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elsevier

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ELSEVIER SCIENTIFIC PUBLISHING COMPANY
Amsterdam — Oxford — New York 1978

ELSEVIER SCIENTIFIC PUBLISHING COMPANY
335 Jan van Galenstraat
P.O. Box 211, Amsterdam, The Netherlands

Distributors for the United States and Canada:

ELSEVIER NORTH-HOLLAND INC.
52, Vanderbilt Avenue
New York, N.Y. 10017

Library of Congress Cataloging in Publication Data

Wisniak, Jaime.

Mixing and excess thermodynamic properties.

(Physical sciences data ; v. 1)

I. Mixing--Bibliography. 2. Heat--Transmission--
Bibliography. I. Tamir, Abraham, joint author.

II. Title. III. Series.

Z7914.M65W57 [TP156.M5] 660.2'84292 78-3424

ISBN 0-444-41687-0

ISBN 0-444-41687-0 (Vol. 1)

ISBN 0-444-41689-7 (Series)

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Printed in The Netherlands

ראשית חכמה קנה חכמה
ובכל-קנינך קנה בינה :
משלי ד'

THE ACQUIRING OF WISDOM IS THE BEGINNING
OF WISDOM, THEREFORE GET UNDERSTANDING
WITH THY SUBSTANCE.

Book of Proverbs 4:7

To

Anita, Daniel, Debora, Miriam and Ariel Wisniak

Dalia, Idan, Guy and Hadas Tamir

PREFACE

The last few years have seen a tremendous increase in the data published on excess thermodynamic properties, since the concept was first defined by Scatchard in 1931. Properties of mixing and excess properties are proving to be increasingly useful in the development of solution theories, data prediction, and design of physical separation equipment. This is a very challenging area in Thermodynamics and more and more people are being attracted to it. Modern chemical industry, requiring more precise and sophisticated methods of calculation will certainly benefit from these developments.

This book is intended to provide a quick and organized literature reference source for the data published on mixing properties and excess properties between 1900 and early 1977. The information reported here has been gathered mainly from Chemical Abstracts and allied publications in Chemistry, Chemical Engineering and Metallurgical Engineering. Over 10,000 references have been scanned and of these, about 6,000 found to contain pertinent material. The material has been organized in an easy to reach manner, following the general framework given by Wichterle, Linek and Hala in their book on Vapor-Liquid Equilibrium. We expect to continue to up-date this reference with material published afterwards. The systems covered include non-electrolyte solutions, electrolyte solutions and metallurgical systems. We thus expect that this literature source will be useful to people working in chemistry, chemical engineering, materials and metallurgical engineering, and process design.

We would like to express our deepest thanks to the Ben-Gurion University of the Negev for providing encouragement and generous assistance, to the Computation Center for their technical help, and, in particular, to our assistants Yehudit Reizner and Moshe Golden for long devoted hours of computer operations for handling the data.

JAIME WISNIAK

ABRAHAM TAMIR

INTRODUCTION

In dealing with multicomponent solutions one is always faced with two questions:

(a) How much does the molar property of a real solution deviate from the molar property obtained by a linear combination of the molar property of the pure components?

(b) How much does the behavior of a real mixture deviate from that of an ideal mixture of the same composition?

If it is found that the deviations are negligible, then the behavior of the mixture can be easily determined. If, however, as in most practical situations, the deviations are significant and their magnitude is not even predictable, one must resort to experimental measurements to determine the real behavior of the solution.

In thermodynamics it is common practice to describe the deviation from ideal solution behavior by means of the so-called properties of mixing and excess properties. The rapid development of research in this field has been particularly motivated by the importance of these variables in developing new classical and statistical theories of solutions, as well as their use in the design of separation equipment.

FUNDAMENTAL RELATIONSHIPS AND DEFINITIONS

In dealing with the extensive properties of solutions, it is convenient to consider separately the contribution attributable to each component present. In ideal systems these contributions are the same as the properties of the pure components existing separately at the temperature and pressure of the solution. However, in many systems, this additivity of properties does not exist and the overall property is quite different from the sum of the pure-component properties.

Assume that M is the value of a property on a molar basis, then

$$nM = M(P, T, n_1, n_2, \dots, n_i) \quad (1)$$

where P is the pressure, T the temperature, n_i is the number of moles of component i in a system containing k components and n is the total number of moles

$$\sum_{i=1}^k n_i = n$$

x

Differentiating we get

$$dnM = \left(\frac{\partial nM}{\partial P} \right)_{T,n} dP + \left(\frac{\partial nM}{\partial T} \right)_{P,n} dT + \sum_{i=1}^k \left(\frac{\partial nM}{\partial n_i} \right)_{P,T, n_{j \neq i}} dn_i \quad (2)$$

The first two terms represent the changes associated with the effect of pressure and temperature in a system of constant composition, while the last terms represent the effect of composition changes at constant pressure and temperature. The derivative

$$\bar{M}_i = \left(\frac{\partial nM}{\partial n_i} \right)_{P,T, n_{j \neq i}} \quad (3)$$

is called the partial property \bar{M}_i of component i .

Equation 2 can be easily integrated at constant pressure and temperature using Euler's theorem for homogeneous functions. Thus,

$$nM = \sum_{i=1}^k \bar{M}_i n_i \quad (4)$$

or

$$M = \sum_{i=1}^k \bar{M}_i X_i \quad (5)$$

on a one mole basis. Equation 3 shows that \bar{M}_i is an intensive property since nM is an extensive property of the first degree in the composition.

Differentiating Equation 4 and comparing it with Equation 2 gives

$$\sum_{i=1}^k n_i d\bar{M}_i = 0 \quad (6)$$

which is a particular form of the general Gibbs-Duhem equation.

The partial property will seldom be equal to the molar property M_i of the pure component at the same pressure and temperature. Although we cannot write that

$$M = \sum_{i=1}^k X_i M_i \quad (7)$$

we can correct for non-linearity by adding a term ΔM called the property of mixing.

$$M = \sum_{i=1}^k X_i M_i + \Delta M \quad (8)$$

Writing Equation 8 in the form

$$\Delta M = M - \sum_{i=1}^k X_i M_i \quad (9)$$

we can see that ΔM is the actual property change that takes place when the pure components are mixed at constant P and T to form one mole of solution. Application of the definition of a partial property leads to

$$\Delta M = \sum_{i=1}^k X_i \overline{\Delta M}_i \quad (10)$$

where

$$\overline{\Delta M}_i = \overline{M}_i - M_i \quad (11)$$

From the fact that $\sum_{i=1}^k X_i = 1$, we obtain

$$dX_k = - \sum_{i=1}^{k-1} dX_i \quad (12)$$

and

$$dM = \sum_{i=1}^k \overline{M}_i dX_i \quad (13)$$

Eliminating X_k we get

$$dM = \sum_{i=1}^{k-1} (\overline{M}_i - \overline{M}_k) dX_i \quad (14)$$

Since X_1, X_2, \dots, X_{k-1} are independent variables

$$\left(\frac{\partial M}{\partial X_i} \right)_{P,T} = \overline{M}_i - \overline{M}_k \quad (15)$$

so that

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$$\bar{M}_k = M - \sum_{i=1}^{k-1} X_i \left(\frac{\partial M}{\partial X_i} \right)_{P,T} \quad (16)$$

and

$$\bar{M}_i = M + \left(\frac{\partial M}{\partial X_i} \right)_{P,T} - \sum_{i=1}^{k-1} X_i \left(\frac{\partial M}{\partial X_i} \right)_{P,T} \quad (17)$$

Equation 17 allows the calculation of the partial property for every component except the k th component.

An ideal solution may be defined as one that follows the Lewis-Randall rule

$$\hat{f}_i = X_i f_i \quad (18)$$

where \hat{f}_i is the fugacity of component i in a solution of composition X_i at P and T , and f_i is the fugacity of pure component i at the same P and T . The strict application of Equation 18 (and Equation 9) may require the definition of one or more components in a hypothetical state of aggregation.

The definitions of fugacities f_i and \hat{f}_i are

$$dG_i = RT d \ln f_i \quad (19)$$

$$d\bar{G}_i = RT d \ln \hat{f}_i \quad (20)$$

so that

$$\bar{G}_i^{id} - \bar{G}_i = \Delta \bar{G}_i^{id} = RT \ln X_i \quad (21)$$

$$\Delta G^{id} = \sum_{i=1}^k X_i \Delta \bar{G}_i^{id} = RT \sum_{i=1}^k X_i \ln X_i \quad (22)$$

Differentiation of Equation 21 with respect to P at constant T and composition gives

$$\left[\frac{\partial \bar{G}_i^{id}}{\partial P} - \frac{\partial \bar{G}_i}{\partial P} \right]_{T,n} = 0 \quad (23)$$

From Maxwell's relations we obtain

$$\bar{V}_i^{id} - \bar{V}_i = \Delta \bar{V}_i^{id} = 0 \quad (24)$$

As a result of Equation 10 it follows that $\Delta V^{\text{id}} = 0$, that is

$$V = \sum_{i=1}^k X_i V_i \quad (25)$$

By proper use of function definition and Maxwell's relations, it can be shown that with the exception of nA , nG and nS , all the extensive properties of mixing of an ideal solution are nil.

Differentiating Equation 21 with respect to T at constant P and composition yields

$$\overline{\Delta S}_i^{\text{id}} = -R \ln X_i \quad (26)$$

so that

$$\Delta S^{\text{id}} = -R \sum_{i=1}^k X_i \ln X_i \quad (27)$$

Equations 22 and 27 show that the isothermal mixing of k components to form an ideal solution is always accompanied by a negative value of ΔG and a positive value of ΔS .

Another important auxiliary concept is that of the apparent molar property. Although it does not have a direct thermodynamic significance, it is usually capable of direct experimental determination in cases where the partial molar properties are not. By definition, the apparent molar property ϕ_M of component 2 is

$$\phi_M = \frac{nM - n_1 M_1}{n_2} \quad (28)$$

Equation 28 shows that ϕ_M is the apparent contribution of one mole of component 2 to property M of the mixture.

The apparent molar property can be related to the partial molar property as follows. From Equation 28 we obtain

$$nM - n_1 M_1 = n_2 \phi_M$$

Differentiation with respect to n_2 , assuming P, T and n_1 to be constant, yields

$$\overline{M}_2 = \left(\frac{\partial nM}{\partial n_2} \right)_{P, T, n_1} = n_2 \left(\frac{\partial \phi_M}{\partial n_2} \right)_{P, T, n_1} + \phi_M \quad (29)$$

Since the molarity m is equivalent to n_2 , when n_1 is constant, Equation 29 may be written

$$\bar{M}_2 = m \frac{d\phi_M}{dm} + \phi_M \quad (30)$$

$$\bar{M}_2 = \frac{d(m\phi_M)}{dm} \quad (31)$$

Integration between the limits $(0,0)$ and $(m, m\phi_M)$ gives

$$\phi_M = \frac{1}{m} \int_0^m \bar{M}_2 dm \quad (32)$$

Equation 8 indicates that the concept of property of mixing is associated with a particular combination of the properties of the pure components. It is of more interest to inquire about the direct comparison of the real property with the ideal property. The excess property [1] is then defined as the difference between the actual property and the property which one would obtain for an ideal solution. According to Missen [2] this definition is sufficiently flexible with respect to the choice of reference state, which affects the ideal solution model, as well as to the choice of pressure or volume. It may then be stated in terms of the same temperature and composition while leaving open the other condition. Thus for mixture property M , the possible excess functions are:

$$M^E [T, J(s), X] = M [T, J(s), X] - M^{id(s)} [T, J(s), X] \quad (33)$$

$$\bar{M}_i^E [T, J(s), X] = \bar{M}_i [T, J(s), X] - \bar{M}_i^{id(s)} [T, J(s), X] \quad (34)$$

$$\Delta M^E [T, J(s), X] = \Delta M [T, J(s), X] - \Delta M^{id(s)} [T, J(s), X] \quad (35)$$

$$\bar{\Delta M}_i^E [T, J(s), X] = \bar{\Delta M}_i [T, J(s), X] - \bar{\Delta M}_i^{id(s)} [T, J(s), X] \quad (36)$$

where $J(s)$ is a property (normally pressure or volume) which must be specified, and superscript id(s) refers to an ideal solution model which must also be specified.

It should be clear that Equation 33 can be applied to any thermodynamic property and is not restricted to extensive properties. For example, McLaughlin [3] has applied it to transport properties like viscosity and thermal conductivity; Masood, *et al.* [4] to the isentropic compressibility; and Wisniak and Tamir [5] to the boiling temperature of a multicomponent mixture.

Missen [2] has discussed the different possible definitions for the ideal state, according to the reference state in which real behavior is considered to approach ideal behavior. The numerical value of the excess property will depend on the choice of ideal solution model and the system description will be asymmetric if different reference states are used for different components in the same solution.

It should be noted that for extensive properties, the definitions given in Equations 33-36 are not independent and that

$$M^E = \Delta M^E \quad (37)$$

$$\overline{M}_i^E = \overline{\Delta M}_i^E \quad (38)$$

$$M^E = \Delta M^E = \sum_{i=1}^k X_i \overline{\Delta M}_i^E = \sum_{i=1}^k X_i \overline{M}_i^E \quad (39)$$

It has been indicated previously that only ΔG^{id} , ΔA^{id} and ΔS^{id} are different from zero so that for all other extensive properties, the excess property is identical with the property of mixing. No new property is defined for those variables. In what follows, the exponent E will be retained for purposes of consistency only.

According to the definition of excess property

$$\overline{\Delta G}_i^E = \overline{\Delta G}_i - \overline{\Delta G}_i^{id} \quad (40)$$

and the definition of the chemical potential μ_i of component i in solution

$$\mu_i \equiv \overline{G}_i = \mu_i^0 + RT \ln \hat{a}_i \quad (41)$$

Where μ_i^0 is the chemical potential of component i pure at P,T and \hat{a}_i is its activity in the solution, we get

$$\overline{\Delta G}_i^E = RT \ln \hat{a}_i - RT \ln X_i \quad (42)$$

$$\overline{\Delta G}_i^E = RT \ln \gamma_i \quad (43)$$

γ_i is the activity coefficient of component i, defined as \hat{a}_i/X_i . For the overall change, ΔG^E , we have

$$\Delta G^E = RT \sum_{i=1}^k X_i \ln \gamma_i \quad (44)$$

Equations 43 and 44 point out that a knowledge of ΔG^E allows calculation of

the activity coefficients and vice versa.

In a similar way, it can be shown that

$$\Delta S^E = \Delta S + R \sum_{i=1}^k X_i \ln \gamma_i \quad (45)$$

It is instructive, at the present stage, to summarize the significance of excess thermodynamic properties:

- (a) Excess properties provide key values for calculation of multicomponent mixture properties from pure component data;
- (b) Excess properties are often used to define the various kinds of solutions;
- (c) Excess properties are used in testing solution theories;
- (d) Excess properties can provide data for evaluation of parameters characterizing interactions between unlike species in a mixture;
- (e) The excess of the Gibbs function of mixing, ΔG^E , is one of the most useful thermodynamic concepts for expressing non-ideality of a liquid mixture;
- (f) ΔG^E is the most useful quantity for determining phase stability and phase separation;
- (g) The excess enthalpy of mixing, $\Delta H^E \equiv \Delta H$, is a very useful quantity in predicting isothermal vapor-liquid equilibrium and testing the thermodynamic consistency of non-isothermal vapor-liquid equilibrium data.

REPRESENTATION OF EXCESS PROPERTIES

The construction of theoretical or empirical expressions for the excess properties of mixtures has been, and is, the subject of much research. As yet, none of the expressions postulated are so generally superior to others that it can be cited as being the best. Proper selection of an appropriate form for a given application depends on such considerations as (1) the need for simplicity of equations, (2) the availability of data with which to evaluate the parameters, (3) the need to make predictions without excessive data (multicomponent systems from binary systems), (4) the desire for accurate correlations, (5) the desire to assign physical meaning to the parameters, (6) unusual non-idealities like partial miscibility, or (7) the nature of the system (aqueous, non-aqueous, metallic).

In the following pages, the most important theories and equations are described. For simplicity, they are grouped in three arbitrary categories (1) Non-electrolyte systems, (2) Alloys and metallic systems, and (3) Electrolyte systems, although some of the equations may be used in more than one category.

1. Non-Electrolyte Systems

This category includes mainly non-aqueous solutions and gas mixtures.

1.1 Regular Solution Theory

The regular solution theory given by Scatchard [6] and Hildebrand [7,8] describes a substitutional solution in which every atom is surrounded by z nearest neighbors, z having the same value whatever central atom is considered, and for which the same composition is similar to the rest of the solution. Since no ordering is considered in the solution, the excess entropy and the excess volume are nil. Development of the theory starts with the definition of the cohesive energy density

$$c = \frac{\Delta U}{V} \quad (46)$$

where ΔU is the energy required for the isothermal vaporization of a saturated liquid of specific volume V to the state of ideal gas.

For a binary mixture, Equation 46 is written

$$-\Delta U = \frac{c_{11}V_1^2X_1^2 + 2c_{12}V_1V_2X_1X_2 + c_{22}V_2^2X_2^2}{X_1V_1 + X_2V_2} \quad (47)$$

The constant c_{ii} refers to interactions between like molecules, while c_{ij} refers to interactions between unlike molecules. Parameter c_{ij} is assumed to be the geometric mean of c_{ii} and c_{jj}

$$c_{ij}^2 = c_{ii}c_{jj} \quad (48)$$

Define the volume fraction of component i as

$$\phi_i = \frac{X_i V_i}{\sum_{i=1}^k X_i V_i} \quad (49)$$

where V_i is the volume of pure i liquid. For a binary mixture, Equation 47 then becomes after rearrangement

$$-\Delta U = (X_1V_1 + X_2V_2)(c_{11}\phi_1^2 + 2c_{12}\phi_1\phi_2 + c_{22}\phi_2^2) \quad (50)$$

Since the excess entropy and excess volume are assumed to be nil, we have

$$\Delta G^E = \Delta A^E = \Delta U^E = \Delta H^E \quad (51)$$

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so that

$$\Delta G^E = \phi_1 \phi_2 (c_{11} + c_{22} - 2c_{12})(X_1 V_1 + X_2 V_2) \quad (52)$$

Defining the solubility parameter δ_i as

$$\delta_i = c_{ii}^{1/2} = \left(\frac{\Delta U}{V} \right)_i^{1/2} \quad (53)$$

gives

$$\Delta G^E = \phi_1 \phi_2 (\delta_1 - \delta_2)^2 (X_1 V_1 + X_2 V_2) \quad (54)$$

Equation 54 may be extended to multicomponent mixtures as follows:

$$\Delta G^E = \sum_{i=1}^{m-1} \sum_{j=i+1}^m \lambda_{ij} X_i X_j \quad (55)$$

with

$$\lambda_{ij} = z N_0 (\frac{1}{2} \epsilon_{ii} + \frac{1}{2} \epsilon_{jj}) \quad (56)$$

where ϵ represents the energy of formation of the different pairs involved and λ_{ij} is the interaction parameter in the binary solution ij .

Weimer and Prausnitz [9] have extended Equation 54 to include the effect of a polar solvent by expressing the energy of vaporization as a function of polar and non-polar solubility parameters in the following way:

$$\frac{\Delta U}{V_1} = \frac{\Delta U_1}{V_1} (\text{non-polar}) + \frac{\Delta U_2}{V_1} (\text{polar}) = \beta_1^2 + \tau_1^2 \quad (57)$$

where β_1 is the non-polar and τ_1 the polar solubility parameter. Equation 54 becomes

$$\Delta G^E = \phi_1 \phi_2 \left[(\beta_1 - \beta_2)^2 + \tau_1^2 - 2\psi_{12} \right] (X_1 V_1 + X_2 V_2) \quad (58)$$

where the energy term ψ_{12} was introduced to account for the induction effect between a polar and non-polar molecule.

1.2 Barker-Guggenheim Lattice Theory [10,11,12]

The category of lattice theories covers a number of particular theories that are variations of the same basic model. The cell theory, hole theory, tunnel theory, Monte Carlo method, and Molecular Dynamics method, all start with a lattice model of the liquid state and the various features of each method are the result of different levels of occupation of the lattice, disorder, available free volume, and averaging procedures. The reader is referred to reference [11] for a detailed mathematical description of the different models.

In Barker's theory, a quasi-lattice picture of the liquid is used, each molecule occupying a certain number of sites on a well-defined lattice. The values of the excess properties of mixing are derived on the basis of energy interactions of surface atoms of each molecule. Only pair interactions are taken into account, no attraction between adjacent pairs is assumed. To specify the model, it is then required to calculate the type and surface of interacting contact points, and the associated energy. The development of the formalism begins with the assumption that the Hamiltonian for the wave equation separates into a kinetic energy term and another term dealing with internal degrees of freedom of the molecules. The kinetic term of the Hamiltonian further separates into a momentum term and a configurational term. The separation of the Hamiltonian can also be expressed in terms of a factored partition function. The configurational part of the partition function is a $3N$ -fold integral and is very difficult to evaluate. The lattice approach replaces this integral with a discrete sum. If we assume that the μ th segment of an A molecule occupies a particular site and the μ th segment of a B molecule occupies a neighbor site, the excess properties become:

$$\Delta G^E = \sum X_{A\mu} E_A^E \quad (59)$$

$$\mu_A^E = RT \left[\sum_{\mu} Q_{\mu}^A \ln (X_{\mu}^A / X_A X_{\mu}^{A1}) + r_A (z/2 - 1) \ln \left(\sum_B r_B X_B / r_A \right) \right] \quad (60)$$

$$\Delta H^E = -2RT \left[\sum_A \sum_{\mu\nu} (X_{\mu}^A X_{\nu}^A - X_A X_{\mu}^{A1} X_{\nu}^{A1}) \eta_{\mu\nu}^{AA} \ln \eta_{\mu\nu}^{AA} + \sum_{A \neq B} \sum_{\mu\nu} X_{\mu}^A X_{\nu}^B \eta_{\mu\nu}^{AB} \ln \eta_{\mu\nu}^{AB} \right] \quad (61)$$

In these equations X_A represents the mole fraction of component A and Q_{μ}^A is the number of μ type contacts of an A molecule. Terms like X_{μ}^A correspond to the frequency factor for interaction of an A molecule through its μ segments and can be calculated from

$$X_{\mu}^A \sum \eta_{\mu\nu}^{AB} X_{\nu}^B = (Q_{\mu}^A / 2) X_A \quad (62)$$

with X_{μ}^{A1} being the value of X_{μ}^A for $X_A = 1$.