The data on the pure compound are m.p. 28–29°, b.p. 196–198°.

Anal. Calcd. for $C_6HBr_2F_3$: C, 24.86; H, 0.35; F, 19.66. Found: C, 25.02; H, 0.40, F, 19.44.

A large excess of bromine along with heating converted the monobromo compound to the tribromo derivative. Alternate vacuum sublimation and recrystallization from ethanol gave pure 2,4,6-tribromo-1,3,5-trifluorobenzene, m.p. 98–98.5°.

Anal. Calcd. for $C_6Br_3F_3$: C, 19.54. Found: C, 19.55.

2-Nitro-1,3,5-trifluorobenzene.—To a well-stirred mixture of 36 g. of 1,3,5-trifluorobenzene in 50 cc. of concd. sulfuric acid, a nitrating solution of 19 cc. of concd. nitric and 17 cc. of concd. sulfuric acids was added at such a rate that the temperature was controlled at 50°. At the end, the temperature was raised to 70° for sixty minutes. The reaction mixture was poured over ice, and the yield of crude nitro compound was 41 g. or 85%. Pure 2-nitro-1,3,5-trifluorobenzene is a heavy, pale yellow liquid, f.p. *ca.* 3.5°, b.p. 81° (20 mm.) or 172° (atm.), $n^{20}D$ 1.47833.

Anal. Calcd. for $C_6H_2O_2NF_3$: C, 40.69; H, 1.14; N, 7.91. Found: C, 40.76; H, 1.16; N, 8.17.

2-Amino-1,3,5-trifluorobenzene.—This amine was prepared from the preceding nitro compound by the same general method as indicated for IV. A 90% yield of crude amine was obtained. Vacuum distillation gave pure 2-amino-1,3,5-trifluorobenzene as a white solid, m.p. 33–34°, b.p. 57° (22 mm.).

Anal. Calcd. for $C_6H_4NF_3$: C, 48.99; H, 2.74; N, 9.52. Found: C, 48.99; H, 2.69; N, 9.58.

The amine forms a very soluble hydrochloride and hydrosulfate in contrast to most other fluorinated anilines.

The acetyl derivative was sublimed after preliminary recrystallizations from ethanol and benzene, m.p. 152–153°.

Anal. Calcd. for $C_8H_6ONF_3$: C, 50.80; H, 3.20; N, 7.41. Found: C, 50.70; H, 3.11; N, 7.58.

Summary

The synthesis and properties of 1,3,5-trifluorobenzene, its intermediates and some of its derivatives have been described.

URBANA, ILLINOIS RECEIVED JUNE 9, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BARNARD COLLEGE, COLUMBIA UNIVERSITY, AND THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

The Ionization Constants of Glycine and the Effect of Sodium Chloride upon its Second Ionization

BY EDWARD J. KING

In a previous contribution[1] the electromotive forces of cells without liquid junction containing glycine ($Z^{\pm}$), glycine hydrochloride (HZCl), and sodium chloride buffers were used to determine the effect of sodium chloride on the first ionization of glycine, $k_1 = m_H m_Z/m_{HZ}$. Extrapolation of these results to zero ionic strength gave values for the first thermodynamic ionization constant of glycine, $K_1 = a_H a_Z/a_{HZ}$, which were in good agreement with those of Owen[2] at 25° but not at higher and lower temperatures. Since these extrapolations were from ionic strengths no lower than 0.1 molal, the ionization constants were subject to considerable uncertainty. The desirability of accurate knowledge of the ionization of so important an amino acid as glycine has led to a redetermination of its ionization constants using the methods of Owen.[2] The electromotive forces of the cells

$$H_2 \mid Z^{\pm} (m_1), \text{HZCl } (m_2) \mid \text{AgCl–Ag} \qquad \text{I}$$

and

$$H_2 \mid Z^{\pm} (m_1), \text{NaG } (m_2), \text{NaCl } (m_3) \mid \text{AgCl–Ag} \qquad \text{II}$$

have been redetermined at 5° intervals from 10 to 50°. The first ionization constant, K_1, has been calculated from the measurements of Cell I and the second ionization constant,[3]

$$K_2 = \frac{a_H a_G}{a_Z} = \frac{m_H m_G}{m_Z} \frac{\gamma_H \gamma_G}{\gamma_Z} = k_2 \gamma_2 \qquad (1)$$

from the measurements of Cell II. In the above expressions NaG represents sodium glycinate and the concentrations m_1, m_2 and m_3 are in moles per kilogram of solvent.

The investigation of the effect of sodium chloride on the second ionization, $k_2 = m_H m_G/m_Z$, has also been carried out. The electromotive forces of cells of the type

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

were measured from 5 to 55° and at constant ionic strengths (M) of 0.1 and 0.3. From these, the second ionization of glycine at infinite dilution in a sodium chloride solution of concentration M could be calculated by the method of Owen and King.[4]

Experimental

Apparatus.—The investigation of the effect of sodium chloride upon the second ionization of glycine was carried out at Yale University with the same apparatus and the same samples of glycine and sodium chloride previously described.[1] The redetermination of the ionization constants was done at Barnard College with somewhat different equipment. A Rubicon Type B high precision potentiometer was used in conjunction with a Rubicon No. 3415 spotlight galvanometer. One of the two Eppley standard cells employed was certified by the National Bureau of Standards in October, 1949. A Deoxo catalytic purifier (Baker and Co.) was used to remove traces of oxygen from the hydrogen. Temperatures were measured with a thermometer certified by the National Bureau of Standards. The temperature of the water-bath in which the cells were immersed was controlled within ±0.01° except at 10 and 15° where the fluctuations were somewhat larger. The cells were those used previously[1] except that the stopcock in the connecting tube between the two electrode chambers was replaced by a short length of capillary tubing for most of the measurements. The electrode compartments were closed with HR-108 rubber stoppers (A. H. Thomas Co.), a grade of stopper which in some work with acetic acid–sodium acetate buffers was found to absorb practically no acetic acid.[5]

Materials.—The glycine was the same as that previously described.[1] Its purity as determined by formol titration[6]

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(1) King, THIS JOURNAL, **67**, 2178 (1945).

(2) Owen, *ibid.*, **56**, 24 (1934).

(3) The ionization constant K_2 is related to K_B calculated by Owen by $K_2 = K_w/K_B$.

(4) Owen and King, THIS JOURNAL, **65**, 1612 (1943). According to the conventions of that paper, the second ionization would be represented by the symbols $[k_2]_{0,M}$ or K_2^*.

(5) The use of these stoppers was suggested by Dr. Roger G. Bates.

(6) Dunn and Loshakoff, *J. Biol. Chem.*, **113**, 359 (1936).

TABLE I

PARAMETERS OF EQUATION (2)

Cell I $m_1 = m_2$				Cell II						Cell III $M = 0.1$; $m_1 = m_2$ $b = -2.10 \times 10^{-6}$		
$m_1 \times 10^6$	$E_{25} \times 10^5$	$a \times 10^6$	$-b \times 10^8$	$m_1 \times 10^6$	$m_2 \times 10^6$	$m_3 \times 10^6$	$E_{25} \times 10^5$	$a \times 10^6$	$-b \times 10^8$	$m_1 \times 10^6$	$E_{25} \times 10^5$	$a \times 10^6$
4979[b]	52253	310	180	4979	5316	5188	93692	221	250	5255	86244	45.5
5268	52052	292	120	5818	9163	7506	93785	221	242	7267	86337	38.4
6750[a]	51182	260	148	7591	11955	9794	93140	198	225	8576	86389	37.0
8248	50483	234	180	10145	6563	10238	90768	115	232	11292	86463	34.7
8810[b]	50274	225	145	11667	12456	12156	91616	150	250	12955	86536	32.6
9198	50130	217	133	13341	20988	17194	91769	151	220	16985	86667	28.2
11288	49473	196	145	14381	15353	14984	91106	132	232	19775	86759	22.5
13405	48934	170	150	16291	11168	16557	89731	84	222	25529	86966	15.6
15013[a]	48579	156	130	20147	13811	20476	89208	67	235			
19379	47819	126	113	20923	13828	17942	89422	71	205			
19675[b]	47770	125	127	21317	13789	21511	88934	54	235	$M = 0.3$; $m_1/m_2 = 0.9924$ $b = -2.00 \times 10^{-6}$		
21212	47547	115	100	25534	17503	25951	88628	45	220			
22438	47387	107	120	31630	20906	27123	88432	32	205	4924	83506	148
25192	47057	98	100	33312	22018	28566	88299	24	205	7567	83559	142
30027	46570	78	96	36816	23816	37153	87589	9	222	10589	83599	141
31076	46473	78	106							10715	83596	141
34166	46211	66	98							20605	83720	133
38475[a]	45899	54	86							28833	83806	132
53931	45025	20	91									

[a] Measurements at 20° omitted. [b] Measurements only at 15, 20, 25 and 50°.

was 99.98 ± 0.14%. Titration with Karl Fischer reagent[7] indicated that the glycine contained less than 0.01% water. A stock solution of hydrochloric acid was prepared by dilution of concentrated, reagent-grade acid and was standardized with a precision of ±0.05% by conversion to silver chloride, by titration with standard sodium hydroxide solution, and by titration with three different samples of sodium carbonate. Reagent-grade sodium chloride was found to contain 0.001% bromide by the uranine test.[8] It was further purified by precipitation with hydrogen chloride followed by recrystallization three times from conductivity water. After long drying at room temperature and at 120°, it was heated in a platinum crucible at 400° for six hours. The final product contained 0.004% water as determined by a titration with Karl Fischer reagent. Stock solutions of sodium hydroxide were prepared by dilution of a clear, saturated solution and were standardized with a precision of ±0.04% against potassium acid phthalate from the National Bureau of Standards. Buffers for use in the cells were prepared from weighed amounts of the stock solutions of hydrochloric acid or sodium hydroxide, redistilled water, solid glycine and sodium chloride. The probable error in concentration of the buffer solutions is less than 0.1%. The solutions were prepared in such a way as to exclude oxygen and carbon dioxide.

Measurements were made in duplicate in almost all cases. In the determination of the two ionization constants the temperature range was covered in the following way: an initial reading of electromotive force at 25° was followed on the first day by readings at 5° intervals either from 10 to 25° or from 30 to 50° and then again at 25°. Then the cells were closed off overnight. The following day, readings were made first at 25°, then over that portion of the tem-

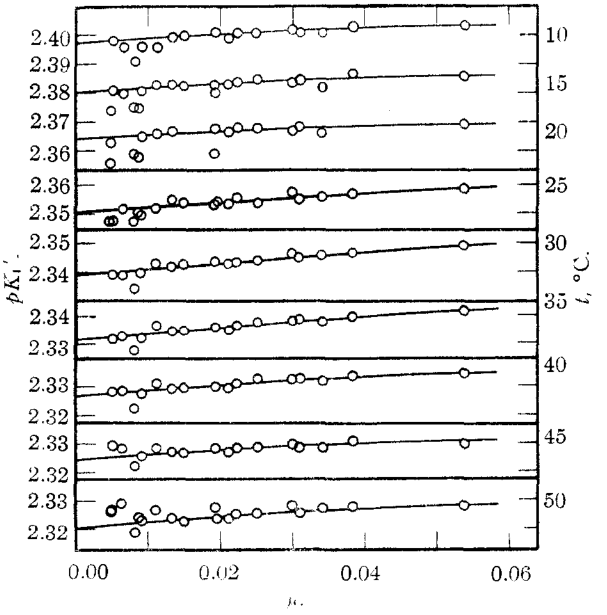

Fig. 1.—Evaluation of pK_1'.

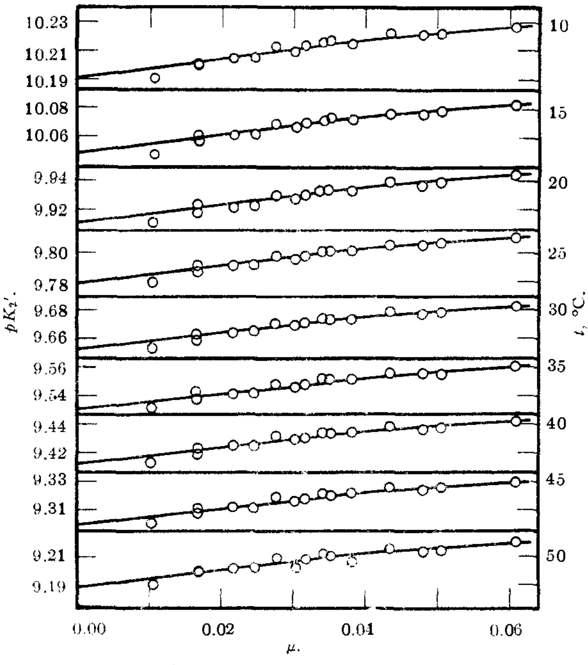

Fig. 2.—Evaluation of pK_2'.

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[7] Seaman, McComas and Allen, *Anal. Chem.*, **21**, 510 (1949).

[8] Pinching and Bates, *J. Research Natl. Bur. Standards*, **37**, 311 (1946).

perature range which was not covered in the preceding day, and finally at 25° for the fourth time. Thus the performance of the electrodes could be checked by comparison of the readings at 25°. With the acid solutions of Cell I, overnight standing caused an average decrease of electromotive force of 0.03 mv. If two successive readings at 25° differed by more than 0.10 mv., the series was discarded. With the alkaline solutions of Cell II, the electromotive force at 25° showed an average decrease of 0.13 mv. after the cell had stood closed off overnight. This is attributed to the solubility of silver chloride in alkaline glycine solution.[9] The average decreases in electromotive force at 25° over the high and low temperature sequences of readings were 0.14 and 0.05 mv., respectively. In order to make consistent the measurements over a period of two days, the values of the electromotive force of Cell II obtained during the second day were increased by an amount equal to the difference between the first and third readings at 25°. Here it is assumed that the temperature coefficient of electromotive force is not significantly affected by dissolved silver chloride. In some series, measurements were made at the higher temperatures on the first day, in others, on the second; when the corrections just discussed were applied, concordant results were obtained.

The electromotive forces of cells containing solutions of given concentrations corrected to a hydrogen pressure of one atmosphere can be represented as a function of temperature by the equation

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

The parameters of this equation are given in Table I. The electromotive forces are expressed in international volts. The average deviation of the values calculated by the equation from the observed values is ±0.029 mv. and only 1.6% of the deviations are greater than 0.10 mv.

Results and Discussion

Since the methods of evaluating the constants K_1, K_2 and k_2 have been given previously,[2,4] they will not be described here in detail. The negative logarithm of the first ionization constant, pK_1, is found by extrapolating to zero ionic strength ($\mu = 0$) a plot of the function $pK'_1 = -\log[(m_1 + m'_H)m'_H/(m_2 - m'_H)]$ against μ. The apparent molality of hydrogen ion, m'_H, is related to the electromotive forces of Cell I by equation [20'] given by Owen.[2] To obtain pK_2, a plot of the function $pK'_2 = (F/2.3026RT)(E_{II} - E^0) + \log[m_3(m_1 + m_{OH})/(m_2 - m_{OH})]$ against μ is extrapolated to $\mu = 0$. The negative logarithms of the second ionization of glycine in sodium chloride solutions are obtained as the extrapolated values at zero concentration of glycine in M-molal chloride solutions of the function $pk'_2 = (F/2.3026RT)(E_{III} - E^0) + [\log \gamma_H\gamma_{Cl}]_{0,M} + \log[m_3(m_1 + m_{OH})/(m_2 - m_{OH})]$ where the double subscript $(0,M)$ refers to the concentrations of glycine and sodium chloride, respectively. These extrapolations are illustrated in Figs. 1 to 3.

Values of the negative logarithms of the constants obtained by extrapolation are recorded in Table II together with values previously reported by Owen[2] and King.[1] The results of Owen have been increased by 0.0020 to 0025 to make them comparable with the values in this paper and reference (1) which have been calculated using the constants given by Birge.[10]

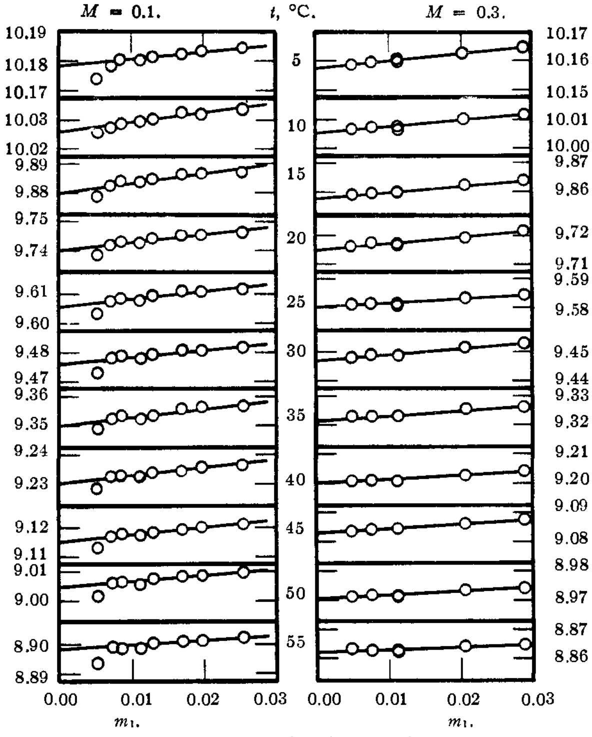

Fig. 3.—Evaluation of pk_2.

The parameters of the Harned and Robinson equation[11] have been calculated from the data in

$$pK = A/T + B + CT \qquad (3)$$

Table II and are given in Table III. The differences between the original and smoothed values of pK times 10^4 are given in parentheses in Table II. The average deviation is ±0.00055. The probable error in pK is estimated to be about ±0.0025 on the basis of errors of 0.1 mv. in the electromotive forces and 0.1% in each concentration.

The values of pK_1 from the present investigation and those reported in the earlier paper[1] are in excellent agreement. The largest difference, 0.0030 at 45°, corresponds to a difference of about 0.12 mv. in electromotive force and is within the error of extrapolation of the results in salt solutions to zero ionic strength. To determine whether the slightly higher results now obtained at 40 to 50° was a consequence of a systematic error, the electromotive forces of some cells containing acetic acid–sodium acetate–sodium chloride buffers[12] were measured. Values of pK for acetic acid at 25 and 50° calculated from these measurements were 0.0013 and 0.0030 larger, respectively, than those reported by Harned and Ehlers. These differences correspond to 0.08 and 0.18 mv. and are not believed to indicate any sizable systematic error.

When the values of pK_1 and pK_2 reported in this paper and those of Owen[2] are compared, good agreement is found at 25°, but the present values are lower than his below that temperature and higher above it. No definite explanation of such strongly temperature-dependent deviations has

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(9) See Keefer and Reiber, THIS JOURNAL, **63**, 689 (1941).

(10) Birge, *Revs. Modern Phys.*, **13**, 233 (1941).

(11) Harned and Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).

(12) Harned and Ehlers, THIS JOURNAL, **55**, 652 (1933).

TABLE II

OBSERVED VALUES OF pK_1, pK_2 AND pk_2

Numbers in parentheses are the deviations (observed − smoothed) × 10^4 in pK_1, pK_2 or pk_2

t, °C.	pK_1[a]	pK_1[1]	pK_1[2]	pK_2[a]	pK_2[2]	pk_2[a] $M = 0.1$	pk_2[a] $M = 0.3$
5		2.4176				10.1786(−2)	10.1588(−10)
10	2.3971(−6)	2.3980	2.407	10.1928(4)	10.208	10.0262(−2)	10.0049(9)
15	2.3800(8)	2.3795	2.386[b]	10.0493(1)	10.058	9.8801(−5)	9.8573(5)
20	2.3640(4)	2.3640	2.368	9.9103(−9)	9.916	9.7397(4)	9.7155(−5)
25	2.3503(−3)	2.3508	2.352	9.7796(3)	9.780	9.6048(8)	9.5791(13)
30	2.3394(−8)	2.3404	2.340	9.6517(−4)	9.650	9.4753(7)	9.4479(−8)
35	2.3312(−9)	2.3318	2.329	9.5300(3)	9.527	9.3507(−7)	9.3217(−2)
40	2.3266(3)	2.3252	2.320	9.4124(5)	9.409	9.2309(−6)	9.2002(−3)
45	2.3242(16)	2.3212	2.315[b]	9.2988(3)	9.295	9.1156(−4)	9.0832(−2)
50	2.3200(−10)	2.3194	2.310[b]	9.1887(−6)		9.0047(−3)	8.9705(0)
55		2.3194				8.8979(7)	8.8619(3)

[a] Present investigation. [b] Calculated values.

TABLE III

THE PARAMETERS OF EQUATION (3)

	pK_1 $M = 0$	pK_2 0	pk_2 0.1	pk_2 0.3
A	1332.17	2686.95	2787.82	2761.73
B	−5.8870	−0.5103	−1.2148	−0.9710
C	0.012643	0.0042857	0.0049287	0.0043182

been found. A difference in quality of the two glycine preparations is the most probable explanation. It may be noted that the presence of small amounts of an electrolytically inert impurity such as water would cause an error which is almost independent of temperature.

Other Thermodynamic Quantities.—The parameters of equation (3) can be used to calculate by conventional thermodynamic methods[11] the changes in free energy, ΔF^0, heat content, ΔH^0, heat capacity, $\Delta C_p{}^0$, and entropy, ΔS^0, associated with the ionizations of glycine in water and in sodium chloride solutions. Values of these functions at 25° are given in Table IV.

TABLE IV

THERMODYNAMIC FUNCTIONS ASSOCIATED WITH THE IONIZATION OF GLYCINE AT 25°

	M	ΔF^0 cal. mole^{-1}	ΔH^0 cal. mole^{-1}	$\Delta C_p{}^0$ cal. deg.$^{-1}$ mole^{-1}	ΔS^0 cal. deg.$^{-1}$ mole^{-1}
		First ionization			
Owen[2,13]	0	3205	1156	−32.2	−6.9
Owen[2,14]	0	3204	1100	−33.8	−7.3
This investigation	0	3206	953	−34.5	−7.6
		Second ionization			
Owen[2,13]	0	13,336	10,806	−24.6	−8.5
Owen[2,14]	0	13,328	10,600	−28.5	−9.2
This investigation	0	13,340	10,550	−11.7	−9.4
This investigation	0.1	13,102	10,749	−13.4	−7.9
This investigation	0.3	13,067	10,879	−11.8	−7.3

As is well-known, the values of ΔH^0, $\Delta C_p{}^0$ and ΔS^0 are strongly dependent on the form of the equation used for expressing pK as a function of temperature[15] as well as on the accuracy of the experimental measurements.[16] This point is illustrated by the inclusion in Table IV of values of the thermodynamic functions calculated from the data of Owen[2] with equation (3)[13] and with an equation developed by Everett and Wynne-Jones.[14] A comparison of the thermodynamic functions derived from the data of Owen and of the present investigation shows reasonably good agreement except for the quantities $\Delta H_1{}^0$, $\Delta H_2{}^0$ and $\Delta C_{p2}{}^0$. The heats of ionization can be compared with values obtained by Sturtevant[17] from calorimetric measurements. For the first ionization the calorimetric value of $\Delta H_1{}^0$ is 930 cal. mole^{-1} in excellent agreement with 953 reported here, but for the second ionization the calorimetric value of $\Delta H_2{}^0$, 10,748, is somewhat higher than 10,550 derived from the present investigation. The value of −11.7 cal. deg.$^{-1}$ mole^{-1} for $\Delta C_{p2}{}^0$ reported here is in reasonable agreement with the average value of −14 for the other amino acids.[18] According to the present results ΔC_{p^0} for the isoelectric reaction $^+NH_3CH_2COOH + OH^- \rightleftarrows NH_2CH_2COO^- + H_3O^+$ is 0.3 cal. deg.$^{-1}$ mole^{-1} or practically zero.[19]

The activity coefficient function $\log \gamma_2 = [\log(\gamma_H\gamma_G/\gamma_Z)]_{0,M}$ for the second ionization of glycine at infinite dilution in M-molal sodium chloride solutions can be calculated from the data in Table II and the relation $pk_2 - pK_2 = \log \gamma_2$[20]. Combination of this with $\log \gamma_W = [\log \gamma_H\gamma_{OH}/a_{H_2O}]_{0,M}$[21] leads to the function $\log \gamma_{h_2} = [\log(\gamma_Z\gamma_{OH}/\gamma_G a_{H_2O})]_{0,M} = \log(\gamma_W/\gamma_2)$ corresponding to the hydrolysis reaction represented by $H_2O + G^- \rightleftarrows Z^{\pm} + OH^-$. Values of these functions at 25° are given in Table V together with the functions $\log \gamma_1 = [\log(\gamma_H\gamma_Z/\gamma_{HZ})]_{0,M}$ for the first ionization and $\log \gamma_{h_1} = [\log(\gamma_{HZ}\gamma_{OH}/\gamma_Z a_{H_2O})]_{0,M}$ for the hydrolysis reaction represented by $H_2O + Z^{\pm} \rightleftarrows HZ^+ + OH^-$ calculated from the data previously obtained.[1]

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(13) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1950, p. 514.

(14) Everett and Wynne-Jones, *Trans. Faraday Soc.*, **35**, 1380 (1939).

(15) See reference 13, pp. 514–516.

(16) Use of the new values of the physical constants[10] leads to an average increase of 0.0025 in pK but does not significantly affect ΔH^0, $\Delta C_p{}^0$, and ΔS^0.

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

(18) Reference 13 and also Cohn and Edsall, "Proteins, Amino Acids, and Peptides," Reinhold Publishing Corporation, New York, N. Y., 1943, p. 80.

(19) Reference 13, p. 534.

(20) In equation (11) of reference 1 pK_1* (or pk_1) and pK_1 should be transposed.

(21) Harned and Mannweiler, THIS JOURNAL, **57**, 1873 (1935).

TABLE V

THE ACTIVITY COEFFICIENT FUNCTIONS OF GLYCINE AT INFINITE DILUTION IN SODIUM CHLORIDE SOLUTIONS AT 25°

M	$\log \gamma_1$	$\log \gamma_{h_1}$	$\log \gamma_2$	$\log \gamma_{h_2}$
0.1	0.003	−0.217	−0.174	−0.039
.3	.009	− .278	− .200	− .069

It is seen from Table V that sodium chloride has a much more pronounced effect on the two functions, log γ_{h_1}, and log γ_2, which involve a product of two ionic activity coefficients than on log γ_1 and log γ_{h_2} which involve a ratio of ionic activity coefficients. The effect of sodium chloride on log γ_{h_1} and log γ_2 is similar to that found for the activity coefficient functions of other weak acids.[22]

The data in Table II can also be used to calculate $[-\log m_H]_{0.M} \equiv pI$ for the isoelectric point of glycine at infinite dilution in water and salt solutions. From the relation $pI = -(^1/_2) \log (K_1K_2/\gamma_1\gamma_2) = (pk_1 + pk_2)/2$ values of pI at 25° in water and 0.1 and 0.3 molal sodium chloride solutions are, respectively, 6.065, 5.979 and 5.969.

Acknowledgment.—The author wishes to thank Professors B. B. Owen and H. S. Harned for their helpful advice.

Summary

The thermodynamic ionization constants, K_1 and K_2, of glycine have been redetermined at 5° intervals from 10 to 50°. Good agreement with the results of Owen is obtained at 25° but not at higher and lower temperatures.

The effect of sodium chloride upon the second ionization of glycine, $k_2 = [m_H m_G/m_Z]_{0.M}$, has been determined from the electromotive forces of hydrogen–silver chloride cells containing glycine–sodium glycinate–sodium chloride buffers at 5° intervals from 5 to 55° and at constant ionic strengths of 0.1 and 0.3 molal.

Equations for computing $-\log K_1$, $-\log K_2$ and $-\log k_2$ as functions of the temperature are given. From them, the derived thermodynamic quantities ΔF^0, ΔH^0, ΔC_p^0, and ΔS^0 associated with the two ionization reactions as well as $[\log \gamma_H\gamma_G/\gamma_Z]_{0.M}$, $[\log \gamma_{OH}\gamma_Z/\gamma_G a_{H_2O}]_{0.M}$ and $[-\log m_H]_{0.M}$ at the isoelectric point have been calculated and discussed.

NEW YORK 27, N. Y.

RECEIVED JULY 7, 1950

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[22] Reference 4, Fig. 4, or reference 13, p. 525.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Application of the Onsager Theory of Ionic Mobilities to Self-diffusion

BY LOUIS J. GOSTING[1] AND HERBERT S. HARNED

Recently, by the use of radioactive tracer techniques, the self-diffusion of a number of ions[2,3,4,5] has been studied. Since there has been some confusion in the interpretation of these data, it seems desirable to view the situation from the standpoint of an expression derived by Onsager[6] which reduces to a limiting law for self-diffusion of an ion as a special case. In this way a clear-cut and direct presentation of the problem can be effected and the experimental accuracy required in its solution estimated.

The phenomena involved are best visualized by considering two different types of diffusion:

1. **Diffusion of a Single Salt.**—When a salt diffuses, electrical neutrality requires that both the positive and negative ions move with the same velocity. Under this condition, the ionic atmospheres suffer no deformation and the "time-of-relaxation effect" vanishes.[6–9] Further, the electrolyte moves in one direction and the solvent by replacing it moves in the opposite direction. This "electrophoretic" effect is an important factor in single salt diffusion and its computation is necessary. Finally, since the activity coefficient of the electrolyte is not constant throughout the diffusing system, it appears in the theoretical equation for the diffusion coefficient as a thermodynamic term $(1 + c\partial\ln y_\pm/\partial c)$ where $y_\pm$ is the activity coefficient of the salt and c is in moles per liter. The theoretical computation of some examples of salt diffusion has been examined in detail in a number of recent contributions.[10–13]

2. **Diffusion in a Solution Containing Three or More Kinds of Ions.**—Since more than two ions are present in the solution, they need not move with the same velocity. While a general treatment of this case is very complicated, a simple limiting law has been derived by Onsager[6] for the diffusion coefficient of an ion at very low concentration compared to that of the other ions present whose concentrations are essentially constant throughout the solution. The activity coefficient of the ion in question is then sensibly constant, since the ionic strength of the solution containing it is kept constant, and the thermodynamic term given above is simply unity. Since, however, the migrating ion has a velocity relative to the other ions, its atmosphere is asymmetric and the time-of-relaxation effect is not zero, and its computation provides the necessary and sufficient basis for the calculation of the limiting law for the variation of the diffusion coefficient of the "trace" ion with the total ionic concentration. The electro-

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