Solution Thermodynamics

using
Wagner Notation

by
Stanley M. Howard

Department of Materials and Metallurgical Engineering
South Dakota School of Mines and Technology
Rapid City, SD 57701

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This treatment of solution thermodynamics describes common solution parameters involving volume, enthalpy, entropy and Gibbs energy. Furthermore, it contains the natural constraints placed on solutions by mathematical considerations. Solution terms are either “integral” or “partial” properties. Integral properties describe the properties of the entire solution while ”partial” is used to describe the properties of any one component in the solution.

Before formal considerations begin, it is useful to consider an example situation where there is a need for partial molar quantities. Such a case is easily illustrated by the following situation. The reaction between MgO and SiO_2 to form solid Forsterite is

$$2MgO_{(1)} + SiO_{2(1)} = Mg_2SiO_{4(s)}. \tag{1}$$

At equilibrium there is one liquid phase consisting of a solution of MgO and SiO_2 and one solid phase consisting of pure Mg_2SiO_4. If one needed to know what temperature-pressure loci are required to maintain a fixed equilibrium distribution of the constituents in this reaction, one would use the Clausius-Clapeyron equation

$$\frac{dP}{d \ln T} = \frac{\Delta H}{\Delta V} \tag{2}$$

The use of this equation requires knowing the volume and enthalpy changes for the reaction. The volume change is

$$\Delta V = \left[\begin{array}{c}\text{Volume of 1 mole of}\\ \text{pure, solid}\\ \text{Forsterite}\end{array}\right] - \left[\begin{array}{c}\text{Volume of 2 moles of}\\ \text{MgO in the liquid solution}\\ \text{of MgO and SiO}_2\end{array}\right] - \left[\begin{array}{c}\text{Volume of 1 mole of}\\ \text{SiO}_2\text{ in the liquid solution}\\ \text{of MgO and SiO}_2\end{array}\right]$$

The enthalpy change may be written in a corresponding way. It is of interest to note that it is possible to measure each of the partial molar volumes to obtain ΔV but it is not possible to ever measure the absolute partial molar enthalpies. However, it is a fairly straightforward mater to measure the *change* in the enthalpies, ΔH.

A second process that illustrates the need for solution properties is the reaction that describes equilibrium in the Betterton Process where Pb is dezinced using $PbCl_2$.

$$PbCl_{2(1)} + Zn_{(1)} = ZnCl_{2(1)} + Pb_{(1)} \tag{3}$$

At equilibrium there exist two liquid phases: a liquid metallic phase of Pb and Zn, and a molten salt phase of $ZnCl_2$ and $PbCl_2$. The volume change for the reaction in this case is

$$\Delta V = \left[\begin{array}{l}\text{Volume of 1}\\ \text{mole of}\\ \text{ZnCl}_2\text{ in the}\\ \text{molten salt}\\ \text{phase of}\\ \text{equilibrium}\\ \text{composition.}\end{array}\right] + \left[\begin{array}{l}\text{Volume of}\\ \text{1 mole of}\\ \text{PbCl}_2\text{ in the}\\ \text{molten salt}\\ \text{phase of}\\ \text{equilibrium}\\ \text{composition}\end{array}\right] - \left[\begin{array}{l}\text{Volume of 1}\\ \text{mole of Pb in}\\ \text{the molten}\\ \text{metallic phase}\\ \text{of equilibrium}\\ \text{composition.}\end{array}\right] - \left[\begin{array}{l}\text{Volume of 1}\\ \text{mole of Zn in}\\ \text{the molten}\\ \text{metallic phase}\\ \text{of equilibrium}\\ \text{composition.}\end{array}\right]$$

Absolute Values

The volume that one mole of a constituent occupies in solution rarely equals the volume of the constituent in the pure state because the interaction forces in solution are different from those in the pure component. The volume of one mole of i in solution is denoted by the symbol V_i and may be determined experimentally by the methods described below.

Measurement and Definition of Absolute Partial Molar Volume

There are three methods of measuring $V_{i.}$

1. The absolute partial molar volume is equal to the increase in the total volume V_T of solution when one mole of species i is added to a very large quantity of the initial solution.

$$V_i = \Delta V_T \qquad (4)$$

   Since V_i varies with composition, a large quantity of solution is specified so that the initial solution's concentration is essentially unaffected by the addition of one mole of i.

2. The second method for measuring V_i is only a minor modification of the first method. The only difference is that rather than adding one mole of i to a large quantity of solution, a smaller quantity of i is added. Consequently, the volume change is for the smaller quantity of i and to obtain the volume change per mole one must divide by Δn_i which is the moles of i added to the solution.

$$V_i = \left[\frac{\Delta V_T}{\Delta n_i}\right] \qquad (5)$$

   This procedure becomes more precise as $\Delta n_i \rightarrow 0$ because the change in solution composition becomes smaller. Therefore, the best value of V_i is in the limit.

$$V_i = \underset{n_i \to o}{Lim}\left(\frac{\Delta V_T}{\Delta n_i}\right) = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} \qquad (6)$$

   The subscripts T,P, and n_j indicate that V_i is measured while T, P, and the number of moles of other solution components remain fixed. Since V_i is defined as a partial derivative it is easy to see why V_i is called the "partial molar volume of species i" in solution.

3. The definition in Eq. [6] implies another method which may be used to determine the partial molar volume, V_i. If one starts with n_j moles of component j at temperature T and pressure P and adds to it species i in several increments, a curve like that shown in Figure1 is obtained. According to Eq. [6], the slope of the line in Figure 1 equals the partial molar volume of species i at the composition selected. For example, the partial molar volume of i at $n_i = 0.06$ is $38.9\, cm^3/mole$.

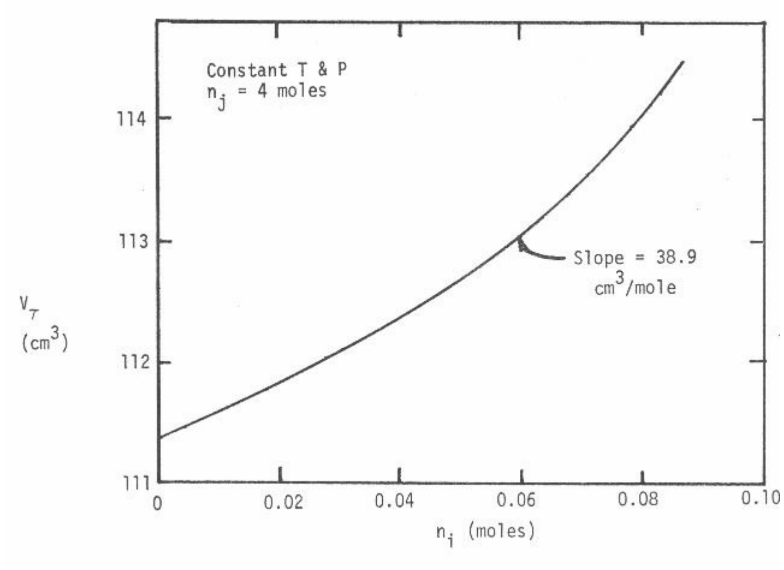

Figure 1. Partial Molar Volume of i, V_i, from Volume vs. n_i

<u>Gibbs-Duhem Equation</u>

The Gibbs-Duhem Equation describes a constraint on the behavior of the partial molar quantities in a solution. The following derivation is in terms of volume but applies to H, S, and G, as well. Constant temperature and pressure are assumed throughout the development.

The total volume V_T of a binary solution composed of n_1 moles of component 1 and n_2 moles of component 2 is

$$V_T = n_i V_1 + n_2 V_2 \tag{7}$$

which may be divided by ($n_1 + n_2$) to give the integral molar volume

$$V = X_1V_1 + X_2V_2 \tag{8}$$

where X_1 = the mole fraction of component 1
X_2 = the mole fraction of component 2.

Consideration of Figure 1 shows that a binary solution's volume is dependent upon the number of moles of each component. That is, $V_T = f(n_1, n_2)$ at constant T and P.

The total differential of V_T gives

$$dV_T = \left(\frac{\partial V_T}{\partial n_1}\right)_{T,P,n_j} dn_1 + \left(\frac{\partial V_T}{\partial n_2}\right)_{T,P,n_j} dn_2 = V_1dn_1 + V_2dn_2 \tag{9}$$

However, the following expression for dV_T is obtained from Eq. [7]:

$$dV_T = n_1dV_1 + n_2dV_2 + V_1dn_1 + V_2dn_2 \tag{10}$$

Subtracting Eq. [9] from Eq. [10] gives

$$n_1dV_1 + n_2dV_2 = 0 \tag{11}$$

Dividing by $(n_1 + n_2)$ gives

$$X_1dV_1 + X_2dV_2 = 0 \tag{12}$$

This important result is called the Gibbs-Duhem Equation. It shows that change in one partial molar volume is related to change in the partial molar volume of the other component.

The Slope-Intercept Method

Two valuable relationships are obtained by differentiating Eq. [8] with respect to X_2 and combining the result with Eq. [12] to give

$$\frac{\partial V}{\partial x_2} = V_2 - V_1 \tag{13}$$

Note that $dX_1 = -dX_2$ since $X_1 + X_2 = 1$. Elimination of V_1 or V_2 with Eq. [8] yields

$$V_1 = V - X_2\left(\frac{\partial V}{\partial x_2}\right) \tag{14}$$

$$V_2 = V + (1 - X_2)\left(\frac{\partial V}{\partial x_2}\right) \tag{15}$$

These two equations are the basis of the Tangent-Intercept Method of graphically determining partial molar volumes from a plot of V versus X_2. As indicated on Figure 2, V_1 equals the intercept at pure component 1 and V_2 equals the tangent intercept at pure component 2.

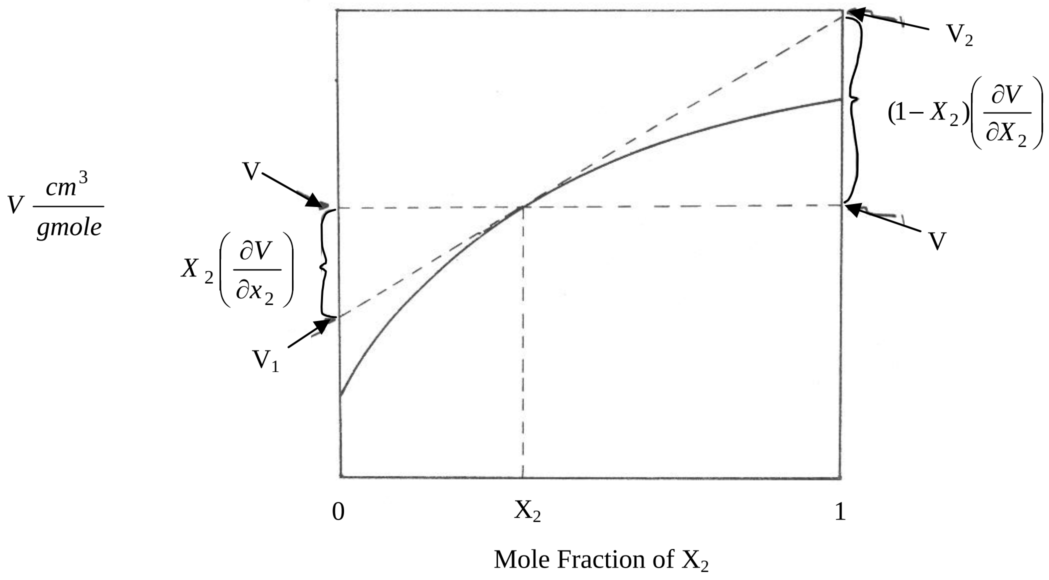

Figure 2. The Tangent –Intercept Method of Finding Partial Molar Volumes

Summary of Absolute Quantities

As stated previously, the above development is directly applicable to the thermodynamic properties H, S, and G. In general, the partial molar quantity is defined as

$$Q_i = \left(\frac{\partial Q_T}{\partial n_i} \right)_{T,\,P,\,n_j} \qquad (16)$$

The integral molar quantity for a binary solution is related to the partial molar quantities as

$$Q = X_1 Q_I + X_2 Q_2 \qquad (17)$$

and the Gibbs-Duhem Equation requires that

$$X_1 \partial\, Q_I + X_2 \partial\, Q_2 = 0$$

The Tangent-Intercept Method may be used to obtain the partial molar quantities Q_i from the integral molar quantity Q. The quantity Q can be V, H, S, or G.
Absolute values are determinable for V and S, but not for H and G. Since only changes in H and G are required for thermochemical calculations, there is no need for the absolute values of H and G. However, the changes in H and G must be related to some standard (or reference) state. When this is done the changes in H and G are called the relative enthalpy and relative Gibbs energy. The next section considers these relative values.

Relative Values (or "…of Mixing")

To assign numerical values to the thermodynamic solution functions of enthalpy and Gibbs energy it is necessary to relate them to a reference state. Since absolute heat energy cannot be measured, all tabulated energy and enthalpy data equals the change from some reference state. For solids and liquids this state is the pure component at the pressure and temperature of interest.

The difference between the partial molar volume in solution V_1 and the molar volume of the pure species is V_i° called the "relative partial molar volume" and is denoted by the symbol V_i^M

$$V_i^M \equiv V_i - V_i^\circ \qquad (18)$$

In general,

$$Q_i^M \equiv Q_i - Q_i^\circ \qquad (19)$$

The parameters on the left side of Eqs. [18] and [19] are also called "partial molar quantities of mixing," because the term 'mixing' implies a quantity relative to the reference state which is the pure component.

The discussion of relative quantities began by citing the necessity of relating the enthalpy and free energy quantities to a reference state so that the change from the reference state could be measured. Methods of measuring these changes for H and G are presented below.

Measurement of Relative Partial Molar Enthalpy and Gibbs Free Energy

The partial molar heat of mixing of species i can be measured calorimetrically by dropping a small amount of liquid component i at temperature T into a solution at temperature T. The transfer of heat required to return the solution to the original temperature equals the heat of mixing for the small quantity Δ n$_{i.}$

Therefore,

$$H_i^M = \lim_{\Delta n_i \to o} \left(\frac{\Delta H_T}{\Delta n_i} \right)_{T,P,n_{other}} = \left(\frac{\partial H_T}{\partial n_i} \right)_{T,P,n_{other}} \qquad (20)$$

Of course, the quantity Δ n$_{i.}$ must be small enough so as not to change the solution's composition, because H_i^M =f(X$_i$).

The partial free energy of mixing may be determined by measuring the partial pressure of species i above the solution and above pure i providing ideal behavior of the gas prevails.

$$G_i^M = G_i - G_i^\circ = RT \ln a_i = RT \ln \left(\frac{P_i}{P_i^o} \right) \qquad (21)$$

Here P_i^o is the pressure of the pure component i.

A second method of measuring G_i^M is by a galvanic cell. If the galvanic cell shown in Figure 3 creates the potential E, then the partial molar Gibbs free energy of mixing is

$$G_i^M = -nFE \qquad (22)$$

where n = the number of equivalents for the cell

F = Faraday's constant: $96{,}525 \dfrac{Joules}{volt * equivalent}$

The relative partial molar entropy of species i may be calculated from the equation

$$G_i^M = H_i^M - TS_i^M \qquad (23)$$

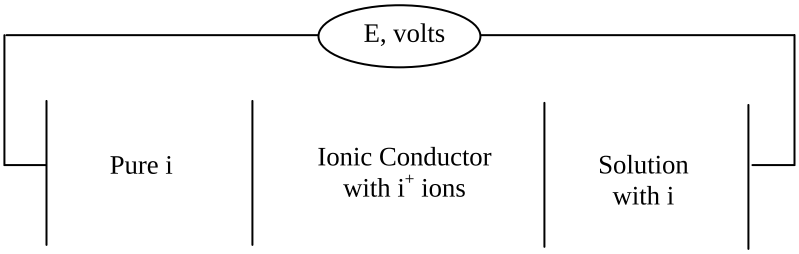

Figure 3. Galvanic Cell for Determining Activities of Component i

Relative Integral Molar Quantities

The integral quantities refer to one mole or solution. Like partial quantities, integral quantities are both absolute and relative. For example, the absolute volume of one mole of a binary solution (two components) is given by equation

$$V^M = x_1 V_1^M + x_2 V_2^M \tag{24}$$

and in general

$$Q^M = x_1 Q_1^M + x_2 Q_2^M \tag{25}$$

The "relative integral molar quantity" Q^M may also be called the "integral molar quantity of mixing."

The Tangent-Intercept Method and Relative Quantities

Relative partial molar quantities may be obtained from the relative integral molar quantities by the Tangent-Intercept Method as illustrated in Figure 2. The same procedure used to derive Eqs. [13] and [14] is followed to obtain

$$Q_1^M = Q^M - x_2 \left(\frac{\partial Q^M}{\partial x_2} \right) \tag{26}$$

$$Q_2^M = Q^M + (1 - x_2) \left(\frac{\partial Q^M}{\partial x_2} \right) \tag{27}$$

Gibbs-Duhem Equation

Likewise, the Gibbs-Duhem Equation for relative quantities has the general form

$$X_1 \partial Q_1^M + X_2 \partial Q_2^M = 0 \tag{28}$$

Excess Values

The excess quantities are defined merely for convenience. They are simply the difference between the actual value of the relative quantity and the value of the relative quantity were the solution ideal.

$$Q_i^{xs} = Q_i^M - Q_i^{M,\,ideal} \tag{29}$$

An ideal solution is a solution in which the interaction among the atoms and molecules of unlike components is the same as the interactions among like atoms and molecules. In such case

$$V_i^{M_1\,ideal} = 0 \tag{30}$$

$$H_i^{M_1\,ideal} = 0 \tag{31}$$

$$G_i^{M_1\,ideal} = RT \ln X_i \tag{32}$$

$$S_i^{M_1\,ideal} = -R \ln X_i \tag{33}$$

Therefore,

$$V_i^{xs} = V_i^M \tag{34}$$

$$H_i^{xs} = H_i^M \tag{35}$$

$$G_i^{sx} = RT \ln a_i - RT \ln X_i = RT \ln\left(\frac{a_i}{X_i}\right) = RT \ln \gamma_i \tag{36}$$

$$S_i^{xs} = S_i^M + R \ln X_i \tag{37}$$

For the integral excess molar quantities

$$V^{xs} = V^M \tag{38}$$

$$H^{xs} = H^m \tag{39}$$

$$S^{xs} = S^M + R\left(X_1 \ln X_1 + X_2 \ln X_2\right) \tag{40}$$

$$G^{xs} = G^M - RT\left(X_1 \ln X_1 + X_2 \ln X_2\right) \tag{41}$$

As with all other partial quantities, the Gibbs-Duhem Equation is valid.

$$X_1 \partial Q_1^{xs} + X_2 \partial Q_2^{xs} = 0 \tag{42}$$

Likewise, the Tangent-Intercept Method may be used to obtain excess partial molar quantities from the corresponding excess integral molar quantity.

Summary

The four thermodynamic quantities V, H, S, and G may refer to either one mole of a solution component (partial molar quantity) or to one mole of solution (integral molar quantity). These quantities may be reported as the absolute value (except for H and G), relative value, or excess value.
The Gibbs-Duhem Equation applies to any of the partial molar quantities and has the general form

$$X_1 \partial Q_1 + X_2 \partial Q_2 = 0 \tag{43}$$

where $Q_1 =$ any partial molar quantity for component 1
$Q_2 =$ any corresponding partial molar quantity for component 2

Likewise, the Tangent-Intercept Method may be used to find any partial molar quantity from the corresponding integral molar quantity

$$Q_1 = Q - X_2\left(\frac{\partial Q}{\partial X_2}\right) \tag{44}$$

$$Q_2 = Q + \left(1 - X_2\right)\left(\frac{\partial Q}{\partial X_2}\right) \tag{45}$$

Any integral molar quantity may be found from the corresponding partial molar quantities according to the following summation

$$Q = X_1 Q_1 + X_2 Q_2 + \ldots \tag{46}$$