APPARENT AND PARTIAL MOLAL HEAT CAPACITIES IN AQUEOUS SOLUTIONS OF 19 UNI-UNIVALENT STRONG ELECTROLYTES

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ABSTRACT

Φ_c, the apparent molal heat capacity of the solute, is shown, within the accuracy of the best experimental data, to be a linear function of the square root of the molality for aqueous solutions of uni-univalent strong electrolytes from infinite dilution to about 2.5 molal. Consequently, $\overline{C}_{p2}$, the partial molal heat capacity of the solute, and $\overline{C}_{p1}$, the partial molal heat capacity of the H_2O, are linear functions of the square root of the molality and the 3/2 power of the molality respectively.

In convenient form are tabulated data from which may be quickly computed values of Φ_c, $\overline{C}_{p2}$, and $\overline{C}_{p1}$ for aqueous solutions of the chlorides, bromides, iodides, nitrates, and hydroxides of hydrogen, lithium, sodium, and potassium for any molality in the given range, at 18°, 21.5°, and 25° C.

CONTENTS

I. INTRODUCTION

The development of a complete set of correlated data on the heat changes associated with reactions involving aqueous solutions of strong electrolytes has been somewhat retarded because of the lack of appropriate and accurate data for computing the relatively large temperature coefficients of such reactions.

These temperature coefficients can be easily and directly computed from values for Φ_c, the apparent molal heat capacity of the solute, for the given solutions.[1] Reliable values for Φ_c can be obtained indirectly from accurate measurements of the heat capacity of any aqueous solution, or from direct measurements of Φ_c. The present writer, requiring reliable values for Φ_c for the computation of the temperature coefficient of heats of dilution [2] and heats of neutralization,[3] reviewed the data on heat capacities in aqueous solutions of uni-univalent strong electrolytes. Values of Φ_c were computed from the various data and plotted against $m^{1/2}$, the square root of the molality.[4]

[1] For a discussion of Φ_c, $\overline{C}_{p_2}$, and $\overline{C}_{p_1}$, the reader is referred to—
(*a*) Lewis and Randall, Thermodynamics, Chapter VIII, McGraw-Hill Book Co., New York; 1923.
(*b*) Randall and Ramage, J. Am. Chem. Soc., **51**, p. 323; 1929.
(*c*) Randall and Rossini, J. Am. Chem. Soc., **49**, p. 93; 1927.
(*d*) Rossini, B. S. Jour. Research, **4**, p. 313; 1930.
[2] Rossini, B. S. Jour. Research, **6**, p. 791; 1931.
[3] Rossini, B. S. Jour. Research, **6**, p. 847; 1931.
[4] Following Lewis and Randall, m is the molality in moles of solute per 1,000 g of H_2O.

II. TREATMENT OF THE DATA

The data [5] are plotted in Figures 1, 2, 3, and 4.

In all cases where the data were obtained at other temperatures the values were corrected to 25° or to 18° C.

An inspection of the plotted data, in which are included the actual experimental data of Randall and Rossini,[6] shows definitely that Φ_c can be represented, within the accuracy of the best experimental data, as a linear function of $m^{1/2}$, from the lowest measured concentration to about 2.5 molal.[7]

Randall and Ramage [8] found that the value of $\overline{C}_{p_2}$ for solutions of sodium chloride increased with temperature, but gave no quantitative information. Randall and Rossini,[9] from a comparison of their data with that of others at lower temperatures, estimated that the change in $\overline{C}_{p_2}$ or Φ_c with temperature was about 0.2 cal mole^{-1}°C^{-2}. From the data of Richards et al., Rossini [10] calculated for aqueous solutions of 3 uni-univalent strong electrolytes, in the region from infinite dilution to about 1 molal, that the change in Φ_c with temperature was 0.26 to 0.29 cal mole^{-1} °C^{-2}. From the data of Richards and Gucker,[11] who measured the specific heats of solutions of $NaOH \cdot 25H_2O$ and $NaC_2H_3O_2 \cdot 25H_2O$ at 16°, 18° and 20°C, the change in Φ_c with temperature over this range is computed to be 0.32 and 0.28 cal mole^{-1} °C^{-2}, respectively. For the purpose of the present work, $\frac{d\Phi_c}{dT}$ is taken as $\frac{2.0}{7}$ cal mole^{-1} °C^{-2}, for the temperature range 18° to 25° C. The same value is used for all the uni-univalent strong electrolytes from infinite dilution to about 2.5 molal and, while probably not strictly valid, this assumption is well within the accuracy of the experimental data.

Randall and Rossini [6] showed from their experimental data that $\overline{C}^{\circ}_{p_2}$ for individual ions is an additive property. This knowledge permits the accurate computation of Φ°_c (which is equal to $\overline{C}^{\circ}_{p_2}$) for a number of solutes for which no data are available in the dilute range of concentration, or for which the data are inadequate to permit reliable extrapolation to infinite dilution.

The curves for the various solutes were drawn in the following order, that the greatest advantage might be obtained in predicting

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[5] (*a*) Richards and Rowe, J. Am. Chem. Soc., **43**, p. 770; 1921; **42**, p. 1621; 1920; Proc. Am. Acad., **49**, p. 173; 1913; on LiCl, NaCl, KCl, $LiNO_3$, $NaNO_3$, KNO_3, LiOH, NaOH, KOH, HNO_3, HCl, HBr, HI, 18° C.
(*b*) Richards and Hall, J. Am. Chem. Soc., **51**, p. 707; 1929; on NaOH, KOH, 18° C.
(*c*) Richards, Mair, and Hall, J. Am. Chem. Soc., **51**, p. 727; 1929; on HCl, 18° C.
(*d*) Richards and Gucker, J. Am. Chem. Soc., **51**, p. 712; 1929; **47**, p. 1876; 1925; on NaOH, NaCl, $NaNO_3$, KNO_3, 18° C.
(*e*) Randall and Rossini, J. Am. Chem. Soc., **51**, p. 323; 1929; Rossini, Thesis, University of California; 1928; on NaCl, KCl, NaBr, KBr, NaI, KI, $NaNO_3$, KNO_3, 25° C.
(*f*) Marignac, Ann. chim. phys., 8, p. 410; 1876; on NaCl over the range 16° to 20° C., KCl at 17° to 22° C., $NaNO_3$ and KNO_3 at 18° to 23° C., NaBr, KBr, NaI, and KI at 20° to 51° C., HNO_3 at 21° to 52° C., HCl at 20° to 24° C.
(*g*) Thomsen, Thermochemische Untersuchungen, **1**, p. 38, Barth, Leipzig; 1882; on HCl, 18° C.
(*h*) Jauch, Z. Physik, **4**, p. 441; 1921; on LiCl, LiBr, LiI, 18° C.
(*i*) Thorvaldson, Brown and Peaker, J. Am. Chem. Soc., **52**, p. 3927; 1930; on HCl, 20° C.
(*j*) Wrewsky and Kaigorodoff, Z. physik. Chem., **112**, p. 83; 1924; on HCl, 20.5° C.

[6] See footnote 5 (*e*), p. 48.

[7] For solutions of HCl and NaCl, Randall and Ramage (see reference 1 (*b*), p. 47) reported $\overline{C}_{p_2}$ as a linear function of $m^{1/2}$, but their data were not precise enough to establish this fact.

[8] See footnote 1 (*b*), p. 47.

[9] See footnote 5 (*e*), p. 48.

[10] See footnote 1 (*d*), p. 47.

[11] See footnote 5 (*d*), p. 48.

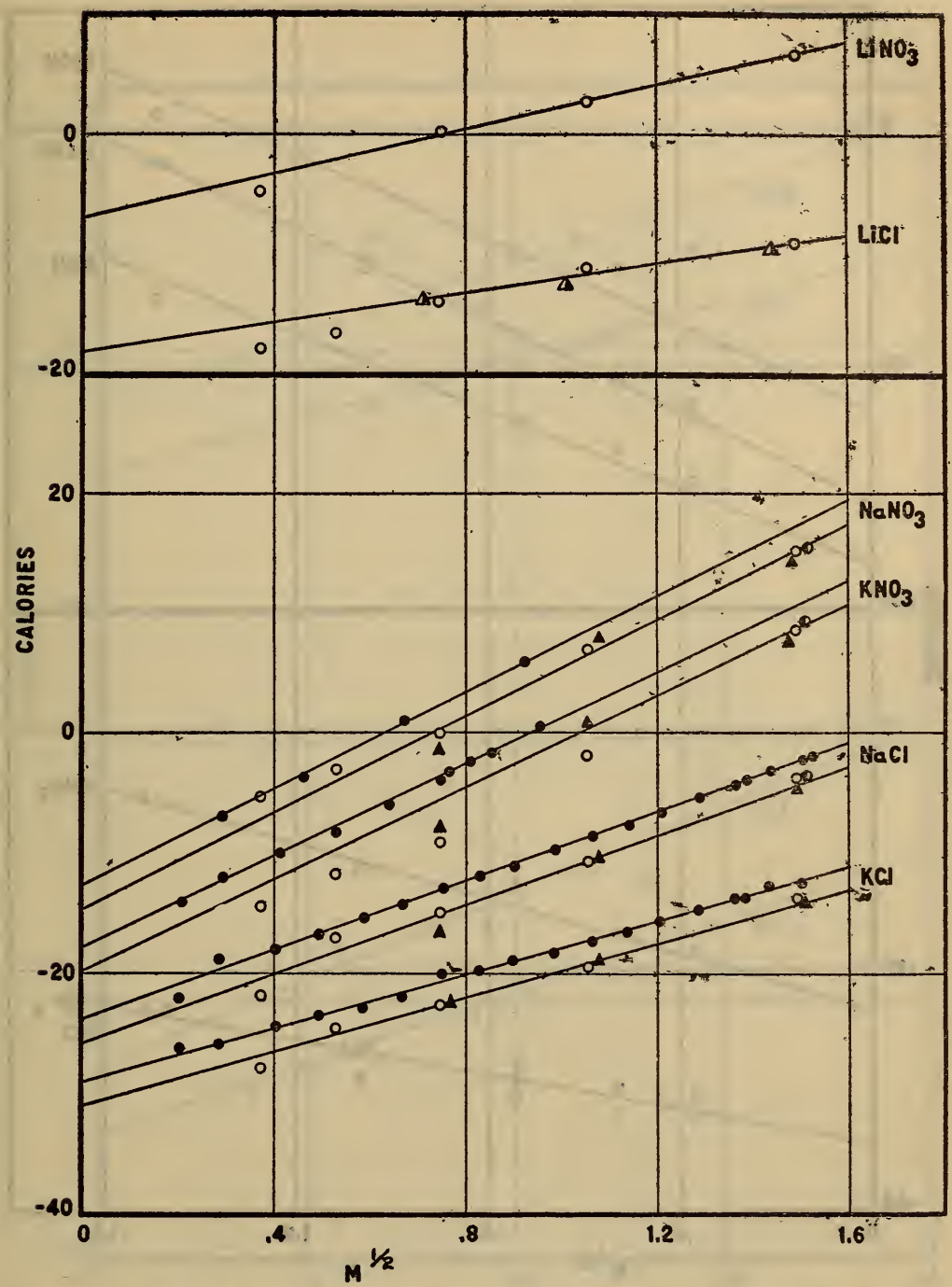

FIGURE 1.—*The apparent molal heat capacity of the solute in aqueous solutions of LiCl and $LiNO_3$ at 18° C., and NaCl, $NaNO_3$, KCl, and KNO_3 at 18' and 25° C*

The apparent molal heat capacity, in calories per mole, is plotted against the square root of the molality. Where two lines are drawn for one solute, the lower is for 18° C., and the upper for 25° C. The data of the various investigators are designated as follows:

- ● Randall and Rossini (25° C.).
- ○ Richards and Rowe (18° C.).
- ◐ Richards and Gucker (18° C.).
- ▲ Jauch (18° C.).
- ▲ Marignac (corrected from 16° to 23° to 18° C.).

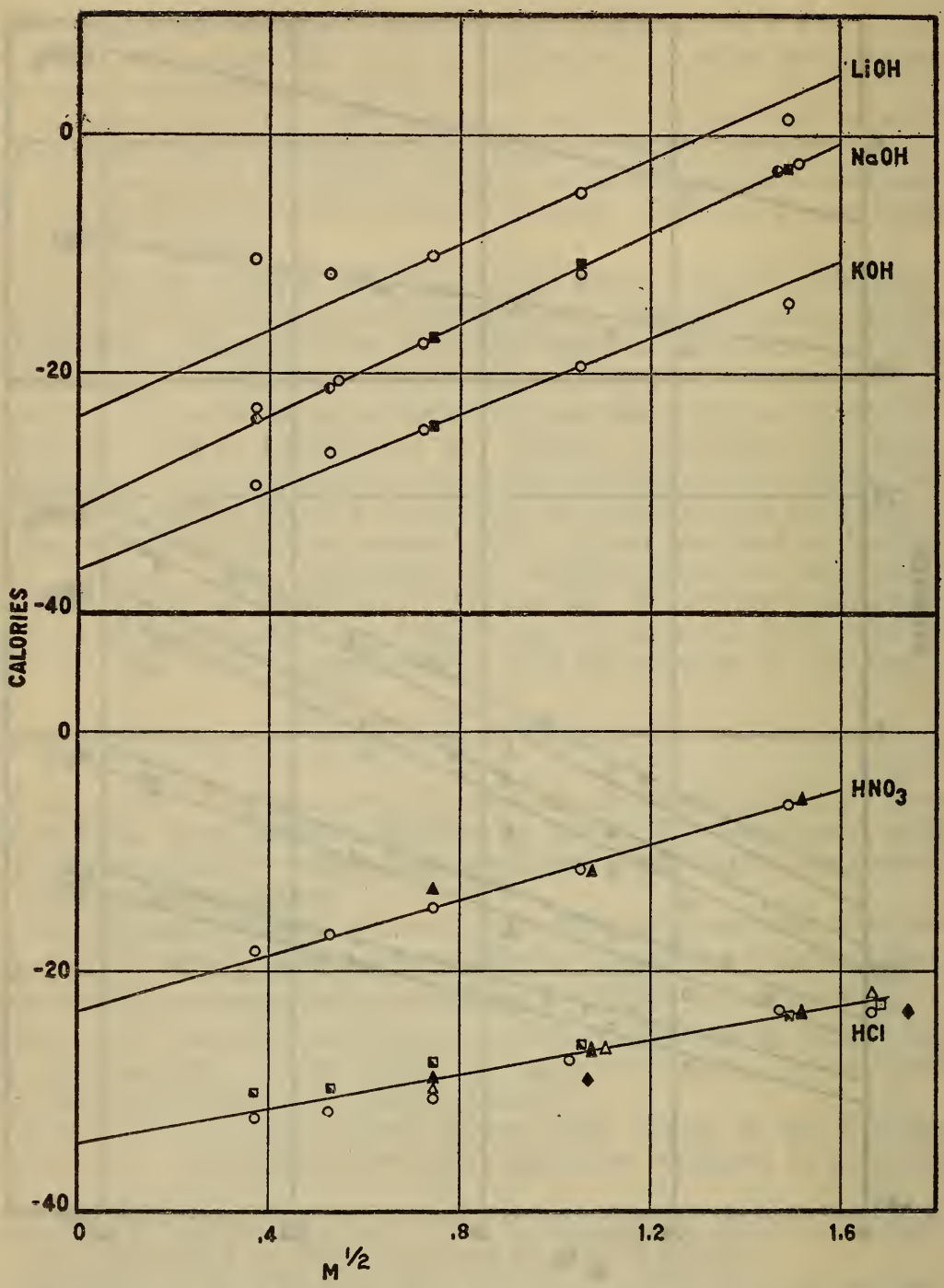

FIGURE 2.—*The apparent molal heat capacity of the solute in aqueous solutions of HCl, HNO_3, LiOH, NaOH, and KOH at 18° C.*

The apparent molal heat capacity, in calories per mole, is plotted against the square root of the molality The data of the various investigators are designated as follows:

○ Richards and Rowe (18° C.).
▣ Richards and Hall (18° C.).
◱ Richards, Mair, and Hall (18° C.).
◐ Richards and Gucker (18° C.).
△ Thomsen (18° C.).
□ Thorvaldson, Brown, and Peaker (corrected from 20° to 18° C.).
◆ Wrewsky and Kaigorodoff (corrected from 20.5° to 18° C.).
▲ Marignac (data on HCl corrected from 22° to 18° C; on HNO_3 from 21° to 52° to 18° C.).

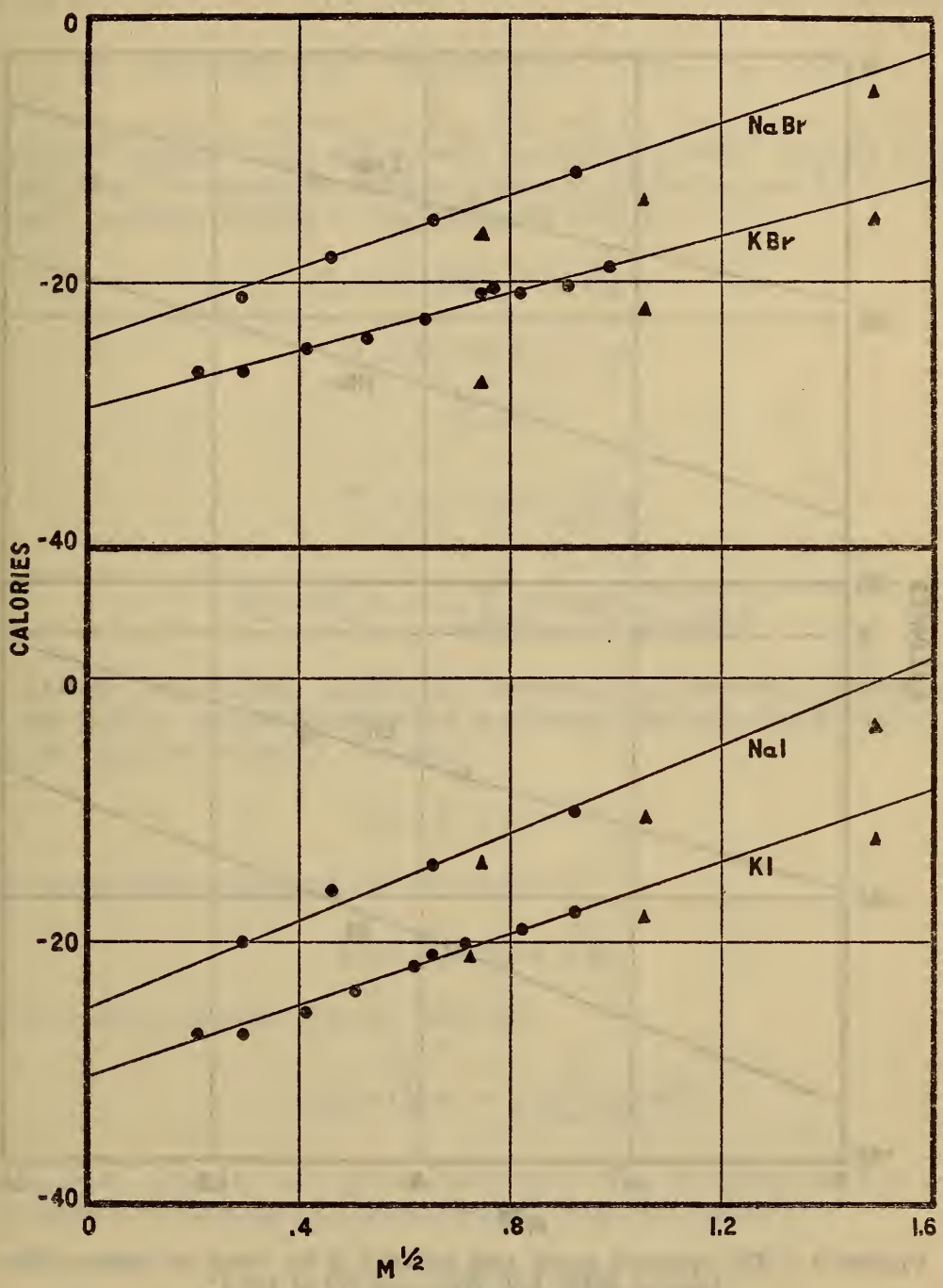

FIGURE 3.—*The apparent molal heat capacity of the solute in aqueous solutions of NaBr, KBr, NaI, and KI at 25° C.*

The apparent molal heat capacity, in calories per mole, is plotted against the square root of the molality. The data of the various investigators are designated as follows:

● Randall and Rossini (25° C.).
▲ Marignac (corrected from 25° to 51° to 25° C.).

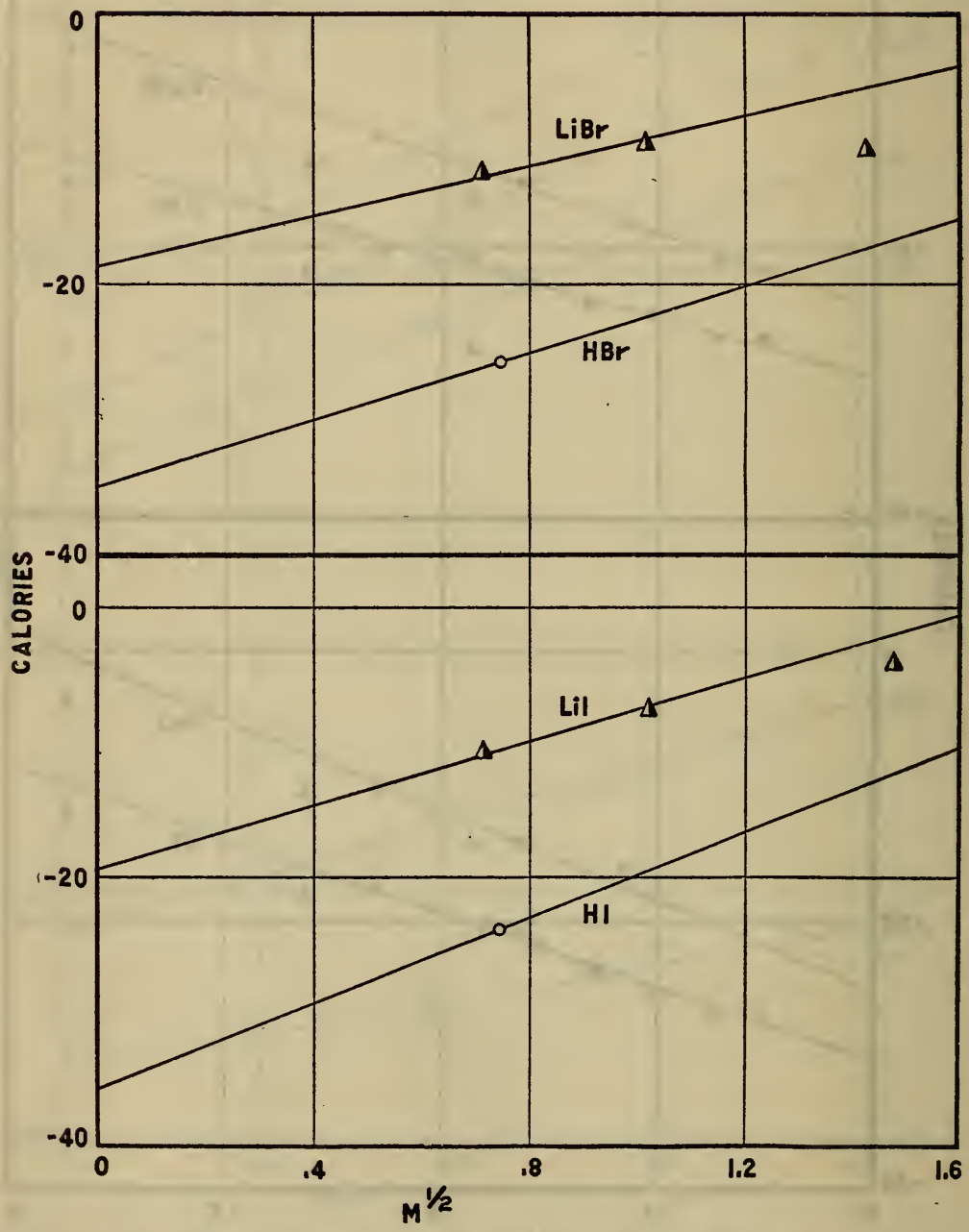

FIGURE 4.—*The apparent molal heat capacity of the solute in aqueous solutions of LiBr, LiI, HBr, and HI at 18° C.*

The apparent molal heat capacity, in calories per mole, is plotted against the square root of the molality. The data of the various investigators are designated as follows:

○ Richards and Rowe (18° C.).
△ Jauch (18° C.).

values for Φ_c for those substances on which the data are meager or unreliable: (1) NaCl; (2) KCl; (3) KNO_3 and $NaNO_3$; (4) LiCl and $LiNO_3$; (5) HCl and HNO_3; (6) NaOH; (7) LiOH and KOH; (8) KBr and NaBr; and (9) KI and NaI; (10) HBr, HI, LiBr and LiI.

III. METHOD OF COMPUTING Φ_c, $\overline{C}_{p_2}$, $\overline{C}_{p_1}$, AND C_p

The equations relating Φ_c, $\overline{C}_{p_2}$, $\overline{C}_{p_1}$ and C_p have been derived in previous papers [12] and will merely be repeated here. In this discussion C_p will be taken as the heat capacity of that amount of solution which contains 1,000 g or 55.508 moles of H_2O.

$$C_p = 55.508\overline{C}_{p_1} + m\,\overline{C}_{p_2} \tag{1}$$

$$C_p = 55.508\,\overline{C}^{\circ}_{p_1} + m\Phi_c \tag{2}$$

$$\Phi^{\circ}_c = \overline{C}^{\circ}_{p_2} \tag{3}$$

$$\overline{C}_{p_1} = \Phi_c + \tfrac{1}{2}m^{\frac{1}{2}}\frac{d\Phi_c}{d(m^{\frac{1}{2}})} \tag{4}$$

$$\overline{C}_{p_1} - \overline{C}^{\circ}_{p_1} = -\frac{m}{55.508}\left(\tfrac{1}{2}m^{\frac{1}{2}}\frac{d\,\Phi_c}{d(m^{\frac{1}{2}})}\right) \tag{5}$$

It has been shown, within the accuracy of the best experimental data, that Φ_c can be represented as a linear function of $m^{\frac{1}{2}}$ within the given range of molality. Hence

$$\Phi_c = \Phi^{\circ}_c + A\,m^{\frac{1}{2}} \tag{6}$$

By combining equations (6), (3), and (4)

$$\overline{C}_{p_2} = \overline{C}^{\circ}_{p_2} + \tfrac{3}{2}\,A\,m^{\frac{1}{2}} \tag{7}$$

and, from equations (6), (3), and (5)

$$\overline{C}_{p_1} - \overline{C}^{\circ}_{p_1} = -\frac{A}{2(55.508)}m^{\frac{1}{2}} \tag{8}$$

The heat capacity of a given solution at the temperature t in g-cal$_t$ per gram of solution can be computed from the formula

$$c_p = \frac{1{,}000 + m\Phi_c}{1{,}000 + mM} \tag{9}$$

where M is the molecular weight of the solute.

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[12] See footnote 1, p. 47.

IV. TABULATED RESULTS

In Table 1 are given, for each of the 19 aqueous solutions, the following information:

1. The value of A, $3/2A$, and $-\frac{A}{2(55.508)}$. These values are the same for the three given temperatures, 18°, 21.5°, and 25° C.

2. The value of $\Phi_v^\circ (=\overline{C}^\circ_{p_2})$ for each of the three temperatures.

From these values one may compute, for any one of the 19 solutions, at any molality between 0 and 2.5, the values of the properties Φ_v, $\overline{C}_{p_2}$, $\overline{C}_{p_1}$, and C_p at 18°, 21.5°, and 25° C.

TABLE 1.—*Table of values for computing* Φ_v, $\overline{C}_{P_2}$ *and* $\overline{C}_{P_1}$

(In cal. mole^{-1}°C $_v^{-1}$)

Solute	A	$3/2A$	$-\frac{A}{2(55.508)}$	$\Phi^\circ_v=\overline{C}^\circ_{p_2}$		
	18°–25° C.	18°–25° C.	18°–25° C.	18° C.	21.5° C.	25° C.
HCl	7.2	10.8	−0.065	−34.5	−33.5	−32.5
HBr	12.4	18.6	−.112	−35.0	−34.0	−33.0
HI	15.9	23.95	−.143	−35.7	−34.7	−33.7
HNO_3	11.5	17.25	−.104	−23.3	−22.3	−21.3
LiCl	6.1	9.15	−.055	−18.2	−17.2	−16.2
LiBr	9.2	13.8	−.083	−18.7	−17.7	−16.7
LiI	11.8	17.7	−.106	−19.4	−18.4	−17.4
$LiNO_3$	9.3	13.95	−.084	−7.0	−6.0	−5.0
LiOH	17.9	26.85	−.161	−23.6	−22.6	−21.6
NaCl	14.4	21.6	−.130	−25.8	−24.8	−23.8
NaBr	13.6	20.4	−.123	−26.3	−25.3	−24.3
NaI	16.6	24.9	−.150	−27.0	−26.0	−25.0
$NaNO_3$	20.0	30.0	−.180	−14.6	−13.6	−12.6
NaOH	19.0	28.5	−.171	−31.2	−30.2	−29.2
KCl	11.2	16.8	−.101	−31.0	−30.0	−29.0
KBr	10.8	16.2	−.097	−31.5	−30.5	−29.5
KI	13.6	20.4	−.123	−32.2	−31.2	−30.2
KNO_3	19.1	28.65	−.172	−19.8	−18.8	−17.8
KOH	16.1	24.15	−.145	−36.4	−35.4	−34.4

In Table 2 are given values for Φ_v°, which is equal to $\overline{C}_p^\circ$, for the individual ions at 25° C. These values have been computed by assuming Φ_v° for K^+ equal to Φ_v° for Cl^-. The temperature coefficient can be taken as half that for two ions.

TABLE 2.—*Values of* Φ°_v $(=\overline{C}^\circ_{p_2})$ *for individual ions at 25° C.*

(Computed by assuming Φ°_v $(K^+)=\Phi^\circ_v$ (Cl^-))

Ion	Φ°_v cal. mole^{-1} °$_v^{-1}$	Ion	Φ°_v cal. mole^{-1} °$_v^{-1}$
H^+	−18.0	Br^-	−15.0
Li^+	−1.7	I^-	−15.7
Na^+	−9.3	NO_3^-	−3.3
K^+	−14.5	OH^-	−19.9
Cl^-	−14.5		

NOTE.—The temperature coefficient of Φ°_v for a single ion can be taken as $\frac{2.0}{14}$ cal. mole^{-1} °C^{-2} at 18° to 25°C.

V. DISCUSSION

The accuracy of the present values for the apparent molal heat capacity can be judged from the figures. The data on NaCl at 25° C. and NaOH at 18° C. are the most consistent. The meager data on LiBr, LiI, HBr and HI indicate the need for accurate measurements at one or two concentrations, preferably at 1 and 2 molal. The data on HCl are at great variance, relatively. The line for HCl, drawn so as to be consistent with Φ°_c for HNO_3 and the known difference between Φ°_c for NO_3^- and for Cl^-, was passed through the middle of all the data. The resulting line, remarkably enough, passed almost directly through the three points from the data of Marignac. An inspection of the various plots shows that the data of Marignac, except, apparently, in the case of NaBr, KBr, NaI, and KI, are remarkably accurate. This was pointed out by Richards and Rowe.[13]

The values for Φ_c, $\overline{C}_{p_2}$ and $\overline{C}_{p_1}$ at 21.5° C. can be used to convert values for Φ_h, $\overline{H}_2$ and $\overline{H}_1$ from 18° to 25° C., or vice versa.

The desirability of having reliable values for Φ_c has already been discussed. $\overline{C}_{p_2}$ and $\overline{C}_{p_1}$ are, respectively, the temperature coefficients of $\overline{H}_2$ and $\overline{H}_1$, the partial molal heat content of the solute and the solvent. These properties occur frequently in thermodynamic equations involving solutions, as they serve to measure the change with temperature of $\overline{F}_2$ and $\overline{F}_1$, the partial molal free energy of the solute and the solvent, respectively.

WASHINGTON, March 27, 1931.

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[13] See footnote 5 (a), p. 48.