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Vector Notation for Partial Molar Properties in Single-Phase Simple Systems

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VECTOR NOTATION FOR PARTIAL MOLAR PROPERTIES IN SINGLE-PHASE SIMPLE SYSTEMS

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ABSTRACT

Conventional coordinate systems used in thermodynamic analysis of mixtures use either mole numbers or mole fractions as independent variables. The definition of quantities and the derivation of relationships in these systems entail formidable algebra. The introduction of a position vector for the amount and composition of a multi-component mixture allows the expression of useful derivative quantities in vector and tensor notation, independently of the coordinate system used.

INTRODUCTION

Multicomponent systems have important applications in chemical and phase equilibria, but are not treated very extensively in the literature because of their complex behavior and the large amounts of data needed for their analysis. In addition, the formidable notation required for their theoretical treatment (Modell and Reid, 1983) makes the mathematics hard to assimilate and may hinder the development of theoretical concepts and techniques.

The discussion is restricted here to single-phase systems which are not at phase boundaries. An n-component mixture is fully determined by the number of moles of each component N_1, N_2, ..., N_{n-1}, N_n, and two other thermodynamic properties, such as the temperature, T, and pressure, P.

$$N_i\text{-set: } (N_1, N_2, ..., N_{n-1}, N_n, T, P) \qquad (1)$$

An alternative formulation involves replacing the mole numbers with mole fractions $x_i = N_i/N$ where $N = \sum_{i=1}^{n} N_i$. Because $\sum_{i=1}^{n} x_i = 1$, only n-1 mole fractions are independent; one can simply drop x_n from the set of independent variables. For the same reason, one additional variable must be introduced, and, since the x_is, T, and P are all intensive variables, the additional variable must be extensive. It is convenient to use N as the extra necessary variable.

$$x_i\text{-set:}\ (x_1, x_2, \ldots, x_{n-1}, N, T, P) \tag{2}$$

All other thermodynamic properties are functions of the independent variables of any of the two above sets.

Following the notation of Modell and Reid (1983), the symbol $\underline{B}$ denotes any of the extensive variables $\underline{V}$ (volume), $\underline{S}$ (entropy), $\underline{U}$ (internal energy), $\underline{H}$ (enthalpy), $\underline{A}$ (Helmholts free energy), and $\underline{G}$ (Gibbs free energy); the symbol B similarly denotes any of the corresponding intensive variables ($B = \underline{B}/N$). The corresponding partial molar properties (PMPs), denoted as $\overline{B}_i$, are defined for the components of the mixture as partial derivatives within the N_i-set of independent variables:

$$\overline{B}_i = \frac{\partial \underline{B}}{\partial N_i} \tag{3}$$

At the same temperature and pressure, pure-component properties are denoted as B_i. Some thermodynamic relationships (taken from Modell and Reid, 1983) demonstrating the difficulties associated with the conventional notation will be listed below. Thermodynamic relationships will then be presented in a more concise vector notation.

Differentials of extensive variables are conveniently expressed in terms of differentials of the independent variables in the N_i-set:

$$d\underline{B} = \frac{\partial \underline{B}}{\partial T} dT + \frac{\partial \underline{B}}{\partial P} dP + \sum_{i=1}^{n} \overline{B}_i \, dN_i \tag{4}$$

The additivity rule gives extensive properties in terms of partial molar properties:

$$\underline{B} = \sum_{i=1}^{n} N_i \overline{B}_i \tag{5}$$

The Duhem relationship is:

$$\sum_{i=1}^{n} N_i \, d\overline{B}_i = \frac{\partial \underline{B}}{\partial T} dT + \frac{\partial \underline{B}}{\partial P} dP \tag{6}$$

From (6), at constant T and P:

$$\sum_{i=1}^{n} N_i \, d\overline{B}_i = 0 \quad \text{(const. T, P)} \tag{8}$$

The definition of $\overline{B}_i$ cannot be given by a simple expression in the x_i-set which uses mole fractions as the independent variables. Partial differentiation rules applied to the previous definition (3) transform it to the x_i set of coordinates. For i≠n:

$$\overline{B}_i = \frac{1}{N}\left(\underline{B} + \frac{\partial \underline{B}}{\partial x_i} - \sum_{j=1}^{n-1} x_j \frac{\partial \underline{B}}{\partial x_j}\right) = B + \frac{\partial B}{\partial x_i} - \sum_{j=1}^{n-1} x_j \frac{\partial B}{\partial x_j} \qquad (9)$$

For i=n, i.e., for the component whose mole fraction was omitted from the x_i-set:

$$\overline{B}_n = \frac{1}{N}\left(\underline{B} - \sum_{j=1}^{n-1} x_j \frac{\partial \underline{B}}{\partial x_j}\right) = B - \sum_{j=1}^{n-1} x_j \frac{\partial B}{\partial x_j} \qquad (10)$$

Conversely, the partial derivatives in the x_i-set can be expressed in terms of PMPs:

$$\frac{\partial \underline{B}}{\partial x_i} = N\,(\overline{B}_i - \overline{B}_n); \qquad \frac{\partial B}{\partial x_i} = \overline{B}_i - \overline{B}_n \quad (i \neq n) \qquad (11)$$

Generally, it is easier to use extensive properties in the N_i-set but intensive properties in the x_i-set. The differential of B in the x_i-set can be expressed as:

$$dB = \frac{\partial B}{\partial T}\, dT + \frac{\partial B}{\partial P}\, dP + \left[\sum_{i=1}^{n-1} (\overline{B}_i - \overline{B}_n)\, dx_i\right] \qquad (12)$$

The addivity rule for B as a function of partial molar properties, can be expressed as:

$$B = \sum_{i=1}^{n} x_i \overline{B}_i = \left[\sum_{i=1}^{n} x_i (\overline{B}_i - \overline{B}_n) + \overline{B}_n\right] \qquad (13)$$

Using (13) in (12), we obtain:

$$dB = \sum_{i=1}^{n} \left[x_i \frac{\partial \overline{B}_i}{\partial T}\, dT + x_i \frac{\partial \overline{B}_i}{\partial P}\, dP + \overline{B}_i\, dx_i\right] \qquad (14)$$

The Duhem relation for the intensive property is:

$$\sum_{i=1}^{n} x_i\, d\overline{B}_i = \frac{\partial B}{\partial T}\, dT + \frac{\partial B}{\partial P}\, dP \qquad (15)$$

A comparison of the two sets of independent variables, shows that the use of mole numbers as independent variables (N_i-set) allows for a simple definition of the partial molar properties and treats all components uniformly; the use of mole fractions (x_i-set) makes the definition of partial molar properties obscure and requires that one component be treated in a special way (since only n-1 mole fractions are independent). Also, the x_i-set is not appropriate for (real or fictional) processes involving addition of a component to an existing mixture, because all mole fractions change simultaneously. The x_i-set produces simpler direct relationships for intensive properties, while the N_i-set produces simpler relationshis for extensive properties. The x_i-set may be more suitable for dilute solutions in which the solvent can be designated as the n-th component and its partial molar property assumed equal to the pure component property B_n:

$$\overline{B}_n \cong B_n \Rightarrow \overline{B}_i = \frac{\partial B}{\partial x_i} + B_n \quad (i \neq n) \tag{16}$$

It appears, then, that each set is more convenient for some tasks or systems. However, the use of both sets of independent variables can be confusing, because in order to switch from one set to the other, one must transform all the partial derivatives. Furthermore, in other situations a different set of independent variables may be more suitable, depending on how the independent variables are related (and how they vary) in a particular physicochemical transformation, or what fictional path makes the computation of thermodynamic properties from available data easier for a particular mixture. The cumbersome notation makes the identification of other coordinate systems difficult. Finally, no single choice of independent variables provides compact notation. The vector notation discussed below provides for relations independent of coordinate systems and may facilitate the conceptual understanding of the behavior of multicomponent mixtures.

VECTOR NOTATION

We define a position vector, **N**, in a n-dimensional space, to denote the composition and amount of a mixture. The position vector can be viewed as having n components, corresponding to mole numbers, i.e., $\mathbf{N} = (N_1, N_2, \ldots, N_n)$. It should be remembered however that the vector itself is a fundamental concept and its components in a particular coordinate system are only derivative quantities; the vector itself is independent of the choice of coordinate systems.

All extensive variables $\underline{B}$ are scalar functions (i.e., potentials) in the space defined by the position vector **N**, with T and P as additional independent variables; note that the presence of the additional variables T and P is similar to the (additional) time variable used with the x, y, z physical space. Apart from the variables mentioned earlier ($\underline{V}$, $\underline{S}$, $\underline{U}$, $\underline{H}$, $\underline{A}$, and $\underline{G}$), we may also treat the total number of moles, N, as another potential in this space; this particular potential is independent of T and P, while the other functions are not.

In standard vector notation, we define a PMP vector $\overline{\mathbf{B}}$ as the gradient of the potential function $\underline{B}$:

$$\overline{\mathbf{B}} = \nabla \underline{B} \tag{17}$$

This vector $\overline{\mathbf{B}}$ is also independent of the coordinate system.

The differential of the general extensive function is:

$$d\underline{B} = \frac{\partial \underline{B}}{\partial T} dT + \frac{\partial \underline{B}}{\partial P} dP + \overline{\mathbf{B}} \cdot \mathbf{dN} \tag{18}$$

The additivity rule takes the form of a dot (inner) product of the position vector and the PMP vector:

$$\underline{B} = \mathbf{N} \cdot \overline{\mathbf{B}} \tag{19}$$

The Duhem relation in vector form is:

$$N \cdot d\,\overline{\mathbf{B}} = \frac{\partial \underline{B}}{\partial T} dT + \frac{\partial \underline{B}}{\partial P} dP \tag{20}$$

or, eliminating $\underline{B} = \mathbf{N} \cdot \overline{\mathbf{B}}$ from the relationship::

$$N \cdot d\,\overline{\mathbf{B}} = N \cdot \left(\frac{\partial \overline{\mathbf{B}}}{\partial T} dT + \frac{\partial \overline{\mathbf{B}}}{\partial P} dP\right) \tag{21}$$

$$\Rightarrow \qquad N \cdot \left(d\,\overline{\mathbf{B}} - \frac{\partial \overline{\mathbf{B}}}{\partial T} dT - \frac{\partial \overline{\mathbf{B}}}{\partial P} dP\right) = 0 \tag{22}$$

Now, writing $d\,\overline{\mathbf{B}}$ as a function of the independent variables (N, T, and P), we have:

$$d\,\overline{\mathbf{B}} = \frac{\partial \overline{\mathbf{B}}}{\partial T} dT + \frac{\partial \overline{\mathbf{B}}}{\partial P} dP + \frac{\partial \overline{\mathbf{B}}}{\partial N} \cdot dN \tag{23}$$

where $\frac{\partial \overline{\mathbf{B}}}{\partial N}$ is just alternative notation for $\nabla \overline{\mathbf{B}}$:

$$d\,\overline{\mathbf{B}} = \frac{\partial \overline{\mathbf{B}}}{\partial T} dT + \frac{\partial \overline{\mathbf{B}}}{\partial P} dP + \nabla \overline{\mathbf{B}} \cdot dN \tag{24}$$

Substitution of this relationship in (22) shows that:

$$\Rightarrow \qquad N \cdot (\nabla \overline{\mathbf{B}} \cdot dN) = 0 \tag{25}$$

$$\Rightarrow \qquad (N \cdot \nabla \overline{\mathbf{B}}) \cdot dN = 0 \tag{26}$$

$$\Rightarrow \qquad N \cdot \nabla \overline{\mathbf{B}} = \mathbf{0} \tag{27}$$

with $\nabla \overline{\mathbf{B}}$ a n×n tensor expressing the dependence of the PMP vector $\overline{\mathbf{B}}$ on position. The equation is significant only for non-ideal mixtures; for ideal mixtures all elements of the tensor $\nabla \overline{\mathbf{B}}$ will be zero. The whole analysis is independent of the particular coordinate system that is used for **N**; the relationships are valid in the N_i-set, the x_i-set or any other coordinate system. Generally, the terms in the equations are dependent on **N**, T, and P. Note that although $\nabla \overline{\mathbf{B}}$ does depend on temperature and pressure, the product $\mathbf{N}\cdot\nabla \overline{\mathbf{B}}$ does not, because equation (27) must be satisfied at any temperature and pressure.

A one-dimensional curve (path) can be defined parametrically by a position vector **C** which is a function of a parameter g; i.e., **N** = **C**(g) along the curve in question. The differential in the position vector along this curve is $d\mathbf{N} = \frac{\partial \mathbf{C}}{\partial g}\,dg$. Under constant temperature and pressure, the change in the potential function $\underline{B}$ along this path is given by:

$$d\underline{B} = \overline{\mathbf{B}}\cdot d\mathbf{C} = \left(\overline{\mathbf{B}}\cdot\frac{\partial \mathbf{C}}{\partial g}\right)dg \quad \text{(constant T, P)} \tag{28}$$

For many conceptual paths which represent tools for calculating differences in a property from one system to another (rather than real processes), the temperature and pressure are held constant. If the path in question is a physical process in which T and P vary, then they might be construed as functions of the same parameter, g, used in the parametric definition of the path. Thus, if T=T(g) and P = P(g):

$$d\underline{B} = \left(\overline{\mathbf{B}}\cdot\frac{\partial \mathbf{C}}{\partial g} + \frac{\partial \underline{B}}{\partial T}\frac{\partial T}{\partial g} + \frac{\partial \underline{B}}{\partial P}\frac{\partial P}{\partial g}\right)dg \tag{29}$$

For this fully specified path, we can also use the total derivative notation:

$$\frac{D\underline{B}}{Dg} = \overline{\mathbf{B}}\cdot\frac{\partial \mathbf{C}}{\partial g} + \frac{\partial \underline{B}}{\partial T}\frac{\partial T}{\partial g} + \frac{\partial \underline{B}}{\partial P}\frac{\partial P}{\partial g} \tag{30}$$

The additivity rule can be used to eliminate $\underline{B}$ from the right-hand sides of equation (29):

$$\frac{D\underline{B}}{Dg} = \left(\frac{\partial \mathbf{C}}{\partial g} + \frac{\partial T}{\partial g}\mathbf{N}\frac{\partial}{\partial T} + \frac{\partial P}{\partial g}\mathbf{N}\frac{\partial}{\partial P}\right)\cdot\overline{\mathbf{B}} \tag{31}$$

Again, the terms in these equations are generally dependent on g, but not on the particular coordinate system that is used for the position and PMP vectors. Note also that g may be either a new variable, such as an extensive thermodynamic property, or one of the variables already appearing in the equation.

Consider as an example a closed system in which a single reaction is occuring, and take g as the reaction extent. In the N_i coordinate system, the path of progress of the reaction is a straight line, defined by a linear **C**(g). Thus, the components of the vector $\frac{\partial \mathbf{C}}{\partial g}$ will be independent of position; furthermore, the vector components that correspond to inert compounds (not participating in the reaction in any way) will be zero. The linear nature of **C**(g) will not change if the coordinate system is rotated, or, more generally, subjected to a linear transformation. Thus, one could define a new coordinate system such that $\frac{\partial \mathbf{C}}{\partial g}$ lies on one of the axis and has only one non-zero component. Even spherical or cylindrical coordinate systems might be appropriate for other situations.

In summary, vector and tensor notation allows relations to be written irrespective of coordinate systems and facilitates the theoretical analysis of multicomponent mixtures. Its further development is currently in progress.

References

Modell, M., and Reid, R. C., 1983, *Thermodynamics and its Applications, 2nd edition*, Prentice-Hall, Englewood Cliffs.

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