[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Effect of Sodium Chloride upon the First Ionization of Glycine

BY EDWARD J. KING

The interaction of neutral salts and weak acids may be studied from the point of view of the effect of the salt on the ionization, $m_{H}m_{A}/m_{HA}$, of the acid. In recent years, the ionizations of several weak acids at infinite dilution in aqueous solutions of sodium chloride have been determined from measurements on cells without liquid junction.[1–6] This method is also applicable to investigations of the interaction of sodium chloride with ampholytes.[7] Batchelder and Schmidt[8] have used cells without liquid junction to determine the effect of several salts on the ionization of alanine at 25°. Their study of the effect of salts on glycine[9] was confined to basic solutions of the ampholyte and made use of cells with liquid junctions.

In the present investigation, the procedure which was used for determination of the effect of sodium chloride on boric acid[4] has been applied, with slight modifications, to the ionization of glycine in acidic solutions. The concentration of sodium chloride has been varied from 0.1 to 3 molal. The measurements have been made over a wide range of temperature so that thermodynamic properties associated with the ionization could be calculated.

The cells used in this investigation were of the following type

$$H_2 \mid Z^{\pm}(m_1),\ HZCl(m_2),\ NaCl(M\text{-}m_2) \mid AgCl\text{-}Ag$$

in which $Z^{\pm}$ represents the dipolar ion, $^{+}NH_3\text{-}CH_2COO^{-}$, and HZCl represents glycine hydrochloride. The concentrations m_1, m_2, and $M\text{-}m_2$, the ionic strength, are in moles per kilogram of water. The thermodynamic equation for the cell is

$$E = E^0 - k[\log \gamma_H\gamma_{Cl}]_{m_1, M-m_2} - k \log m_H m_{Cl} \quad (1)$$

where $k = 2.3026\ RT/F$ and the subscripts refer to the molalities of glycine and sodium chloride, respectively. The first ionization of glycine is represented by $HZ^+ \rightleftarrows H^+ + Z^{\pm}$ and the corresponding ionization constant is

$$K_1 = \frac{a_H a_Z}{a_{HZ}} = \frac{m_H m_Z}{m_{HZ}} \cdot \frac{\gamma_H \gamma_Z}{\gamma_{HZ}} \equiv k_1\gamma_1 \quad (2)$$

The effect of sodium chloride on the ionization, k_1, of glycine is conveniently studied in terms of the conventions introduced by Owen and King.[4] A thermodynamic ionization constant is defined by

$$K_1^* \equiv \left[\frac{\gamma_H^*\gamma_Z^*}{\gamma_{HZ}^*}\, k_1\right]_{m_1, M-m_2} = [k_1]_{0, M} \quad (3)$$

The asterisk indicates that the standard state is chosen so that activity coefficients are unity at infinite dilution of glycine in a sodium chloride solution of concentration M. As before, the subscripts refer to the molalities of glycine and sodium chloride, respectively. The standard state of all activity coefficients without an asterisk is infinite dilution in pure water. These activity coefficients are related as follows

$$[\gamma]_{m_1, M-m_2} = [\gamma]_{0, M} \cdot [\gamma^*]_{m_1, M-m_2} \quad (4)$$

To correspond with the new standard states, a set of standard potentials is defined by the relation

$$E^{0*} = E^0 - [k \log \gamma_H\gamma_{Cl}]_{0, M} \quad (5)$$

The thermodynamic equation for the cell may now be written as

$$E = E^{0*} - [k \log \gamma_H^*\gamma_{Cl}^*]_{m_1, M-m_2} - k \log m_H m_{Cl} \quad (6)$$

For a description of the evaluation of the standard potentials, E^{0*}, and a discussion of the utility of these conventions in studies of the salt effect the reader is referred to the paper by Owen and King.[4] The method by which K_1^* is calculated from the electromotive force data will be discussed below.

Experimental

The glycine was obtained from the Amino Acid Manufactures of the University of California at Los Angeles. Its analysis was reported as follows: assay by formol titration, 100.0%; moisture, less than 0.02%; ash, 0.026 ± 0.013%; negative tests for chloride, ammonia, phosphate, iron and heavy metals. It was stored over potassium hydroxide. Arsenic-free hydrochloric acid was diluted to give an approximately one molal solution. This acid was standardized by conversion to silver chloride and by titration against purified borax. The results of the two methods agreed to within one part in a thousand. The sodium chloride was similar in quality to that used in the previous investigation. The solutions were prepared from weighed amounts of these chemicals and conductivity water. All solutions contained equal stoichiometric concentrations of glycine and its hydrochloride. In order to minimize errors caused by fermentation of the glycine, the solutions were prepared either the evening before or the morning of a series of measurements.

The cells were constructed with a stopcock in the bridge connecting the two electrode chambers. Diffusion of the complex silver chloride ion toward the hydrogen electrode could be prevented by closing this stopcock between measurements. The technique used in the preparation of the solutions and manipulation of the cells ensured the exclusion of oxygen. The temperature range was covered in the following way: an initial reading at 25° was succeeded by readings at 5° and at five-degree intervals to 55° and finally a third reading was taken at 25°. This procedure required between eleven and fourteen hours. If two successive readings at 25° differed by more than 0.1

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

(2) Harned and Hickey, *ibid.*, **59**, 1284 (1937).

(3) Hickey, *ibid.*, **62**, 2916 (1940).

(4) Owen and King, *ibid.*, **65**, 1612 (1943).

(5) Alpert, Dissertation, Yale University, 1944.

(6) Harned and Bonner, THIS JOURNAL, **67**, 1026 (1945).

(7) An alternative approach is to consider the effect of the salt on the activity coefficient of the un-ionized ampholyte. This is fully discussed in Cohn and Edsall, "Proteins, Amino Acids and Peptides," Chapter 11, Reinhold Publishing Corporation, New York, N. Y., 1943.

(8) Batchelder and Schmidt, *J. Phys. Chem.*, **44**, 880 (1940).

(9) Batchelder and Schmidt, *ibid.*, **43**, 1121 (1939).

TABLE I

PARAMETERS OF EQUATION (7)

$m_1 \times 10^3$	E_{25}	$a \times 10^5$	$b \times 10^6$	$m_1 \times 10^3$	E_{25}	$a \times 10^5$	$b \times 10^6$	$m_1 \times 10^3$	E_{25}	$a \times 10^5$	$b \times 10^6$
	M = 0.1				M = 0.3				M = 0.725		
4.946	0.45425	8.35	−1.50	7.273	0.42520	−1.75	−1.18	7.301	0.40362	− 9.00	−0.94
7.677	.44918	5.75	−1.34	8.833	.42320	−3.10	−1.12	8.608	.40200	− 9.90	− .89
7.880	.44890	5.30	−1.34	10.005	.42203	−3.57	−1.22	10.375	.40024	−10.80	− .88
10.548	.44613	3.70	−1.10	11.75	.42058	−4.80	−1.12	16.08	.39693	−13.4	− .66
15.00	.44324	2.00	−1.20	13.00	.41978	−5.00	−1.00	17.56	.39632	−13.8	− .66
16.29	.44253	1.90	−1.22	13.11	.41982	−5.00	−1.00	21.16	.39514	−14.5	− .68
20.60	.44107	0.50	−1.02	16.88	.41790	−6.30	−0.96	22.25	.39485	−14.7	− .62
25.36	.43987	−0.10	−0.92	20.03	.41670	−7.30	−1.02	29.00	.39352	−15.8	− .64
31.29	.43870	−1.10	−0.84	22.25	.41621	−7.40	−0.94	30.62	.39324	−16.2	− .52
				27.34	.41484	−8.75	−0.76				
	M = 1.25				M = 2				M = 3		
6.872	0.38893	−13.9	−0.76	5.080	0.35981	−22.6	−0.40	6.032	0.37466	−18.3	−0.67
7.864	.38769	−14.6	− .82	6.496	.35756	−24.7	− .32	8.281	.37167	−20.5	− .46
7.883	.38763	−14.7	− .68	7.811	.35601	−25.7	− .32	94.97	.37060	−21.3	− .50
13.07	.38336	−17.7	− .62	10.041	.35422	−27.4	− .26	10.687	.36960	−21.9	− .56
14.45	.38266	−18.0	− .53	15.81	.35160	−29.8	− .20	15.27	.36724	−24.0	− .35
17.84	.38132	−18.9	− .51	20.02	.35048	−31.0	− .20	20.45	.36560	−25.6	− .40
22.67	.37980	−20.3	− .35	24.01	.34977	−31.5	− .22	28.01	.36424	−26.7	− .38
24.09	.37967	−20.2	− .56								

mv. the series was discarded. Measurements were almost always made in duplicate.

Small corrections were applied to the observed electromotive forces to bring them to prescribed temperatures and ionic strengths and to a hydrogen pressure of one atmosphere. Corrections were also made for errors in the slide wire of the potentiometer. The corrected electromotive forces at given concentrations of glycine and sodium chloride can be represented by the equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \qquad (7)$$

The parameters of this equation are given in Table I. The average deviation of the values calculated by the equation from the observed values is ±0.023 mv. and only 1.8% of the deviations are greater than 0.10 mv.

Calculation of K_1*.—The procedure which was used in the evaluation of the ionization constants of boric acid in sodium chloride solutions[4] is not feasible for the first ionization of glycine because the latter is a much stronger acid. Accordingly, an apparent hydrogen ion concentration, m_H', and an apparent ionization constant, $K_1^{*\prime}$, are defined by the following equations

$$\begin{aligned} -\log m_H' &\equiv (E - E^{0*})/k + \log (M - m_2) \\ &= -\log m_H - [\log \gamma_H{}^*\gamma_{Cl}{}^*]_{m_1, M-m_1} \qquad (8) \end{aligned}$$

and

$$K_1^{*\prime} \equiv m'_H(m_1 + m'_H)/(m_2 - m'_H) \qquad (9)$$

At infinite dilution of glycine and its hydrochloride in an M-molal sodium chloride solution $m_1 = m_2 = 0$, $m_H' = m_H$, and $K_1^{*\prime} = K_1^*$. Hence, if $-\log K_1^{*\prime} = pK_1^{*\prime}$ is plotted against m_1 and the curve is extrapolated to zero concentration of glycine, the intercept is pK_1^* or $-\log K_1^*$. Values of k required for the calculation of the extrapolation function, $pK_1^{*\prime}$ were computed from the constants recently given by Birge.[10] The standard potentials, E^{0*}, were taken from the paper by Owen and King.[11]

All of the extrapolations to zero concentration of glycine were drawn as straight lines parallel to the concentration axis. In several cases, extrapolations with a slope were possible but no definite trends were noted. Some of these extrapolations are illustrated in Fig. 1. The average uncertainty in drawing the extrapolations was estimated to be less than ±0.001 in pK_1^*; the

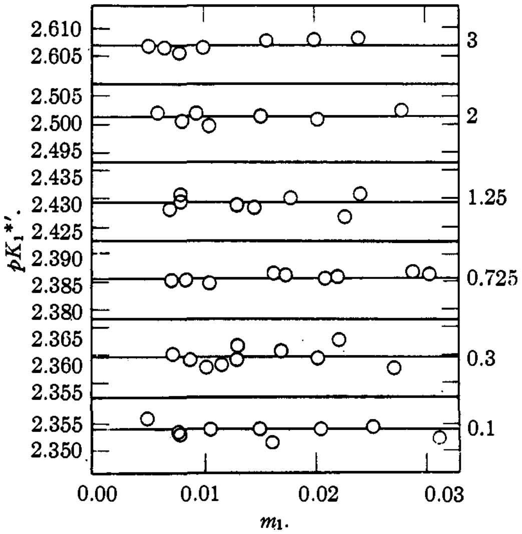

Fig. 1.—Evaluation of pK_1^* at 25° for various values of M. Diameters of circles represent 0.10 mv.

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(10) Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

(11) Alpert[6] estimated that changes in the standard potentials resulting from the shift to the new values of the gas constant and the ice point on the absolute scale are less than 0.08 mv. and therefore negligible.

TABLE II

OBSERVED VALUES OF pK_1^* IN M-MOLAL SODIUM CHLORIDE SOLUTIONS

Numbers in parentheses are the deviations (observed − smoothed) × 10^4 in pK_1^*

	M...0.00	0.1	0.3	0.725	1.25	2.00	3.00
5	2.4176(−7)	2.4216(−6)	2.4298(−3)	2.4588(−7)	2.5089(−9)	2.5886(−7)	2.7034(−6)
10	2.3980(6)	2.4014(5)	2.4090(6)	2.4378(9)	2.4864(7)	2.5640(5)	2.6768(4)
15	2.3795(2)	2.3830(6)	2.3904(9)	2.4180(10)	2.4649(4)	2.5408(6)	2.6516(5)
20	2.3640(1)	2.3672(5)	2.3736(2)	2.4007(8)	2.4457(−2)	2.5196(0)	2.6278(−3)
25	2.3508(−1)	2.3540(5)	2.3595(−3)	2.3855(2)	2.4293(−7)	2.5014(0)	2.6069(0)
30	2.3404(2)	2.3432(6)	2.3478(−8)	2.3737(5)	2.4161(−3)	2.4852(−2)	2.5877(2)
35	2.3318(−1)	2.3345(4)	2.3386(−12)	2.3638(3)	2.4054(−3)	2.4714(−3)	2.5707(2)
40	2.3252(−5)	2.3275(3)	2.3310(−22)	2.3560(2)	2.3958(−2)	2.4593(−8)	2.5545(−5)
45	2.3212(−4)	2.3237(3)	2.3266(−20)	2.3518(14)	2.3895(6)	2.4500(−3)	2.5414(3)
50	2.3194(0)	2.3216(4)	2.3236(−26)	2.3486(17)	2.3845(6)	2.4426(1)	2.5289(1)
55	2.3194(3)	2.3222(14)	2.3236(−19)	2.3475(20)	2.3818(10)	2.4361(−4)	2.5181(0)

equivalent of ±0.045 mv. Uncertainties greater than either +0.001 or −0.001 in pK_1^* were possible in 28% of the extrapolations. The largest uncertainties were found between 40° and 55° for an ionic strength of 0.3. Values of pK_1^* are recorded in Table II.

A smoothed set of ionization constants was obtained by the following procedure. First, values of pK_1^* at a given temperature were smoothed graphically against the ionic strength. The smoothed values for a given ionic strength were next fitted to the Harned and Robinson[12] equation

$$pK_1^* = A^*/T + B^* + C^*T \qquad (10)$$

Finally, the constants of this equation were smoothed graphically against the ionic strength. These parameters are given in Table III. The differences between the original and smoothed values of pK_1^* times 10^4 are given in the parentheses in Table II. The average deviation of the smoothed from the original pK_1^* is ±0.00063. This precision of fit is not an indication of the accuracy of the results. A maximum uncertainty of ±0.002 in pK_1^* would result from errors of ±0.05 mv. in the electromotive force and ±0.1% in the ionic strength. In addition, the appreciable solubility of silver chloride in glycine[13] and sodium chloride solutions may have given rise to systematic errors.

TABLE III

SMOOTHED VALUES OF THE PARAMETERS OF EQUATION (10)

M	A^*	B^*	C^*
0.0000	1259.9	−5.3980	0.011817
.1000	1278.0	−5.5030	.011974
.3000	1292.4	−5.5727	.012067
.7250	1297.4	−5.5234	.011931
1.250	1277.1	−5.2559	.011412
2.000	1213.1	−4.6187	.010234
3.000	1026.6	−3.0809	.007529

Although this investigation is primarily concerned with the ionization of glycine in sodium chloride solutions, it is also of interest to obtain the ionization constants of glycine in pure water by extrapolation of pK_1^* in salt solutions to zero ionic strength. Combination of equations (2), (3) and (4) leads to the relation

$$pK_1^* = pK_1 - [\log(\gamma_H\gamma_Z/\gamma_{HZ})]_{0,M} \qquad (11)$$

The logarithm of the activity coefficient of the dipolar ion, Z, is proportional to the ionic strength[14] and the limiting slope may be calculated from Kirkwood's theory. But the logarithm of the ratio of the two ionic activity coefficients is also proportional to the ionic strength, and the limiting slope is essentially an empirical constant with a value larger than the slope for the dipolar ion. Because of this fact and the small number of experimental points the extrapolations to zero concentration of salt were performed without the aid of theory. The values of pK_1 so obtained are given in Table II. The lack of experimental points at very low ionic strengths and the relatively large uncertainties in pK_1^* for an ionic strength of 0.3 at the higher temperatures result in larger uncertainties in the ionization constants in pure water than in the ionizations in salt solutions. Comparison of the ionization constants in water with those of Owen[15] reveals excellent agreement at 25° but poor agreement at either end of the temperature range.[16]

Other Thermodynamic Quantities.—The activity coefficient function $[\log(\gamma_H\gamma_Z/\gamma_{HZ})]_{0,M}$ for the first ionization of glycine at infinite dilution in M-molal sodium chloride solutions may be calculated from equation (11) and the data of Table II. Because it contains the ratio of two ionic activity coefficients, this function does not behave like those of other weak acids[17] but is positive

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[12] Harned and Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940); see also Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., 1943, pp. 508–514.

[13] Dunning and Shutt, *Trans. Faraday Soc.*, **34**, 1192 (1938).

[14] Scatchard and Kirkwood, *Physik. Z.*, **33**, 297 (1932); Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934); *Chem. Rev.*, **19**, 275 (1936); and ref. 7, chapter 12.

[15] Owen, THIS JOURNAL, **56**, 24 (1934).

[16] The smaller temperature coefficient of the ionization constant leads to a heat of ionization, 958 calories per mole at 25°, which is 198 calories less than that found by Owen but is in good agreement with 930 calories obtained by Sturtevant, THIS JOURNAL, **63**, 88 (1941), from calorimetric measurements.

[17] Reference 4, Fig. 4.

throughout the experimental concentration range. In contrast, the function

$$[\log \gamma_h]_{0,M} = \left[\log \frac{\gamma_{HZ}\gamma_{OH}}{\gamma_Z a_{H_2O}}\right]_{0,M} = \log \frac{K_1{}^*K_w}{K_w{}^*K_1} \quad (12)$$

corresponding to the hydrolysis of glycine, $H_2O + Z^{\pm} \rightleftarrows HZ^+ + OH^-$, contains the product of two ionic activity coefficients. The ionization constant of water in sodium chloride solutions $K_w{}^*$, can be calculated from the data of Harned and Mannweiler.[18] The plot of $[\log \gamma_h]_{0,M}$, or $[\log \gamma_h a_{H_2O}]_{0,M}$, against the square root of the ionic strength lies between plots of the activity coefficient functions of acetic and boric acids[17] and exhibits a minimum at an ionic strength of about 1.1.

The changes in free energy, $\Delta F_1{}^0{}^*$, heat content, $\Delta H_1{}^0{}^*$, heat capacity, $\Delta C_{p_1}{}^0{}^*$, and entropy $\Delta S_1{}^0{}^*$ associated with the first ionization of glycine at infinite dilution in salt solutions can be obtained from equation (10) and Table III by the usual thermodynamic methods.[12] This equation can also be used to find the centigrade temperature, ϑ, at which the ionization is a maximum. Values of the functions at 25° and of ϑ are given in Table IV.

The variations of the changes in heat content, heat capacity, and entropy with salt concentration are illustrated in Figs. 2 to 4. The effect of temperature on these functions becomes smaller as the ionic strength increases, but the decrease is not as pronounced as that shown by boric acid.[4] All of the curves approach zero ionic strength with a positive slope except those of $\Delta C_{p_1}{}^0{}^*$. It

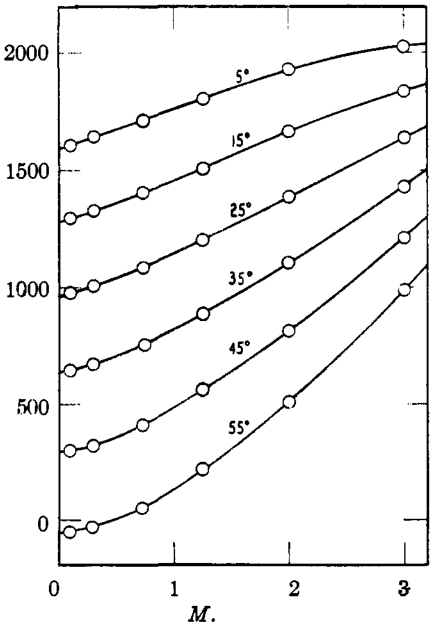

Fig. 2.—$\Delta H_1{}^0{}^*$ for the ionization of glycine at infinite dilution in M-molal sodium chloride solutions; diameters of circles 50 cal. mole^{-1}.

TABLE IV

THERMODYNAMIC FUNCTIONS ASSOCIATED WITH THE IONIZATION OF GLYCINE AT INFINITE DILUTION IN M-MOLAL SODIUM CHLORIDE SOLUTIONS AT 25°

M	$\Delta F_1{}^0{}^*$	$\Delta H_1{}^0{}^*$	$-\Delta C_{p_1}{}^0{}^*$	$-\Delta S_1{}^0{}^*$	ϑ
0.0000	3206.8	958	32.2	7.54	53.4
.1000	3210.4	977	32.7	7.49	53.5
.300	3218.9	1005	32.9	7.43	54.1
.725	3253.6	1083	32.6	7.28	56.6
1.250	3314.7	1201	31.1	7.09	61.4
2.000	3412.2	1388	27.9	6.79	71.1
3.000	3556.1	1635	20.5	6.44	96.1

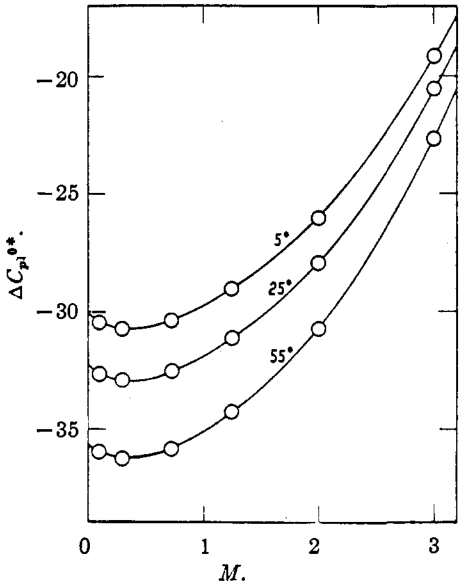

Fig. 3.—$\Delta C_{p_1}{}^0{}^*$ for the ionization of glycine at infinite dilution in M-molal sodium chloride solutions; diameters of circles 0.5 cal. deg.$^{-1}$ mole^{-1}.

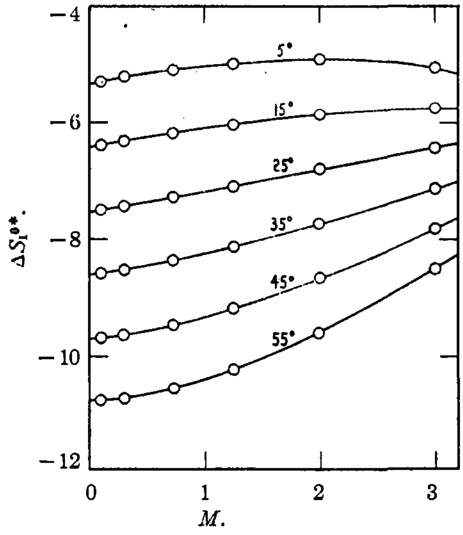

Fig. 4.—$\Delta S_1{}^0{}^*$ for the ionization of glycine at infinite dilution in M-molal sodium chloride solutions; diameters of circles 0.2 cal. deg.$^{-1}$ mole^{-1}.

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[18] Harned and Mannweiler, THIS JOURNAL, 57, 1873 (1935).

is doubtful whether any significance can be attached to the negative slopes of the latter, because in the range M = 0 to 0.725 the variation of $\Delta C_{p_1}{}^{0*}$ is only 0.7 cal. deg.$^{-1}$ mole^{-1}, which is probably less than the experimental error.

The author wishes to thank Professors H. S. Harned, B. B. Owen and S. E. Wood for many helpful discussions.

Summary

Electromotive forces of the cells $H_2 \mid Z^* (m_1), HZCl(m_2), NaCl(M-m_2) \mid AgCl\text{-}Ag$ have been determined at five-degree intervals from 5 to 55° and at six constant ionic strengths from 0.1 to 3 molal.

From these, the first ionization constants of glycine in salt solutions, $K_1^* = [m_H m_Z/m_{HZ}]_{0,M}$, have been computed. The first ionization constants of glycine in water have been obtained by extrapolation of the results in salt solutions.

Equations for computing $-\log K_1^*$ as a function of temperature are given. From them, the derived thermodynamic quantities $[\gamma_H \gamma_Z/\gamma_{HZ}]_{0,M}$, $[\gamma_{HZ}\gamma_{OH}/\gamma_Z a_{H_2O}]_{0,M}$, ΔF_1^{0*}, ΔH_1^{0*}, $\Delta C_{p_1}{}^{0*}$, and ΔS_1^{0*} have been calculated and their variations with salt concentration illustrated by plots and tables.

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Surface Area Measurements of Activated Carbons, Silica Gel and other Adsorbents

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Since the development by Brunauer, Emmett and Teller (BET)[2] of an equation for an adsorption isotherm based on a multilayer theory, considerably increased interest has been shown in the physical adsorption of gases on solids. The BET equation was the first to give good agreement with the experimental data for all types of vapor-on-solid adsorption and made possible the calculation of a reasonably accurate value for the area of the adsorbent.

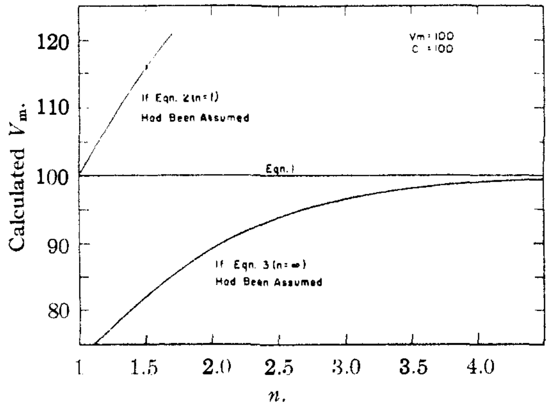

Fig. 1.—Error involved by the use of equations 2 and 3 as approximations for equation 1 at various values of n. Equation 1 was used to calculate a series of isotherms with various values of n assuming V_m = 100 and C = 100. These isotherms were plotted separately according to equation 2 and equation 3, and V_m determined for each, assuming the plots linear in the relative pressure region 0.1 to 0.2. The V_m so calculated are shown by the equation 2 and equation 3 curves, respectively.

The BET equation for the isothermal adsorption is

$$V = \frac{V_m CX}{(1-X)}\left(\frac{1-(n+1)X^n + nX^{n+1}}{(1+(C-1)X - CX^{n+1})}\right) \quad (1)$$

where V_m is the volume of gas (S.T.P.) necessary to form a monolayer; C is related to the heat of adsorption of the monolayer (E_l) and the heat of liquefaction (E_L) by the relation $RT \ln C = E_l - E_L$; n is the number of layers to which the gas is limited; X is the relative pressure and V the volume of gas (S. T. P.) adsorbed.

For the purpose of calculating the surface area of solids, equation 1 is commonly used in one of its two limiting forms

$$\frac{X}{V} = \frac{1}{CV_m} + \frac{X}{V_m} \qquad n = 1 \quad (2)$$

or

$$\frac{X}{V(1-X)} = \frac{1}{V_m C} + \frac{C-1}{V_m C}X \qquad n = \infty \quad (3)$$

For values of n greater than 3 or 4 and for values of X up to 0.25, equation 3 is a fair approximation to equation 1, providing C is considerably greater than unity. On the other hand, equation 2 can be used only for isotherms which have an n value very close to unity.

Figure 1 demonstrates the approximate error involved in the use of either equation 2 or 3 rather than the full BET equation for isotherms with n less than 4 and C equal to 100. The curves of Fig. 1 were prepared by assuming an adsorbent with a fixed true value of V_m and C. Isotherms with various values of n were calculated from equation 1 and from them, apparent values for V_m and C were recalculated by equation 2 or 3, assuming a linear plot between X = 0.1 and 0.2. From Fig. 1, it is apparent that neither equation 2 or 3 will give V_m within 5% of the true value, if the isotherm has an n in the range 1.15 to 2.7.

In the course of the examination of a great many and variety of isotherms, we have found a number, for which n was less than 4 and greater than 1.

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[1] Present address, Mellon Institute of Industrial Research, Pittsburgh, Pa.

[2] Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309 (1938).