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

The molal volumes of acetic acid are appreciably affected by ionization even at relatively high concentrations. The values ϕ_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 α 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 ϕ_u are represented by

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

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 ϕ_u, ± 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 $\phi(NaOAc)$ and $\phi_u(HOAc)$ satisfy the conditions $(d\phi/dc^{1/2})_{c=0} = 1.86$ and $(d\phi_u/dc)_{c=0} =$ finite.[3] 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°, 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).

Calorimetric Investigations of Organic Reactions. IV. The Heats of Ionization of dl-Alanine at 25°

By Julian M. Sturtevant

In a previous publication[1] 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.[2] 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.[2] 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° 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° by a small General Electric refrigerating unit.[3] Fine control of the temperature of the oil-bath was obtained by the heater-thyratron control circuit previously described.[2,4]

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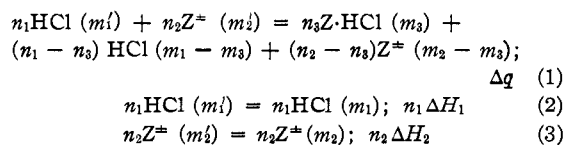(2) Sturtevant, J. Phys. Chem., **45**, 127 (1941).

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

lows. The total heat evolution accompanying the opening of the dilution cup at 25° was found to be 0.090±0.019 joule, or ±0.05 microvolt. The deviations here are largely to be attributed to the impossibility of obtaining entirely reproducible closures, and to variations in the amount of tearing from run to run. While the type of dilution cup used in this apparatus has proven very satisfactory in most respects, it now appears that this lack of reproducibility in the closure imposes a definite limitation on the useful sensitivity which can be obtained. The additional correction mentioned here would affect the results which have been previously published only very slightly, except in dilution experiments extending to low concentrations. It may be mentioned that the data on the heats of dilution of glycine[5] are brought into better agreement with those of Gucker, Pickard and Ford[6] by application of this correction, the average deviation being changed from −110 microdegrees to ±60 microdegrees.

The stock solutions of hydrochloric acid and sodium hydroxide were made up from Baker analyzed materials and boiled distilled water saturated with nitrogen. The sodium hydroxide solution, prepared by dilution of a saturated solution filtered through asbestos, gave no precipitate with barium hydroxide. The hydrochloric acid was analyzed gravimetrically, and the sodium hydroxide was compared twice during the measurements by weight titrations with freshly made-up and analyzed hydrochloric acid. The concentrations of these stock solutions were known to better than ±0.05%. The exclusion of carbon dioxide was attempted by the previously described technique.[7] Eastman *dl*-alanine was recrystallized twice from 25% alcohol and dried over sodium hydroxide *in vacuo* at 70° for thirty-six hours. It was stored *in vacuo* over sodium hydroxide.

The appropriate vapor pressure corrections were applied to all the results.

Experiments with Hydrochloric Acid.

—Three series of measurements were made; in the runs in a given series, the hydrochloric acid concentration before reaction and the final ionic strength were held constant, while the initial alanine concentration was decreased, in order to allow extrapolation to zero alanine concentration. From the observed heat effect there was deducted in each case the heat of the dilution of the hydrochloric acid. In all cases but one the heat of the dilution of the alanine[8] was negligible. In the notation of the previous publication,[1] the reactions involved may be written

$$n_1HCl\ (m_1^i) + n_2Z^\pm\ (m_2^i) = n_3Z\cdot HCl\ (m_3) +$$
$$(n_1 - n_3)\ HCl\ (m_1 - m_3) + (n_2 - n_3)Z^\pm\ (m_2 - m_3);$$
$$\Delta q \quad (1)$$
$$n_1HCl\ (m_1^i) = n_1HCl\ (m_1);\ n_1\Delta H_1 \quad (2)$$
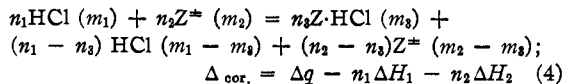$$n_2Z^\pm\ (m_2^i) = n_2Z^\pm(m_2);\ n_2\Delta H_2 \quad (3)$$

(5) Sturtevant, THIS JOURNAL, **62**, 1879 (1940).

(6) Gucker, Pickard and Ford, *ibid.*, **62**, 2698 (1940).

(7) Sturtevant, *ibid.*, **62** 2276 (1940).

(8) Data kindly supplied by Professor Frank T. Gucker, Jr., of Northwestern University, in advance of publication, were used for the calculation of the appropriate heats of dilution of alanine.

$$n_1HCl\ (m_1) + n_2Z^\pm\ (m_2) = n_3Z\cdot HCl\ (m_3) +$$
$$(n_1 - n_3)\ HCl\ (m_1 - m_3) + (n_2 - n_3)Z^\pm\ (m_2 - m_3);$$
$$\Delta_{cor.} = \Delta q - n_1\Delta H_1 - n_2\Delta H_2 \quad (4)$$

where $Z^\pm$ represents alanine zwitterion.

The ionization process the heat of which is desired may be written:

$$ZH^+ = Z^\pm + H^+;\ \Delta H_A \quad (5)$$
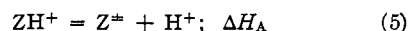
for which the thermodynamic ionization constant is

$$K_A = \frac{(m_1 - m_3)(m_2 - m_3)}{m_3} \frac{\gamma_{Z^\pm}\gamma_{H^+}}{\gamma_{ZH^+}}$$
$$= \frac{1 - \alpha}{\alpha}\ (m_1 - \alpha m_2) \frac{\gamma_{Z^\pm}\gamma_{H^+}}{\gamma_{ZH^+}} \quad (6)$$

where α is the degree of association. To eliminate possible medium effects on the reactions represented by Eqs. (2) and (3), and to eliminate the unknown quantity $\gamma_{Z^\pm}/\gamma_{ZH^+}$ from the final results, experiments were made at decreasing values of total amino acid concentration and the quantity $\Delta H_A' = -\Delta q_{cor.}/\alpha'n_2$, where α' is calculated from the equation

$$\frac{1 - \alpha'}{\alpha'}\ (m_1 - \alpha'm_2) = K_A/\gamma_{H^+} \quad (7)$$

was extrapolated to $m_2 = 0$. The values of K_A determined by Nims and Smith[9] were employed. For γ_{H^+}, values of the activity coefficient of hydrochloric acid determined by Harned and Ehlers[10] were used.

Because of the fact that the previously published[11] data on the heat of dilution of aqueous hydrochloric acid had not been corrected for the heat of opening the dilution cup, it seemed desirable to redetermine the small number of dilution heats needed for the present purposes. The results of these measurements are given in Table I. The relatively large discrepancy between the new value and the value read from the previous graph in the case of the dilution of 3.2723 *m* hydrochloric acid is presumably due to the difficulty of establishing the form of the apparent heat content curve

TABLE I

HEATS OF DILUTION OF HYDROCHLORIC ACID AT 25°

Series	Initial molality of HCl	Final molality of HCl	Heat of diln., joules (int.) per mole Observed	Previous value[a]	Diff. micro-degrees
1	3.2723	0.2056	−2994	−2974	897
1	3.2723	.2055	−2988	−2974	631
2	1.4994	.0871	−1648	−1648	0
3	0.3675	.02009	− 768	− 771	− 13

[a] Sturtevant, ref. 11.

(9) Nims and Smith, *J. Biol. Chem.*, **101**, 401 (1933); Harned and Owen, *Chem. Rev.*, **25**, 31 (1939).

(10) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).

(11) Sturtevant, *ibid.*, **62**, 584, 3265 (1940).

TABLE II

HEAT OF REACTION OF ALANINE WITH AQUEOUS HYDROCHLORIC ACID AND THE HEAT OF ACID IONIZATION OF ALANINE AT 25°

Series 1: $m_1' = 3.2723$; $m_1 = 0.2056$; $K_A/\gamma_{H^+} = 5.97 \times 10^{-3}$.

Series 2: $m_1' = 1.4995$; $m_1 = 0.08704$; $K_A/\gamma_{H^+} = 5.70 \times 10^{-3}$.

Series 3: $m_1' = 0.3674$; $m_1 = 0.02007$; $K_A/\gamma_{H^+} = 5.22 \times 10^{-3}$.

Run	Moles of HCl, n_1	Moles of alanine, n_2	Final total molality of alanine, m_2	Observed heat effect, Δq, joules (int.)[a]	Cor. heat effect, $\Delta q - n_1 \Delta H_1 - n_2 \Delta H_2$, joules (int.)	α'	$\Delta H_A'$, joules (int.) per mole[c]	Deviation from mean joules per mole Observed	Deviation from mean joules per mole Expected
1a	0.02722	0.008344	0.06302	−104.03	−22.57[b]	0.9605	2820	+20	± 5
1b	.02592	.006276	.04979	− 94.46	−16.89	.9635	2793	− 7	6
1c	.02675	.004189	.03217	− 91.32	−11.24	.9669	2780	−20	9
1d	.02258	.002233	.02032	− 73.60	− 6.03	.9689	2790	−10	14
1e	.02386	.001140	.00982	− 74.49	− 3.10	.9704	2806	+ 6	28
						Weighted mean	2800	±13	±12
2a	.01195	.006281	.04572	− 34.98	−15.27	0.8903	2733	+ 3	± 4
2b	.01187	.002816	.02065	− 26.64	− 7.06	.9226	2726	− 4	14
2c	.01179	.001358	.01004	− 22.91	− 3.44	.9317	2719	−11	29
						Weighted mean	2730	± 6	±19
3a	.002684	.002090	.01563	− 5.677	− 3.616	0.6538	2651	+11	±27
3b	.002804	.001682	.01204	− 5.238	− 3.087	.6922	2650	+10	32
3c	.002660	.001417	.01070	− 4.650	− 2.609	.7059	2609	−31	36
3d	.002874	.001133	.00791	− 4.401	− 2.195	.7322	2645	+ 5	46
						Weighted mean	2640	±14	±35

[a] After application of corrections for vapor pressure changes and heat of opening dilution cup. [b] In this experiment the heat of dilution of the alanine, $n_2 \Delta H_2$, amounted to −0.01 joule. [c] Corrected to 25° using the temperature coefficient given by Nims and Smith, ref. 9.

near the upper end of the concentration range studied. In the present calculations the newer dilution heats have been employed.

Table II summarizes the experimental data and the calculated heats of ionization. In computing the weighted means of the $\Delta H_A'$, the individual values were assigned weights inversely proportional to the "expected deviations" listed in the last column of Table II, and calculated by the equation[1]

$$\delta(\Delta H_A') = \pm 0.05 \frac{c}{\alpha' n_2} \sqrt{2 + \left(\frac{\Delta \mu_1}{\Delta \mu_2}\right)^2} \quad (8)$$

In this expression c is total heat capacity (solution plus calorimeter) in joules per microvolt, $\Delta \mu_1$ is the observed temperature rise in microvolts minus that due to the hydrochloric acid dilution, and $\Delta \mu_2$ is the temperature rise in the heat capacity determination. In deriving this expression, an uncertainty of ± 0.05 microvolt (± 40 microdegrees) has been assigned to each temperature interval involved.

From the last two columns of Table II it is evident that in each series of measurements the values of $\Delta H_A'$ are independent of alanine concentration to within less than the expected uncertainty. Therefore no significance can be attributed

to the slight trends evident in Series 2 and 3, and to the fact that the values in Series 1 happen to fall on a smooth curve when plotted as a function of alanine concentration. The fact that $\Delta H_A'$ is independent of m_2 indicates either that medium effects due to the amino acid are of negligible magnitude, or that the various individual effects happen to cancel each other. If the former alternate is correct, one is led to the conclusion that the heat of dilution of hydrochloric acid solutions by alanine solutions is essentially the same as that by pure water, and that $\gamma_{Z\pm}/\gamma_{ZH^+}$ is very nearly unity, in the concentration ranges covered.

In the paper on the heats of ionization of glycine it was shown that a fair value of the ionization constant could be obtained from the thermal data. In the present experiments, the ratio n_1/n_2 did not closely enough approach unity in any case to allow a good value of the ionization constant to be obtained. From the data of runs 3a and 3d, using Eq. (7) and setting $\alpha' = -\Delta q_{cor.}/n_2 \Delta H_A'$, we find $\Delta H_A' = 2595$ and $K_A = 0.00427$, which is somewhat below the value 0.00457 found by Nims and Smith.[9]

The mean values of $\Delta H_A'$ are found to vary linearly with the square root of the ionic

strength. They lie on the straight line

$$\Delta H'_A = 2585 + 474\sqrt{m_1} \qquad (9)$$

with an average deviation of ± 6 joules per mole. In Fig. 1 the individual values in each series have been plotted against the square root of the ionic strength. The intercept of this line, 2585 joules per mole, may be identified as the heat of ionization at infinite dilution, ΔH^0_A. Omission of Run 3c would not change the value of ΔH^0_A materially. A reasonable value for the purely calorimetric uncertainty in ΔH^0_A would appear to be ± 20 joules per mole.

It is rather important to consider how these results would be affected by an error in K_A. Using the value $K_A = 0.00427$, we find $\Delta H'_A = 2795$, 2715 and 2590 for Series 1, 2 and 3, respectively. The points lie fairly well on a smooth curve and would extrapolate to a considerably smaller value for ΔH^0_A, about 2490. A larger value of K_A would cause a corresponding change in ΔH^0_A in the opposite direction. It is evident therefore that the present results are more strongly dependent on the values of K_A and γ_{H^+} than one would wish; no means of avoiding this dependence has been discovered.

In Table III are listed the values of the heat capacities of the final solutions. The heat capacities of the hydrochloric acid solutions agree within the expected error (about ± 0.0010 cal.$_{25}$ per °C. per g.) with those given by Gucker and Schminke.[12]

TABLE III

HEAT CAPACITIES OF ALANINE–HYDROCHLORIC ACID SOLUTIONS AT 25°

Molality of HCl, m_1	Molality of alanine, m_2	Heat capacity cal.$_{25}$ per °C. per g.[a]
0.2056	0	0.9876
.2055	0	.9886
.2056	0.06302	.9863
.2056	.04979	.9867
.2055	.03217	.9855
.2055	.02032	.9871
.2055	.00982	.9873
.08709	0	.9933
.08698	0.04572	.9940
.08702	.02065	.9927
.08713	.01004	.9931
.02009	0	.9976
.02008	0.01563	.9987
.02007	.01204	.9978
.02008	.01070	.9959
.02006	.00791	.9966

[a] 1 cal.$_{25}$ = 4.1788 joules (int.); Osborne, Stimson and Ginnings, *Bur. Standards J. Research*, **23**, 197 (1939).

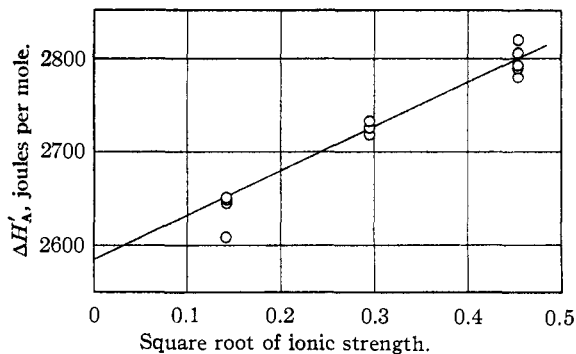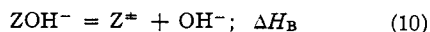(12) Gucker and Schminke, THIS JOURNAL, **54**, 1358 (1932).

Fig. 1.—The heat of the acid ionization of alanine at 25°.

Experiments with Sodium Hydroxide.—The procedure followed in the experiments with sodium hydroxide was entirely analogous to that of the acid experiments. The ionization process studied can be written

$$ZOH^- = Z^{\pm} + OH^-; \quad \Delta H_B \qquad (10)$$

for which

$$K_B = \frac{1-\alpha}{\alpha}(m_1 - \alpha m_2)\frac{\gamma_{Z^{\pm}}\gamma_{OH^-}}{\gamma_{ZOH^-}} \qquad (11)$$

In the calculations the K_B of Nims and Smith[9] and the activity coefficients of sodium hydroxide given by Harned and Hecker[13] have been used.

As in the case of the hydrochloride acid experiments, new determinations have been made of the sodium hydroxide dilution heats used in the calculations. These data appear in Table IV. The values for Series 1 agree well with the value reported previously.[7] The values for Series 2 agree well with each other, but are larger than the earlier value by about twice the estimated uncertainty in the earlier value; a part of this difference is probably due to the fact that after these experiments were performed it was discovered that the ethereal paraffin solution used in closing the dilution cup contained a small amount of some acidic substance, so that a small neutralization heat may be

TABLE IV

HEATS OF DILUTION OF SODIUM HYDROXIDE AT 25°

Series	Initial molality of NaOH	Final molality of NaOH	Heat of diln., joules (int.) per mole Observed	Previous value[a]	Diff., micro-degrees
1	1.5254	0.08672	+255.8	+258.5	+ 50
1	1.5254	.08671	+260.7	+258.5	+ 42
2	.5564	.03468	−189.9	−160.2	−225
2	.5564	.03470	−181.8	−160.2	−163
3	.2382	.01454	−317.6	−282.8	−110
4	.1063	.00645	−341	(−281)	− 84
4	.1063	.00439	−553	(−306)	−234

[a] Sturtevant, ref. 7.

(13) Harned and Hecker, *ibid.*, **55**, 4838 (1933).

TABLE V

HEAT OF REACTION OF ALANINE WITH AQUEOUS SODIUM HYDROXIDE AND THE HEAT OF BASIC IONIZATION OF ALANINE
AT 25°

Series 1: $m_1' = 1.5254$; $m_1 = 0.08671$; $K_B/\gamma_{OH^-} = 9.48 \times 10^{-5}$.
Series 2: $m_1' = 0.5564$; $m_1 = 0.03470$; $K_B/\gamma_{OH^-} = 8.80 \times 10^{-5}$.
Series 3: $m_1' = 0.2405$; $m_1 = 0.01548$; $K_B/\gamma_{OH^-} = 8.35 \times 10^{-5}$.
Series 4: $m_1' = 0.1063$; $m_1 = 0.004390$; $K_B/\gamma_{OH^-} = 7.91 \times 10^{-5}$.

Run	Moles of NaOH, n_1	Moles of alanine, n_2	Final total molality of alanine, m_2	Observed heat effect, Δq, joules (int.)[a]	Cor. heat effect, $\Delta q - n_1 \Delta H_1 - n_2 \Delta H_2$, joules (int.)	α'	$\Delta H_B'$, joules (int.) per mole[b]	Deviation from mean, or straight line, joules per mole Observed	Expected
1a	0.01172	0.004450	0.03293	−43.16	−46.19	0.9982	10,398	+53	±15
1b	.01132	.004251	.03257	−40.78	−43.70	.9983	10,297	−45	15
1c	.01292	.004457	.02994	−42.58	−45.91	.9983	10,318	0	14
1d	.01028	.002806	.02365	−25.97	−28.62	.9985	10,216	−47	15
1e	.01242	.002802	.01956	−25.48	−28.68	.9985	10,249	+22	18
1f	.01188	.0007314	.00534	− 4.306	− 7.376	.9988	10,097	− 6	54
1g	.01200	.0007142	.00516	− 4.119	− 7.216	.9988	10,116	+15	56
					Extrapolated value		10,056	±27	±27
2a	.004309	.004463	.03592	−44.39	−43.59	0.9320	10,481	+ 4	±12
2b	.004417	.002799	.02195	−29.91	−29.09	.9932	10,466	−11	16
2c	.004287	.001107	.00896	−12.41	−11.61	.9966	10,487	+10	32
					Weighted mean		10,477	± 8	±20
3a	.001976	.004410	.03455	−21.17	−20.55	0.9957	10,442	−16	± 9
3b	.001826	.002675	.02269	−19.51	−18.94	.9888	10,491	+33	14
3c	.001900	.001118	.00911	−12.11	−11.52	.9873	10,438	−20	31
					Weighted mean		10,458	±23	±18
4a	.0006570	.001681	.01122	− 6.997	− 6.634	0.9886	10,214	− 3	±62
4b	.0005567	.0008911	.007035	− 5.898	− 5.590	.9722	10,328	+ 3	62
4c	.0006015	.0005962	.004350	− 5.771	− 5.438	.8780	10,388	− 5	63
					Extrapolated value		10,505	± 4	±62

[a] After application of corrections for vapor pressure changes and heat of opening dilution cup. [b] Corrected to 25° using the temperature coefficient given by Nims and Smith, ref. 9.

included in the newer dilution heats. The last two dilution heats in Table V are to concentrations considerably below the concentration range studied in the earlier work. It should be noted that the procedure of using very dilute sodium hydroxide as the diluent in all experiments with low final concentrations, a procedure employed in the earlier work to avoid errors due to carbon dioxide in the diluent, could not be employed in the present experiments because of the presence of alanine.

The experimental data on the neutralization reactions are given in Table V. The alanine dilution heats were negligible in all cases. The calculated values of $\Delta H_B'$ indicate that the medium effects are larger in the experiments with sodium hydroxide than in those with hydrochloric acid. None of the alanine concentrations is small enough that any allowance need be made for the presence of the amino acid in a form other than

zwitterions in the solutions before reaction.[14] The values for Series 1 are plotted in Fig. 2, and indicate a strong dependence of $\Delta H_B'$ on m_2. This dependence will not be significantly altered by any reasonable change in the value of K_B/γ_{OH^-} used in the calculations. The values of $\Delta H_B'$ for Series 4, also plotted in Fig. 2, seem to show a dependence on m_2 of slope opposite in sign to that of Series 1, though in this case the experimental uncertainties are large enough to throw considerable doubt on the exact form of the dependence. The data of Series 4 are much more susceptible to changes in K_B/γ_{OH^-} than are those of Series 1; thus, if $K_B/\gamma_{OH^-} = 7.00 \times 10^{-5}$ instead of 7.91 $\times 10^{-5}$ is used, one calculates for Runs 4a, 4b, 4c that $\Delta H_B' = 10202, 10297, 10307$, respectively. These quantities no longer show a linear dependence on m_2, and would extrapolate to a value some 200 joules per mole less than that given in Table V.

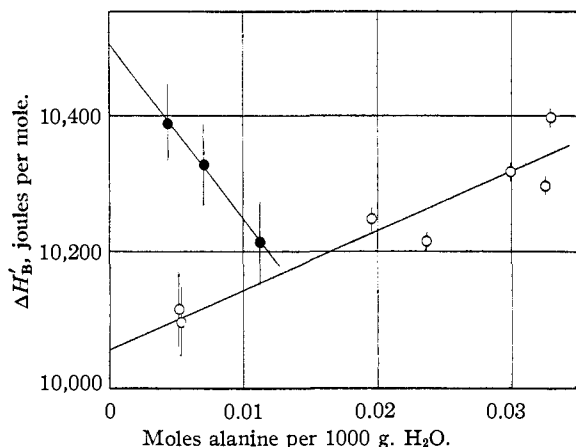(14) Sturtevant, THIS JOURNAL, **62**, 3519 (1940).

Fig. 2.—The heat of the basic ionization of alanine; vertical lines indicate estimated uncertainties: O, Series 1; ●, Series 4.

The values of $\Delta H'_B$ in Series 2 and 3 appear to be independent of alanine concentration, perhaps because in these series the ionic strength is intermediate between that of Series 1, with positive medium effect, and that of Series 4, with negative medium effect.

The extrapolated values of $\Delta H'_B$ for the first and last series and the weighted mean values for Series 2 and 3 are plotted as a function of the square root of the ionic strength in Fig. 3. The extrapolation of these values to zero ionic strength is a rather uncertain procedure, partly because of their strong dependence on ionic strength and partly because of the doubt in the value for Series 4. The extrapolated value is $\Delta H^0_B = 10,540$ joules per mole; a reasonable value for the uncertainty in this quantity would appear to be ± 150 joules per mole.

In Table VI are listed the heat capacities for the various alanine–sodium hydroxide solutions. The values for the solutions of zero alanine concentration agree satisfactorily with those given by Gucker and Schminke.[15]

Comparison with Previous Results.—As mentioned above, the heats of ionization of glycine given in an earlier paper[1] were not determined in a way that allowed unambiguous elimination of any medium effects which may have been present. It is therefore impossible to assume that the values obtained are directly comparable with the present quantities for alanine. However, it seems probable that the glycine values would not be greatly altered if the method used for alanine were employed.

Table VII gives a comparison between the

(15) Gucker and Schminke, THIS JOURNAL, **55**, 1013 (1933).

TABLE VI

HEAT CAPACITIES OF ALANINE–SODIUM HYDROXIDE SOLUTIONS AT 25°

Molality of NaOH, m_1	Molality of alanine, m_2	Heat capacity cal.$_{25}$ per °C. per g.[a]
0.08672	0	0.9939
.08671	0	.9959
.08672	0.03293	.9947
.08674	.03257	.9951
.08670	.02994	.9939
.08665	.02365	.9953
.08669	.01956	.9938
.08676	.00534	.9933
.08673	.00516	.9941
.03468	0	.9975
.03470	0	.9971
.03468	0.03592	.9980
.03472	.02195	.9975
.03469	.00896	.9981
.01454	0	not determined
.01595	0	0.9991
.01548	0.03455	.9969
.01548	.02269	.9980
.01548	.00911	.9981
.00645	0	1.0014
.00439	0	not determined
.00439	0.01122	0.9987
.00439	.00703	.9979
.00439	.00435	.9985

[a] 1 cal.$_{25}$ = 4.1788 joules (int.); Osborne, Stimson and Ginnings, *Bur. Standards J. Research*, **23**, 197 (1939).

values for glycine and alanine, together with the ionization heats of these amino acids calculated in two different ways from the temperature variation of the ionization constants as determined by measurements of the e. m. f.'s of cells without liquid junctions. As was found to be true for glycine, it is seen that the calorimetric and e. m. f. values for alanine show only fair agreement in the acid ionization heat and excellent agreement in the case of ΔH^0_B (leaving out of consideration the second e. m. f. value given for ΔH^0_B). It is particularly interesting to note the close parallelism between the e. m. f. and calorimetric values for ΔH^0_A; the e. m. f. value for glycine is about 46%
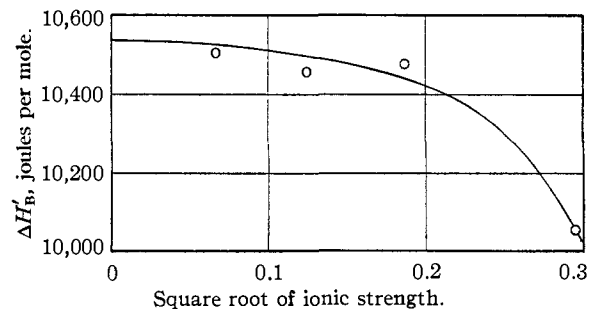

Fig. 3.—The heat of the basic ionization of alanine at 25°.

TABLE VII

IONIZATION HEATS OF GLYCINE AND *dl*-ALANINE AT 25°

		Glycine			*dl*-Alanine	
		E. m. f.		Calorimetric	E. m. f.		Calorimetric
ΔH_A^0	joules per mole	$4915^{b,c}$	4602^d	3891^e	$3368^{f,c}$	3347^g	2585^h
	calories^a per mole	$1175^{b,c}$	1100^d	930^e	$805^{f,c}$	800^g	615^h
ΔH_B^0	joules per mole	$11570^{b,c}$	11710^d	11591^e	$10713^{f,c}$	7605^g	10540^h
	calories^a per mole	$2765^{b,c}$	2800^d	2771^e	$2561^{f,c}$	1818^g	2520^h

^{a} One calorie (defined) = 4.1833 international joules. ^{b} Owen, THIS JOURNAL, **56**, 24 (1934). ^{c} Harned and Owen, *Chem. Rev.*, **25**, 31 (1939). ^{d} Recalculation of Owen's data by Everett and Wynne-Jones, *Trans. Faraday Soc.*, **35**, 1380 (1939). ^{e} Sturtevant, ref. 1. ^{f} Smith, Taylor and Smith, *J. Biol. Chem.*, **122**, 109 (1937). ^{g} Recalculation of data of Smith, Taylor and Smith by Everett and Wynne-Jones, ref. d. ^{h} Present research.

higher than that for alanine, while the calorimetric value for glycine is about 51% higher. Thus this large difference between glycine and alanine can be considered as firmly established.

If we consider ZH^+ as a dibasic acid, then its ionization heats are related to ΔH_A^0 and ΔH_B^0 as follows: $\Delta H_{A_1}^0 = \Delta H_A^0$; $\Delta H_{A_2}^0 = \Delta H_W^0 - \Delta H_B^0$. Taking the value $\Delta H_W^0 = 55,881$ joules per mole given by Pitzer,[16] we obtain $\Delta H_{A_2}^0 = 45,341$ joules per mole, or 10,838 defined calories per mole.

(16) Pitzer, THIS JOURNAL, **59**, 2365 (1937).

Summary

Calorimetric measurements of the heats of neutralization of *dl*-alanine by hydrochloric acid and sodium hydroxide at 25° are reported. A double extrapolation of the results is employed to give values of the acidic and basic ionization heats. The heat of the acid ionization of alanine is about two-thirds that of glycine, while the heat of the basic ionization of alanine is about nine-tenths that of glycine.

The Dipole Moments and Structures of Diketene and of Certain Acid Anhydrides and Related Oxygen and Sulfur Compounds

BY PETER F. OESPER AND CHARLES P. SMYTH

The dipole moments of diketene, benzoic anhydride, benzoyl peroxide, benzoyl persulfide, and diphenyl sulfone have been measured in benzene solution in order to study their molecular structures. These structures have in common the fact that carbonyl or sulfone groups may rotate about some axis in them giving rise to the possibility of change in dipole moment, which may be influenced by steric hindrances, resonance or both.

Purification of Materials

Diketene.—A sample, kindly presented to us by Dr. A. B. Boese of the Carbide and Carbon Chemicals Corporation, was brought by hand from Pittsburgh and kept at low temperature until the measurements were made.

Benzoic Anhydride.—Material from the Eastman Kodak Company was used without purification; m. p. 43°.

Benzoyl Peroxide.—Material from the Eastman Kodak Company was recrystallized from alcohol; m. p. 104–105°.

Benzoyl Persulfide.—Material from the Eastman Kodak Company was recrystallized from ether; m. p. 127–128°.

Diphenyl Disulfone.—A sample was kindly given us by Dr. H. E. Westlake.

Benzene.—The purification was carried out in the usual manner.[1] The dielectric constant and density of the benzene were measured every day on which the solutions in it were run, the values being given in Table I.

Experimental Results

The dielectric constants, ϵ, at 520 kilocycles and the densities, d, of benzene solutions containing mole fractions c_2 of the polar compound were measured as in previous work.[2] The data are listed in Table I, together with the polarizations calculated from them. Table II lists in the second column the values of MR_D, the molar refraction for the D sodium line, the value for diketene being

(1) Smyth and Walls, THIS JOURNAL, **54**, 1854 (1932).
(2) Lewis and Smyth, *J. Chem. Phys.*, **7**, 1085 (1939); THIS JOURNAL, **61**, 3063 (1939).