Wagner Interaction Coefficients and Modified Margules Equations

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The relationships between the Wagner interaction and Margules coefficients are derived to discuss their limitations and to clarify incorrect construction of the excess Gibbs energy from the partial excess Gibbs energies, expressed as linear functions of mole fractions. Margules-type equations with Henrian reference states are obtained, and their significance is discussed. An estimate for the Gibbs energy of melting of graphite is obtained, and the use of activity coefficients for deriving the Gibbs energy of melting of refractory elements is suggested. This research is part of the effort in materials properties at the U.S. Bureau of Mines.

Introduction

The Wagner interaction coefficients (WIC) for dilute ternary solutions [52Wag] continue to be the subject of a number of interesting publications [86Pel, 90Bal, 90Ni, 90Yua, 92Haj, 92Wei]. The concept introduced by Wagner [52Wag] was used extensively for liquid metals (each as component 1 = the solvent) in which the activity coefficient of a solute metal or metalloid (component 2) was affected by another solute (component 3). It was shown that WIC exhibited a very interesting pattern in a metal for each selected component 2, as component 3 followed Group I to VIII in the Periodic Table of the Elements [60Oht, 60Sch]. The purpose of the present paper is (1) to show the relationships between WIC and the Margules coefficients to elucidate their usefulness, (2) to clarify incorrect construction of the excess Gibbs energy, G^{ex}, from the excess partial Gibbs energies, g_i, expressed as linear functions of mole fractions, X_i, (3) to obtain the Margules equations with Henrian reference states, and (4) to suggest a method for the estimation of Gibbs energies of melting of refractory elements. (We use g_i for the excess partial Gibbs energy to avoid the cumbersome notation, G_i^{ex}).

Wagner and Margules Equations

The WIC, designated as $\varepsilon_{ij} = \partial g_i/\partial X_{ij}$, in terms of g_i, are the coefficients of X_i in the Taylor expansion for g_2 as in a dilute ternary solution:

$$g_2 = RT\ln\gamma_2 = A_{12} + \varepsilon_{22}X_2 + \varepsilon_{23}X_3 = A_{12} + \left(\frac{\partial g_2}{\partial X_2}\right)X_2 + \left(\frac{\partial g_2}{\partial X_3}\right)X_3 \qquad \text{(Eq 1)}$$

where $X_1 \rightarrow 1$, R is the gas constant, T is the temperature in K, γ_2 is the activity coefficient, and A_{12} is the value of g_2 for $X_2 = X_3 = 0$. Note that the coefficient of X_3 in the last term is ε_{23}, which is also equal to ε_{32}, as can be obtained by differentiation of the Margules equation (Eq 3 that follows) and thereafter setting X_2 and X_3 to zero. The subscripts on ε_{ij} are in the same succession as in $\partial g_i/\partial X_j$. Equation 1 is for dilute solutions; hence the lowest order Margules equations for the excess molar Gibbs energy, G^{ex}, and for the excess partial Gibbs energy, g_2, are sufficient for our immediate purposes:

$$G^{ex} = A_{12}X_1X_2 + A_{13}X_1X_3 + A_{23}X_2X_3 \qquad \text{(Eq 2)}$$

$$g_2 = A_{12}X_1^2 + A_{23}X_3^2 + (A_{12} + A_{23} - A_{13})X_1X_3 \qquad \text{(Eq 3)}$$

A higher order Margules equation [86Gok] can be used when the precision of a set of data justifies it. The standard state for each component is the pure element in the same state of aggregation as the alloy so that $g_i = 0$ for each X_i set to unity. The exchange of two subscripts leaves Eq 2 unaffected, if we let $A_{ij} = A_{ji}$; therefore, the equation for g_3 can be obtained from Eq 3 by interchanging the subscripts 2 and 3. The same procedure can be used to obtain the equation for g_1 of the solvent. We differentiate g_2 of Eq 3 as in [75Gok] by using ($dX_1 = -dX_2$) at constant X_3, and ($dX_1 = -dX_3$) at constant X_2 to obtain $\varepsilon_{22} = -2A_{12}$, and $\varepsilon_{23} = A_{23} - A_{12} - A_{13}$ and substitute them in Eq 1 to derive the Wagner equation with the Margules coefficients:

$$g_2 = A_{12} - 2A_{12}X_2 + (A_{23} - A_{12} - A_{13})X_3 \qquad \text{(Eq 4)}$$

A cubic Margules equation [86Gok] would yield the same type of equation with an additional ternary constant inside the parentheses in Eq 4. The corresponding equation for g_3 can be obtained from Eq 4 by interchanging the subscripts 2 and 3:

$$g_3 = A_{13} - 2A_{13}X_3 + (A_{23} - A_{13} - A_{12})X_2 = A_{13} + \varepsilon_{33}X_3 + \varepsilon_{32}X_2 \qquad \text{(Eq 5)}$$

There are 3 additional terms for a quaternary system in Eq 2, ($A_{14}X_1X_4$, $A_{24}X_2X_4$, and $A_{34}X_3X_4$), and the corresponding extra terms for g_2 of Eq 4 can be readily derived. As evident, g_1 and ε_{1j} for the solvent are both zero at very low solute concentrations if ε_{ij} formulation of Eq 1 is used.

It has been shown correctly by [67Dar], [85Sch], [86Pel], [88Sri] and [90Bal] that the relationships such as Eq 1 and 4, and those based on Taylor or Maclaurin expansion, violate the

Gibbs-Duhem relation for finite concentrations of solutes even if they represent the experimental data reasonably well. An additional point is to be made here regarding the linear equations, such as Eq 1 with ε_{ij}. When G^{ex} is obtained by substituting g_2 and g_3, both containing ε_{ij}, in $G^{ex} = X_2\, g_2 + X_3\, g_3$, as was carried out in [65Lup], and g_2 is rederived herein from G^{ex}, we obtain:

$$g_2 = G^{ex} + (1 - X_2)\left(\frac{\partial G^{ex}}{\partial X_2}\right)_{X_1/X_3} =$$

$$A_{12} + 2\varepsilon_{22}\, X_2 + 2\varepsilon_{23}\, X_3 \qquad \text{(Eq 6)}$$

where the additional quadratic terms are ignored for dilute solutions. This equation contains the extra coefficients 2 in the second and the third terms after the second equality as can be seen by comparing it with Eq 1. Therefore, Eq 1 and 5 are not in the proper functional forms to yield an appropriate functional form of G^{ex}. The mathematical reason for this is that the linear functions for g_i yield quadratic functions for G^{ex}.

The use of the first and the higher order WIC to construct various equations created staggeringly and unnecessarily complicated equations when far simpler Margules equations or other polynomials have already existed since 1895; see [67Hal], [75Gok], and [86Gok]. Further, it was shown that the activity coefficient data on one solute (e.g., g_2) in the dilute range could be used to obtain all the coefficients in Eq 2 and 3, and additional data for g_3 could determine the coefficients in the higher order Margules equations [82Gok]. Therefore, it is far better to use Eq 3 than Eq 1, even with the second order WIC as the coefficients of the additional quadratic terms for Eq 1. Experimental data seldom justify the use of the second and third order WIC, but even then, it would be preferable to use the third order Margules equations. Most importantly, use of Eq 3 avoids the difficulties ably pointed out by [92Wei] in the numerical computation of WIC. Further, the coefficients from Eq 3, based on the data for g_2, may be used to obtain reliable values of the WIC if desired. However, it seems preferable to use the existing reliable values of WIC to obtain the coefficients of Eq 3, or reexamine the original data and substitute them in Eq 3 to accomplish this purpose. Also, Eq 3 and its higher order forms would permit convenient optimization of data, e.g. by the least squares approximation.

A wealth of data has been presented in terms of WIC [82Sig, 84Ans, 88STE] and is useful to metallurgists. Therefore, to save the WIC formalism, first [85Sch] and later [86Pel] suggested adding $g_1 = -0.5\varepsilon_{22}X_2^2 - \varepsilon_{23}\, X_2X_3 - 0.5\varepsilon_{33}\, X_3^2$ to Eq 1 to eliminate successfully the thermodynamic inconsistency of Eq 1. Their resulting equation for a dilute ternary solution contains two more terms than Eq 9 to be presented later. All the controversies among [84Suk], [86Pel], [88Sri], and [89Nag] on the WIC formalism were resolved by [85Sch] and [90Bal].

It is evident that the Margules-type equations are preferable to the equations with linear terms even after their successful modification by [85Sch] and [86Pel]. Other proper power series satisfying the boundary conditions and the Gibbs-Duhem relation can also be used, and such equations for multicomponent solutions should reduce to lower-component equations for each X_i set to zero. Here we stress that any other type of proper equation representing a set of data is equivalent to the Margules equation with an adequate number of terms. Therefore, it is recommended that a Margules-type equation be used for representing the data on activity coefficients. The use of one type of equation, preferably the Margules equation, would enhance communication among thermodynamicists of alloys.

Other Standard States

Next, we consider the equations based on other standard states than those in the foregoing equations. For this purpose, we consider first a binary system for which G^{ex} for a single phase can be represented by the following Margules power series:

$$G^{ex} = X_1X_2(A_{21}X_1 + A_{12}X_2) + X_1^2X_2^2(B_{21}X_1 + B_{12}X_2) \qquad \text{(Eq 7)}$$

$$+ \ldots$$

If we retain the first term (with the first set of parentheses), it is third order. If we set $A_{12} = A_{21}$, it then is quadratic, i.e. $G^{ex} = A_{12}X_1X_2$. We note that for a third order equation, g_2 is given by

$$g_2 = X_1^2[A_{21} + 2X_2\,(A_{12} - A_{21})] \qquad \text{(Eq 8)}$$

The limiting value of g_2 for $X_2 = 0$ is A_{21} here, which also should be equal to A_{12} in $g_2 = A_{12}X_1^2$ (see also Eq 3). Thus the limiting value would be the same for whatever the appropriate selected maximum power is for Eq 8, provided that the data are reliable at low concentration ranges of component 2, where the contribution from higher power terms becomes negligible. Further, in an appropriate power series with a proper number of terms representing a set of data, the coefficients should not be inordinately different from one another in their numerical values. However, it has been the author's experience that most high-temperature data yield different limiting values with different maximum powers in Eq 7, attributable to the uncertainties in experimental data, particularly at low concentrations.

When the standard state is changed to the Henrian scale, i.e., g_2(Henrian) = 0, (or $\gamma_2 \rightarrow 1$) for $X_2 = 0$, then Eq 8 must contain the separate added term $-A_{21}$, and its quadratic equivalent, $-A_{12}$ so that for the latter g_2 (Henrian) $= -A_{12} + A_{12}X_1^2$. A constant added term c, as in g_2 (Henrian) $= \mathrm{c} + A_{12}X_1^2$, changing the activity to the Henrian scale, is therefore not an adjustable parameter, contrary to [67Dar], despite the fact that such an arbitrary adjustment could not violate the Gibbs-Duhem relation when used with $g_1 = A_{12}X_2^2$ for the solvent. Since any set of data, however complicated, can be represented with a Margules equation having an adequate number of terms, an arbitrary value of c cannot be assigned to A_{21} in the Henrian modification of Eq 7 or 8. It is believed that the arbitrary assignment of values to c by [67Dar], based on experimental data as stated in [67Dar], was intended to extend optimistically the compositional range of validity of the quadratic Margules equation. Therefore, Eq 2 for G^{ex}, with component 2 and 3 on the proper Henrian scale is:

$$G^{ex}\ \text{(Henrian)} = -A_{12}X_2 + A_{12}X_1X_2 - A_{13}X_3$$

$$+ A_{13}X_1X_3 + A_{23}X_2X_3 \qquad \text{(Eq 2a)}$$

This equation is used to derive:

$$g_2\,(\text{Henrian}) = -A_{12} + A_{12}X_1^2 + A_{23}X_3^2 + (A_{12} + A_{23} - A_{13})X_1X_3 \qquad \text{(Eq 9)}$$

A similar equation for g_3 can be obtained by exchanging the subscripts 2 and 3. It can be seen that the elements, such as H, N, O, and S, could each be taken as component 2, and the variation of g_2(Henrian) could be investigated by using Eq 9; see, among numerous such applications, [73Wag], [93Gok1], and [93Gok2].

Next, we consider a pure solid high melting element as a standard state and use the resulting excess Gibbs energy equation to estimate the Gibbs energy of melting of a pure high melting element, e.g., graphite, (gr.). Pure graphite is not in the same state of aggregation as the liquid Fe-C alloys below 4130 K. The partial (molar) Gibbs energy G_2 of dissolved C then refers to graphite:

$$G_2 = G^0\,(gr.) + RT \ln X_2\gamma_{22} \qquad \text{(Eq 10)}$$

where G^0(gr.) is for pure graphite, the remaining symbols are for the liquid, and γ_{22} in liquid alloy refers to graphite as the standard state. The activity measurements are usually made conveniently by investigating the equilibria in 2CO = [C in Fe] + CO_2, in which the activity of carbon is one when C(gr.) is present in this reaction instead of [C in Fe]. The partial (molar) Gibbs energy of [C in Fe] in the dilute range with pure hypothetically existing liquid C as the standard state is:

$$G_2 = G_2^0\,(\text{L}) + R\,T \ln X_2\gamma_{2\text{L}} \qquad \text{(Eq 11)}$$

where $\gamma_{2\text{L}}$ indicates that the activity coefficient refers to the hypothetically existing pure liquid as the standard state. The partial (molar) Gibbs energy G_2 is independent of the choice of standard states so that Eq 10 and 11 are equal; hence, we derive:

$$G_2^0\,(L) - G^0\,(gr.) = \Delta G_2^0\,(\text{melt}) = R\,T \ln[\gamma_{22}/\gamma_{2\text{L}}] \qquad \text{(Eq 12)}$$

Thus, the ratio of activity coefficients is a constant at a given temperature because the left-hand side is a constant equal to the standard Gibbs energy of melting of graphite. If, in a sufficiently dilute range, we can write $g_2\,(\text{ref.L}) = R\,T \ln\gamma_{2\text{L}} = A_{12}\,X_1^2$, where (ref.L) refers to liquid C, then from Eq 12, we obtain g_2(ref.gr.), referring to graphite. Thus, we obtain:

$$g_2\,(\text{ref.gr.}) = R\,T \ln \gamma_{22} = \Delta G_2^0\,(\text{melt}) + A_{12}X_1^2 \qquad \text{(Eq 13)}$$

Therefore, A_{12} (and the additional coefficients of X_i if Eq 8 were used) would be the same irrespective of the choice of standard states, i.e., A_{ij} is the same whether a pure liquid or a pure solid is used as a standard state for a component of a liquid alloy. We consider that the equality of A_{ij} in both types of standard states, as obtained from Eq 13, is an important new correlation. Two selected best values of g_2 (ref.gr.) would be sufficient to determine the constants in Eq 13 for a selected temperature, which is 1833 K in this case. The range of composition where the experimental data are likely to be more reliable is about $X_2 = 0.02$ to 0.07 (0.44 to 1.59 mass% C). If we take $X_2 = 0.02$ and 0.07, and use the results in [58Ris], [61Ban], and [84Oht (also quoted in [86Gok])], we obtain the following approximate result:

$$g_2 = 68\,000 - 80\,000X_1^2 \text{ J/mol} \qquad \text{(Eq 14)}$$

where the constants are probably reliable to within 10 000. (A more extensive analysis on the activity of C in liquid Fe will be in a forthcoming paper). The first term on the right in Eq 14 is the standard Gibbs energy of melting of graphite at 1833 K, i.e. 68 kJ/mol. It is possible to justify this value by using the following estimates for graphite based on the properties of Sn, Ge, and Si from [89Bar] in the following table:

Element	ΔS^0(melt), J/mol · K,	C_p(liquid) – C_p(solid), J/mol · K	Melting point, K
Sn.................	13.9	–1.0	505
Ge.................	30.5	–1.1	1210
Si..................	29.8	–2.0	1685
C	30(a)	–3.0(a)	4130

(a) Estimated by the author.

The melting point of graphite, determined by [76Gok], using an HF-laser, is 4130 K. The standard enthalpy of melting of graphite is given by ΔH^0(melt) = 30 × 4130 = 123 900 J/mol at 4130 K. From the heat capacity change of –3.0, we derive

$$\Delta G^0\,(\text{melt}) = 136\,290 - 57.98\,T + 3.0\,T \ln T \text{ J/mol} \qquad \text{(Eq 15)}$$

From this equation, ΔG^0 (melt) = 71 330 J/mol at 1833 K. The foregoing value from Eq 15 is within ~ 3.3 kJ of the value in Eq 14, which is in fortuitously good agreement. Thus, it is suggested here that similar but more accurate activity coefficient measurements be carried out for solid elements having high melting points as one of the components in binary liquid alloys for reasonable estimation of their standard Gibbs energies of melting. Suitable galvanic cells could be used for this purpose, particularly at temperatures below 1500 K to obtain reliable data. For example, the alloys of Zr-Sn, W-Al, Ta-Au, Hf-Au, and Th-Ag [90Mas] are suitable for such measurements on Zr, W, Ta, Hf, and Th, respectively. In fact, highly accurate data, not yet attainable, could also give the temperature dependence of ΔG^0(melt), the standard enthalpy of melting, and even the melting point.

Cited References

52Wag: C. Wagner, *Thermodynamics of Alloys*, Addison-Wesley Press, Cambridge, MA (1952).

58Ris: A. Rist and J. Chipman, *Physical Chemistry of Steelmaking*, J.F. Elliott, Ed., John Wiley & Sons, New York, 3-12 (1958).

60Oht: M. Ohtani and N.A. Gokcen, *Trans. Met. Soc. AIME, 218*, 533-540 (1960).

60Sch: H. Schenck, *Stahl Eisen, 80*, 1377-1382 (1960).

61Ban: S. Ban-ya and S. Matoba, Physical Chemistry of Process Metallurgy, G.R. St. Pierre, Ed., Interscience Publishers, New York, 373-402 (1961).

65Lup: C.H.P. Lupis and J.F. Elliott, *Trans. Met. Soc. AIME, 233*, 829-830 (1965).

67Dar: L.S. Darken, *Trans. Met. Soc. AIME, 239*, 80-89, 90-96 (1967).

67Hal: E. Hala, J. Pick, V. Fried, and O. Vilim, *Vapour-Liquid Equilibrium*, 2nd ed., Pergamon Press, 54 (1967).

73Wag: C. Wagner, *Acta Metall.*, 21, 1297-1303 (1973).

75Gok: N.A. Gokcen, *Thermodynamics*, Ch. 11, Techscience, Inc. (1975).

76Gok: N.A. Gokcen, E.T. Chang, T.M. Poston, and D.J. Spencer, *High Temp. Sci.*, *8*, 81-97 (1976).

82Gok: N.A. Gokcen, *High Temp. Sci.*, *15*, 293-300 (1982).

82Sig: G.K. Sigworth and T.A. Engh, *Scand. J. Metall.*, *11*, 143-149 (1982).

84Ole: M. Olette, *Ironmaking and Steelmaking*, *11*, 67-72 (1984).

84Oht: H. Ohtani, M. Hasebe, and T. Nishizawa, *Trans. Iron Steel Inst. Jpn.*, *24*, 857-864 (1984).

85Sch: R. Schuhmann, Jr., *Metall. Trans. B*, *16*, 807-813 (1985).

86Gok: N.A. Gokcen, *Statistical Thermodynamics of Alloys*, Ch. 1. Plenum Press, New York (1986).

86Pel: A.D. Pelton and C.W. Bale, *Metall. Trans. A*, *17*, 1211-1215 (1986).

88Sri: S. Srikanth and K.T. Jacob, *Metall. Trans.* B, *19*, 269-275 (1988).

88STE: *Steelmaking Data Sourcebook*, Japan Society for the Promotion of Science, 19th Committee on Steelmaking, Gordon & Breach Science Publishers (1988).

89Bar: I. Barin, *Thermodynamic Data of Pure Substances*, VCH Publishers, Inc., New York (1989).

89Nag: M. Nagamori, *Metall. Trans. B*, *20*, 434-440 (1989).

90Bal: C.W. Bale and A.D. Pelton, *Metall. Trans. A*, *21*, 1997-2002 (1990).

90Mas: T.B. Massalski, P.R. Subramanian, H. Okamoto, and L. Kacprzak, *Binary Alloy Phase Diagrams*, ASM International, Materials Park, OH (1990).

90Ni: R. Ni, Z. Ma, and S. Wei, *Steel Res.*, *61*, 113-116 (1990).

90Yua: G. Yuanchang and W. Changzhen, *Metall. Trans. B*, *21*, 543-547 (1990).

92Haj: J.P. Hajra and M.G. Frohberg, *Metall. Trans. B*, *23*, 23-28 (1992).

92Wei: S. Wei, *Steel Res.*, *63*(4), 159-165 (1992).

93Gok1: N.A. Gokcen and Z. Moser, *J. Phase Equilibria*, *14*(3), 288-295 (1993).

93Gok2: N.A. Gokcen, T. Tanaka, and Z. Morita, *J. Chim. Phys.*, *90*, 233-248 (1993).