

### Summary

The heat capacities of the metatitanates of iron, calcium, and magnesium were measured in the temperature range 52 to 298°K. Ferrous metatitanate has a marked "hump" in its heat-capacity curve, the maximum being at 57°K. There is approximately 0.95 unit of excess entropy in the "hump" above the "normal" curve.

The following molal entropies at 298.16°K.

were computed: ferrous metatitanate,  $25.3 \pm 0.3$ ; calcium metatitanate,  $22.4 \pm 0.1$ ; and magnesium metatitanate,  $17.8 \pm 0.1$  E.U.

Combination of the above entropies with related entropy data yields the following molal entropies of formation of the metatitanates from the respective oxides and rutile: ferrous metatitanate,  $-0.4$ ; calcium metatitanate,  $+0.5$ ; and magnesium metatitanate,  $-1.1$  E.U.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

## The Ionization Constant of Acetic Acid in 50% Glycerol-Water Solution from 0 to 90°

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From electromotive force measurements of the cells,  $H_2 | HAc (m_1), NaAc (m_2), NaCl (m_3), Glycerol (X), H_2O (Y) | AgCl-Ag$  in which the solvent mixture was 50% by weight of glycerol, the ionization constant of acetic acid has been determined at 5° intervals from 0 to 90°. This is the widest temperature range over which measurements of this kind have been made.

### Experimental Results

The measurements were carried on in cells and by the technique of Harned and Morrison.<sup>2</sup> Glycerol purified and analyzed by methods described by us in an earlier communication<sup>3</sup> was used. The stock buffer solution was prepared by neutralizing half the weight of acetic acid taken with sodium hydroxide. Water formed in the neutralization reaction was taken into consideration in computing its total weight in the cell solution. The concentrations were:  $m_1 = 0.3947$ ,  $m_2 = 0.3947$  and  $m_3 = 0.3997$ . The cell solutions were prepared from this solution.

Two series of cell measurements were made at given concentrations of cell electrolytes, one through a temperature range from 0 to 50° and another from 50 to 90°. After the temperature readings were recorded, the cell was brought to 25° for the low temperature series and to 50° for the high temperature series. Excellent recovery values were obtained at 25°. Recovery values at the higher temperatures were not so good but were considerably better for these cells containing a buffered solution than for those containing only hydrochloric acid.<sup>3</sup> Since the cells were run in triplicate at six concentrations, eighteen recovery checks at 50° were made. Of these four were within 0.1 mv. and sixteen within 0.3 mv. of the initial values at this temperature.

(1) This communication contains material from a dissertation presented by F. H. Max Nestler to the Graduate School of Yale University in partial fulfillment of the Degree of Doctor of Philosophy, June, 1943.

(2) Harned and Morrison, *Am. J. Sci.*, **33**, 161 (1937).

(3) Harned and Nestler, *THIS JOURNAL*, **68**, 665 (1946).

The experimental results obtained at nineteen temperatures have been expressed by the equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \quad (1)$$

The constants,  $a$ ,  $b$  and the electromotive force,  $E_{25}$ , were obtained from the first order five degree differences in electromotive forces by the graphical method described by Harned and Nims.<sup>4</sup> These are given in Table I as well as the average and maximum deviations between the observed electromotive forces and those calculated by the equation. The average deviations are quite small and the maximum always occurs in the higher range of temperature. Although this shows that less reproducibility is obtained from 70 to 90°, the discrepancies are not large and we believe that considerable confidence may be placed in the results over the entire temperature range.

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS,  $H_2 | HAc(m_1), NaAc(m_2), NaCl(m_3), GLYCEROL (X), WATER (Y) | AgCl-Ag$  ACCORDING TO EQUATION  $E = E_{25} + a(t - 25) + b(t - 25)^2$

Valid from 0 to 90°;  $m_1 = 0.99992$ ,  $m_2 = 0.98756$   $m_3$ ;  $\mu = m_2 + m_3 = 2.0125$   $m_2 = 1.9876$   $m_3$ .  $\Delta$  (av.) and  $\Delta$  (max.) equal average and maximum deviations of calculated from observed electromotive forces.  $X = Y = 50\%$  by weight.

$\mu$	$E_{25}$	$a \times 10^4$	$b \times 10^7$	$\Delta$ (av.)	$\Delta$ (max.)
0.02234	0.61131	6.55	-4.00	0.05	0.21 <sup>a</sup>
.03805	.59756	6.06	-2.25	.10	.44 <sup>a</sup>
.06878	.58231	5.50	-2.00	.05	.19 <sup>a</sup>
.11281	.56972	5.04	-2.00	.05	.13 <sup>b</sup>
.14211	.56393	4.82	-2.50	.04	.13 <sup>c</sup>
.18439	.55727	4.59	-2.35	.05	.15 <sup>b</sup>

<sup>a</sup> At 90°. <sup>b</sup> At 50°. <sup>c</sup> At 60°.

### The Ionization Constant and Derived Thermodynamic Quantities

The ionization constant was determined by using the equation of the cell in the form<sup>5</sup>

(4) Harned and Nims, *ibid.*, **54**, 423 (1932).

(5) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., 1943, p. 497.

$$\frac{(E - E^0)F}{2.303RT} + \log \frac{m_{\text{HAc}} m_{\text{Cl}}}{m_{\text{Ac}}} = -\log K_A - \log \frac{\gamma_{\text{HAc}} \gamma_{\text{Cl}}}{\gamma_{\text{Ac}}} \equiv -\log K'_A \quad (2)$$

$E$  is the electromotive force of the cell,  $E^0$  its standard potential,  $K_A$  the ionization constant and  $m_{\text{HAc}}$  etc.,  $\gamma_{\text{HAc}}$  etc. are the molalities and activity coefficients of the species denoted by the subscripts. Since the activity coefficient function is unity at infinite dilution and very close to unity at all ionic strengths employed, the plots of the left side of the equation or  $(-\log K'_A)$  versus the ionic strength are nearly horizontal straight lines. The slopes of these plots are given in Table II. We note that the activity coefficient function,  $\log (\gamma_{\text{HAc}} \gamma_{\text{Cl}} / \gamma_{\text{Ac}})$  changes sign with variations of temperature. As a result the extrapolation to zero ionic strength where  $(-\log K'_A)_{m=0}$  equals  $(-\log K_A)$  can be carried out graphically with a high degree of accuracy. The values of  $E^0$  employed are given by the equation<sup>3</sup>

$$E^0 = 0.18392 - 7.45 \times 10^{-4}(t - 25) - 3 \times 10^{-6}(t - 25)^2 \quad (3)$$

TABLE II

## IONIZATION CONSTANT

$K_\theta = 5.379 \times 10^{-6}$ ;  $T_\theta = 304.3^\circ$ ;  $\Delta K_A = (K_A(\text{calcd.}) - K_A(\text{obs.})) \times 10^6$ .  $\alpha$  is slope defined by equation:  $-\log K'_A = -\log K_A + \alpha\mu$ .

	$\alpha$	$\frac{K_A(\text{obs.})}{\times 10^{-6}}$	$\frac{\Delta K_A}{\times 10^6}$		$\alpha$	$\frac{K_A(\text{obs.})}{\times 10^6}$	$\frac{K_A}{\times 10^6}$
0	0.070	4.778	+0.007	50	0.020	5.184	+0.004
5	.065	4.960	-.001	55	.015	5.068	+.011
10	.060	5.097	+.007	60	.010	4.951	+.003
15	.060	5.222	-.003	65	.005	4.806	+.005
20	.055	5.316	-.013	70	.000	4.654	+.002
25	.050	5.352	+.004	75	-.015	4.475	+.010
30	.045	5.378	-.001	80	-.020	4.315	-.008
35	.040	5.373	-.004	85	-.025	4.137	-.012
40	.035	5.330	+.003	90	-.030	3.935	-.004
45	.030	5.270	+.005				

The results of this computation are compiled in Table II. The ionization constant as a function of temperature may be expressed by the equation

$$\log K_A = -\frac{A^*}{T} + D^* - C^*T \quad (4)$$

which was shown by Harned and Robinson<sup>6,5</sup> to be valid for many weak electrolytes over the temperature range from 0 to 60°. Analysis of our results indicates that this equation may be employed successfully from 0 to 90°. In other words, the results are not sufficiently accurate to show a deviation from a quadratic function for the variation of the free energy of ionization with the temperature.

The standard free energy, heat content, specific heat and entropy of the ionization reaction as functions of temperature can be calculated by the equations

$$\Delta F_1^0 = A' + D'T + C'T^2 \quad (5)$$

$$\Delta H_1^0 = A' - C'T^2 \quad (6)$$

$$\Delta C_{p1}^0 = -2C'T \quad (7)$$

$$\Delta S_1^0 = D' - 2C'T \quad (8)$$

where  $A'$ ,  $D'$  and  $C'$  equal 2.3026  $R$  times  $A^*$ ,  $D^*$  and  $C^*$ . The maximum value of  $K_A$  denoted  $K_\theta$  and the temperature  $T_\theta$  at which  $K_A$  is a maximum may be calculated by the functions

$$T_\theta = (A^*/C^*)^{1/2} \quad (9)$$

$$\log K_\theta = D^* - 2(C^*A^*)^{1/2} \quad (10)$$

The constants of equation (4), obtained by the method of least squares, are  $A^* = 1321.4256$ ,  $D^* = 3.4148$  and  $C^* = 0.014268$ . Table II contains the deviations of the observed from the values calculated by equation (4). The average deviation in  $\Delta K_A \times 10^6$  is 0.006 which is less than 0.2% in  $K_A$ .

## Summary

1. The ionization constant of acetic acid in 50% by weight glycerol-water solutions has been determined from 0 to 90° by means of cells without liquid junctions.

2. The results may be expressed within the accuracy of the method by an equation which is a quadratic in temperature for the free energy of ionization.

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(6) Harned and Robinson, *Trans. Faraday Soc.*, **36**, 673 (1940). see also Harned and Owen, ref. 5, p. 583.