Thermodynamically Consistent Composition Dependence of Quantities of Mixture in Multicomponent Systems

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The paper gives an evidence that isobaric-isothermal composition dependence of molar quantities of mixing in binary systems $\Delta_{mix}E = x(1 - x)\varphi(x)$, introduced by Guggenheim, which is the only one consistent with the method of intercepts equation, can be generalized to an analogous relation valid for k-component systems ($k > 2$) and all quantities of mixture.

Isobaric-isothermal composition dependence of molar quantities of mixing $\Delta_{mix}E$ is in thermodynamic calculations for binary systems used in the form

$$\Delta_{mix}E = x(1 - x)\varphi(x) \tag{1}$$

which was introduced by *Guggenheim* for excess Gibbs energy [1] (x is the mole fraction of the second component). If $\varphi(x)$ is proper, definite regression function, eqn (1) satisfies the boundary conditions which are by definition

$$\Delta_{mix}E \ (x = 0) = 0 \tag{2}$$
$$\Delta_{mix}E \ (x = 1) = 0 \tag{3}$$

There are, however, additional dependences satisfying these conditions, e.g. $\exp[-1/x(1 - x)]\varphi(x)$ or $\sin(\pi kx)\varphi(x)$. Parameters characterizing a system are in these functions involved only in the function $\varphi(x)$.

Guggenheim [1], *Redlich* and *Kister* [2], and *Scatchard* [3] selected the function $\varphi(x)$ for $\Delta_{mix}G^E$ (excess Gibbs energy of mixing) to be of the form

$$\varphi(x) = A_0 + A_1(2x - 1) + A_2(2x - 1)^2 + \tag{4}$$

where A_0, A_1,..., are constants. The only criteria to choose this form of $\varphi(x)$ were that the function (1) satisfies conditions (2) and (3), it is smooth and has the simplest possible form. However, this selection requires an additional criterion for quantities of mixing, in particular, the function $\varphi(x)$ to be finite.

If we replace $\Delta_{mix}E$ with $\Delta_{mix}G^E/(RT)$ and the function $\varphi(x)$ we write as

$$\varphi(x) = Ax + B(1 - x) \tag{5}$$

where A, B are constants and substitute both into eqn (1), it is then possible to derive for $\Delta_{mix}\overline{G_i}^E$ the relations that are identical with those obtained by *Margules* [4]. Margules, however, started with the regression functions for a fraction p_i/P_i that could be thought of as, in those times not yet introduced, activity a_i

$$\ln \frac{p_1}{P_1} = \alpha_0 \ln(1 - x) + \sum_i \frac{\alpha_i}{i} x^i \tag{6}$$

$$\ln \frac{p_2}{P_2} = \beta_0 \ln x + \sum_i \frac{\beta_i}{i}(1 - x)^i \tag{7}$$

in which α_i's and β_i's are Margules' constants. In the case of $\alpha_0 = \beta_0 = 1$ and $\alpha_1 = \beta_1 = 0$, right-hand sides of eqns (6) and (7) are equal to $\Delta_{mix}\overline{G_i}^E/(RT)$. *Carlson* and *Colburn* [5] rewrote these equations to the form consistent with eqn (5).

If we write the function $\varphi(x)$ for $\Delta_{mix}G^E/(RT)$ in the form

$$\varphi(x) = \frac{AB}{A(1 - x) + Bx} \tag{8}$$

and substitute it into eqn (1), then it is possible to derive for $\Delta_{mix}\overline{G_i}^E$ the relations identical with *van Laar* functions [6]

$$\Delta_{mix}\overline{G_1}^E = \frac{\alpha x^2}{(1 + rx)^2} \tag{9}$$

$$\Delta_{mix}\overline{G_2}^E = \frac{\alpha(1 - x)^2}{(1 + r)(1 + rx)^2} \tag{10}$$

which were also rewritten to the form consistent with eqn (8) by *Carlson* and *Colburn* [5] (α and r are constants). *Van Laar* did not derive eqns (9) and (10) starting with eqn (1), either, but he started with the van der Waals equation for a binary liquid mixture [7].

The purpose of this paper is to prove that the relations analogous to eqn (1) are the only ones consistent with the general method of intercepts equation.

THEORETICAL

Let the composition of k-component system be given by the mole fractions x_j of components and let the mole fraction of the f-th component

$x_f = 1 - \sum_{\substack{i=1 \\ i \neq f}}^{k} x_i$ be the dependent variable. It is then

possible for an extensive quantity E of 1 mol of mixture (temperature and pressure being constant), which is a homogeneous function of the 1st homogeneity with respect to amount of substance n_i, to write down an equation

$$E = \sum_{i=1}^{k} x_i \overline{E}_i = \sum_{\substack{i=1 \\ i \neq f}}^{k} x_i \overline{E}_i + \left(1 - \sum_{\substack{i=1 \\ i \neq f}}^{k} x_i\right) \overline{E}_f =$$
$$= \overline{E}_f + \sum_{\substack{i=1 \\ i \neq f}}^{k} x_i (\overline{E}_i - \overline{E}_f) \qquad (11)$$

where $\overline{E}_i$ is the partial molar quantity of the i-th component. Differentiating eqn (11) and using the Gibbs—Duhem equation in its differential form we obtain a relation

$$dE(x_1,..,x_{f-1},x_{f+1},..,x_k) = \sum_{\substack{i=1 \\ i \neq f}}^{k} (\overline{E}_i - \overline{E}_f) dx_i +$$
$$+ \sum_{\substack{i=1 \\ i \neq f}}^{k} x_i d\overline{E}_i + \left(1 - \sum_{\substack{i=1 \\ i \neq f}}^{k} x_i\right) d\overline{E}_f = \sum_{\substack{i=1 \\ i \neq f}}^{k} (\overline{E}_i - \overline{E}_f) dx_i \quad (12)$$

Hence using eqn (12) we have $(k-1)$ relations for dependent variable mole fraction of the f-th component

$$\left[\frac{\partial E(x_1,...,x_{f-1},x_{f+1},...,x_k)}{\partial x_i}\right]_{x_{j \neq i}} = \overline{E}_i - \overline{E}_f \quad (13)$$

where $\overline{E}_i$, $\overline{E}_f$ are the functions of $x_1,...,\ x_{f-1},\ x_{f+1},\ ...,\ x_k$. Substituting eqn (13) into eqn (11) we have the partial differential equation

$$E(x_1,..,x_{f-1},x_{f+1},..,x_k) = \overline{E}_f +$$
$$+ \sum_{\substack{i=1 \\ i \neq f}}^{k} x_i \left[\frac{\partial E(x_1,...,x_{f-1},x_{f+1},...,x_k)}{\partial x_i}\right]_{x_{j \neq i}} \quad (14)$$

Eqn (11) is the equation of a $(k-1)$-dimensional figure (curve, surface and/or hypersurface) and the partial derivatives $\partial E(x_1,...,\ x_{f-1},\ x_{f+1},...,\ x_k)/\partial x_l$ are the slopes of tangent, of $(k-1)$-dimensional, linear surface at the point $(x_1,...,\ x_{f-1},\ x_{f+1},...,\ x_k)$. Eqns (11), (13), and (14) imply that $\overline{E}_f$ is the intercept of this surface with the E-axis at the point $x_f = 1$. Eqn (11), derived by *Gibbs* [8] for a ternary system, is thus a general equation of the method of intercepts

and eqn (14) is the partial, differential equation consistent with this method.

The above relations are also valid in a particular case when we consider a quantity of mixing $\Delta_{mix}E$ instead of E. The boundary conditions are in this special case

$$\Delta_{mix}E(x_i = 0, x_h = 1) = 0, \ i = 1, 2, ..., k, \ i \neq h \quad (15)$$

Assuming $\partial \Delta_{mix}E(x_1, ..., x_{f-1}, x_{f+1}, ..., x_k)/\partial x_i$ for $i \neq f, h$ is finite, eqn (14) implies for the quantities of mixing at $x_{h \neq f} = 1$ (i.e. $x_{i \neq h} = 0$) the relation

$$\partial \Delta_{mix}E(x_1, ..., x_{f-1}, x_{f+1}, ..., x_k)/\partial x_i = -\Delta_{mix}\overline{E}_f \quad (15a)$$

Rewriting eqn (14) to integrable form we obtain, for dependent variable mole fraction of the f-th component and for chosen h-th component, $(k-1)$ the following relations

$$\left[\frac{\partial E(x_1,..,x_{f-1},x_{f+1},..,x_k)}{\partial x_h}\right]_{x_{j \neq h}} - \frac{E(x_1,..,x_{f-1},x_{f+1},..,x_k)}{x_h} =$$
$$= -\left\{\frac{\overline{E}_f}{x_h} + \sum_{\substack{i=1 \\ i \neq f,h}}^{k} \frac{x_i}{x_h} \left[\frac{\partial E(x_1,..,x_{f-1},x_{f+1},..,x_k)}{\partial x_i}\right]_{x_{j \neq i}}\right\} \quad (16)$$

Multiplying eqns (16) by integrating factor $1/x_h$, their left-hand sides turn into partial derivative $\partial[E(x_1,..., x_{f-1}, x_{f+1},..., x_k)/x_h]/\partial x_h$. Partially integrating in such manner rearranged equations we obtain, for constant values of $x_{i \neq f, h}$, relations as follows

$$\frac{E(x_1,..,x_{f-1},x_{f+1},..,x_k)}{x_h} =$$
$$= -\int \frac{1}{x_h}\left\{\frac{\overline{E}_f}{x_h} + \sum_{\substack{i=1 \\ i \neq f,h}}^{k} \frac{x_i}{x_h} \left[\frac{\partial E(x_1,..,x_{f-1},x_{f+1},..,x_k)}{\partial x_i}\right]_{x_{j \neq i}}\right\} \partial x_h$$
$$= F(x_1,..,x_{f-1},x_{f+1},..,x_k) +$$
$$+ C(x_1,..,x_{f-1}, x_{f+1},...,x_{h-1}, x_{h+1},..,x_k) =$$
$$= \Phi(x_1,..,x_{f-1},x_{f+1},..,x_k) \quad (17)$$

Integration constant in eqn (17) is thus a function of mole fractions of $k-2$ components and therefore is composition-independent in a binary system.

If the function E is expanded into the McLaurin series, the partial derivative $\{\partial[E(x_1,..., x_{f-1}, x_{f+1}, ..., x_k)/x_h]/\partial x_h\}_{x_{i \neq f, h}}$ does not contain the sum of coefficients λ_ζ in the part of expansion $x_h \sum_\zeta \lambda_\zeta$. Therefore, this sum is involved in the integration constant $C(x_1,..., x_{f-1}, x_{f+1},..., x_{h-1}, x_{h+1},..., x_k)$ in eqn (17).

Assuming the mentioned expansion of $E(x_1,..., x_{f-1}, x_{f+1},..., x_k)$, the same sum is equal to the first partial derivative $[\partial E(x_1,..., x_{f-1}, x_{f+1},..., x_k)/\partial x_h]_{x_{i \neq f, h}}$ for $x_h = 0$. When this is the case, the relation

$$C(x_1,..., x_{f-1}, x_{f+1},..., x_{h-1}, x_{h+1},..., x_k) =$$
$$= [\partial E(x_1,..., x_{f-1}, x_{f+1},..., x_k)/\partial x_h]_{x_{i \neq f, h}} \quad (18)$$

is valid.

Eqn (17) may be rewritten for all $x_h \in \{x_1,..., x_{f-1}, x_{f+1},..., x_k\}$ to the $(k-1)$ relations

$$E(x_1,.., x_{f-1}, x_{f+1},.., x_k) = x_1 \Phi_1(x_1,.., x_{f-1}, x_{f+1},.., x_k)$$
$$= x_2 \Phi_2(x_1,.., x_{f-1}, x_{f+1},.., x_k)$$
$$\quad (19)$$
$$= x_k \Phi_k(x_1,.., x_{f-1}, x_{f+1},.., x_k)$$

When $x_h = 0$, Φ_h goes to infinity but the uncertain expressions on the right-hand side of the last equation limit to the right value E.

Multiplying the right-hand sides of eqn (19) by the unit term

$$\prod_{\substack{i=1 \\ i \neq f, h}}^{k} x_i \left(\prod_{\substack{i=1 \\ i \neq f, h}}^{k} x_i \right)^{-1} \quad (20)$$

we can formally transform them to the frequently used form

$$E(x_1,.., x_{f-1}, x_{f+1},.. x_k) = \left(\prod_{\substack{i=1 \\ i \neq f}}^{k} x_i \right) \Phi(x_1,.., x_{f-1}, x_{f+1},.. x_k) \quad (21)$$

The function $\Phi(x_1,..., x_{f-1}, x_{f+1},..., x_k)$ has the same value for any h-th component. If some of x_i $(i \neq f, h)$ are equal to zero, the function $\Phi(x_1,..., x_{f-1}, x_{f+1},..., x_k)$ goes to infinity but again, the uncertain term on the right-hand side of eqn (21) limits to the E-value.

If we select mole fraction of the g-th component

$$x_g = 1 - \sum_{\substack{i=1 \\ i \neq g}}^{k} x_i$$ to be the dependent variable in eqn

(11), using the same procedure we obtain an equation analogous to eqn (21)

$$E(x_1,.., x_{g-1}, x_{g+1},.. x_k) = \left(\prod_{\substack{i=1 \\ i \neq g}}^{k} x_h \right) \Phi(x_1,.., x_{g-1}, x_{g+1},.. x_k) \quad (22)$$

The function $\Phi(x_1,..., x_{g-1}, x_{g+1},..., x_k)$ has the same properties as the one $\Phi(x_1,..., x_{f-1}, x_{f+1},..., x_k)$.

For the mole fractions $x_1,..., x_k$, x_f and x_g being as dependent variables among them, we obtain, join-

ing eqns (21) and (22), an equation

$$E(x_1,.., x_{f-1}, x_{f+1},.. x_k) = E(x_1,.., x_{g-1}, x_{g+1},.. x_k) =$$
$$= \left(\prod_{\substack{i=1 \\ i \neq f}}^{k} x_i \right) \Phi(x_1,.., x_{f-1}, x_{f+1},.., x_k) =$$
$$= \left(\prod_{\substack{i=1 \\ i \neq g}}^{k} x_i \right) \Phi(x_1,.., x_{g-1}, x_{g+1},.., x_k) \quad (23)$$

Multiplying the right-hand sides in eqn (23) by the unit term $x_f x_f^{-1}$ and $x_g x_g^{-1}$ we obtain the relation

$$E(x_1,..., x_k) = \left(\prod_{i=1}^{k} x_i \right) \varphi(x_1,..., x_k) \quad (24)$$

For some zero values of x_i, the function $\varphi(x_1,..., x_k)$ has similar properties as the above functions $\Phi(x_1,..., x_{f-1}, x_{f+1},..., x_k)$ and $\Phi(x_1,..., x_{g-1}, x_{g+1},..., x_k)$. If some of x_i's had zero or other constant values, it is impossible to derive fitting the experimental data the term $\varphi(x_1,..., x_k)$ as a function of mole fractions of all components.

Theory Application — Binary and Ternary Systems

For the binary systems eqn (23) is simplified to the relation $(x_f \equiv x_2; x_g \equiv x_1)$

$$E(x_1) = E(x_2) = x_1 \Phi(x_1) = x_2 \Phi(x_2) \quad (25)$$

Because

$$x_1 + x_2 = 1 \quad (26)$$

eqn (25) can be written as

$$x_1 \Phi(x_1) = (1 - x_1) \Phi(x_2) \quad (27)$$

Substituting $\Phi(x_2)$ from eqn (27) into eqn (25) we obtain a relation analogous to eqn (24)

$$E(x_1) = E(x_2) = x_1 \Phi(x_1) = (1 - x_1) x_1 [\Phi(x_1) + \Phi(x_2)] =$$
$$= x_1 x_2 \varphi(x_1, x_2) \quad (28)$$

which is valid for both zero and nonzero values of x_i. The uncertain forms on the right-hand side of eqn (28) at $x_1 = 0$ or $x_1 = 1$ limit to the finite values (in the special case $\lim_{x_1 \to 0,1} \Delta_{mix} E = 0$).

For the ternary systems eqns (21, 22) and (24) are simplified to the relations

$$E(x_1, x_2) = x_1 x_2 \Phi(x_1, x_2) \quad (29)$$

$$E(x_1, x_3) = x_1 x_3 \Phi(x_1, x_3) \qquad (30)$$

$$E(x_2, x_3) = x_2 x_3 \Phi(x_2, x_3) \qquad (31)$$

and

$$E(x_1, x_2, x_3) = x_1 x_2 x_3 \varphi(x_1, x_2, x_3) \qquad (32)$$

Multiplying both sides of eqns (29—32) by positive numbers α, β, γ, and δ the sum of which is equal to 1 and adding the obtained relations we get a new formal equation ($E(x_1, x_2) \equiv E(x_1, x_3) \equiv E(x_2, x_3) \equiv E(x_1, x_2, x_3)$).

$$E(x_1, x_2, x_3) = x_1 x_2 \alpha \Phi(x_1, x_2) + x_1 x_3 \beta \Phi(x_1, x_3) + \\ + x_2 x_3 \gamma \Phi(x_2, x_3) + x_1 x_2 x_3 \delta \varphi(x_1, x_2, x_3) \qquad (33)$$

Using the relations

$$\alpha = f(x_1, x_2)/\Phi(x_1, x_2) \qquad (34)$$

$$\beta = f(x_1, x_3)/\Phi(x_1, x_3) \qquad (35)$$

$$\gamma = f(x_2, x_3)/\Phi(x_2, x_3) \qquad (36)$$

$$\delta = f(x_1, x_2, x_3)/\varphi(x_1, x_2, x_3) \qquad (37)$$

eqn (33) transforms to the form

$$E(x_1, x_2, x_3) = x_1 x_2 f(x_1, x_2) + x_1 x_3 f(x_1, x_3) + \\ + x_2 x_3 f(x_2, x_3) + x_1 x_2 x_3 f(x_1, x_2, x_3) \qquad (38)$$

This is a frequently used equation identical with the Redlich—Kister equation [2].

Eqns (29—31) are valid (when $x_i + x_j = 1$) for all three binary subsystems of a ternary system. Because one of the mole fractions is always equal to zero it is impossible to derive the general forms of these equations using only the determined relations (28). If the functions $f(x_1, x_2)$, $f(x_1, x_3)$, $f(x_2, x_3)$ in eqn (38) and $\Phi(x_1, x_2)$, $\Phi(x_1, x_3)$, $\Phi(x_2, x_3)$ in eqns (29—

31) are expressed as regression polynomials of the same form, the ratios of coefficients referring to the same powers of variables in the corresponding f- and Φ-functions are equal to α, β, and γ, respectively. If $x_i + x_j = 1$ and $x_{k \neq i, j} = 0$ are valid relations for eqn (38), then this equation is transcribed to the equation of the only unknown in a binary system i—j.

CONCLUSION

It was proved that general relations analogous to eqn (1) are the only ones consistent with the method of intercepts for binary systems; formal relations analogous to eqn (1) are generally valid for the k-component systems ($k = 2, 3, ...$) — if some of the mole fractions are equal to zero, the uncertain expressions tend to the right value of a quantity under consideration; relations analogous to eqn (1) are valid for all quantities of mixture (not only for quantities of mixing).

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