

$\Lambda_{\infty}\text{HCl}$ , respectively,  $\Lambda_{\infty}(\text{H}^+ + \text{H}_2\text{PO}_4^-)$  has been calculated to be 340.5 at that same temperature.

2. Values for the first stoichiometric dissociation constant of phosphoric acid alone in aqueous solution at 18° have been calculated from the data of Noyes and Eastman.  $pK_1'$  (*i. e.*,  $pK_1$  at infinite dilution) has been assigned the value 2.09. An equation well fitting the data is  $pK_1 = 2.09 - \sqrt{\mu}/(1 + 1.0\sqrt{\mu}) - 1.8\mu$ .

3. An approximate equation for the activity coefficient of the undissociated fraction in pure dilute aqueous solutions of phosphoric acid at 18° is  $p\gamma_{\text{H}_3\text{PO}_4} = -1.8\mu$ , where  $\mu$  is calculated from the equivalent ion concentration.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

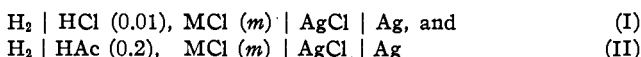
### THE TEMPERATURE COEFFICIENT OF DISSOCIATION OF ACETIC ACID IN POTASSIUM AND SODIUM CHLORIDE SOLUTIONS<sup>1</sup>

BY HERBERT S. HARNED AND GEORGE M. MURPHY

RECEIVED JULY 15, 1930

PUBLISHED JANUARY 12, 1931

It has been shown by Harned and Robinson, and Harned and Owen<sup>2</sup> that the ionization constant, hydrogen- or hydroxide-ion concentrations, and ionic activity coefficients of weak acids and bases may be determined from measurements of cells without liquid junction. Their measurements were all made at 25°. Since it is a matter of considerable importance to study the effect of temperature on the dissociation of a weak electrolyte both in a pure solvent and in salt solutions, the present study was undertaken. To this end accurate measurements of the cells



at 20, 25 and 30° have been made, in which HAc is acetic acid, and MCl sodium and potassium chlorides.

#### Experimental Procedure and Results

The cells employed were of the usual H-type, and were equipped with a three-way stopcock through which the hydrogen entered the cell. By the proper manipulation of this stopcock, the cell could easily be transferred from a thermostat maintained at one temperature to one at another temperature without danger of the hydrogen electrode coming into contact with air. Equilibrium in the cell was considered established when

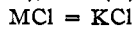
<sup>1</sup> The present investigation represents part of the thesis presented by George M. Murphy in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Yale University, 1930.

<sup>2</sup> Harned and Robinson, *THIS JOURNAL*, 50, 3157 (1928); Harned and Owen, *ibid.*, 52, 5079 (1930).

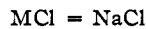
the readings of the electromotive force were constant to  $\pm 0.02$  mv. Cells of this type without employing a vacuum technique are reproducible to within  $\pm 0.2$  mv. The mean temperature coefficients may be reproduced to within  $\pm 0.005$  mv.

TABLE I

## (1) ELECTROMOTIVE FORCES OF CELLS

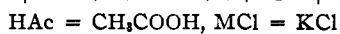


<i>M</i>	$E_{20}$	$E_{25}$	$E_{30}$	$10^4 a_{25}$	$10^6 b_{25}$
0.00	0.46359	0.46456	0.46533	374.55	-86.1
.05	.42359	.42394	.42400	96.71	-13.7
.1	.41060	.41068	.41058	-4.87	-8.8
.2	.39585	.39575	.39537	-121.29	-14.15
.5	.37628	.37588	.37526	-271.36	-11.71
1	.35820	.35754	.35664	-436.31	-13.43
1.5	.34668	.34582	.34475	-558.09	-12.15
2	.33691	.33591	.33471	-654.94	-11.91
3	.32175	.32055	.31914	-814.23	-13.10



0.05	0.42327	0.42361	0.42375	113.31	-9.44
.1	.41021	.41030	.41025	9.75	-6.82
.2	.39568	.39552	.39524	-111.25	-6.07
.5	.37503	.37458	.37404	-264.30	-4.81
1	.35541	.35473	.35393	-417.22	-6.77
1.5	.34170	.34088	.33991	-525.11	-8.80
2	.32973	.32879	.32772	-611.33	-7.91
3	.30984	.30866	.30738	-796.99	-6.48

## (2) ELECTROMOTIVE FORCES OF THE CELLS



<i>M</i>	$E_{20}$	$E_{25}$	$E_{30}$	$10^4 a_{25}$	$10^6 b_{25}$
0.05	0.46451	0.46540	0.46618	356.68	-5.16
.1	.44901	.44962	.45012	241.00	-4.45
.2	.43298	.43294	.43325	154.76	-2.31
.5	.41174	.41170	.41158	-38.86	-3.89
1	.39444	.39406	.39356	-223.32	-6.09
1.5	.38451	.38394	.38324	-333.39	-7.29
2	.37702	.37632	.37550	-406.57	-7.44
3	.36576	.36492	.36396	-493.26	-6.58



0.05	0.46378	0.46475	0.46564	398.06	-3.87
.1	.44792	.44860	.44920	285.33	-3.57
.2	.43146	.43188	.43220	171.34	-4.63
.5	.40938	.40940	.40935	-73.28	-3.42
1	.39050	.39024	.38984	-171.69	-5.64
1.5	.37862	.37815	.37756	-280.31	-5.29
2	.36868	.36804	.36732	-366.81	-4.89
3	.35308	.35222	.35126	-513.88	-6.25

In Table I are given the observed electromotive forces of the cells designated at 20, 25, and 30°.

The frequently employed equation

$$E_t = E_{25} (1 + a_{25} (t - 25) + b_{25} (t - 25)^2) \quad (1)$$

is sufficient to express the electromotive force as a function of  $t$ . The constants  $a_{25}$  and  $b_{25}$  are given in the fifth and sixth columns of the table.

**The Activity Coefficients and Partial Heat Content of Hydrochloric Acid in the Chloride Solutions.**—The activity coefficient of the acid in the salt solutions may be computed from the well-known equation

$$\ln \gamma = \frac{E_o - E}{2RT} F \ln \gamma_o - \ln \frac{\sqrt{0.01(0.01 + m)}}{0.01} \quad (2)$$

where  $E$  is the electromotive force of the cell containing salt,  $E_o$  that of the cell containing acid only, and  $\gamma_o$ , the activity coefficient of the acid of 0.01  $M$  concentration at a temperature  $T$ .

According to the computations of Randall and Young,<sup>3</sup> the activity coefficient of  $\approx 0.01 M$  acid at the freezing point of the solution differs by 0.2% from that at 25°. Fortunately, sufficient heat data are available to estimate the variation of  $\gamma_o$  with the temperature in the neighborhood of 25°. The variation of the activity with the temperature is given by

$$\frac{d \ln a}{dT} = - \frac{\bar{L}}{RT^2} \quad (3)$$

where  $\bar{L}$  is the partial heat content relative to  $o$  at zero concentration of solute. The variation of  $\bar{L}$  with temperature may be represented by the equation

$$\bar{L} = \bar{L}_{25} + (\bar{c}_p - \bar{c}_p^o) (T - 298.1) \quad (4)$$

where  $\bar{c}_p$  and  $\bar{c}_p^o$  are the partial molal heat capacities of the solute at concentrations  $m$  and  $o$ , respectively, and  $\bar{L}_{25}$  is the relative partial heat content at 25°. Substituting this expression in Equation 3 and performing the integration, it is found that

$$\log \frac{a_{25}}{a_t} = -\bar{L}_{25}y + \Delta C_p z \quad (5)$$

where

$$y = \frac{298.1 - T}{2.303 \times 298.1 \times RT} \quad (6)$$

and

$$z = 298.1y - \frac{1}{R} \log \frac{298.1}{T} \quad (7)$$

Values of  $y$  and  $z$  have been computed and tabulated by Lewis and Randall.<sup>4</sup> Since

$$\log a = 2 \log a_{\pm} = 2 \log m\gamma \quad (8)$$

<sup>3</sup> Randall and Young, THIS JOURNAL, 50, 989 (1928).

<sup>4</sup> Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, pp. 613-616.

we readily find that

$$\log \frac{\gamma_{25}}{\gamma} = -\frac{1}{2} (\bar{L}_{25}y - \Delta C_p Z) \quad (9)$$

The value of  $\bar{L}_{25}$  for 0.01 *M* hydrochloric acid has been computed by Harned<sup>5</sup> from the electromotive force measurements of Ellis, and Noyes and Ellis<sup>6</sup> and is 78.9 calories. The values of  $C_p$  and  $C_p^\circ$  have been determined calorimetrically by Randall and Ramage<sup>7</sup> and are:  $\bar{C}_p^\circ = -41$ ;  $\bar{C}_p = -41 + 14m^{1/2} = -39.6$ , whence  $\Delta\bar{C}_p = 1.4$  cal. Substituting these values in (9) and performing the calculation, we find that the value of the ratios,  $\gamma_{25}/\gamma_{20}$  and  $\gamma_{30}/\gamma_{25}$  is 0.999, corresponding to a variation of about 0.1% for a change in temperature of 5°. Since only a 0.2% variation is obtained in going from the freezing point of the acid at 25° and 0.1% for 5° change, it appears that  $\gamma$  is changing most rapidly in the neighborhood of 25° provided that the method of extrapolation from the freezing point data is accurate. Since the change in  $\gamma_0$  with the temperature at the concentration in question is so small, and because of the uncertainty in the heat data, we have taken  $\gamma_0$  to be the same at 20, 25 and 30°. The value used was 0.902,<sup>8</sup> which upon substitution in Equation 2 gives

$$\log \gamma = \frac{2520}{T} (E^\circ - E) - 0.04479 - \log \frac{\sqrt{0.01(0.01 + m)}}{0.01} \quad (10)$$

The activity coefficients given in Table II were computed by this equation from the electromotive forces in the first half of Table I.

The data in the table show that  $\gamma$  decreases slightly with the increase of temperature and that this decrease becomes greater at higher salt concentrations. Such a decrease of  $\gamma$  is to be expected.

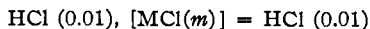
If we substitute the value for the free energy of the cell reaction derivable from Equation 1 in the Gibbs-Helmholtz equation

$$\frac{d(-\Delta E/T)}{dT} = \frac{\Delta H}{T^2} \quad (11)$$

we obtain

$$-\Delta H_{25} = \Delta F_{25} (1 - 298a_{25}) \quad (12)^9$$

by means of which the heat content of the cell reaction at all salt concentrations may be computed. By subtracting the values of  $(-\Delta H)_{25}$  at a given salt concentration,  $M$ , from the value at zero salt concentration, we obtain the heat content change corresponding to the transfer



<sup>5</sup> Harned, in Taylor, "Treatise on Physical Chemistry," D. Van Nostrand and Co., New York, 1924, Chap. XII, p. 723.

<sup>6</sup> Ellis, THIS JOURNAL, 38, 737 (1916); Noyes and Ellis, *ibid.*, 39, 2352 (1917).

<sup>7</sup> Randall and Ramage, *ibid.*, 49, 93 (1927).

<sup>8</sup> Harned and Åkerlöf, *Physik. Z.*, 27, 411 (1926).

<sup>9</sup> Ellis, THIS JOURNAL, 38, 737 (1916).

TABLE II  
ACTIVITY COEFFICIENTS AND RELATIVE PARTIAL HEAT CONTENT OF 0.01 *M* HYDROCHLORIC ACID IN POTASSIUM AND SODIUM CHLORIDE SOLUTIONS

MCl = KCl				
<i>m</i>	$\gamma_{\pm 0}$	$\gamma_{\pm}$	$\gamma_{\pm 0}$	$(-\Delta\bar{H})_{\pm}$ , cal.
0.0	0.902	0.902	0.902	0
.05	.813	.812	.812	46
.1	.777	.776	.776	65
.2	.753	.751	.751	122
.5	.711	.710	.708	291
1	.723	.720	.719	400
1.5	.743	.740	.738	433
2	.781	.778	.775	518
3	.862	.857	.853	663
MCl = NaCl				
0.05	0.818	0.817	0.816	155
.1	.783	.782	.780	111
.2	.756	.755	.752	188
.5	.730	.728	.724	398
1	.765	.761	.756	640
1.5	.822	.815	.810	853
2	.901	.894	.886	1108
3	1.091	1.081	1.069	1418

or the partial heat content of the acid in the salt solution relative to its value at zero salt concentration.<sup>10</sup> The values of  $(-\Delta\bar{H}_{\pm})$  are given in the fifth column of Table II, and are plotted in Fig. 1 along with values

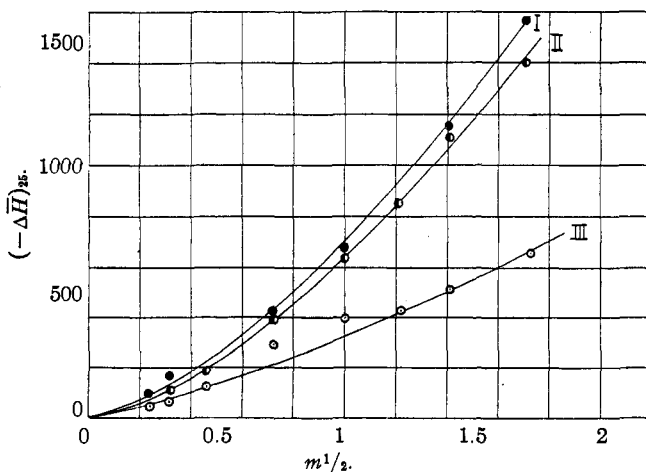
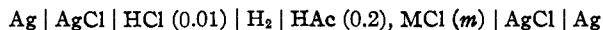


Fig. 1.—The relative partial heat content of hydrochloric acid in potassium and sodium chloride solutions. ●, HCl; ○, HCl in NaCl; ⊙, HCl in KCl.

<sup>10</sup> Harned, THIS JOURNAL, 42, 1808 (1920).

for the partial heat content of the pure aqueous acid solution relative to 0.01 *M*. These latter were taken from the results computed by Harned from the data of Ellis, and of Noyes and Ellis.<sup>5,11</sup> The results appear reasonable and agree in magnitude at least with the less accurate results obtained by Harned.<sup>10</sup> In fact, great accuracy is not to be expected since an error of 0.01 mv. in the temperature coefficient of the cell causes an error of 130 calories in the partial heat content.

**The Dissociation of Acetic Acid in Sodium and Potassium Chloride Solutions and its Temperature Coefficient.**—From the electromotive forces of cells given in Table I, we may readily obtain those of the cells



The electromotive forces of the latter are given by

$$E = E_1 - E_0 = 0.00019844 T \log \frac{(0.902)^2 (0.01)^2}{\gamma_{\text{H}} \gamma_{\text{Cl}} m_{\text{H}} m} \quad (13)$$

It is important to note that  $\gamma_{\text{H}} \gamma_{\text{Cl}}$  is the activity coefficient of hydrochloric acid in a solution containing both the weak acid and the salt. Harned and Owen<sup>2</sup> have carefully analyzed Equation 13. If the values of  $\gamma_{\text{H}}^{\circ} \gamma_{\text{Cl}}^{\circ}$  obtainable from Table II are substituted in (13), an "apparent" hydrogen-ion concentration,  $m'_{\text{H}}$ , is obtained because these values of  $\gamma_{\text{H}}^{\circ} \gamma_{\text{Cl}}^{\circ}$  are obtained in pure aqueous salt solutions and do not equal similar values obtained in the presence of undissociated acetic acid. By introducing  $\gamma_{\text{H}}^{\circ} \gamma_{\text{Cl}}^{\circ}$  for  $\gamma_{\text{H}} \gamma_{\text{Cl}}$  in Equation 13, we obtain

$$\log m'_{\text{H}} = - \frac{E}{0.00019844T} - 4.09858 - 2 \log \gamma_{\text{HCl}}^{\circ} - \log m \quad (14)$$

Further, from Equation 17 of Harned and Owen's study, we find that the relation between the real and apparent hydrogen-ion concentration at a given temperature is

$$SM = \log \frac{m'_{\text{H}}}{m_{\text{H}}} \quad (15)$$

where *S* is a constant which corrects for the effect of the undissociated acetic acid molecule, and *M* is the concentration of the acetic acid. They found that *S* equals 0.047 and, consequently, *SM* equals 0.0094. By combining (14) and (15), we obtain

$$\log m_{\text{H}} = - \frac{E}{0.00019844T} - 4.09858 - 2 \log \gamma_{\text{HCl}}^{\circ} - \log m - 0.0094 \quad (16)$$

by which the values of  $m_{\text{H}}$  contained in Table III were computed in the manner described by Harned and Robinson. In making this step, we have assumed that *SM* is the same at 20, 25 and 30°. This assumption involves no error greater than the experimental, since *M* is not high and since the temperature range under consideration is only ten degrees.

<sup>11</sup> See Chap. XII, Table VII, p. 723, of Taylor's "Treatise on Physical Chemistry," D. Van Nostrand and Co., New York, 1924.

TABLE III  
HYDROGEN-ION CONCENTRATIONS OF 0.2 *M* ACETIC ACID IN POTASSIUM AND SODIUM CHLORIDE SOLUTIONS

MCl = KCl				MCl = NaCl			
<i>m</i>	<i>m</i> <sub>H20</sub>	<i>m</i> <sub>H25</sub>	<i>m</i> <sub>30</sub>	<i>m</i>	<i>m</i> <sub>H20</sub>	<i>m</i> <sub>H25</sub>	<i>m</i> <sub>30</sub>
0.05	0.002323	0.002337	0.002339	0.05	0.002361	0.002367	0.002363
.1	.002352	.002364	.002366	.1	.002418	.002424	.002424
.2	.002399	.002415	.002410	.2	.002492	.002495	.002497
.5	.002451	.002476	.002486	.5	.002562	.002574	.002583
1	.002354	.002385	.002405	1	.002462	.002482	.002501
1.5	.002203	.002234	.002259	1.5	.002281	.002309	.002330
2	.002009	.002039	.002065	2	.002104	.002134	.002160
3	.001718	.001746	.001765	3	.001772	.001802	.001830

Our next step is to obtain values for the dissociation constant of the acetic acid at 20, 25 and 30°. Conductance data at temperatures other than 25° are unreliable although they indicate little change of the dissociation constant with temperature in the neighborhood of 25°. We have very good evidence to show that this is the case. The dissociation constant, *K*, is given thermodynamically by

$$K = \frac{\gamma_{\text{HAc}}}{\gamma_{\text{H}}\gamma_{\text{Ac}}} \frac{m_{\text{H}}^2}{0.2 - m_{\text{H}}} = \gamma_{\text{A}}^2 K_{\text{c}} \quad (17)$$

Taking the logarithm, we obtain

$$\log K = \log K_{\text{c}} + 2\log \gamma_{\text{A}} \quad (18)$$

But we know that in dilute and moderately concentrated solutions the variation of  $\gamma_{\text{A}}$  with the ionic strength is given by

$$2\log \gamma_{\text{A}} = -\sqrt{\mu} + B\mu \quad (19)$$

Substituting in (18) and transposing,

$$\log K - B\mu = \log K_{\text{c}} - \sqrt{\mu} \quad (20)$$

is obtained. Thus if we plot  $(\log K_{\text{c}} - \sqrt{\mu})$ , computed from the data in Table III, against  $\mu$ , straight lines should be obtained in the more dilute solutions. Further, when  $\mu = 0$ , the right-hand member of Equation 20 equals  $\log K$ . The plots of these quantities at the three temperatures are shown in Fig. 2. The plots are all drawn to the point at  $\mu = 0$  corresponding  $1.75 \times 10^{-5}$  for *K* found by Harned and Owen. It is clear that the data at all three temperatures fall closely on these lines. We feel justified for the present in employing  $1.75 \times 10^{-5}$  for the dissociation constant at all three temperatures.

In Table IV are given the values of  $\gamma_{\text{A}}$  or  $\sqrt{\gamma_{\text{H}}\gamma_{\text{Ac}}/\gamma_{\text{HAc}}}$  in the solution of the two chlorides computed by Equation 17 from the values of  $m_{\text{H}}$  given in Table III.

It is apparent from these results that the activity coefficient of acetic acid decreases slightly with rising temperature at the higher ionic strengths. This is similar to the behavior of hydrochloric acid in the same salt solu-

TABLE IV  
THE ACTIVITY COEFFICIENT OF ACETIC ACID IN THE SALT SOLUTIONS

<i>M</i>	MCl = KCl			<i>M</i>	MCl = NaCl		
	$\gamma_{A20}$	$\gamma_{A25}$	$\gamma_{A30}$		$\gamma_{A20}$	$\gamma_{A25}$	$\gamma_{A30}$
0.05	0.798	0.796	0.796	0.05	0.787	0.785	0.785
.1	.790	.786	.786	.1	.769	.767	.766
.2	.776	.771	.770	.2	.747	.745	.742
.5	.758	.751	.747	.5	.727	.722	.717
1	.790	.779	.773	1	.756	.749	.741
1.5	.844	.834	.824	1.5	.815	.805	.798
2	.927	.911	.903	2	.884	.871	.863
3	1.084	1.067	1.057	3	1.051	1.033	1.017

tions. Further, this temperature effect is somewhat greater the higher the salt concentration. Finally, at a given ionic strength the activity coef-

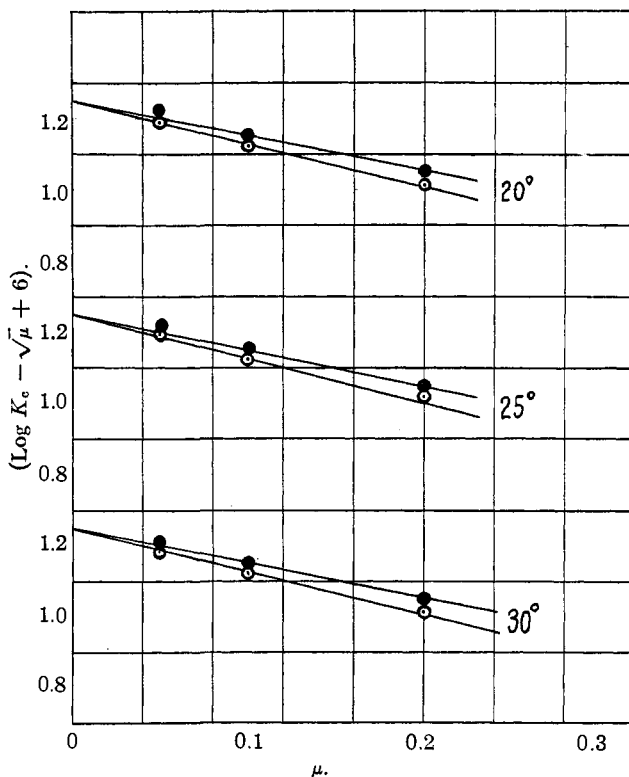


Fig. 2.—Graphical extrapolation to determine the dissociation constant of acetic acid at 20, 25 and 30°. ○, KCl; ●, NaCl.

ficient is greater in potassium than in sodium chloride solutions, a fact observed by Harned and Robinson.<sup>2</sup> Indeed, at 25°, our electromotive force measurements closely check those of Harned and Robinson.



**Calculation of the Electrical Heat Content Decrease.**—We have made no calculations of the heat content decreases of the cell reaction from the electromotive force of the cells containing acetic acid. The only difference from the previous calculations would be that the hydrochloric acid is transferred from the salt solution containing some acetic acid. Moreover, since there is no convenient reference state upon which the calculations can be based, we cannot readily obtain the partial molal heat content.

It is a matter of some interest, however, to compute the excess or electrical partial heat content of hydrochloric acid from the results which we have so far derived.

According to theory, the partial free energy of an electrolyte may be divided into two parts as follows

$$\Delta\bar{F} = \Delta\bar{F}_c + \Delta\bar{F}_e \quad (21)$$

where

$$\left. \begin{aligned} \Delta\bar{F}_c &= RT \ln m, \text{ and } \\ \Delta\bar{F}_e &= RT \ln \gamma \end{aligned} \right\} \quad (22)$$

$\Delta\bar{F}_c$  is the contribution to the free energy due to the change in concentration,  $\Delta\bar{F}_e$  is the contribution to the partial free energy caused by the electrostatic forces, and is denoted "the electrical free energy" or the excess free energy caused by the ionic atmosphere. Since  $\gamma$  is unity when  $m$  equals zero,  $\Delta\bar{F}_e$  equals zero when  $m$  equals zero.

$\Delta\bar{F}_e$  may be computed readily, but we are more interested at present in the corresponding values of  $\Delta\bar{H}_e$ , or the excess heat content. The Gibbs-Helmholtz equation is

$$\frac{d(\Delta\bar{F}_e/T)}{dT} = \frac{d(R \ln \gamma)}{dT} = -\frac{\Delta\bar{H}_e}{T^2} \quad (23)$$

whence

$$(-\Delta H_e) = 2.303RT^2 \frac{d \log \gamma}{dT} = 2.303 \frac{RT^2}{\gamma} \frac{d\gamma}{dT} = 2.303 RT^2 A_{25} \quad (24)$$

The values of  $d\gamma/dT$  have been determined in the following manner. The temperature variation of  $\gamma$  was computed by an empirical equation similar to Equation 1. The values of  $a_{25}$  thus obtained were plotted and

TABLE V

THE EXCESS HEAT CONTENT DECREASE OF HYDROCHLORIC ACID IN POTASSIUM AND SODIUM CHLORIDE SOLUTIONS AT 25° IN CALORIES

M	KCl		NaCl	
	$(-\Delta\bar{H}_e)_{25}$	$10^4 A_{25}$	$(-\Delta\bar{H}_e)_{25}$	$10^4 A_{25}$
0.05	+40.6	-10.0	99.6	-24.5
.1	65.0	-16.0	143.1	-35.2
.2	111.7	-25.0	186.6	-52.0
.5	160.0	-41.8	335.1	-82.4
1	243.1	-59.8	490.8	-120.7
1.5	297.6	-73.2	618.9	-152.2
2	342.3	-84.2	701.4	-172.5
3	406.6	-100.0	827.5	-203.5

a smooth curve drawn through the points. From this curve  $A_{25}$  could be computed with considerable accuracy. The values of  $A_{25}$  and the decrease in the excess partial heat content,  $-\Delta\bar{H}_e$ , of the acid in the salt solutions computed by Equation 24 are given in Table V. In Fig. 3 these values of  $(-\Delta\bar{H}_e)_{25}$  are plotted against  $m^{1/2}$ , and it is seen that the points fall on straight lines. Similar calculations for acetic acid were made but since at present the results appear to have no particular value, they have not been included.

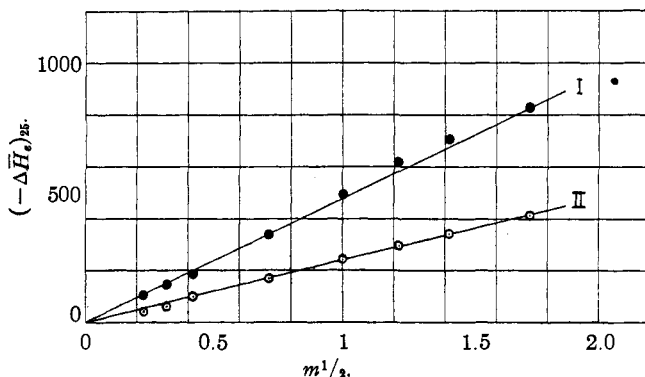
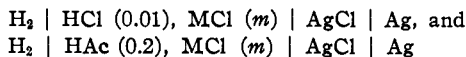


Fig. 3.—The excess relative heat content of hydrochloric acid in potassium and sodium chloride solutions. ●, HCl in NaCl; ○, HCl in KCl.

### Summary

1. Measurements of the cells



have been obtained at 20, 25 and 30°. Potassium and sodium chlorides were the salts employed.

2. The activity coefficients of hydrochloric acid in the salt solutions at the three temperatures have been computed.

3. The hydrogen-ion concentrations of the acetic acid salt solutions have been computed.

4. The dissociation constant of acetic acid was found to vary very little if at all through the temperature range of from 20 to 30°.

5. The ionic activity coefficient of acetic acid in sodium and potassium chloride solutions at the three temperatures were computed.

6. The excess or electrical contribution to partial molal heat content of hydrochloric acid in the chloride solutions was computed and found as a first approximation to be proportional to the square root of the total molality.