LETTERS TO THE EDITOR

Methods to Calculate Thermodynamic Partial Molar Quantities from Known Quantity of One Component in a Multicomponent Alloy

The purpose of this communication is to present a general method of calculation (eqs. (12), (13) and (14)) of the thermodynamic properties from known values of the corresponding property of one component or from known differences of the corresponding properties of two components in a multicomponent alloy. A method of calculation of this type was initiated by Darken⁽¹⁾, and later, several others were proposed^{(2)~(16)}. In these methods, except two⁽¹⁾⁽¹⁶⁾, applications are limited to ternary systems or to systems with particular conditions (e.g., saturation w.r.t. one component). The present method, on the other hand, is applicable to general multicomponent systems, and has noticeable advantages over the two methods⁽¹⁾⁽¹⁶⁾. In the following, calculations will be made with partial molar free energies, though they are equally applicable to the molar quantity of any other thermodynamic property.

The excess molar free energy G^E and the excess partial molar free energies G_i^E of mixing in an n -component system ($n \geq 2$) have the following relationships under isothermal isobaric conditions

$$dG^E = \sum_i G_i^E dX_i \quad (1)$$

$$\frac{\partial G_i^E}{\partial X_k} = -\frac{\partial(G_m^E - G_k^E)}{\partial X_i} + \frac{\partial G_m^E}{\partial X_k}, \quad i \neq m. \quad (4)$$

Substitution of eq. (4) in eq. (3) produces

$$\frac{\partial G_m^E}{\partial X_k} = \sum_{i \neq m} X_i \left\{ \frac{\partial(G_m^E - G_k^E)}{\partial X_i} \right\} \quad (5)$$

or

$$\sum_{i \neq k, m} X_i \left\{ \frac{\partial(G_m^E - G_k^E)}{\partial X_i} \right\} = (1 - X_k) \left\{ \frac{\partial(G_m^E - G_k^E)}{\partial X_k} \right\} + \frac{\partial G_k^E}{\partial X_k}. \quad (6)$$

If X_k is changed, keeping constant the ratio of all the other atom fractions, namely $X_i/X_m = \text{constant} \equiv C_{ik} (i \neq k)$, then

and

$$\sum_i X_i dG_i^E = 0 \quad (2)$$

where the summation goes from $i=1$ to n , and X_i is the atom fraction. Let us suppose that values of G_k^E are known and values of G_m^E are going to be calculated. Let us select $X_1, \dots, X_{m-1}, X_{m+1}, \dots, X_n$ as independent variables. Dividing eq. (2) by dX_k at constant $X_j (j \neq m, k)$ yields

$$\sum_i X_i \left(\frac{\partial G_i^E}{\partial X_k} \right)_{X_j (j \neq m, k)} = 0, \quad k \neq m. \quad (3)$$

In the following text, partial derivatives are taken under similar constant-composition conditions, unless otherwise noted. There are $(n-1)$ independent equations similar to eq. (3), and therefore, one additional equation makes it possible to calculate all the n G_i^E 's. In the present paper, one additional equation is either known values of the excess partial molar free energy of one component or known differences of the free energies of two components. Since the sequence of differentiation of G^E with X_i and X_k is immaterial, $(\partial/\partial X_k)(\partial G^E/\partial X_i) = (\partial/\partial X_i)(\partial G^E/\partial X_k)$, and hence, by the aid of eq. (1) we obtain

$$X_i = (1 - X_k)(C_{ik} / \sum_{j \neq k} C_{jk}), \quad i \neq k. \quad (7)$$

Differentiating eq. (7) yields

$$X_i dX_k = -(1 - X_k) dX_i, \quad i \neq k. \quad (8)$$

Equation (8) leads to the following identity under the constant-ratio condition:

$$\left[-dX_k \sum_{i \neq k, m} X_i \left\{ \frac{\partial(G_m^E - G_k^E)}{\partial X_i} \right\} = (1 - X_k) \sum_{i \neq k, m} \left\{ \frac{\partial(G_m^E - G_k^E)}{\partial X_i} \right\} dX_i \right]_{C_{ik}}. \quad (9)$$

Substituting eq. (6) in eq. (9) yields

$$\left[(1 - X_k) \sum_{i \neq m} \left\{ \frac{\partial(G_m^E - G_k^E)}{\partial X_i} \right\} dX_i = - \left(\frac{\partial G_k^E}{\partial X_k} \right) dX_k \right]_{C_{ik}} \quad (10)$$

Since the summation term in the last equation is the total differential of $(G_m^E - G_k^E)$, eq. (10) becomes

$$\left[d(G_m^E - G_k^E) = - \left\{ \left(\frac{\partial G_k^E}{\partial X_k} \right) / (1 - X_k) \right\} dX_k \right]_{C_{ik}}. \quad (11)$$

Integrating the last equation from $X_k = X_k^0$ to X_k gives

$$G_m^E = G_k^E + (G_m^E - G_k^E)_{X_k = X_k^0} - \left[\int_{X_k^0}^{X_k} \left\{ \left(\frac{\partial G_k^E}{\partial X_k} \right) / (1 - X_k) \right\} dX_k \right]_{C_{ik}}. \quad (12)$$

If the value of G_m^E at $X_k = X_k^0$ is known, values of G_m^E can be calculated from eq. (12). Since m is arbitrary, the partial molar free energies of the other components are calculable in a similar way. A choice of X_k^0 will depend on availability of the G_k^E data. In the most favorable case, X_k^0 will be chosen as unity, since G_m^E for this composition can be determined from the k - m binary data.

Another interesting use can be made of eq. (11), from which it follows that

$$\left(\frac{\partial G_k^E}{\partial X_k} \right)_{X_j(j \neq m, k)} = -(1 - X_k) \left\{ \frac{\partial(G_m^E - G_k^E)}{\partial X_k} \right\}_{C_{ik}}.$$

Integrating the last equation from $X_k = X_k^0$ to X_k at constant $X_j(j \neq m, k)$ yields

$$G_k^E = (G_k^E)_{X_k = X_k^0} - \left[\int_{X_k^0}^{X_k} (1 - X_k) \left\{ \frac{\partial(G_m^E - G_k^E)}{\partial X_k} \right\}_{C_{ik}} dX_k \right]_{X_j(j \neq m, k)}. \quad (13)$$

Once G_k^E has been known, the partial molar free energies of any other components are calculable from the difference $(G_m^E - G_k^E)$ by eq. (12).

When values of $(G_m^E - G_k^E)$ are known, eq. (5) can be integrated to

$$G_m^E = \left[(G_m^E)_{X_k = X_k^0} + \int_{X_k^0}^{X_k} X_k \left\{ \frac{\partial(G_m^E - G_k^E)}{\partial X_k} \right\} dX_k + \sum_{i \neq k, m} X_i \int_{X_k^0}^{X_k} \left\{ \frac{\partial(G_m^E - G_k^E)}{\partial X_i} \right\} dX_k \right]_{X_j(j \neq m, k)}. \quad (14)$$

Equations (13) and (14) are of particular use, when the difference $(G_m^E - G_k^E)$, or the ratio of the activity coefficients, of two components are experimentally known, e.g. by the Knudsen cell-mass spectrometer combination. To obtain expressions in terms of activity coefficients γ_i , $RT \ln \gamma_i$ is substituted for G_i^E in eqs. (12), (13), and (14).

As compared with Darken's technique⁽¹⁾, eq. (12) has great advantages. In Darken's

technique, from known values of the excess partial molar free energy of one component, is firstly calculated the excess molar free energy, from which the excess partial molar free energy of another component is calculable. In the first step of calculation, the limiting value at $X_k = 1$ of the partial molar quantity of every component must be known. On the other hand, in eq. (12), the excess partial molar free energy of another component, G_m^E , is calculated directly

from known values for one component, G_k^E . In addition to G_k^E , only the value of G_m^E at $X_k = X_k^0$ is required, and X_k^0 may take any value between 0 and 1. For the same reason as the above discussion, eq. (13) is more favorable than Belton and Fruehan's technique⁽¹⁶⁾ for the cases where differences of the excess partial molar free energies of two components are known. To calculate the excess molar free energy G^E , however, Darken's⁽¹⁾ and Belton and Fruehan's⁽¹⁶⁾ techniques are simpler than the present technique. The former techniques require a single step of calculation, while the latter needs as many steps as the number of components except the k component.

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