

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE COLLEGE OF WASHINGTON]

**Molal Volumes of Solutes. VII. Sodium Acetate and Acetic Acid**

BY O. REDLICH AND L. E. NIELSEN

For the test of Born's equation discussed in the fifth paper<sup>1</sup> of this series precise data for the apparent molal volumes of sodium acetate and acetic acid were required. The experimental method has been described in the preceding paper.

**Materials and Analyses.**—Mallinckrodt Analytical Reagents were used. Sodium acetate was recrystallized from redistilled water, the wet crystals were dissolved to give approximately 3 *M* stock solutions. Acetic acid was distilled under reduced pressure.

Several methods of analyzing the sodium acetate solutions were tested. Neither heating in the platinum dish with sulfuric acid nor conversion to sodium carbonate in an atmosphere of oxygen and carbon dioxide was satisfactory. Finally we adopted the method described by Kolthoff and Sandell, *i. e.*, heating with sulfuric acid and then with ammonium carbonate to convert the acid sulfate to the normal sulfate. The sodium sulfate, heated to constant weight with the full flame of two bunsen burners, was considered neutral if the reaction was acidic with phenolphthalein and basic with methyl orange. If not, more acid or carbonate, as required, was added, and the residue heated again. Three analyses of the first stock solution checked within 0.03%, two analyses of the second within 0.07%; NaOAc = 82.041.

Acetic acid was titrated with sodium hydroxide solution

TABLE I

APPARENT MOLAL VOLUMES OF SODIUM ACETATE IN AQUEOUS SOLUTIONS AT 25.00° (ML./MOLE)

<i>c</i>	$10^4(d - d^0)/d^0$	$\phi$	$10^3\delta\phi$	$10^3\delta d$
0.006903	2953	39.500	100	- 7
7206	3093	358	- 45	3
8192	3513	392	- 22	2
8425	3617	351	- 65	5
0.010402	4468	326	-110	11
20773	8896	455	- 61	13
23281	9963	488	- 45	10
26068	11134	572	23	- 6
26421	11284	581	30	- 7
5110	21782	659	- 16	8
5850	24912	698	- 8	5
5972	25413	726	15	- 9
6871	29219	754	8	- 5
0.23717	99787	40.207	7	
29724	124723	321	1	
34426	144064	435	27	
39144	163584	492	2	
44157	184185	570	- 2	
48845	203412	638	- 8	
5746	238412	788	14	
6421	266188	824	- 44	
6758	279636	905	- 9	
8189	336337	41.107	11	

(1) O. Redlich and J. Bigeleisen, *Chem. Rev.* (1942).

TABLE II

APPARENT MOLAL VOLUMES OF ACETIC ACID IN AQUEOUS SOLUTION AT 25.00°

<i>c</i>	$10^4(d - d^0)/d^0$	$\phi$	$10^3\delta\phi$	$\phi_u$	$10^3\delta\phi_u$
0.2174	18187	51.8631	- 7.9	51.967	+6
.4483	37278	9132	- 1.8	985	+1
.5677	47139	9243	+ 1.4	988	-8
.8363	69019	9756	+11.5	52.028	+2
1.1258	92513	52.0108	+ 1.0	056	-5
1.5792	128616	0836	- 0.9	123	-1
2.0222	163237	1560	- 5.3	190	-9
2.9126	230083	3292	+ 0.7	357	+7
4.1076	313911	5860	+ 1.0	609	-3

and phenolphthalein. A precision of 0.1% was considered sufficient as this corresponds to 0.008 cc. mole in the molal volume; HOAc = 60.052.

**Results.**—Tables I and II contain the results in the arrangement used in the preceding paper. The data for sodium acetate are represented by

$$\phi = 39.244 + 1.86c^{1/2} + 0.209c \quad (\text{NaOAc, } 25.00^\circ)$$

with the deviations  $\delta\phi$  (observed - calculated) listed in Table I. The accidental errors are estimated to be  $\pm 0.017$ , the total error  $\pm 0.03$ . Influence of hydrolysis is neither to be expected nor noticed.

Watson and Felsing<sup>2</sup> represent the results of their pycnometer determinations in the range of 0.3 to 3 *M*, according to Masson's rule, by

$$\phi = 38.75 + 2.53c^{1/2} \quad (\text{NaOAc, } 25.00^\circ)$$

This is a new example of the fact that Masson's rule is unsuitable for extrapolation to infinite dilution.

Within the range and precision of our measurements, the apparent molal volume of acetic acid is a linear function of the molality, *m*

$$\phi = 51.8397 + 0.14184m \quad (\text{HOAc, } 0.2 \leq m \leq 5; 25.00^\circ)$$

The deviations  $\delta\phi$  are listed in Table II. As a consequence of this equation, we obtain the formula

$$\frac{d - d_0}{d_0} = m \frac{w_2 + d_0\phi}{1000 - md_0\phi} = \frac{0.008364 - 0.000141425m}{1 + 0.051688m + 0.000141425m^2}$$

(*w*<sub>2</sub> molal weight of acetic acid) fitting our data with an average deviation  $5.10^{-6}$ . These purely empirical equations must never be extrapolated

(2) G. M. Watson and W. A. Felsing, *THIS JOURNAL*, **63**, 410 (1941).

to lower molalities because the increasing ionization effects a drop of  $\phi$  to the limit  $\phi_0(\text{H}^+ + \text{OAc}^-) = 40.47$ .

The molal volumes of acetic acid are appreciably affected by ionization even at relatively high concentrations. The values  $\phi_u$  of the apparent molal volume of the undissociated acid, as recorded in Table II, have been obtained by means of the equation

$$\phi_u = \phi + 11.47\alpha$$

where  $\alpha$  denotes the degree of ionization and the change of volume accompanying ionization at infinite dilution is assumed to be  $-11.47$  ml./mole (*cf.* ref. 1).

The experimental values of  $\phi_u$  are represented by

$$\phi_u = 51.942 + 0.0846c + 0.0191c^2 \quad (25.00^\circ)$$

The influence of the errors in the density determination itself is small in the concentration range

covered by the measurements. Therefore, as discussed in the preceding paper, the mean square error of  $\phi_u$ ,  $\approx 0.006$ , is significant. Taking into account the error of the analysis the estimated total uncertainty amounts to 0.01 cc./mole.

The equations used for representing  $\phi(\text{NaOAc})$  and  $\phi_u(\text{HOAc})$  satisfy the conditions  $(d\phi/dc^{1/2})_{c=0} = 1.86$  and  $(d\phi_u/dc)_{c=0} = \text{finite}$ .<sup>3</sup> The experimental results agree, therefore, with the predicted dependence on concentration of the apparent molal volume.

### Summary

The apparent molal volumes of sodium acetate and acetic acid in aqueous solutions at  $25.00^\circ$ , required for a test of Born's equation, have been determined with an estimated uncertainty of 0.03 and 0.01 cc./mole, respectively.

(3) *Cf.* O. Redlich, *J. Phys. Chem.*, **44**, 619 (1940).

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## Calorimetric Investigations of Organic Reactions. IV. The Heats of Ionization of *dl*-Alanine at $25^\circ$

BY JULIAN M. STURTEVANT

In a previous publication<sup>1</sup> measurements of the heats of reaction of glycine with hydrochloric acid and sodium hydroxide were described. The interpretation of the results given in that paper was not entirely satisfactory, since the experiments were not performed in such a manner that medium effects could be completely eliminated in the calculations. In the present work these objections have been partially overcome by using a double extrapolation procedure.

### Experimental

The calorimetric measurements were made in the apparatus described elsewhere.<sup>2</sup> A few minor changes have been made in the apparatus. The main thermel has been increased from twenty to thirty junctions, and the sensitivity of the galvanometer used has been increased somewhat. The calorimeter heater is contained in a 0.3 by 7-cm. tantalum well welded into the bottom of the calorimeter. The heater is a 39.4 ohm, bifilar coil of no. 36 double silk insulated Advance wire; the coil was given several coats of Glyptal varnish and baked, and inserted into the well with the latter filled with molten Wood's metal. The heater is equipped with potential and current-carrying leads. The precision of the timing of the

electrical heating periods has been increased by employing a quick-acting, mechanical lock-in relay actuated by a contactor on the 100-cycle General Radio Company clock described in the earlier paper.<sup>2</sup> The contactor closes once every thirty seconds, so that heating periods of a half minute or multiple thereof may be employed.

The oil thermostat was maintained at  $25^\circ$  during the summer months, in which the present measurements were made, by circulating through a coil submerged in it a slow stream of water from a water thermostat maintained at about  $15^\circ$  by a small General Electric refrigerating unit.<sup>3</sup> Fine control of the temperature of the oil-bath was obtained by the heater-thyratron control circuit previously described.<sup>2,4</sup>

As might be expected, considerable difficulty was experienced with leakage currents during the months of July and August. It was found to be necessary to evacuate the apparatus after each run and to fill it with dry nitrogen. All possible parts of the electrical apparatus were enclosed in boxes containing calcium chloride.

A small additional correction was discovered which had not been applied to any of the previous data which were obtained with this calorimeter. It was found that there was a small evolution of heat arising from tearing open the gold foil and paraffin closure of the dilution cup, in addition to that due to expanding the platinum-iridium bel-

(1) Sturtevant, *THIS JOURNAL*, **63**, 88 (1941).

(2) Sturtevant, *J. Phys. Chem.*, **45**, 127 (1941).

(3) The author is indebted to the George Sheffield Fund for a grant with which the refrigerating unit was purchased.

(4) Sturtevant, *Rev. Sci. Instruments*, **9**, 276 (1938).