LETTERS TO THE EDITOR

To the Editor:

In a recent paper by Reid and Beegle [*AIChE J.*, 23, 726 (1977)], the authors state in "Conclusions and Significance" that "There is, however, no general one-to-one correspondence between extensive thermodynamic derivatives with respect to mole numbers and intensive derivatives with respect to mole fractions." Perhaps I have misunderstood what the authors meant but anyway, there exists a well-defined one-to-one correspondence which may be obtained as follows.

Let us consider a homogeneous mixture characterized by the extensive composition variables $N_1, \ldots, N_n$ plus some additional thermodynamic state variables $u_1, \ldots, u_m$; N_k are mole numbers or masses of individual species constituting the mixture. If Z is an extensive thermodynamic quantity we have $Z(N_1, \ldots, N_n; u_1, \ldots, u_m) = N\overline{Z}(x_1, \ldots, x_n; u_1, \ldots, u_m)$ where $N = N_1 + \ldots + N_n > 0$, $x_k = N_k/N$. Let us fix $(u_1, \ldots, u_m)$ and write $Z(N_1, \ldots, N_n)$ instead of $Z(N_1, \ldots, N_n; u_1, \ldots, u_m)$. So Z is a homogeneous function of order one and we have

$$Z = \sum_{i=1}^{n} N_i Z_i \quad \text{where} \quad Z_i = \frac{\partial Z}{\partial N_i} \tag{1}$$

The definition of Z_i depends on the definition of $(u_1, \ldots, u_m)$; usually, one considers $m = 2$, $u_1 = T$ (temperature), $u_2 = P$ (pressure) and Z_i are called partial quantities (on the molar or mass basis). The functions Z_i *and* Z/N *are homogeneous functions of* order zero, so we may put $(Z/N)(N_1, \ldots, N_n) = \overline{Z}(x_2, \ldots, x_n)$ and $Z_i(N_1, \ldots, N_n) = \overline{Z}_i(x_2, \ldots, x_n)$.

If F is a homogeneous function of order zero, putting $F(N_1, \ldots, N_n) = \overline{F}(x_2, \ldots, x_n)$ yields

$$\left.\begin{aligned} &k = 2, \ldots, n: \\ &\frac{\partial F}{\partial N_k} = \frac{1}{N}\left(\frac{\partial \overline{F}}{\partial x_k} - \sum_{i=2}^{n} x_i \frac{\partial \overline{F}}{\partial x_i}\right) \\ &\text{and} \\ &\frac{\partial F}{\partial N_1} = -\frac{1}{N}\sum_{i=2}^{n} x_i \frac{\partial \overline{F}}{\partial x_i} \end{aligned}\right\} \tag{2}$$

hence

$$k = 2, \ldots, n: \quad \frac{\partial \overline{F}}{\partial x_k} = N\left(\frac{\partial F}{\partial N_k} - \frac{\partial F}{\partial N_1}\right) \tag{3}$$

The relations (2) and (3) represent the sought-for one-to-one correspondence. Putting $F = Z/N$ we get, with (1),

$$k = 2, \ldots, n: \quad \frac{\partial \overline{Z}}{\partial x_k} = \overline{Z}_k - \overline{Z}_1, \qquad \overline{Z} = \sum_{i=1}^{n} x_i \overline{Z}_i \tag{4}$$

Putting $F = Z_i$ we obtain the relations for $\partial^2 Z/\partial N_i \partial N_k$; etc.

Making use of (4), other useful relations may be obtained, such as

$$\sum_{j=1}^{n} x_j \frac{\partial \overline{Z}_j}{\partial x_k} = 0,$$

$$\frac{\partial(\overline{Z}_k - \overline{Z}_1)}{\partial x_j} = \frac{\partial(\overline{Z}_j - \overline{Z}_1)}{\partial x_k} \quad \text{for } j, k = 2, \ldots, n \tag{5}$$

(if $\overline{Z}$ is 2-times continuously differentiable) and the like. Observe that for a (generally) non-homogeneous medium, the partial quantities $\overline{Z}_k$ can be defined by (4) as local quantities. These definitions and the resulting relations are particularly convenient in continuum thermodynamics.

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Reply:

Dr. Veverka has misinterpreted the statement quoted above in his letter. We find no fault with his thermodynamic relations; in fact they are well known (Modell and Reid, 1974).

What we were attempting to question was whether one could write equations (13) through (16) in terms of intensive state functions and mole fractions. We showed that this could be done only if the Legendre transform employed was A, H or G but not if any other transform were used.

As an example, consider equations (17) and (36). Clearly, a derivative such as $G_{12} = \partial^2 \underline{G}/\partial N_1 \partial N_2$ is not equal to $\partial^2 G/\partial z_1 \partial z_2$. However, the determinants [equations (17) and (36)] both are zero on the spinodal curve. If G' had been used to delineate the stability and critical phenomena, then the determinant in mole fraction notation would not go to zero on the spinodal curve, but the mole number determinant [equations (13), (14)] would still be applicable.

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LITERATURE CITED

Modell, M. and R. C. Reid, "Thermodynamics and Its Applications," Chapter 8, Prentice-Hall, Englewood Cliffs, NJ (1974).