

UNITED STATES DEPARTMENT OF COMMERCE • John T. Connor, *Secretary*
NATIONAL BUREAU OF STANDARDS • A. V. Astin, *Director*

Thermal Properties of Aqueous Uni-univalent Electrolytes

Vivian Barfield Parker



NSRDS-NBS 2
National Standard Reference Data Series
National Bureau of Standards 2
(Category 5—Thermodynamic and Transport Properties)

Issued April 1, 1965

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C., 20402 - Price 45 cents

Foreword

In 1963 the President's Office of Science and Technology established the National Standard Reference Data System to ensure that the technical community of the United States has maximum access to compilations of critically evaluated data in the physical sciences. The National Bureau of Standards was assigned administrative responsibility for this Government-wide activity.

The National Bureau of Standards, as well as other groups both in this country and abroad, has been active in the compilation of standard reference data for many years. However, in view of the great accumulation of unevaluated data, the accelerated production of new data, the known time lag in incorporating these data into critically evaluated compilations, and the urgent needs of the scientific and technical community, it was decided by the Federal Council for Science and Technology that a substantially greater effort, planned and coordinated on a national basis, was needed. The National Standard Reference Data System (NSRDS) is the outgrowth of that decision.

The NSRDS is conducted as a decentralized operation across the country, with central coordination by the NBS. It comprises a complex of data centers and other activities, carried on in government agencies, academic institutions, and non-government laboratories. The independent operational status of existing critical data projects is maintained and encouraged. The activities of data centers which are components of the NSRDS include the preparation of compilations of critically evaluated data, the preparation of critical reviews of the quantitative state of knowledge in a specialized area, and computations of useful functions derived from standard reference data.

The present publication is considered to be a product of the National Standard Reference Data System activities at the NBS. It consists of a compilation of critically evaluated data on the thermodynamic properties of aqueous uni-univalent electrolytes, prepared as one of the continuing projects of the NBS Thermochemistry Section.

A. V. ASTIN, *Director.*

Preface

Since 1940 the National Bureau of Standards has maintained in its Thermochemistry Section a program on the collection, analysis, and evaluation of chemical thermodynamic data on chemical substances. One of the important areas of consideration has been the thermochemistry of aqueous electrolyte solutions. Because of the comparatively regular behavior of dilute univalent electrolyte solutions in water, as predicted by classical theoretical considerations, one can establish consistent values for the heats and free energies of formation and entropies of the hypothetical single-ion species, once a value for one particular ion is assigned.

As part of the planned total review of the available chemical thermodynamic data, a systematic review of the heat-capacity, heat-of-solution, and heat-of-dilution data on simple 1-1 electrolytes has been made. From the analysis of these data, tables of selected "best" values of "apparent" heat capacities, and heats of dilution are given, as well as selected values of the heats of solution to infinite dilution. Also included is a review of data on the heats of neutralization of monobasic acids which has led to a selected "best" value for the heat of ionization of water.

The author wishes to acknowledge the many stimulating and fruitful discussions with D. D. Wagman and W. H. Evans of the Thermochemistry Section. The continued financial assistance by the Division of Research of the U.S. Atomic Energy Commission is also gratefully acknowledged.

VIVIAN B. PARKER.

Contents

	Page
Foreword.....	III
Preface.....	IV
I. Introduction.....	1
II. Units of energy and constants.....	2
III. Uncertainties.....	2
IV. The apparent molal heat capacity.....	2
V. Heats of dilution.....	10
VI. Heat of neutralization.....	19
VII. Heat of solution at infinite dilution.....	20
VIII. Review papers.....	33
IX. References.....	34
X. Tables.....	41

List of Figures

Figure I. The apparent molal heat capacity of KCl at 25 °C.....	8
Figure II. The apparent molal heat capacity: acids and lithium compounds.....	8
Figure III. The apparent molal heat capacity: ammonium and sodium compounds.....	8
Figure IV. The apparent molal heat capacity: potassium, rubidium, and cesium compounds.....	9
Figure V. The apparent molal heat capacity: the oxyanions of hydrogen, sodium and potassium.....	9
Figure VI. The apparent molal heat capacity: the chlorides.....	9
Figure VII. The apparent molal heat capacity: carboxylates.....	9
Figure VIII. The apparent molal heat capacity: partially ionized compounds.....	9
Figure IX. The chord area plot for NaCl at 25 °C.....	17
Figure X. The relative apparent molal enthalpy: acids and ammonium and lithium compounds.....	18
Figure XI. The relative apparent molal enthalpy: sodium compounds.....	18
Figure XII. The relative apparent molal enthalpy: potassium, rubidium and cesium compounds.....	18
Figure XIII. The relative apparent molal enthalpy: the hydroxides and chlorides.....	18
Figure XIV. The relative apparent molal enthalpy: concentrated solutions.....	19

Thermal Properties of Aqueous Uni-univalent Electrolytes

Vivian Barfield Parker

The available specific heat, heat of dilution, and heat of solution data for aqueous solutions of uni-univalent electrolytes have been critically reviewed and tables of selected "best" values at 25 °C prepared. In addition, the neutralization data have been critically reviewed in order to obtain the "best" value, 13,345 cal/mole, for the heat of ionization of water at 25 °C.

The electrolytes reviewed include the hydroxides, halides and oxyhalides, nitrates and nitrites, formates and acetates, cyanides, cyanates and thiocyanates, and permanganates of hydrogen, ammonium and the methyl ammonium derivatives, silver, and the alkali metals.

I. Introduction

The data on the thermal properties of aqueous uni-univalent electrolytes have been critically reviewed by Rossini [1, 2, 3, 4, 5],¹ Bichowsky and Rossini [6], Rossini et al. [7], Harned and Owen [8, 9], Pitzer and Brewer [10], Britske et al. [11], Lange and Robinson [12], and Lange and Monheim [13]. In view of the current program of the Thermochemistry Section on the revision of the tables of Selected Values of Chemical Thermodynamic Properties of chemical substances, it was felt advisable to re-examine all the available data on the thermal properties of the aqueous uni-univalent electrolytes and select systematically the most consistent set of values. It is hoped that this review, in addition to making available the experimental data, will serve to indicate areas where the data are inadequate or completely nonexistent.

The terminology and conventions used are those of Lewis and Randall [14], Lewis, Randall, Pitzer, and Brewer [10], Rossini [2, 3, 4], Harned and Owen [9], and Glasstone [15]. A summary of the terms used and their definitions follows:

Φ_C is the apparent molal heat capacity of the solute, equal to $[(1000 + mM_2)C - 1000 C^\circ]/m$ where C and C° are the specific heats (per unit mass) of the solution and pure solvent, respectively, m is the molality, and M_2 is the molecular weight of the solute.

ΔH_{diln} , the integral heat of dilution, is the change in enthalpy, per mole of solute, when a solution of concentration m_1 is diluted to a final finite concentration m_2 .

If the dilution is carried out by the addition of an infinite amount of solvent, so that the final solution is infinitely dilute, the enthalpy change is the integral heat of dilution to infinite dilution. Since Φ_L , the relative apparent molal enthalpy, is equal to and of opposite sign to this, only Φ_L is referred to here when discussing dilution to infinite dilution.

\bar{L}_2 is the relative partial molal enthalpy of the solute in the given solution, equal to $\Phi_L + \frac{1}{2}m^{1/2}(d\Phi_L/dm^{1/2})$.

\bar{L}_1 is the relative partial molal enthalpy of the solvent in the given solution, equal to $-(M_1m^{3/2}/2000)(d\Phi_L/dm^{1/2})$, where M_1 is the molecular weight of the solvent. It is also the partial or differential heat of dilution and may be defined as the change

in enthalpy per mole of solvent when it is added to a large volume of the solution at the given concentration.

\bar{J}_2 is the relative partial molal heat capacity of the solute, equal to $\bar{C}_2 - \bar{C}_2^\circ$, which is equal to $(\partial\bar{L}_2/\partial T)_p$, where \bar{C}_2 is equal to $\Phi_C + \frac{1}{2}m^{1/2}(d\Phi_C/dm^{1/2})$ and \bar{C}_2° is equal to Φ_C° .

Φ_C° is the value of the apparent molal heat capacity of the solute at infinite dilution. It is not to be confused with the heat capacity of the pure solvent.

The limiting slopes of the apparent molal properties were taken as two thirds the limiting slopes for the partial molal properties given by Harned and Owen [9].

ΔH_{soln} is the total or integral heat of solution of one mole of solute to form a solution of concentration m . It is equal to $(H_m - 55.506H_1 - mH_2)/m$, where H_m is the enthalpy of the solution, and H_1 and H_2 are the molar enthalpies of the pure solvent and solute, respectively.

The partial or differential heat of solution is the increase in enthalpy per mole of solute when it is dissolved in a large volume of solution at a concentration m , so that there is no appreciable change in the latter. It is equal to $\bar{L}_2 - L_2$ where L_2 is the relative partial molal enthalpy of the pure solute.

ΔH_∞ is the heat of solution at infinite dilution, equal to $\Delta H_{\text{soln}}(m) - \Phi_L(m)$.

ΔH_N° is the heat of neutralization at infinite dilution. In a reaction between a strong acid and a strong base at finite and equal concentrations, given by $\text{HX} \cdot n\text{H}_2\text{O} + \text{MOH} \cdot n\text{H}_2\text{O} = \text{MX} \cdot (2n + 1)\text{H}_2\text{O}$, ΔH_N° is equal to $\Delta H_N - [\Phi_L\text{MX} \cdot (2n + 1)\text{H}_2\text{O} - \Phi_L\text{MOH} \cdot n\text{H}_2\text{O} - \Phi_L\text{HX} \cdot n\text{H}_2\text{O}]$.

ΔH_i is the heat of ionization or dissociation of a weak acid or base into its ionic species, such as, $\text{HA} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{A}^-$ and $\text{RNH}_2 + \text{H}_2\text{O} = \text{RNH}_3^+ + \text{OH}^-$.

K_i refers to the equilibrium constant of the above type reactions, with K_a and K_b referring specifically to the equilibrium constants of the acid and base reactions, respectively.

The properties were calculated, wherever possible, over the entire range from infinite dilution to approximate saturation or to a 1:1 mole ratio. Use was made of Seidell's and Linke's compilations [615, 616, 617] to obtain the saturation concentrations. Values for Φ_L and Φ_C were estimated for some electrolytes when there was enough information available on the other members of the family.

¹ Figures in brackets indicates the literature references on pages 34-41.

II. Units of Energy and Constants

The unit of energy used is the thermochemical calorie, defined by the relation 1 thermochemical calorie = 4.1840 J. The 1961 atomic weights are used [16]. The values for the specific heat of water are those recommended by the International Committee of Weights and Measures as given by Stimson [17]. The conversion factors for correction to the thermochemical calorie are taken from [18] and [618]. Unless otherwise mentioned the specific heats of the pure solutes used to correct ΔH_{soln} to 25 °C have been obtained from Kelley [19] and Kelley and King [20]. The values of the limiting slopes appearing in the Debye-Hückel theory of strong electrolytes are taken from Harned and Owen [9]. The emf data, on the whole, were used as summarized by Harned and Owen. The heats of vaporization of H₂O used in the calculations on the dissociation pressures of the hydrates were obtained from Osborne, Stimson, and Ginnings [649]. Whenever sufficient data appeared in the original article, the results were completely recalculated, making appropriate corrections for the specific heat of water, atomic weights, calorie used, etc. When the details given were insufficient to make exact corrections, the experimental results were corrected on the basis of reasonable estimates of the quantities employed by the authors.

III. Uncertainties

The uncertainties assigned to the various values have been based on many factors—the experimental technique used, the details given, the number of measurements, the standard deviation, the magnitude of the corrections to 25 °C (and to infinite dilution, for $\Delta H_{\infty}^{\circ}$), the inherent error in the methods used, the reliability of previous work of the investigators, etc. A strictly mathematical evaluation can therefore not be made. The personal appraisal is an important part of the overall evaluation. For example, the standard deviation of Wüst and Lange's [21] work on KCl is ± 1 cal, but the assigned uncertainty is larger; the value selected as the "best" value is 40 cal lower than theirs. As in the above case, the standard deviation and also the assigned uncertainty can be misleading. In other cases it is not possible to assign an uncertainty because of the lack of information.

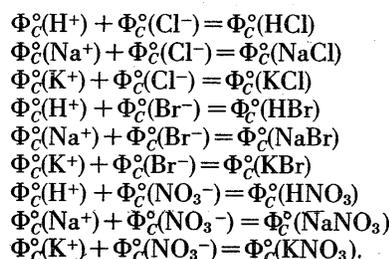
IV. The Apparent Molal Heat Capacity

A great many investigators have measured the specific heats of aqueous electrolyte solutions although only a few have done so with sufficient precision to give reliable results for the apparent molal heat capacity of the solute. Harned and Owen [8] have pointed out the difficulty in obtaining satisfactory results in very dilute solutions. They show, for example, that at a concentration of 0.01 molal an error of 0.01 percent in the specific heat measurements results in an error of about 10 cal/deg mole

in the apparent molal heat capacity of the solute, whereas an error of 1 percent in the determination of the concentration results in an error of only 0.5 cal/deg mole. For this reason a great deal of reliance has been placed on the Debye-Hückel theory in the very dilute region.

The measurements of specific heat were converted to Φ_c . The values for Φ_c were plotted against $m^{1/2}$ on large scale graphs. The first three systems treated were NaCl, HCl, and NaOH, at the various experimental temperatures. This was done to determine the temperature coefficients, which in general were applied to other systems when necessary to correct to 25 °C. In general the curve was drawn down to $m^{1/2}=0.4$ following the data available as closely as possible. The curve was continued so that as $m^{1/2} \rightarrow 0$, the slope, $d\Phi_c/dm^{1/2}$, approached the limiting value (6.13 at 25 °C).

Preliminary values for Φ_c° at 25 °C for the hydroxides, chlorides, bromides, iodides, and nitrates of H, Li, Na, and K were obtained. It was assumed that the heat capacities of the individual ionic species are additive at infinite dilution. Equations of the following sort were set up:



$\Phi_c^{\circ}(\text{H}^+)$ was set equal to 0. The values of Φ_c° for each electrolyte were weighted proportionally to their estimated reliability. By cross substituting values, values for the individual ions were obtained. The various values for each ion were weighted, depending on the source, and averaged. The Φ_c° values of the electrolytes were then adjusted to be self-consistent.

The values obtained were checked by the method of Guggenheim and Prue [22] as adapted by Pitzer and Brewer [10]. The results agreed well within the uncertainties. Thus, Pitzer and Brewer's values of Φ_c° for NaCl (−22.1 cal/deg mole) and KCl (−27.7) compare favorably with −21.5 and −27.4, respectively, obtained here by the above simple approach. If their method is used with the experimental data used here, values of −21.9 and −27.8 are obtained. The difference between $\Phi_c^{\circ}(\text{Na}^+)$ and $\Phi_c^{\circ}(\text{K}^+)$ in this work is 5.9 as compared to 5.6; for Cl[−] and Br[−], 1.3 as compared to 1.2. It was therefore felt that there was no appreciable difference in results due to the method of extrapolation, but rather that it was which data were used and how the experimental data were treated that was more important. It was also felt advantageous

to treat each system individually. Very few adjustments were found to be necessary to make the results consistent, not only for Φ_C° , but also for Φ_L , ΔH_∞° , and ΔH_N° , at 25 °C.

Once the values for the above mentioned ions were determined, they were subtracted from the Φ_C° values obtained later for other compounds to obtain the values for the other ions in table I.

The values of Φ_C° of HCl, NaOH, and NaCl (table II) at temperatures other than 25 °C were not adjusted, since there were insufficient data available on the other systems to give an adequate number of values of Φ_C° for smoothing.

The values of Φ_C° for all compounds considered are given in tables III to IX. Graphic representation of the various families of curves, as well as a detailed curve for KCl, are given in figures I through VIII.

The available data for each compound are summarized in the following section. For each substance are listed the various investigations, with the temperature and range of concentrations measured. The investigations given the greatest weight in the evaluation of Φ_C are marked with an asterisk. The substances are discussed in the order: acids, ammonium and amine salts, silver salts, and salts of the alkali metals.

HF

The specific heat has been measured by Baud [23] (15 °C, $m=11.72$), Pranschke and Schwiete [24]* (18 °C, $m=34.30$ to 5.44), Kolesov, Skuratov, and Uvarov [25]* (25 °C, $m=2.01$ to 0.01), Thorvaldson and Bailey [26]* (19 °C, $m=46.37$ to 0.28), Roth and Chall [27] (50 °C, and between 20 and 50 °C, $m=13.26$), Roth, Pahlke, Bertram, and Börger [28]* (20 °C, $m=2.22$ to 0.11), and Mulert [29] (17–18 °C, $m=17.5$ to 2.63).

HCl

The specific heat has been measured by Thomsen [30]* (18 °C, $m=5.55$ to 0.56), Marignac [31, 32]* (22 °C, $m=2.22$ to 0.56), Richards and Rowe [33, 34] (18 °C, $m=0.28$), [35, 36] (18 °C, $m=0.56$ and 0.28), and [37]* (18 °C, $m=5.55$ and 2.77), Richards, Rowe, and Burgess [38] (20 °C, $m=6.30$ and 2.78), Roth and Chall [27] (50 °C, and between 22.5 and 50 °C, $m=2.25$), Ackermann [39]* (10, 20, 40 to 120 °C, $m=2.00$ to 0.50), Vrevskii and Kaigorodov [40, 41]* (3.3, 20.5, 40.4, and 60.5 °C, $m=16.60$ to 0.17), Tucker [42] (10 °C, $m=12.67$ to 2.57), Richards, Mair, and Hall [43]* (16, 18, and 20 °C, $m=2.22$ to 0.56), Thorvaldson, Brown, and Peaker [44]* (18 and 19 °C, $m=2.78$), Drucker [45]* (18 °C, $m=2.65$ and 1.25), Radulescu and Jula [46]* (15 °C, $m=2.08$), Wicke, Eigen, and Ackermann [47]* (20, 40, 60 to 130 °C, $m=1.91$ to 0.59), Randall and Ramage [48]* (25 °C, $m=1.05$ to 0.08), Gucker and Schminke [49]* (25 °C, $m=2.01$ to 0.01), and Sturtevant [50]* (25 °C, $m=0.87$ to 0.02). The J_2 values obtained here agree well with Bates and Bower's [51] values of J_2 from emf measurements below $m=0.1$ and

Harned and Owen's [9] tabulation of J_2 obtained from the extended Debye-Hückel equation. For $0.1 \leq m \leq 4.0$ the J_2 values are below and within 2 cal/deg mole of the values tabulated by Harned and Owen from Harned and Ehlers' emf data. As $m \rightarrow 4.0$ the difference becomes 1 cal/deg mole.

Other emf measurements since 1955 have been reported by Hayes and Lietzke [52] (25 to 50 °C, $m=0.1$ to 0.001), Greeley [53] (25 to 200 °C, $m=1.0$ to 0.005), Covington and Prue [54] (25 °C, $m=0.07$ to 0.005) and [55] (25 °C, $m=0.1$ to 0.005), Oiwa [56] (25 °C, $m=0.1$ to 0.001), Taylor and Smith [57] (10 to 45 °C, $m=1.5$ to 0.9) and Aston and Gittler [58] (25 °C, $m=4.0$ to 1.2).

HClO₄

The specific heat has been measured by Berthelot [59, 60] (between 15 and 40 °C, $m=9.0$ to 0.05), and Richards and Rowe [36] (18 °C, $m=0.56$).

The data were not considered reliable for a Φ_C curve.

HBr

The specific heat has been measured by Toloczko and Meyer [61] (13.25 °C, $m=4.1$), Richards and Rowe [35, 36]* (18 °C, $m=0.56$), Roozeboom [62]* (between 12 and 30 °C, $m=30.17$ to 0.28), and Johnson, Gilliland, and Prosen [63]* (25 °C, $m=11.10$).

J_2 values were compared with Harned and Owen's [9], and Biermann and Yamasaki's [64] emf data. The agreement is good.

HI

The specific heat has been measured by Richards and Rowe [36]* (18 °C, $m=0.56$), and Johnson, Gilliland, and Prosen [63]* (25 °C, $m=7.60$).

HIO₃

The specific heat has been measured by Randall and Taylor [65]* (25 °C, $m=3.60$ to 0.07).

HNO₃

The specific heat has been measured by Thomsen [30]* (18 °C, $m=5.55$ to 0.23), Marignac [66]* (between 21 and 52 °C, $m=1.10$ to 0.56), Mishchenko and Ponomareva [67]* (21 °C, extremely concentrated solutions to 1.24), Forsythe and Giauque [68]* (25 °C, $m=35.55$ and 18.50), Roth [69]* (20 °C, $m=0.27$ to 0.03), Drucker [45]* (18 °C, $m=2.41$ to 1.06), Richards and Rowe [36] (18 °C, $m=0.56$) and [70]* (18 °C, $m=5.55$ to 0.14), Lloyd and Wyatt [71] (0 °C, extremely concentrated solutions), Bump et al. [72] (0 to 26.7 °C, extremely concentrated solutions), and Booman, Elverum, and Mason [73] (0 °C, extremely concentrated solutions).

CH₂O₂

The specific heat of aqueous formic acid has been measured by Bury and Davies [74]* (15 °C, $m=10.06$ to 1.33), Ackermann and Schreiner [75]* (0, 10, 20, 30 to 130 °C, $m=2.84$ to 0.49), and Glagoleva and Cherbov [76]* (25, 60, and 80 °C, 100% to $m=4.185$).

The specific heat of $\text{CH}_2\text{O}_2(1)$ has been measured by von Reis [77], Radulescu and Jula [46], Berthelot and Ogier [78], Pettersson [79], Glagoleva and Cherbov [76], Gibson, Latimer, and Parks [80]*, and Stout and Fisher [81]*.

$\text{C}_2\text{H}_4\text{O}_2$

The specific heat of aqueous acetic acid has been measured by Marignac [32, 66]* (between 21 and 52 °C, $m=22.2$ to 2.22), Neiman [82, 83]* (23.9, 42.0, 59.5, and 80.5 °C, 100% to $m=0.96$), Richards and Gucker [84]* (16, 18, and 20 °C, $m=2.22$), von Reis [85]* (18 °C, $m=2.22$), Bury and Davies [74]* (15 °C, $m=8.66$ to 0.91), and Ackermann and Schreiner [75]* (10, 20, 30 to 130 °C, $m=3.00$ to 0.50).

Richards and Gucker [84]* calculated the specific heat (18 °C, $m=1.11$ to 0.07) from ΔH_{dil} and the value of the specific heat at $m=2.22$.

The specific heat of $\text{C}_2\text{H}_4\text{O}_2(1)$ has been measured by Radulescu and Jula [46]*, von Reis [77], Parks and Kelley [86]*, Swietoslowski and Zielenkiewicz [87], Neiman [82, 83]*, Marignac [32], and Berthelot [88].

$\text{C}_3\text{H}_6\text{O}_2$

The specific heat of aqueous propionic acid has been measured by Bury and Davies [74]* (15 °C, $m=5.84$ to $m=0.49$) and Ackermann and Schreiner [75]* (0, 10, 20, 30 to 130 °C, $m=2.00$ to 0.50).

NH_3

The specific heat has been measured by Rühle-mann [89] (between 22 and 99 °C, $m=1.35$), Vrevskii and Kaigorodov [40, 41]* (2.4, 20.6, 41, and 60.9 °C, $m=28.01$ to 0.84), and Hildenbrand and Giauque [90]* (25 °C, $m=55.51$, and -73 to -18 °C, more concentrated solutions).

NH_4F

The specific heat has been measured by Labowitz and Westrum [91]* (25 °C, $m=0.50$ to 0.005).

NH_4Cl

The specific heat has been measured by Thomsen [30]* (18 °C, $m=7.40$ to 0.28), Marignac [32]* (between 20 and 52 °C, $m=4.44$ to 0.56), Drucker [45]* (18 °C, $m=4.73$ to 1.10), Mishchenko and Ponomareva [67, 92]* (25 °C, $m=7.03$ to 0.31), D'Ans and Tollert [93]* (21, 41, 70, and 86 °C, $m=3.28$ and 1.67), Winkelmann [94]* (15 to 28.6 °C, $m=6.23$ to 0.58), Faasch [95]* (18 °C, $m=3.96$ to 0.47), and Urban [96]* (20, 25, 30, 35, and 40 °C, $m=2.00$).

The value for $\Phi_C^\circ\text{NH}_4^+$ was obtained by subtracting $\Phi_C^\circ\text{Cl}^-$ from $\Phi_C^\circ\text{NH}_4\text{Cl}$.

NH_4Br

The specific heat has been measured by Thomsen [30] (19 °C, $m=0.28$) and Faasch [95] (18 °C, $m=4.02$ to 0.50). The Φ_C line, however, was estimated.

$\Phi_C^\circ\text{NH}_4\text{Br}$ was obtained from $\Phi_C^\circ\text{NH}_4^+$ and $\Phi_C^\circ\text{Br}^-$.

NH_4I

Thomsen [30] measured the specific heat (18 °C,

$m=0.28$). The Φ_C curve was essentially estimated, using $\Phi_C^\circ\text{NH}_4\text{I}$ from the ions.

NH_4NO_3

The specific heat has been measured by Thomsen [30]* (18 °C, $m=11.10$ to 0.56), Marignac [32, 66]* (between 20 and 50 °C, $m=11.10$ to 0.56), Tollinger [97]* (23.5 °C, $m=0.56$), Zwicky [98] (20 °C, $m=28.61$ to 1.39), Lerner-Steinberg [99]* (21.6 °C, $m=0.60$ and 0.44), Chauvenet [100] (15 °C, $m=1.33$), Drucker [45]* (20 °C, $m=4.99$ and 1.05), Rutskov [101, 102]* (25, 50, and 75 °C, $m=18.50$ to 0.56), Winkelmann [94]* (16 to 38 °C, $m=8.33$ to 0.39), Cohen, Helderman, and Moesveld [103, 104] (32.3 °C, $m=28.41$ to 1.39), and Gucker, Ayres, and Rubin [105, 106]* (25 °C, $m=24.00$ to 0.10).

$\text{CH}_3\text{NH}_3\text{Cl}$

The specific heat has been measured by Whitlow and Felsing [107]* (25 °C, $m=0.96$ to 0.09). Φ_C is tabulated only in the range from $m=1.11$ to 0.09 since the data available are not considered reliable for extrapolation to infinite dilution. A rough extrapolation leads to a value for Φ_C° of -1 cal/deg mole.

$(\text{CH}_3)_2\text{NH}_2\text{Cl}$

The specific heat has been measured by Whitlow and Felsing [107]* (25 °C, $m=0.98$ to 0.11). Φ_C is tabulated only in the range from $m=1.11$ to 0.09 since the data available are not considered reliable for extrapolation to infinite dilution. A rough extrapolation leads to a value for Φ_C° of +2 cal/deg mole.

$(\text{CH}_3)_3\text{NHCl}$

The specific heat has been measured by Whitlow and Felsing [107]* (25 °C, $m=1.0$ to 0.09). Φ_C is tabulated only in the range from $m=1.11$ to 0.09 since the data available are not considered reliable for extrapolation to infinite dilution. A rough extrapolation leads to a value for Φ_C° of +4 cal/deg mole.

AgF

The specific heat has been measured by Jahn-Held and Jellinek [110]* (25 °C, $m=14$ to 1). Values for Φ_C are given at infinite dilution and above $m=2$.

AgNO_3

The specific heat has been measured by Marignac [66]* (between 25 and 52 °C, $m=2.22$ to 0.56) and Kapustinskii, Yakushevskii, and Drakin [111]* (25 °C, $m=1.80$ to 0.28). Róth [69]* gives an equation for the range $m=0.22$ to 0.08 at 18.5 °C.

LiOH

The specific heat has been measured by Richards and Rowe [70]* (18 °C, $m=2.22$), and [36] (18 °C, $m=0.56$), and Gucker and Schminke [112]* (25 °C, $m=2.27$ to 0.04).

Richards and Rowe [70]* calculated the specific heat (18 °C, $m=1.11$ to 0.14) from ΔH_{dilin} at 16 and 20 °C and the specific heat at $m=2.22$.

The Φ_C curve was based primarily upon Gucker and Schminke's measurements.

LiCl

The specific heat has been measured by Tucker [42] (14 to 22 °C, $m=16.34$ to 2.52), Chernyak [113] (25 °C, $m=1.0$), Bennowitz and Kratz [114]* (20 °C, $m=1.0$ to 0.05), White [115]* (25 °C, $m=0.05$), Jauch [116] (18 °C, $m=4.06$ to 0.50) Hess [117]* (25 °C, $m=0.15$), Drucker [45]* (18 °C, $m=9.8$ to 1.3), Gucker and Schminke [49]* (25 °C, $m=2.46$ to 0.04), Richards and Rowe [70]* (18 °C, $m=2.22$), and Lange and Dürr [118]* (25 to 28 °C, $m=19.89$ to 0.56).

Richards and Rowe [70]* calculated the specific heat (18 °C, $m=1.11$ to 0.14) from ΔH_{dilin} and the specific heat at $m=2.22$.

The Φ_C lines of Gucker and Schminke, and Lange and Dürr are parallel to one another. There seems to be a systematic error in the latter's work. The final Φ_C line is based primarily on Gucker and Schminke's work.

LiBr

The specific heat has been measured by Jauch [116]* (18 °C, $m=4.45$ to 0.51), Lange and Schwartz [119]* (26.5 °C, $m=17.92$ to 0.04), and Eigen and Wicke [120]* (10, 20, 40, 60 to 120 °C, $m=0.56$, 0.91, and 1.32).

Here as in LiCl, the Φ_C lines of Eigen and Wicke and Lange and Schwartz are parallel. Eigen and Wicke's line was essentially used, with Lange and Schwartz's Φ_C values lowered by a constant amount to coincide with Eigen and Wicke's.

LiI

The specific heat has been measured by Jauch [116]* (18 °C, $m=3.17$ to 0.51).

LiNO₃

The specific heat has been measured by Chauvenet [100] (15 °C, $m=2$), Drucker [45]* (18 °C, $m=1.89$ to 0.91), and Richards and Rowe [70]* (18 °C, $m=2.22$). The latter also used ΔH_{dilin} at 16 and 20 °C to calculate the specific heat from $m=1.11$ to 0.14 at 18 °C.

NaOH

The specific heat has been measured by Thomsen [30]* (19 °C, $m=7.40$ to 0.28), Bertetti and McCabe [121]* (3.12 to 60 °C, $m=22.81$ to 1.06), Richards and Rowe [36]* (18.1 °C, $m=0.56$ and 0.28), Ackermann [39, 122]* (10, 20, 40, 60 to 130 °C, $m=2.00$ to 0.50), Richards and Gucker [84]* (16, 18, and 20 °C, $m=2.22$), Sturtevant [50]* (25 °C, $m=0.087$ to 0.006), Tucker [42] (16 to 21 °C, $m=22.54$ to 4.92), Richards and Hall [123]* (18 °C, $m=2.22$ to 0.56), Roth, Wirths, and Berendt [124] (19.8 °C, $m=10.11$), Wilson and McCabe [125]* (29.8 to 122 °C, $m=26.76$ to 25.20), and Gucker and Schminke [112]* (25 °C, $m=2.55$ to 0.04).

The values of \bar{J}_2 obtained here agree well with those given by Harned and Owen [9] and Akerlöf and Kegeles [126] below $m=2$.

NaCl

The specific heat has been measured by Thomsen [30] (19 °C, $m=5.55$ to 0.28), Marignac [32] (18 °C and between 22 and 52 °C, $m=2.22$ to 0.56), Stakhanova and Vasilev [127]* (25 °C, $m=4.37$ to 0.20), Biron [128] (19 °C, $m=0.28$ to 0.07), Blaszkowska [129]* (21.4 °C, $m=2.22$ to 0.28), Zdanovskii [130]* (25 °C, $m=2.33$), Zdanovskii and Suslina [131]* (25 °C, $m=1.89$), Zdanovskii and Matsenok [132]* (25 °C, $m=6.11$ to 1.75), Eigen and Wicke [120]* (10, 20, 40 to 130 °C, $m=1.12$ to 0.41), D'Ans and Tollert [93] (21 and 41 °C, $m=5.75$ to 1.66), Drucker [45]* (20 °C, $m=4.36$ to 1.02), Chipman, Johnson, and Maass [133]* (18.8 and 25.4 °C, $m=2.54$ to 0.43), Nikolaev, Kogan, and Ogorodnikov [134]* (25 °C, $m=6.15$ to 0.34), Winkelmann [94] (17 to 46 °C, $m=5.48$ to 0.53), Leitner [135] (25.7 to 95.7 °C, $m=5.97$), Hess [117]* (25 °C, $m=0.15$ to 0.003), White [136]* (35 to 45 °C, $m=0.20$ to 0.01), Hess and Gramke [137]* (15, 25, 35, 45 °C, $m=1.03$ to 0.01), Voskresenskaya and Yankovskaya [138] (50 °C, $m=57.6$ to 3.45), Lipsett, Johnson, and Maass [139]* (25 °C, $m=6.01$ to 0.17), Bousefield and Bousefield [140]* (7, 20, and 33 °C, $m=5.70$ to 0.25), Rutskov [101, 102]* (25, 50, and 75 °C, $m=5.55$ to 0.20), Ackermann [39]* (10, 20, 40, 60 to 130 °C, $m=2.00$ to 0.50), Randall and Ramage [48]* (25 °C, $m=1.90$ to 0.07), Sandonnini and Gerosa [141] (18.5 °C, $m=1.12$ to 0.20), Person [142] (0 to 13 °C, $m=9.05$ to 1.88), Randall and Bisson [143]* (25 °C, $m=6.20$ and 4.04), Randall and Rossini [144]* (25 °C, $m=2.30$ to 0.04), and Richards and Gucker [84]* (18 °C, $m=2.22$).

The \bar{J}_2 values which were checked with those obtained from emf data as given by Harned and Owen [9]. The agreement is excellent below $m=1$ and within 3 cal/dmole between $m=1$ and 4.

NaClO₃

The specific heat has been measured by Colomina and Nicolas [145]* (24 °C, $m=15.39$ to 0.20) and Ferrer [146]* (25 °C, $m=3.11$ to 0.19).

NaClO₄

The specific heat has been measured by Colomina and Nicolas [145]* (24.5 °C, $m=12.22$ to 0.13), and Ferrer [146]* (25 °C, $m=2.59$ to 0.24).

The values of Φ_C chosen were based on Ferrer's data up to $m=2.6$ and above that on Colomina's.

NaBr

The specific heat of aqueous NaBr has been measured by Marignac [32, 66]* (between 20 and 52 °C, $m=2.22$ to 0.56), Chipman, Johnson, and Maass [133] (25.4 and 18.8 °C, $m=1.88$ to 0.24), Bender and Kaiser [147]* (25 and 30 °C, $m=8.37$ to 0.97), Rossini [148]* (25 °C, $m=0.43$ to 0.08), and Randall and Rossini [144]* (25 °C, smoothed values from $m=1.00$ to 0.01).

Below $m=2.0$ the values obtained here for \bar{J}_2 were below but within 3 cal/deg mole of the emf values listed in Harned and Owen [9].

NaBrO₃

The specific heat has been measured by Ferrer [146]* (25 °C, $m=2.34$ to 0.21).

NaI

The specific heat has been measured by Thomsen [30]* (18 °C, $m=0.28$), Marignac [32, 66]* (between 20 and 51 °C, $m=2.22$ to 0.56), Rossini [148]* (25 °C, $m=0.85$ to 0.9), and Randall and Rossini [144]* (25 °C, smoothed values from $m=1.00$ to 0.01).

NaNO₂

The specific heat has been measured by Ferrer [146]* (25 °C, $m=2.25$ to 0.10) and Perreu [149] (15 °C, $m=11.87$ to 1.45).

NaNO₃

The specific heat has been measured by Thomsen [30]* (18 °C, $m=5.55$ to 0.28), Marignac [66]* (20.5 °C and between 22 and 52 °C, $m=2.22$ to 0.56), Biron [128] (19 °C, $m=0.28$ to 0.03), Person [142] (0 to 20 °C, $m=7.7$ to 0.59), Magie [150] (room temperature, $m=1.11$ to 0.19), D'Ans and Tollert [93]* (21 °C, $m=5.0$), Winkelmann [94, 151] (2 to 60 °C, $m=2.35$ to 0.37), Gerlach [152] (between 20 and 95 °C, $m=10.2$), Richards and Gucker [84]* (18 °C, $m=2.22$), Zdanovskii [130]* (25 °C, $m=2.58$), Rossini [148]* (25 °C, $m=0.85$ to 0.08), Randall and Rossini [144]* (25 °C, smoothed values at $m=1.00$ to 0.01), Richards and Rowe [70]* (18 °C, $m=2.22$), Drucker [45]* (18 °C, $m=4.59$ to 1.03), and Chauvenet [100] (15 °C, $m=2.13$).

Richards and Rowe [70]* calculated the specific heat (18 °C, $m=1.11$ to 0.14) from the dilution data at 16 and 20 °C and the specific heat at $m=2.22$.

NaCHO₂

The specific heat of aqueous sodium formate has been measured by Ackermann and Schreiner [75]* (10, 20, 30 to 120 °C, $m=2.85$ to 0.50).

NaC₂H₃O₂

The specific heat of aqueous sodium acetate has been measured by Thomsen [30]* (17 °C, $m=2.78$ to 0.28), Marignac [32, 66]* (22.5 °C, and between 19 and 52 °C, $m=2.22$ to 0.56), Richards and Gucker [84]* (16, 18, and 20 °C, $m=2.22$), Perreu [153]* (19 °C, $m=4.78$ to 1.36), Bindel [154] (21 °C, $m=5.55$ to 1.11), Ferrer [146]* (25 °C, $m=2.79$ to 0.23), Kapustinskii and Stakhanova [155]* (25 °C, $m=17.13$ to 3.14), Ackermann and Schreiner [75]* (10, 20, 30 to 120 °C, $m=2.53$ to 0.60). Gnesotto and Fabris [156] measured the specific heat of the liquid trihydrate at 0 to 100 °C.

Richards and Gucker [157]* calculated the specific heat ($m=1.09$ to 0.03) from dilution data and the specific heat at $m=2.22$, obtained in [84].

NaC₃H₅O₂

The specific heat of aqueous sodium propionate

has been measured by Ackermann and Schreiner [75]* (10, 20, 30 to 120 °C, $m=2.24$ to 0.50).

KOH

The specific heat has been measured by Thomsen [30]* (18 °C, $m=1.85$ to 0.28), Jaquerod [158] (18 °C, $m=4.92$ to 0.95), Gawlik [159]* (20 °C, $m=0.33$ to 0.04), Voskresenskaya [160]* (20 °C, $m=4.24$), Richards and Hall [123]* (18 °C, $m=0.56$), Gucker and Schminke [49]* (25 °C, $m=2.59$ to 0.04), Richards and Rowe [36]* (18 °C, $m=0.56$) and [70]* (18 °C, $m=13.38$ and 5.55), Sabatier [161] (temperature uncertain, $m=13.37$).

Richards and Rowe [70]* calculated the specific heat (18 °C, $m=2.22$ to 0.14) from the dilution data and specific heats of the more concentrated solutions.

The agreement of the calculated \bar{J}_2 values with those given by Harned and Owen [9] for the emf values is excellent.

KCl

The specific heat has been measured by Thomsen [30]* (18 to 20 °C, $m=3.7$ to 0.28), Marignac [32, 66]* (19.5 °C and between 20 and 51 °C, $m=1.11$ to 0.56), Andrews [162] (18 °C, $m=0.25$), Stakhanova and Vasilev [127]* (25 °C, $m=4.60$ to 0.20), Voskresenskaya and Rutskov [163]* (25 °C, $m=1.40$), Biron [128] (19 °C, $m=0.28$ to 0.03), Winkelmann [94] (0 to 55 °C, $m=5.59$ to 0.42), and [151] (20 °C, $m=0.71$), Chipman, Johnson, and Maass [133]* (18.8 and 25.4 °C, $m=2.48$ to 0.33), Magie [150] (room temperature, $m=1.11$ to 0.14), Sandonnini and Gerosa [141] (18.5 °C, $m=0.75$ to 0.17), Jaquerod [158] (18 °C, $m=3.8$ to 0.95), Cobb and Gilbert [164]* (25 °C, $m=1.00$ and 0.50), D'Ans and Tollert [93]* (21 and 41 °C, $m=4.40$ to 1.7), Nikolaev, Kogan, and Ogorodnikov [134]* (25 °C, $m=4.80$ to 0.07), Zdanovskii [130]* (25 °C, $m=2.56$), Rutskov [101, 102]* (25 °C, $m=4.63$ to 0.10), Popov, Bundel, and Choller [165]* (20 °C, $m=0.56$ to 0.14), Popov, Khomyakov, Feodos'ev, and Schirokikh [166]* (same data as [165]), Urban [96]* (10 to 40 °C, $m=2.00$ to 0.10), Ferrer [146]* (25 °C, $m=2.98$ to 0.05), Hess and Gramkee [137]* (15, 25, 35, 45 °C, $m=1.03$ to 0.01), Clews [167]* (15.6 to 43.2 °C, $m=2.50$ to 0.10), Gucker [168]* (20 °C, $m=2.22$), Kapustinskii, Yakushevskii, and Drakin [111]* (25 °C, $m=1.71$ to 0.52), Varasova, Mishchenko, and Frost [169]* (25 °C, $m=4.85$ and 2.73), Randall and Bisson [143] (25 °C, $m=4.85$ and 2.73), Bousefield and Bousefield [140]* (20 and 33 °C, $m=3.40$ to 0.25), Randall and Rossini [144]* (25 °C, $m=2.50$ to 0.05), Rossini [148]* (25 °C, $m=2.25$ to 0.04), Cohen and Moesveld [170]* (19 °C, $m=3.39$ and 1.03), Parshikov [171]* (25 °C, $m=0.41$), and Richards and Rowe [70]* (18 °C, $m=2.22$).

Richards and Rowe [70]* calculated the specific heat (18 °C, $m=1.11$ to 0.14) from the directly determined specific heat at $m=2.22$ and their dilution data. The ΔH_{soln} and ΔH_{diln} experiments of Wüst and Lange [21]* were sufficiently detailed

to permit the computation of the heat capacity of the solutions. The ΔH_{soln} measurements of KCl at various temperatures were also used to compute Φ_C at the mean temperature.

The calculated J_2 values were compared with those obtained from the emf measurements as given by Harned and Owen [9]. The agreement was good, within 1 cal/deg mole below $m=2$.

KBr

The specific heat has been measured by Thomsen [30]* (18 °C, $m=0.28$), Marignac [32, 66]* (between 20 and 51 °C, $m=2.22$ to 0.56), Popov, Bundel, and Choller [165]* (20 °C, $m=0.19$), Bender and Kaiser [147]* (25 and 35 °C, $m=5.52$ to 1.00), Rossini [148]* (25 °C, $m=0.97$ to 0.04), Randall and Rossini [144]* (25 °C, smoothed values from $m=1.00$ to 0.01), Chipman, Johnson, and Maass [133]* (25.4 and 18.4 °C, $m=1.57$ to 0.21), Urban [96]* (10, 15, 20, 25, 30, 35, and 40 °C, $m=2.00$), Popov, Skuratov, and Strel'tsova [172]* (20.2 °C, $m=0.32$).

KI

The specific heat has been measured by Thomsen [30]* (18 °C, $m=0.28$), Marignac [32] (between 20 and 51 °C, $m=2.22$ to 0.56), Drucker [45]* (18 °C, $m=3.24$ to 0.68), Popov, Skuratov, and Strel'tsova [172]* (20.2 °C, $m=1.63$), Rossini [148]* (25 °C, $m=0.85$ to 0.04), and Randall and Rossini [144] (25 °C, smoothed values from $m=1.00$ to 0.01).

KIO₃

The specific heat has been measured by Randall and Taylor [65]* (25 °C, $m=0.38$ to 0.04).

KNO₃

The specific heat has been measured by Thomsen [30]* (18 °C, $m=2.22$ to 0.23), Marignac [32, 66]* (20.5 °C and between 22 and 52 °C, $m=2.22$ to 0.56), Person [142] (0.6 to 20.6 °C, $m=2.00$ to 0.50), Drucker [45]* (19 °C, $m=2.18$ and 1.05), Voskresenskaya [160]* (30 °C, $m=2.10$), Rutskov [101, 102]* (25, 50, and 75 °C, $m=0.50$ to 6.94), Zdanovskii [130]* (25 °C, $m=3.12$), Magie [150] (room temperature, $m=2.22$ to 0.14), Biron [128] (19 °C, $m=0.28$ and 0.14), D'Ans and Tollert [93] (41 °C, $m=2.78$), Winkelmann [94, 151] (4 to 60 °C, $m=2.44$ to 0.30), Chauvenet [100] (15 °C, $m=2.18$), Richards and Gucker [84]* (18 °C, $m=2.22$), Andrews [162] (16.6 °C, $m=0.26$), Gucker [168]* (20, 50, and 80 °C, $m=2.22$), Richards and Rowe [70]* (18 °C, $m=2.22$), Rossini [148]* (25 °C, $m=1.05$ to 0.05), Randall and Rossini [144]* (25 °C, smoothed values at $m=1.00$ to 0.01).

Lange and Monheim [173]* calculated the specific heat at 18.75 °C from the solution and dilution experiments at 12.5 and 25.0 °C at $m=0.146$ to 0.0004. Richards and Rowe [70]* calculated the specific heat (18 °C, $m=1.11$ to 0.14) from dilution data and the measured specific heat at $m=2.22$.

KCNS

Urban [96]* has measured the specific heat (10, 15, 20, 25, 30, 35, and 40 °C, $m=2.63$ to 0.50).

KC₂H₃O₂

The specific heat of aqueous potassium acetate has been measured by Marignac [32, 66]* (between 20 and 51 °C, $m=11.11$ to 2.22), Drucker [45]* (18.6 °C, $m=5.62$ to 1.05), Urban [96]* (10, 15, 20, 25, 30, 35, and 40 °C, $m=2.36$ to 0.25), and Andrews [162] (18 °C, $m=0.25$).

KMnO₄

The specific heat has been measured by Perreu [174]* (19 °C, $m=0.40$ to 0.063) and Kapustinskiĭ and Klokman [175]* (25 °C, $m=0.32$ to 0.03).

KClO₃

The specific heat has been measured by Bindel [154] (20 °C, $m=2.78$ to 0.56). The data were not considered reliable for a Φ_C line.

Cs and Rb Compounds

The scarcity of concordant information on the Cs compounds makes the selection of $\Phi_C^{\circ}\text{Cs}^+$ difficult. The selection depends on whether the data of Richards and Rowe [70] at 18 °C on CsCl or CsNO₃, or the data of Kapustinskiĭ and coworkers [176, 177, 178, 179] on CsI at 25 °C are utilized. It was felt that the more recent measurements on CsI are the more reliable. This choice necessitated estimating the other Φ_C lines, which were drawn to be consistent with the CsI and the K compounds.

Since there was no reliable information available on the Rb compounds to determine $\Phi_C^{\circ}\text{Rb}^+$, the value was estimated on the basis of values of Φ_C° of Cs⁺, K⁺, and Na⁺.

The data available for each compound follow:

RbI

Jauch [116] has measured the specific heat (18 °C, $m=3.14$ to 0.05).

RbNO₃

Chauvenet [100] has measured the specific heat (15 °C, $m=1.45$).

CsCl

The specific heat has been measured by Bennewitz and Kratz [114]* (20 °C, $m=0.41$ to 0.01) and Richards and Rowe [70]* (18 °C, $m=1.11$ to 0.14).

CsI

The specific heat has been measured by Kapustinskiĭ, Yakushevskii, and Drakin [176]* (25 °C, $m=0.73$ to 0.15), and Kapustinskiĭ, Lipilina, and Samoïlov [177, 178]* (25 °C, $m=1.06$ to 0.22). Kapustinskiĭ [179]* reported the same values.

CsNO₃

The specific heat has been measured by Chauvenet [100] (15 °C, $m=0.61$) and Richards and Rowe [70]* (18 °C, $m=0.93$ to 0.14).

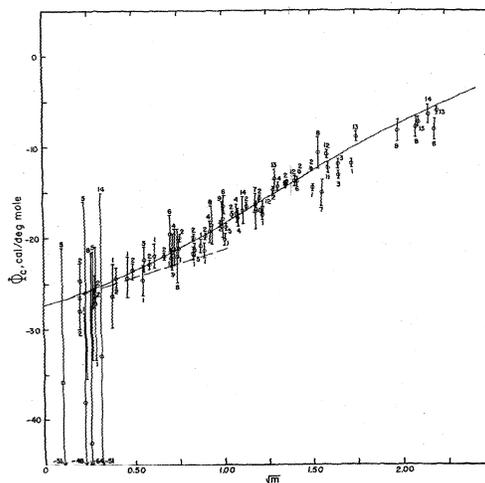


FIGURE 1. The apparent molal heat capacity, Φ_c , of KCl in cal/deg mole, at 25°C as a function of m^w . The vertical line indicates the assigned uncertainty of the determination. The series of the determinations are:

- | | |
|--|---|
| (1) Ferrer [146] | (8) Nikolae, Kogan, and Ogorodnikov [134] |
| (2) Rosina [148] | (9) Cobb and Gilbert [164] |
| (3) Randall and Bisson [143] | (10) Vokresenskaya and Rutskov [163] |
| (4) Kaputinski, Yakushevskii, and Drakin [111] | (11) Zdanovskii [130] |
| (5) Hess and Gramke [137] | (12) Clews [167] |
| (6) Urban [96] | (13) D'Amico and Toller [93] |
| (7) Varasova, Mischenko, and Frost [169] | |

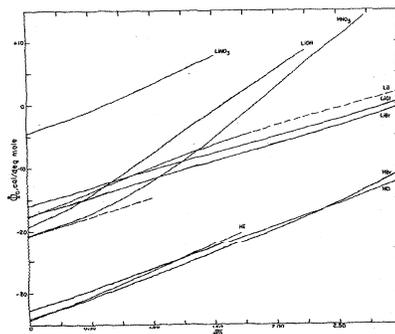


FIGURE 2. Φ_c as a function of m^w in aqueous solutions of HCl, HBr, HI, HNO₃, LiOH, LiCl, LiBr, LiI, and LiNO₃ at 25°C.

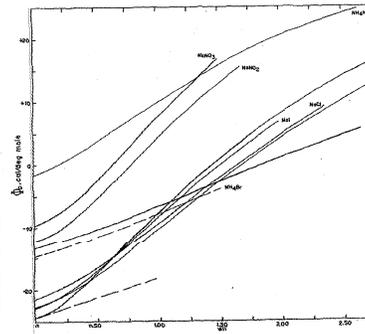


FIGURE 3. Φ_c as a function of m^w in aqueous solutions NH₄Cl, NH₄Br, NH₄NO₃, NaOH, NaCl, NaBr, NaI, NaNO₂ and NaNO₃ at 25°C. NH₄Br is estimated.