

Lawrence Berkeley National Laboratory

Recent Work

Title

MATHEMATICAL REPRESENTATION OF SIZE AND ELECTRONIC FACTORS

Permalink

<https://escholarship.org/uc/item/4dz7n9q6>

Author

Brewer, L.

Publication Date

1982-11-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY

Materials & Molecular Research Division

JAN 11 1983

LIBRARY AND
DOCUMENTS SECTION

Presented at the 1982 Annual Meeting of the Materials
Research Society, Boston, MA, November 1-4, 1982

MATHEMATICAL REPRESENTATION OF SIZE AND ELECTRONIC
FACTORS

Leo Brewer

November 1982

TWO-WEEK LOAN COPY
*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782.*



LBL-15220 2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

MATHEMATICAL REPRESENTATION OF SIZE AND ELECTRONIC FACTORS

(Presented at the 1982 Annual Meeting of the Materials Research Society,
November 1-4, 1982, Boston, Massachusetts.)

LEO BREWER

Materials and Molecular Research Division, Lawrence Berkeley Laboratory and
Department of Chemistry, University of California, Berkeley, CA 94720

ABSTRACT

The relative sizes of the atoms and their electronic configurations are important factors in determining the thermodynamic properties of metallic phases. The regular solution model provides for an asymmetric excess Gibbs energy when there is a size difference, but the actual degree of asymmetry does not correspond to crystallographic sizes. This is due in part to the effect of electronic configurations upon the asymmetry of the Gibbs energy. The Hume-Rothery Rules indicate that the bcc, hcp, and ccp structures are associated with characteristic outer-shell electron per atom concentrations. The electronic factors require modification of the usual definition of internal pressure as used in the regular solution theory. Rather than using the energy of vaporization to the ground atomic state, the energy of vaporization to the valence state atom, which has the same electronic configuration as in the condensed state, is a more appropriate measure of the degree of cohesion and the internal pressure. The problems of providing mathematical expressions that accommodate the contributions of internal pressure, electronic factors, and size factors are discussed.

The starting model for treating size effects is the regular solution [1,2,3] which yields for a binary liquid solution of components 1 and 2, $\ln \gamma_1 = v_1 a \phi_2^2$ and $\ln \gamma_2 = v_2 a \phi_1^2$. The activity coefficients γ_1 and γ_2 are taken with respect to the pure standard states. ϕ_1 and ϕ_2 are the volume fractions

$\frac{x_1 v_2}{x_1 v_1 + x_2 v_2}$ and $\frac{x_2 v_1}{x_1 v_1 + x_2 v_2}$ where v_1 and v_2 are the molal volumes of pure 1 and

2, respectively, and x_1 and x_2 are the respective molefractions. With the assumption that the interaction between pairs of unlike atoms or molecules is the geometric mean of the interaction between pairs of like atoms or molecules, $a = (1/RT)[(\Delta E_1/v_1)^{1/2} - (\Delta E_2/v_2)^{1/2}]^2$ where ΔE_1 and ΔE_2 are the ener-

gies of vaporization of pure liquids 1 and 2. The above equations also assume that the mixing occurs under constant volume conditions and that the entropy of mixing is ideal.

It is more convenient to work with powers of molefraction than powers of volume fraction and the expansion of the ϕ^2 terms as a power series in molefraction yields, with truncation after the cubic term,

$$\ln \gamma_1 = bx_2^2 + cx_2^3 \text{ and}$$

$$\ln \gamma_2 = (b + 1.5c)x_1^2 - cx_1^3$$

where $b = v_1 a$ and $(b + c)/(b + 0.5c) = v_2/v_1$.

These equations are merely a first approximation as the mixing is normally not at constant volume and $\Delta E/v$ is not independent of temperature. Thus the entropy of mixing can not be ideal and the b and c terms include contributions from the excess entropy of mixing [9]. In addition, the assumption that the interaction between unlike atoms will be the geometric mean of the interaction between like atoms is not rigorous. Some modifications of the equations provided by the simple theory are necessary.

The relationship between b and c and the ratio of molal volumes is rarely found to hold for metallic solutions. This is due to the fact that there are other contributions to the Gibbs energy in addition to those assumed in the regular solution equation derivation. The cohesion between atoms is described in terms of the internal pressure parameters $\Delta E/v$ where ΔE is the energy of vaporization. For most metals the vaporization takes place to a gaseous atom which is in a different electronic state than the predominant electronic state of the metal. The lanthanide metals provide a most striking example. The energies of vaporization drop off rapidly from lanthanum to samarium and from gadolinium to thulium which would indicate according to the variation of $\Delta E/v$ that the metals become more weakly bound with increasing atomic number. However, the melting points vary in the opposite direction indicating that the cohesion increases with increasing atomic number. Also the use of the normal energies of vaporization of the lanthanides to evaluate the internal pressures would indicate that their solubilities in one another would be rather small, which is contrary to observation. If one takes the energy of vaporization of the metal to a gaseous atom of the same electronic configuration as in the metal, then one has a more correct measure of the cohesion [5]. Thus a simple mathematical modification of replacing ΔE_1 and ΔE_2 in the expressions for the internal pressure parameters by ΔE_1^* and ΔE_2^* , the energies of vaporization to the valence state of the gaseous atom with the same electronic configuration as in the condensed metal, removes most of the discrepancy.

Additional modifications are necessary to adapt the regular solution model to metals. The geometric-mean assumption has no rigorous basis and actual behavior corresponds more closely to the interaction between unlike atoms being half way between the arithmetic and the geometric means. This is due in part to an effect of size disparity discussed below. The resulting equation for the b and c terms of the activity coefficient equations becomes

$$b + c = (v_1/2RT) [(\Delta E_1^*/v_1)^{1/2} - (\Delta E_2^*/v_2)^{1/2}]^2$$

where the ΔE^* values are the energies of vaporization to the gaseous valence state. For example, for Lu metal, ΔE^* would be for the vaporization to the electronic gaseous state corresponding to the $4f^{14}5d6s6p$ configuration rather than to the $4f^{14}5d6s^2$ configuration of the gaseous ground state. Brewer [5,6] has compiled the spectroscopic data needed to evaluate the promotion energies and Lamoreaux [7] has tabulated the values of v and ΔE^* needed to more accurately represent the internal pressures of the elements.

There are additional contributions in the solid state due to size disparities and there are additional electronic interactions that must be considered in general. However, when one is mixing transition metals of the left hand side of the periodic table, the equations given above can represent the thermodynamic data for the liquid solutions with good accuracy. In the compilation [8] of thermodynamic data and phase diagrams for the one hundred binary systems of molybdenum from hydrogen to lawrencium, it was possible to calculate the phase diagrams for mixtures of molybdenum and the lanthanides as well as molybdenum with transition metals of the first six groups using the modified regular solution equations described above for the liquid solutions.

More generally, additional modifications are necessary. When atoms of different sizes are mixed in a solid lattice with equivalent sites such as cc(cI2), hcp(hP2), or ccp(cF4) lattices, there will be a strain energy which increases the activity coefficient and increases the values of b and c over that given by the regular solution equation. On the other hand, there are structures with non-equivalent lattice sites such as σ (tP30), μ (hR39), R(hR59), the Laves phases (cF24, hP24, hP12), and similar phases which achieve better space utilization with components of unequal size and appropriate size disparity will reduce the values of b and c . The atoms in the liquid phase are not restricted to equivalent sites and size disparity in a liquid can result in reduction of the values of b and c . As mentioned above, this is part of the basis for reducing the values of b and c below the values indicated in the initial regular solution equation based on the geometric mean assumption.

The effect of size disparity in increasing the b and c values for solid phases with equivalent lattice sites and decreasing the b and c values for liquid phases is shown by the restricted ranges of composition for the solid phases even when the liquid phases are miscible. The effect of size disparity and internal pressure differences on the b and c values in the solid is particularly clear when one compares the solubilities of various metals in the bcc and ccp phases of Th and Pu which have markedly different sizes and internal pressures [9]. The solubilities in Th of the alkali metals, alkaline earth metals from calcium through radium and Eu and Yb will be very small because of the small internal pressures compared to thorium. The size disparity will greatly reduce the solubilities of the third period elements from Sc to Ge even when the internal pressure differences are not large. Because of the much higher internal pressures of transition metals of the fourth and fifth periods for groups five through eight, their solubilities in thorium will be small. The solubilities in Th of the platinum group metals will be greatly reduced because of the strong General-Lewis-Acid-Base interaction producing very stable intermetallic compounds. This leaves only Y, Zr, La, Hf, and most of the lanthanides and lighter actinides with large solubilities in thorium. In contrast, plutonium with a smaller size will dissolve much larger amounts of the metals of the third period from Sc to Ge. The metals

with appreciable solubility in Pu will be restricted to Al, Sc, Ti, Ga, Zr, Hf, Ce-Lu except Eu and Yb, and Np to Fm.

The major difficulty with the simplest form of the regular solution equation is that it does not provide the proper asymmetry. The simple regular solution equation provides for asymmetric equations for γ_1 and γ_2 as given by $(b+c)/(b+0.5c) = v_2/v_1$, but the actual degree of asymmetry or the ratio of c to b does not correspond to the crystallographic sizes. This is due in part to the effect of changing electronic configurations upon the asymmetry of the Gibbs energy. The Hume-Rothery Rules indicate that the bcc, hcp, and ccp structures are associated with characteristic outer-shell electron per atom concentrations. As metals with differing electron concentrations are mixed, the atoms will change their electronic configurations and therefore their sizes. Thus the metals do not have one characteristic size, but in some instances a series of sizes depending upon the electronic environment. Normally, a solid metal will melt to a liquid of higher molal volume and the melting point will increase with increasing pressure. However, increasing pressure will favor those electronic configurations which use the greatest number of inner shell electrons for bonding [10]. Upon increasing the pressure, the increasing number of atoms with different electronic configurations and different sizes will result in a higher space utilization as in the Laves phases and the liquids will become more dense than the simple solid, e.g. bcc. Thus the melting points which initially increase with increasing pressure are expected to reach a maximum and then decrease until a solid with non-equivalent lattice sites can compete in space-utilization with the liquid. Also addition of various solutes will alter the electronic configurations. Non-transition solutes will make it more difficult to bond inner shell d orbitals efficiently and the electronic configurations with a reduced number of d electrons will be favored. Ellner [11] presents some striking examples of the drastic change in size with change in electronic configuration. Metals such as Ni, Pd, and Pt must promote several d electrons to p orbitals to achieve the high degree of cohesion that is observed. Thus Pd which has the gaseous ground state $4d^{10}$ must promote to approximately $4d^7 5s 5p^2$ in the fcc structure to make a total of five to six electrons available for bonding. Au which has the gaseous ground state $5d^{10} 6s$ must promote to approximately $5d^8 6s 6p^2$ to make a total of four to five electrons available for bonding and to achieve the high level of cohesion demonstrated by its high boiling point. However, if these metals are alloyed with non-transition metals whose outer shell orbitals have a much different distribution in space than the inner shell d orbitals, the bonding contribution of the d electrons is reduced so much that it is not possible to offset the high promotion energy penalty that must be paid and the degree of promotion is reduced. With fewer electrons used in bonding, the atoms are less tightly held and the molal volumes increase dramatically when there is an excess of non-transition metal. When transition metals such as Cu, Ag, and Au which are making good use of d electron bonding are mixed with other transition metals such as Ni, Pd, and Au, Vegard's Law is obeyed and the atoms are able to retain their normal sizes. However, addition of Zn, Ga, In and other non-transition metals cause a dramatic decrease in the bonding of the transition metals and a resulting striking increase in size when an excess of non-transition metal has been added.

There are other interrelations of size and electronic configuration such as the Generalized Lewis-Acid-Base interactions [12,13], which produce very strong interactions between transition metals from the left hand side of the

Periodic Table with transition metals from the right hand side of the Periodic Table. In such circumstances the usually positive values of b in the Regular Solution equations must be replaced by negative values.

In spite of all these complications, it is possible to maintain a relatively simple mathematical expression. For example, if one wishes to calculate the boundaries of two binary phases saturating one another, one rarely has to go to more complicated mathematics than the equations representing equal fugacities of the two components as given here [14].

$$\ln x + b_x(1-x)^2 + c_x(1-x)^3 + e_x = \ln(1-y) + (b_y + 1.5c_y)y^2 - c_y y^3$$

$$\ln y + b_y(1-y)^2 + c_y(1-y)^3 + e_y = \ln(1-x) + (b_x + 1.5c_x)x^2 - c_x x^3$$

x is the molefraction of component 1 in the phase richest in component 2 and y is the molefraction of component 2 in the phase richest in component 1. The subscript x refers to the value of the regular solution parameters in the phase where x is smallest and the subscript y refers to the value in the phase where y is smallest. The e terms come from the standard Gibbs energy changes. For example for a solid with largely component 1 in equilibrium with a liquid phase $e_x = \Delta G_{f,1}^\circ/RT = \Delta H_{f,1}^\circ/RT - \Delta S_{f,1}^\circ/R$ and $e_y = -\Delta G_{f,2}^\circ/RT = -\Delta H_{f,2}^\circ/RT + \Delta S_{f,2}^\circ/R$ where the subscript f refers to the fusion process. As noted above, any real solution will rarely have ideal entropies of mixing and the regular solution parameter values are given by $b = b_h/T - b_s$ and $c = c_h/T - c_s$ where the subscript h refers to the enthalpy contribution and subscript s refers to the excess entropy contribution. In some instances, when it may be more convenient to use hypothetical Henry's Law standard states in place of the pure standard states, then additional enthalpy and entropy terms are added to the e_x and e_y values.

The solution of the two equations to obtain the boundary concentrations is simple and can be readily done with a programable hand calculator and programs for such calculations are available [14]. In some instances a more complicated equation can be avoided by change of components. Darken [15] has pointed out that the b and c values will behave in a simple way for part of the composition range and then change very drastically. This happens when there is a change in electronic configuration at a titration point. When this region of rapid change is close to the composition of a congruently melting phase, it is often convenient to take that composition, e.g. AB_2 , as a component and treat the system as an $A-AB_2$ system for compositions richer in A than AB_2 and treat it as a $B-AB_2$ system for the other half. The equations for calculating the solidus and liquidus boundaries of the AB_2 are considerably simplified by this process. There is the slight disadvantage that the calculated curves will violate thermodynamics in yielding a pointed liquidus and solidus at the maximum melting point, but the difference between the approximately calculated compositions and the correctly calculated compositions is negligible.

Time does not permit a detailed discussion of the various models that can be used to estimate some of the regular solution parameters. Chemical bonding models are particularly useful because they are equally applicable to metals and non-metals and to condensed and gaseous species [16,17]. Because of their wide applicability, it is almost always possible to find data that can be used to check the accuracy of a given model. The use of a model that starts with

the core electrons already accurately represented through the availability of spectroscopic data for the various valence states considerably increases the accuracy because the desired Gibbs energy is not obtained from the small difference between large numbers but is directly obtained from enthalpies and entropies of bonding that are provided by the models. It is particularly important to be able to use these predictive models, not only when no data are available, but also when data are available that might be seriously in error [18]. The process of carrying out mathematical operations to calculate phase diagrams can not be an automatic process without input of serious thought at every step. It is particularly important not to let the experimental data fix the values of all the parameters b_h , b_s , c_h , c_s , e_x , and e_y . Even extremely small experimental errors will cause these parameters to work against one another and take quite unreasonable values [18]. It is most important to use predictive models to select values of at least e_x , e_y , b_s , and c_s if they are not available from direct experiments. Then with only b_h and c_h as independent parameters, the fitting procedure is less likely to yield ridiculous values.

ACKNOWLEDGEMENT

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC03-76SF00098.

REFERENCES

1. J. H. Hildebrand, R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed., Reinhold Publishing Co., New York, 1950, reprinted by Dover, 1964.
2. J. H. Hildebrand, R. L. Scott, "Regular Solutions," Prentice-Hall, 1962.
3. J. H. Hildebrand, J. M. Prausnitz, R. L. Scott, "Regular and Related Solutions," Van Nostrand Reinhold, 1970.
4. G. N. Lewis, M. Randall, "Thermodynamics," 2nd ed., revised by K. S. Pitzer and L. Brewer, McGraw-Hill, 1961.
5. L. Brewer, J. Opt. Soc. Am. 61, 1101-11 (1971).
6. L. Brewer, "Phase Stability in Metals and Alloys," ed. by R. Rudman, J. Stringer, R. I. Jaffee, pp. 39-61, 241-9, 344-6, and 560-8, McGraw-Hill, 1967.
7. R. H. Lamoreaux, Melting Point Gram-Atomic Volumes and Enthalpies of Atomization for Liquid Elements, Lawrence Berkeley Laboratory, Rep. LBL-5159, July 1976.

8. L. Brewer, R. Lamoreaux, "Molybdenum, Physiochemical Properties of its Compounds and Alloys," At. Energy Rev., Special Issue 7, Parts I and II, IAEA, Vienna, 1980.
9. L. Brewer, Plutonium 1970 and Other Actinides," TMS Metallurgy Series, Vol. 17, pp. 650-58, Ed. W. N. Miner, TMS AIME, N.Y. (1970).
10. L. Brewer, Science 161, 115-22 (1968).
11. M. Ellner, J. Less-Common Metals 75, P5-P16 (1980).
12. L. Brewer, Acta Met. 15, 553-6 (1967).
13. L. Brewer, P. R. Wengert, Metall. Trans. 4, 83-104, 2674 (1973).
14. L. Brewer, "Calculator Programs for Thermodynamic Data and Phase Diagrams Calculations," Lawrence Berkeley Laboratory report LBL-5485, May 1978.
15. L. S. Darken, Trans. Met. Soc. AIME 239, 80-96 (1967).
16. L. Brewer, The Role and Significance of Empirical and Semiempirical Correlations, pp. 155-74, in: Structure and Bonding in Crystals, Vol. I, Academic Press, 1981.
17. L. Brewer, J. S. Winn, Models for Calculation of Dissociation Energies of Homonuclear Diatomic Molecules, Faraday Discussions No. 14, 126-35 (1980).
18. L. Brewer, Principles of Critical Evaluation and Compilation of Phase Diagrams and Thermodynamic Data, pp. 196-206, in: Calculation of Phase Diagrams and Thermochemistry of Alloy Phases, Ed. Y. A. Chang, J. F. Smith, AIME Conf. Proceedings, 1979.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720