little with the ionic strength of the solution. Its value between $\mu = 0.5$ and 1.0 may be considered to be -0.741 v.

Acknowledgment.—For various helpful suggestions and for assistance in the interpretation of the experimental data we are glad to acknowledge our indebtedness to Professor George Scatchard of this Institute.

Summary

The molal ferric–ferrous electrode potential has been obtained from electromotive force measurements in perchloric acid solution of cells of the type described in the introduction. The value found is -0.7701 v. The electromotive force data have been corrected for hydrolysis of ferric iron and plotted in such a way that errors from liquid junction potentials and changing activity coefficients are removed by extrapolation.

A table of values of the formal ferric–ferrous electrode potential of $Fe(ClO_4)_3$–$Fe(ClO_4)_2$ mixtures in $HClO_4$ solution from an ionic strength of 0.1 to 1.0 has been prepared. For the ionic strength range 0.5 to 1.0, the value is -0.741 v.

A new method for the determination of free acid in the presence of ferrous and ferric iron is described.

CAMBRIDGE, MASS. RECEIVED JULY 28, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heats of Ionization of Water, Ammonium Hydroxide, Carbonic, Phosphoric, and Sulfuric Acids. The Variation of Ionization Constants with Temperature and the Entropy Change with Ionization

BY KENNETH S. PITZER[1]

In addition to their value as thermochemical data, these heats of ionization make possible the calculation of the changes of entropy with ionization, and the entropies of some of the ions involved. The latter calculations will be presented in another paper. Also it is found that certain approximate generalizations can be made concerning the change in entropy and heat capacity with ionization, and that these results lead to equations for the variation of ionization constants with temperature.

Throughout this paper a defined calorie equal to 4.1833 international joules will be used, and extrapolations to infinite dilution will be made consistent with the Debye–Hückel theory. The uncertainties given for the various results are from two to three times the probable errors and should, therefore, outline a region within which the true value almost certainly lies. An attempt has been made to include all possible sources of error, including questionable assumptions and estimates made as part of the calculations.

Apparatus.—The chief aim in the design of this calorimeter was the attainment of high sensitivity in temperature determination. This makes possible heat of reaction measurements at sufficiently low concentration so that heats of dilution may be estimated without too great uncertainty. Another feature is the economy in electrical equipment.

The calorimeter itself consists of a Pyrex vacuum flask with a ground glass joint in the neck. Into this fits a stopper which is also evacuated, and which carries the electrical leads and stirrer through a central tube of small diameter. Thus, when the flask is so filled that the water surface is just up in the small central tube, there is little opportunity for evaporation. The flask is 25 cm. long and has a volume of 885 ml. The entire unit is completely submerged in a water thermostat controlled to within 0.003° during a single run. For heat of solution measurements the sample is placed in a very thin glass bulb sealed with paraffin on to a glass rod which in turn slides through the hollow stirrer shaft. An additional propeller is placed just above the sample where it will be most effective after the bulb has been broken against the bottom of the flask. When two solutions are to be mixed one is used at relatively high concentration and placed in a glass tube with silver disks sealed into its ends by means of paraffin. This is supported just below the stirrer through which a rod may be thrust, breaking the seals.

A resistance thermometer consisting of 96 ohms of no. 38 silk insulated copper wire and a heater composed of 100 ohms of no. 30 manganin are wound on a silver tube 5.2 cm. in diameter and 16 cm. long. The leads are of no. 24 manganin and no. 24 copper, respectively, and single in each case. The windings are afforded protection by a cover of thin silver welded in place. This thermometer serves also as a stirrer tube which with its large surface gives excellent heat exchange.

The electrical circuits are shown in Fig. 1. The three constant arms of the thermometer bridge are of manganin, wound in a manner similar to the thermometer itself and submerged in a three-liter oil-bath. The heat exchange is such that a current of 0.01 amp. may be used if desired. The connections to the thermometer have so low

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[1] Shell Research Fellow, Academic Year, 1936–1937.

a resistance that moderate temperature changes introduce a negligible error. The only switch contacts in this circuit are in the parallel, adjustable resistance, R, which is a high grade Leeds and Northrup resistance box with 10,000, 1000, 100, and 10-ohm dials. With this set at 20,000 ohms or more, contact resistances are estimated to introduce errors of less than 0.00003° in the temperatures.

Although the use of a measuring current of 0.01 amp. makes the resistance thermometer sensitive to 0.00001°, and the temperature drift before and after heating is consistent to about this amount, the results of calibration runs with a temperature rise of 0.1° spread over about 0.0003°, which suggests that the temperature readings after comparatively large changes are reproducible only to that accuracy. For this reason a smaller measuring current, say 0.003 amp., may be used without loss of accuracy and with a reduction in heating.

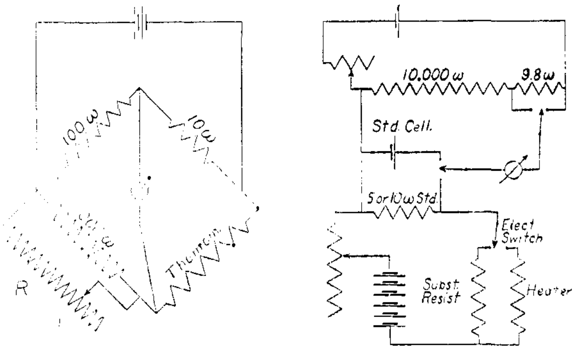

Fig. 1.—Resistance thermometer and heater circuits for the calorimeter.

The heater circuit is very simple, its chief requirements being that the resistances of the heater and the comparing standard be known accurately. These were calibrated by comparison with standard resistances of nearly equal resistance, a White potentiometer being used for this purpose. The electrically actuated timing switch is so connected to a timing circuit from the University Observatory that it may be thrown on any given second with an error of not more than one or two hundredths of a second.

Materials.—The chemicals used were all of "c. p." grade and were purified further if necessary. The hydrochloric acid was redistilled in an all-glass still, diluted with freshly distilled water, and stored in a bottle which previously had contained hydrochloric acid for a period of at least one year. Analysis by weighing precipitated silver chloride gave as the average of three determinations 1.1414 ± 0.0001 moles of hydrochloric acid per kg. of soln. The series of experiments on the heat of ionization of water was completed within three weeks after making up a fresh solution, thus avoiding any possible errors due to reaction of the acid with the glass. The sodium hydroxide solution was carefully freed from carbonate by the addition of a very slight excess of barium hydroxide. A paraffin-lined bottle was used to hold the sodium hydroxide solution, which was analyzed by comparison with the hydrochloric acid. Weight burets were used except for experiments where the precision needed was only about 1%. Unless the presence of carbon dioxide was of no significance, the distilled water was boiled and was protected from the air thereafter. The preparation of the other solutions which were used was carried out in a similar fashion, except that in several cases less precise analyses sufficed.

The Heat of Ionization of Water.—The best available value for the heat of ionization of water is that obtained by Rossini,[2] after a review of the available data, principally that of Richards and co-workers. The value thus obtained for 18° (ΔH° = 13,709 ± 16 cal.) seems quite satisfactory; however, the temperature coefficient is somewhat uncertain. Rossini[3] has also reviewed the available data on the heat capacities of aqueous solutions, but the extrapolations to infinite dilution were carried out in a manner not entirely consistent with the Debye–Hückel theory. The recent work of Gulbransen and Robinson[4] and Young and Machin[5] on the relative heat capacity of sodium chloride solutions establishes the validity of the limiting form of the Debye–Hückel theory for heat capacities in the very dilute region, and, moreover, gives probably the best value for the limiting slope. Consequently, it seemed desirable to recalculate the heat capacity of the pertinent aqueous solutions making use of this more recent information. The data for lithium, sodium, and potassium chlorides and hydroxides, and hydrochloric acid appeared most reliable in the dilute region and were therefore employed. The experimental values of the apparent molal heat capacity (Φ_c) were plotted against the square root of the molality as in Fig. 2. Three requirements were imposed in drawing the curves: first, that all experimental data be fitted within their reasonable uncertainties; second, that the limiting slope $d\Phi_c/d\sqrt{m}$ equal 8.0 (this is an average value obtained from both heat of dilution and dielectric constant data); and, third, that the heat capacities at infinite dilution be the sums of those of the individual ions. These criteria fortunately leave but little uncertainity in the course of the heat

TABLE I

MOLAL HEAT CAPACITIES OF AQUEOUS IONS AT INFINITE DILUTION AND 25°

(Potassium and Chloride Assumed Equal)

Ion	Φ_c^0, cal./deg.	Ion	Φ_c^0, cal./deg.
K^+	−14.1	H^+	−15.9
Na^+	− 7.5	OH^-	−16.1
Li^+	− 2.4	Cl^-	−14.1

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[2] Rossini, *Bur. Standards J. Research*, **6**, 847 (1931).

[3] Rossini, *ibid.*, **7**, 47 (1931).

[4] Gulbransen and Robinson, THIS JOURNAL, **56**, 2637 (1934).

[5] Young and Machin, *ibid.*, **58**, 2254 (1936).

capacity curves. The values for infinite dilution are summarized in Table I.

Combining the values in Table I for hydrogen and hydroxide ions with the heat capacity of water, one obtains for the reaction $H_2O = H^+ + OH^-$, $\Delta C_p^0 = -50.0$ cal./deg. at 25° and, using Rossini's results, $d(\Delta C_p^0)/dT = 0.3$ and $\Delta H^0 = 13{,}709$ cal./mole at 18°, one finds $\Delta H^0 = 13{,}352 - 50.0(t - 25) + 0.15(t - 25)^2$ cal./mole.

While the error in the above value could hardly be very large, nevertheless an accurate experimental value for 25° seemed desirable. Consequently, a single series of experiments was carried out with the greatest care. The reactions whose heats were measured are the following

$$HCl{\cdot}46.5H_2O + NaOH{\cdot}1065.5H_2O = NaCl{\cdot}1113H_2O \quad (1)$$

$$HCl{\cdot}46.5H_2O + 1165.5H_2O = HCl{\cdot}1112H_2O. \quad (2)$$

The results for these reactions may then be combined with the heats of dilution of $HCl{\cdot}1112H_2O$,[6] $NaOH{\cdot}1065.5H_2O$,[7] and $NaCl{\cdot}1113H_2O$[4] to give the heat of neutralization at infinite dilution, or the heat of ionization of water.

In the heat of neutralization experiments (Equation 1) the temperature intervals of the reaction and calibration runs were made to coincide as nearly as possible. The calculations were made in the usual manner, using the rate of temperature drift before and after heating periods to correct for heat conduction to the thermostat and other small losses or gains of heat. The average of three experiments gave 13,828 ± 12 cal. for the heat of the reaction in Equation (1) at 25°. The heat effect for Equation (2), being small, was easily measured, the result being 352 ± 8 cal. at 25°. Since this result is subtracted from that for Equation (1), any constant errors will be removed from the final value. Thus the value here obtained for the heat of the dilution of hydrochloric acid indicated in Equation (2) is to be preferred for the present calculations even though equally accurate values have been given previously.[7] The final calculation of the heat of ionization of water is summarized in Table II.

TABLE II

THE HEAT OF IONIZATION OF WATER

$$HCl{\cdot}46.5H_2O + NaOH{\cdot}1065.5H_2O = NaCl{\cdot}1113H_2O + 13{,}828 \pm 12 \text{ cal.} \quad (1)$$

$$HCl{\cdot}46.5H_2O + 1065.5H_2O = HCl{\cdot}1112H_2O + 352 \pm 8 \text{ cal.} \quad (2)$$

$$HCl{\cdot}1112H_2O + \infty H_2O = HCl{\cdot}(\infty + 1112)H_2O + 100 \text{ cal.} \quad (3)$$

$$NaOH{\cdot}1065.5H_2O + \infty H_2O = NaOH{\cdot}(\infty + 1065.5)H_2O + 86 \text{ cal.} \quad (4)$$

$$NaCl{\cdot}1113H_2O + \infty H_2O = NaCl{\cdot}(\infty + 1113)H_2O + 73 \text{ cal.} \quad (5)$$

(1) + (5) − (2) − (3) − (4) gives

$$HCl{\cdot}(\infty + 1112)H_2O + NaOH{\cdot}(\infty + 1065.5)H_2O = NaCl{\cdot}(\infty + 1113)H_2O \quad (6)$$
$$+ (\infty + 1065.5)\,H_2O + 13{,}363 \pm 16 \text{ cal.}$$

or $H_2O(l.) = H^+(aq.) + OH^-(aq.) \quad \Delta H = 13{,}363 \pm 16$ cal.

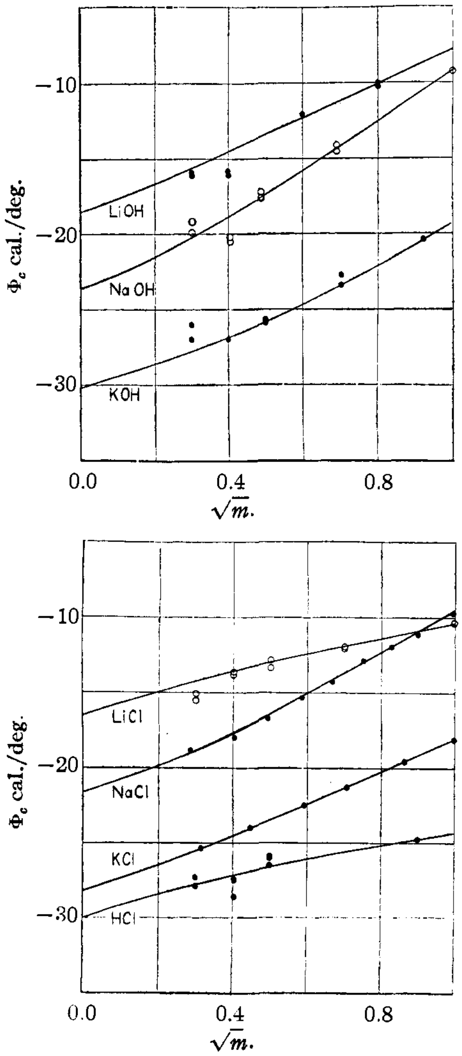

Fig. 2.—Apparent molal heat capacity of aqueous solutions[8] at 25°.

The result given in Table II is thus in excellent agreement with that calculated above, and as the uncertainties in the two values are not signifi-

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[6] Landolt-Börnstein, "Tabellen."

[7] Rossini, *Bur. Standards J. Research*, **6**, 791 (1931), converted to 25°.

[8] (a) NaCl and KCl, Randall and Rossini, THIS JOURNAL, **51**, 323 (1929). (b) LiCl, HCl and KOH, Gucker and Schminke, *ibid.*, **54**, 1358 (1932). (c) LiOH and NaOH, Gucker and Schminke, *ibid.*, **55**, 1013 (1933). See ref. 3 for older data.

TABLE III

HEATS OF IONIZATION

Subst.	Vol. (1), ml.	Soln. (1)	Soln. (2) vol. (2) = 885 − vol. (1)	Heat evolved, cal.	Molal ΔH^0, cal.		
					This research	Other research	"Best value"
NH_4OH	35	0.956 M NaOH	0.05 M NH_4Cl	29.4 ± 0.5	865 ± 30	....	865 ± 30
H_2CO_3	10	1.162 M HCl	.015 M $NaHCO_3$	26.6 ± .6	1843 ± 60	....	1843 ± 60
HCO_3^-	10	1.162 M HCl	.015 M $NaHCO_3$ .015 M Na_2CO_3	46.7 ± .5	3500 ± 100	....	3500 ± 100
H_3PO_4	15	1.000 M HCl	.020 M NaH_2PO_4	−9.0 ± .5	−1950 ± 80	−1750[9]	−1880 ± 80
$H_2PO_4^-$	5	1.000 M HCl	.009 M Na_2HPO_4 .001 M NaH_2PO_4	6.8 ± .3	800 ± 80	740[10]	800 ± 80
HPO_4^{--}	15	1.000 M HCl	.080 M Na_2HPO_4 .020 M Na_3PO_4	76.4 ± .5	3500 ± 500	....	3500 ± 500
HSO_4^-	10	0.790 M Na_2SO_4	1.000 M HCl	−45.1 ± 1.0	−5200 ± 500	−2229[11]	−5200 ± 500

TABLE IV

THERMODYNAMIC CONSTANTS FOR THE IONIZATION OF WEAK ACIDS IN AQUEOUS SOLUTION AT 25°

Acid	ΔH^0, cal./mole	ΔF^0, cal./mole	$-\Delta S^0$, cal./deg. mole	$-\Delta C_p^0$, cal./deg. mole
Acetic[13]	−112	6,488	22.1	34
Metaboric[14]	3,360	12,599	31.0	43
Butyric[15]	−691	6,574	24.4	46
Carbonic (1st)[16]	1,843	8,683	22.9	
Chloroacetic[17]	−1,170	3,900	17.0	35
Chlorous[18]	−4,100	2,670	22.7	
Formic[19]	−13	5,120	17.2	41
Hypochlorous[20]	3,320	10,100	22.8	
Phosphoric (1st)[9]	−1,880	2,898	16.0	
Propionic[21]	−168	6,650	22.9	38
Sulfurous (1st)[22]	4,000	2,725	22.6	
Water[23]	13,358	19,093	19.24 (27)[12]	50
Carbonic (2d)[24]	3,500	13,983	35.2	
Phosphoric (2d)[10]	800	9,830	30.3	
Sulfuric (2d)[11]	−5,200	2,620	26.3	
Phosphoric (3d)[25]	3,500	16,300	43	

cantly different, their average may be taken as a final "best" value

$$\Delta H = 13{,}358 - 50.0(t - 25) + 0.15(t - 25)^2 \text{ cal./mole}$$

The uncertainty in this value appears to be about 12 cal. in or near the 18 to 25° interval. It is impossible to say how much this expression may be in error at temperatures considerably above or below this region.

The Heats of Ionization of Ammonium Hydroxide, Carbonic, Phosphoric, and Sulfuric Acids.—Because of the lack of accurate heat of dilution data it was desirable to measure most of these heat effects in very dilute solution, with resulting loss of precision. Otherwise the estimation of heats of dilution would have led to even greater uncertainty. In each case the heat of ionization itself was measured rather than the heat of neutralization of the weak acid or base. The latter method is less satisfactory because it gives the desired heat of ionization, itself relatively small, as the difference between two large quantities. As an example of the former method, the heat of ionization of ammonium hydroxide was obtained by measuring the heat of reaction of sodium hydroxide with ammonium chloride in dilute aqueous solution. The final solution thus contains both sodium chloride (ionized) and am-

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(9) Nims, THIS JOURNAL, **56**, 1110 (1934).

(10) Harned and Embree, *ibid.*, **56**, 1050 (1934); Nims, *ibid.*, **55**, 1946 (1933).

(11) Hamer, *ibid.*, **56**, 860 (1934). See also discussion below.

(12) The standard state of water is the 55 molal liquid. In order to make the value for water comparable, a value of the entropy R ln 55 larger has been placed in parentheses.

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

(14) Owen, *ibid.*, **56**, 1695 (1934).

(15) Harned and Sutherland, *ibid.*, **56**, 2039 (1934).

(16) Shedlovsky and MacInnes, *ibid.*, **57**, 1705 (1935).

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

(18) Barnett, Thesis, University of California, 1935.

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

(20) (a) Ingham and Morrison, *J. Chem. Soc.*, 1200 (1933); (b) Neumann and Müeller, *Z. anorg. allgem. Chem.*, **185**, 428 (1930).

(21) Harned and Ehlers, THIS JOURNAL, **55**, 2379 (1933).

(22) (a) Johnstone and Leppla, *ibid.*, **56**, 2233 (1934); (b) Roth and Zeumer, *Z. Elektrochem.*, **38**, 164 (1932).

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

(24) MacInnes and Belcher, *ibid.*, **55**, 2630 (1933).

(25) Prideaux and Ward, *J. Chem. Soc.*, **125**, 423 (1924).

monium hydroxide (principally un-ionized); however, the latter should not significantly affect the heat of dilution, except by change of the fraction ionized. This is apparent when one considers that only long range, *i. e.*, coulombic, forces should give a heat of dilution in the range of low concentration.

The experimental results are given in Table III together with values of the molal heats of ionization at infinite dilution calculated therefrom. In these calculations, heats of dilution were taken from sources given above, or were estimated using the Debye–Hückel theory. Where the reaction was not complete, the amount of reaction was calculated from the ionization constant, using estimated activity coefficients if necessary.

No comparisons will be made with the early work of Thomsen, Berthelot, and others because of the difficulty of reducing their results to 25° and infinite dilution, and because improved calorimetric methods have rendered their work comparatively inaccurate.

The Entropy of Ionization of Weak Acids

The changes in heat, free energy, entropy, and heat capacity with ionization are tabulated in Table IV for a number of weak acids. While an exhaustive search of the literature has not been made, it is believed that the values listed are in most cases the best available. On inspection of the data in Table IV it is at once apparent that although ΔH and ΔF have values varying over a wide range, ΔS and ΔC_p are always negative, and for a first ionization have roughly the values -22 and -40 cal./deg. mole, respectively. It is of interest to note that rough theoretical considerations also lead to this result.

The entropy change in the reaction $HA = H^+ + A^-$ may be taken as the absolute entropy of the hydrogen ion plus the entropy difference between A^- and HA. The absolute entropy of the hydrogen ion is known accurately enough for the present purpose from the value of Eastman and Young[26] for the absolute entropy of chloride ion, and the sum of the entropies of hydrogen and chloride ions given by Latimer, Schutz, and Hicks.[27] The value thus obtained is -4.6 cal./deg. mole. The difference between the entropies of the negative acid ion and neutral molecule in solution may be considered as arising from the difference in entropy of the gas ion and molecule, and the difference in their entropies of solution.

The entropy of the gas molecule (HA) will differ from that of the ion (A^-) because of several factors. The increased mass of HA will contribute, at most, about 0.1 cal./deg. mole. If A^- is a non-linear polyatomic molecule, then no rotational degrees of freedom will be lost, although the moments of inertia will be slightly changed. This will have only a small effect on the entropy. In water, hypochlorous acid, and analogous molecules the ion is linear and has then only two degrees of rotational freedom. The loss of the other rotation may mean a loss of the order of five cal./deg. mole in the entropy at 25°. In all of the molecules here considered, the removal of the hydrogen will mean the loss of two vibrations, both of such frequency that they contribute but slightly to the entropy, and, where one rotation of the entire molecule was not lost, an additional vibration of torsional character will be lost. This, of course, assumes that the two bonds of the oxygen atom adjacent to the hydrogen form an angle less than 180°, and that rotation of the OH group with respect to the remainder of the molecule is appreciably hindered.[28] This torsional vibration will contribute in the neighborhood of three cal./deg. mole to the entropy. The symmetry number may be changed by the ionization, thus contributing a difference of the order of one cal./deg. mole. It is thus apparent that the entropy of the gas ion will be less than that of the neutral molecule, and in almost every case by an amount between three and six cal./deg. mole.

The difference in the entropies of solution is less easily discussed. In all the acids in Table IV and, in fact, in almost all weak acids the ionizing proton is attached to an oxygen atom. Since the acid is weak, one presumes that most of the negative charge lies on this oxygen. Then, unless some radical rearrangement of charge occurs on ionization, we may consider the resulting negative ion as an essentially neutral molecule attached to a charged oxygen atom. Applying now the ideas developed by Latimer and co-workers[29] concerning the entropy of solution of simple ions, one finds that the difference in entropies of solution will arise from the compression, due to the electrostatic field, of the water near the charged oxygen atom. Since the effective charge is probably less than one unit, and because the rest of the molecule

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[26] Young, M. B., Thesis, University of California, 1935.

[27] Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 82 (1934).

[28] See Kemp and Pitzer, THIS JOURNAL, **59**, 276 (1937); Pitzer, *J. Chem. Phys.*, **5**, 473 (1937).

[29] (a) Latimer and Kasper, *ibid.*, **51**, 2293 (1929); (b) Latimer, *Chem. Rev.*, **18**, 349 (1936).

excludes water from some of the region around the oxygen, this difference in entropies will probably be considerably less than, possibly one-half of, the entropy of solution of OH^- ion which is -26 cal./deg. mole.[30] In cases where the ion has several equivalent oxygens among which the charge is divided, the above description must be suitably amended, although the expected entropy of solution should be very similar. The entropy of ionization is then the sum of three terms: the absolute entropy of the hydrogen ion, -4.6, the difference in the entropies of the gas ion (A^-) and the molecule (HA), about -4, and the difference in the entropies of solution of the gas ion and molecule which will be considerably smaller than -26. If the last term is taken as $-26/2 = -13$, we find the entropy of ionization to be -22, or roughly the average of the values for the first ionizations listed in Table IV. The weaker acids show larger entropies of ionization, as is to be expected due to the greater concentration of negative charge on the oxygen atom. The entropies of second or third ionizations are larger, because the entropy of solution term depends on the square of the charge.

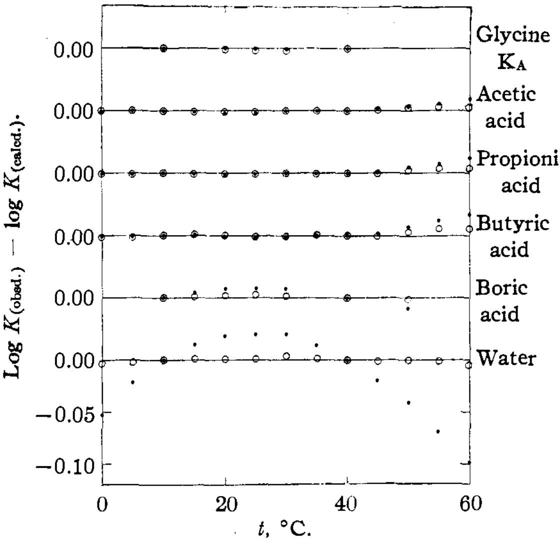

Fig. 3.—Test of equations (10) and (11) with glycine, acetic, propionic, butyric, boric acids and water: open circles, eq. (10); solid circles, eq. (11).

This discussion gives, of course, only a very approximate value for the entropy of ionization, but it does seem to show why this quantity is approximately the same for various weak acids and why it is of the order of magnitude found experimentally. Since the derivation was valid for any ordinary temperature, we may take the derivative of the entropy of ionization with respect to the logarithm of the temperature and obtain the change in heat capacity with ionization. The latter quantity should then have about the same magnitude for different acids, as is found experimentally.

We may now test further the values of the heat of ionization of sulfuric acid given in Table III. It is apparent from Table IV that the value of the entropy of ionization given there, -26.3 cal./deg. mole, is about as small as one would expect. The fact that the heat of ionization found by Hamer[11] gives a still smaller value of the entropy, -16.3, argues strongly against that result.

Variation of Ionization Constants with Temperature.—Using the results of the preceding section, we may now set up approximate expressions which give the ionization constant as a function of temperature, provided a single value of the constant is available. Assuming a constant ΔC_p, thermodynamics gives

$$\Delta H = \Delta H_0 + \Delta C_p T$$

$$\Delta S = \Delta S_0 + \Delta C_p \ln T$$

$$\Delta F = RT \ln K = \Delta H - T\Delta S = \Delta H_0 - T\Delta S_0 + \Delta C_p\,(T - T \ln T)$$

If K and thereby ΔF is known for some temperature say T_1

$$\Delta F = \Delta F_{T_1} + \Delta S_0\,(T_1 - T) + \Delta C_p\,(T - T_1 + T_1 \ln T_1 - T \ln T) \quad (7)$$

If $T_1 = 298.1$, $\Delta C_p = -40$, $\Delta S_{298.1} = -22$

$$\Delta F = \Delta F_{298.1} + 5425 - 246T + 40T \ln T \quad (8)$$

or

$$\log K = (\text{const.}/T) + 53.78 - 20 \log T \quad (9)$$

This expression should be useful for a great many approximate calculations.

If the data on an ionization constant cover a sufficient range of temperature to determine accurately the first derivative (heat of ionization), nevertheless, the knowledge that ΔC_p is probably near -40 cal./deg. should be useful. This gives an equation for the form

$$\log K = A + B/T - 20 \log T \quad (10)$$

Harned and Embree[10] also have discussed the variation of ionization constants with temperature, and have proposed the equation

$$\log K = \log K_m - 5.0 \times 10^{-5}(t - \theta)^2 \quad (11)$$

in which the constants K_m and θ are the maximum value of the ionization constant and the temperature at which the maximum is attained.

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[30] The rotational contribution was excluded from the entropy of the OH^- gas ion since rotation is certainly not present in solution and only the "electrostatic" entropy of solution was desired.

The range of validity of the equation is given as $t - \theta = \pm 75$. The authors make no attempt to interpret this equation theoretically.

It may be noted that both equations (10) and (11) have two undetermined constants, and, since it is known that both can be fitted satisfactorily to the experimental data for many acids, it seems likely that the fundamental assumptions in equation (11) are essentially the same as those of (10), *i. e.*, ΔC_p is a constant and has a value of about -40 cal./deg. Application of the usual thermodynamic equations to (11) yields

$$\Delta C_p = -2.3 \times 10^{-4} RT[T + 2(t - \theta)] \quad (12)$$

or at $T = 298.1$°K.

$$\Delta C_p = -40.6 - 0.273(25 - \theta)$$

Thus for the case in which both θ and t are near 25° it becomes apparent that equations (10) and (11) are essentially the same, and that the theoretical considerations given above are applicable to equation (11) also.

It remains then to consider which of the two equations is more satisfactory when either t or θ is considerably different from 25°. Figure 3 presents graphically the deviations of the experimental from the calculated values of K, for several acids, when the constants of each equation are evaluated from the data at 10 and 40°. The data for other acids which to save space were omitted from Fig. 3, give results similar to those shown, the greater number being similar to glycine. It is thus apparent that equation (10) gives better agreement in virtually every instance where there is an appreciable difference between the two equations.

The writer wishes to acknowledge with thanks the many valuable suggestions made by Professor W. M. Latimer.

Summary

A calorimeter for the precise measurements of heats of reaction in aqueous solution is described. The available data on the heat of ionization of water are considered, and a revised value for the ΔC_p of the reaction obtained. Accurate measurements of the heat of neutralization of hydrochloric acid with sodium hydroxide at 25° are described, which give a value of the heat of ionization of water that is in good agreement with the revised value calculated from previous measurements. The selected "best" value of ΔH^0 for the ionization of water is: $13{,}358 - 50.0(t - 25) + 0.15(t - 25)^2$ cal./mole. The heat of ionization was measured for several weak acids and ammonium hydroxide with the following results

Substance	ΔH^0 of ionization at 25°, 30 cal./mole
NH_4OH	865 ± 30
H_2CO_3	1843 ± 60
HCO_3^-	3500 ± 100
H_3PO_4	−1880 ± 80
$H_2PO_4^-$	800 ± 80
HPO_4^{--}	3500 ± 500
HSO_4^-	−5200 ± 500

The changes in heat, free energy, entropy, and heat capacity with ionization are tabulated for sixteen weak acids. It is discovered that for all "first" ionizations, ΔS° is near -22 cal./mole and ΔC_p near -40 cal./mole, and an explanation of this fact is offered. Use is also made of these generalizations to develop the following formula which gives approximately the ionization constant over a range of temperature, provided a single experimental value is known: $\log K = \text{const.}/T + 53.78 - 20 \log T$. When a series of values of an ionization constant are available, an equation of the form: $\log K = A + B/T + 20 \log T$ is suggested. It is also pointed out that within its limited range of applicability the equation recently suggested by Harned and Embree is essentially equivalent to the second one given above.

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