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Some Individual Ion Correlations
Among Aqueous Freezing Point Measurements

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Guy R. B. Elliott

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SOME INDIVIDUAL ION CORRECTIONS AMONG AQUEOUS

FREEZING POINT MEASUREMENTS

by

Guy R. B. Elliott

ABSTRACT

The experimental basis for thermodynamic solution theory is discussed, and a revised application of Debye-Hückel theory to the solvent behavior is examined. Over much of the concentration range of freezing point measurements for 1-1 electrolytes (up to approximately 1.2 molal, but excluding the most dilute solutions), the freezing point depressions, θ , can be described by equations of the form

$$\theta = \theta^{st} + k_1^* m + b_1^* m^2$$

where θ^{st} is derived from Raoult's law plus Debye-Hückel interactions, m is molality, and k_1^* and b_1^* are constants. The experimental values of k_1^* and b_1^* for 1-1 salts of strong acids can be correlated through empirical individual ion parameters which can be added to give approximate values of k_1^* and b_1^* . With few exceptions, the calculated and experimental values agree well. 2-2 electrolytes appear to obey the same equation form in dilute solutions but to show changes in the constants at about 0.05 molal. Alcohol solutes also lead to a similar behavior except that θ^{st} is replaced by a simple Raoult's law term.

I. INTRODUCTION

In recent years growing doubts have been discussed (see Appendix and Ref. 1a) as to whether the theory of thermodynamics as presently formulated can exactly describe the behavior of real solutions. Therefore it seemed legitimate to reconsider solvent theory, particularly the assumption of asymptotic approach to the Raoult's law slope for all dilute solution activity-mole fraction relationships. This paper considers both the determination of solvent activity by freezing point depression measurements and the relationship of these activities to other theories.

For many years it has been possible to obtain

very precise aqueous freezing point depression measurements.¹⁻¹¹ Because of their precision, and because so many interrelated systems have been studied carefully (especially by Scatchard, Prentiss, and Jones), these data offer an excellent group to check for theoretical correlations.

The present paper reconsiders certain conclusions drawn from these freezing point data.

(A) The extended Debye-Hückel theory, as applied to the solvent with a constant 3-Å distance of closest ionic approach assumed, is modified so as to offer an empirically better fit to the higher concentration freezing point data, i.e., up to 1.4 molal. (B) Using these new parameters, simple correlations are developed which sort out parameters

associated with individual ions. These ion parameters can roughly predict the solvent behavior associated with different salts. (C) The behavior of aqueous solutions (while approaching limiting slopes not greatly off the Raoult's law slope) seems to be significantly different from theoretical predictions based on Raoult's law with only Debye-Hückel corrections.

II. PLOTTING

Consider measured freezing point depressions, θ , at solute molalities, m . Let standard freezing point depressions, including Debye-Hückel effects, θ^{st} , be calculated as will be shown. If the ideal freezing point depressions, as calculated from a complex theoretical relationship, are subtracted from the measured values, and if a simple form of deviation from the ideal is observed, then it seems likely that the theoretical hypothesis used for the calculation was at least close to correct. As will become apparent, such subtraction does lead to simple relationships.

θ^{st} has been calculated with a standard 3-Å ion size using a function from Pitzer and Brewer: the function is $3.720 m \left[1 - 0.3777 m^{\frac{1}{2}} \sigma(m^{\frac{1}{2}}) \right]$ where $\sigma(m^{\frac{1}{2}})$ is $(3/m^{3/2}) \left[(1 + m^{\frac{1}{2}}) - 1 / (1 + m^{\frac{1}{2}}) - 2 \ln(1 + m^{\frac{1}{2}}) \right]$. See Ref. 12, pp. 409, 411, and 342-348 for the development of this function; a very similar calculation has also, however, been used by Brown and Prue⁸ and Garnsey and Prue.⁹ The use of standard ion sizes is discussed at the end of this section.

Where the calculation of $(\theta - \theta^{st})$ had already been carried out by Brown and Prue or Garnsey and Prue, their values were sometimes used (as indicated in the text). These values were rounded in the last figure in the original papers, and this rounding sometimes leads to some scatter at low concentrations in the $(\theta - \theta^{st})/m$ plots. The maximum error resulting from this rounding is indicated by Curve A of Fig. 1. The rounding corrections may be positive or negative.

The function used in Fig. 1 avoids certain assumptions which appear in other methods of plotting. For example, when $(\theta - \theta^{st})$ is plotted against m^2 and the data are represented by a straight line extrapolated to the origin, the extrapolation tacitly assumes that the only important deviations

Fig. 1. Curves corresponding to various assumed experimental errors mentioned in text.

from Raoult's law are described by the Debye-Hückel terms and terms in m^2 . Since θ , θ^{st} , and m^2 all go to zero for the pure solvent, this zero intercept is trivial. On the other hand, if $(\theta - \theta^{st})/m$ is plotted against m and if the behavior assumed above is physically real, the dilute solution data will lie on a meaningful straight line passing through the origin.

If the behavior on this latter plot is not linear, there still may be some test of the Raoult's law limit so long as the extrapolation can be made to the intercept on the ordinate. To demonstrate a correspondence with the Raoult's law slope* it is necessary to show that the data extrapolate to zero or that all systems extrapolate to some other single value, in which case the value chosen for the heat of fusion of water was probably in error.

Correction for the so-called "ion sizes" or distance of closest approach should be discussed. When ionic activity data (such as those from emf measurements) are evaluated, then distances of closest ionic approach must be chosen. It has repeatedly been emphasized (e.g., Ref. 13) how arbitrary is the assignment of these "ion sizes" -- changes of several percent in the ion sizes can be compensated for by changes in the corollary constant, B' , in the $B'm^2$ term, and an equally good fit to the data can be achieved.

Even allowing for this arbitrariness, the "ion sizes" or "distances of closest ionic approach" from emf data do not seem to correspond well with Debye-Hückel behavior in freezing point studies.

*Because unit activity for the pure solvent is set by the definition of activity, the approach to unit activity is also trivial, and it is only in the slope that an approach to limiting Raoult's law behavior is tested.

Fig. 2. Curves showing the deviations from horizontal caused by the use of different distances of closest approach. (Dilute solutions.)

In turn, these latter "ion sizes" are often very different from those predicted by the Pauling ionic radii which are sometimes used for ionic solution predictions. Furthermore, what Brown and Prue⁸ have called a "paradoxical situation" can arise in that the apparent distance of closest approach may be less than the sum of the ionic radii. These problems will be discussed further in Section III.

The curves in Figs. 2 and 3 show the corrections for dilute and more concentrated solutions, which should be subtracted if a different distance of closest approach by the ions were appropriate

Fig. 3. Curves showing the deviations from horizontal caused by the use of different distances of closest approach. (Concentrated solutions.)

to replace the 3-Å standard value. A plot of $(\theta - \theta^{st})/m$ vs m for a real system might follow a curve corresponding to that shown in Fig. 2. Such a situation would suggest that the appropriate distance of closest ionic approach was not 3-Å but was that indicated, and that B' was zero. B' corrections might, of course, be appropriate, and a line of constant slope would be added to the curve calculated. Some of the distance calculations shown correspond with LiCl, KCl, and NaCl values determined by other techniques; others are included for rough interpolation purposes.

III. DILUTE 1-1 ELECTROLYTES

Figure 4 shows the agreement among aqueous KCl freezing point depression results from several sources. The systems in Figs. 4 to 11 show the

Fig. 4. Freezing point results for dilute alkali chlorides.

Fig. 5. Freezing point results for dilute alkali bromides.

sort of behavior exhibited by dilute 1-1 electrolyte solutions.

In the less dilute regions, these solutions all approach closely to the Debye-Hückel-Raoult's law slope, or actually pass through that slope, at $(\theta - \theta^{st})/m = 0$. (An intercept of 0.0372 corresponds to an experimental deviation of only 1% from the ideal slope.)

A downward curvature at low concentrations is usually shown even in the cases where an upward curvature would be required to reach 0 at infinite dilution. Although this curvature occurs in a region where the plotted function is about to "blow up" due to experimental scatter, the trends seem too systematic to be ignored. Also, no matter what ionic radii are selected, in theory, the zero limit

Fig. 6. Freezing point results for dilute alkali nitrates.

should not change. The curvature follows no obvious function to extrapolate to infinite dilution. Correspondingly, from the most dilute solution data for the several salts, one probably cannot make a solid argument as to whether one limit or several are being approached.

Much of the curvature could be eliminated by the use of different distances of closest approach for the different ionic species. For example, consider KCl. The curvature for 3.98-Å is shown in Fig. 2; subtracting this curve from the experimental curve in Fig. 4 would lead to a nearly horizontal line agreeing with the ideal freezing point

Fig. 7. Freezing point results for dilute ammonium salts.

depressions and $R' = 0$ --- at least for the concentrations below 0.5 molal. (There may well be some difference in the curve shapes, but this argument requires analysis of the trends in the individual groups of data. At larger concentrations the prediction breaks down. See KCl in the Appendix, page 26.) $3.98\text{-}\text{\AA}$ is the value used with KCl emf data.¹³ On the other hand, for NaCl, the freezing point difference would be best (but poorly) represented by $\sim 5.6\text{ \AA}$, while 4 or $4.45\text{ \AA}$ has been used for the emf results (see Appendix Ref. 58a).

By comparing the curves in Figs. 2 and 3 with the course of the experimental points in Fig. 4 and with Fig. 13 which will be presented later, one can establish that the ionic radii for LiCl, KCl, and NaCl ($3.14\text{-}\text{\AA}$, $2.76\text{-}\text{\AA}$, and $2.41\text{-}\text{\AA}$) do not correspond well with the distances of closest approach for the freezing point results.

To summarize, one can "interpret" some of the

Fig. 8. Freezing point results for dilute alkali chlorates.

results by making assumptions about "ion sizes," but the conclusions cannot be checked by independent methods, and, in fact, they seem to be in contradiction with many of the independent determinations.

One can look at possible sources of experimental difficulty. First, one might wonder if the 1436-cal heat of fusion of ice is wrong -- should the zero for $(\theta - \theta^{\text{st}})/m$ fall at -0.04 rather than where it is plotted? Then the data (with reasonable scatter of magnitude like that shown for

Fig. 9. Freezing point results for dilute alkali perchlorates.

Fig. 10. Freezing point results for dilute alkali formates.

Fig. 11. Freezing point results for dilute alkali acetates.

Curve A of Fig. 1) could all approach the same limit. This postulate would be close to the one frequently made (e.g., Ref. 12, p. 413) when it is assumed that the dilute-solution changes in molal freezing point depressions are the corollary of the thermodynamic requirement* that all solvent behavior approach a Raoult's law limit. A more positive statement is sometimes made to the effect that the curvature is because of the thermodynamic requirement.

The corresponding error in the accepted heat

*Actually solute behavior consistent with Henry's law is also assumed, e.g., see Ref. 12, p. 232-233.

of fusion of ice would be $(0.04/3.72) 1436$, or 15 cal per mole. This error is considerably beyond the accepted ± 1 cal for the uncertainty (Ref. 12, p. 409) as represented by B in Fig. 1. There was enough confidence in the value of 1436 cal per mole so that λ , the ideal freezing point depression per mole in aqueous solutions, was changed from 1.858 to 1.860°K per mole as represented by C in Fig. 1.

One source of possible experimental error which would lead to a curvature at low concentrations would be a constant absolute error in all measurements of θ , the freezing point depression. For example, what if the potentiometer zero were off? Curve D corresponds to a 0.0003°K error of this type, and Curve A is close to 0.0001°K error.

On the other hand, one might ask if there is a source of potential curvature in the solvent activity data -- is there experimental evidence of interactions which are not covered by Debye-Hückel theory and the ideal solvent entropy of mixing implied by Raoult's law?

Consider the fact that adding ionic solutes to pure water often leads to a reduction in the total volume occupied by the water. MgSO_4 offers a good example. (See Ref. 12, Fig. 17-1, and p. 379.)

A reaction can, of course, be driven by entropy effects, and the enthalpy may increase or decrease. When enough shrinkage in the water has taken place to give a negative apparent volume to the added electrolyte, then it is not easy to assert that the only important effects influencing the solvent behavior are the charge interactions described by Debye-Hückel and the ideal entropy of mixing described by Raoult's law. It would seem almost reasonable to anticipate departures from Raoult's law-Debye-Hückel prediction at low solute concentrations. At larger concentrations, however, where very many ions were involved, the departures would be masked by the larger total effects from all the other ions.

At this point in the consideration of the data, one might suppose there had been a wrong choice of the heat of fusion of ice plus a neglect of small effects from the breakup of water aggregates when a small amount of ionic solute is added to water.

IV. DILUTE AMMONIUM HALIDE SOLUTIONS

Recently Scatchard and Orttung¹⁴ have recon-

sidered Scatchard and Prentiss¹³ ammonium bromide results in light of some concentration cell measurements they made which did not agree thermodynamically with the freezing point results. They state: "We regard this as certain evidence that the effect is not in the liquid solution, and that the freezing point depressions are not true measures of the activity of the water, particularly in dilute solutions." They, however, "find no evidence to indicate that the other freezing points determined by Scatchard and Prentiss are not precise measures of the water activity."

Garnsey and Prue⁹ have remeasured the freezing point depressions for very dilute solutions, with the results shown in Fig. 12. Their results are not so precise as those of Scatchard and Prentiss. For NH_4Cl , about half the "discrepancy" in the apparent dilute solution limit is removed if the Garnsey and Prue data are accepted. For NH_4Br , most of the "discrepancy" is removed. Without the theoretical assumptions, no basis to reject the

Fig. 12. A comparison of very dilute ammonium halide freezing point depression results.

Scatchard and Prentiss results would exist, however. Some correlations to be developed later are more consistent with the older data than the newer data and suggest that the Scatchard and Prentiss data are substantially correct.

Scatchard and Orttung¹⁴ offered a possible explanation for the NH_4Br behavior which was unsatisfactory to Garnsey and Prue, but the explanation given by Garnsey and Prue is in turn unsatisfactory to Scatchard.¹⁵

V. MORE CONCENTRATED 1-1 ELECTROLYTES

The problems, posed in the previous sections and in the appendix, lead to a question of what theoretical deductions can logically be drawn from the results of freezing point studies. For dilute solutions, the curvature apparently cannot be predicted from any theory tied to independent measurements. For the more concentrated solutions, it is therefore important to see if new correlations can be developed either between different systems or within individual chemical systems.

For empirical reasons, and because one could not be confident of the corrections anyway, the use of θ^{st} as calculated without individual ion size corrections will be carried forward. (A good discussion of problems with concentrated ionic solution theory is given in Ref. 16; see also p. 343 of Ref. 12.) Hopefully, the ion size effects might be absorbed in other purely empirical parameters.

The results of Scatchard, Prentiss, and Jones for several electrolytes for concentrations above 0.05 molal are presented in Figs. 13 to 19. Over large ranges of composition and at concentrations as great as 1.4 molal, these data can be represented by straight lines of the form

$$\theta - \theta^{\text{st}} = k_1^* m + b_1^* m^2. \quad (1)$$

Rounded constants, k_1^* and b_1^* , for the different salts are given in Table I. The representation can be made precise, often within 0.1% of the measured freezing point depression per mole of solute over a considerable range of concentration. (For the rounded constants used in the tables, however, the representation may be off by 0.5%)

In glancing over the plots, one can see certain correlations: Fig. 13 looks much like Fig. 14; in Fig. 15, the nitrate slopes are negative except for

Fig. 13. Freezing point results for alkali chlorides.

LiNO_3 which contains Li^+ , and Li^+ seems to produce a strong positive slope in Figs. 13 and 14; the ammonium salts in Fig. 16 show trends like the alkali salts. Further correlations can be noted.

An examination of the correlations among the constants for the straight lines characteristic of the different salts (excluding the formates and acetates, for which it did not work) has permitted the assignment of specific values to the particular individual ions. These individual ion parameters, k_1^* and b_1^* , can be added together to predict the k_1^* and b_1^* values for the various salts. The individual ion parameters, the predicted constants, and the difference between observation and prediction are shown on the table.

To show the level of empirical usefulness of the calculations, Table II has been prepared. It

Fig. 14. Freezing point results for alkali bromides.

examines the observed freezing point depression for the measured composition closest to 0.8 molal, comparing it with calculated values (a) using the rounded constants for the "observed" k_1^* and b_1^* taken from the lines drawn on the graphs, and (b) using "predicted" k_1^* and b_1^* values calculated from the individual ion parameters in Table I. The (a) values fall within 0.5% of the measured values; for the (b) values, only three measured freezing point depressions are more than 2% different from the values obtained from the individual ion parameters.

Fig. 15. Freezing point results for alkali nitrates.

The correlations for k_1^* in Table I seem to be good enough to rule out impurities in the salts as the source of the deviations of the k_1^* values (the deviation of the extrapolated intercepts on Figs. 4 to 11) from zero. If all the ions were really seeking an ideal limit and the discrepancies were due to impurities alone, one would not expect the deviations from that limit to be predicted by adding individual ion parameters applicable to any salt.

If curvature at low concentrations is accepted as real, then the effect upon more concentrated

Fig. 16. Freezing point results for ammonium salts.

solutions of those factors which cause the curvature in dilute solutions should also be discussed. When a straight line is drawn through the data plotted as $(\theta - \theta^{st})/m$ vs m , it is tacitly assumed that all the experimentally significant factors can be lumped into three terms as in Eq. (1). Thus, θ^{st} describes Debye-Hückel deviations from Raoult's law. k_1^* describes further effects which are applicable, using a single constant, over the whole range of composition covered by the fitting line; these are in excess of Raoult's law. The $b_1^* m^2$ term represents the effects which are applicable over the same range with unchanging constant as a function of the solute molality squared.

Nowhere in this equation is there a term giving curvature at low values of m ; such a term is required if the curvature is real. Successive additions of solute ions produce less and less effect per ion added, however, when salt is gradually added to originally pure water. Presumably the effect per ion becomes so small as to be experi-

Fig. 17. Freezing point results for chlorates and perchlorates.

mentally undetectable at the larger concentrations.

VI. FURTHER DISCUSSION OF THE RELATIONSHIPS FOUND FOR MORE CONCENTRATED 1-1 ELECTROLYTES

This section is not necessary in describing the thermodynamic problems of dealing with dilute aqueous solutions. However, it is included to offer a small part of one answer to the question, "If we accept the Duhem activity relationship as really an approximation, then what do we use in its place?"

Fig. 18. Freezing point results for formates.

The solvent equation form we have used here is closely related to the form

$$a_1 - c_1 = -k_1 N_2 + b_1 N_2^2 \quad (2)$$

which has been observed experimentally for the solvent activity-mole fraction relationships for dilute and concentrated liquid alloys. (See appendix.) The Debye-Hückel term in Eq. (1) is, of course, irrelevant for the alloys. The constant, c_1 , establishes an appropriate reference state; for very dilute solutions c_1 is 1 and the reference is pure solvent.

In Eq. (1), freezing point depressions replace activities, molalities are used instead of mole fractions, and k_1^* refers to deviations from Raoult's law instead of including the Raoult's law portion as in k_1 . Thus, k_1^* is almost proportional to $(k_1 - 1)$, with the difference resulting from the units used. Also, b_1^* may be related to b_1 . Some other factors, in practice, are absorbed in k_1^* and b_1^* because a_1 is not precisely proportional to θ

Fig. 19. Freezing point results for acetates.

except near infinite dilution.

If the Duhem relationship is relaxed to an approximation, the equation is not unexpected. The solute form

$$a_2 = k_2 N_2 + b_2 N_2^2 \quad (3)$$

is well accepted and appears well verified experimentally. Using a pure-solute (not hypothetical) reference state, $k_2 \neq 1$ except by accident; it is unique to each solute-solvent pair used, and it is a measure of the effect of solute-solvent interactions

Table I

Individual Ion Parameters for the Correlation of k_1^* and b_1^* in the
Freezing Point Depression Equation, $\theta = \theta^{st} + k_1^*m + b_1^*m^2$.

Assigned b_1^* values			Assigned k_1^* values		
$K^+ = 0.00$	$Cl^- = 0.00$	$NO_3^- = -0.33$	$K^+ = 0.03$	$Cl^- = 0.00$	$NO_3^- = -0.04$
$Na^+ = 0.08$	$Br^- = 0.03$	$ClO_3^- = -0.17$	$Na^+ = 0.05$	$Br^- = 0.01$	$ClO_3^- = -0.01$
$Li^+ = 0.63$	$I^- = 0.00$	$ClO_4^- = -0.04$	$Li^+ = 0.06$	$I^- = 0.04$	$ClO_4^- = 0.00$
$NH_4^+ = 0.04$			$NH_4^+ = 0.01$		

	b_1^* for the m^2 Interaction Term			k_1^* for the Core Interaction Term		
	Observed	Predicted ^a	Obs.-Pred.	Observed	Predicted ^a	Obs.-Pred.
KCl	0.00	0.00	0.00	0.03	0.03	0.00
KBr	0.00	0.03	-0.03	0.04	0.04	0.00
KNO ₃	(-0.65)	-0.33	(-0.32)	(-0.06)	-0.01	(-0.05)
KClO ₃	(-0.73)	-0.17	(-0.56)	0.01	0.02	-0.01
NaCl	0.09	0.08	0.01	0.05	0.05	0.00
NaBr	0.16	0.11	0.05	0.07	0.06	0.01
NaNO ₃	-0.25	-0.25	0.00	0.01	0.01	0.00
NaClO ₃	-0.17	-0.09	-0.08	0.04	0.04	0.00
NaClO ₄	-0.06	0.04	-0.10	0.04	0.05	-0.01
LiCl	0.52	0.63	-0.11	0.05	0.06	-0.01
LiBr	0.64	0.66	-0.02	0.06	0.07	-0.01
LiNO ₃	0.41	0.30	0.11	(0.08)	0.02	(0.06)
LiClO ₃	0.50	0.46	0.04	0.07	0.05	0.02
LiClO ₄	0.67	0.59	0.08	0.08	0.06	0.02
NH ₄ Cl	0.05	0.04	0.01	0.01	0.01	0.00
NH ₄ Br	0.06	0.07	-0.01	0.02	0.02	0.00
NH ₄ I	0.04	0.04	0.00	0.05	0.05	0.00
NH ₄ NO ₃	-0.29	-0.29	0.00	-0.02	-0.03	0.01
Total ^b	3.91		0.65	0.65		0.10

^a Prediction from adding positive and negative ion parameter values.

^b Excluding salt values in parentheses. These totals are offered, not as exact descriptions of the accuracy of the prediction, but rather as some indication of the level of correlation.

Table II

Comparisons of Predictions with Experiment for the Freezing Point
Depressions Observed in Near 0.8-Molal Solutions.

Salt	Molal Concentration, m	Observed Freezing Point Depression, θ °K	Calculated from "Observed" k_1^* and b_1^* , °K	Calculated from Individual Ion Parameters, °K
KCl	0.77852	2.555	2.556 ^a	2.556
KBr	0.80717	2.659	2.657	2.676
KNO ₃	0.79342	2.129	2.124	(2.366)
NaCl	0.80120	2.707	2.704	2.697
NaBr	0.77676	2.689	2.680	2.642
NaNO ₃	0.79637	2.444	2.449	2.449
NaClO ₃	0.76747	2.425	2.419	2.476
NaClO ₄	0.83302	2.695	2.699	2.694
LiCl	0.82305	3.062	3.069	3.150
LiBr	0.82116	3.146	3.149	3.171
LiNO ₃	0.81478	2.985	2.986	2.964
LiClO ₃	0.83324	3.115	3.113	3.069
LiClO ₄	0.78603	3.052	3.036	2.980
NH ₄ Cl	0.80055	2.643	2.644	2.638
NH ₄ Br	0.76415	2.537	2.538	2.544
NH ₄ I	0.78434	2.620	2.614	2.614
NH ₄ NO ₃	0.83275	2.490	2.489	2.481

^a Most of the discrepancy between columns 3 and 4 results from rounding k_1^* and b_1^* .

upon the solute activity.

The $b_2N_2^2$ term is often ascribed to the effects upon the solute activity if two solute species happen by random chance to approach each other closely (e.g., Ref. 12, p. 240).

If the Duhem integration is accepted, these secondary effects (from the solute interactions upon each other) lead to a $b_1N_2^2$ term affecting the solvent activity. The primary interactions between solute and solvent are denied as an influence upon the solvent activity, however; that is a consequence of the mathematical relationships applied in thermodynamics.

But if the Duhem integration is an approximation, i.e., if something is wrong with the prac-

tical use of the thermodynamic definition of equilibrium, then those effects which lead to $k_2 \neq 1$ can be postulated as leading to $k_1 \neq 1$ as well.

In the freezing point results, k_1^* would be expected to differ for each salt, but one would anticipate k_1^* values for the individual ions which would be at least approximately the same in the different solutions. This behavior appears to be in accord with the experimental results.

Whether or not one accepts the interpretation given to the k_1^* and b_1^* constants above, their applicability over wide ranges of concentration does demonstrate that the interactions reflecting the first power of m are highly ideal (near to Raoult's law) over the whole range of concentration measured.

To test the general validity of the limiting Raoult's law, one would like to find systems for which the behavior was very nonideal for the more concentrated solutions and approached the Raoult's law limiting slope as dilution proceeded. In this sense these aqueous solutions do not offer a good test of the general applicability of Raoult's law to all dilute solutions.

Various other dilute solution treatments and their extension to larger concentrations are discussed briefly below.

In their ionic solute activity correlations, Åkerlöf and Thomas¹⁷ plot $(\log \gamma_2 - \log \gamma_2 \text{ ref})$ vs m . For dilute solutions this equals $-(a_2 - a_2 \text{ ref})/m$ vs m and is closely related to $(\theta - \theta^{\text{st}})/m$ for the solvent. These correlations exist over even larger ranges of composition than can be tested in the freezing point studies; the behavior suggests that the solvent correlations developed in the present report could quite possibly be extended further if the appropriate data were available.

Many theoretical treatments use Raoult's law as a base line and predict or correlate solvent behavior as deviations from that line. Often the deviations are bN_2^2 . For aqueous solutions as treated in this report, the error introduced by this assumption is small; the base line as experimentally established is not very much off Raoult's law, and the Raoult's law base line is adequate as an approximation.

For organic solvents (e.g., see Ref. 18), the vapor pressure measurements seem to indicate larger deviations of this base line from the ideal. Since the data are pushed severely in demonstrating this, the statement does not deny usefulness of regular solution theory for organic materials.

For metallic solutions, it is obvious that theories must be used for some predictions since the possible metallic-solution combinations are numerically astronomical. Present metallic theories (e.g. Refs. 19 to 21) are undoubtedly useful as approximations, and it does not seem that they are intended as more. Even without the Raoult's law base line problems, the theories often must become inexact because they assume smoothly curving solution behavior as a function of composition; particularly for strongly bonded solutions, this

assumption is contrary to some recent precise results (e.g. Refs. 22 to 25). The rough behavior is usually adequately treated by the theoretical approximations, however.

As an example of the effect of the approximations, Fig. 20 (see Ref. 18) represents a case in which the base line is wrong but structuring seems to be absent. The Raoult's law-based slope with bN_2^2 curvature (dashed) was fitted to the data at 0.89 mole fraction. In the dilute solution region, the slope is wrong but the activity is usually $< 0.5\%$ off. Even at 0.75 mole fraction, the activity prediction is only about 5% off. Clearly the assumption of a Raoult's law base line is practical and useful in the absence of better data.

VII. 2-2 ELECTROLYTES

Some apparently excellent 2-2 electrolyte data are available from Brown and Prue.⁸ It is interesting to see if the behavior of such solutions is distinctly different from that of the 1-1 electrolyte case.

As plotted in Figs. 21 and 22, the solutions appear to show abrupt changes in curvature at around

Fig. 20. A comparison of different base lines (Raoult's law and $a_{Cd} = 1 - 0.856 N_{Cd}$) used with b_1N_2 solvent activity deviations.

Fig. 21. Freezing point results for CoSO_4 , NiSO_4 , and CaSO_4 .

0.04 to 0.06 molal. Whether the less-curving regions are better represented by curves or straight lines is not experimentally clear; also, in view of the solution structure effects mentioned in the previous section, it is not obvious that slope changes should be rejected as impossible. In any case, the use of two straight lines in each system does give an empirically adequate description of almost all the data. (Again, as m and θ approach zero, there is greater uncertainty for a given precision in measuring the quantities. However, the scatter of the results for the more concentrated

Fig. 22. Freezing point results for MgSO_4 , ZnSO_4 , and CuSO_4 .

solutions indicates other sources of error, as well.)

As with the 1-1 electrolytes, it is not possible to assert, on the basis of the experiments, that a Raoult's law limit is being approached. The base lines corresponding to the more dilute lines drawn on the figures are all 3 or 4% off of the Raoult's law slope. In this case also, Duhem integrations of these values are difficult because of the abrupt changes of slope for $d \log \gamma_1/dm$.

To retain consistency with the Raoult's law limit, Brown and Prue treated the deviations from Raoult's law plus Debye-Hückel theory as if they resulted from ion association. It was recognized that ions moved toward and away from each other. Their treatment assumed that within a certain distance the ions could be considered as being associated; the associated ions in the species now could be treated mathematically as a single uncharged nonelectrolyte molecule obeying Raoult's law, while outside the cutoff distance they would be described as two species obeying Raoult's law plus Debye-Hückel terms.

The ion association curves in Figs. 21 and 22 are taken from Brown and Prue's Fig. 4. Their method of calculation is only outlined, and slight discrepancies may exist between their curves and our reproductions of them. Also they calculated curves by several other assumptions, none of which gave good fits to the data.

Friedman and Miller²⁶ have made theoretical calculations which avoid the arbitrary assignment of inter-ion distances inside which the ions are considered as associated.⁸ However, mathematical assumptions which lead to calculated Raoult's law behavior are still incorporated in the Friedman and Miller treatment, and their curves look much like Brown and Prue's.

VIII. ALCOHOLS

To show what some nonionic solute freezing point depressions can look like, various alcohols' results are shown in Figs. 23 and 24. Many of the results for more concentrated solutions can be adequately described by equations of the form

$$\theta = \theta^{\text{ideal}} + k_1^* m + b_1^* m^2, \quad (4)$$

where θ^{ideal} from Raoult's law replaces θ^{st} from Raoult's law-Debye-Hückel terms as in Eq. (1).

If solutions are ideal and obey Raoult's law throughout, they offer little test of the Duhem prediction. The Duhem integration must fit such solutions. If the measured behavior is close to ideal ($k_1^* \approx 0$) in the whole range of measurement, it is not possible to distinguish whether the apparent ideality is the result of cancelling molecular interactions or a corollary of Duhem integration.¹⁹ Darken¹⁹ has defined Raoult's law as follows:

Fig. 23. Aqueous freezing point depressions by some alcohols.

"Raoult's law (that the activity approaches the atom or mole fraction tangentially as both approach one)---." Only if the data deviate from ideality in the midregions can one test for an asymptotic approach to Raoult's law in the end regions.

These alcohol results in many cases are too ideal to offer much test of thermodynamic theory. Note that the reported deviations from ideality are often not much greater for the most concentrated solutions than for the apparent intercept. Often the plots are fairly linear. Linearity suggests that the major aspects of solution behavior might be explained by a small number of unchanging types of interaction with the changes of activity

Fig. 24. Aqueous freezing point depressions by various butyl alcohols.

resulting from the changes in the amount of solute present to undergo these interactions.

IX. CONCLUSIONS

Some of the difficulties in reconciling aqueous freezing point depression results with thermodynamic theory are pointed out. If the Duhem relationship is considered a thermodynamic approximation to physical reality, the necessity of approach to Raoult's law is relaxed and closer correlations of solution behavior become possible. For example, individual ion parameters can be chosen which can be used to calculate freezing point lowering values, agreeing in most cases within 2% with the observed values.

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APPENDIX: THE EXPERIMENTAL BASIS FOR THERMODYNAMIC SOLUTION THEORY
AS APPLIED TO AQUEOUS ELECTROLYTES

I. INTRODUCTION

This paper uses a theoretical treatment which does not follow thermodynamic theory as it is usually applied to real systems. This appendix explains why it seems legitimate to me to consider modifications of the theory.

By early 1963 we had developed the isopiestic balance technique (1a-3a) enough so that precise vapor pressure measurements could probably be made on the solvent in dilute solutions. Earlier unpublished molecular reasoning had led us to the consideration of a solvent activity-dilute solute mole fraction equation

$$a_1 = 1 - k_1 N_2 \quad (1a)$$

which differed from Raoult's law for which $k_1 = 1$ in all cases. Here, from the molecular reasoning, each different kind of solute molecule would, perhaps, interact differently with its immediate solvent neighbors with a net effect described by k_1 times the amount of solute added. k_1 would not be expected to have unit value except for ideal solutions; in this and other respects k_1 is much like k_2 for Henry's law with the pure (not hypothetical) solute reference state,

$$a_2 = k_2 N_2 \quad (2a)$$

Measurements were made on Ga-Cd solutions (4a,5a) because these show large deviations from ideality: at lower temperatures broad two-liquid regions exist. If the molecular reasoning were correct, one might find significant deviations from ideality, and the difference between $k_1 = 1$ and $k_1 \neq 1$ could be tested experimentally. The results indicated that, within small experimental uncertainty,

$$P_{\text{Cd alloyed}}/P_{\text{Cd pure}} = 1 - 0.856 N_{\text{Ga}} + 0.943 N_{\text{Ga}}^2 \quad (3a)$$

i.e., $k_1 \neq 1$. This behavior is consistent with the molecular reasoning and inconsistent with such treatments as regular solution theory.(6a)

(Regular solution theory is only partially thermodynamic in origin. However, its advocates have had enough confidence in the approach to

Henry's plus Raoult's law behavior in dilute solutions so that often it was not felt necessary to take measurements at less than 7 at. % solute.)

A general survey of the experimental support for thermodynamic theory was also undertaken.(4a) In many instances, otherwise apparently good data have been rejected in the literature as thermodynamically improper. Even results [e.g. from von Zawidzki (7a)] which have been accepted in the literature as demonstrating validity of the Duhem relationship on closer examination often showed regions of serious thermodynamic contradiction. Later papers and correspondence (8a-19a) elaborated the discussion, pointed out other sources of difficulty, and showed other cases where equations of the forms 1a or 3a were followed for rather dilute solutions. The Second Law of Thermodynamics was specifically suggested as the source of difficulty.(19a) More recently there has been indication that a group under P. Oshchepkov in Moscow has been set up to study related problems.(20a)

In our earlier literature search, the ionic aqueous solution measurements were not examined in detail. This appendix is an examination of data bearing on the activities of 183 such systems. Only a few new systems have been found to add to those already treated by Robinson and Stokes (21a) in their classic compilation of activity determinations on aqueous solutions.

Several preliminary comments need to be made. First, one cannot become an expert on ionic theory in a few months — I am no expert in this area. Second, although I have attempted to examine all the most important references, I may have missed some important ones, partly by oversight and partly because they were not readily available. Third, although statements will be made to the effect that experiments are not definitive in offering experimental answers to certain questions, no criticism of the experiments is thereby intended. On the contrary, I have been very much impressed with the excellence of several of the techniques. I would suggest that the results might properly be accepted

at face value if there is none but theoretical reason to question them.

II. THE COLLECTIVE RESULTS OF ACTIVITY MEASUREMENTS

Since most thermodynamic activity measurements have been made in isopiestic studies, and since most of that work has been done by Robinson or Stokes and their coworkers, it is proper that their work should be used as much of the basis of the values in the activity tables. This has been done in their tables.(21a) In general, little attention was given to the aqueous freezing point depression measurements: if they seemed to agree, this was noted; if they seemed not to agree, all the necessary heat of dilution data were seldom available, anyway. Likewise, in the present discussion the reader is referred to the body of this report for most of the discussion of freezing point depressions. Only in a few cases of special interest have I carried out the Duhem integration of the EMF data to compare with freezing point plus heat of dilution data.

Sharp discrepancies frequently exist when it is assumed that a single activity may be calculated even though different methods of measurement (e.g., freezing point, vapor pressure, EMF, osmotic pressure) are used. The following study evaluates the agreement when a single set of such activities is assumed to exist with aqueous solutions for the solute and for the solvent. In effect, the rhetorical questions are asked, "Do the aqueous solution experiments justify the thermodynamic definition of equilibrium as an exact description of physical reality? Is the simple mathematical description only a good approximation to all the complexity of real equilibrium?"

It is frequently emphasized that a true law is always valid; no exceptions are allowed. The analysis of thermodynamic data, however, is very complicated, and apparent exceptions to the laws (i.e., thermodynamically anomalous data) can be excused because of possible secondary effects such as anomalous pressure-fugacity ratios or residual gas pressures in vapor pressure studies, nonelectrochemical side reactions or unexpected electrochemical reactions in EMF studies, leaky membranes in osmotic pressure studies, and impure solids in

freezing point depressions. Therefore, an analysis of the experimental justification for thermodynamic solution theory must examine the weight of evidence to see what conclusions are justified by the group, in spite of the weakness of any single measurement.

One must be careful to consider the functions used. For example, the solute activity coefficient and the solvent osmotic coefficient are designed to go to unit value at infinite dilution. One should not consider that the error in the measurement is only 1% if the function is measured as 0.89 when it should have been 0.90; the real error is $0.01 / (1.00 - 0.90)$ or 10% in the change from the arbitrary initial unit value. Likewise, if a γ of 0.700 for the solute at 0.1 m is the initial value to which the isopiestic measurements are tied, it is this value from which the changes of γ should be considered.

Activity coefficients are commonly tabulated to three or four figures after the decimal point. If an activity coefficient is listed as changing from 0.726 to 0.529 in a range of composition, it is implied that the change is 0.197 ± 0.001 ; perhaps the discrepancy is a bit larger, but a 5% different change of 0.207 is greater than the precision of the tabulated values would suggest. Since this and much larger activity coefficient changes are commonly observed in the tabulated values, a 5% deviation in changes of comparable size would suggest significant experimental discrepancy. If the overall change were very much less, a good test of the thermodynamic prediction could not be made within the scatter of the data.

Our experiments with alloys referred to earlier in this appendix had indicated that the apparent limiting slopes of the activity-mole fraction relationships for vapor pressures seldom fell within 5% of the ideal Raoult's law value. By long extrapolation, then, it seemed reasonable to anticipate Duhem integration discrepancies of greater than 5% if our predictions based on molecular models were correct for aqueous solutions.

Table Ia summarizes the results of the experiments. The positioning of the reference numbers by columns indicates the types of measurements which have been made on the systems. If the discrepancy in the changes of γ is greater than 5%, the system was not considered as demonstrating thermodynamic

consistency. "Yes" or "No" indicates the results of the comparison. Sometimes the agreement was good (< 4% discrepancy) in some regions but not in others; in other cases some methods of measurement agreed thermodynamically while others did not.

"Yes, No" indicates these conditions. The footnotes should be read in all cases; the Yes or No ratings are only a quick summary to help show the overall picture.

Table Ia

A Summary of Activity Measurements with a Comparison of the Results
by Different Types of Measurement

Solute	Number of Properties Considered (VP,EMF,FP)	Vapor Pressure		EMF		Freezing Point	Notes	
		Isopiestic	Direct	With Transference	Without Transference		Thermodynamic Consistency Demonstrated	Comments
HCl	3	22a		23a	24a - 26a	25a	No	See below
HBr	1				29a			
HI	1	30a						
HClO ₄	1	30a	31a					See below
HNO ₃	2		32a			33a	No	See below
LiOH	1				35a,36a			
LiCl	3	37a - 39a	39'a		40a	40a,42a	No	See below

- HCl - (25a) considered that the direct vapor pressure (VP) measurements were all in error, especially below 3 M. (22a) believed that the values selected by (25a) were in small error above 1.2 M. The (25a) values are consistent with selected freezing point depression measurements, but differ from EMF measurements (26a) at large concentrations. Transference cell values (23a), mostly at lower concentrations, do not tie in well with the values selected by (22a), but this may well be an extrapolation error. There is fair agreement between calorimetric and EMF heat data (27a). Solubility determinations (28a) do not agree with EMF values (25a).
- HClO₄ - Problems in reconciling isopiestic and absolute pressure results suggest problems as to what should be used as the pressures for the isopiestic reference solutions.
- HNO₃ - (34a) develops a single equation to fit γ from freezing point (FP) measurements (33a) and VP (32a). The equation is tied to γ from VP at 36 M; equation and VP measurement differ by a factor of 2 at 3 M.
- LiCl - If the EMF values for γ (40a) and the Duhem integrated values from VP (38a) are set equal at 0.1 M, they diverge by 6% of the change in γ at 2 M, and above 2 M the deviations become very large. The lithium amalgam electrode is "known to be erratic." (41a) has compared VP and EMF data from 1 to 0.1 M; there is a 42% discrepancy between the changes of activity by EMF or Duhem VP. In comparing EMF and FP the integration error is 15% (40a), but these are not his more recent FP data. A Duhem integration comparing the more recent FP data (42a) and the same EMF results also fails by 15% in representing the change of γ . Absolute VP data (39'a) disagree with the selected values.

Table Ia (continued)

Solute	Number of Properties Considered (VP, EMF, FP)	Vapor Pressure		EMF		Freezing Point	Notes	
		Isopiestic	Direct	With Transference	Without Transference		Thermodynamic Consistency Demonstrated	Comments
LiBr	3	39a, 43a			40a	40a, 42a	No	See below
LiI	1	37a						
LiClO ₄	2	44a				45a	No	See below
LiNO ₃	2	46a, 47a	39'a			48a, 49a	No	See below
LiAc	2	46a				50a	No	See below
LiToI	1	46a						
NaOH	2	51a	54a		27a, 36a, 52a, 53a		No	See below
NaF	3	55a			56a	48a	No	See below

LiBr - Major discrepancies are shown (39a). γ Duhem-integrated from the VP in the range 0.1 to 3 M is 12% larger than the EMF value. The γ change from FP is over twice as great as that from EMF in the range 0.1 to 1 M, but the temperatures are different.

LiClO₄ - γ from the VP rises 17% more rapidly than γ from FP in the range 0.1 to 1 M. Calculation for heat effects might eliminate the discrepancy.

LiNO₃ - The VP (46a) and FP (49a) γ curves have different shapes with large percentage errors in the changes of γ (without heat of solution corrections). Direct VP data show a hump which was smoothed for calculation purposes (39'a).

LiAc - The VP (46a) and FP (50a) γ curves have different shapes; the changes of γ in the range 0.1 to 1 M are 82% larger for the VP than for the FP. New heat data might resolve the discrepancies.

NaOH - Regarding the comparison of VP (51a) and concentrated solution EMF (53a) results, (51a) states, "It must be remembered that at high concentrations the water activity is very sensitive to small errors in the electromotive force. Even so, the agreement cannot be considered satisfactory." (27a) notes difficulties with amalgam cells but concludes the agreement with the EMF work by (52a) is satisfactory. "The agreement with calorimetric data is only fair," however. There is not good agreement between these latter EMF data and those from VP, but the region of overlapping measurement is not large. Direct bithermal isopiestic equilibrations (54a) give results which "are in fair agreement with those obtained by combining the isopiestic ratios of sodium hydroxide to sulfuric acid with the static vapor pressure measurements of Shankman and Gordon on sulfuric acid, and support the latter against electromotive force results."

NaF - If the γ values by VP and EMF are assumed equal at 0.1 M, there is a 16% discrepancy in the change of γ to 0.983 M. FP data are in rough agreement with the VP data (at different temperatures, however.)

Table Ia (continued)

Solute	Number of Properties Considered (VP, EMF, FP)	Vapor Pressure		EMF		Freezing Point	Notes	
		Isopiestic	Direct	With Transference	Without Transference		Thermodynamic Consistency Demonstrated	Comments
NaCl	3	57a		58a	40a	42a	Yes, No	See below
NaBr	3	39a, 60a			40a	42a	Yes, No	See below
NaI	3	39a			40a	48a	No	See below
NaClO ₃	2	61a				45a	No	See below
NaClO ₄	2	44a				45a	No	See below

NaCl - Recently an attempt was made to compare glass-electrode EMF data with other NaCl results. The author (59a) commented, "Comparison with literature values is somewhat difficult since the values from different sources disagree with each other by as much as 1 mV. The present results agree best with Harned's over the range he measured, diverge sharply from those given by Robinson and Scatchard at intermediate concentrations, and agree with the values of Scatchard but disagree with those of Robinson near saturation. The divergence between the sets of values reported by such distinguished sources is disturbing, especially since NaCl is frequently used as a reference solute in isopiestic measurements."

In the range 0.005 to 0.1 M, the transference cell data (58a) fail by about 5% in predicting the freezing point depression changes. (Note that these were the measurements which agreed for KCl.)

Since the reader may be unfamiliar with the functions used in describing aqueous solutions, the deviation function plot (21a, Fig. 8.11) should be discussed. The quantity ($\phi - 0.07$ M NaCl) goes to unity as long as a finite solute activity coefficient at ∞ dil. is assumed. According to Debye-Hückel theory, the quantity is dropped rapidly in value as the concentration rises, and for NaCl the value is ~ 0.86 at 1 M. What is significant in testing thermodynamic theory is not the magnitude of the numbers but rather how accurately the changes in the numbers can be predicted. Here the scatter is some 30% of the changes in the function on the plot, and very little justification of theory is demonstrated.

In his early selection of the NaCl γ values, Robinson (39a) split the discrepancy between the EMF and FP results, but his newer selection (21a) is outside both types of measurement. Serious discrepancies are shown in the comparison at higher concentrations.

Calorimetric and EMF heat data are not in agreement (27a).

NaBr - The change of γ from EMF is 13% greater than that from FP in the range 0.1 to 1 M, but the VP and EMF values are very close (39a). (The reference solution VP values are in doubt, however; see KCl). From 1 to 4 M the integration discrepancy is 12% for EMF vs. VP.

NaI - From 0.1 to 1 M the Duhem integration of the VP results (39a) originally led to a 10% error in the change of γ , but the newer choice of KCl reference values has reduced the discrepancy to 6% (21a).

NaClO₃ - The γ change as integrated from the FP data at 273°K is some 25% larger than the γ change at 298°K from integration of the VP data (61a). The discrepancy might be resolved by more heat of solution data.

NaClO₄ - γ from FP measurements changes 35% more rapidly than γ from VP measurements. More heat data might bring the γ changes into agreement.

Table Ia (continued)

Solute	Number of Properties Considered (VP,EMF,FP)	Vapor Pressure		EMF		Freezing Point	Notes	
		Isopiestic	Direct	With Transference	Without Transference		Thermodynamic Consistency Demonstrated	Comments
NaBrO ₃	1	62a						
NaNO ₃	2	46a				49a	Marginal	See below
NaForm	2	63a				50a	No	See below
NaAc	2	46a,63a				50a	No	See below
NaProp	1	63a						
NaBut	1	63a						
NaVal	1	63a						
NaCapro	1	63a						
NaHept	1	63a						
NaCapryl	1	63a						
NaPelarg	1	63a						
NaCapra	1	63a						
NaHMal	1	64a						
NaHSucc	1	64a						
NaHADip	1	64a						
NaTol	1	46a						
NaCNS	1	65a						
NaH ₂ PO ₄	1	66a						
KOH	1				36a,67a,68a			See below
KF	2	55a				48a	No	See below

NaNO₃ - There is discrepancy as to the value of γ (46a), and the shapes of the γ curves from VP and FP are different even when corrected for heat effects. The agreement here is better than for most systems, however.

NaForm - The γ from FP changes 16% more rapidly than that from VP when heat terms are ignored. Perhaps heat data would resolve the discrepancies.

NaAc - The γ values as calculated from VP and FP are of very different shapes. Heat data might resolve the discrepancies.

KOH - Within experimental precision $\bar{L}_2$ data agree and $\bar{C}_{p2}$ data disagree, comparing EMF and calorimetry.

KF - The γ curves from VP and FP have very different shapes

Table Ia (continued)

Solute	Number of Properties Considered (VP,EMF,FP)	Vapor Pressure		EMF		Freezing Point	Notes	
		Isopiestic	Direct	With Transference	Without Transference		Thermodynamic Consistency Demonstrated	Comments
KCl	3	57a	70a	71a	72a	42a	Yes, No	See below
KBr	3	39a,60a			40a	42a	No	See below

KCl - The KCl situation is very complex. KCl is used as a standard for many thermodynamic purposes, and much very careful work has been done on its solutions. Even though the work was done just after the First World War, the vapor pressure studies (70a) are quite possibly the best absolute pressure determinations which have ever been made. There was an anomalous hump in the VP results in the range 0.4 to 0.8 M about which (70a) said, "The points of the curve between 0.4 M and 0.8 M were determined with great care and the irregularities here observed are entirely too great to be attributed to experimental error. We have no explanation to offer for the peculiar shape of the curve in this region other than possible changes in the state of molecular aggregation of the solvent." The same sort of hump, but only about half as large, shows in the best FP data (42a; also see plot in this paper). As pointed out elsewhere (73a), the accepted KCl vapor pressures (22a) have wiped out his hump; all isopiestic activities tied to these KCl values are correspondingly erroneously "corrected," at least as far as the vapor pressure data can show. The reason for "correcting" the vapor pressures was to bring them into agreement with the EMF values. From (74a), "In an earlier paper, however, it has been shown that the EMF data on some alkali halides can be reconciled with the isopiestic data by taking a set of reference values for γ_{KCl} which are considerably higher above 1.5 M KCl than those adopted by Scatchard, Hamer and Wood. The discrepancy is largely due to the greater emphasis I have placed on the EMF results, and until a direct determination of the osmotic or activity coefficient of potassium chloride is made by another method, both sets of reference values for γ_{KCl} must be regarded as equally probable."

KCl EMF cells without transference do not agree with cells with transference. This can be seen by the different values of the transference number. From the EMF ratio of cells with and without transference, it is 0.498, (72a); the supposedly accurate transference number is 0.4905 from moving boundary measurements (71a). Using the latter transference number and EMF data for cells with transference (71a), there is excellent agreement with activities from FP data (42a) corrected for heats of dilution.

This latter agreement for KCl cells with transference is clouded by the fact that for NaCl it is the cells without transference which agree best with the FP data. Furthermore, there is considerable disagreement as to the heat of solution of KCl (e.g., 75a) although this does not greatly alter the calculation.

γ for KCl as selected earlier (39a) by Robinson split the discrepancy between the dropping amalgam EMF and the FP values. Now (21a) he accepts values closer to those from the EMF.

KBr - There is sharp initial discrepancy between γ values from VP and EMF on one hand and FP on the other, (39a) but there is again agreement by 1 M. (The reference solution VP values are in doubt, however; see KCl). From 1 to 4 M the VP and EMF γ changes diverge sharply.

Table Ia (continued)

Solute	Number of Properties Considered (VP, EMF, FP)	Vapor Pressure		EMF		Freezing Point	Notes	
		Isopiestic	Direct	With Transference	Without Transference		Thermodynamic Consistency Demonstrated	Comments
KI	2	39a, 76a			40a		No	See below
KClO ₃	2	62a				45a	No	See below
KBrO ₃	1	77a						
KNO ₃	2	46a				49a	Yes	See below
KAc	2	46a				50a	No	See below
KHMal	1	64a						
KHSucc	1	64a						
KHAdip	1	64a						
KTol	1	46a						
KCNS	1	65a						
KH ₂ PO ₄	1	66a						
NH ₄ Cl	2	78a				48a, 135a	Yes, No	See below
NH ₄ NO ₃	2	78a				48a, 135a	Yes, No	See below
RbCl	2	37a, 79a				48a	Yes	See below
RbBr	1	39a, 79a						
RbI	1	39a, 79a						
RbNO ₃	1	79a						
RbAc	1	79a						

- KI - From 0.1 to 1 M the VP and EMF results indicate about 25% more change in γ than the FP results. Above 1 M all results diverge sharply. From 1 to 2 M the VP change is 3 times larger than the EMF change, while from 1 to 4 M the FP change is 2.5 times greater than the VP change. (See 39a).
- KClO₃ - The data do not overlap enough to give a significant test.
- KNO₃ - When FP results, as corrected for heat effects, are compared with VP results, the discrepancies in the γ changes are small ($\sim 3\%$).
- KAc - The γ values from VP and FP change very differently. Perhaps the heat data would reconcile the discrepancy.
- NH₄Cl - In (78a), the VP results are compared with the FP results as corrected to 298°K by heat of dilution data as in 48a. They consider that an error of 3% in the γ change from 0.1 to 2 M is satisfactory agreement. By 4.58 M the error is 24%. A discrepancy as with NH₄Br (last listing) seems to exist.
- NH₄NO₃ - When γ is assumed identical for FP and VP at 0.1 M, the γ changes of fairly rough data are in good agreement. A discrepancy as with NH₄Br (last listing) seems to exist, however.
- RbCl - From 0.1 to 0.5 M the agreement between VP and FP is good (39a) and the newer selection of a hypothetical KCl-H₂O VP as reference has reduced the discrepancy still further (21a). The range covered is small.

Table Ia (continued)

Solute	Number of Properties Considered (VP, EMF, FP)	Vapor Pressure		EMF		Freezing Point	Notes	
		Isopiestic	Direct	With Transference	Without Transference		Thermodynamic Consistency Demonstrated	Comments
CsOH	1				80a			
CsCl	2	37a			80a		Yes, No	See below
CsBr	1	39a, 37a						
CsI	1	39a, 79a						
CsNO ₃	1	79a						
CsAc	1	79a						
AgNO ₃	1	81a						
TlClO ₄	1	79a						
TlNO ₃	1	79a						
TlAc	1	79a						
MgCl ₂	2	82a, 83a, 83'a				48a	No	See below
MgBr ₂	1	82a, 83'a						
MgI ₂	1	82a, 83'a						
Mg(ClO ₄) ₂	2	84a				85a	No	See below
Mg(NO ₃) ₂	1	86a, 87a						

CsCl - There is excellent agreement between the γ values from VP and EMF. What little discrepancy exists could be reduced by changing the extrapolation to ∞ dil. The test is less convincing, however, because the KCl-H₂O reference "vapor pressure" is not a real measured quantity but rather an idealized quantity made to compromise the KCl solution discrepancies. As pointed out, (37a) beyond 2 M a discrepancy develops.

MgCl₂ - The older (82a) reference vapor pressures led to about 5% discrepancy in the change of γ by VP and by FP from 0.2 to 1 M and 19% discrepancy from 1 to 2 M. The newer values (21a) are in ~ 7% disagreement throughout.

Mg(ClO₄)₂ - If the γ values from FP (85a) and VP (84a, see 96a) are assumed equal at 0.1 M, there is a 14% discrepancy in the change to the value for 1 M. Perhaps heat of solution data would resolve the discrepancy.

Table Ia (continued)

Solute	Number of Properties Considered (VP, EMF, FP)	Vapor Pressure		EMF		Freezing Point	Notes	
		Isopiestic	Direct	With Transference	Without Transference		Thermodynamic Consistency Demonstrated	Comments
MgAc ₂	1	88a						
CaCl ₂	3	73a, 89a	89'a, 90a	91a, 92a	36a, 93a, 94a	36a	No	See below
CaBr ₂	1	43a, 97a						
CaI ₂	1	97a						
Ca(ClO ₄) ₂	2	96a				85a	No	See below

CaCl₂ - These γ values are based on isopiestic VP measurements (89a) which do not overlap, but are tied to, EMF cells with transference (91a) using moving boundary transference numbers (95a). NaCl and H₂SO₄ are used as standards. (89a) states, "As a result it is believed that the water activities and activity coefficients of calcium chloride at 25° are now known more accurately and over a wider concentration range than those of any other normal 1:2 salt."

The thermodynamic picture, however, is far from clear. First, see NaCl and H₂SO₄ discussions regarding problems with these reference solutions. The EMF results for cells without transference using dropping amalgam electrodes (36a, 93a) are in sharp disagreement with the VP results (89a) and are considered (89a) to be in error. Certainly, dropping amalgam electrodes are always subject to question - the very reason for using them is to provide fresh surfaces because the amalgam is reacting continuously in a side nonelectro-chemical reaction. For CaCl₂ there is, indeed, a discrepancy between transference numbers from the moving boundary method (95a) and from the EMF ratio for cells with and without transference (91a). But the discrepancy is comparable for that for KCl (q.v.), and with KCl the dropping amalgam EMF data have been used to reject absolute vapor pressure measurements.

Dynamic pressure measurements at three compositions (89'a) agree at two compositions with the selected values; dew point measurements (90a) disagree. It is reported (36a) that FP results agree with the amalgam EMF results. The reference VP values have smoothed a hump similar to that for KCl, as pointed out elsewhere (73a).

Ca(ClO₄)₂ - The change in γ from 0.1 to 1 M is 7% larger from VP than from FP. This discrepancy might be resolved if heat of solution data were available.

Table Ia (continued)

Solute	Number of Properties Considered (VP, EMF, FP)	Vapor Pressure		EMF		Freezing Point	Notes	
		Isopiestic	Direct	With Transference	Without Transference		Thermodynamic Consistency Demonstrated	Comments
Ca(NO ₃) ₂	2	98a	99a, 100a			48a	No	See below
SrCl ₂	2	73a, 101a, 83'a			36a, 93a		No	See below
SrBr ₂	1	97a						
SrI ₂	1	97a						
Sr(ClO ₄) ₂	2	96a				85a	No	See below
Sr(NO ₃) ₂	1	86a						
BaCl ₂	2	79a, 73a, 101a	89'a, 101'a, 103'a		36a, 93a, 102'a		Yes, No	See below
BaBr ₂	3	97a, 102a			103a	48a	No	See below
BaI ₂	1	97a						
Ba(ClO ₄) ₂	2	96a				85a	No	See below

- Ca(NO₃)₂ - The direct vapor pressure measurements are in sharp disagreement with the isopiestic values based on the selected KCl reference "vapor pressures." The FP data are meager and are not in disagreement with the isopiestic results. However, this γ changes only in the range 0.48 to 0.35 with deviations of 0.02 from the isopiestic values; large percentage discrepancies could be hidden in the scatter.
- SrCl₂ - Robinson considers that, "The results for strontium chloride are in reasonable agreement with the EMF determinations of Lucasse." The newer γ values (21a) lead to about 10% greater change of γ than for these EMF values (93a).
- Sr(ClO₄)₂ - The change in γ from 0.1 to 1 M is 54% larger from VP than from FP. This discrepancy might be resolved if heat of solution data were available.
- BaCl₂ - Again comparing the new (21a) standard values from the VP measurements with the same EMF values (93a) used with SrCl₂, the VP values for γ change about 10% faster than the EMF values. Other EMF values (102'a) agree with dynamic pressures (89'a, 101'a) and are closer to the selected values but differ from the dew point measurements (103'a). The EMF values are not for equilibrium, however, since reaction with water was continuously destroying the amalgam.
- BaBr₂ - The changes of γ from FP are 20% greater than the changes from VP in the range 0.1 to 1 M.
- Ba(ClO₄)₂ - Ref. (96a) authors are dubious about their VP data. The change in γ from 0.1 to 1 M is five times larger from FP than from VP. This discrepancy might be resolved if heat of solution data were available.

Table Ia (continued)

Solute	Number of Properties Considered (VP, EMF, FP)	Vapor Pressure		EMF		Freezing Point	Notes	
		Isopiestic	Direct	With Transference	Without Transference		Thermodynamic Consistency Demonstrated	Comments
Ba(NO ₃) ₂	1	86a						
BaAc ₂	1	88a						
MnCl ₂	1	104a, 83'a						
FeCl ₂	1	105a						
CoCl ₂	1	104a, 106a						
CoBr ₂	1	107a						
CoI ₂	1	107a						
Co(NO ₃) ₂	1	86a						
NiCl ₂	1	104a, 83'a						
CuCl ₂	1	104a						
Cu(NO ₃) ₂	1	86a						
ZnCl ₂	2	22a, 108a, 83'a			108a - 111a		Yes, No	See below
ZnBr ₂	2	112a			109a, 113a, 114a		No	See below
ZnI ₂	2	115a, 116a			109a, 117a		No	See below
Zn(ClO ₄) ₂	2	84a		84a			No	See below

ZnCl₂ - The newer reference pressures and newer isopiestic measurements now yield γ values (21a) of different size but in overall good agreement with early EMF values using zinc amalgam (110a) if the extrapolation to ∞ dil. is changed; comparison with their own EMF work (108a) is now poorer. There is a general disagreement between VP and EMF as to the form of the changes in the region below 1 M.

ZnBr₂ - At one time the agreement between VP and EMF (113a) was better than now with the new reference activities (21a). The changes of γ are small and the percentage errors large.

ZnI₂ - From 0.1 to 0.8 M, γ from EMF (117a) using zinc amalgam and Ag-AgI electrodes changes 13% faster than the VP integration value used (21a). The measurements using Zn-ZnI₂ and Hg-HgI₂ as electrodes (116a) were very different and were considered by (115a) as being in error. The older accepted γ values were in better agreement, but reevaluation of the reference "vapor pressures" has led to about half of the discrepancies now existing.

Zn(ClO₄)₂ - No test of thermodynamic prediction is involved because no independently measured transference numbers are available.

Table Ia (continued)

Solute	Number of Properties Considered (VP, EMF, FP)	Vapor Pressure		EMF		Freezing Point	Notes	
		Isopiestic	Direct	With Transference	Without Transference		Thermodynamic Consistency Demonstrated	Comments
Zn(NO ₃) ₂	1	84a						
CdCl ₂	2	118a			119a - 121a		No	See below
CdBr ₂	3	118a			119a, 122a, 123a	124a	No	See below
CdI ₂	2	76a			125a, 126a		Yes	See below
Cd(NO ₃) ₂	1	86a						
Pb(ClO ₄) ₂	1	87a						
Pb(NO ₃) ₂	2	87a, 127a				48a	No	See below
UO ₂ Cl ₂	1	128a						
UO ₂ (ClO ₄) ₂	1	128a						
UO ₂ (NO ₃) ₂	1	86a, 128a						

CdCl₂ - There have been several EMF measurements. It is pointed out (118a) that the EMF agreement is good at low concentrations with discrepancy between 0.1 and 1 M. Best agreement with VP is found for (119a), but even here the curve shapes are different. There is about 7% discrepancy from 0.1 to 0.5 M and about 4% overall discrepancy at the largest concentrations.

CdBr₂ - Because of experimental difficulties, the VP results are presented only "as affording support for" the EMF results. The EMF results are not in good agreement, three different electrodes yielding three sets of values. The closest EMF values (122a) to the FP value (124a) disagree by 8% in the integration, and the furthest values (123a) differ by 33%.

CdI₂ - The EMF values using three different electrodes are in good agreement, and their scatter overlaps the VP results. All measurements used cadmium amalgam as the other electrode. It is this latter electrode which is generally suspect and should be tested. The vapor pressures are compared with KI which in turn is compared with KCl (q.v.) and its difficulties, however.

Pb(NO₃)₂ - When γ is assumed to be 0.369 at 0.1 M and the changes of γ to 1 M are considered, the freezing point changes considered in the paper (48a) are 10% less, and the other vapor pressure measurements (127a) are 13% greater, than the selected values (87a). Heat of solution measurements might resolve the discrepancy.

Table Ia (continued)

Solute	Number of Properties Considered (VP, EMF, FP)	Vapor Pressure		EMF		Freezing Point	Notes	
		Isopiestic	Direct	With Transference	Without Transference		Thermodynamic Consistency Demonstrated	Comments
Li_2SO_4	2	129a			36a		Marginal	See below
Na_2SO_4	2	129a			36a, 130a		Yes, No	See below
Na_2CrO_4	1	131a, 83'a						
$\text{Na}_2\text{S}_2\text{O}_3$	1	129a						
Na_2Fum	1	132a						
Na_2Mal	1	132a						
K_2SO_4	3	129a			36a	48a	Yes	See below
K_2CrO_4	1	133a						
$(\text{NH}_4)_2\text{SO}_4$	2	134a				135a	No	See below
Rb_2SO_4	1	135'a						
Cs_2SO_4	1	135'a						
BeSO_4	1	136a						
MgSO_4	2	137a				48a, 140a	No	See below
MnSO_4	2	137a				48a	No	See below
NiSO_4	2	137a				48a	No	See below

Li_2SO_4 - While earlier comparison of VP and sparse EMF data was good, the new choice of reference pressures for isopiestic comparison has led to overall 4% discrepancy in the γ changes with greater discrepancies around 0.5 M.

Na_2SO_4 - The newer reference vapor pressures for isopiestic work have partially destroyed the very good earlier agreement between VP and EMF. The present discrepancy (3%) is small compared to most other systems, however. The calorimetric heats of dilution do not agree well with those from EMF. There are still problems connected with the KCl (q.v.) reference pressures used for calculation. Two different reference electrodes were used in the EMF work, and agreement is still good; the doubtful amalgam electrode was not changed, however.

K_2SO_4 - Except in the range 0.1 to 0.5 M where the curve shapes are different, the VP and meager EMF data are in good agreement. Likewise meager FP data agree.

$(\text{NH}_4)_2\text{SO}_4$ - In (134a) the VP values are not compared with the FP values (135a) apparently because of the absence of satisfactory heat of dilution data.

MgSO_4 - γ from FP as tied to VP (137a) at 0.1 M is in 5% disagreement at 1 M. The VP data are not presented. Newer FP data cannot be integrated. See CuSO_4 .

MnSO_4 - γ from FP as tied to VP (137a) at 0.1 M is in 14% disagreement at 2 M. The VP data are not presented.

NiSO_4 - γ from FP as tied to VP (137a) at 0.1 M is in 11% disagreement at 2 M. The VP data are not presented. Newer FP data cannot be integrated. See CuSO_4 .

Table Ia (continued)

Solute	Number of Properties Considered (VP,EMF,FP)	Vapor Pressure		EMF		Freezing Point	Notes	
		Isopiestic	Direct	With Transference	Without Transference		Thermodynamic Consistency Demonstrated	Comments
CuSO ₄	3	137a			138a,139a	48a,140a	Yes, No	See below
ZnSO ₄	3	137a			139'a	48a,140a	No	See below
CdSO ₄	3	137a			141a	48a	Yes, No	See below
UO ₂ SO ₄	1	136a				142a	No	See below
AlCl ₃	1	143a						
ScCl ₃	1	143a						
CrCl ₃	1	144a						
YCl ₃	1	143a						
LaCl ₃	1	143a,74a,79a						
CeCl ₃	1	143a						
PrCl ₃	1	143a						
NdCl ₃	1	143a						
SmCl ₃	1	145a						
EuCl ₃	1	145a						
Cr(NO ₃) ₃	1	144a						

CuSO₄ - To prevent precipitation 138a and 139a added reactive acid to the EMF cells. When Pb-PbSO₄ is used to replace Hg-HgSO₄ there is "complete disagreement with the freezing point data" (139a). The vapor pressure data and their precision are not shown. The EMF and FP data are meager. When tied at 0.1 M, the γ values agree within exptl. error to 1.5 M. Recent precise FP data (140a) show rapidly changing $d \log \gamma / dm$ changes which cannot be integrated accurately. This problem is discussed elsewhere in this present report.

ZnSO₄ - γ from FP as tied to VP (137a) at 0.1 M is in 12% disagreement at 2 M. The VP data are not presented. Newer FP data cannot be integrated. See CuSO₄.

CdSO₄ - γ from FP as tied to VP (137a) at 0.1 agrees at 3 points to 1 M. EMF γ (140a) as tied at 0.1 M is off by 23% at 3.5 M. The VP data are not presented.

UO₂SO₄ - There is a sevenfold discrepancy between VP and FP γ -value at 3.5 M if the activity coefficients are assumed equal at 0.1 M. Heat of solution data might resolve the discrepancy.

Table Ia (continued)

Solute	Number of Properties Considered (VP, EMF, FP)	Vapor Pressure		EMF		Freezing Point	Notes	
		Isopiestic	Direct	With Transference	Without Transference		Thermodynamic Consistency Demonstrated	Comments
$K_3Fe(CN)_6$	1	146a						
$K_4Fe(CN)_6$	2	79a				48a	No	See below
$Al_2(SO_4)_3$	1	79a						
$Cr_2(SO_4)_3$	1	144a						
$Th(NO_3)_4$	1	146a						
Five Sulfonic Acids	1	147a						
	1	147a						
	1	148a						
	1	148a						
	1	148a						
NaH_2AsO_4	1	149a						
KH_2AsO_4	1	149a						
Na_2CO_3	3		150a, 151a		151a, 152a	150a	No	See below
Na_2HPO_4	1	149a						
Na_2HASO_4	1	149a						
K_2HPO_4	1	149a						
K_2HASO_4	1	149a						
$Ga(ClO_4)_3$	1	153a						
$Co(en)_3Cl_3$	1	154a						
Na_3PO_4	1	149a						

$K_4Fe(CN)_6$ - FP data mentioned in 79a, but I could not find them. FP data used only to set original activity.

Na_2CO_3 - The Duhem integration of the EMF data from (151a) is 6% off his measured vapor pressures (gas saturation method). γ values from (152a) by EMF and from (150a) by VP and FP are still more different, but a large part of this latter discrepancy can be removed by changing the extrapolations to ∞ dil. Heat of dilution values from EMF do not agree with the estimates of Bichowski and Rossini. (There is a fourfold discrepancy.)

Table Ia (continued)

Solute	Number of Properties Considered (VP,EMF,FP)	Vapor Pressure		EMF		Freezing Point	Notes	
		Isopiestic	Direct	With Transference	Without Transference		Thermodynamic Consistency Demonstrated	Comments
Na ₃ AsO ₄	1	149a						
K ₃ PO ₄	1	149a						
K ₃ AsO ₄	1	149a						
ThCl ₄	1	155a						
Ky ₄ Mo(CN) ₈	1	156a						
Pt(en) ₃ Cl ₄	1	156a						
Pt(en) ₃ (ClO ₄) ₄	1	154a						
UO ₂ F ₂	1					157a		See below
KH ₂ PO ₄	1	66a,149a						
NaH ₂ PO ₄	1	66a,149a						
In ₂ (SO ₄) ₃	1				158a,159a	158a		See below
NH ₄ Br	2			160a		135a,161a	No	See below
H ₂ SO ₄	2	38a	161'a,162a 162'a		163a,164a		No	See below
LiForm	1					50a		
KForm	1					50a		
LiClO ₃	1					45a		
KClO ₄	1					45a		
NH ₄ I	1					135a		
<u>UO₂F₂</u>	- The behavior is complex and in only rough agreement with theoretical treatments assuming very incomplete dissociation of UO ₂ F ₂ as well as extensive polymerization to (UO ₂ F ₂) _x species.							
<u>In₂(SO₄)₃</u>	- The measurements are affected by major hydrolysis of HgSO ₄ and minor hydrolysis of In ₂ (SO ₄) ₃ . Rough correlations between predicted and measured solubilities are noted. EMF tied to a single FP measurement.							
<u>NH₄Br</u>	- Scatchard and Orttung consider that the FP measurements of Scatchard and Prentiss do not give the water activity. Recent FP measurements are discussed in the present text.							
<u>H₂SO₄</u>	- As already discussed (38a) there is a problem with what to use for H ₂ SO ₄ reference pressures because the VP and EMF data "differ considerably" from each other. 162a suggested that the cell reaction (163a) was, perhaps, not that which was postulated, and that the VP data should be accepted. "The agreement between the EMF results from the two types of cell is extraordinarily good, whilst the calorimetric data are in fair agreement." (164a) (The $\bar{L}$ values by the two methods follow curves of different shapes, the calorimetric value being 9% larger at 7 M, and 3% smaller at 17 M.)							

III. DISCUSSION OF TABLE Ia

Of the 183 systems considered and for which thermodynamic activities have been determined, 17 show agreement within 5% for the γ changes as established by different techniques, at least in some areas of measurement.

Of these 17 systems, four (RbCl , KNO_3 , and K_2SO_4 in FP vs VP; and K_2SO_4 and CdI_2 in EMF vs VP) show close agreement throughout. These isopiestic VP correlations are less convincing because the reference vapor pressures for KCl , NaCl , CaCl_2 , and H_2SO_4 are all hypothetical values (rather than measured values) based on compromises among the thermodynamic discrepancies by different methods of measurement. Likewise, the EMF measurements cannot stand alone: To quote from Harned and Owen, (195a) "It should be emphasized at this point that the nature of the chemical reaction, corresponding to a particular electrode or cell, cannot be determined by electromotive force measurements alone. Cell reactions, no matter how simple and obvious, must be treated as hypothetical until it can be shown that thermodynamic quantities calculated from the electromotive force, ΔF , ΔH , equilibrium constants, etc., have been checked by other evidence."

Perhaps the best thermodynamic correlation existing is for KCl solutions as measured by freezing point depressions with heat of dilution corrections, and by EMF cells with transference plus transference numbers by the moving boundary method. This correlation falls within the experimental scatter of very precise freezing point data. Unfortunately transference cell data are seldom reported above 0.1 M, and isopiestic data are seldom taken below 0.1 M, so comparison is not possible in most cases.

Two other systems should also be emphasized. For NaBr the γ values from isopiestic VP and EMF without transference are close; this might reflect the similarity of KCl and NaBr — those hypothetical VP values which are used to bring EMF and isopiestic VP into agreement for KCl might lead to appropriate corrections for the NaBr comparison by VP and EMF. For BaCl_2 there is good agreement between the EMF and dynamic VP values; in judging this agreement one should bear in mind that the water and amalgam were continuously reacting as

shown by the destruction of the amalgam on standing in water.

I have not found the data to convince me that the thermodynamic definitions of activity and equilibrium are correct. On the other hand, since any measurement is subject to legitimate thermodynamic question (see The Collective Results of Activity Measurements), one cannot assert that the data prove that the theory is wrong. What probably can be concluded is that the results do not demonstrate an adequate experimental basis for the thermodynamic thesis.

APPENDIX REFERENCES

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