ionic strength and, further, we believe that it is valid, or very nearly so at all salt concentrations. This latter statement may be verified by computing the activity coefficients relative to unity in a given solvent at various concentrations of the undissociated acid molecule. The results thus obtained agree reasonably with what is to be expected according to the Debye and Hückel theory. Since Harned and Robinson considered this matter, we have not considered it in detail in the present investigation.

3. Our value of 1.75×10^{-5} for the dissociation constant of acetic acid agrees closely with 1.785×10^{-5}, recently computed by Davies[8] by applying viscosity corrections to the conductivity data of Kendall.[9] On the other hand, our value of 1.77×10^{-4} for formic acid is considerably lower than 1.87×10^{-4} obtained by Davies with an extrapolation of Auerbach and Zeglin's[10] conductivity data at 18°.

4. Values for the dissociation constants of ammonia, and the mono-, di- and trimethylamines were computed by the same method from Harned and Robinson's data, and compared with those recently compiled.

5. The present investigation, following that of Harned and Robinson, demonstrates how it is possible, from measurements of cells without liquid junction, to evaluate the thermodynamic behaviors of weak acids and bases in salt solutions, and to determine their dissociation constants by a method which is thermodynamically exact.

New Haven, Connecticut

[Contribution from the Sterling Chemistry Laboratory of Yale University]

THE ACID AND BASE CONSTANTS OF GLYCINE FROM CELLS WITHOUT LIQUID JUNCTION[1]

By Herbert S. Harned and Benton B. Owen

Received June 11, 1930 Published December 18, 1930

In this study of aqueous solutions of glycine, we shall assume with Bjerrum[2] that the neutral ampholyte molecule in solution exists as "zwitterion," to be designated hereafter "amphion," but our numerical results do not depend upon the validity of this assumption. We further assume complete dissociation of sodium glycinate and glycine hydrochloride in the solutions with which we are concerned, thus

$$ClNH_3CH_2COOH \longrightarrow Cl^- + {}^+NH_3CH_2COOH, \text{ and}$$
$$NH_2CH_2COONa \longrightarrow Na^+ + NH_2CH_2COO^-$$

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[8] Davies, *Phil. Mag.*, [7] **4**, 244 (1927).

[9] Kendall, *J. Chem. Soc.*, 101, 1285 (1912).

[10] Auerbach and Zeglin, *Z. physik. Chem.*, **103**, 191 (1923).

[1] This paper represents part of the dissertation presented by Benton B. Owen to the Graduate School of Yale University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Bjerrum, *Z. physik Chem.*, **104**, 147 (1923).

or if the sodium glycinate be hydrated

$$\mathrm{HONH_3CH_2COONa} \longrightarrow \mathrm{Na^+ + HONH_3CH_2COO^-}$$

The amphcation and amphanion being weak electrolytes, their incomplete dissociation may be represented by

$$\begin{gathered}
\mathrm{^+NH_3CH_2COOH} \rightleftharpoons \mathrm{^+NH_3CH_2COO^- + H^+}, \text{ and}\\
\mathrm{H_2O + NH_2CH_2COO^-} \rightleftharpoons \mathrm{^+NH_3CH_2COO^- + OH^-}, \text{ or}\\
\mathrm{HONH_3CH_2COO^-} \rightleftharpoons \mathrm{^+NH_3CH_2COO^- + OH^-}
\end{gathered}$$

For reasons of simplicity we shall hereafter write G^- for the amphanion, $\mathrm{NH_2CH_2COO^-}$, $Z^{\pm}$ for the amphion, $\mathrm{^+NH_3CH_2COO^-}$, $\mathrm{ZOH^-}$ for the hydrated amphanion, $\mathrm{HONH_3CH_2COO^-}$, and $\mathrm{ZH^+}$ for the amphcation, $\mathrm{^+NH_2CH_2COOH}$. The above equations then become

$$\mathrm{ClZH} \longrightarrow \mathrm{Cl^- + ZH^+} \tag{1}$$

$$\mathrm{NaG} \longrightarrow \mathrm{Na^+ + G^-} \tag{2}$$

$$\mathrm{NaZOH} \longrightarrow \mathrm{Na^+ + OH^-} \tag{2a}$$

and

$$\mathrm{ZH^+} \rightleftharpoons \mathrm{Z^{\pm} + H^+} \tag{3}$$

$$\mathrm{H_2O + G^-} \rightleftharpoons \mathrm{Z^{\pm} + OH^-} \tag{4}$$

$$\mathrm{ZOH^-} \rightleftharpoons \mathrm{Z^{\pm} + OH^-}, \text{ and} \tag{4a}$$

$$\mathrm{H_2O + G^-} \rightleftharpoons \mathrm{ZOH^-} \tag{5}$$

The exact thermodynamic equations for the acid and base equilibria in water, in the absence of any effect upon the medium due to the presence of glycine, we represent by

$$K_{\mathrm{A}} = \frac{\gamma_{\mathrm{Z^{\pm}}}\,\gamma_{\mathrm{H^+}}}{\gamma_{\mathrm{ZH^+}}}\,\frac{m_{\mathrm{Z^{\pm}}}\,m_{\mathrm{H^+}}}{m_{\mathrm{ZH^+}}} = \gamma_{\mathrm{A}}^2\,k_{\mathrm{A}} \tag{6}$$

$$K_{\mathrm{B}} = \frac{\gamma_{\mathrm{Z^{\pm}}}\,\gamma_{\mathrm{OH^-}}}{\gamma_{\mathrm{G^-}}\,a_{\mathrm{H_2O}}}\,\frac{m_{\mathrm{Z^{\pm}}}\,m_{\mathrm{OH^-}}}{m_{\mathrm{G^-}}} = \gamma_{\mathrm{B}}^2\,k_{\mathrm{B}}, \text{ or} \tag{7}$$

$$K_{\mathrm{B}} = \frac{\gamma_{\mathrm{Z^{\pm}}}\,\gamma_{\mathrm{OH^-}}}{\gamma_{\mathrm{ZOH^-}}}\,\frac{m_{\mathrm{Z^{\pm}}}\,m_{\mathrm{OH^-}}}{m_{\mathrm{ZOH^-}}} = \gamma_{\mathrm{Bh}}^2\,k_{\mathrm{Bh}}, \text{ and} \tag{7a}$$

$$K_{\mathrm{h}} = \frac{\gamma_{\mathrm{ZOH^-}}}{\gamma_{\mathrm{G^-}}\,a_{\mathrm{H_2O}}}\,\frac{m_{\mathrm{ZOH^-}}}{m_{\mathrm{G^-}}}. \tag{8}$$

The "γ's" are the activity coefficients, and the "m's" the molal concentrations of the species denoted by the subscripts. K_{h} is the equilibrium constant for the hydration of the glycinate ion, and K_{A} and K_{B} are the dissociation constants defined by Bjerrum for glycine as acid and base, respectively. k_{A}, and k_{B} or k_{Bh}, are the concentration terms in these constants, and γ_{A}, and γ_{B} or γ_{Bh}, the corresponding activity coefficients

$$\sqrt{\frac{\gamma_{\mathrm{Z^{\pm}}}\,\gamma_{\mathrm{H^+}}}{\gamma_{\mathrm{ZH^+}}}},\quad \sqrt{\frac{\gamma_{\mathrm{Z^{\pm}}}\,\gamma_{\mathrm{OH^-}}}{\gamma_{\mathrm{G^-}}\,a_{\mathrm{H_2O}}}}\quad \text{or}\quad \sqrt{\frac{\gamma_{\mathrm{Z^{\pm}}}\,\gamma_{\mathrm{OH^-}}}{\gamma_{\mathrm{ZOH^-}}}}$$

Now in the measured solutions some neutral glycine is always present in varying amounts. This alters the properties of the medium, the dielectric constants for example,[3] and, therefore, influences the activity coefficients. This "medium effect" has been examined in some detail in a pre-

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[3] Neutral glycine increases the dielectric constant of water [Fürth, *Ann. Physik*, **70**, 63 (1923)].

vious communication by the authors,[4] and will be referred to later in this paper, so for the present it will only be necessary to state that our measurements yield "apparent" values of the concentrations and activity coefficients defined by the equations

$$K_A = \frac{\gamma'_{Z\pm}\,\gamma'_{H^+}}{\gamma'_{ZH^+}}\,\frac{m'_{Z\pm}\,m'_{H^+}}{m'_{ZH^+}} = \gamma'^2_A k'_A \tag{6'}$$

$$K_B = \frac{\gamma'_{Z\pm}\,\gamma'_{OH^-}}{\gamma'_{G^-}\,a'_{H_2O}}\,\frac{m'_{Z\pm}\,m'_{OH^-}}{m'_{G^-}} = \gamma'^2_B k'_B, \text{ or} \tag{7'}$$

$$K_B = \frac{\gamma'_{Z\pm}\,\gamma'_{OH^-}}{\gamma'_{ZOH^-}}\,\frac{m'_{Z\pm}\,m'_{OH^-}}{m'_{ZOH^-}} = \gamma'^2_{Bh} k'_{Bh}, \text{ and} \tag{7a'}$$

$$K_h = \frac{\gamma'_{ZOH^-}}{\gamma'_{G^-}\,a'_{H_2O}}\,\frac{m'_{ZOH^-}}{m'_{G^-}} \tag{8'}$$

It is important to note that the present investigation does not enable us to differentiate between the hydrated and unhydrated amphanion. We obtain numerical values for a "γ" which may be either γ_B or γ_{Bh}, and a "k" which may be either k_B or k_{Bh}. This is another illustration of the fact that thermodynamics alone does not yield information regarding the nature of the species present or the process taking place. Therefore, for reasons of convenience, we shall employ Equations 6, 7, 6′ and 7′ and keep the mathematical expressions in formal agreement with those of Bjerrum.

The "medium effect" is a function of the concentration, M, of the weak electrolyte causing a variation in the medium, and its evaluation requires the study of a series of apparent concentrations for several values of M. In this first study of ampholytes by cells without liquid junction, time restricted the measurements to one value of M only, and for this value we selected 0.1. This concentration is high enough to prevent certain experimental difficulties with the electrodes, and small enough to involve only a very small medium effect (probably of the order of 1%). Although we cannot evaluate the small medium effect in this research, we will consistently employ equations which take it into account (primed equations), so that this preliminary paper may serve both as an illustration of the method, and as an exact basis for a more detailed investigation, now under way, concerning the medium effect in glycine solutions.

Experimental Procedure

The cell measurements involved the use of 0.1 molal solutions of glycine hydrochloride, sodium glycinate and sodium hydroxide. Although alkaline solutions of glycine are relatively stable toward boiling, they are rapidly decomposed by oxygen in the presence of finely divided copper.[5] Because of the platinum black on the hydrogen electrodes, it was considered necessary to remove all traces of oxygen from the solutions

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[4] Harned and Owen, THIS JOURNAL, **52**, 5079 (1930).

[5] Traube and Schönewald, *Ber.*, **39**, 184 (1906).

during their preparation, and to take every precaution to exclude contact with air during transfer to the cells. An approximately molal solution of sodium hydroxide was prepared by decanting sufficient saturated sodium hydroxide into a flask of thoroughly boiled distilled water, cooled in a stream of hydrogen, and kept thereafter under a pressure of this gas slightly above atmospheric. The solution was standardized against molar hydrochloric acid by means of a 500-cc. weight buret fitted with stopcocks allowing it to be filled and used in an atmosphere of hydrogen only. Next, a six-liter pyrex flask was fitted with a siphon tube bearing a three-way stopcock, an inlet tube with stopcock and a short filling tube bearing a 5-mm. bore stopcock through which the tip of the weight buret could be thrust against a stream of escaping hydrogen. Thirty-five grams of dry ammonia-free glycine was weighed into this flask with sufficient water to make the solution 0.1 molal in sodium glycinate (allowance being made for the water to be added later with the alkali). The glycine solution was boiled and cooled in a stream of pure hydrogen, and kept under a slight pressure of this gas. The boiling was done before the alkali was added to avoid the remote possibility that there might be some decomposition before the last traces of oxygen were removed. Then, by an approximate calibration of the weight buret, the calculated amount of sodium hydroxide solution was delivered into the flask through the large bore stopcock against a brisk counter current of hydrogen. Several weighings were necessary as the last few tenths of a cc. were added, but no air came in contact with the solutions during the manipulations. Since the flask had been tared, the weight of water lost during boiling was calculable, and an equal amount of water, previously boiled and cooled in hydrogen, was admitted through the large stopcock. A similar six-liter flask was fitted up, and in it was prepared an oxygen-free 0.1 molal solution of sodium hydroxide in the manner just described. This solution was to serve as reference solution in one side of the amalgam double cells. Since the same cells and technique are to be employed later with the glycine hydrochloride cells, the 0.1 molal glycine hydrochloride solution was prepared from glycine and molar hydrochloric acid solution in a manner similar to the sodium glycinate solution.

The addition of known amounts of salt to portions of the sodium glycinate solution was carried out in the following manner, and this method also applies *mutatis mutandis* to the glycine hydrochloride solution. Pure dry sodium chloride was weighed into 200-cc. solution flasks fitted with intake and delivery tubes bearing stopcocks. The flasks were then warmed and alternately evacuated and filled with hydrogen to remove the last traces of air, and finally filled with hydrogen. The delivery tube of the flask was then connected to the siphon tube of the sodium glycinate storage flask through a T-tube arranged so that it could be alternately evacuated and filled with hydrogen, thus permitting transfer of solution without the slightest contamination with air. The amount of solution received by the solution flask was then determined by weighing, and the molality of the sodium chloride calculated. The reference solution of 0.1 molal sodium hydroxide was transferred in a similar manner to solution flasks containing no salt.

The amalgam cells employed were of the usual type described by Harned[6] and Åkerlöf[7] except for minor alterations, and a slight reduction in size. In operation each cell contained about 75 cc. of solution, and each bubble tube about 25 cc. Before filling the cells they were fitted with solid rubber stoppers, and connected to the bubble tubes and solution flasks with thick rubber tubing, wired in place. Then the cells, bubble tubes and connections together were alternately exhausted and filled with hydrogen, and finally exhausted, so that when the stopcocks to the solution flasks were opened, the solutions were drawn into cells and bubble tubes containing traces of hydrogen and water vapor only. At this point the cells contained more solution than needed, so the

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[6] Harned, THIS JOURNAL, **47**, 676 (1925).

[7] Åkerlöf, *ibid.*, **48**, 1160 (1926).

excess was made to serve the purpose of excluding air while the limbs of the amalgam droppers and hydrogen electrodes were being substituted for the solid rubber stoppers closing the cells. Thus, while this replacement was being quickly made, the pressure of hydrogen from a bubble tube was forcing excess solution out of a cell between the rim and a stopper bearing an electrode, so that the time of simultaneous contact between electrode, air and solution was quite negligible. The amalgam droppers were fitted similarly.

The flow of hydrogen through the cells was begun immediately, and continued at the rate of about three bubbles per second for two or three hours before the flow of amalgam was begun. The droppers contained about 30 cc. of amalgam and required about six minutes to empty. The potentiometer was read thirty seconds after the flow of amalgam was begun, and then two or three times per minute thereafter. In general, the readings increased slightly during the first two or three readings, and then decreased steadily. The difference between the maximum and minimum readings varied roughly in an inverse manner with the salt concentration. Thus, for cells with zero salt concentration, the variation was 0.3 to 0.5 millivolt, while for 2 molal salt the difference was less than 0.1 millivolt.

The Determination of the Dissociation Constant and Activity Coefficient of Glycine as Base.—The electromotive force of the cell

$$\mathrm{H_2/NaOH(0.1)/Na_xHg/NaG(0.1),\ NaCl_{(m)}/H_2} \qquad \text{(I)}$$

at 25° is given by

$$E = 0.05915 \log \frac{(0.766)^2\,(0.1)^2\,a_{\mathrm{H_2O}}}{(\gamma_{\mathrm{NaOH}})^2\,(m + 0.1)\,m_{\mathrm{OH}}\,a_{\mathrm{H_2O(0.1)}}} \qquad (9)$$

where $a_{\mathrm{H_2O(0.1)}}$ is the activity of water in 0.1 M sodium hydroxide, and $a_{\mathrm{H_2O}}$ is its activity in the sodium glycinate–chloride solution; 0.766 is the value of the activity coefficient of 0.1 M sodium hydroxide given by Harned and Åkerlöf.[8] It is important to note that our final results are independent of this choice of reference value. We shall let $a_{\mathrm{H_2O(0.1)}}$ equal unity, and write Equation 9 as

$$16.9062\,E + 2.2315 + 2\log \frac{\gamma_{\mathrm{NaOH}}}{\sqrt{a_{\mathrm{H_2O}}}} + \log \mu = -\log m_{\mathrm{OH}} \qquad (10)$$

by which m_{OH} can be evaluated if we know $\gamma_{\mathrm{NaOH}}/\sqrt{a_{\mathrm{H_2O}}}$, the activity coefficient of sodium hydroxide in sodium glycinate–chloride solutions. This we do not know, but $\gamma^{\circ}_{\mathrm{NaOH}}/\sqrt{a^{\circ}_{\mathrm{H_2O}}}$, the activity coefficient of sodium hydroxide in sodium chloride solutions has been determined by Harned.[9] Substituting this value in Equation 10 we can calculate an apparent (unreal) hydroxyl-ion concentration defined by

$$16.9062\,E + 2.2315 + 2\log \frac{\gamma^{\circ}_{\mathrm{NaOH}}}{\sqrt{a^{\circ}_{\mathrm{H_2O}}}} + \log \mu = -\log m'_{\mathrm{OH}} \qquad (10')$$

and anticipated in Equations 6′ and 7′. Values[10] of $\gamma^{\circ}_{\mathrm{NaOH}}/\sqrt{a^{\circ}_{\mathrm{H_2O}}}$ were

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[8] Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

[9] Harned, THIS JOURNAL, **47**, 648 (1925).

[10] So long as m_{OH} is of the order of 0.01 molal or less, the values of the activity coefficient of sodium hydroxide in salt solutions are practically independent of m_{OH} and depend only upon μ. Consequently, we have employed the 0.01 sodium hydroxide series throughout.

recalculated from the data of Harned[9] to conform to the value 0.901, given by Harned and Åkerlöf,[8] for the activity coefficient of 0.01 molal sodium hydroxide in pure water. Table I contains these values at corresponding values of μ read from a plot. The electromotive force, E, is the mean of all the readings made on each cell while the amalgam was flowing, and differs only slightly from the weighted average, using only readings of greatest constancy, or the graphical average from a plot of e. m. f. against time. In the particular case of the cell for which $m = 0$, E is the mean of the "E's" of four such cells, which were 0.09771, 0.09713, 0.09713 and 0.09840. This illustrates the poor agreement at lowest salt concentrations. The values of m'_{OH} were calculated by Equation 10′, of log k'_B by the relation $\log k'_B = 2 \log m'_{OH} - \log (0.1 - m'_{OH})$ which follows from (7′). The value of log k'_B given in parentheses was obtained by extrapolation to infinite dilution of electrolyte, and is therefore log $\overset{\circ}{k}_B$, where $\overset{\circ}{k}_B$ is the apparent basic dissociation constant of glycine. Obviously, $\overset{\circ}{k}_B$ must differ from the real dissociation constant, K_B, because its calculation involves extrapolation with a line whose slope is a function of the specific properties of both sodium chloride and sodium glycinate, through the region $\mu = M$ to $\mu = 0$, in which sodium glycinate alone is present. The same kind of difficulty is encountered in the calculation of activity coefficients of slightly soluble substances by extrapolation of solubility data in salt solutions. K_B equals $\overset{\circ}{k}_B$ in the experimentally unrealizable case in which $M = 0$, or, as we have shown in our previous paper, K_B can be evaluated exactly by extrapolation of values of $\overset{\circ}{k}_B$ corresponding to several different values of M. In Fig. 1 (I) are plotted as plain circles the values of log k'_B against the ionic strength. The equation of the straight line drawn through the points is

TABLE I

THE THERMODYNAMIC PROPERTIES OF SODIUM GLYCINATE SOLUTIONS

0.1 Molal sodium glycinate, m molal sodium chloride. Amalgam electrodes (approximately 0.1% Na).

$\mu = 0.1 + m$	E	$2 \log \frac{\overset{\circ}{\gamma}_{NaOH}}{\sqrt{\overset{\circ}{a}_{H_2O}}}$	m'_{OH}	Log k'_B	Log γ_B
0.0	.....	....	......	(−4.2550)	0.0
.1	0.09759	$\bar{1}$.7532	0.002320	−4.2590	+ .0020
.2059	.08145	$\bar{1}$.6940	.002420	−4.2216	− .0167
.3241	.07216	$\bar{1}$.6610	.002382	−4.2357	− .0097
.4837	.06299	$\bar{1}$.6306	.002446	−4.2124	− .0213
.6163	.05786	$\bar{1}$.6136	.002437	−4.2155	− .0198
.7465	.05234	$\bar{1}$.5892	.002639	−4.1456	− .0547
1.0755	.04445	$\bar{1}$.5830	.002526	−4.1841	− .0355
1.5647	.03379	$\bar{1}$.5742	.002683	−4.1310	− .0620
1.7750	.03058	$\bar{1}$.5740	.002681	−4.1316	− .0617
2.1573	.02327	$\bar{1}$.5754	.002923	−4.0555	− .0998
2.7311	.01591	$\bar{1}$.5796	.003045	−4.0194	− .1178

$$\log k_B^\circ - \log k'_B = 2B_B\mu \tag{11}$$

and its intercept corresponds to $k_B^\circ = 5.56 \times 10^{-5}$. To calculate γ_B, the real basic activity coefficient of glycine, we cannot employ Equation 7 directly, because we know neither K_B or k_B. We have, however, demonstrated in our previous paper that $\log k'_B/k_B$ extrapolated to zero ionic strength becomes $\log k_B^\circ/K_B$, if we are justified in applying to a base this relation discovered for acids. We must also make use again of the hypothesis that this relationship is valid over a considerable range of ionic strengths, so that we may write

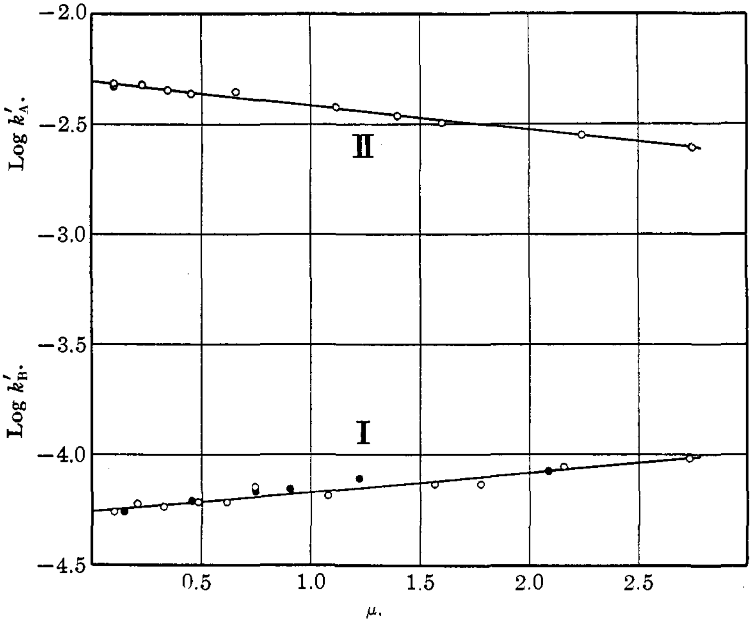

Fig. 1.—Apparent dissociation constants. I, basic; II, acidic.

$$\log \frac{k'_B}{k_B} = \log \frac{k_B^\circ}{K_B} \tag{12}$$

By combining this with Equation 7, we obtain

$$2 \log \gamma_B = \log k_B^\circ - \log k'_B \tag{13}$$

by which the values given in Table I were calculated. Substituting Equation 11 in 13, we deduce the important relation

$$\log \gamma_B = B_B\mu \tag{14}$$

illustrated by Fig. 2 (I). Indeed this linear variation of $\log \gamma_B$ with μ is to be expected from the nature of γ_B, for, by definition

$$2 \log \gamma_B = \log \gamma_{Z\pm} + \log \frac{\gamma_{OH^-}}{\gamma_{G^-}} - \log a_{H_2O} \tag{15}$$

Since $Z^{\pm}$ is neutral, the logarithm of its activity coefficient will vary linearly with the salt concentration in dilute or moderately dilute solutions. This is also to be expected for a ratio of ionic activity coefficients of ions of the same valence type. Furthermore, the linear variation of log a_{H_2O} will be a close approximation. Hence

$$\left.\begin{aligned} \log \gamma_{Z^{\pm}} &= B_Z\,\mu \\ \log \frac{\gamma_{OH^-}}{\gamma_{G^-}} &= (B_{OH} - B_G)\mu \\ \log a_{H_2O} &= B_{H_2O}\,\mu \end{aligned}\right\} \qquad (16)$$

and consequently (14) follows immediately from (15) and (16) by writing $2B_B = B_Z + B_{OH} - B_G - B_{H_2O}$. These considerations obviously account for the simple linear extrapolation of log k'_B through Equation 13.

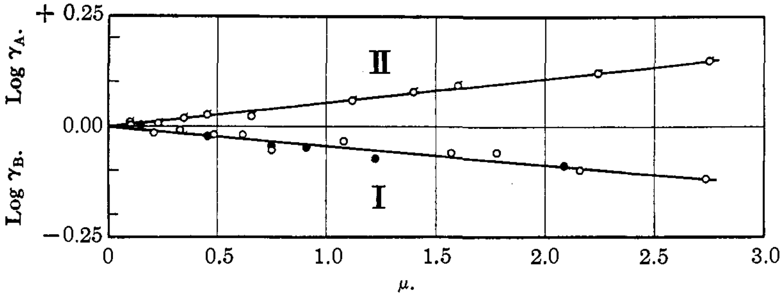

Fig. 2.—Activity coefficient of glycine. I, basic; II, acidic.

As an important check on the method just outlined, cells in which the silver–silver chloride electrode replaces the amalgam electrode have been employed, and found to give the same numerical results.[11] Since the use of silver–silver chloride single cells in place of amalgam double cells represents a considerable simplification of technique, and a great saving of time, we shall outline the method of calculating our results. It is realized, of course, that the general applicability of the method is limited by the fact that a large number of organic bases have a considerable solvent action upon silver chloride.

If the electromotive force of the reference cell

$$H_2/HCl(0.01)/AgCl/Ag;\quad +0.4644 \qquad (II)$$

be subtracted from that of the cell

$$H_2/NaG(0.1),\ NaCl(m)/AgCl/Ag,\ \text{or } + E \qquad (III)$$

we obtain the electromotive force, $E - 0.4644$, of a concentration cell without liquid junction. Thus

$$H_2/NaG(0.1),\ NaCl(m)/AgCl/Ag/AgCl/HCl(0.01)/H_2 \qquad (IV)$$

The equation relating E to the concentrations and activity coefficients is

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[11] Suggested by work recently conducted in this Laboratory by Dr. E. J. Roberts, [THIS JOURNAL, **52**, 3877 (1930)].

$$E - 0.4644 = 0.05915 \log \frac{(0.904)^2\ (0.01)^2}{(\gamma_{\mathrm{HCl}})^2\ m_{\mathrm{H}}m} \tag{17}$$

if the activity coefficient of 0.01 molal hydrochloric acid is taken to be 0.904, as given by Randall and Young.[12] m_{H} Is the hydrogen-ion concentration in the sodium glycinate solution. This equation permits the calculation of m_{H}, but since m_{OH} is desired, we must introduce the equilibrium expression for the dissociation of water

$$K_{\mathrm{w}} = \frac{\gamma_{\mathrm{H^+}}\ \gamma_{\mathrm{OH^-}}}{a_{\mathrm{H_2O}}}\, m_{\mathrm{H}}m_{\mathrm{OH}} = \gamma_{\mathrm{w}}{}^2 m_{\mathrm{H}}m_{\mathrm{OH}} \tag{18}$$

Giving K_{w} the numerical value[13] 1.005×10^{-14} and combining (17) and (18), we obtain

$$16.9062\, E - 17.7614 + 2 \log \gamma_{\mathrm{HCl}} - 2 \log \gamma_{\mathrm{w}} + \log m = -\log m_{\mathrm{OH}} \tag{19}$$

Just as in the derivation of Equation (10′), we must introduce known activity coefficients in sodium chloride solutions, in the place of unknown activity coefficients in sodium chloride solutions containing sodium glycinate also. In so doing, we define an apparent hydroxyl-ion concentration, m'_{OH}, thus

$$16.9062\, E - 17.7614 + 2 \log \gamma^{\circ}_{\mathrm{H}} - 2 \log \gamma^{\circ}_{\mathrm{w}} + \log m = -\log m'_{\mathrm{OH}} \tag{19′}$$

Table II contains the results of the measurements with silver–silver chloride electrodes. The average electromotive force, E, was measured (Cell III) over a period of at least four hours during which the maximum deviation from the mean did not exceed 0.05 millivolt. The values of $\log \gamma^{\circ}_{\mathrm{HCl}}$ were read from a plot of the data of Harned,[8] and the values of $\log \gamma^{\circ}_{\mathrm{w}}$ were obtained from a similar plot of $\gamma^{\circ}_{\mathrm{HCl}}$ and $\gamma^{\circ}_{\mathrm{NaOH}}/\sqrt{a^{\circ}_{\mathrm{w}}}$, and more recent values of $\gamma^{\circ}_{\mathrm{NaCl}}$ determined by Harned.[14] Column 5 contains the values of m'_{OH} computed by Equation 19′. The values of $\log k'_{\mathrm{B}}$ and $\log \gamma_{\mathrm{B}}$ were computed as in the preceding section, and are included in Figs. 1 and 2 as inked-in circles. It is obvious that the same straight

TABLE II

THE THERMODYNAMIC PROPERTIES OF SODIUM GLYCINATE SOLUTION BY THE SECOND METHOD

0.1 Molal Sodium Glycinate, m Molal Sodium Chloride; Silver Chloride Electrodes

$\mu = 0.1 + m$	E	$2 \operatorname{Log} \gamma^{\circ}_{\mathrm{w}}$	$2 \operatorname{Log} \gamma^{\circ}_{\mathrm{HCl}}$	m'_{OH}	$\operatorname{Log} k'_{\mathrm{B}}$	$\operatorname{Log} \gamma_{\mathrm{B}}$
0.1470	0.97173	$\bar{1}.7422$	$\bar{1}.7700$	0.002326	−4.2566	+0.0008
.4659	.92023	$\bar{1}.6980$	$\bar{1}.7286$	.002456	−4.2088	− .0231
.7459	.90620	$\bar{1}.7002$	$\bar{1}.7426$	.002579	−4.1657	− .0447
.9049	.90058	$\bar{1}.7120$	$\bar{1}.7584$	.002607	−4.1563	− .0494
1.2223	.89290	$\bar{1}.7378$	$\bar{1}.7938$	.002755	−4.1075	− .0738
2.0875	.87760	$\bar{1}.8314$	$\bar{1}.9144$	.002863	−4.0738	− .0906

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[12] Randall and Young, THIS JOURNAL, **50**, 989 (1928).

[13] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 486.

[14] Harned, THIS JOURNAL, **51**, 416 (1929).

lines will serve to represent both the plain and inked-in circles within the experimental error.

The Determination of the Dissociation Constant and Activity Coefficient of Glycine as Acid.—The type of cell used to evaluate the acid constants of glycine is identical to that used previously in the study of acetic[15] and formic[4] acids, and to Cell III of this research. Thus E, the measured electromotive force, applies to the cell

$$H_2/HZCl(0.1),\ NaCl(m)/AgCl/Ag;\quad E \qquad \text{(V)}$$

from which we subtract, as before, the electromotive force of Cell II to obtain the electromotive force of the complete concentration cell without liquid junction, *viz.*

$$H_2/HZCl(0.1),\ NaCl(m)/AgCl/Ag/AgCl/HCl(0.01)/H_2 \qquad \text{(VI)}$$

The equilibrium expression for this cell is

$$E - 0.4644 = 0.05915 \log \frac{(0.904)^2\ (0.01)^2}{(\gamma_{HCl})^2(m + 0.1)m_H} \qquad (20)$$

in which the significance of the symbols and numerical values is obvious from the discussion of Cell III. In simplifying this equation we shall simultaneously replace γ_{HCl} by the known function $\overset{\circ}{\gamma}_{HCl}$ and solve for the apparent hydrogen-ion concentration, thus

$$16.9062\,E - 3.7636 + 2 \log \overset{\circ}{\gamma}_{HCl} + \log \mu = -\log m'_H \qquad (20')$$

The experimental values of E are the averages of the readings taken on each cell over a period of at least four hours in which the maximum deviation from the mean was not over 0.08 millivolt. The values of log $\overset{\circ}{\gamma}_{HCl}$ were read from the same plot used for this purpose in Equation 19′, and are shown in Table III along with E, and m'_H calculated therefrom with the

TABLE III

THE THERMODYNAMIC PROPERTIES OF GLYCINE HYDROCHLORIDE IN SODIUM CHLORIDE SOLUTIONS

0.1 Molal Glycine Hydrochloride, m Molal Sodium Chloride; Silver Chloride Electrodes

$\mu = 0.1 + m$	E	2 Log $\overset{\circ}{\gamma}_{HCl}$	m'_H	Log k'_A	Log γ_A
0.0	.....	....	.....	(−2.3080)	0.0
.1	0.39531	$\bar{1}.7915$	0.01945	−2.3283	.0101
.1	.39495	$\bar{1}.7915$	.01972	−2.3146	.0033
.2278	.37644	$\bar{1}.7492$	.01962	−2.3198	.0059
.3436	.36746	$\bar{1}.7342$	.01910	−2.3460	.0190
.4525	.36110	$\bar{1}.7288$	.01881	−2.3607	.0263
.6546	.35101	$\bar{1}.7354$	.01897	−2.3527	.0224
1.1155	.33643	$\bar{1}.7816$	.01765	−2.4221	.0570
1.3961	.32980	$\bar{1}.8146$	.01692	−2.4627	.0774
1.5997	.32504	$\bar{1}.8408$	.01635	−2.4953	.0936
2.2424	.31254	$\bar{1}.9408$	.01542	−2.5509	.1215
2.7468	.30371	0.0292	.01449	−2.6100	.1510

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[15] Harned and Robinson, THIS JOURNAL, 50, 3158 (1928).

aid of Equation 20′. The values of $\log k'_A$ given in the fifth column were calculated by the relation $\log k'_A = 2 \log m'_H - \log (0.1 - m'_H)$, and are plotted in Fig. 1 (II). As in the case of the basic system, $\log k'_A$ is a linear function of μ, and the equation of the straight line is

$$\log k^\circ_A - \log k'_A = 2B_A\mu \qquad (21)$$

From similar concentrations to those by which we derived Equation 13, we may obtain the expression

$$2 \log \gamma_A = \log k^\circ_A - \log k'_A \qquad (22)$$

by which the values of $\log \gamma_A$ shown in Table III were calculated. Combination of Equations 21 and 22 leads to the important relation

$$\log \gamma_A = B_A\mu \qquad (23)$$

This linear variation of $\log \gamma_A$ with μ is demonstrated experimentally in Fig. 2 (II), and follows theoretically from the definition of γ_A. Thus, for

$$\log \gamma_A = \log \gamma_{Z\pm} + \log \frac{\gamma_{H^+}}{\gamma_{ZH^+}} \qquad (24)$$

we may write

$$\log \gamma_A = B_Z\mu + (B_H - B_{ZH})\mu = B_A\mu \qquad (25)$$

because the logarithm of the activity coefficient of a neutral particle and the ratio of two ionic activity coefficients of the same valence type are both linear functions of the ionic strength. The extrapolated value of $\log k'_A$ at infinite dilution of electrolyte is $\log k^\circ_A$, and is given in Table III in parentheses. This corresponds to the value 4.92×10^{-3} for k°_A.

Summary

1. Making use of 0.1 molal sodium glycinate and glycine hydrochloride solutions, the apparent dissociation constants of glycine have been measured at 25°. The values obtained are $k^\circ_A = 4.92 \times 10^{-3}$ and $k^\circ_B = 5.56 \times 10^{-5}$. For purposes of comparison, we may write $k^\circ_A = K_A$, and $k^\circ_B = K_B$, because, for the dilution we have used, the error introduced by this approximation is negligible compared to the discordance among the various values of K_A and K_B recorded in the literature. Branch and Miyamoto[16] list the results of six independent electrometric studies of glycine besides their own. If we include our results and those of Bjerrum and Unmack,[17] the mean values for the nine determinations are $K_A = 4.26 \times 10^{-3}$ and $K_B = 5.14 \times 10^{-5}$, with average deviations from the means of 10 and 13.6%, respectively. This unsatisfactory agreement in the literature can be traced, in no small part, to uncertainties inherent in the methods used. Among these, liquid junctions and unrecognized medium effects are sources of error that are eliminated in the method we have just described. The elimination of liquid junction has actually been carried out

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[16] Branch and Miyamoto, THIS JOURNAL, **52**, 863 (1930); cf. Kirk and Schmidt, *U. of California Pub. Physiol.*, **7**, 57 (1929).

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

in this paper, but the complicated and laborious study of the medium effect of glycine has just been begun experimentally.

2. It has been demonstrated that the use of silver–silver chloride electrodes or amalgam electrodes leads to identical results in the measurements with alkaline glycine solutions.

3. In the absence of any information concerning the medium effect of glycine, we have drawn, by analogy, upon our study of this subject with acetic and formic acids, and have calculated the activity coefficients of the 0.1 molal amphanion and amphcation in sodium chloride solutions. The logarithms of the activity coefficients are linear functions of the ionic strength, which is in accord with theory.

4. By an exact thermodynamic method which eliminates the use of liquid junctions and which takes into account certain medium effects heretofore neglected, we have shown that the acid and base constants of an ampholyte may be evaluated. Further, in the case of glycine, the first steps toward an experimental solution have been made, and preliminary values of the important constants determined.

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[Contribution from the Department of Chemical Engineering of the Massachusetts Institute of Technology]

A MANOMETER FOR THE MEASUREMENT OF SMALL PRESSURE DIFFERENTIALS AT HIGH PRESSURES[1]

By James H. Boyd, Jr.[2]

Received July 12, 1930 Published December 18, 1930

Introduction

In an investigation of the viscosity of compressed gases by the author a new instrument was developed[3] for the measurement of the small pressure differentials which existed between the two ends of a capillary tube through which flowed compressed gas. It relies on electrical means for determining the pressure differential but requires no calibration and does not demand the use of clean mercury to gain accurate results. This manometer is primarily a laboratory precision instrument though by suitable calibration it may be used as a high pressure flowmeter.

The only other instrument for this use at high pressures described in the literature and known to the author is that used by Wildhagen.[4] It

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[1] This article is based on a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Science from the Massachusetts Institute of Technology.

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[3] J. H. Boyd, Jr., *Phys. Rev.*, **35**, 1284 (1930).

[4] Wildhagen, *Z. angew. Math. Mech.*, **3**, 181 (1923).