SOME CONSIDERATIONS IN ESTABLISHING THERMODYNAMIC ACTIVITIES FROM HIGH TEMPERATURE EMF MEASUREMENTS*

Guy R. B. Elliott
University of California, Los Alamos Scientific Laboratory
Los Alamos, New Mexico 87545

ABSTRACT

Various sources of uncertainty and error in establishing thermodynamic properties from experimental data are discussed and evaluated. These problems reflect experimental difficulties, the frequent absence of necessary data, some dubious assumptions in the absence of data, certain fallacies when simple models are combined with thermodynamic manipulations to correlate limited or imprecise data, and some ill-chosen methods of describing data. Effects of metal solubility in molten salts, of reactions between electrolyte and metal, of experimental errors, and of poor models are considered.

I. INTRODUCTION

Certain kinds of molten salt emf measurements surpass most aqueous emf measurements in precision, accuracy, stability, reliability of temperature coefficients, and versatility in the systems which can be studied --- many sources of aqueous system uncertainty can be avoided with molten salts. Specifically, measurements taken at room temperature with aqueous solutions often need correction for nonequilibrium effects, e.g., continuing side reaction with the water component of the solutions, strains and concentration gradients in the solids, and effects of deposited surface films. Frequently molten salts and molten metals can be reacted to equilibrium, except, of course, for the concentration gradients across the salt bridges. As corollary, certain aspects of electrochemical behavior which cannot be studied in aqueous solutions can be detected and analyzed in molten systems.

This paper describes the results of some such analyses we have carried out; it deals with problems which can be met and with solutions to these problems. Many of our examples use data from our own laboratory because that is the work we know best. Other equally important problems upon which we have done little work are discussed in other papers of this symposium, and elsewhere.

Areas of our research interest include (a) the structure of liquid and solid alloys, (b) the validity of usual solution models in light of such structure, (c) the development of better models and the reconciliations of the newer models with established models of proven validity, (d) solution metastability, (e) treatment of the effects arising from the solubility of metals in their salts, primarily where significant electronic conductivity is not introduced, (f) correction for the
effects of exchange reactions between alloys and electrolytes, and (g) bare electrode emfs which pass many tests cursorily applied to "establish" equilibrium but which in truth are not equilibrium values. The analyses will be discussed from three points of view, namely: theoretically weak assumptions, missing data, and experimental hazards.

II. THEORETICALLY WEAK ASSUMPTIONS

IIA. Asymptotic Approach to the Slope of Raoult's Law for the Activity of the Dilute Solvent - A widespread misconception asserts (barring Debye-Hückel or other obvious interactions) that dilute solution data are probably in error if the solvent activities do not approach Raoult's Law behavior at solvent concentrations of perhaps 0.95 mole fraction or greater. Figure 1 represents the sort of treatment often accorded such data: As drawn the experimental evidence is for approach to a slope of ~0.5 where the Raoult's Law slope is 1.000.

There are several problems with the Raoult's Law assertion:
1. If there is experimental error, the S-curve is a poor way to correct the errors.
2. Metallic solutions tend to impose order on even dilute solutes because there is less loss of metallic resonance that way. Therefore metallic solutions can have order at relatively great dilution, thus invalidating one assumption implied by the Raoult's Law assertion. (See IIB and IID.)
3. Detectable effects of structure at great dilution can occur even with aqueous systems, e.g., with divalent sulfates. After making Debye-Hückel corrections, such solutions still do not approach the Raoult's Law slope at the greatest dilution measured by freezing point depression (1,2).
4. The thermodynamic requirement for Raoult's Law behavior applies only at unmeasurable infinite dilution, as is well known. Extending the conclusion about Raoult's Law behavior to finite dilution requires the use of simple, and possibly simplistic, models --- neither our mathematics nor our chemistry is adequate to develop an exact description. As corollary it is perhaps surprising to see our simple models working as well as they do --- sometimes these models can give excellent descriptions of reality, but (as has been said so many times to students) mixing simple models with thermodynamics can be dangerous. (See next paragraph, IIB, IIC, and IID.)
5. The slopes of the activity-composition relationships for real solutions often do not vary smoothly with composition; as a consequence of the irregular slope variation, the common power series descriptions of solution activities can be unsatisfactory. The S-curve neglects the slope problem. (See IIB, IIC, and IID.)
Figures 2-4 show experimental data bearing on the question of asymptotic approach to the Raoult's Law slope. The emf data (3,4) for molten alloys of gold in tin with molten SnCl₂ electrolyte appear to approach the ideal slope indicated in Fig. 2. As will be discussed (IID), however, for > 0.01 mole fraction of Au in Sn (log N<sub>Sn</sub> > 0.004) the activities do not approach Raoult's Law behavior asymptotically. The dilute solution vapor pressure data by isopiestic balance (5) for molten solutions of lead in cadmium do not show asymptotic approach to Raoult's Law behavior even at 0.005 mole fraction of Pb in Cd. For both silicon and iron by vapor pressure (6), the solvent activities over wide ranges of composition are much lower than the Raoult's Law values, with slopes more like 1.5 and 2.

These three systems show behavior which is rather typical of different classes of alloys. Some alloys approach Raoult's Law behavior closely at measurable concentration ranges (Fig. 2); often the precise asymptotic approach does not appear until the solute atoms are separated by three or four solvent atoms (-0.01 mole fraction of solute) on average (see IID); then the solution becomes random and Raoult's Law is approached systematically. Other alloys have behavior far from Raoult's Law even at great dilution (Fig. 3). Also (Fig. 4) some solvent activities do not seem even remotely related to Raoult's Law behavior at any measured composition.

IIB. Effects of Structural Changes Upon Component Activities - It is, of course, obvious that structure and thermodynamic properties must be interrelated. As early as 1923 Taylor (7) postulated a dissolved intermetallic compound to explain the nature of the activity-composition relationships in molten alloys which he had determined by emf using molten salt electrolytes.

For alloys the energy levels of the solvent and solute metals will normally be different, often requiring a two-band model for their description in concentrated solutions. In the case of dilute and widely-separated solute atoms, their original resonance band may disappear completely, with the bonding of such solutes to their solvent neighbors being ionic or covalent. Such nonmetallic groups of atoms (but made up from the original metallic components) may also order further in the still primarily metalliclly-bonded solvent because such ordering relieves stresses on the metallic resonance.

The concepts mentioned in the previous paragraph, or closely-related concepts, have been discussed under a wide variety of names; cybotactic groups or microheterogeneous regions (e.g., 8), interaction units (e.g., 9), complex species (5), pseudomolecules, ionic assemblies, chemical bond groups, and clusters — the last four terms are all used in one volume (10). The term clusters will be used throughout the remainder of this paper because it seems to have the most wide acceptance for describing chemically-bonded groups of atoms around a solute in a metallic solvent, especially at great dilution.
Cluster formation and the ordering of clusters, along with more extensive interactions best described by two-band models, can all work to produce sharp changes in the activity-composition relationships being followed in different composition regions by molten alloys. Examples of broad range relationships and abrupt shifts of those relationships are shown by Figs. 5 and 6, namely heat of mixing data by Kleppa (11) using molten metal calorimetry. As will be discussed (IIC, IID) the changes of behavior at ~0.8 mole fractions of Cd with Sn or Pb solutes are also shown by other kinds of measurements.

Figure 7 shows activity coefficient-mole fraction relationships for Au-Cd molten alloys from vapor pressures as measured by isopiestic balance (12). These precise and detailed data show both changes of behavior at AuCd5 and Au2Cd9 and a two-liquid region at ~0.86 mole fraction of Au. Similar behavior (no figure here) is shown in precise emf studies on Au-Sn solutions at elevated temperatures (13) wherein the Sn activities approximately follow broad range solution equations (much like the calorimetric Cd solutions, Figs. 5 and 6), but the precise behavior can only be described by equations applicable to limited compositions (as in Fig. 7).

Other examples of broad range structural relationships, as well as further comments on broad trends of structural effects with added finer detail, will be discussed after describing some sensitive ways of evaluating precise data. The present section is included merely to show examples where experimental results appear to correlate with structural phenomena.

IIC. The Random Solution Assumption for Molten Alloys - The long linear portions of the plots of heats of mixing per mole vs mole fraction in Figs. 5 and 6 correspond to the equation form, underlined letters being constants,

\[ \Delta H_{mix} = a_{\text{Cd}} + b_{\text{Cd}}^2 \]  

(1)

To the extent that the equation form is exact in describing the data, it is also true that \( \Delta H_{\text{Sn}} \) or \( \Delta H_{\text{Pb}} \) = \( -b_{\text{Cd}}^2 \), thus satisfying one criterion of regular solution theory. It is tempting to argue that the \( a_{\text{Cd}} \) terms result from the formation of essentially identical clusters of CdSnx, or of CdPbx, when solute is added to the Cd solvent. The argument seems to be an eminently plausible explanation of the experimental fact that the heat of mixing is proportional (first approximation) to the solute added. The \( b_{\text{Cd}}^2 \) term then is ascribed to the effects of random close approaches of solute-based clusters to each other; such close approaches would temporarily alter the energy associated with each cluster, and the number of such interactions occurring at any time would be directly proportional to the number of close approaches, i.e., proportional to the square of the number of solute atoms present at different compositions. A very similar argument, applied to deduce Henry’s Law plus a term to modify it for more concentrated solutions,
is given in a standard text (14); also we have elaborated and extended the reasoning to apply to the solvent behavior (15), but see IID.

Following the lines of argument discussed in the previous paragraph can lead to the development of equation forms which can be very useful in giving remarkably precise descriptions of certain experimental results. For example, there are many systems for which the solute activity closely follows Henry's Law plus $bN_2^2$ terms, i.e.,

$$a_2 = k_2N_2 + b_2N_2^2$$  \(2\)

and solutions fitting into another broad class demonstrate compliance with Elliott's Law $bN_2^2$ corrections (both sections of Fig. 3, both components in Fig. 4, and numerous other examples to be presented, including data not yet presented and lying beyond the plots in Fig. 2)

$$a_4 = 1 - k_4N_2 + b_4N_2^2$$  \(3\)

Equations 2 and 3 are not corollary through the Duhem relationship, however, and they cannot both be followed simultaneously by a single solute-solvent pair --- if the solute obeys Eq. 2 closely then the solvent closely follows Raoult's Law plus $bN_2^2$ terms, dropping higher terms,

$$a_1 = 1 - k_1N_2 + b_1N_2^2$$  \(4\)

and if the solvent obeys Eq. 3 then a close, but not mathematically exact, description of the corollary solute equation is

$$a_2 = kN_2^2 + bN_2^2$$  \(5\)

Random solutions are implicit in the derivations of all these equation forms. As noted, the equation forms are indeed followed for real systems, but some hazards of assuming random solution entropies will now be discussed. Twenty-five years ago we were warned (25) of the dangers of using too simple entropy assumptions, and the warning is still valid. Figure 8 demonstrates an example of the problem, considering data from calorimetric data (Fig. 5) and from emf measurements also taken at high temperature (7).

The temperature coefficients of emf at the various compositions establish partial molal enthalpies in agreement with those derived from the heat of mixing equation on Fig. 5, and one can consider that these values are correct. This system was chosen as a textbook example for \[ \log \gamma_1 = 2bN_2^2 \] with ideal entropies of mixing as corollary (16), and indeed if one looked only at the variation of activity with composition he could readily be lulled into thinking the solution equations do represent a random solution form. The error of the random solution assumption, combined either with the data as received or with the data plotted as regular solutions, can be seen in Fig. 8; in each case from the random solution assumption one would deduce a $\Delta H_{cd}$ in error by around 500 cal per mole in a large composition region. Correspondingly,
if one had combined measured heats with entropies estimated as ideal, he would have arrived at activities which were off by over 40%. Yet it is not uncommon to find temperature coefficients being rejected as unreliable as compared with estimated entropies, and certainly there can be problems with experimental temperature coefficients. The point here is that one may not have data available, and he may have to make the random solution assumption as better than other guesses. The random solution assumption, however, may be simplistic because it neglects the local entropy changes as nonmetallic clusters form in the metallic host.

Figure 9 for Zn-Sn by calorimetry (11) and by emf (7,17) again shows weakness of the random solution assumption. (The theory behind the Houseman plot of emf data will be discussed in the next section.) Although the calorimetric data would seem to be consistent with random solution behavior, the activities established by emf are very different from those one would calculate if he used the form of the heat of mixing equations to justify regular solution treatments, including the assumption of ideal entropies of mixing. Note that both kinds of measurements, i.e., calorimetry and emf, show a structural change at about 0.35 mole fraction of Sn; such a change of behavior often reflects nonrandom solutions.

IID. Some Useful But Unorthodox Plots of Thermodynamic Data - The nature of many kinds of experimental errors, and their effects on the uncertainties of activity calculations, made the experimental testing of Eq. 2 much easier than similar testing of Eq. 3 — systems unequivocally and closely following Eq. 2 were noted long ago, but equipment developed since WW-II has been needed to demonstrate clear obedience to Eq. 3. In consequence most ways of plotting and presenting data have been designed to be consistent with the Eq. 2 - Eq. 4. Duhem corollaries, and correspondence with Eq. 3 has often been missed, as will be demonstrated shortly.

Dundee plots of changes of solvent activity with changes of solute composition vs solute composition, i.e., \( (1 - a_i)/N_2 \) vs \( N_2 \), can be very useful both in detecting changes of solution behavior and in distinguishing between obedience to solvent Eqs. 3 or 4. If a straight line describes the data then Eq. 3 at least is valid; if the line passes the ordinate at 1.000 then the special case of Eq. 4 is obeyed.

Such a plot is shown in Fig. 10. Also included are four data points for concentrations greater than those plotted in Fig. 2. Note that a change of slope appears at \( N_{Au} = 0.01 \). For smaller concentrations the data lie on \( (1 - a_i)/N_2 = 1.000 \) --- thus \( a_1 = 1 - N_2 = N_1 \) and Raoult's Law is followed. At larger concentrations the apparent intercept is not 1,000, and Eq. 3 is followed, although the system still is very close to asymptotic approach to the Raoult's Law slope.

The Au-Sn behavior is not unusual, e.g., see plots of Ni-Cd and Sn-Hg behavior in later sections. We offer the following interpreta-
tion of the behavior shown in the plots: (1) In line with the concept of clusters discussed in IIB, the slope shift occurs when the clusters lose the order imposed on them by the metallic resonance; below 0.01 mole fraction of Au the AuSn\textsubscript{x} clusters remain in nonmetallic bonding to their neighbors, but the clusters themselves move randomly about the solution. For the higher concentrations of Au-Sn the AuSn\textsubscript{x} clusters, or other clusters, have an additional ordering imposed by the metallic resonance of the liquid Sn solvent. (2) The trends of random solution free energy are followed approximately in spite of the differing details of solution behavior, and regular solution theory in this case remains a very good approximation of the broad trends of solution activity although, of course, the solution fine structure is too complex to be truly regular.

Solution fine structure such as that shown for Au-Sn in the Dundee plot above is not distinguishable in many other kinds of plots. As was already noted the plot in Fig. 2 was not adequate, and a plot of activity vs mole fraction is also not sensitive enough. Another group of plots involves the log of the activity coefficient and the Margules (18) power series in constants and the mole fraction of the other component

\[
\log \gamma_i = aN_2 + bN_2^2 + cN_2^3 + \ldots
\]

Margules assumed that a single set of constants would apply over the whole mole fraction range, 0 to 1, and he evaluated \(a = 0\) at infinite dilution. Also, he truncated the remaining series at a single term. Similar reasoning is followed today, although now the constants are accepted normally for smaller ranges of composition, e.g., a range of 0.2 in mole fraction at the ends of the presumed single phase region.

There is no thermodynamic reason to assert that the Margules series has any validity in interpolating between uncertain experimental measurements, although experience may show that a truncated series has practical usefulness --- clearly some way is needed to arrive at the slopes of the activity-composition relationships because only isolated points can be measured. Furthermore, the major basis for asserting that \(a = 0\) is lost for all finite compositions if the measurements show structured solutions of the types being discussed here for alloys. Thus common plots such as \(\log \gamma_i\) vs \(N_2\) or \((\log \gamma_i)/N_2^2\) vs \(N_2\) can be misleading since often \(a \neq 0\).

The Houseman plot of \((\log \gamma_i)/N_2\) vs \(N_2\) is usually far better than the two plots mentioned in the preceding paragraph. Here a straight line indicates conformity to the first two power series terms in Eq. 6. If such a plot does indeed show that \(a = 0\), then one may be justified in seeking higher terms with a plot involving \(N_2^2\). Recall that the Houseman plot in Fig. 9 brought out the structural phenomenon which was also disclosed by the heat of mixing data.
Figure 11 compares the Pb-Cd vapor pressure data from Fig. 3 using Houseman and linear \( \alpha \)-function plots. Examination of the activity-mole fraction plot in Fig. 3 will show a structural shift at about 0.99 mole fraction of Cd, although random solution behavior (asymptotic approach to the slope of Raoult's Law) is not yet demonstrated. The same structural effect is clear in the upper Houseman plot. In contrast, the linear \( \alpha \)-function plot wipes out that information and is most difficult to extrapolate to unmeasured dilution.

The relationship between the Houseman and Dundee plots is as follows: The Houseman plot is tied to an empirical power series for which it is not easy to deduce a physical model; it does, however, offer a better broad range fit (neglecting the fine structure) for many systems than does the Dundee plot. Where fine structure is being analyzed it usually is not experimentally possible to distinguish between the aptness of use whether the Houseman or the Dundee form has been chosen. The Dundee plot can be modified better for midregion use in some cases (e.g., where the structural change occurs at \( \text{Au}_2\text{Cd}_9 \) in Fig. 7); here the Dundee plot uses \( (c - a_0)/N^2 \) vs \( N^2 \), effectively changing the solution standard state being used for reference. Thus \( 1 \) (associated with the pure solvent) is replaced by \( c \) (a constant associated with a different reference state, in this case the liquid intermetallic compound, \( \text{Au}_2\text{Cd}_9 \)).

The Dundee plot is tied to the useful but simplistic molecular model which leads to prediction of Eqs. 2 and 3 as reasonable equation forms for certain solute and solvent behaviors. The developments are simplistic because they assume only short-range bonding forces and neglect the long-range movement of solvent atoms far from a solute --- such movement is necessary if microscopic reversibility is to be maintained for the liquid-vapor equilibrium for the solvent.

Figure 12, again for Pb-Cd, offers a phase diagram and a Houseman plot confirming the existence of the structural change pointed out in Fig. 6. Judging from the demonstrated fine structure in dilute solutions shown in Fig. 11, it seems reasonable to surmise that the data might also show more details of structure if the present data were more precise.

IIE. Corrections in EMF Calculations - One must be careful in some cases in converting emf readings to activities, as when metal dissolves into the molten salt electrolyte. In some cases (e.g., Ca-CaCl\(_2\), 19) an element of electronic conduction is introduced, leading to internal drain of the cell. In other cases (e.g., Cd-CdI\(_2\)) there is no significant electronic conduction but the value of \( n \) in \( \Delta G = -nF \varepsilon \) is changed significantly. Figure 13 for Ni-Cd molten alloys with molten CdI\(_2\) electrolyte (20) shows a Dundee plot with a structural break at about 0.01 mole fraction of Ni. Below this composition the solution is apparently random, and Raoult's Law behavior is approached asymptotically.
These calculations required the use of $n = 1.87$, not 2, for the average ion charge, thus correcting for the Cd$_{4}^{++}$ formed when Cd dissolves in CdI$_{2}$ electrolyte. If $n$ is assumed to be 2 in $\Delta G = -nFE$ then the apparent activities lie several percent off the Raoult's Law slope in the dilute limit. Both correction for $n$ and correction for exchange reactions between solvent metals and the electrolyte will be discussed further in III.

Bare electrodes can also necessitate correction or rejection of emf measurements, if these electrodes contact the electrolyte. The problem develops when a surface film (e.g., an oxide layer) passes current but is stable against direct reaction with the electrolyte. Then the system can be electrochemically active but chemically at equilibrium with the outer surface of the film, and such a system can pass many usual tests of equilibrium yet give spurious emf values.

IIIF. Duhem Integrations - The Sn-Hg system has been measured by emf using electrolytes of pure SnCl$_{2}$ (21,22) and of SnCl$_{3}$ dissolved in water, glycerine, or mixed molten halides (refs. in 21). All measurements agree in showing an unusual variation of emf with composition. Figure 14 shows emf data plotted along with calculated lines based on random solution entropies and on solution entropies with 2/3 the random solution values; the latter entropy values could be broken out of the temperature coefficients of emf at various compositions (21); the 0.0916 is based on the composition of the reference electrode.
This system shows again a transformation from structured (Sn chains in Hg matrix?) to random at about 0.01 mole fraction of Sn in Hg. The structural complexity can be considered well documented by several groups of workers, and the data can be accurately Duhem integrated to predict the Hg vapor pressures at the same temperature. Conant has applied a correction to his earlier calculations (23) and the Hg vapor activities now agree very closely with prediction from Duhem integration from the emf values for these structured solutions.

In spite of excellent agreement with theory shown by the Sn-Hg system, however, one must be very careful in his Duhem integrations of alloy data. For solids the CeCd.5 microphases indicate the sorts of problems one can meet: In this case what appears to be a single phase region was demonstrated by vapor pressure (24) and X-ray crystallography to contain at least 70 interrelated superlattices, each of which thermodynamically constitutes a separate phase. These phases can rapidly reach equilibrium of the Cd component with the nucleated structure, but nucleation of more stable structures can be difficult, and one cannot accurately establish the path of integration which would correspond to equilibrium through the microphases.

For this CeCd.5 region, N_{Cd}/N_{Ce} is not huge, and errors in the integration path used for calculation are not too critical. For similar behavior in the end regions of composition where the ratio would be very large, however, large integration errors could be introduced if one tried to extrapolate to infinite dilution.

For molten alloys, as well, there can be long-lasting metastability, and there is some indication that structural complexity can "pile up" in dilute solutions --- apparently the structural changes reflect distance between atoms more than mole fraction; so long as the system is not so dilute as to become random, the structural changes become more and more frequent in dilute solution on a mole fraction basis. Again such complexity can cause problems in extrapolating Duhem integrations to infinite dilution, but the problem is less serious for concentrated solutions.

III. MISSING DATA

When one attempts to correct measured emfs for the effects of metal solubility in the molten salt, or for the exchange reaction between the electrolyte and the less active alloy component, he usually needs unmeasured data: The accurate calculations (20) require ionic concentrations and mobilities. Although extensive free energy tables are available to start the exchange reaction calculations, the activity coefficients usually are missing, and few mobilities have been determined in the electrolytes of interest. Usually one must guess the activity coefficients and mobility ratios.
IV. EXPERIMENTAL ERRORS

In concluding this presentation, it is probably worthwhile to point out some sources of experimental error or insufficiency which frequently lead to data scatter. With such scatter, sensitive plots of the types discussed can have little value with those data.

Inadequate stirring can be a major problem with molten salt emfs. Apparently the clusters in the alloys can have very slow rates of diffusion, and even a five cc sample standing at high temperature overnight may not have come close to equilibrium. In the electrolyte the reaction with the alloy or reference electrode can take place very slowly across the interface, and again much stirring is needed to bring the system to equilibrium.

Temperature control is very important at the level of precision needed for studies such as those discussed here. Concentric, heavy-walled, metal cylinders placed around the emf cell and next to the furnace control thermocouple can smooth controller variation and give very uniform temperatures around the cell.

Electrode lead insulation can be very important where the leads pass through the electrolyte. (See IIE.)

Mixed electrolytes are a source of serious problems because it is essentially impossible to get identical starting compositions in the two sections of the emf cell. In addition they add to the activity coefficient and mobility uncertainties. Finally common mixed electrolytes, e.g., LiCl-KCl, sometimes add to the problem of formation of reactive hydroxide impurities.

Cell movement in the furnace changes temperatures and heat flow patterns and can be a source of experimental scatter. If possible one would like to add solute from a sidearm and into the cell to avoid re-positioning the cell as material is added.

ACKNOWLEDGMENTS

It is not practical to name all the people who contribute to our understanding of scientific problems, but especially important help to me came from D. R. Conant and B. L. Houseman. This work was supported by the U. S. Energy Research and Development Agency.

REFERENCES

1. G. R. B. Elliott, "Some Individual Ion Correlations Among Aqueous Freezing Point Depression Measurements," Los Alamos Scientific Laboratory Report No. LA-3891, 1968.
2. D. R. Conant, "The Relationship of Certain Measurements on Aqueous Electrolyte Systems to the Debye-Hückel Theory, to Raoult's Law, and to Thermodynamics," Los Alamos Scientific Laboratory Report No. LA-4428, 1970.
3. J. A. Yanko, A. E. Drake, and F. Hovorka, Trans. Electrochem. Soc., 89, 357 (1946).
4. G. R. B. Elliott and J. F. Lemons, J. Electrochem. Soc., 114, 935 (1967).
5. H. S. Swofford, Jr. and G. R. B. Elliott, Inorg. Chem., 7, 666 (1968).
6. Ts. Syuu, A. Yu. Polyakov, and A. M. Samarin, Izv. VUZ Chern. Met., 1961, No. 1, 12.
7. N. W. Taylor, J. Amer. Chem. Soc., 45, 2865 (1923).
8. S. F. Khokhlov, "Some Problems Pertaining to the Structure of Liquids" in A. M. Samarin, "Structure and Properties of Liquid Metals," Academy of Sciences of the USSR, Baikov's Institute of Metallurgy, Moscow, 1960, translated in AEC-tr-4879, May 1962.
9. G. R. B. Elliott, D. R. Conant, H. S. Swofford, Jr., and B. L. Houseman, "Liquid Structure as Deduced from Precise Thermodynamic Measurements," in "High Temperature Technology," Proceedings of the Third International Symposium, Asilomar, California, 1967, Butterworths, London, 1969, Organizer, D. D. Cubicciotti.
10. S. Takeuchi, "The Properties of Liquid Metals," John Wiley and Sons, New York, 1973.
11. O. J. Kleppa, J. Phys. Chem., 59, 354 (1955).
12. G. R. B. Elliott, C. C. Herrick, J. F. Lemons, and P. C. Nordine, High Temp. Sci., 1, 58 (1969).
13. P. L. Robinson and G. R. B. Elliott, High Temp. Sci., 4, 1 (1972).
14. K. S. Pitzer and L. Brewer, revision of G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1961, p. 240.
15. G. R. B. Elliott, J. F. Lemons, and H. S. Swofford, Jr., J. Phys. Chem., 69, 933 (1965).
16. J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Third Edition, Reinhold Publishing Co., New York, 1950, p. 35.
17. Z. Kozuka, J. Moriyama, and I. Kushima, J. Electrochem. Soc., Japan, 29, E106.
18. M. Margules, Sitzber. Akad. Wiss. Wien., 104, 1243 (1895).
19. D. R. Morris, C. Aksaranan, B. S. Waldron, and S. H. White, J. Electrochem. Soc., 120, 570 (1973).
20. D. R. Conant, J. Chem. Eng. Data, 16, 430 (1971).
21. G. R. B. Elliott, J. Electrochem. Soc., 115, 1143 (1968).
22. C. S. Weaver, R. C. Whitelatch, D. J. Jerome, and G. R. B. Elliott, High Temp. Sci., 5, 155 (1973).
23. D. R. Conant and G. R. B. Elliott, High Temp. Sci., in press.
24. G. R. B. Elliott and J. F. Lemons, "Nonstoichiometry, Order, and Microphases in CeCd₃-x Solid Solutions," Advances in Chemistry Series, No. 39, Ed. R. F. Gould, American Chemical Society, Washington, D.C., 1963, p. 153.
25. J. F. Elliott and J. Chipman, J. Amer. Chem. Soc., 73, 2682 (1951).
ACTIVITY

Fig. 1 - Hypothetical representation of an unjustified asymptotic approach to the Raoult's Law slope at measurable concentrations.

Fig. 2 - Experimental data showing apparently asymptotic approach to the slope of Raoult's Law for dilute, molten solutions of Au in Sn as measured by molten salt emf cells. However, see text and Fig. 11.

Fig. 3 - Experimental data which fail to show asymptotic approach to the slope of Raoult's Law even for molten alloys containing less than 0.01 mole fraction of Pb in Cd as measured by isopiestic balance vapor pressures.

Fig. 4 - Experimental vapor pressure data for liquid Fe-Si solutions showing slopes far larger than the Raoult's Law slope. These slopes hold over large concentration regions, and no experimentally significant evidence of asymptotic approach to the Raoult's Law slope is shown.

Fig. 5 - Experimental data showing apparent non-ideal behavior of a binary system at 1823 °K.

Fig. 6 - Experimental vapor pressure data for liquid Fe-Si solutions showing slopes far larger than the Raoult's Law slope. These slopes hold over large concentration regions, and no experimentally significant evidence of asymptotic approach to the Raoult's Law slope is shown.
Fig. 5 - Calorimetric heat of mixing data showing structural change for liquid Sn-Cd solutions at about 0.8 mole fraction of Cd.

Fig. 6 - Calorimetric heat of mixing data showing structural change for liquid Pb-Cd solutions at about 0.8 mole fraction of Cd. See phase diagram and emf data in Fig. 11 which also show the structural change.

Fig. 7 - Detailed isopiestic balance vapor pressure data showing changes of Cd activity coefficient with composition at 928K. Structural changes in the liquid occur at the stoichiometry for AuCd and AuCd⁺, and a two-liquid region appears near 0.86 mole fraction of Au.

Fig. 8 - Experimental heat of mixing data for liquid Sn-Cd solutions derived from the temperature coefficients of emf and from calorimetry (see Fig. 5) as compared with evaluated heats of mixing assuming ideal entropies of mixing. Although the experimental values agree reasonably well, and although the heat of mixing equation (Fig. 5) suggests regular solution behavior, still the entropies of mixing are far from ideal and regular solution calculations will not produce accurate activities from calorimetric data in this case.
Fig. 9 - Calorimetric (upper plot) and emf (lower plot) data for Zn-Sn molten alloys. The Houseman plot of the emf data emphasizes the structural effects upon the Zn activity as composition is shifted. Both methods of measurement show the structural change at about 0.35 mole fraction of Sn. Although the calorimetric data suggest regular solution behavior, the emf data show that the entropies of mixing are far from ideal.

Fig. 10 - Molten Au in Sn emf data as in Fig. 2 are plotted using a Dundee plot of changes of solvent activity with solute composition vs solute composition, i.e., \( \log \gamma_i / \gamma_N \) vs \( x_i \). These plots show that, although the activities seemed in Fig. 2 to be asymptotically approaching the slope of Raoult's Law throughout the range of measurement, in fact only the measurements at less than 0.31 mole fraction of Au do actually follow such asymptotic approach. At larger concentrations there is a different liquid structure which is described by a different equation form.

Fig. 11 - A Houseman plot of the Pb-Cd data in Fig. 3 shows the change of behavior at about 0.01 mole fraction of Pb (upper portion of plot). Lower points are plotted according to linear alpha-function which is indeterminate at low concentrations and does not show solution structural effect. The other line which dips below the graph and rises later corresponds to an attempt to fit the data by regular solution theory.

Fig. 12 - Phase diagram and Houseman plot of Pb-Cd molten alloys. These exhibits confirm the change shown in Fig. 5 based on calorimetric work.