201. *The Thermochemistry of Solutions. Part VI. The Heat of Ionisation of Succinic Acid.*

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Using a technique similar to that described in Part V (preceding paper), we have measured calorimetrically the heats of the first and the second ionisation of succinic acid at two concentrations over the temperature range 5—30°. The results have been used to obtain the heat-content change and the heat-capacity change at infinite dilution, and have been combined with ionisation-constant data to give the thermodynamic functions for the two stages of ionisation. The thermodynamics of the ionisation of dibasic acids is discussed in the light of the results, with special reference to the Kirkwood–Westheimer theory.

SINCE the publication of Kirkwood and Westheimer's theory of the electrostatic effect of substituents on the dissociation constants of organic acids (*J. Chem. Physics*, 1938, **6**, 506, 513), considerable interest has been taken in the dissociation constants of dibasic acids (cf. Westheimer and Shookhoff, *J. Amer. Chem. Soc.*, 1939, **61**, 555; Wynne-Jones and Rushbrooke, *Trans. Faraday Soc.*, 1944, **40**, 99; Westheimer and Kirkwood, *Trans. Faraday Soc.*, 1947, **43**, 77). It is agreed that the theory is inadequate to explain the temperature dependence of the effect, but there are no very reliable measurements of the variation of both ionisation constants of dibasic acids with temperature against which the theory can be checked. The present work is an attempt to contribute relevant data towards such a discussion.

In Part V the difficulty of obtaining ΔH values at infinite dilution from calorimetric results was discussed, and it was shown that use of the Debye–Huckel limiting law gave results which were comparable with those obtained by other means. Although the limiting law therefore has been shown to give a reasonably good approximation to the behaviour of uni-univalent electrolytes, the validity of the correction for uni-bivalent electrolytes is much less certain; ΔH was therefore measured both in 0·05M- and in 0·025M-solutions, in order to obtain some indication of how ΔH varies with concentration.

As some of the results in Part V suggested the possibility that ΔC_p was not independent of

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* Although Harned and Embree's equation is only an approximation, it was applied in preference to the other empirical equations for the variation of log K with T because it is easier to fit to the data, and because in any case Rule and La Mer's results are not sufficiently precise to warrant fitting to a more exact expression.

temperature, the temperature range was extended downward to 5°. It would have been useful to extend the measurements to higher temperatures also, but control of the temperature of the bath surrounding the calorimeter was not sufficiently good above 30° to make this worth while.

EXPERIMENTAL.

Calorimeter.—The calorimeter was of similar design to that used previously, but was larger, its capacity being 100 instead of 50 ml. A new thermel was constructed; it consisted of 112 junctions of chromel–constantan. The junctions were spot-welded instead of soldered as previously, the chromel being introduced because a chromel–constantan junction has a greater thermal E.M.F. than a copper–constantan one (cf. Weber, " Temperature Measurement and Control ", Philadelphia, 1941, Chap. IV), and because chromel gives a better spot-weld.

The sensitivity of the thermel was very much greater than that of those previously used, partly on account of the increased thermal sensitivity of the new junctions, and partly because mechanical improvements resulting in more accurate rotation of the calorimeter enabled the junctions to be mounted closer to it. The resistance of the thermel and leads was 15·5 ohms, and by using a Tinsley galvanometer of sensitivity 790 mm. per micro-amp., and internal resistance 134 ohms, a sensitivity of 10,000 mm. per ° c. was obtained. This is to be compared with 3,000 mm. for the thermel described in Part IV, and about 1,000 for that constructed by McEwan and used for some of the other work on acids.

The chief advantage of a sensitive thermel is not that increased accuracy is obtained, because thermel sensitivity does not appear to be the limiting factor, but that operation of the adiabatic control is made easier and the effect of any parasitic e.m.f.'s which might arise in the thermel circuit, and which tend to cause temperature drifts, is minimised.

The heat capacity of the calorimeter was determined by carrying out the dilution of $KNO_3,50H_2O$ to $KNO_3,100H_2O$, for which accurate values of ΔH and its temperature coefficient have been given by Richards and Rowe (*J. Amer. Chem. Soc.*, 1921, **43**, 770).

Reaction measured.—Essentially the same reaction was carried out as described in Part V, but modifications in the concentrations of the reactants were necessary. For the first ionisation, the reaction was

$$NaHA + HCl \longrightarrow NaCl + H_2A \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

To ensure that none of the doubly-charged anion was present in the sodium hydrogen succinate solution, a large excess of free succinic acid was present. The solution was 0·05M in sodium hydrogen succinate, and approximately 0·25M in free succinic acid. A 10% excess of hydrochloric acid solution was used. Half these concentrations were used in the measurements at higher dilution. For the second ionisation, the reaction was

$$Na_2A + 2HCl \longrightarrow 2NaCl + H_2A \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

The solutions were 0·05M and 0·025M in sodium succinate, and the same excess of hydrochloric acid was used as before. Thus the reactions for which ΔH is recorded are :—

$$H_2A = H^+ + HA^- \quad (\Delta H_1)$$
$$\text{and} \quad H_2A = 2H^+ + A^{=} \quad (\Delta H_1 + \Delta H_2)$$

and contributions due to the heats of dilution of the reactants are included. These may not be small, and are discussed below.

Materials.—" AnalaR " Succinic acid was used, and standard methods were used for the preparation of sodium hydroxide and hydrochloric acid solutions. The solutions of the acid salt were found to be readily affected by fungoid contamination. They were therefore used immediately after being prepared.

Results.—The specific heat of the solution from reaction (1) was taken to be 0·990, and that from reaction (2) 0·995. The experimental results are set out in the table.

Observed ΔH *values.*

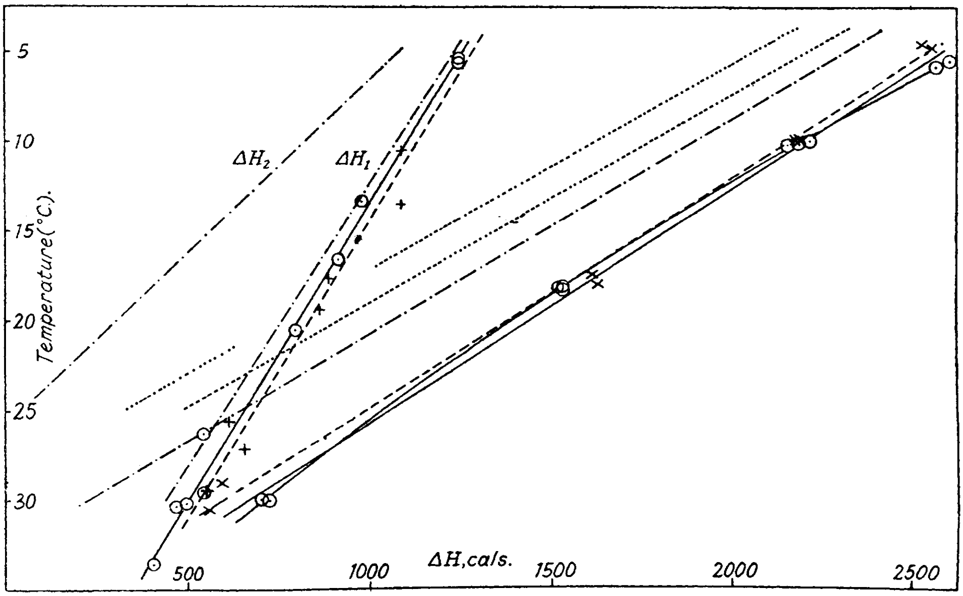
(ΔH_1).				($\Delta H_1 + \Delta H_2$).			
0·05M.		0·025M.		0·05M.		0·025M.	
Temp.	ΔH (cals.).	Temp.	ΔH.	Temp.	ΔH.	Temp.	ΔH.
5·30°	1245	10·44°	1085	5·51°	2608	4·65°	2532
5·54	1245	13·50	1085	5·84	2573	4·89	2555
13·37	978	17·64	882	9·93	2221	9·80	2175
16·58	913	19·33	860	10·14	2188	9·95	2185
20·44	794	25·61	613	10·20	2153	17·39	1615
26·25	558	27·11	656	18·07	1529	17·86	1627
29·69	547	29·49	558	18·10	1512	29·13	594
30·14	496	—	—	18·20	1529	30·58	560
30·34	468	—	—	29·93	702	—	—
33·64	408	—	—	30·00	722	—	—

For the first stage of ionisation in 0·05M-solutions, the plot of ΔH against temperature was linear, and the results were fitted to a straight line by the method of least squares, giving the result $\Delta H = 1399 - 29{\cdot}99t$ cals., where t is the temperature in °c. The probable error of a single determination was $\pm$ 18 cals., which is comparable with the precision attained in the earlier work using the McEwan thermel, but slightly less than that attained with the aliphatic acids. Estimation of the probable error in the expression for ΔH gives $\Delta H = (1399 \pm 5{\cdot}6) - (29{\cdot}99 \pm 0{\cdot}24)t$ cals. The plot of ΔH against T was also linear for 0·025M-solutions, and the results were fitted to a straight line by the method of least squares, giving $\Delta H = (1429 \pm 13) - (29{\cdot}78 \pm 0{\cdot}61)t$ cals. The probable error of a single determination was ± 35 cals., almost exactly double that for 0·05M-solutions. This is, of course, in agreement with expectation.

For the first and the second stage of ionisation together, the results for 0·05M-solutions were fitted to a straight line by the method of least squares, giving $\Delta H = 2975 \pm 77{\cdot}03t$ cals. When fitted to a straight line, the probable error of a single determination comes out at ± 39 cals., which is much greater than that found for ΔH_1 in 0·05M-solutions. The results were better fitted by a parabolic expression, which gives $\Delta H = 1722{\cdot}5 - 80{\cdot}60\,(t - 15{\cdot}592) + 0{\cdot}708\,(t - 15{\cdot}592)^2$ cals., and the probable error of a single determination ± 12 cals. The overall accuracy of the results is not, however, in our opinion sufficient to place this deviation from linearity beyond doubt. The results for 0·025M-solutions were fitted to a straight line, giving $\Delta H = (2948 \pm 11) - (78{\cdot}37 \pm 0{\cdot}64)t$ cals., and ± 33 cals. for the probable error of a single determination; this is in agreement with the expected probable error.

It should be noted that the probable errors quoted above refer only to the random errors. As in Part V, allowance must be made for systematic errors, such as those in the heat capacities of calorimeter and solutions, and possible inaccuracies in preparation of solutions. This may contribute an uncertainty of not more than 1% to the observed ΔH.

Variation of heat of ionisation with temperature.



——O—— ΔH_1, ($\Delta H_1 + \Delta H_2$) *at* 0·05M; – – + – – ΔH_1 *at* 0·025M; – – × – – ($\Delta H_1 + \Delta H_2$) *at* 0·025M; — . — . — *values adopted for* ΔH_1°, ΔH_2°, *and* ($\Delta H_1^\circ + \Delta H_2^\circ$). *The two dotted lines represent the values of* ($\Delta H_1 + \Delta H_2$) *obtained by direct application of the limiting law for heats of dilution to the experimental results at* 0·05M (*upper line*) *and* 0·025M (*lower line*).

Dilution Corrections.—In obtaining ΔH_1°, the heat content for the first ionisation at infinite dilution, there are two uncertainties to be taken into account: (1) The uncertainty in the heat of dilution of excess succinic acid, which is too great to be neglected, but too small to be measured accurately by our methods. (2) The usual uncertainty in the application of the limiting law to the heat of dilution of electrolytes.

(1) As a guide to the magnitude of this correction, the heat of dilution of 0·25M-succinic acid to 0·125M was measured at 20°. The result was $\Delta H = +13$ cals. per mole, the uncertainty in this value being about ± 3 cals. This means that the correction to ΔH per mole of sodium salt for 0·05M-solutions is about + 65 cals. If it is assumed that the heat of dilution varies linearly with concentration, the molar heat of dilution of 0·125M-succinic acid to half that concentration will be 6·5 cals., and the correction to ΔH in 0·025M-solutions about + 33 cals. In view of the fairly large uncertainty of this correction, it was taken to be temperature independent. With this correction applied, ΔH_1 in 0·05M- and 0·025M-solutions is given respectively by $\Delta H_1 = 1464 - 30{\cdot}0t$ cals., and $\Delta H_1 = 1462 - 29{\cdot}8t$ cals.

(2) The limiting law predicts a fall of about 45 cals. in ΔH from 0·05M to 0·025M, while the experimental results show no significant alteration, although in view of the probable errors a drop of some 20—30 cals. is not ruled out. The deviation from the limiting law is in the expected direction. However, the limiting law might be expected to apply more nearly to the dilution to infinity of 0·025M-solutions than that of 0·05M-solutions, and the correction has therefore been applied to the results at the former concentration. Although the predicted limiting-law correction does not vary linearly with temperature, the nature of the approximations made is such that the small predicted deviation from linearity of the ΔH_1° plot against temperature is not significant. Adopting this procedure between 5° and 30°, we may represent our results for ΔH_1° by the equation $\Delta H_1^\circ = 1390 - 31{\cdot}5t$ cals.

To obtain ΔH°_2 we have to subtract ΔH_1° from the measured value of ΔH for reaction (2), corrected to infinite dilution. The correction of ΔH for reaction (2) is difficult because of the inapplicability of the limiting law for multivalent electrolytes except at very low concentrations. The situation is further complicated by the fact that, although at 5° and 30° the drop in ΔH from 0·05M to 0·025M is not much less than that required by the theory, yet the curvature of the plot of ΔH against T for the 0·05M-solution means that in the region 15—20° the drop is very small compared with the theoretical value of about 150 cals. (For a uni-bivalent electrolyte, the limiting slope for heat of dilution is $3\sqrt{3}$ times that for a uni-univalent electrolyte.) There is no obvious explanation for this discrepancy.

Accordingly, we have adopted a rather arbitrary procedure for obtaining ΔH°. We have taken values for ΔH at 0·05M and 0·025M as obtained from the linear equations, and obtained a value at 0·01M by extrapolation, assuming a linear dependence of ΔH on concentration. We have then applied the limiting law to these values. The result of this procedure may be expressed as $(\Delta H_1^{\circ} + \Delta H_2^{\circ}) = 2737 - 83{\cdot}7t$ cals. On this basis $\Delta H_2^{\circ} = 1347 - 52{\cdot}2t$ cals.

It is obvious that the results at infinite dilution, particularly for the second stage of ionisation, are subject to considerable uncertainty. The figure shows the experimentally determined heats of ionisation, and the heats of ionisation at infinite dilution derived from them by the method described above, and gives some idea of the nature of the approximations involved. For the first and the second stage of ionisation together, the effect of applying the limiting law directly is shown.

DISCUSSION.

The only e.m.f. data on succinic acid which appear to be sufficiently accurate to warrant their use in the derivation of the thermodynamic functions for ionisation are those of Jones and Soper (*J.*, 1936, 133), who measured K_1 and K_2 for ten dibasic acids at 25°, 50°, and 74°. We have combined our data with theirs at 25° to give the following values for ΔH°, ΔC_p°, ΔS°, and ΔG°:

	$\Delta H^{\circ}_{298\cdot1}$.	$\Delta C_p{}^{\circ}_{298\cdot1}$.	$\Delta S^{\circ}_{298\cdot1}$.	$\Delta G^{\circ}_{298\cdot1}$.
First ionisation	+602	−31·5	−17·0	+5680
Second ionisation	+ 42	−52·2	−25·5	+7650

The results for the second ionisation are rather less reliable than those for the first.

By using Jones and Soper's data for the temperature variation of K, it should be possible to obtain values of ΔH and ΔC_p. The accuracy claimed in K is 1%, which should allow at least roughly reliable values of ΔC_p to be obtained.

Plotting Jones and Soper's log K against T for succinic acid showed that for the first ionisation K cannot reach a maximum until somewhere between 50° and 74°, whereas our results show on extrapolation that $\Delta H_1^{\circ} = 0$ at about 45°, and therefore that K must have a maximum at this temperature. The disagreement is marked, but might possibly be explained by a decrease in the numerical value of our ΔC_p above 30°, though this is rather unlikely, in view of the fact that none of Harned's precise e.m.f. measurements of ionisation constants over the range 0—60° shows any appreciable variation of ΔC_p in this range. For the second ionisation, a plot of Jones and Soper's results showed that log K has a maximum at about 25°, in agreement with our result that $\Delta H_2^{\circ} = 0$ at about 26°.

The disagreement with our results for ΔH_1° made us interested in the results which might be obtained by applying three-constant expressions to the ionisation constants of all the acids investigated by Jones and Soper. We used expressions of the forms used by Harned and Robinson (*Trans. Faraday Soc.*, 1940, **36**, 973) and by Everett and Wynne-Jones (*ibid.*, 1939, **35**, 1380) to calculate ΔC_p. The two equations gave results in close agreement. Since only three points are available it is not possible to say how well the true variation of K with T is represented, and therefore any conclusions based on such a treatment must be tentative. Below we give values of ΔC_p, rounded to the nearest 5 cals., for the acids investigated by Jones and Soper.

	ΔC_p.	
Acid.	1st Ionisation.	2nd Ionisation.
cis-Caronic	−50	−25
*cyclo*Hexane-1 : 1-diacetic	−25	− 5
Succinic	−15	−50
β-Methylglutaric	−45	−65
Adipic	−10	−30
ββ-Dimethylglutaric	+20	+10
trans-Caronic	+10	−25
Glutaric	−55	−80
β-*iso*Propylglutaric	−40	−50
DL-βγ-Diphenyladipic	−70	−60

For succinic acid, agreement with our ΔC_p for the second ionisation is good, but for the first ionisation it is poor. In view of this fact, and the fact that the other results give values of ΔC_p

which vary over a wider range than the data for ΔC_p for any other acids in the literature, it is perhaps reasonable to suggest that their data are not sufficiently accurate for a discussion of the thermodynamics of the ionisation of dibasic acids. Soper (private communication) has pointed out that errors in E.M.F. of 1 millivolt would be sufficient to change the sign of ΔC_p for ββ-dimethylglutaric acid, for example, to make it about − 30 cals. per degree. The possibility of such errors arising from small errors in E.M.F. work emphasises the value of calorimetric work in this field. Even the uncertainty in the dilution correction is unlikely to introduce uncertainties as great as those obviously present in thermodynamic functions derived from all but the most precise E.M.F. work.

Consideration of the values obtained from our result shows that for the first ionisation, ΔC_p is quite normal compared with ΔC_p values found for other fatty acids (cf. Part V; Everett and Wynne-Jones, *loc. cit.*; Harned and Owen, *op. cit.*), but that ΔS is significantly less numerically than that for unsubstituted fatty acids except formic acid. This result is as might be expected, for Magee, Ri, and Eyring (*J. Chem. Physics*, 1941, **9**, 419) have already pointed out that the more polar an acid the smaller the entropy loss on ionisation, because more orientation of water molecules might be expected round a polar than round a non-polar solute. For the second ionisation ΔC_p and ΔS are comparable with those for oxalic, but both rather less numerically than those for malonic acid (cf. Harned and Owen, *op. cit.*). In view of the uncertainties in the results, the significance of the difference is not certain, and an attempt to explain it at this stage would be premature.

Kirkwood and Westheimer (*loc. cit.*) have stated that their theory does not provide a satisfactory explanation for the temperature dependence of the electrostatic effect of substituents. In their amplification of this statement, Wynne-Jones and Rushbrooke (*loc. cit.*) used Jones and Soper's data for the temperature variation of the dissociation constants of the dibasic dicarboxylic acids, and various data for aliphatic amino-acids. Westheimer and Kirkwood (*loc. cit.*) have since pointed out that the use by Wynne-Jones and Rushbrooke of the latter data is inadmissible from a theoretical point of view, and our analysis of the former data casts some doubt on their suitability for detailed discussion. It is therefore of interest to consider our results in the light of the electrostatic theory of substituent effect.

The simple Bjerrum theory (*Z. physikal. Chem.*, 1923, **106**, 219) to which the Kirkwood–Westheimer treatment of a dibasic acid reduces as the length between the ionising centres becomes great, gives a value for the interprotonic distance of succinic acid of 3·65 A., which is not very much too small. For succinic acid, Westheimer and Shookhoof (*loc. cit.*) give 5·75 A. as the interprotonic distance obtained by applying the Kirkwood–Westheimer theory to Jones and Soper's value for ΔpK at 25°, 6·66 A. as the maximum interprotonic distance calculated on the basis of accepted valency angles and bond-lengths, and 4·66 A. as the root mean square separation of the protons calculated on the basis of free rotation according to Eyring (*Physical Rev.*, 1932, **39**, 746). Levi (Thesis, Oxford, 1941) has pointed out that the Bjerrum theory gives for the difference between the first and the second heats of ionisation

$$\Delta H_1 - \Delta H_2 = -\frac{\mathbf{e}^2\mathbf{N}}{a}\cdot\frac{1}{\varepsilon}\left(1 + \frac{T}{\varepsilon}\frac{\partial\varepsilon}{\partial T}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where a is the distance between the ionising centres and the other symbols have their usual significance. Taking a as 5 A., we have that $\Delta H_1 - \Delta H_2$ is about 200 cals. at 0°. Smaller values of a give larger values of $\Delta H_1 - \Delta H_2$. The experimental value of ΔH_1 is almost equal to that of ΔH_2 at 0°, and to secure even approximate agreement with experiment, a fairly large value of a would be necessary.

Differentiating again, we have for the difference in heat capacity changes for the successive stages of ionisation :

$$\Delta C_{p_1} - \Delta C_{p_2} = \frac{\mathbf{Ne}^2}{a}\cdot T\cdot\frac{\partial^2}{\partial T^2}\left(\frac{1}{\varepsilon}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The value for succinic acid obtained from this research is about 20 cals. per degree which would require an interprotonic distance (a) of 1 A. Thus we find that in order to fit $\Delta H_1 - \Delta H_2$ at low temperatures, we must use a larger value of a than is physically plausible, whereas to fit its temperature dependence, we must use an impossibly small value of a. This means, of course, that for any given reasonable value of a there is a temperature at which the Bjerrum expression gives the correct value of $\Delta H_1 - \Delta H_2$, but this can hardly be regarded as satisfactory agreement with experiment, although it emphasises the need to take ΔC_p into account.

If the approximations introduced into the Kirkwood–Westheimer theory by Wynne-Jones and Rushbrooke are accepted, the expression for the difference in heat capacity change is equivalent to the right-hand side of equation (2) multiplied by a factor f, where $f < 1$, and is probably about 0·7.* This refinement of the Bjerrum theory is therefore seen to exaggerate rather than to diminish the discrepancy between theory and experiment for changes in heat capacity (cf. Westheimer and Kirkwood, *loc. cit.*, p. 85).

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