HEAT CONTENT VALUES FOR AQUEOUS SOLUTIONS OF THE CHLORIDES, NITRATES, AND HYDROXIDES OF HYDROGEN, LITHIUM, SODIUM, AND POTASSIUM AT 18° C.

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ABSTRACT

The existing data on the heats of dilution of the chlorides, nitrates, and hydroxides of hydrogen, lithium, sodium, and potassium at various temperatures and concentrations have been converted to one temperature, and a series of values for the concentration range from infinite dilution to about 2 molal have been obtained. The extrapolation to infinite dilution has been made with the aid of the Debye-Hückel theory of strong electrolytes.

The data, exhibited in tabular and graphic form, give values for $\Phi_h - \Phi_h{}^\circ$, the relative apparent molal heat content of the solute, $\overline{H}_2 - \overline{H}_2{}^\circ$, the relative partial molal heat content of the solute, and $\overline{H}_1 - \overline{H}_1{}^\circ$, the relative partial molal heat content of the H_2O. The procedure employed in calculating the above quantities is given in detail.

CONTENTS

		Page
I.	Definitions	791
II.	Introduction	792
III.	Methods of calculation and treatment of the data	796
IV.	The available data	800
V.	The calculated results	801
VI.	Discussion	803

I. DEFINITIONS

In this discussion the nomenclature of Lewis and Randall[1] will, in the main, be followed:

m is the molality in moles of solute per 1,000 g H_2O.

The subscripts 1 and 2 refer to the solvent and solute, respectively.

The superscript zero on any symbol refers to the given property at infinite dilution.

H (printed in italic caps) is the symbol for the total heat content of a given solution.

$\overline{H}_1$ and $\overline{H}_2$ (printed in italic caps with bar) are the partial molal heat content [2] of the solvent and of the solute, respectively, and are defined by the following equations:

$$\overline{H}_1 = \left(\frac{\delta H}{\delta n_1}\right)_{n_2,\, P,\, T} \tag{1}$$

$$\overline{H}_2 = \left(\frac{\delta H}{\delta n_2}\right)_{n_1,\, P,\, T} \tag{2}$$

[1] Lewis and Randall, Thermodynamics, Chap. VIII. McGraw-Hill Book Co., New York; 1923.

[2] In the partial molal symbols, the use of the italic cap letter indicates a molal property while the overhead bar is the differential mark.

where n_1 and n_2 are the number of moles of the solvent and solute, respectively.

Φ_h is the apparent molal heat content of the solute.

$MX \cdot n_1 H_2O$ designates a solution composed of 1 mole of the solute MX and n_1 moles of the solvent H_2O.

The heat content of any solution is given by the equation:[3]

$$H = n_1\overline{H}_1 + n_2\overline{H}_2 \tag{3}$$

or by definition of Φ_h,

$$H = n_1\overline{H}_2{}^\circ + n_2\Phi_h \tag{4}$$

For the reaction

$$n_2 MX \cdot n_1 H_2O + (\infty - n_1)H_2O = n_2 MX \cdot \infty H_2O \tag{5}$$

$$\Delta H = [n_2\overline{H}_2{}^\circ + \infty\overline{H}_1{}^\circ] - [n_2\overline{H}_2 + n_1\overline{H}_1 + (\infty - n_1)\overline{H}_1{}^\circ] = n_2(\overline{H}_2{}^\circ - \overline{H}_2) + n_1(\overline{H}_1{}^\circ - \overline{H}_1) \tag{6}$$

or, using the apparent molal heat content function, for the same reaction,

$$\Delta H = [n_2\Phi_h{}^\circ + \infty\overline{H}_1{}^\circ] - [n_2\Phi_h + n_1\overline{H}_1{}^\circ + (\infty - n_1)\overline{H}_1{}^\circ] = n_2(\Phi_h{}^\circ - \Phi_h) \tag{7}$$

Combination of equations (6) and (7) gives

$$n_2(\Phi_h - \Phi_h{}^\circ) = n_2(\overline{H}_2 - \overline{H}_2{}^\circ) + n_1(\overline{H}_1 - \overline{H}_1{}^\circ) \tag{8}$$

or

$$\Phi_h - \Phi_h{}^\circ = \overline{H}_2 - \overline{H}_2{}^\circ + \frac{n_1}{n_2}(\overline{H}_1 - \overline{H}_1{}^\circ) \tag{9}$$

$\Phi_h - \Phi_h{}^\circ$ will be called the relative apparent molal heat content[4] of the solute; $\overline{H}_2 - \overline{H}_2{}^\circ$, the relative partial molal heat content of the solute[5], and $\overline{H}_1 - \overline{H}_1{}^\circ$, the relative partial molal heat content of the solvent.

II. INTRODUCTION

Values for $\Phi_h - \Phi_h{}^\circ$, $\overline{H}_2 - \overline{H}_2{}^\circ$, and $\overline{H}_1 - \overline{H}_1{}^\circ$ are needed in many thermodynamic calculations involving aqueous solutions. If values are known for the relative apparent molal heat content of the solute, and for the heat change in a given reaction at one concentration, one can calculate the heat change for the given reaction at any desired concentration.

The partial molal heat content of the solute and of the H_2O serve as a measure of the change of the respective partial molal free energies with temperature, according to the thermodynamic formula

$$\frac{d}{dT}\left(\frac{\overline{F} - \overline{F}^\circ}{T}\right) = -\frac{\overline{H} - \overline{H}^\circ}{T^2} \tag{10}$$

[3] See Chap. IV of reference 1.

[4] See footnote 3.

[5] Lewis and Randall (see footnote 1, p. 791) use the symbol L_2 for this property, but in order to better keep in mind the physical significance of it, we shall use the complete designation

One application of this formula is in the calculation of activity coefficients from freezing point data, where the value for $\overline{H}_1-\overline{H}_1°$ is needed.

In order to evaluate $\Phi_h-\Phi_h°$, $\overline{H}_2-\overline{H}_2°$, and $\overline{H}_1-\overline{H}_1°$, there must be available data on heats of dilution, or heats of solution, extending to very small concentrations from which extrapolation to infinite dilution will introduce no appreciable uncertainty. Until recently, the only extensive data on the heats of dilution of uni-univalent electrolytes in aqueous solution were those of Richards and Rowe,[6] who measured heats of dilution from $MX \cdot 25\ H_2O$ to $MX \cdot 400\ H_2O$, and those of Pratt,[7] who covered about the same range of concentration but at many more temperatures. Without additional information, the extrapolation from $MX \cdot 400\ H_2O$ to $MX \cdot \infty\ H_2O$ is, however, over too large a gap to bridge with any measure of certainty. Later, Richards and coworkers extended the data on HCl to 800 H_2O and on NaOH to 3,200 H_2O. Following 1927, there began to appear the data of Lange [8] and coworkers, who measured the heats of dilution of salts at extremely small concentrations.

However, the Richards data were obtained at 16° to 20° C., while the Lange measurements were made at 25° C. Inasmuch as the temperature coefficient of the heat of dilution is rather large, correlation of the two sets of data with those of Pratt would be impossible without sufficiently accurate data on heat capacities in the given solutions. These data are available from values which have been compiled by the present author,[9] chiefly from the experimental data of Randall and Rossini,[10] and Richards and coworkers.[11]

For extrapolating the data to infinite dilution, a new tool has been made available with the extension to heats of dilution of the Debye-Hückel [12] theory of strong electrolytes. This extension [13] involves simply taking the temperature coefficient of the original expression given by Debye and Hückel. That the heat of dilution of strong electrolytes in the region of very small concentrations follows more or less closely the predictions of this theory was first shown by the work of Nernst and Orthmann,[14] and Lange and Messner,[15] and later by Lange [16] and others.

A short derivation of the equations expressing the change of the apparent and partial molal heat content with concentration, as derived theoretically from the Debye-Hückel theory, is given here.

Consider the two systems A and B. A is an infinitely dilute solution and B is a dilute solution of molality m. The difference in the free energy of 1 mole of solute in the two systems is

$$\Delta F = \overline{F}_2 - \overline{F}_2° \tag{11}$$

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[6] Richards and Rowe, J. Am. Chem. Soc., **43**, p. 770; 1921.
[7] Pratt, J. Frank. Inst., **185**, p. 663; 1918.
[8] Lange, Fortschritte der Chemie, Physik, und physikalische Chemie, **19**, No. 6, p. 1; 1928.
[9] These data will appear in B. S. Jour. Research, 1931.
[10] Randall and Rossini, J. Am. Chem. Soc., **51**, p. 323; 1929.
[11] Richards and Hall, Mair, Gucker, Dole, J. Am. Chem. Soc., **51**, pp. 507, 712, 727, 731, 740, and 794; 929. Richards and Rowe, J. Am. Chem. Soc., **43**, p. 770; 1921.
[12] Debye and Hückel, Physikalische Zeit., **24**, p. 185; 1923. Debye, ibid., **25**, p. 97; 1924.
[13] Gross and Halpern, Physikalische Zeit., **26** p. 403; 1925. Bjerrum, Z. physik. Chem. **119**, p. 156; 1926. Gross, Monatshefte f. Chemie, **48**, p. 243; 1927. Lewis and Randall, "Thermodynamics," German translation by Redlich, Berlin; 1927.
[14] Nernst and Orthmann, Sitzb. Preuss. Akad. Wiss., p. 51; 1926.
[15] Lange and Messner, Z. Elektrochem., **33**, p. 431; 1927.
[16] For a complete list of this work see Lange, Z. Elektrochem., **36**, p. 772; 1930.

Following Debye and Hückel, this free energy difference may be separated into two parts: (1) The "classical" or that due to the free energy change with concentration where the molecules of solute are considered as particles of an "ideal" solution, and (2) the "electrical" or that due to the free energy change resulting from the electrical forces of the ions. Then

$$\overline{F}_2-\overline{F}_2{}^\circ=[\overline{F}_{2\,(\text{class.})}-\overline{F}_2{}^\circ{}_{(\text{class.})}]+[\overline{F}_{2\,(\text{elec.})}-\overline{F}_2{}^\circ{}_{(\text{elec.})}] \tag{12}$$

For very low concentrations, one may write

$$\overline{F}_2-\overline{F}_2{}^\circ=R\ T\ ln\ m+\left[-\frac{N^{3/2}\ e^3}{D^{3/2}\ T^{1/2}}\left(\frac{\pi}{1{,}000\ k}\right)^{1/2}(\Sigma\nu_i z_i{}^2)^{3/2}m^{1/2}\right] \tag{13}$$

where the last term is that given by Debye and Hückel for the change in "electrical" free energy for the very dilute range with the exception that m has been substituted for the concentration. In this expression N is Avogadro's number, e is the electronic charge, D is the dielectric constant of the medium, k is Boltzmann's constant, T is the absolute temperature, z is the charge on the ith kind of ions whose number per molecule of solute is ν, and m is the molality as already defined.

By operating upon equation (13) according to the thermodynamic relation expressed by equation (10)

$$\frac{d}{dT}\left(\frac{\overline{F}_2-\overline{F}_2{}^\circ}{T}\right)=-\frac{\overline{H}_2-\overline{H}_2{}^\circ}{T^2} \tag{10}$$

one obtains the expression

$$\overline{H}_2-\overline{H}_2{}^\circ=-\tfrac{3}{2}\frac{N^{3/2}e^3}{D^{3/2}T^{1/2}}\left(\frac{\pi}{1{,}000\ k}\right)^{1/2}\left(1+\frac{T}{D}\frac{dD}{dT}\right)(\Sigma\nu_i z_i{}^2)^{3/2}\ m^{1/2} \tag{14}$$

New data on the dielectric constant of water and its temperature coefficient have recently been published.[17] These have been reviewed and compared with the existing data [18] by Lange and Robinson.[19] Following the suggestion of these latter authors, the values for D and $\frac{dD}{dT}$ used in the present work were obtained by averaging the values of Drude, Wyman, and Drake, Pierce, and Dow. This gives the following values for 18° C.

$$D=81.15 \qquad \frac{dD}{dT}=-0.37$$

Then, for a uni-univalent electrolyte at 18° C., evaluation of equation (14) gives

$$\overline{H}_2-\overline{H}_2{}^\circ=653\ m^{1/2}\ \text{calories per mole of solute} \tag{15}$$

[17] Drake, Pierce, and Dow, Phys. Rev., 35, p. 613; 1930. Wyman, Phys. Rev., 35, p. 623; 1930. Cuthbertson and Maass, J. Am. Chem. Soc., 52, p. 483; 1930.
[18] Drude, Wied. Ann., 59, p. 48; 1896. Kockel, Ann. Physik., 77, p. 430; 1925.
[19] Lange and Robinson, J. Am. Chem. Soc., 52, p. 2811; 1930.

This expression gives the variation with concentration of the relative partial molal heat content of the solute from the region of very low concentration to infinite dilution.

The expression for the like property of the solvent, H_2O, can be deduced from the partial molal equation.[20]

$$55.508\ d\overline{H}_1 + m\ d\overline{H}_2 = 0 \tag{16}$$

On substituting in equation (16) the value for $d\overline{H}_2$ obtained by differentiating equation (15), and then integrating, one obtains for an aqueous solution of a uni-univalent electrolyte at 18° C.

$$\begin{aligned}\overline{H}_1 - \overline{H}_1{}^\circ &= -\frac{(\overline{H}_2 - \overline{H}_2{}^\circ)\ m}{3\ (55.508)} = -\frac{653\ m^{3/2}}{3\ (55.508)} \\ &= -3.92\ m^{3/2} \text{ calories per mole of } H_2O\end{aligned} \tag{17}$$

For a solution composed of m moles of solute and 1,000 g or 55.508 moles of H_2O, equation (9) may be written

$$\Phi_h - \Phi_h{}^\circ = \overline{H}_2 - \overline{H}_2{}^\circ + \frac{55.508}{m}(\overline{H}_1 - \overline{H}_1{}^\circ) \tag{18}$$

Substituting into equation (18), $-\frac{(\overline{H}_2 - \overline{H}_2{}^\circ)\ m}{3\ (55.508)}$ for $(\overline{H}_1 - \overline{H}_1{}^\circ)$ (from equation (17)) gives

$$\Phi_h - \Phi_h{}^\circ = \frac{2}{3}(\overline{H}_2 - \overline{H}_2{}^\circ) \tag{19}$$

This relation always holds whenever a partial molal property of the solute is directly proportional to $m^{1/2}$.

Evaluating equation (19), one obtains

$$\Phi_h - \Phi_h{}^\circ = 435\ m^{1/2} \text{ calories per mole of solute} \tag{20}$$

This equation gives the theoretical variation of the relative apparent molal heat content with concentration in the very dilute region for a uni-univalent electrolyte at 18° C., and is the device used in this paper to extrapolate the experimental data from regions of low concentration to infinite dilution.

The uncertainty in the value of the numerical cœfficient in equation (20) is in large part due to the uncertainty in the value of $\frac{dD}{dT}$ used in evaluating equation (14). If the uncertainty [21] in the value of $\frac{dD}{dT}$ is taken as about 3 per cent, the resulting uncertainty in the value of the numerical cœfficient in equation (20) is about 50 calories. However, since this equation is used in extrapolating only over a small range, the uncertainty due to lack of knowledge of the exact value of this cœfficient introduces a possible error in the extrapolated values of only several calories in most cases. As can be seen from an inspection of Figures 1, 2, and 3, where are plotted the experimentally

[20] See footnote 3, p. 792. [21] See footnote 19, p. 794.

observed values for the heats of dilution, the error in locating the intercept at infinite dilution is due more to lack of knowledge of the exact position of the curve in the region of low concentration than to the selection of the slope used in extrapolation.

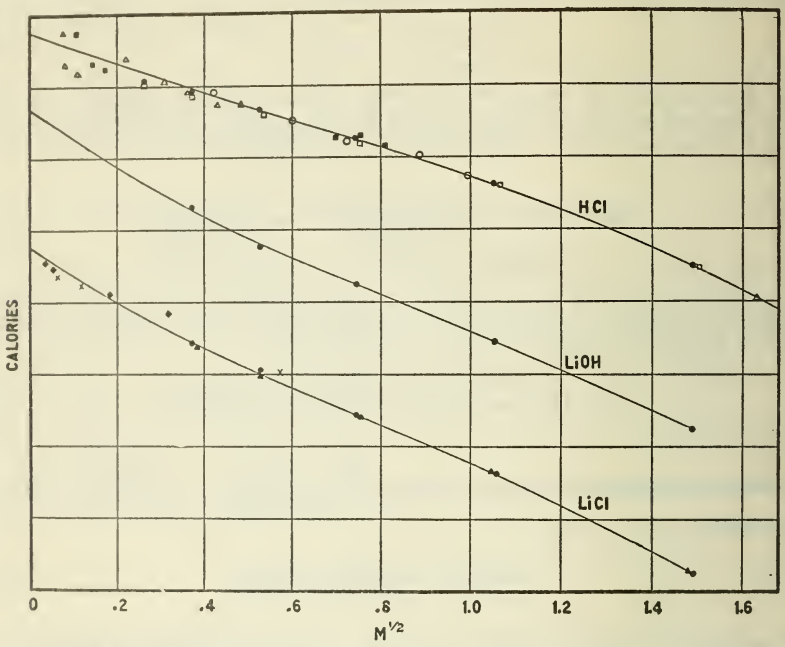

FIGURE 1.—*Plot of the experimental data on the heats of dilution of HCl, LiCl, and LiOH*

The data have been calculated to 18°C., in calories per mole of solute.

The ordinate scale measures the apparent molal heat content in calories per mole while the abscissa scale gives the square root of the molality. Each unit of the ordinate scale is for HCl, 200 calories, and for LiCl and LiOH, 100 calories.

The data of the various investigators are:

● Richards and Rowe.
□ Richards, Mair, and Hall.
■ Muller.
△ Steinwehr.
○ Wrewsky and Savaritzky.
◆ Nernst and Orthmann.
× Nernst and Naudé.
▲ Lange and Durr.

III. METHODS OF CALCULATION AND TREATMENT OF DATA

The starting point for the evaluation of $\Phi_h - \Phi_h°$, $\overline{H}_2 - \overline{H}_2°$, and $\overline{H}_1 - \overline{H}_1°$ lies in equation (7) where the quantity ΔH can be determined by proper extrapolation of the experimental data to infinite dilution. This may be illustrated by the following procedure:

Given the solution $HCl \cdot 25H_2O$. The heat content of this solution is

$$H = \overline{H}_2 + 25\overline{H}_1 \tag{21}$$

or

$$H = \Phi_h + 25\overline{H}_1° \tag{22}$$

The heat change which occurs when this solution is diluted, for example with an equal amount of H_2O, is measured. We have the reaction

$$HCl \cdot 25H_2O + 25H_2O = HCl \cdot 50H_2O \tag{23}$$

The heat content of the newly formed solution is H′.

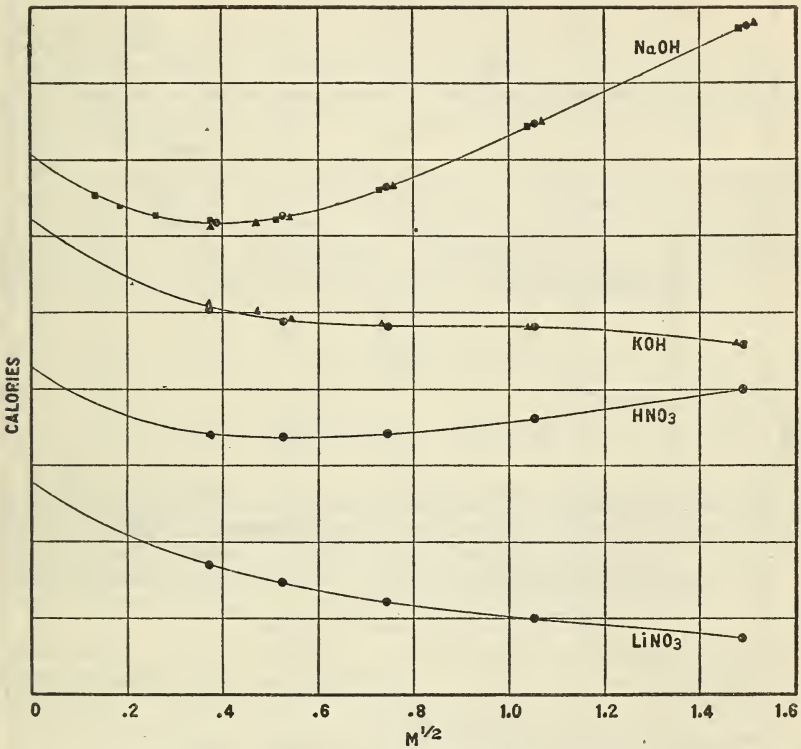

FIGURE 2.—*Plot of the experimental data on the heats of dilution of NaOH, KOH, HNO_3, and $LiNO_3$*

The data have been calculated to 18°C., in calories per mole of solute.
The ordinate scale measures the apparent molal heat content in calories per mole while the abscissa scale gives the square root of the molality. Each unit of the ordinate scale is 100 calories.
The data of the various investigators are:
● Richards and Rowe. ■ Richards and Gucker. ▲ Pratt.

Then

$$\Delta H = \Phi'_h + 50\overline{H}_1{}^\circ - [(\Phi_h + 25\overline{H}_1{}^\circ) + 25\overline{H}_1{}^\circ] = \Phi_h' - \Phi_h \tag{24}$$

One then proceeds to measure the heat change when this new solution is further diluted:

$$HCl \cdot 50H_2O + 50H_2O = HCl \cdot 100H_2O \tag{25}$$

This gives

$$\Delta H = \Phi_h'' - \Phi_h' \tag{26}$$

Combining with equation (24), one obtains for the reaction

$$HCl \cdot 25H_2O + 75H_2O = HCl \cdot 100H_2O \tag{27}$$

the heat change

$$\Delta H = \Phi_h'' - \Phi_h \tag{28}$$

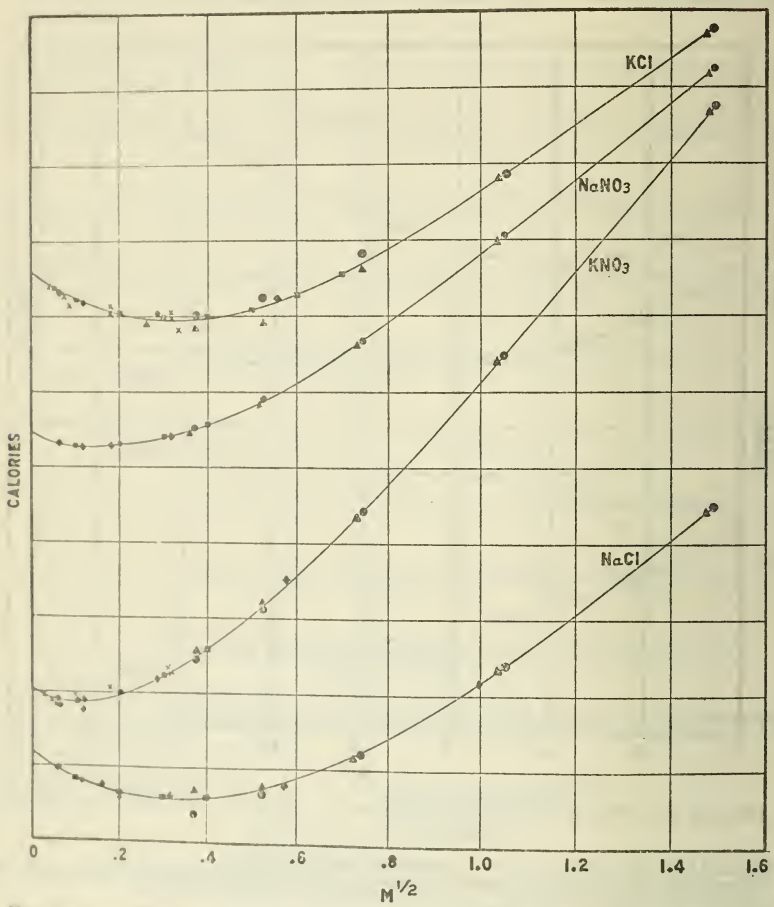

FIGURE 3.—*Plot of the experimental data on the heats of dilution of NaCl, KCl, $NaNO_3$, and KNO_3*

The data have been calculated to 18° C., in calories per mole of solute.

The ordinate scale measures the apparent molal heat content in calories per mole while the abscissa scale gives the square root of the molality. Each unit of the ordinate scale is for NaCl and KCl, 100 calories, and for $NaNO_3$ and KNO_3, 200 calories.

The data of the various investigators are:

● Richards and Rowe.
■ Lange et al.
▲ Pratt.
◆ Nernst and Naudé.
× Nernst and Orthmann.

Proceeding in this manner, one can measure, with sufficiently accurate and sensitive apparatus, heats of dilution to very small concentrations. When a proper extrapolation to infinite dilution is made, then, for the reaction

$$HCl \cdot 25H_2O + (\infty - 25)\ H_2O = HCl \cdot \infty H_2O \tag{29}$$

the heat change becomes

$$\Delta H = H^\circ - H = \Phi_h^\circ - \Phi_h \tag{30}$$

or for the reverse change

$$\Phi_h - \Phi_h^\circ = H - H^\circ \tag{31}$$

where 1 mole of solute is concerned.

When the data obtained for $\Phi'_h - \Phi_h$, $\Phi''_h - \Phi_h$, $\Phi_h''' - \Phi_h$, etc., are plotted against the square root of the molality and extrapolated by means of equation (20) to infinite dilution, values of $\Phi_h - \Phi_h^\circ$ can be read off.

Where sufficiently accurate values of the apparent molal heat capacity of the solute are available, the calculation to 18°C. of the heat of dilution data obtained at other temperatures introduces no uncertainty. The temperature coefficient of the apparent molal heat content is equal to the apparent molal heat capacity:

$$\frac{d\Phi_h}{dT} = \Phi_c \tag{32}$$

or

$$\frac{d}{dT}(\Phi_h - \Phi_h^\circ) = \Phi_c - \Phi_c^\circ \tag{33}$$

Having obtained values for $\Phi_h - \Phi_h^\circ$, the values for $\overline{H}_2 - \overline{H}_2^\circ$ and $\overline{H}_1 - \overline{H}_1^\circ$ can be derived by a procedure similar to that employed by Randall and Rossini [22] and Rossini [23] for heat capacities.

From equation (28), one may write, for m moles of solute,

$$H - H^\circ = m\,(\Phi_h - \Phi_h^\circ) \tag{34}$$

Differentiating with respect to m,

$$\frac{d}{dm}(H - H^\circ) = (\Phi_h - \Phi_h^\circ) + m\frac{d}{dm}(\Phi_h - \Phi_h^\circ) \tag{35}$$

But

$$\frac{d}{dm}(H - H^\circ) = \overline{H}_2 - \overline{H}_2^\circ \tag{36}$$

Hence

$$\overline{H}_2 - \overline{H}_2^\circ = \Phi_h - \Phi_h^\circ + m\frac{d}{dm}(\Phi_h - \Phi_h^\circ) \tag{37}$$

substituting $2m^{1/2}\,d\,m^{1/2}$ for dm, we obtain

$$\overline{H}_2 - \overline{H}_2^\circ = \Phi_h - \Phi_h^\circ + \tfrac{1}{2}m^{1/2}\frac{d}{dm^{1/2}}(\Phi_h - \Phi_h^\circ) \tag{38}$$

From a plot of values of $\Phi_h - \Phi_h^\circ$ against $m^{1/2}$, one obtains values for $\overline{H}_2 - \overline{H}_2^\circ$ from equation (38).

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[22] See footnote 10, p. 793.

[23] Rossini, B. S. Jour. Research, 4, p. 313; 1930.

Now by equation (18)

$$\Phi_h - \Phi_h^\circ = \overline{H}_2 - \overline{H}_2^\circ + \frac{55.508}{m}(\overline{H}_1 - \overline{H}_1^\circ) \tag{18}$$

Combination of equations (38) and (18) gives

$$\overline{H}_1 - \overline{H}_1^\circ = -\frac{m^{3/2}}{2(55.508)}\frac{d}{dm^{1/2}}(\Phi_h - \Phi_h^\circ) \tag{39}$$

Values of the slope of $\Phi_h - \Phi_h^\circ$ against $m^{1/2}$ have already been obtained in evaluating $\overline{H}_2 - \overline{H}_2^\circ$. There remains only the multiplication of this slope by the coefficient, $-\frac{m^{3/2}}{2(55.508)}$, to obtain values for $\overline{H}_1 - \overline{H}_1^\circ$.

IV. THE AVAILABLE DATA

The data which have been used in this paper to carry out the procedure and calculations described in the foregoing section are plotted, for the various solutes, in Figures 1, 2, and 3. The plotted data have, of course, all been calculated to 18° C. from whatever temperature they were measured. Only those data which give heats of dilution in the range from $MX \cdot 25H_2O$ to infinite dilution were considered.

Richards and Rowe [24] measured the heats of dilution of HCl at 16° and 20° C. over the range $HCl \cdot 25H_2O$ to $HCl \cdot 400H_2O$. These same authors [25] obtained data at the same temperatures and for the same range of concentration on HNO_3, $LiNO_3$, $NaNO_3$, KNO_3, LiCl, NaCl, KCl, LiOH, NaOH, and KOH. For the purposes of the present work, the measurements at 16° and 20° C. were averaged to give the heat of dilution at 18° C.

Richards, Mair, and Hall [26] repeated the measurements on HCl and extended them to $HCl \cdot 800\ H_2O$. Richards and Gucker [27] reported new measurements on NaOH, extending the data to $NaOH \cdot 3200H_2O$.

Pratt [28] measured the heats of dilution of NaCl, KCl, $NaNO_3$, NaOH and KOH over the range of concentration $MX \cdot 25H_2O$ to about $MX \cdot 400H_2O$ at many temperatures from 0° to 33.5° C. For NaCl and KCl, data at 18° C. were available, but for the other electrolytes data for 18° C. were obtained by interpolating the measurements made by Pratt at 15° and 20° C.

Data on HCl were available from the measurements of Muller [29] at 16° C., of Steinwehr [30] at 18° C., and the data of Wrewskii and Savaritzky,[31] who measured the heat of solution of HCl gas in water at 21.5° C. for various concentrations.

In the very dilute range of concentrations there are the measurements of Lange and coworkers at 25° C. and of Nernst and coworkers

[24] Richards and Rowe, J. Am. Chem. Soc., 42, p. 1621; 1920.
[25] Richards and Rowe, J. Am. Chem. Soc., 43, p. 770; 1921.
[26] Richards, Mair, and Hall, J. Am. Chem. Soc., 51, p. 727; 1929.
[27] Richards and Gucker, J. Am. Chem. Soc., 51, p. 712; 1929.
[28] Pratt, J. Frank. Inst., 185, p. 663; 1918.
[29] Muller, Bull. Soc. Chim., 13, p. 1053; 1913.
[30] Steinwehr, Z. physik. Chem., 38, p. 185; 1903.
[31] Wrewskii and Savaritzky, Z. physik. Chem., 112, p. 90; 1924.

at 18° C. Lange and Robinson[32] obtained data on $NaNO_3$ and NaCl; Lange and Leighton,[33] on KCl; and Lange and Monheim,[34] on KNO_3. The original work of Lange and Messner[35] contained a few data on LiCl, NaCl, KCl, and KNO_3. The measurements of Nernst and Orthmann[36] include data on LiCl and KCl, while Nernst and Naudé[37] record some measurements on LiCl, NaCl, KCl, $NaNO_3$, and KNO_3.

All of the foregoing data, where obtained at other temperatures, were calculated to 18° C. by means of the apparent molal heat capacity values already mentioned.[38] The experimental data for the heats of dilution have been plotted against $m^{1/2}$ in Figures 1, 2, and 3. The extrapolation to infinite dilution has been made by the use of equation (20).

V. THE CALCULATED RESULTS

By a shift of the ordinate scale so that the intercept of the curve for the heat of dilution on the ordinate axis becomes the origin, $m=0$ and $\Phi_h-\Phi_h^\circ=0$, the curves in Figures 1, 2, and 3 give immediately values for $\Phi_h-\Phi_h^\circ$, by equation (30).

In Table 1 are given values of $\Phi_h-\Phi_h^\circ$, the relative apparent molal heat content of the solute, for the 11 different solutions at dilutions expressed in terms of the number of moles of H_2O associated with 1 mole of solute.

From the curves of $\Phi_h-\Phi_h^\circ$ against $m^{1/2}$, values of $\overline{H}_2-\overline{H}_2^\circ$, the relative partial molal heat content of the solute, were determined by means of equation (38). Then by application of equation (39) values for $\overline{H}_1-\overline{H}_1^\circ$, the relative partial molal heat content of the H_2O, were obtained. In Table 2 are given values of $\Phi_h-\Phi_h^\circ$, $\overline{H}_2-\overline{H}_2^\circ$, and $\overline{H}_1-\overline{H}_1^\circ$, for the 11 different solutions at concentrations from $m=0$ to $m=1.96$.

TABLE 1.—$\Phi_h-\Phi_h^0$, *relative apparent molal heat content, at 18° C. in g-cal.*$_{18}$ *per mole of solute* [a]

Solution ↓ MX→	HCl	LiCl	NaCl	KCl	HNO_3	$LiNO_3$	$NaNO_3$	KNO_3	LiOH	NaOH	KOH
MX· ∞ H_2O	0	0	0	0	0	0	0	0	0	0	0
MX· 6,400 H_2O	41	38	35	33	36	36	30	31	40	38	38
MX· 3,200 H_2O	58	53	45	42	48	49	34	29	55	50	52
MX· 1,600 H_2O	81	73	55	51	61	65	31	18	77	63	70
MX· 800 H_2O	115	100	61	58	74	85	18	−17	106	76	90
MX· 400 H_2O	162	132	61	58	85	108	−15	−90	141	86	113
MX· 200 H_2O	222	175	47	45	90	133	−86	−233	188	78	130
MX· 100 H_2O	305	231	−5	−13	86	157	−246	−465	243	39	137
MX· 50 H_2O	430	312	−120	−128	66	180	−520	−885	323	−45	137
MX· 25 H_2O	655	450	−330	−318	28	205	−960	−1,530	443	−173	162

[a] The composition of the solution is given in terms of the number of moles of water associated with 1 mole of solute.

[32] Lange and Robinson, Z. physik. Chem., A, **148**, p. 197; 1930.
[33] Lange and Leighton, Z. Elektrochem., **34**, p. 566; 1928.
[34] Lange and Monheim, Z. physik. Chem., A, 150, p. 349; 1930.
[35] Lange and Messner, Naturwissenschaften, **15**, p. 521; 1927.
[36] Nernst and Orthmann, sitzb. preuss. Akad. Wiss., p. 51; 1926; p. 136; 1927.
[37] Nernst and Naudé, Z. Elektrochem., **33**, p. 532; 1927.
[38] See footnote 9, p. 793.

TABLE 2.—*Apparent and partial molal heat content of solute and partial molal heat content of H_2O in aqueous solutions of HCl, LiCl, NaCl, KCl, HNO_3, $LiNO_3$, $NaNO_3$, KNO_3, LiOH, NaOH, and KOH at 18° C*

Solute	m moles of solute per 1,000 g H_2O	$m^{1/2}$	$\Phi_A-\Phi_A°$ g-cal.18 per mole of solute	$\overline{H}_2-\overline{H}_2°$ g-cal.18 per mole of solute	$\overline{H}_1-\overline{H}_1°$ g-cal.18 per mole of H_2O
HCl	0	0	0	0	0
	.01	.1	44	66	−.0040
	.04	.2	88	131	−.0310
	.09	.3	131	196	−.105
	.16	.4	173	257	−.242
	.25	.5	213	310	−.437
	.36	.6	251	367	−.752
	.64	.8	327	482	−1.78
	1.00	1.0	408	623	−3.87
	1.44	1.2	500	792	−7.57
	1.96	1.4	604	983	−13.38
LiCl	0	0	0	0	0
	.01	.1	41	61	−.0036
	.04	.2	78	113	−.0252
	.09	.3	112	159	−.0762
	.16	.4	141	197	−.162
	.25	.5	168	234	−.297
	.36	.6	194	271	−.499
	.64	.8	245	347	−1.18
	1.00	1.0	297	433	−2.45
	1.44	1.2	355	537	−4.72
	1.96	1.4	419	658	−8.44
NaCl	0	0	0	0	0
	.01	.1	38	52	−.0025
	.04	02	56	66	−.0072
	.09	.3	62	64	−.0032
	.16	.4	60	47	+.037
	.25	.5	48	14	.153
	.36	.6	33	−31	.415
	.64	.8	−23	−154	1.51
	1.00	1.0	−97	−303	3.71
	1.44	1.2	−188	−477	7.50
	1.96	1.4	−287	−638	12.39
KCl	0	0	0	0	0
	.01	.1	35	49	−.0025
	.04	.2	52	63	−.0079
	.09	.3	59	63	−.0064
	.16	.4	58	51	+.020
	.25	.5	49	14	.158
	.36	.6	30	−44	.480
	.64	.8	−33	−165	1.53
	1.00	1.0	−108	−306	3.57
	1.44	1.2	−188	−442	6.59
	1.96	1.4	−277	−605	11.58
HNO_3	0	0	0	0	0
	.01	.1	38	54	−.0029
	.04	.2	64	84	−.0144
	.09	.3	79	111	−.052
	.16	.4	86	97	−.032
	.25	.5	90	96	−.027
	.36	.6	90	88	+.013
	.64	.8	84	58	.30
	1.00	1.0	70	32	.68
	1.44	1.2	54	6	1.25
	1.96	1.4	37	−32	2.44
$LiNO_3$	0	0	0	0	0
	.01	.1	38	55	−.0031
	.04	.2	69	94	−.0180
	.09	.3	93	125	−.052
	.16	.4	113	148	−.101
	.25	.5	129	166	−.167
	.36	.6	142	176	−.221
	.64	.8	162	195	−.38
	1.00	1.0	177	213	−.65
	1.44	1.2	190	224	−.88
	1.96	1.4	201	235	−1.20
$NaNO_3$	0	0	0	0	0
	.0025	.05	20	30	−.00045
	.01	.1	32	39	−.0013
	.04	.2	30	18	+.0087
	.09	.3	8	−34	.068
	.16	.4	−25	−102	.222
	.25	.5	−71	−208	.617
	.36	.6	−135	−349	1.388
	.64	.8	−290	−635	3.98
	1.00	1.0	−475	−942	8.42
	1.44	1.2	−667	−1260	15.38
	1.96	1.4	−868	−1584	25.28
KNO_3	0	0	0	0	0
	.0025	.05	20	30	−.00045
	.01	.1	32	33	−.0002
	.04	.2	13	−26	+.026
	.09	.3	−39	−136	.157
	.16	.4	−113	−276	.470
	.25	.5	−207	−456	1.122
	.36	.6	−313	−636	2.195
	.64	.8	−551	−1060	5.87
	1.00	1.0	−823	−1525	12.65
	1.44	1.2	−1108	−1993	22.96
	1.96	1.4	−1408	−2476	37.71
LiOH	0	0	0	0	0
	.01	.1	42	63	−.0038
	.04	.2	82	119	−.0267
	.09	.3	118	168	−.081
	.16	.4	150	212	−.179
	.25	.5	180	252	−.328
	.36	.6	208	286	−.506
	.64	.8	258	360	−1.18
	1.00	1.0	310	440	−2.34
	1.44	1.2	362	525	−4.23
	1.96	1.4	418	615	−6.96
NaOH	0	0	0	0	0
	.01	.1	40	57	−.0031
	.04	.2	65	84	−.0137
	.09	.3	81	97	−.026
	.16	.4	86	84	+.006
	.25	.5	81	58	.136
	.36	.6	68	20	.311
	.64	.8	26	−75	1.16
	1.00	1.0	−30	−170	2.52
	1.44	1.2	−86	−254	4.36
	1.96	1.4	−143	−319	6.21
KOH	0	0	0	0	0
	.01	.1	40	58	−.0032
	.04	.2	74	103	−.0218
	.09	.3	99	131	−.052
	.16	.4	117	145	−.081
	.25	.5	129	148	−.086
	.36	.6	133	147	−.091
	.64	.8	137	137	.000
	1.00	1.0	137	139	−.036
	1.44	1.2	142	164	−.57
	1.96	1.4	154	207	−1.87

The data for $\Phi_h - \Phi_h{}^\circ$ and $\overline{H}_2 - \overline{H}_2{}^\circ$ are plotted against $m^{1/2}$ in Figures 4 and 5, respectively, while Figure 6 shows values of $\overline{H}_1 - \overline{H}_1{}^\circ$ plotted against $m^{3/2}$.

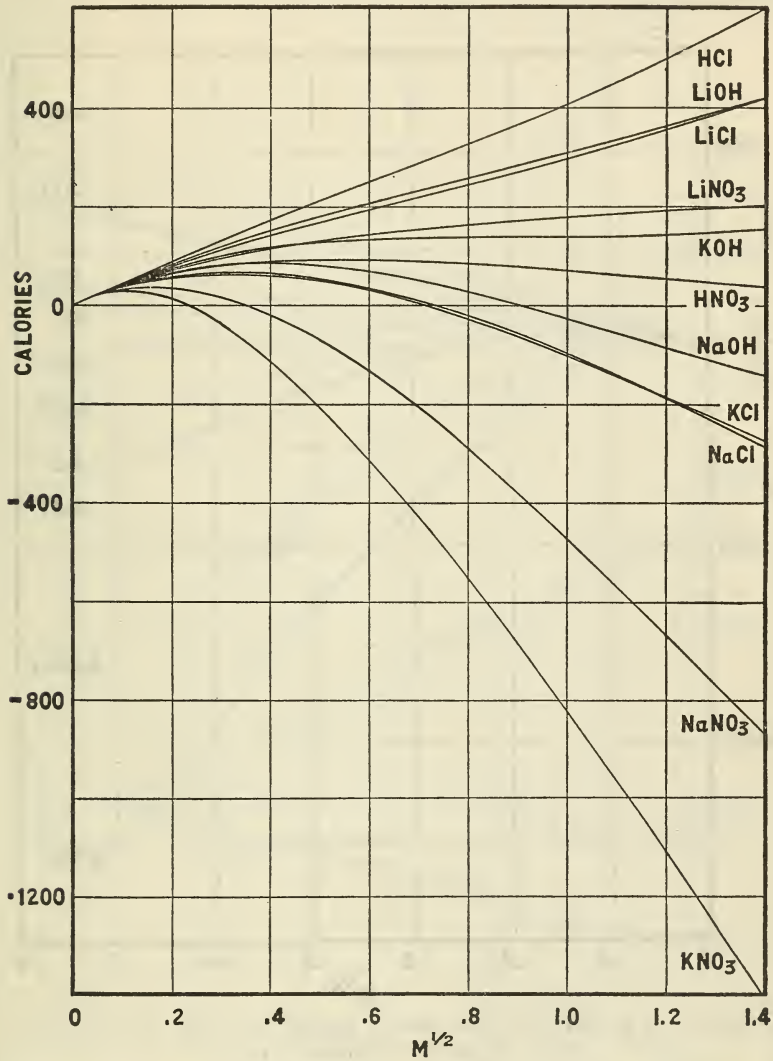

FIGURE 4.—*Plot of $\Phi_h - \Phi_h{}^\circ$, the relative apparent molal heat content of the solute, in aqueous solutions at 18° C.*

The ordinate scale gives $\Phi_h - \Phi_h{}^\circ$ in calories per mole of solute while the abscissa scale gives the square root of the molality.

VI. DISCUSSION

The character of the family of curves shown in Figure 4, in which the relative apparent molal heat content is plotted against the square

root of the molality, has already been discussed, in the very dilute region by Lange[39] and coworkers, and in the more concentrated range by Richards and Rowe.[40] The curves in Figures 5 and 6, showing the relative partial molal heat content of the solute and of the H_2O, are self-explanatory.

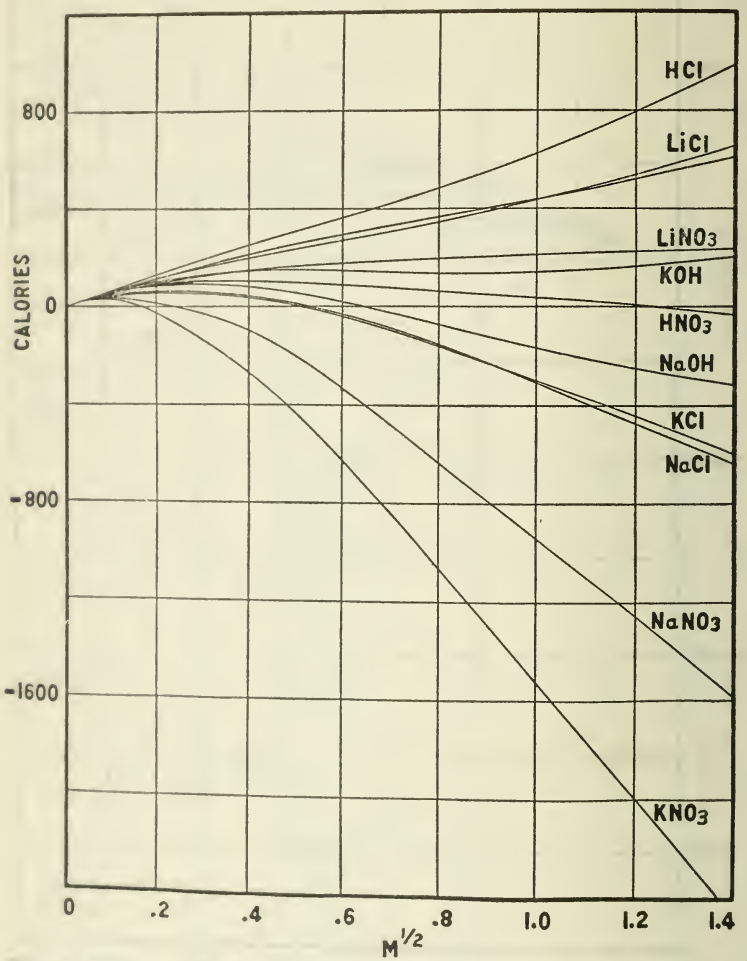

FIGURE 5.—*Plot of $\overline{H}_2-\overline{H}_2°$, the relative partial molal heat content of the solute, in aqueous solutions at 18° C.*

The ordinate scale gives $\overline{H}_2-\overline{H}_2°$ in calories per mole of solute while the abscissa scale gives the square root of the molality.

The usefulness of a complete compilation of values of $\Phi_h-\Phi_h°$, $\overline{H}_2-\overline{H}_2°$, $\overline{H}_1-\overline{H}_1°$, for the given concentration range will be apparent to whoever has need of such data in the calculation of heats of reaction at various concentrations from a heat of reaction measured at

[39] See footnote 16, p. 793.

[40] See footnote 6, p. 793.

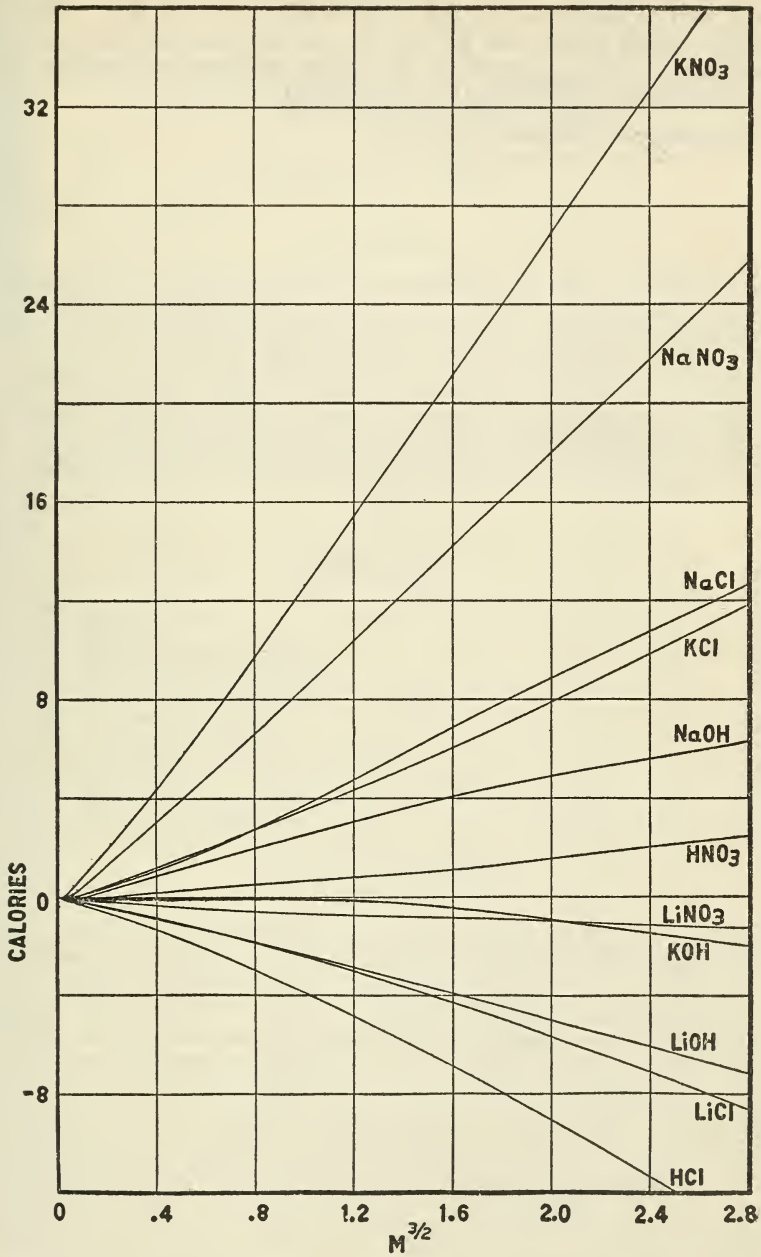

FIGURE 6.—*Plot of $\overline{H}_1-\overline{H}_1°$, the relative partial molal heat content of the H_2O, in aqueous solutions at 18° C.*

The ordinate scale gives $\overline{H}_1-\overline{H}_1°$ in calories per mole of H_2O while the abscissa scale gives the 3/2 power of the molality.

one concentration, or in the calculation of the temperature coefficient of the partial molal free energy of the solute or of the H_2O. The heat content values given here for 18° C. can be converted to other temperatures by the appropriate use of the apparent and partial molal heat capacities of the substances involved.

WASHINGTON, January 23, 1931.