on the temperature, and the absolute accuracy of the bath depends solely on the purity of the water. By repeating the washing occasionally the constancy can be maintained almost indefinitely. Air-saturation is easily secured and still more easily tested.

With a sealed bulb giving the triple point of water as a temperature standard there should be no error from conduction down the thermometer. Impurity in the water, however, is exceedingly troublesome, since it is both concentrated and transported by the freezing, and the configuration is continually changing. A particular method of freezing gives a relief which is excellent but only temporary, and then there seems to be no way to avoid beginning preparations all over again. Hence the triple point, while convenient and reliable for a short job, is less so than the above-described "ice-point" for continuous work. If the impurity is small enough in comparison to the requirements, however, the triple-point apparatus is excellent, though it requires more attention and work than the cold cell.

WASHINGTON, D. C. RECEIVED AUGUST 2, 1933

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Dissociation Constants of Glycine at Various Temperatures

BY BENTON BROOKS OWEN

Recently[1,2,3] it was shown that the dissociation constants and activity coefficients of weak electrolytes (including ampholytes) can be obtained from measurements of the electromotive forces of cells without liquid junctions. In applying the method to glycine,[2] the activity coefficient calculations were complete, but it was pointed out that the dissociation constants were "apparent" because insufficient data were at hand to correct for the medium effect of the glycine ions. The true (thermodynamic) dissociation constants have been evaluated in the present paper.

Discussion of the Methods

The acid dissociation constant was determined by the method of Harned and Owen,[2] making use of cells of the type

$$H_2/Z^{\pm}(m_1),\ HZCl(m_2)/AgCl,\ Ag \qquad (A)$$

Neutral glycine is represented by $Z^{\pm}$, and glycine hydrochloride by HZCl. Two stock solutions were prepared with slightly different values of the ratio, m_1/m_2, and these, in various dilutions, constitute Series A1 and A2 for which the data are given in Table I. The "apparent" hydrogen ion concentrations, m'_{H^+}, were calculated by the equation

$$E/k - E^\circ/k + 2 \log \overset{\circ}{\gamma}_{HCl} + \log m_2 = -\log m'_{H^+} \quad [20']^4 \qquad (1)$$

in which $k = RT2.3026/F$, and $\overset{\circ}{\gamma}_{HCl}$ is the activity coefficient of hydrochloric acid in pure water solution at the concentration m_2. Values of $\overset{\circ}{\gamma}_{HCl}$ were read from plots of the data of Harned and Ehlers,[5] and E° was calculated from Equation (7) of the same paper.

Representing the acid dissociation of glycine by $ZH^+ = Z^{\pm} + H^+$, and the true and apparent dissociation constants, respectively, by

$$K_A = k'_A \gamma'_{Z^{\pm}} \gamma'_{H^+}/\gamma'_{ZH^+} \quad [6'] \qquad (2)$$

and

$$k_A = m'_{Z^{\pm}} m'_{H^+}/m'_{ZH^+} = (m_1 + m'_{H^+})m'_{H^+}/(m_2 - m'_{H^+}) \qquad (3)$$

it follows that K_A is obtained by extrapolation to $\mu = 0$ on a plot of log k'_A against μ. The necessary data are given in Table I. The extrapolation is illustrated in Fig. 1, and the values of log K_A are collected in Table II.

The basic dissociation constant was determined by the method of Harned and Ehlers,[3] making use of cells of the type

$$H_2/Z^{\pm}(m_1),\ NaG(m_2),\ NaCl(m_3)/AgCl,\ Ag \qquad (B)$$

in which NaG represents sodium glycinate. The electromotive force of this cell is expressed by

$$E/k - E^\circ/k = -\log m_{H^+} m_{Cl^-} \gamma_{H^+} \gamma_{Cl^-} \qquad (4)$$

Representing the basic dissociation of glycine by $G^- + H_2O = Z^{\pm} + OH^-$, and the true dissociation constant by

$$K_B = \frac{m_{Z^{\pm}} m_{OH^-} \gamma_{Z^{\pm}} \gamma_{OH^-}}{m_{G^-} \gamma_{G^-} a_w} \quad [7] \qquad (5)$$

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(1) Harned and Owen, THIS JOURNAL, **52**, 5079 (1930).

(2) Harned and Owen, *ibid.*, **52**, 5091 (1930).

(3) Harned and Ehlers, *ibid.*, **54**, 1350 (1932).

(4) Numbers enclosed in brackets refer to the corresponding Equation numbers in Ref. 2.

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

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS OF TYPES A AND B

$m_2 \times 10^6$	10°	15°	20°	25°	30°	35°	40°	45°
	Series A1		$m_1/m_2 = 1.1301$					
5126			0.52135	0.52281	0.52416		0.52656	
6449	0.51122		.51376	.51502	.51618		.51827	
6833			.51157	.51282	.51389		.51599	
8483			.50450	.50556	.50659		.50834	
10237	.49665		.49870	.49967	.50038		.50197	
14107	.48728		.48890	.48956	.49030		.49146	
14833			.48725	.48797	.48860		.48988	
27022			.47043	.47084	.47113		.47157	
37740	.46144		.46195	.46210	.46230		.46241	
37740	.46151		.46203	.46224	.46235		.46257	
	Series A2		$m_1/m_2 = 1.2981$					
6917	0.51025		0.51301	0.51434	0.51553		0.51750	
6970	.51014		.51275	.51411				
7263	.50895		.51158	.51262	.51386		.51579	
9497	.50083		.50315	.50404	.50501		.50667	
11948	.49412		.49599	.49696				
15016	.48764		.48933	.49011	.49076		.49190	
25696	.47353		.47456	.47510	.47545		.47605	
41200	.46223		.46269	.46285	.46301		.46315	
41200	.46235		.46274	.46294				
$m_3 \times 10^6$	Series B1		$m_1/m_3 = 1.0187$		$m_2/m_3 = 0.98487$			
4659	0.93427	0.93542	0.93651	0.93750		0.93920		0.94042
5477			.93264	.93356	0.93441	.93510	0.93573	.93627
5661			.93161	.93252	.93335	.93408	.93469	.93528
6998				.92734		.92867		.92961
8627			.92132	.92208	.92271	.92318	.92372	.92407
11892	.91240	.91315	.91383	.91439	.91486	.91527		
23135	.89656	.89705	.89747	.89778	.89800	.89820		
24530	.89511	.89566	.89609	.89637		.89674		.89664
25440				.89555		.89588		.89571
34488	.88710	.88750	.88779	.88796	.88799	.88804		
36960			.88609	.88627	.88635	.88626	.88612	.88588
50907			.87830	.87841	.87835	.87823	.87794	.87758
	Series B2		$m_1/m_3 = 0.83826$		$m_2/m_3 = 0.95276$			
6231			0.93316	0.93411	0.93498	0.93572	0.93637	0.93692
8902			.92472	.92547	.92616	.92675	.92722	.92763
9166			.92389	.92472	.92541	.92600	.92649	.92687
16218			.90992	.91056	.91104	.91140	.91165	.91186
26604			.89794	.89829	.89852	.89865	.89866	.89865
40535			.88778	.88799	.88806	.88798	.88786	.88765
54955			.88048	.88058	.88052	.88035	.88009	.87974

equations (4) and (5) may be combined with the dissociation constant for water, K_w, to yield

$$E/k - E^\circ/k + \log K_w + \log m_{Cl^-} m_{Z^\pm}/m_{G^-} = \log K_B - \log \gamma_{Cl^-} \gamma_{Z^\pm}/\gamma_{G^-} \quad (6)$$

Here $m_{Cl^-} = m_3$, $m_{G^-} = m_2 - m_{OH^-}$, and $m_{Z^\pm} = m_1 + m_{OH^-}$. The left side of equation (6) is therefore known if m_{OH^-} can be estimated. For this purpose it is sufficient to set $m_{OH^-} = K_B m_2/m_1$ as a first approximation, and use a rough value of K_B obtained from equation (6) by neglecting m_{OH} and the last term on the right. Then by plotting the left side of equation (6) against μ, log K_B is obtained by extrapolation to $\mu = 0$. If the value of K_B thus obtained differs[6] from the one employed, m_{OH^-} must be reapproximated using the new value of K_B. Finally, by successive approximations and extrapolations, a correct, unvarying value of K_B is obtained. The values of K_w were taken from the paper of Harned and Hamer.[7] The necessary data are given in Table I, and the extrapolations illustrated in Fig. 2. Table II contains the values of log K_B.

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[6] *Cf.* footnote, Reference 3, p. 1351.

[7] Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933).

Materials and Technique

Eastman ammonia-free glycine was precipitated once by methanol and recrystallized four times from conductivity water. It was kept thereafter in a vacuum desiccator over solid potassium hydroxide, occasionally renewed. Its moisture content was determined as follows.

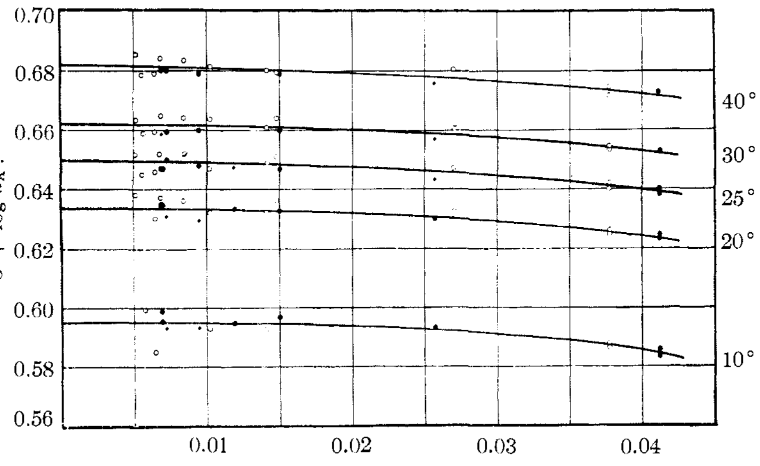

Fig. 1.—The acid dissociation of glycine: ○, series A1; ●, series A2.

A 20-g. sample, maintained at 103 to 107° in air, lost 0.19% in weight in two days, and a further 0.02% in ten days. A fifteen gram sample, maintained at 100° in the vacuum produced by a Cenco-megavac pump, operating continuously, was weighed hourly for thirteen hours. The loss in weight approached 0.16% asymptotically. The purity of the glycine was therefore taken as 99.8%. A series of small samples and stock solution B1 were analyzed by a micro-Kjeldahl method,[8] which confirmed this figure.

Baker "Analyzed" sodium chloride was precipitated by hydrogen chloride, ignited and recrystallized three times from conductivity water. It was dried overnight at 110° before being used.

The sodium hydroxide was Baker "Analyzed." The carbonate was allowed to settle from a 50% solution of the hydroxide. Standardization, storage, dilution and all subsequent manipulation of this, as well as all other solutions, were carried out in an atmosphere of tank hydrogen purified by passage over red hot copper turnings, and through a soda-lime tower. Full details of this technique are given elsewhere.[2] Benzoic acid and acid potassium phthalate from the Bureau of Standards were used as alkalimetric standards.

The hydrochloric acid was Baker "Analyzed," redistilled. It was standardized gravimetrically, and also against the sodium hydroxide. All standardizations were repeated before the preparation of each of the stock solutions. All concentrations were known to the nearest 0.1%.

For Series A1, B1 and B2 the cells were those previously employed by Ehlers,[3,5] and were filled under vacuum. For Series A2 simpler, smaller cells were used, and filling was carried out under pressure of pure hydrogen. In this series the electrodes were allowed to stand overnight in small portions of the solutions. Electrodes were of the usual type employed by Harned and his co-workers, and were freshly prepared for each cell. Cells were measured in duplicate, and the mean of their electromotive forces recorded. The average difference between duplicate cells was about 0.05 mv. Where this difference exceeded 0.2 mv. the measurements were discarded.

Discussion of Results

The observed dissociation constants contained in Table II can be accurately expressed by the empirical equations

$$\log K_A = -2.4514 + 0.0052t - 0.000047t^2 \quad (7)$$

and

$$\log K_B = -4.4200 + 0.0093t - 0.000050t^2 \quad (8)$$

By substituting the derivatives in the van't Hoff equation, the corresponding heats of dissociation were calculated at various temperatures and included in Table II. These values can be reproduced exactly by

$$\Delta H_A = 1773 - 18.6t - 0.24t^2 \text{ calories} \quad (9)$$

and

$$\Delta H_B = 3170 - 10.2t - 0.24t^2 \text{ calories} \quad (10)$$

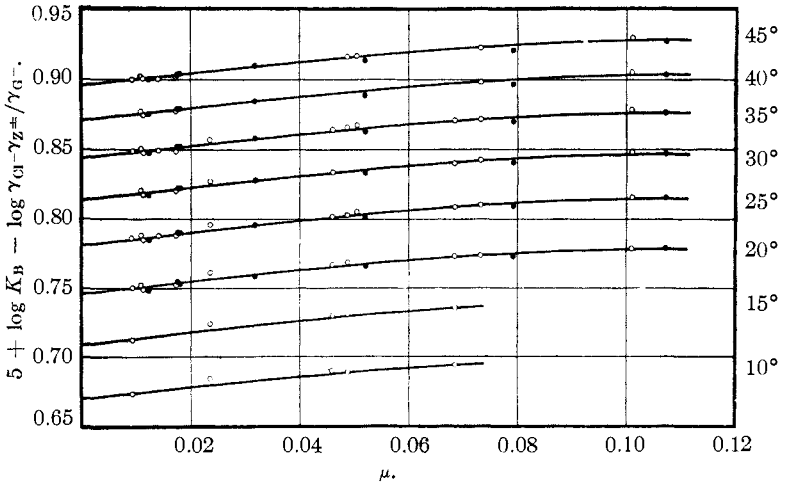

Fig. 2.—The basic dissociation of glycine: ○, series B1; ●, series B2.

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[8] The author takes pleasure in acknowledging his indebtedness to Professor David I. Hitchcock, of the Department of Physiology, for these analyses [Hitchcock and Belden, *Ind. Eng. Chem., Anal. Ed.*, **5**, 402 (1933)].

TABLE II

THE DISSOCIATION CONSTANTS AND HEATS OF DISSOCIATION OF GLYCINE

t, °C.	10°	15°	20°	25°	30°	35°	40°	45°
$3 + \log K_A$	0.595	0.616[a]	0.634	0.650	0.662	0.673[a]	0.682	0.687[a]
$5 + \log K_B$	.670	.709	.746	.781	.814	.844	.871	.896
ΔH_A (cal.)	1562	1439	1305	1159	1000	829	646	449
ΔH_B (cal.)	3044	2962	2869	2765	2648	2519	2377	2222

[a] Calculated by Equation (7).

In view of the wide disagreement among the values of K_A and K_B reported in the literature, and the fact that their evaluation involved the estimation or "elimination" of liquid junction potentials, a critical comparison with earlier values will not be attempted.[9] Heats of dissociation, depending upon the temperature coefficient of the electromotive force rather than upon its absolute magnitude, are in more satisfactory agreement. Thus, Bjerrum and Unmack[10] found $\Delta H_A = 1510$ cal. between 0 and 37°, and $\Delta H_B = 2710$ cal. at 25°.

Although Harned and Owen[2] expressed the opinion that the apparent constants, k_A° and k_B°, determined by them were probably within 1% of the true constants, K_A and K_B, the observed differences are, respectively, 8 and 6% of the former, recalculated to conform to the same values of E° and RT/F. If this difference is not entirely due to the medium effect of glycine ions, but is due in part to analytical errors, it is obvious that the latter are much less probable in the present research. Moreover, the *effects* of some of the uncertainties, discussed below, are much greater in the former, unbuffered measurements.

The estimated numerical uncertainty of the present results is of the order of ±0.002 in the logarithms of the constants, or ±0.5%. It is difficult to estimate the *absolute* accuracy of these figures. An uncertainty of 0.1 mv. in E or E° causes an error of 0.5% in K_A, and the effect of a 0.2% error in the purity of the glycine, or in the preparation of stock solutions, is almost as great. An uncertainty of only 0.01% in the accepted value of RT/F becomes 0.1% in terms of K_A.[11] Perhaps the limiting factors in the attainment of absolute accuracy are the purity of the glycine and the exclusion of oxygen and carbon dioxide from the solutions. Special attention was given to the former, and experimental precautions were taken to discern contamination by air. Thus duplicate cells and duplicate stock solutions were used to detect flaws in manipulation, and the technique was changed in Series A2 to discover systematic errors.

Summary

The acid and basic dissociation constants and heats of dissociation of glycine have been determined in aqueous solution from 10 to 40°, and from 10 to 45°, respectively. The results observed at 25° are, $K_A = 4.47 \times 10^{-3}$, $K_B = 6.04 \times 10^{-5}$, ($K_a = 1.67 \times 10^{-10}$, $K_b = 2.26 \times 10^{-12}$), $\Delta H_A = 1159$ cal., $\Delta H_B = 2765$ cal., ($\Delta H_a = 10{,}716$ cal., and $\Delta H_b = 12{,}322$ cal.).

NEW HAVEN, CONN. RECEIVED AUGUST 3, 1933

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[9] Readers desiring to make this comparison should consult the compilation by Branch and Miyamoto [THIS JOURNAL, **52**, 863 (1930)], and also Reference 10. The equations $K_a = K_w/K_B$, $K_b = K_w/K_A$, $K_0' = K_A$, and $K_0'' = K_w/K_B$ will correlate the different systems of notation with our own.

[10] Bjerrum and Unmack, *D. Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.*, **9**, 1 (1929).

[11] The value of K_B is of course influenced by any uncertainty in the values of K_w employed (Reference 7), but this error can be eliminated by converting K_B to K'' or K_a (Reference 9) with the same values of K_w.