at less than 0.005M. Parton and Gibbons have measured the dissociation constants of oxalic acid, using cells without liquid junctions, and the present results are in satisfactory agreement with theirs.

These measurements, and to a less extent the similar ones of Jones and Soper (J., 1936, 133; cf. also J., 1934, 1836) on succinic, glutaric, and adipic acids, illustrate the difficulties involved in extrapolating to zero ionic strength from data obtained with cells without liquid junctions. The method retains its experimental advantage of introducing no liquid-junction potentials; but its theoretical advantage is lost when the necessary corrections for ionic dissociation become large and involve assumptions regarding such thermodynamically unsatisfactory quantities as individual ion activity coefficients.

The results of Jones and Soper are given in Table III, where are also included those recent determinations which represent thermodynamic dissociation constants and are based on cells with liquid junctions. (The references are to Sims, *J. Amer. Chem. Soc.*, 1926, **48**, 1251; Kolthoff and Bosch, *loc. cit.*; Gane and Ingold, *loc. cit.*; German and Vogel, *J. Amer. Chem. Soc.*, 1936, **58**, 1546.) The schemes of p_H standardisation adopted by these workers—in so far as they can be inferred—are not identical either with each other or with that adopted here, but discrepancies from this cause will not be large. The three results italicised appear to be considerably in error. Kolthoff and Bosch's method

TABLE III.

Correlation with previously determined dissociation constants.

Acid		Succinic.			Glutaric.			Adipic.		
Ref.	Temp.	p_{K_1} .	p_{K_2} .	Δp_K .	p_{K_1} .	p_{K_2} .	Δp_K .	p_{K_1} .	p_{K_2} .	Δp_K .
J. & S.	25°	4.16	5.61	1.45	4.34	5.41	1.07	4.43	5.41	0.98
S.	25	4.20	5.62	1.42	4.32	5.50	1.18	4.43	5.62	1.19
K. & B. ...	18	4.18	5.57	1.39	—	—	—	4.34	5.44	1.10
G. & I. ...	25	4.19	5.48	1.29	4.34	5.42	1.08	4.42	5.41	0.99
G. & V. ...	25	4.20	5.60	1.40	4.35	5.42	1.07	—	—	—
This paper	20	4.22	5.67	1.45	4.39	5.50	1.11	4.43	5.42	0.99

of calculation seems to involve some inaccuracies; when their data are treated in the manner described above (though their lowest concentrations are somewhat high for the purpose) values of 4.21 for p_{K_1} and 5.66 for p_{K_2} for succinic acid are found.

In general, the agreement between the results obtained in the present work and the most probable values based on the previous data is satisfactory, and confirms the validity of the assumptions necessary in applying equation (1).

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