Open Systems: Chemical Potential and Partial Molar Quantities

Chemical Potential

For closed systems, we have derived the following relationships:

$$dU = TdS - pdV$$

$$dH = TdS + Vdp$$

$$dA = -SdT - pdV$$

$$dG = VdP - SdT.$$

For open systems, in addition to the two variables in each of the above equations, one must also consider the variation of the number of moles of each species, n_i. Therefore, for open systems, we write

$$dU = TdS - pdV + \sum_i \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} dn_i$$

$$dH = TdS + Vdp + \sum_i \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_{j\neq i}} dn_i$$

$$dA = -SdT - pdV + \sum_i \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}} dn_i$$

$$dG = VdP - SdT + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} dn_i$$

The partial derivatives within the summations above are called "chemical potentials" for the i-th species, and denoted by the letter μ. Therefore,

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_{j\neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}} = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}}$$

It may seem strange that the derivatives of all these thermodynamic properties with respect to composition are all equal. One way to think about this is to consider each property as a multidimensional surface in the appropriate space, I.e., the space of (S,V,n_i) for U, (S,p,n_i) for H, and so on. Then the above relationship requires that the slopes of these surfaces in one particular direction, with the other quantities fixed, are the same. Below, we define certain quantities called partial molar quantities, which are also derivatives of state properties with respect to composition, but *always* with T,p fixed. The fact that the partial molar free energy is also equal to the chemical potential is noteworthy.

Partial Molar Quantities

Partial Molar quantities are required to deal with <u>open</u> <u>systems</u>, i.e., systems that permit mass transfer between themselves and surroundings.

Consider an <u>open</u> system with n_1 moles of component 1, n_2 moles of component 2, n_3 moles of component 3, etc.. We would write the free energy change dG for such a system as

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,\dots} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2,\dots} dT + \left(\frac{\partial G}{\partial n_1}\right)_{P,T,,n_2,\dots} dn_1 + \dots$$

$$= VdP - SdT + \overline{G}_1 dn_1 + \overline{G}_2 dn_2 + \dots$$

In the second equality, the quantities G_1, G_2, etc.. are called *partial molar free energies*. Similarly, we may define partial molar volumes, partial molar enthalpies, internal energies, and entropies:

$$\overline{V}_1 = \left(\frac{\partial V}{\partial n_1}\right)_{P,T,,n_2,\dots} ; \overline{H}_1 = \left(\frac{\partial H}{\partial n_1}\right)_{P,T,,n_2,\dots} ; \text{etc..} \qquad (1)$$

Because of their great importance in the thermodynamics of solutions, we discuss partial molar volumes and partial molar free energies further.

Partial Molar Volume:

The total volume of a solution of, say, two miscible liquids is given by

$$\boxed{V = n_1 \overline{V}_1 + n_2 \overline{V}_2} \qquad (2)$$

The units of partial molar volumes are the same as molar volumes. The relationship between the two, i.e., partial molar volume and the molar volume is a subtle but important one.

- In the case of ideal solutions, the partial molar volume of each component will be identical to the molar volume of the pure substance in the absence of the other component.
- However, in the case of non-ideal solutions, the presence of the second component has a measurable influence on the molar volume of the first component and vice versa. Therefore, in general,

  $$\overline{V}_1 \neq V_1^* \text{ and } \overline{V}_2 \neq V_2^*.$$

The standard state for defining partial molar quantities is a 1 **molal** solution, i.e., a solution that contains 1 mol of the substance in 1.0 kg of solvent.

Physical Interpretation of partial molar quantities:

It may appear that there is something "not quite right" about the following two equations:

$$V = n_1 \overline{V}_1 + n_2 \overline{V}_2, \text{where}$$

$$\overline{V}_1 = \left(\frac{\partial V}{\partial n_1} \right)_{P,T,n_2}, \text{and } \overline{V}_2 = \left(\frac{\partial V}{\partial n_2} \right)_{P,T,n_1}.$$

Based on what we have seen so far, the first equation should be $dV = \overline{V}_1 dn_1 + \overline{V}_2 dn_2$, which is simply another application of the chain rule in partial differentiation.

However, Eq. (2) can indeed be justified on physical grounds as follows. Consider a large volume of solution containing ethanol (E) and water (W). We now add a small amount of water, say, Δn_W moles of water, to this solution. We would want to express the new volume of the solution as $V_{new} = V_{old} + \Delta n_W V^*_{W,m}$, where $V^*_{W,m}$ is the molar volume of pure water. However, this will give us the final volume only in the case of an ideal solution. In the ethanol-water solution, the *effective* molar volumes of both substances are different from their molar volumes in the absence of the other substance. Designating the actual molar volume of water in the presence of ethanol as $V_{W,m}$, the change of volume of the solution is

$$\Delta V = \Delta n_W \overline{V}_{W,m}.$$

Therefore, we get $\overline{V}_{W,m} = \dfrac{\Delta V}{\Delta n_W}$.

The partial molar volume of water, V_W, is defined as the value of the fraction on the right hand side in the limit of an infinitesimal change in the number of moles of water. Mathematically, we write

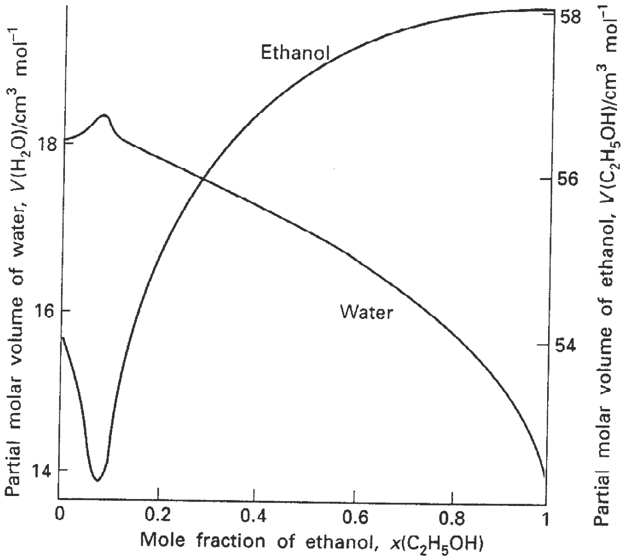
$$\overline{V}_W = \lim_{\Delta n_W \to 0} \frac{\Delta V}{\Delta n_W} = \frac{dV}{dn_W}.$$

Once we impose the conditions that temperature, pressure and the number of moles of ethanol, n_E, are to be held constant, the derivative on the right hand side becomes identical to the definition of the partial molar volumes used above and in Eq. (1):

$$\overline{V}_W = \left(\frac{\partial V}{\partial n_W} \right)_{T,P,n_E}.$$

An example of the applications of Eq. (2):

Consider a 40% by mass ethanol solution of ethanol in water at 25°C. From the figure of partial molar volumes of ethanol and water in the presence of each other, estimate the volume of 1000 g of the solution. Compare this to the volume that would have resulted if the solution was ideal. Density of ethanol = 0.785 g mL^{-1} and pure water = 0.997 g mL^{-1} , at this temperature.



In 1000 g of solution, we have 400 g ethanol (*E*) and 600 g water (*W*).

$$n_E = \frac{400\text{ g}}{46.07\text{ g mol}^{-1}} = 8.68\text{ mol.}$$

$$n_W = \frac{600\text{ g}}{18.02\text{ g mol}^{-1}} = 33.30\text{ mol}$$

$$x_E = 0.207;\ x_W = 0.793.$$

From the figure, we estimate that at these mole fractions, the partial molar volumes are

$$\overline{V}_E = 55.5\text{ mL mol}^{-1};$$

$$\overline{V}_W = 17.2\text{ mL mol}^{-1}.$$

Therefore, using Eq. (5.33), we get

$$V = n_E \overline{V}_E + n_W \overline{V}_W = 8.68 \times 55.5 + 33.30 \times 17.2$$
$$= 1054.5\text{ mL.}$$

If the solution was ideal, we would use the molar volumes of the pure substances to obtain

$$V = 8.68\text{ mol} \times \frac{46.07\text{ g mol}^{-1}}{0.785\text{ g mL}^{-1}} + 33.30\text{ mol} \times \frac{18.02\text{ g mo}}{0.997\text{ g mL}}$$
$$= 1111\text{ mL.}$$

Therefore, we see that the non-ideal nature of the solution is reflected in a contraction of volume.

Another example of applying Eq. (2):

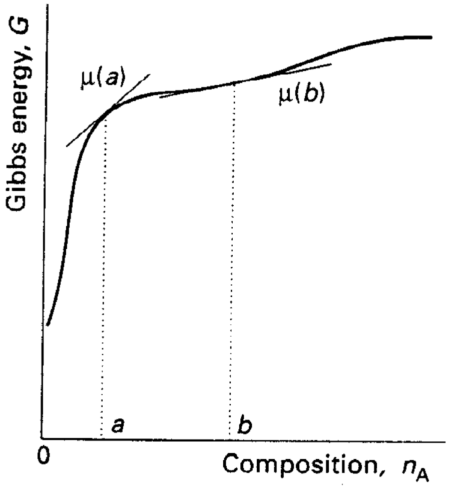
Density of a 50% by mass solution of ethanol in water at 25°C is 0.914 g mL^{-1}. Given that the partial molar volume of water at this composition is 17.4 mL mol^{-1},what is the partial molar volume of ethanol?

No. of moles of ethanol in 100 g of solution: 50 g/46.07 g mol^{-1} = 1.085 mol.
No. of moles of water in 100 g of solution: 50 g/18.02 g mol^{-1} = 2.775 mol.
Now, since $V = n_E \overline{V}_E + n_W \overline{V}_W$, we get

$$\begin{aligned}\overline{V}_E &= \frac{V - n_W \overline{V}_W}{n_E} \\ &= \frac{\left(100\text{ g}/0.914\text{ g mL}^{-1}\right) - 2.775\text{ mol} \times 17.4\text{ mL mol}}{1.085\text{ mol}} \\ &= 56.33\text{ mL mol}^{-1}.\end{aligned}$$

Partial molar Free Energy:

Partial molar free energy is commonly refered to as the "chemical potential," and denoted by the letter μ:



$$\boxed{\begin{aligned}\mu_A &= \overline{G}_A = \left(\frac{\partial G}{\partial n_A}\right)_{P,T,n_B} \\ \mu_B &= \overline{G}_B = \left(\frac{\partial G}{\partial n_B}\right)_{P,T,n_A}\end{aligned}}.$$

The figure to the left shows a plot of the total free energy G vs. n_A. The slope of the plot of G vs. n_A at various compositions yields the partial molar free energy $\overline{G}_A$ at that composition. From this information, $\overline{G}_B$ can be found as in the example above.

For a pure substance, partial molar free energy is simply a measure of the molar free energy since, in this case, $G = nG_m$, and

$$\left(\frac{\partial G}{\partial n}\right)_{T,p} = G_m.$$

Gibbs-Duhem Equation

We now derive an important equation related to partial molar properties. Consider a general property *Z*. Using the definition of partial molar quantities above,

$$dZ = \sum_i \overline{Z}_i dn_i. \tag{3}$$

But, generalizing Eq. (2), we get

$$Z = n_i \overline{Z}_i. \tag{4}$$

At the same time, the general differential of $Z(n_i, \overline{Z}_i)$ (using the chain rule) is

$$dZ = \sum_i n_i d\overline{Z}_i + \sum_i \overline{Z}_i dn_i. \tag{5}$$

Comparing Eq. (3) and (5), we conclude that

$$\sum_i n_i d\overline{Z}_i = 0. \tag{6}$$

This is called the Gibbs-Duhem equation. One application of this equation is illustrated below.

Determination of partial molar quantities

It is often more convenient to express the property (and therefore, the corresponding partial molar properties) in the form of an empirical function of concentration, usually molality. Consider a binary mixture, a solution consisting of one solute and a solvent. Once again, using volume as an example, we write[1]

$$V = a + bm^{1/2} + cm + dm^{3/2} + em^2$$

where *m* is the molality of the solute and (*a*, *b*, *c*, *d*, *e*) are empirical constants. Usually, the solvent is assigned the subscript 1 and the solute, the subscript 2. Therefore,

$$\overline{V}_2 = \left(\frac{\partial V}{\partial n_2}\right)_{T,p,n_1} = \left(\frac{\partial V}{\partial m}\right)_{T,p,n_1} = \tfrac{1}{2}bm^{-1/2} + c + \tfrac{3}{2}dm^{1/2} + 2em$$

Now, recalling the Gibbs-Duhem equation (applied to volume),

$$n_1 d\overline{V}_1 + n_2 d\overline{V}_2 = 0,$$

---

[1] This model seems to work well for volumes.

we conclude that

$$n_1 d\overline{V}_1 + m(-\tfrac{1}{4}bm^{-3/2} + \tfrac{3}{4}dm^{-1/2} + 2e)dm = 0$$

Therefore, $d\overline{V}_1 = \frac{1}{n_1}\left[\tfrac{1}{4}bm^{-1/2} - \tfrac{3}{4}dm^{1/2} - 2em\right]dm.$

Integrating both sides, we get

$$\int_{V^*_{1,m}}^{\overline{V}_1} d\overline{V}_1 = \frac{1}{n_1}\int_0^m \left[\frac{1}{4}bm^{-1/2} - \frac{3}{4}dm^{1/2} - 2em\right]dm.$$

$$\overline{V}_1 = V^*_{1,m} + \frac{1}{n_1}\left[\frac{b}{8}m^{1/2} - \frac{d}{2}m^{3/2} - em^2\right].$$

Thus, in a binary mixture, if we have an expression for the variation of the partial molar volume with concentration for one of the components, we can find an expression for the other. Similar treatments are generally possible for other partial molar properties as well.

Thermodynamic relationships among partial molar quantities

We now show that the thermodynamic relationships derived earlier for state properties also apply to partial molar properties. For example, consider the thermodynamic equation of state

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p. \tag{7}$$

Differentiating both sides with respect to n_i, we get

$$\left[\frac{\partial}{\partial n_i}\left(\frac{\partial H}{\partial p}\right)_T\right]_{T,p,n_{j\neq i}} = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_{j\neq i}} - T\left[\frac{\partial}{\partial n_i}\left(\frac{\partial V}{\partial T}\right)_p\right]_{T,p,n_{j\neq i}}.$$

Since the order of differentiation is immaterial for state properties,

$$\left[\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial n_i}\right)_{T,p,n_{j\neq i}}\right]_T = \overline{V}_i - T\left[\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_{j\neq i}}\right]_p \text{ or}$$

$$\left(\frac{\partial \overline{H}_i}{\partial p}\right)_T = \overline{V}_i - T\left(\frac{\partial \overline{V}_i}{\partial T}\right)_p.$$

Similarly, every equation we have derived for state properties can be applied to partial molar quantities as well.

Criteria for equilibrium

The thermodynamic criterion for equilibrium in open systems is also formulated in terms of partial molar free energies, or chemical potentials.

If A and B are present in two phases α and β, the phase equilibrium condition is:

$$\boxed{\overline{G}_A^{\alpha} = \overline{G}_A^{\beta} \text{ (or } \mu_A^{\alpha} = \mu_A^{\beta}\text{) and } \overline{G}_B^{\alpha} = \overline{G}_B^{\beta} \text{ (or } \mu_B^{\alpha} = \mu_B^{\beta}\text{).}}$$

For chemical equilibria, the net chemical potential of the reactants (weighted by the stoichiometric coefficients) must be equal to the net chemical potential of the products. Consider the equilibrium

$$n_A A + n_B B \rightleftharpoons n_C C + n_D D.$$

Then, the criterion for chemical equilibrium is

$$(n_C \mu_C + n_D \mu_D) = (n_A \mu_A + n_B \mu_B).$$