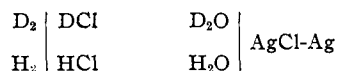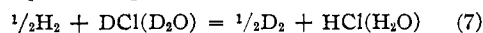ΔF for the dissociation of DOAc increases more rapidly with the temperature than does ΔF for the dissociation of HOAc. On the other hand, the entropy differences are constant. Thus, the greater increase in K_D with increasing temperature is due to the greater increase in ΔH_D over ΔH_H. Since $\Delta F_D - \Delta F_H$ equals $-\Delta F$ for the exchange process (6), the reverse reaction, as expected, is favored on increasing temperature. The values for K_6, the equilibrium constant for the exchange process (6), calculated from $\Delta F_D - \Delta F_H$, are given in Table VII. Also

$$\left(\frac{\partial \Delta H_D}{\partial T}\right)_p - \left(\frac{\partial \Delta H_H}{\partial T}\right)_p = \Delta C_p$$

for process (6) is sensibly independent of temperature and equal to 2.0 cal. deg.$^{-1}$ mole^{-1}. Noonan and LaMer,[13] who made a careful study of the e. m. f. of the cell without transport

$$\left.\begin{array}{l} D_2 \mid DCl \\ H_2 \mid HCl \end{array}\right. \quad \left.\begin{array}{l} D_2O \\ H_2O \end{array}\right| AgCl\text{-}Ag$$

over a wide range of deuterium solvents, found that ΔC_p for the process

$$\tfrac{1}{2}H_2 + DCl(D_2O) = \tfrac{1}{2}D_2 + HCl(H_2O) \quad (7)$$

is also very small if not zero.

The almost zero value of ΔC_p in these exchange processes results from the fact that ions of the

(13) Noonan and LaMer, J. Phys. Chem., **43**, 247 (1939); LaMer and Noonan, THIS JOURNAL, **61**, 1487 (1939).

same valence type and almost identical chemical properties are involved in these equilibria. The partial molal heat capacity of an ionic species is determined primarily by its net charge and only secondarily by its internal constitution.[14]

Summary

1. The equivalent conductances of sodium chloride, sodium acetate, hydrochloric acid, and acetic acid have been measured at 14.36, 25, 35 and 44.86° in a solvent whose deuterium fraction is 0.925. From these data, the dissociation constant of deuteroacetic acid at $F_D = 1$ is calculated at corresponding temperatures.

2. The dissociation constant of deuteroacetic acid follows the Harned–Embree equation and passes through a maximum at 31°; protoacetic acid at 22°.

3. The ratio K_H/K_D decreases with increasing temperature.

4. The differences in the heats, free energies and entropies of ionization of the deutero and proto acids have been calculated. ΔC_p for the exchange process HOAc(H$_2$O) + D$^+$(D$_2$O) + OAc$^-$(D$_2$O) = DOAc(D$_2$O) + H$^+$(H$_2$O) + OAc$^-$(H$_2$O) is sensibly zero; ΔS is sensibly constant and equal to -1.3 cal. deg.$^{-1}$ mole^{-1}.

(14) Rossini, Bur. Standards J. Research, **4**, 313 (1930); **7**, 47 (1931); LaMer and Cowperthwaite, THIS JOURNAL, **55**, 1004 (1933).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Electrostatic Effects on Ionization Constants

BY VICTOR K. LAMER AND FRANK BRESCIA*

In a recent paper, E. C. Baughan[1] derived on the basis of theoretical suggestions of Gurney,[2] the equation

$$\Delta H_T = \Delta H_x + c\, 1/D_T \left[1 + T\frac{\partial \ln D}{\partial T}\right]_T \quad (1)$$

for the heat of ionization ΔH_T of a weak acid of the electric charge type HA + H$_2$O $\rightleftarrows$ H$_3$O$^+$ + A$^-$, as a function of the temperature T, on the assumption that the electrical work involved in creating the electric field is adequately expressed by the well known formula of Born

$$c = \frac{\epsilon^2}{2}\left(\frac{1}{r_+} + \frac{1}{r_-}\right)$$

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(1) E. C. Baughan, J. Chem. Phys., **7**, 951 (1939).
(2) Gurney, ibid., **6**, 499 (1938).

where ϵ is the elementary electric charge, r_+ and r_- are the radii of the cation and anion, and D is the dielectric constant of the solvent.

ΔH_x may be regarded either as the heat of ionization in a medium of infinite dielectric constant where no electrical work would be involved, or as the heat effect if there were no separation of electric charges in the dissociation process.

Since ΔH is zero at the characteristic temperature for which the dissociation constant is a maximum, equation (1) may also be expressed as

$$\Delta H_T = c\left[1/D_T\left(1 + T\frac{\partial \ln D}{\partial T}\right) - 1/D_\theta\left(1 + \theta\frac{\partial \ln \theta}{\partial T}\right)\right] \quad (1a)$$

Hence, ΔH_T is determined solely by the parameters Θ and r.

We have recently completed a series of accurate determinations of the dissociation constants of deuteroacetic acid by the conductance method,[3] which with the data of Harned and co-workers on protoacetic acid should serve as a particularly good test of these equations.

The dielectric behavior of both ordinary water and deuterium oxide has been carefully investigated by Wyman and his collaborators,[4] and is expressible in the form

$$D = ae^{-bT} \qquad (2)$$

When the experimental values of ΔH_T for a given acid are plotted against $X = \frac{1}{D_T}\left(1 + T\frac{\partial \ln D}{\partial T}\right)$ equation (1) requires a linear relationship. The mean radius r, defined by $\frac{2}{r} = \left(\frac{1}{r_+}+\frac{1}{r_-}\right)$, is calculable from the slope and ΔH_x from the intercept at $X = 0$. Both should be constants independent of temperature if equation (1) is valid. Baughan showed that equation (1) held for the best available data on weak acids in H_2O.

In Fig. 1 we plot our data for DOAc and for comparison the corresponding data for HOAc recalculated from Harned and Embree's equation and Wyman's dielectric data.
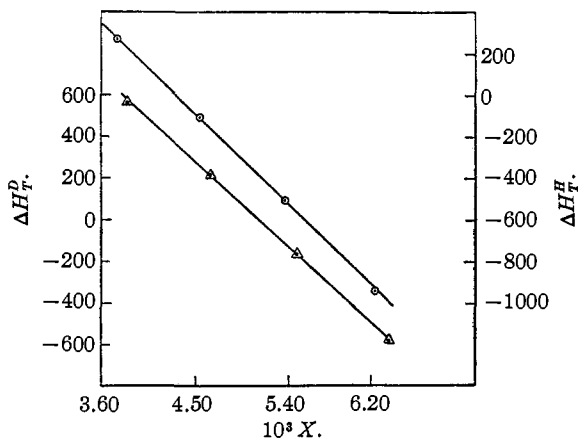

Fig. 1.—$X = \frac{1}{D_T}\left(1 + T\frac{\partial \ln D}{\partial T}\right)$: ⊙, HOAc; ▲, DOAc.

The values of the parameter c for the two acids have been obtained by simultaneous solution for two temperatures using the data[3,4] given in Table I and the equation:

$$\Delta H_T^D - \Delta H_T^H = c^D\left[1/D_T^D\left(1 + T\frac{\partial \ln D^D}{\partial T}\right) - \right.$$

(3) Brescia, LaMer and Nachod, THIS JOURNAL, **62**, 614 (1940).

(4) Wyman, *Phys. Rev.*, **35**, 623 (1930); Wyman and Ingalls, THIS JOURNAL, **60**, 1182 (1938).

$$\left. 1/D_\Theta^D\left(1 + \Theta^D\frac{\partial \ln D^D}{\partial T}\right)\right] + c^H\left[1/D_\Theta^H\left(1 + \Theta^H\frac{\partial \ln D^H}{\partial T}\right) - 1/D_T^H\left(1 + T\frac{\partial \ln D^H}{\partial T}\right)\right] \qquad (3)$$

The superscripts H and D refer to HOAc and DOAc, respectively.

TABLE I

t°C.	$\Delta H^D - \Delta H^H$	
14.36	308.6	$\log D^H = 1.9446 - 0.00198\,t$
25.00	329.1	$\log D^D = 1.9433 - 0.00199\,t$
35.00	348.9	$\Theta^H = 22.09\,°C.$
44.86	368.9	$\Theta^D = 31.06\,°C.$

TABLE II

Temperature, °C.	$c^H \times 10^{-5}$	$c^D \times 10^{-5}$
14.36–25.00	4.725	4.410
25.00–35.00	4.709	4.412
35.00–44.86	4.708	4.408

Av. $c^H = 4.714 \times 10^5$ $c^D = 4.410 \times 10^5$
a. d. = 0.15% a. d. = 0.02%

The values of c (cal. mole^{-1}) are constant. Setting $\epsilon = 4.796 \times 10^{-10}$ e. s. u. and $N = 6.03 \times 10^{23}$ yields for the harmonic mean radius:

r^H (for protoacetic acid) = 0.704 Å.
r^D (for deuteroacetic acid) = 0.753 Å.

Using these values of r, we find as shown in Tables III and IV that $\Delta H_x^D = 2260$ cal. and $\Delta H_x^H = 2030$ cal. The difference, 230 cal., should be independent of electrostatic effects and hence should arise from the differences in fundamental vibration frequencies of the molecules involved in the dissociation process.

TABLE III

DEUTEROACETIC ACID

t,°C.	ΔH_x^D (calcd.)	ΔH^D (exptl.)	ΔH^D (calcd.)
14.36	226×10^1	570.9	569
25.00	227	222.6	210
35.00	226	−154.7	−158
44.86	223	−577.4	−547

TABLE IV

PROTOACETIC ACID

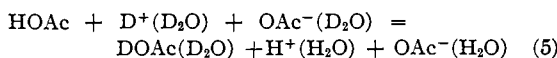| t,°C.	ΔH_x^H (calcd.)	ΔH^H (exptl.)	ΔH^H (calcd.)
14.36	203×10^1	262.3	265
25.00	204	−106.5	−114
35.00	203	−503.6	−502
44.86	200	−946.3	−912

Since r^H and r^D, D_T^H and D_T^D, and $\partial \ln D^H/\partial T$ and $\partial \ln D^D/\partial T$ are practically identical, equation (3) can be reduced to

$$\Delta H_T^D - \Delta H_T^H = c\left[1/D_{\Theta^H}\left(1 + \Theta^H\frac{\partial \ln D}{\partial T}\right) - 1/D_{\Theta^D}\left(1 + \Theta^D\frac{\partial \ln D}{\partial T}\right)\right] \qquad (4$$

According to this equation, the difference between the heats of ionization of the proto and deutero forms of an acid should be independent of temperature and, practically speaking, a function only of their respective characteristic temperatures, Θ. This requires that

$$\left(\frac{\partial \Delta H^D}{\partial T}\right)_p - \left(\frac{\partial \Delta H^H}{\partial T}\right)_p = \Delta C_p$$

should equal zero for the corresponding exchange reaction

$$\text{HOAc} + \text{D}^+(\text{D}_2\text{O}) + \text{OAc}^-(\text{D}_2\text{O}) = \\ \text{DOAc}(\text{D}_2\text{O}) + \text{H}^+(\text{H}_2\text{O}) + \text{OAc}^-(\text{H}_2\text{O}) \quad (5)$$

Experimentally, ΔC_p for the exchange process where HOAc is acetic acid[3] is 2 cal. mole^{-1} deg.$^{-1}$; ΔC_p for the corresponding benzoic acid exchange process[5] is about 9.5 cal. mole^{-1} deg.$^{-1}$; but is exactly zero for the HCl–DCl exchange.[6] Presumably these very small ΔC_p values may be attributed to the small differences in the radii of $\text{H}^+(\text{H}_2\text{O})$ and $\text{D}^+(\text{D}_2\text{O})$, and of the anions in the respective waters, as well as in the dielectric properties of the two waters.

The validity of equation (1) is evidence that $\log K$ can be adequately expressed as

$$\frac{-\Delta F^\circ}{2.3RT} = \log K = A - B/T - \frac{C}{D}\frac{1}{T} \quad (6)$$

where A, $B = \Delta H_x/2.3R$, and $C = c$ (eq. 1)/2.3R are constants for each acid in a given solvent.

As a means of testing whether or not $\log K$ is a function of D and of T only, it may prove helpful to introduce a procedure which recently has found application in the analogous problem of interpreting the energies and entropies of activation in the kinetics of ionic reactions.[7]

The procedure consists in determining the temperature coefficients not only in media of constant composition but also in media of constant dielectric constant (isodielectric temperature coefficient). Thus the customary coefficient is composed of an isodielectric coefficient and a correction term involving $\partial D/\partial T$.

$$\left(\frac{d \log K}{d(1/T)}\right)_{comp.} = \left(\frac{\partial \log K}{\partial(1/T)}\right)_D + \\ \left(\frac{\partial \log K}{\partial D}\right)_T \left(\frac{\partial D}{\partial T}\right)_{comp.} \left(\frac{\partial T}{\partial 1/T}\right) \quad (7)$$

where each term may be identified as

$$\left(\frac{-\Delta H}{2.3R}\right)_{comp.} = \left(\frac{-\Delta H}{2.3R}\right)_D - \frac{C}{D}\left[\frac{T}{D}\frac{\partial D}{\partial T}\right] \quad (8)$$

(5) Rule and LaMer, THIS JOURNAL, **60**, 1974 (1938).

(6) Noonan and LaMer, *J. Phys. Chem.*, **43**, 247 (1939).

(7) LaMer, *J. Franklin Inst.*, **225**, 709 (1938); Amis and LaMer, THIS JOURNAL, **61**, 905 (1939); Svirbely and Warner, *ibid.*, **57**, 1883 (1935); Svirbely and collaborators, *ibid.*, **60**, 330, 1613 (1938); **61**, 3534, 3538 (1939).

$$= -\left(B + \frac{C}{D}\right) - \frac{C}{D}\left[\frac{T}{D}\frac{\partial D}{\partial T}\right]$$
$$= -B - \frac{C}{D}\left[1 + \frac{T}{D}\frac{\partial D}{\partial T}\right] \quad (9)$$

Similarly for the entropy of dissociation in the standard state

$$\left(\frac{\Delta S^0}{2.3R}\right)_{comp.} = \left(\frac{d(T \log K)}{dT}\right)_{comp.} = \\ A + \frac{C}{D}\left[\frac{T}{D}\frac{\partial D}{\partial T}\right] \quad (10)$$

From (9), which is identical with equation (1), it is evident that the slope of $\log K$ vs. $1/T$ should reduce to $-(B + C/D)$ in isodielectric solvents where $\partial D/\partial T = 0$. Similarly from equation (10), $\Delta S^0/2.3R$, obtained by plotting $T \log K$ against T, reduces to A for isodielectric solvents. $2.3RA$ is the increase in entropy in the standard state for the dissociation process corrected for all electrostatic contributions.

It is evident, therefore, that by determining isodielectric temperature coefficients by adjusting the composition of the medium to maintain D constant, one should determine directly the thermodynamic quantities for the process freed from electrostatic contributions; in other words, for a dissociation process which does not involve electrostatic work dependent upon the dielectric constant of the medium surrounding the molecules involved.

The neutral molecule quantities can of course be calculated from the temperature coefficient at constant composition by introducing the correction factors in $\partial D/\partial T$. This is the essence of equations (1) and (9), and their merit resides in the fact that the medium is not changed in composition with changing temperature.

Agreement between such calculated values of $(\partial \ln K/\partial(1/T))_D$ and those determined directly in isodielectric media will only be obtained if it is legitimate to express $\log K$ as function of D and T only (equation 6) and if r remains independent of temperature and of solvent. That $(\partial r/\partial T)$ is negligible now appears to be generally accepted. That r is indeed an adjustable parameter which takes into account undetermined specific solvent effects and only approximates the physical meaning ascribed to it is becoming more generally recognized.

The evidence[7] which is accumulating upon the kinetics of the bromoacetate–thiosulfate replacement and the ammonium cyanate $\longrightarrow$ urea reactions demonstrate that when the isodielectric char-

acter of the medium is maintained by the addition of methanol and ethanol, the kinetic analog of A in equation (10) remains remarkably constant. On the other hand, when isopropanol, diethylene glycol, and particularly dioxane, are employed to produce media of very low dielectric constant, exact constancy of A is not obtained. This is to be expected since the addition of dioxane produces a greater change in specific solvent properties than does the addition of an alcohol most closely resembling water.

Differentiating equation (9) and evaluating coefficients from equation (2) yields

$$\Delta C_p = -b^2 T c/D \tag{11}$$

The value of ΔC_p calculated for protoacetic acid ($r = 0.70$ Å.) is -39.9, whereas the experimental value is -41.3 cal. deg.$^{-1}$ mole^{-1}.

Treating in the same manner the empirical Harned–Embree[8] equation

$$\log K_T = \log K_M - p(T - \Theta)^2 \tag{12}$$
$$[\Delta C_p/2.3R]_{T=\Theta} = -6pT^2 + 4pT\Theta = -2p\Theta^2 \tag{13}$$

Equating (11) and (13)

$$p = \frac{\epsilon^2}{(2.3R)rD^3} \left(\frac{\partial D}{\partial T}\right)^2 \frac{1}{2\Theta} \tag{14}$$

Equation (14) can be shown to be correct by introducing numerical values for $T = \Theta$ and recovering the experimental value of $p \cong 4.5 \times 10^{-5}$.

Since D does not vary much for the values of $T = \Theta$ encountered for this group of acids and r proves to be almost a constant we have an explanation of why equation (12) represents the

(8) Harned and Embree, THIS JOURNAL, **56**, 1050 (1934); Walde, J. Phys. Chem., **39**, 478 (1935).

facts so well with an almost universal value of p.[8]

Summary and Conclusions

1. The equation

$$\Delta H_T = \Delta H_x + c \, 1/D_T \left[1 + T \frac{\partial \ln D}{\partial T}\right]$$

represents with high precision ΔH, the heat of dissociation of deuteroacetic acid as a function of temperature, when $\Delta H_x = 2260$, and $c = 4.410 \times 10^{+5}$. The values for protoacetic acid are 2030 cal. and $4.714 \times 10^{+5}$, corresponding to (Born) r values of 0.75 and 0.70 Å., respectively.

2. ΔC_p for an acid–base exchange reaction involving deuterium and hydrogen in D_2O and in H_2O is practically zero since the radii of the ions and the dielectric properties of the two media are practically identical.

3. The difference in the heats of ionization of deutero and proto acids appears to be a function only of the characteristic temperature Θ at which the maximum value of the dissociation constants occurs.

4. The desirability of determining the temperature coefficients of dissociation constants of acids, not only in solvents of constant composition but also in solvents of constant dielectric constant, is pointed out.

5. The empirical constant $p \cong 4.5 \times 10^{-5}$ in the Harned–Embree equation is shown on theoretical grounds to be equal to

$$p = \frac{\epsilon^2}{(2.3R)rD^3} \cdot \left(\frac{\partial D}{\partial T}\right)^2 \cdot \frac{1}{2\Theta}$$

Thermodynamics of Concentrated Aqueous Solutions of Sodium Hydroxide[1,2]

By Gösta Åkerlöf and Gerson Kegeles

Introduction

The thermodynamic properties of strong electrolytes in highly concentrated solutions over a large temperature range may conceivably be obtained by a number of different methods. In most cases, however, the methods applicable narrow down to a single one, the determination of the

(1) This communication contains part of the material of a dissertation to be presented by Gerson Kegeles to the Graduate School of Yale University in partial fulfillment of the requirements of the degree of Doctor of Philosophy, June, 1940.

(2) The tables of this paper are published with the financial assistance of the authors and of Yale University.

vapor pressure of the solution. The alkali hydroxides and hydrochloric acid belong to the few electrolytes forming exceptions to this general rule since it would appear to be possible to study their solutions using an electromotive force method. The properties of hydrochloric acid already have been studied for a considerable temperature range by Åkerlöf and Teare,[3] who used solutions up to 16 molal. Solutions of the alkali hydroxides have been the subject of a series of studies by Harned

(3) Åkerlöf and Teare, THIS JOURNAL, **59**, 1855 (1937).