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THE CALCULATION OF PARTIAL MOLAL QUANTITIES

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For many applications of thermodynamics to chemical and physical problems it is necessary to employ the partial derivative, with respect to the amount of some substance present, of an extensive[1] quantity **G**, such as the volume, entropy, heat capacity, etc. The role of such quantities in the thermodynamics of mixtures has been discussed by Lewis.[2] The partial derivative of **G** with respect to the number of moles, n_1, of the constituent designated as number one is termed by Lewis and Randall[3] the "partial molal" property of that constituent. They represent it by the symbol $\bar{G}_1$, thus

$$\bar{G}_1 \equiv \left(\frac{\partial G}{\partial n_1}\right)_{n_2, n_3, \ldots P, T}$$

The subscripts indicate that the number of moles of each of the constituents other than number one are held or "considered held" constant, and likewise that the pressure, P, and the temperature, T, are considered constant; in other words, P, T and the amounts of each of the constituents are selected as independent variables.

Several methods for the calculation of partial molal quantities have been discussed by Lewis and Randall. They have described two methods which involve certain intensive properties rather than the extensive ones embodied in the fundamental definition of $\bar{G}$. More recently, Sosnick[4] and Randall and Rossini[5] have suggested other similar procedures which are very useful.

As pointed out by these authors, appropriate changes of variables are frequently very convenient. They permit the use of curves with finite

[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 13.

[2] Lewis, *Proc. Am. Acad.*, **43**, 259 (1907), especially p. 273.

[3] (a) Lewis and Randall, THIS JOURNAL, **43**, 233 (1921); (b) Ref. 1, Chapter IV.

[4] Sosnick, THIS JOURNAL, **49**, 2255 (1927).

[5] Randall and Rossini, *ibid.*, **51**, 323 (1929).

slopes in critical regions, or curves which follow closely, simple empirical equations. Plots of small deviations from such equations can often be manipulated with less effort or more accuracy than the plot of the complete function. A change of variables sometimes aids also in the utilization of data already available in a particular form.

To facilitate changes of variables, two tables have been prepared in this Laboratory which exhibit the relations between a number of common intensive properties, various composition terms, and the corresponding partial molal quantities. These tables are useful aids in the selection and manipulation of convenient functions.

The mathematical methods employed in the construction of the tables are simple and well known. A single illustration will suffice: $\bar{G}_1$ is to be obtained from a plot of $y = \mathbf{G}/(n_1 + n_2)$ against N_1, the mole fraction of constituent number one. For example, **G** might represent volume, and y the volume of one mole of solution.

$$(\partial y)_{n_2, P, T} = \frac{(\partial \mathbf{G})_{n_2, P, T}}{(n_1 + n_2)} - \frac{\mathbf{G}}{(n_1 + n_2)^2}(\partial n_1)_{n_2, P, T} \quad (1)$$

$$(\partial \mathbf{G})_{n_2, P, T} = (n_1 + n_2)(\partial y)_{n_2, P, T} + y(\partial n_1)_{n_2, P, T} \quad (2)$$

The mole fraction $N_1 = \dfrac{n_1}{n_1 + n_2}$

$$(\partial N_1)_{n_2 P, T} = \frac{1}{(n_1 + n_2)}(\partial n_1)_{n_2, P, T} - \frac{n_1(\partial n_1)_{n_2, P, T}}{(n_1 + n_2)^2} \quad (3)$$

$$(\partial n_1)_{n_2, P, T} = \frac{n_1 + n_2}{N_2}(\partial N_1)_{n_2, P, T} \quad (4)$$

$$\bar{G}_1 = N_2\left(\frac{\partial y}{\partial N_1}\right)_{n_2, P, T} + y = N_2\left(\frac{\partial y}{\partial N_1}\right)_{P, T} + y \quad (5)$$

The subscript n_2 may be omitted since the value of $\mathrm{d}y/\mathrm{d}N_1$ is obviously independent of the way in which N_1 is varied at constant pressure and temperature. This formula corresponds to the one in Table I

$$\bar{G}_1 = N_2S + y - C \quad (6)$$

for the special case in which $C = 0$. S represents the slope of the curve.

Symbols

W_1 and W_2 = mass of one mole of constituents 1 and 2, respectively
n_1 and n_2 = numbers of moles of constituents 1 and 2, respectively
N_1 and N_2 = mole fractions of constituents 1 and 2
$r_1 = n_1/n_2$; $r_2 = n_2/n_1 = m\ W_1/1000$
m = moles of constituent 2 (solute) per 1000 g. of constituent 1 (solvent)
G = any extensive property of the mixture consisting of n_1 moles of constituent 1 and n_2 moles of 2
G_1 and G_2 = molal properties of pure constituents 1 and 2
$\Phi = (\mathbf{G} - n_1G_1)/n_2$, apparent molal property of constituent 2
$G = \mathbf{G}/(n_1 + n_2)$
$\Delta = G - (N_1G_1 + N_2G_2)$

TABLE I

FORMULAS FOR THE CALCULATION OF $\overline{G_1}$

	x .... / y	1 N_1	2 N_2	3 m	4 $m^{1/2}$
A	$\frac{\mathrm{G}}{n_2} + C$	N_2^2S	$-N_2^2S$	$-\frac{mS}{r_1}$	$-\frac{m^{1/2}S}{2r_1}$
B	$\frac{\mathrm{G}}{n_1 + n_2} + C$	$N_2S + y - C$	$-N_2S + y - C$	$-\frac{mS}{N_1} + y - C$	$-\frac{m^{1/2}S}{2N_1} + y - C$
C	$\frac{n_1 + n_2}{\mathrm{G}} + C$	$-\frac{N_2S}{(y-C)^2} + \frac{1}{y-C}$	$\frac{N_2S}{(y-C)^2} + \frac{1}{y-C}$	$\frac{mS}{N_1(y-C)^2} + \frac{1}{y-C}$	$\frac{m^{1/2}S}{2N_1(y-C)^2} + \frac{1}{y-C}$
D	$\Phi + C$	$G_1 + N_2^2S$	$G_1 - N_2^2S$	$G_1 - \frac{mS}{r_1}$	$G_1 - \frac{m^{1/2}S}{2r_1}$
E	Δ	$G_1 + y + N_2S$	$G_1 + y - N_2S$	$G_1 + y - \frac{mS}{N_1}$	$G_1 + y - \frac{m^{1/2}S}{2N_1}$
F	G_w	$W_1\left[y + \left(N_1N_2 + \frac{N_2^2W_2}{W_1}\right)S\right]$	$W_1\left[y - \left(N_1N_2 + \frac{N_2^2W_2}{W_1}\right)S\right]$	$W_1\left[y - \left(m + \frac{W_2m^2}{1000}\right)S\right]$	$W_1\left[y - \left(\frac{m^{1/2}}{2} + \frac{m^{3/2}W_2}{2000}\right)S\right]$

	x .... / y	5 m^k	6 $\log_{10}(m^k)$	7 r_2	8 r_1
A	$\frac{\mathrm{G}}{n_2} + C$	$-\frac{km^kS}{r_1}$	$-\frac{kS}{2,303\, r_1}$	$-r_2^2S$	S
B	$\frac{\mathrm{G}}{n_1 + n_2} + C$	$-\frac{km^kS}{N_1} + y - C$	$-\frac{kS}{2.303\, N_1} + y - C$	$-\frac{r_2S}{N_1} + y - C$	$\frac{S}{N_2} + y - C$
C	$\frac{n_1 + n_2}{\mathrm{G}} + C$	$\frac{km^kS}{N_1(y-C)^2} + \frac{1}{y-C}$	$\frac{kS}{2.303N_1(y-C)^2} + \frac{1}{y-C}$	$\frac{r_2S}{N_1(y-C)^2} + \frac{1}{y-C}$	$\frac{-S}{N_2(y-C)^2} + \frac{1}{y-C}$
D	$\Phi + C$	$G_1 - \frac{km^kS}{r_1}$	$G_1 - \frac{kS}{2.303\, r_1}$	$G_1 - r_2^2S$	$G_1 + S$
E	Δ	$G_1 + y - \frac{km^kS}{N_1}$	$G_1 + y - \frac{kS}{2.303\, N_1}$	$G_1 + y - \frac{r_2S}{N_1}$	$G_1 + y + \frac{S}{N_2}$
F	G_w	$W_1\left[y - \left(km^k + \frac{kW_2m^{k+1}}{1000}\right)S\right]$	$W_1\left[y - \frac{k}{2.303}\left(1 + \frac{W_2m}{1000}\right)S\right]$	$W_1\left[y - \left(r_2 + \frac{r_2^2W_2}{W_1}\right)S\right]$	$W_1\left[y + \left(r_1 + \frac{W_2}{W_1}\right)S\right]$

Table II

Formulas for the Calculation of G_2

	x	1	2	3	4
	y	N_1	N_2	m	$m^{1/2}$
A	$\frac{G}{n_2} + C$	$-N_1N_2S + y - C$	$N_1N_2S + y - C$	$mS + y - C$	$\frac{m^{1/2}S}{2} + y - C$
B	$\frac{G}{n_1 + n_2} + C$	$-N_1S + y - C$	$N_1S + y - C$	$\frac{mS}{N_2} + y - C$	$\frac{m^{1/2}S}{2N_2} + y - C$
C	$\frac{n_1 + n_2}{G} + C$	$\frac{N_1S}{(y - C)^2} + \frac{1}{y - C}$	$-\frac{N_1S}{(y - C)^2} + \frac{1}{y - C}$	$-\frac{mS}{N_2(y - C)^2} + \frac{1}{y - C}$	$-\frac{m^{1/2}S}{2N_2(y - C)^2} + \frac{1}{y - C}$
D	$\Phi + C$	$-N_1N_2S + y - C$	$N_1N_2S + y - C$	$mS + y - C$	$\frac{m^{1/2}S}{2} + y - C$
E	Δ	$G_2 + y - N_1S$	$G_2 + y + N_1S$	$G_2 + y + \frac{mS}{N_2}$	$G_2 + y + \frac{m^{1/2}S}{2N_2}$
F	G_w	$W_2\left[y - \left(N_1N_2 + \frac{N_1^2W_1}{W_2}\right)S\right]$	$W_2\left[y + \left(N_1N_2 + \frac{N_1^2W_1}{W_2}\right)S\right]$	$W_2\left[y + \left(m + \frac{1000}{W_2}\right)S\right]$	$W_2\left[y + \left(\frac{1000}{2m^{1/2}W_2} + \frac{m^{1/2}}{2}\right)S\right]$

	x	5	6	7	8
	y	m^k	$\log_{10}(m^k)$	r_2	r_1
A	$\frac{G}{n_2} + C$	$km^kS + y - C$	$\frac{kS}{2.303} + y - C$	$r_2S + y - C$	$-r_1S + y - C$
B	$\frac{G}{n_1 + n_2} + C$	$\frac{km^kS}{N_2} + y - C$	$\frac{kS}{2.303\ N_2} + y - C$	$\frac{S}{N_1} + y - C$	$-\frac{r_1S}{N_2} + y - C$
C	$\frac{n_1 + n_2}{G} + C$	$-\frac{km^kS}{N_2(y - C)^2} + \frac{1}{y - C}$	$-\frac{kS}{2.303N_2(y - C)^2} + \frac{1}{y - C}$	$-\frac{S}{N_1(y - C)^2} + \frac{1}{y - C}$	$\frac{r_1S}{N_2(y - C)^2} + \frac{1}{y - C}$
D	$\Phi + C$	$km^kS + y - C$	$\frac{kS}{2.303} + y - C$	$r_2S + y - C$	$-r_1S + y - C$
E	Δ	$G_2 + y + \frac{km^kS}{N_2}$	$G_2 + y + \frac{kS}{2.303\ N_2}$	$G_2 + y + \frac{S}{N_1}$	$G_2 + y - \frac{r_1S}{N_2}$
F	G_w	$W_2\left[y + \left(\frac{1000km^{k-1}}{W_2} + km^k\right)S\right]$	$W_2\left[y + \frac{k}{2.303}\left(1 + \frac{1000}{mW_2}\right)S\right]$	$W_2\left[y + \left(\frac{W_1}{W_2} + r_2\right)S\right]$	$W_2\left[y - \left(\frac{r_1^2W_1}{W_2} + r_1\right)S\right]$

$G_w = G/(n_1W_1 + n_2W_2)$, specific property (*i. e.*, specific heat, etc.)

$$\bar{G}_1 = \left(\frac{\partial G}{\partial n_1}\right)_{n_2};\ \bar{G}_2 = \left(\frac{\partial G}{\partial n_2}\right)_{n_1}$$

C = any constant
k = any exponent
y = the quantity plotted as ordinate
x = the quantity plotted as abscissa
S = the slope of the curve = dy/dx

The units of quantity chosen for the formulas placed above the double lines are purely arbitrary and may be varied at will. Thus W_1' may represent any desirable amount of constituent 1, and W_2' a convenient quantity of constituent 2. Then n_1' and n_2' will represent the numbers of such units and r_2' the ratio of the numbers of units of constituent 2 to the number of units of constituent 1. Except for the addition of primes to each symbol, the same formulas will represent the partial derivatives for the quantities corresponding to W_1' and W_2'. For example if W_1' represents one gram, $\bar{G}_1'$ represents a partial specific property and must be multiplied by the molal weight of the first constituent to yield a partial molal quantity.

It is sometimes convenient to plot such quantities as heat capacity *per gram* against *mole* (rather than weight) fraction. Below the double lines in the tables are a few formulas arranged for direct calculation of partial molal properties from such typical pairs of dissimilar units.

Some of these formulas have already been used or suggested. 1-*E* is the relation recommended by Sosnick.[4] It is especially useful in those cases in which Δ is very small. 1-*C* is the basis of the method of intercepts used by Lewis and Randall,[3] 6-*D* was also used by Lewis and Randall, and 4-*D* without the constant, was employed by Randall and Rossini.

The list presented is, of course, not complete but contains the formulas which seem to us most likely to be useful. If special problems require other relations, those presented here are sufficiently varied to act as guides in the selection of other formulas which might be of value.

Summary

Formulas have been prepared to facilitate changes of variables in the calculation of partial molal properties of the constituents of solutions. These are presented in tables.

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