equation were determined as before. The following values were found:

n	$B+K$	q	A	$-AB$	D	C
3	0.2519	1.096	4.285	1.862	0.799	0.5818
3.25	.2867	1.225	5.145	4.431	1.391	0.9054
4.375	.4492	1.208	8.792	27.836	5.558	2.1878

This shows that the differences between the constants from the two computations for $n = 3.25$ can be considered to be due to a slight uncertainty in the value of n.

This entire discussion, then, would seem to indicate that the $P-V-T$ relationships between all pure, non-associating and non-dissociating substances are very similar when proper allowance is made for the size of the molecules and the attractive forces between them. The equation given here

$$PV + \frac{4.555V + 7.427}{T^{1/2}V^2 + 0.9382T^{2/3}V + 2.140/(T^{3/2})} = 3.25T + 0.2837P + 1.343 \log (P + 1)$$

is probably as correct in form as can be obtained without going to higher degree in V than the cube, though the values of the constants could probably be improved by a method of choosing points for their determination other than the more or less random one employed here for that purpose. A marked deviation from it on the part of any substance should be rather definite evidence of association or dissociation.

PLACENTIA, CALIFORNIA RECEIVED MARCH 30, 1936

[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGY, YALE UNIVERSITY SCHOOL OF MEDICINE]

The Ionization Constant of Glycolic Acid from 0 to 50°

BY LESLIE FREDERICK NIMS

Recently Harned and co-workers[1,2] have developed a method for the precise determination of the thermodynamic ionization constant of a weak electrolyte at different temperatures. This method was used in obtaining results reported here for glycolic acid, the first member of the homologous series of α-hydroxy acids.

Method and Results

Lithium, potassium and barium glycolates, prepared by neutralizing an aqueous solution of glycolic acid with the respective c. p. carbonates, were recrystallized three times from water, dried and analyzed by conversion to the sulfates. Stock buffer solutions were made by dissolving weighed amounts of the purified salts in the requisite weight of a carefully analyzed hydrochloric acid solution. The buffer solutions were then analyzed by titration with standard sodium hydroxide and evaporation with sulfuric acid. The concentrations of acid and salt determined by these two independent methods agreed to within $\pm 0.1\%$.

Solutions obtained from the stock solutions by weight dilution were used as electrolytes in the cell Pt, H_2/Buffer solution/AgCl/Ag and the electromotive force of the cell was determined at several temperatures. The relation of the electromotive force of such a cell to the ionization constant of the weak acid present is expressed by the equation

$$pK - \log \frac{\gamma_{Cl^-}\gamma_{HG}}{\gamma_{G^-}} = \frac{(E - E_0)F}{2.303RT} - \log \left(\frac{\nu m_2}{m_1 - m_H} - 1\right) + \log m_1 \quad (1)$$

where m_1 is the molality of hydrochloric acid, m_2 the molality of the salt of the weak electrolyte and ν is the valence of the cation of the salt. The other terms have their usual significance. Inspection of equation (1) reveals that the right-hand side consists of known or measured quantities with the exception of m_H, which occurs as a small correction term and may be estimated with sufficient accuracy by a simple approximation. Therefore, at any temperature, if the right-hand side is plotted as a function of the ionic strength, the intercept at zero ionic strength will be the negative logarithm of the ionization constant. Derivations of equations similar to equation (1) as well as a complete description of the experimental technique have been given in former papers.[3,4] Values of E_0 for the cell used in the measurements have been determined by Harned and Ehlers.[5]

The electromotive forces at the indicated tem-

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

[2] Harned and Ehlers, *ibid.*, **54**, 1350 (1932).

[3] Nims, *ibid.*, **55**, 1946 (1933).

[4] Nims and Smith, *J. Biol. Chem.*, **101**, 401 (1933).

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

TABLE I

ELECTROMOTIVE FORCE OF CELLS CONTAINING GLYCOLATE BUFFER SOLUTIONS

m_1	m_2	Observed E corrected to one atmosphere H_2 at				
		0.3°	12.5°	25.9°	37.5°	50°
			Potassium			
0.001958	0.003765	0.59502	0.60320	0.61142	0.61936	0.62721
.004110	.007903	.57599	.58329	.59051	.59758	.60451
.005966	.01147	.56670	.57356	.58037	.58699	.59342
.006100	.01173	.56598	.57289	.57966	.58630	.59276
.007598	.01461	.56074	.56732	.57381	.58018	.58635
.01243	.02391	.54882	.55483	.56077	.56655	.57216
.01318	.02534	.54738	.55336	.55924	.56498	.57055
.02322	.04465	.53392	.53924	.54446	.54954	.55447
.03388	.06515	.52502	.52988	.53473	.53940	.54398
			Lithium			
0.002004	0.004070	0.59644	0.60479	0.61299	0.62096	0.62869
.004037	.008200	.57861	.58601	.59335	.60054	.60759
.005911	.01201	.56907	.57605	.58293	.58966	.59621
.007633	.01653	.56552	.57226	.57902	.58559	.59213
.01086	.02352	.55673	.56305	.56941	.57571	.58181
.01565	.03389	.54789	.55381	.55974	.56558	.57133
.02504	.05421	.53652	.54198	.54737	.55263	.55780
.03088	.06686	.53145	.53665	.54180	.54686	.55178
.03835	.08305	.52617	.53112	.53608	.54095	.54568
			Barium			
0.003640	0.003306	0.57619	0.58347	0.59069	0.59772	0.60452
.005516	.005009	.56543	.57221	.57896	.58554	.59196
.007184	.006524	.55871	.56523	.57164	.57788	.58392
.009395	.008532	.55180	.55800	.56413	.57014	.57597
.01105	.01003	.54764	.55370	.55960	.56541	.57106
.01522	.01382	.53952	.54520	.55075	.55618	.56145
.01866	.01695	.53449	.53994	.54527	.55047	.55548
.03000	.02725	.52224	.52714	.53193	.53660	.54111
.03661	.03325	.51729	.52197	.52651	.53097	.53526

peratures and the concentrations of the constituents of the individual solutions are listed in Table I. From these results the ionization constants were calculated. Figure 1 indicates the extent of agreement among the three series of results obtained at 25°. It is believed that the values of pK derived from the extrapolations at the various temperatures are precise to within ±0.003 of a pK unit.

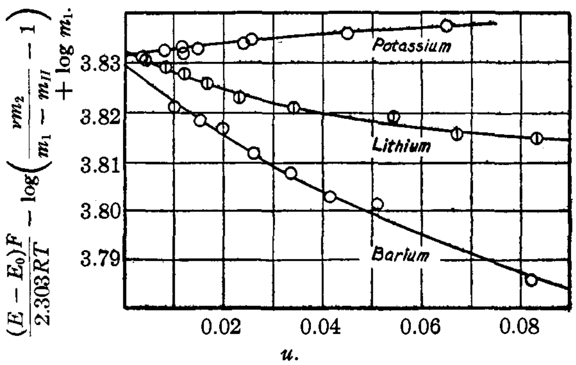

Fig. 1.—A plot of the right-hand side of equation (1) against the ionic strength at 25°. The intercept at zero ionic strength is the negative logarithm of the ionization constant. The three lines were obtained from buffer solutions containing potassium, lithium and barium glycolates, respectively.

Harned and Embree[6] have found that for many weak acids the variation of the ionization constant with temperature can be expressed by a very simple empirical equation. This equation contains two arbitrary constants: θ, the temperature at which the ionization is a maximum, and $pK_{\text{max.}}$, where $K_{\text{max.}}$ is the maximum value of the ionization constant. For glycolic acid the equation was found to be

$$pK = pK_{\text{max.}} + 5 \times 10^{-5}(t - \theta)^2 = 3.829_6 + 5 \times 10^{-5}(t - 30.2)^2 \quad (2)$$

Table II gives values of pK determined by extrapolation of equation (1) as well as those calculated by equation (2). The table also includes values of the increase in free energy, heat content and entropy for the ionization of glycolic acid at infinite dilution. These were computed from re-

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[6] Harned and Embree, THIS JOURNAL, 56, 1050 (1934).

lations obtained by substitution of equation (2) in the proper thermodynamic equations.

TABLE II

THE VALUES OF pK, AND OF VARIOUS THERMODYNAMIC FUNCTIONS FOR THE IONIZATION OF GLYCOLIC ACID AT INFINITE DILUTION

Temp., °C.	pK, extrap.	pK, eq. (2)	$\Delta F°$ cal.	$\Delta H°$ cal.	$\Delta S°$ cal./deg.
0.3	3.875	3.874_3	4850	1020	−14.00
12.5	3.844	3.845_3	5028	660	−15.29
25.0	3.831	3.831_0	5229	210	−16.83
37.5	3.833	3.832_3	5450	−320	−18.59
50.0	3.849	3.849_2	5695	−920	−20.55

For the ionization constant of glycolic acid at 25°, 1.49×10^{-4} is given in the "International Critical Tables"[7] whereas 1.475×10^{-4} is obtained from the present experiments. Larsson and Adell[8] report a value of pK for 18° only 0.002 lower than that given by equation (2), while Pedersen's[9] results are 0.008 lower at 0 and 18°.

The observed differences in the initial slopes of the lines in Fig. 1 are due to the specific effects of the cations present upon the term $-\log \gamma_{\mathrm{Cl}^-}\gamma_{\mathrm{HG}}/\gamma_{\mathrm{G}^-}$ in equation (1). This behavior is not inconsistent with the principle of specific interaction of Brönsted[10] but is in disagreement with the ionic strength principle of Lewis and Randall.[11]

Summary

1. The thermodynamic ionization constant of glycolic acid has been determined over the temperature range of 0 to 50°.

2. The free energy, heat content and entropy change for the ionization of glycolic acid at infinite dilution have been computed.

NEW HAVEN, CONN.

RECEIVED MARCH 25, 1936

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[7] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. VI, p. 262.

[8] Larsson and Adell, *Z. physik. Chem.*, **A157**, 342 (1931).

[9] Pedersen, *J. Phys. Chem.*, **38**, 993 (1934).

[10] Brönsted, THIS JOURNAL, **44**, 877 (1922).

[11] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 380.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Hydrobromic Acid in Aqueous Solution from Electromotive Force Measurements

BY HERBERT S. HARNED, ALBERT S. KESTON[1] AND JOHN G. DONELSON

The activity coefficient and relative partial molal heat content of hydrochloric acid in aqueous solution recently have been evaluated over considerable temperature and concentration ranges from electromotive force measurements by Harned and Ehlers.[2] A similar study of aqueous hydrobromic acid solutions will now be described. A thorough investigation of the electromotive forces of the cell

$$H_2 \mid HBr\ (m) \mid AgBr - Ag$$

has been made at temperatures varying from 0 to 60° and at concentrations of acid varying from 0.003 to 0.2 *M*. These results are supplemented by a few measurements at concentrations between 0.2 and 1 *M*. From these data, the standard potential of the cell, and the thermodynamic properties of aqueous hydrobromic acid solutions have been computed.

To meet the requirements of certain theoretical computations, the densities of these solutions were determined. From these, equations have been derived so that the normal concentrations may be calculated from the molal concentrations and *vice versa* at any temperature at which the cells were measured.

Experimental Procedure and Examination of Silver–Silver Bromide Electrodes

1. Hydrogen electrodes were the customary platinized platinum type.

2. The cells were of the usual U-shaped type. They were arranged so that they could be completely drained through suitable tubes through the bottom of the thermostat and subsequently filled *in vacuo*.

3. All solutions of hydrobromic acid were boiled *in vacuo* until free of dissolved air, saturated with hydrogen and then introduced into the cell.

4. Each solution was introduced into three cells. The electromotive forces were measured from 0 to 60° at 5° intervals. Three cells prepared in this manner possessed electromotive forces which varied from the mean by not more than ±0.05 mv. Triplicate results at twenty-

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[1] The major portion of the material in this communication was taken from a Dissertation presented by Albert S. Keston to the Graduate School of Yale University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1935.

[2] Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).