General Partial Properties

Gustavo A. Iglesias-Silva
Dept. de Ingeniería Química, Instituto Tecnológico de Celaya, Celaya 38010, Guanajuato, México

Kenneth R. Hall
Artie McFerrin Dept. of Chemical Engineering, Texas A&M University, College Station, TX 77843

DOI 10.1002/aic.11894
Published online July 24, 2009 in Wiley InterScience (www.interscience.wiley.com).

Partial molar properties are useful thermodynamic properties because their molar average equals the property itself. In this article, we present a description of partial properties in general, and we show that for many partial properties, partial molar properties being a subset, the property is a molar average of the partial properties. Although partial molar properties remain the most useful, several of the other partial properties could have practical applications. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 2945–2949, 2009
Keywords: thermodynamics, thermodynamic properties, partial molar properties, partial properties

Introduction

Thermodynamic properties of an ideal gas mixture are the molar averages of the pure component ideal gas properties. This simple but rigorous formulation is one of the reasons that the ideal gas is such a useful tool in thermodynamic calculations. The thermodynamic properties of real fluids are the molar average of their partial molar properties, the partial derivative of the total property with respect to the number of moles of one component at constant temperature, pressure, and number of moles of all other components. Because this simple relationship holds, the partial molar properties are also useful tools for thermodynamic calculations. Astarita[1] has presented an elegant description of mathematics and thermodynamics, and O'Connell and Haile[2] provide a similar description in somewhat clearer derivations. In addition, Michelsen and Mollerup[3] discuss partial derivatives in thermodynamics. Of course, the various books dealing with thermodynamics deal extensively with the mathematics of thermodynamics.

Correspondence concerning this article should be addressed to G. A. Iglesias-Silva at gais@iqcelaya.itc.mx

© 2009 American Institute of Chemical Engineers

As we show in this article, partial molar properties are a subset of many partial properties whose molar average equals their thermodynamic property. In general, the partial properties are the partial derivative of the total property with respect to the number of moles of one component at constant intensive and/or extensive variables, and number of moles of all other components. Although the partial molar properties remain the most useful of this set, other partial properties would have practical applications.

The derivation of the general partial properties naturally involves Legendre transforms in some cases. A secondary consequence of deriving these partial properties is the development of general consistency equations.

Partial Properties Derivation

The mechanics of this derivation are familiar, but the results are interesting. Throughout, we use F to denote a molar property, such as: U, H, A, G, S, and V. We further use X and Y to denote intensive variables, such as: U, H, A, G, S, V, P, and T. A total property is:

$$(nF) = nF(X, Y, n_1, n_2, \cdots, n_N) \tag{1}$$

in which n represents number of moles, N is the total number of components, and the subscripts represent individual components. On differentiation, Eq. 1 becomes:

$$d(nF) = \left[\frac{\partial(nF)}{\partial X}\right]_{Y,n} dX + \left[\frac{\partial(nF)}{\partial Y}\right]_{X,n} dY + \sum_{i=1}^{N} \left[\frac{\partial(nF)}{\partial n_i}\right]_{X,Y,n_{j\neq i}} dn_i \tag{2}$$

Expanding and noting that $n_i = z_i n$, where z_i is the mole fraction of component i:

$$ndF + Fdn = n\left(\frac{\partial F}{\partial X}\right)_{Y,n} dX + n\left(\frac{\partial F}{\partial Y}\right)_{X,n} dY + \sum_{i=1}^{N} \left[\frac{\partial(nF)}{\partial n_i}\right]_{X,Y,n_{j\neq i}} (ndz_i + z_i dn) \tag{3}$$

Collecting terms in n and dn, we obtain:

$$\left\{dF - \left(\frac{\partial F}{\partial X}\right)_{Y,n} dX - \left(\frac{\partial F}{\partial Y}\right)_{X,n} dY - \sum_{i=1}^{N} \left[\frac{\partial(nF)}{\partial n_i}\right]_{X,Y,n_{j\neq i}} dz_i\right\} + \frac{dn}{n}\left\{F - \sum_{i=1}^{N} z_i \left[\frac{\partial(nF)}{\partial n_i}\right]_{X,Y,n_{j\neq i}}\right\} = 0 \tag{4}$$

The only way Eq. 4 can always be zero is if the terms in braces equal zero because n and dn can take on arbitrary values. Therefore, we have two equations relating properties:

$$dF = \left(\frac{\partial F}{\partial X}\right)_{Y,n} dX + \left(\frac{\partial F}{\partial Y}\right)_{X,n} dY + \sum_{i=1}^{N} \left[\frac{\partial(nF)}{\partial n_i}\right]_{X,Y,n_{j\neq i}} dz_i \tag{5}$$

which equals Eq. 1 when $n = 1$, and

$$F = \sum_{i=1}^{N} z_i \left[\frac{\partial(nF)}{\partial n_i}\right]_{X,Y,n_{j\neq i}} \tag{6}$$

Equation 6 presents the case of a general partial property:

$$\tilde{F}_i \equiv \left[\frac{\partial(nF)}{\partial n_i}\right]_{X,Y,n_{j\neq i}} \tag{7}$$

and the molar property F is the molar average of its partial property:

$$F = \sum_{i=1}^{N} z_i \tilde{F}_i \tag{8}$$

If F is any of U, H, A, G, S, or V and X is T and Y is P, then $\tilde{F}_i$ is, by definition, the partial molar property, $\overline{F}_i$. However, we have placed no such constraint on X and Y. In fact, they can be any of U, H, A, G, S, V, P, or T; therefore, the partial molar property is a subset of the partial property and Eq. 8 holds for any combination of intensive variables.

Now, let us investigate the case in which X represents an intensive property (U, H, A, G, S, V, P, or T), and Y represents an extensive property, such as: nU, nH, nA, nG, nS, or nV. The total property, nF, is:

$$(nF) = nF(X, nY, n_1, n_2, \cdots, n_N) \tag{9}$$

Following the same line of reasoning as with Eqs. 2–8, the derivation becomes:

$$d(nF) = \left[\frac{\partial(nF)}{\partial X}\right]_{nY,n} dX + \left[\frac{\partial(nF)}{\partial(nY)}\right]_{X,n} d(nY) + \sum_{i=1}^{N} \left[\frac{\partial(nF)}{\partial n_i}\right]_{X,nY,n_{j\neq i}} dn_i \tag{10}$$

$$ndF + Fdn = n\left(\frac{\partial F}{\partial X}\right)_{Y,n} dX + \left(\frac{\partial F}{\partial Y}\right)_{X,n} (ndY + Ydn) + \sum_{i=1}^{N} \left[\frac{\partial(nF)}{\partial n_i}\right]_{X,nY,n_{j\neq i}} (ndz_i + z_i dn) \tag{11}$$

Note: if both nY and n are constant, the Y is also constant.

$$\left\{dF - \left(\frac{\partial F}{\partial X}\right)_{Y,n} dX - \left(\frac{\partial F}{\partial Y}\right)_{X,n} dY - \sum_{i=1}^{N} \left[\frac{\partial(nF)}{\partial n_i}\right]_{X,nY,n_{j\neq i}} dz_i\right\} + \frac{dn}{n}\left\{F - Y\left(\frac{\partial F}{\partial Y}\right)_{X,n} - \sum_{i=1}^{N} z_i \left[\frac{\partial(nF)}{\partial n_i}\right]_{X,nY,n_{j\neq i}}\right\} = 0 \tag{12}$$

$$dF = \left(\frac{\partial F}{\partial X}\right)_{Y,n} dX + \left(\frac{\partial F}{\partial Y}\right)_{X,n} dY + \sum_{i=1}^{N} \left[\frac{\partial(nF)}{\partial n_i}\right]_{X,nY,n_{j\neq i}} dz_i \tag{13}$$

(again Eq. 13 equals Eq. 10 when $n = 1$). The expression in the second set of braces this time contains a Legendre transform of F:

$$\Lambda \equiv F - Y\left(\frac{\partial F}{\partial Y}\right)_{X,n} \tag{14}$$

and:

$$\Lambda = \sum_{i=1}^{N} z_i \left[\frac{\partial(nF)}{\partial n_i}\right]_{X,nY,n_{j\neq i}} \equiv \sum_{i=1}^{N} z_i \tilde{\Lambda}_i \tag{15}$$

We have transformed the function F into a new function, Λ, which is a function of X and $(\partial F/\partial Y)_{X,n}$. Beegle et al.[4] have developed an elegant theory of Legendre transforms that results in Eq. 14. Kumar and Reid[5] use the theory to relate various partial derivatives in a general manner. However, they have not anticipated the results of this article. Therefore, the partial functions are:

$$\tilde{F}_i \equiv \left[\frac{\partial(nF)}{\partial n_i}\right]_{X,Y,n_{j\neq i}} \neq \tilde{\Lambda}_i = \left[\frac{\partial(nF)}{\partial n_i}\right]_{X,nY,n_{j\neq i}} \quad (16)$$

Finally, let us investigate the case in which X and Y represent extensive properties, such as: nU, nH, nA, nG, nS, or nV. The total property, nF, is:

$$(nF) = nF(nX, nY, n_1, n_2, \cdots, n_N) \quad (17)$$

Following the same line of reasoning as with Eqs. 2–16, the derivation becomes:

$$d(nF) = \left[\frac{\partial(nF)}{\partial(nX)}\right]_{nY,n} d(nX) + \left[\frac{\partial(nF)}{\partial(nY)}\right]_{nX,n} d(nY) + \sum_{i=1}^{N}\left[\frac{\partial(nF)}{\partial n_i}\right]_{nX,nY,n_{j\neq i}} dn_i \quad (18)$$

$$ndF + Fdn = \left(\frac{\partial F}{\partial X}\right)_{Y,n}(ndX + Xdn) + \left(\frac{\partial F}{\partial Y}\right)_{X,n}(ndY + Ydn) + \sum_{i=1}^{N}\left[\frac{\partial(nF)}{\partial n_i}\right]_{nX,nY,n_{j\neq i}}(ndz_i + z_i dn) \quad (19)$$

Note: if nX, nY, and n are constant, then X and Y are also constant.

$$\left\{dF - \left(\frac{\partial F}{\partial X}\right)_{Y,n} dX - \left(\frac{\partial F}{\partial Y}\right)_{X,n} dY - \sum_{i=1}^{N}\left[\frac{\partial(nF)}{\partial n_i}\right]_{nX,nY,n_{j\neq i}} dz_i\right\} + \frac{dn}{n}\left\{F - X\left(\frac{\partial F}{\partial X}\right)_{Y,n} - Y\left(\frac{\partial F}{\partial Y}\right)_{X,n} - \sum_{i=1}^{N} z_i\left[\frac{\partial(nF)}{\partial n_i}\right]_{nX,nY,n_{j\neq i}}\right\} = 0 \quad (20)$$

$$dF = \left(\frac{\partial F}{\partial X}\right)_{Y,n} dX + \left(\frac{\partial F}{\partial Y}\right)_{X,n} dY + \sum_{i=1}^{N}\left[\frac{\partial(nF)}{\partial n_i}\right]_{nX,nY,n_{j\neq i}} dz_i \quad (21)$$

(again Eq. 21 equals Eq. 18 when $n = 1$). The expression in the second set of braces this time contains a double-Legendre transform of F (also discussed by Beegle et al.[4]):

$$\mathcal{L} \equiv F - X\left(\frac{\partial F}{\partial X}\right)_{Y,n} - Y\left(\frac{\partial F}{\partial Y}\right)_{X,n} \quad (22)$$

and:

$$\mathcal{L} = \sum_{i=1}^{N} z_i\left[\frac{\partial(nF)}{\partial n_i}\right]_{nX,nY,n_{j\neq i}} \equiv \sum_{i=1}^{N} z_i\tilde{\mathcal{L}}_i \quad (23)$$

We have transformed the function F into a new function, $\mathcal{L}$, which is a function of $(\partial F/\partial X)_{Y,n}$ and $(\partial F/\partial Y)_{X,n}$. Therefore, the partial functions are:

$$\tilde{F}_i \equiv \left[\frac{\partial(nF)}{\partial n_i}\right]_{X,Y,n_{j\neq i}} \neq \tilde{\mathcal{L}}_i = \left[\frac{\partial(nF)}{\partial n_i}\right]_{nX,nY,n_{j\neq i}} \quad (24)$$

Discussion

The gist of the derivations is that many partial properties exist that satisfy the expression that the property equals the molar average of the partial properties, and that Legendre transforms composed of many functions also have molar average expressions. Of course, dealing with canonical variables leads to well-known relationships. For example:

$$(nU) = nU(nS, nV, n_1, n_2, \cdots, n_N) \quad (25)$$

Equation 22 defines the Legendre transform that has the desired property

$$U - S\left(\frac{\partial U}{\partial S}\right)_{V,n} - V\left(\frac{\partial U}{\partial V}\right)_{S,n} = U - TS - PV = G = \sum_{i=1}^{N} z_i\left[\frac{\partial(nU)}{\partial n_i}\right]_{nS,nV,n_{j\neq i}} = \sum_{i=1}^{N} z_i\bar{G}_i \quad (26)$$

If we select the enthalpy or the Helmholtz energy, Eq. 14 defines the applicable transform

$$(nH) = nH(nS, P, n_1, n_2, \cdots, n_N) \quad (27)$$

$$H - S\left(\frac{\partial H}{\partial S}\right)_{P,n} = H - TS = G = \sum_{i=1}^{N} z_i\left[\frac{\partial(nH)}{\partial n_i}\right]_{nS,P,n_{j\neq i}} = \sum_{i=1}^{N} z_i\bar{G}_i \quad (28)$$

$$(nA) = nA(T, nV, n_1, n_2, \cdots, n_N) \quad (29)$$

$$A - V\left(\frac{\partial A}{\partial V}\right)_{T,n} = A + PV = G = \sum_{i=1}^{N} z_i\left[\frac{\partial(nA)}{\partial n_i}\right]_{T,nV,n_{j\neq i}} = \sum_{i=1}^{N} z_i\bar{G}_i \quad (30)$$

Finally, if we select the Gibbs energy, Eq. 6 is applicable and

$$(nG) = nG(T, P, n_1, n_2, \cdots, n_N) \quad (31)$$

$$G = \sum_{i=1}^{N} z_i\left[\frac{\partial(nG)}{\partial n_i}\right]_{T,P,n_{j\neq i}} = \sum_{i=1}^{N} z_i\bar{G}_i \quad (32)$$

and we obtain the well-known result:

$$\left[\frac{\partial(nU)}{\partial n_i}\right]_{nS,nV,n_{j\neq i}} = \left[\frac{\partial(nH)}{\partial n_i}\right]_{nS,P,n_{j\neq i}} = \left[\frac{\partial(nA)}{\partial n_i}\right]_{T,nV,n_{j\neq i}} = \left[\frac{\partial(nG)}{\partial n_i}\right]_{T,P,n_{j\neq i}} = \bar{G}_i \quad (33)$$

which can also result using Beegle et al.[4] Another option would be to examine the following functions with Eq. 6:

$$(nU) = nU(T, V, n_1, n_2, \cdots, n_N) \tag{34}$$

$$U = \sum_{i=1}^{N} z_i \left[\frac{\partial(nU)}{\partial n_i}\right]_{T,V,n_{j\neq i}} = \sum_{i=1}^{N} z_i \tilde{U}_i \tag{35}$$

$$(nH) = nH(T, V, n_1, n_2, \cdots, n_N) \tag{36}$$

$$H = \sum_{i=1}^{N} z_i \left[\frac{\partial(nH)}{\partial n_i}\right]_{T,V,n_{j\neq i}} = \sum_{i=1}^{N} z_i \tilde{H}_i \tag{37}$$

$$(nA) = nA(T, V, n_1, n_2, \cdots, n_N) \tag{38}$$

$$A = \sum_{i=1}^{N} z_i \left[\frac{\partial(nA)}{\partial n_i}\right]_{T,V,n_{j\neq i}} = \sum_{i=1}^{N} z_i \tilde{A}_i \tag{39}$$

$$(nG) = nG(T, V, n_1, n_2, \cdots, n_N) \tag{40}$$

$$G = \sum_{i=1}^{N} z_i \left[\frac{\partial(nG)}{\partial n_i}\right]_{T,V,n_{j\neq i}} = \sum_{i=1}^{N} z_i \tilde{G}_i \tag{41}$$

Smith et al.[6] and Reis[7] anticipate Eqs. 34–41. We could select the following function and use Eq. 14

$$(nU) = nU(T, nV, n_1, n_2, \cdots, n_N) \tag{42}$$

$$U - V\left(\frac{\partial U}{\partial V}\right)_{T,n} = U + PV - T\left(\frac{\partial P}{\partial T}\right)_{V,n} = H - T\left(\frac{\partial P}{\partial T}\right)_{V,n} = \sum_{i=1}^{N} z_i \left[\frac{\partial(nU)}{\partial n_i}\right]_{T,nV,n_{j\neq i}} \tag{43}$$

Obviously, many other functions like Eq. 43 exist that would have molar average equations using partial properties. It is also obvious that many of these functions would find little practical use, but they exist if necessary. The only caution is that the Legendre transforms always operate on the extensive property(s). Reis[7] not only anticipates the partial properties at constant temperature and volume, but also he proposes partial properties at constant pressure and entropy and at constant volume and entropy. However, he does not introduce the completely general partial properties nor does he relate the Legendre transforms to partial properties. Reis also suggested the possibility of having a partial pressure and a partial temperature. While these are certainly possibilities, they reduce to the equations:

$$\tilde{P}_i \equiv \left[\frac{\partial(nP)}{\partial n_i}\right]_{TVn_{j\neq i}} = \frac{RT}{V}\left[\frac{\partial(nZ)}{\partial n_i}\right]_{TVn_{j\neq i}} \Leftrightarrow \tilde{Z}_i = \left[\frac{\partial(nZ)}{\partial n_i}\right]_{TVn_{j\neq i}} \tag{44}$$

For an ideal gas, $\tilde{P}_i = P$, which when combined with Eq. 8 produces Dalton's law.

$$\tilde{T}_i \equiv \left[\frac{\partial(nT)}{\partial n_i}\right]_{PVn_{j\neq i}} = \frac{PV}{R}\left[\frac{\partial(n/Z)}{\partial n_i}\right]_{PVn_{j\neq i}} = ZT\left[\frac{\partial(n^2/nZ)}{\partial n_i}\right]_{PVn_{j\neq i}} = T\left[2 - \frac{\tilde{Z}_i}{Z}\right] \tag{45}$$

In addition to general partial properties, the derivation provides for general consistency relationships. Combining Eqs. 5 and 8 gives:

$$\sum_{i=1}^{N} z_i d\tilde{F}_i - \left(\frac{\partial F}{\partial X}\right)_{Y,n} dX - \left(\frac{\partial F}{\partial Y}\right)_{X,n} dY = 0 \tag{46}$$

which is the Gibbs–Duhem equation if $X = T$ and $Y = P$. However, combining Eqs. 13–15 produces a different consistency test:

$$\sum_{i=1}^{N} z_i d\tilde{\Lambda}_i - \left(\frac{\partial F}{\partial X}\right)_{Y,n} dX + Yd\left(\frac{\partial F}{\partial Y}\right)_{X,n} = 0 \tag{47}$$

Finally, combining Eqs. 21–23 provides yet another consistency test:

$$\sum_{i=1}^{N} z_i d\tilde{\mathcal{L}}_i + Xd\left(\frac{\partial F}{\partial X}\right)_{Y,n} + Yd\left(\frac{\partial F}{\partial Y}\right)_{X,n} = 0 \tag{48}$$

Applications of general partial properties are scarce in the literature. Lupis[8,9] uses the partial property at $X = T$ and $Y = V$ for the energy and other thermodynamic properties in metallurgical applications.

Conclusions

We have demonstrated that all partial properties regardless of the variables held constant (intensive or extensive or mixed) have the characteristic that their molar averages are some molar property of a fluid. Although many of these properties would have little use, many others could be useful. If extensive properties are constant, some form of a Legendre transform is the molar average of the partial property.

In addition, the derivation produces expressions for general consistency tests. One of these becomes the Gibbs–Duhem equation if $X = T$ and $Y = P$, but it applies to any set of intensive properties not only T and P. The other expressions allow consistency tests for systems containing extensive properties.

Because the expressions suggested in this article allow any combination of intensive and/or extensive properties, the number of possible expressions is large. It is also obvious that many of these expressions would have little practical application. However, some of these new expressions could have practical application in some problems. Therefore, we offer this generalization of partial properties and consistency tests.

Literature Cited

1. Astarita G. Thermodynamics: a view from outside. *Fluid Phase Equilib*. 1993;82:1–14.
2. O'Connell JP, Haile JM. *Thermodynamics: Fundamentals for Applications*. Cambridge: Cambridge University Press, 2005.

3. Michelsen ML, Mollerup J. Partial derivatives of thermodynamic properties. *AIChE J*. 1986;32:1389–1392.
4. Beegle BL, Modell M, Reid RC. Legendre transforms and their application in thermodynamics. *AIChE J*. 1974;20:1194–1200.
5. Kumar SK, Reid RC. Derivation of the relationships between partial derivatives of Legendre transforms. *AIChE J*. 1986;32:1224–1226.
6. Smith JM, van Ness HC, Abbott MM. *Introduction to Chemical Engineering Thermodynamics*, 7th ed. New York: McGraw-Hill, 2005.
7. Reis JCR. Theory of partial molar properties. *J Chem Soc Trans*. 1982;78:1595–1608.
8. Lupis CHP. Effects of constant pressure and constant volume conditions on the interaction energies of solutes. *Acta Metallugica*. 1978;26:211–215.
9. Lupis CHP. Effects of constant pressure and constant volume conditions on the composition dependence of chemical potentials and activity coefficients. *Acta Metallugica*. 1978;26:751–757.

Manuscript received Nov. 11, 2008, and revision received Feb. 24, 2009.