[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Temperature Variation of Ionization Constants in Aqueous Solutions

BY HERBERT S. HARNED AND NORRIS D. EMBREE

As a result of recent investigations accurate values of the ionization constants in aqueous solution of formic,[1] acetic,[2] propionic[3] and chloroacetic acids,[4] of the acid and base constants of glycine[5] and alanine,[6] and of the ionization constants of HSO_4^-[7] and $H_2PO_4^-$[8] throughout considerable ranges of temperature are known. It is the purpose of this communication to show that the ionization constants at one atmosphere pressure of all these electrolytes conform to a general empirical law as far as their behaviors with respect to temperature are concerned.

It has been observed that the ionization constants of a number of these electrolytes first increase, then pass through maxima and finally decrease with increasing temperature. If we plot log K, where K is the ionization constant, against t, the centigrade temperature, we find that the curves are superimposable. Consequently, if ($\log K - \log K_m$), where K_m is the maximum value of the ionization constant, is plotted against ($t - \Theta$), where Θ is the temperature of the maximum, all points representing this function derived from the ionization constants of acetic, propionic, formic acids and $H_2PO_4^-$ fall on the same curve as shown by Fig. 1. This relation is quite accurate and is within the probable error of the experimental determinations of these quantities.

Although in the temperature range investigated the ionization constants of chloroacetic acid, glycine and alanine do not exhibit maxima, indications are present which show unquestionably that such maxima exist at other temperatures. It is interesting to note that the ionization of chloroacetic acid decreases with temperature and the ionization constants of glycine and alanine increase with temperature.

From the equation derived by Wright which expresses the variation of log K with the temperature an approximate value of Θ for chloroacetic acid was obtained. Using this preliminary value the values of $\log K - \log K_m$ were found to fall very close to the curve.

From the equations derived by Owen for the temperature variation of the acid and base constants of glycine,[9] the maxima were calculated and the values of ($\log K - \log K_m$) were found to fit accurately on the curve as is also indicated by Fig. 1.

The law demonstrated by Fig. 1 may be stated in the following manner. At constant pressure and in aqueous solutions

$$\log K - \log K_m = f(t - \Theta) \qquad (1)$$

Thus the variation of log K referred to log K_m for all ionizations is a universal function of ($t - \Theta$). The ionization constants of the electrolytes mentioned were all determined by electromotive force measurements. Very few of the points lie further from the curve drawn through them by an amount corresponding to an error in electromotive force greater than ±0.1 mv. or ±0.4% in the value of K.

The ionization constant of ammonium hydroxide which has been evaluated from conductance measurements[10] through a considerable temperature range also shows a maximum and the plot of these results fits our curve. The deviations, however, are so great that we have not included them in Fig. 1.

The ionization constant of water has also been evaluated by conductance measurements up to 300°[11] and has been shown to possess a maximum at about 275°. Unfortunately, these results are not exactly comparable to ours since they were determined at higher pressures. However, from the nature of the results from 0 to 60°, we have reason to believe that the ionization constant of water will also conform to the general relation.

Upon consideration of the curve in Fig. 1, it was observed immediately that in the neighbor-

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(1) Harned and Embree, THIS JOURNAL, **56**, 1042 (1934).

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

(3) Harned and Ehlers, *ibid.*, **55**, 652 (1933).

(4) Wright, *ibid.*, **56**, 314 (1934).

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

(6) Nims and Smith, *J. Biol. Chem.*, **101**, 401 (1933).

(7) Hamer, THIS JOURNAL, **56**, 860 (1934).

(8) Nims, *ibid.*, **55**, 1946 (1933).

(9) These are the acid and base constants as defined by the "zwitter ion" theory of Bjerrum [*Z. physik. Chem.*, **104**, 147 (1923)] $K_A = \frac{a_{z\pm}a_{H^+}}{a_{zH^+}}$ and $K_B = \frac{a_{z\pm}a_{OH^-}}{a_{zOH^-}}$, respectively. It is our opinion that this conformity is good evidence for Bjerrum's theory in the case of glycine and, as we shall show later, alanine.

(10) "International Critical Tables," McGraw-Hill Book Company, New York, 1929, Vol. VI, p. 260.

(11) "International Critical Tables," McGraw-Hill Book Company, New York, 1929, Vol. VI, p. 152.

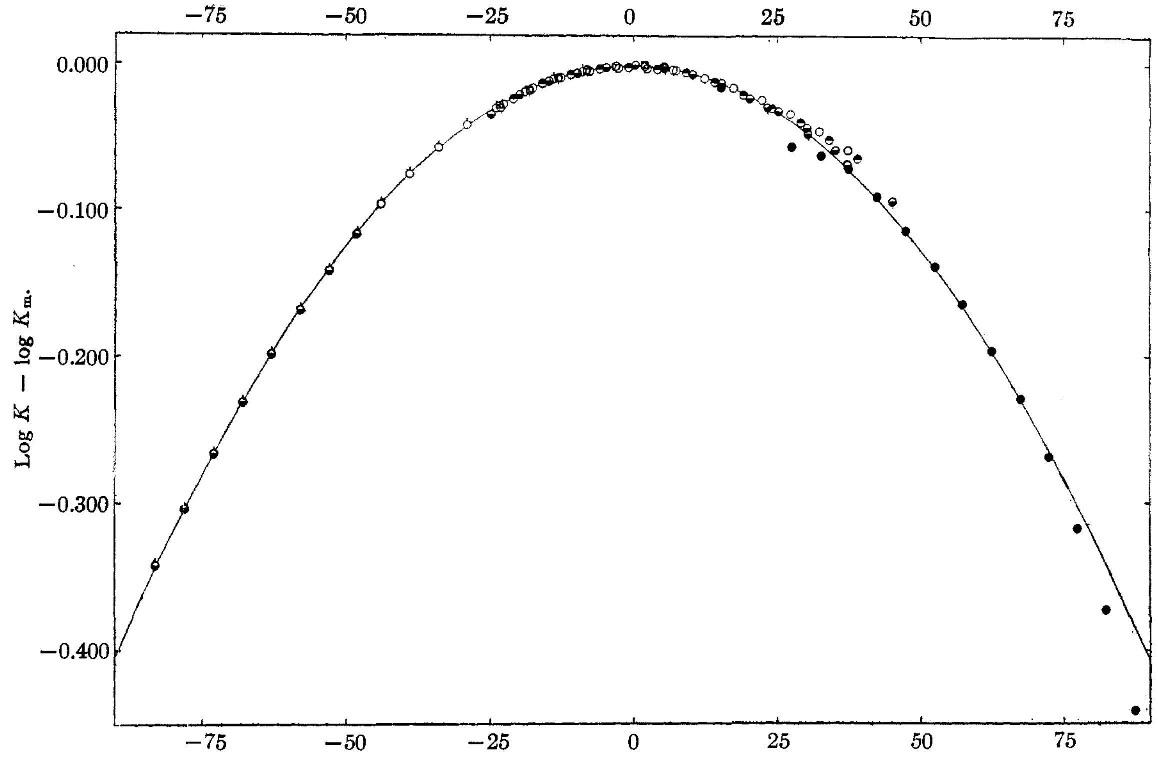

Fig. 1.—The graph of $\log K - \log K_m$ against $(t - \Theta)$: ⦶ glycine (K_B), ○ glycine (K_A), ⊖ formic acid, □ alanine (K_A), ♀ $H_2PO_4^-$, ○ acetic acid, ● propionic acid, ♀ chloroacetic acid, ● HSO_4^-. The smooth curve represents equation (2) where $p = 5.0 \times 10^{-5}$. Diameter of circles representing points corresponds to 1% of the value of K.

hood of its maximum and for a considerable distance from its maximum it is almost exactly a parabola. Therefore, as a first approximation, we shall employ the equation

$$\log K - \log K_m = -p(t - \Theta)^2 \qquad (2)$$

p is a general constant and has a value of 5.0×10^{-5} deg.$^{-2}$. Thus, $\log K$ as a function of t for all electrolytes may be expressed by a quadratic equation

$$\log K = [\log K_m - p\Theta^2] + 2p\Theta t - pt^2 \qquad (3)$$

in which K_m and Θ are constants characteristic of the electrolyte and the constant p is general.

With the actual knowledge represented by equation (2), we are now able to find Θ and K_m for alanine and HSO_4^- and to revise somewhat the values in the cases of some of the other weak electrolytes. These constants are readily obtained by a graphical method. Thus, by rearranging equation (3)

$$\log K + pt^2 = \log K_m - p\Theta^2 + 2p\Theta t \qquad (4)$$

is obtained.

If $(\log K + pt^2)$ is plotted against t a straight line should be obtained the slope of which is $2p\Theta$ and the intercept at t equals 0° is $(\log K_m - p\Theta^2)$. Since p is known, Θ and $\log K_m$ may be evaluated. Incidentally, the intercept at any convenient value of t may be used for the evaluation of $\log K_m$ since Θ is immediately calculable from the slope.

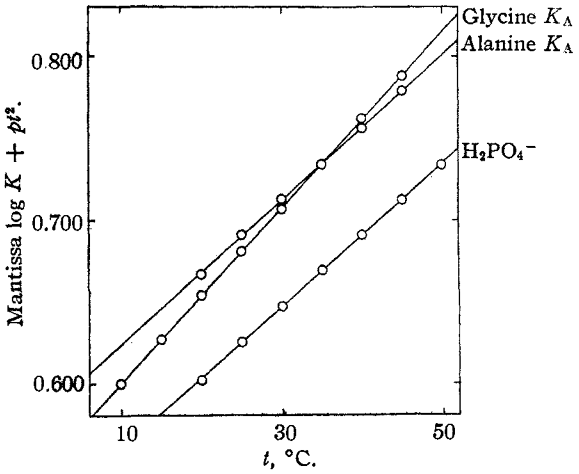

Fig. 2.—Graphs of equation (4) for glycine (K_A), alanine (K_A) and $H_2PO_4^-$.

The plots of this function for $H_2PO_4^-$ and the acid constants of glycine and alanine are shown in Fig. 2. For convenience in graphing the three sets of values on one figure, the mantissas of $\log K_m + pt^2$ have been plotted and 0.2 has been subtracted from the values of this quantity in the case of $H_2PO_4^-$. The points are almost exactly on straight lines. We did not need to use this method for the base constant of glycine since the equation employed by Owen for the variation of $\log K$ with t was a quadratic like equation (3).

The graphs (mantissa of $\log K + pt^2$) for formic, acetic[12] propionic and chloroacetic[12] acids are shown in Fig. 3. In the temperature range of from 0 to 40° it is evident that the points fall on the straight lines within the estimated accuracy, showing that the values of ($\log K - \log K_m$) conform to the equation. We offer no explanation for the slight deviations for the points representing values of K at temperatures from 45 to 60°. In the case of HSO_4^-, there are deviations at 0 and 5° as well as in the range 45–60°, but the probable experimental error as estimated by Hamer is about 2%. Since the values from 10 to 40° are undoubtedly the most accurate and since they fall on a straight line, we feel justified in using them to determine the character of the graph. Values of K_m and Θ determined by this procedure are compiled in Table I.

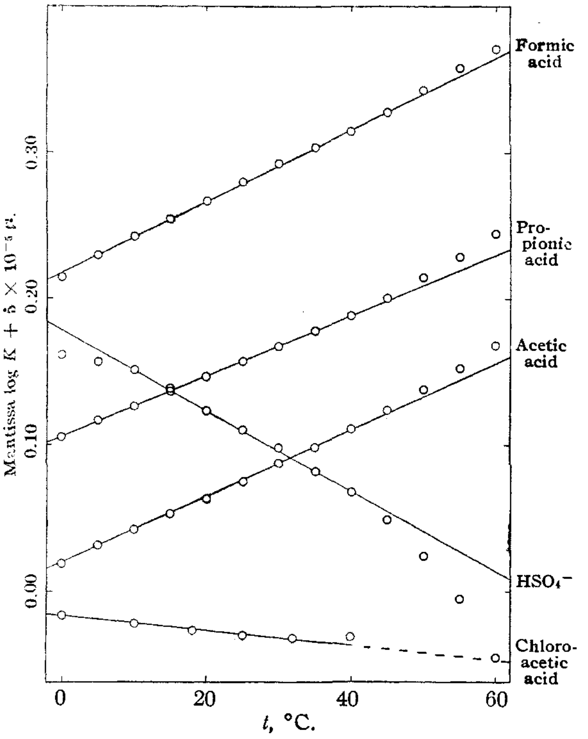

Fig. 3.—Graphs of equation (4) for acetic, propionic, formic and chloroacetic acids, and HSO_4^-.

TABLE I

VALUES OF LOG K_m AND Θ. $p = 5.0 \times 10^{-5}$

	Θ	$10 + \log K_m$
HSO_4^-	−27.6	8.2166
Chloroacetic acid	− 5.4	7.1853
Propionic acid	20.9	5.1278
Acetic acid	22.6	5.2456
Formic acid	24.7	6.2480
$H_2PO_4^-$	43.1	2.8112
Alanine (K_A)	43.3	6.677
Glycine (K_A)	53.9	7.691
Glycine (K_B)	93.0	6.012
Alanine (K_B)	(286)	(3.532)
Water	(360)[a]	(1.58)

[a] Estimated by eq. (4) from the ionization constants from 0 to 60° determined by Harned and Hamer [THIS JOURNAL, **55**, 2194 (1933)].

Since in the cases of alanine (K_B) and water, Θ is so far from the region of temperatures where accurate values of K are known, we place no reliance on the values of Θ and $\log K_m$ for these electrolytes given in Table I. Indeed the approximation represented by equation (2) could not reasonably be expected to hold in these cases. However, as previously mentioned, there is reason to conclude that the general expression in equation (1) is valid for both these cases.

Since equation (1) promises to express a general law for weak electrolytes, we are led to the interesting conclusion that the change in heat content of the ionization reaction, ΔH, is a function of only one characteristic constant Θ, since

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H}{RT^2} = 2.3 \frac{\partial f(t - \Theta)}{\partial T} \qquad (5)$$

Using the approximation given by equation (2), we find that

$$\Delta H = -2.3 \times 10^{-4} RT^2 (t - \Theta) \qquad (6)$$

In Table II, values of ΔH calculated by this equation at 10, 25 and 40° are compared with those previously reported.

The agreement is good in the cases of glycine and alanine where the reported values of ΔH were determined by graphical methods. In some of the other cases in which the agreement is not so good, an equation of an arbitrary form for $\log K$ with four constants derived from the arbitrary equation

$$\Delta H = a + bT + cT^2$$

was employed. The evaluation of ΔH from measurements of K is subject to large errors. The calculation should be considerably improved by

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[12] For convenience in plotting, 0.2 has been subtracted from the values of the function.

TABLE II

VALUES OF HEAT CONTENTS OF THE IONIZATION REACTIONS

		10°	25°	40°
Formic acid	Calcd. Eq. 6	550	− 12	− 690
	Reported	573	− 13	− 657
Acetic acid	Calcd. Eq. 6	470	− 100	− 730
	Reported	389	− 112	− 628
Propionic acid	Calcd. Eq. 6	410	− 170	− 860
	Reported	384	− 168	− 746
Chloroacetic acid	Calcd. Eq. 6	− 560	−1240	−2030
	Reported	− 593	−1170	−1639
$H_2PO_4^-$	Calcd. Eq. 6	1230	740	140
	Reported	..	..	..
HSO_4^-	Calcd. Eq. 6	−1400	−2150	−3040
	Reported	− 934	−2229	−3665
Glycine (K_A)	Calcd. Eq. 6	1670	1180	630
	Reported	1567	1165	655
Glycine (K_B)	Calcd. Eq. 6	3090	2780	2370
	Reported	3044	2765	2377
Alanine (K_A)	Calcd. Eq. 6	920	750	155
	Reported	..	720	210

employing the less arbitrary function represented by equation (6).

There does not appear to be any general quantitative relation between Θ and $\ln K_m$. It appears that the weaker the electrolyte the greater the value of Θ but this is a very rough statement of the facts and a number of exceptions occur.

As a result of this study one important observation concerning any discussion of ionization constants in relation to the constitution of the ionizing electrolytes should be made. For such a comparison to have real value, it will be essential to select the values of the ionization constants at their maxima or at their corresponding temperatures, Θ.

Summary

1. Recent accurate determinations of ionization constants of weak acids, bases and ampholytes reveal that at one atmosphere pressure and in aqueous solution

$$\log K - \log K_m = f(t - \Theta)$$

where $f(t - \Theta)$ is a general function and K_m and Θ are constants characteristic of each ionization reaction. K_m is the maximum value of the ionization constant which occurs at the temperature Θ.

2. The approximation equation

$$\log K = \log K_m - 5.0 \times 10^{-5}(t - \Theta)^2$$

is valid within experimental error in the region near the maximum values of K. As a matter of fact, it can be employed with confidence over a range of $t - \Theta = \pm 75$.

3. The change in heat content of ionization is given by

$$\Delta H = 2.3\ RT^2\ (\partial f(t - \Theta)/\partial T)$$

and its value given by the use of only one characteristic constant Θ.

4. Some values of ΔH given by the approximate equation

$$\Delta H = 2.3 \times 10^{-4}\ RT^2\ (t - \Theta)$$

have been calculated and compared with values computed by other methods.

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

Studies on the Vapor Pressure–Temperature Relations and on the Heats of Hydration, Solution and Dilution of the Binary System Magnesium Nitrate–Water

BY WARREN W. EWING, ERNST KLINGER AND JOHN D. BRANDNER

This article, presenting heat and vapor pressure data obtained on the binary system magnesium nitrate–water, is a continuation of the studies which are being carried out in this Laboratory on the nitrates of certain bivalent metals. These nitrates are peculiarly rich in hydrates and are quite soluble in water, hence they serve as fertile fields for the investigation of hydration phenomena and of the properties of concentrated solutions. Results for calcium nitrate have been presented already. The strontium nitrate system and the zinc nitrate system are being investigated at the present time.

It has been shown[1] that magnesium nitrate exists as the anhydride and in the following hydrated forms: the dihydrate melting at 130.9°, the hexahydrate melting at 89.9°, and the enneahydrate having a transition temperature of −14.7°. In this investigation vapor pressures of unsaturated solutions, of saturated solutions, and of mixed hydrates have been measured. Likewise, heats of dilution and of solution have been determined. From both vapor pressure and calorimetric measurements, partial molal heats of

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[1] Ewing, Brandner, Slichter and Griesinger, THIS JOURNAL, **55**, 4822 (1933); Ewing and Klinger, *ibid.*, **55**, 4825 (1933).