Statistical Molecular Thermodynamics

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Video 10.2

Partial Molar Quantities and the Gibbs-Duhem Equation

Chemical Potential

Continuing to work with 2-component solutions:

$$dG(n_1, n_2, P, T) = \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{P,n_1,T} dn_2 + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2} dT$$

or specifically:

$$dG(n_1, n_2, P, T) = \mu_1 dn_1 + \mu_2 dn_2 + VdP - SdT$$

where the chemical potential is a partial molar free energy

$$\mu_j = \left(\frac{\partial G}{\partial n_j}\right)_{n_{i \neq j}, P, T} = \bar{G}_j$$

for a pure substance, the partial molar free energy is the free energy of one mole of that substance, but μ may be something different for one mole present in a mixture.

Other Partial Molar Quantities

Consider volume:

$$V\left(n_1, n_2, P, T\right)$$

at constant *P* and *T*, *V* is a function only of extensive variables, i.e., homogeneous of degree one, so Euler's theorem provides:

$$V\left(n_1, n_2; P, T\right) = \left(\frac{\partial V}{\partial n_1}\right) n_1 + \left(\frac{\partial V}{\partial n_2}\right) n_2$$

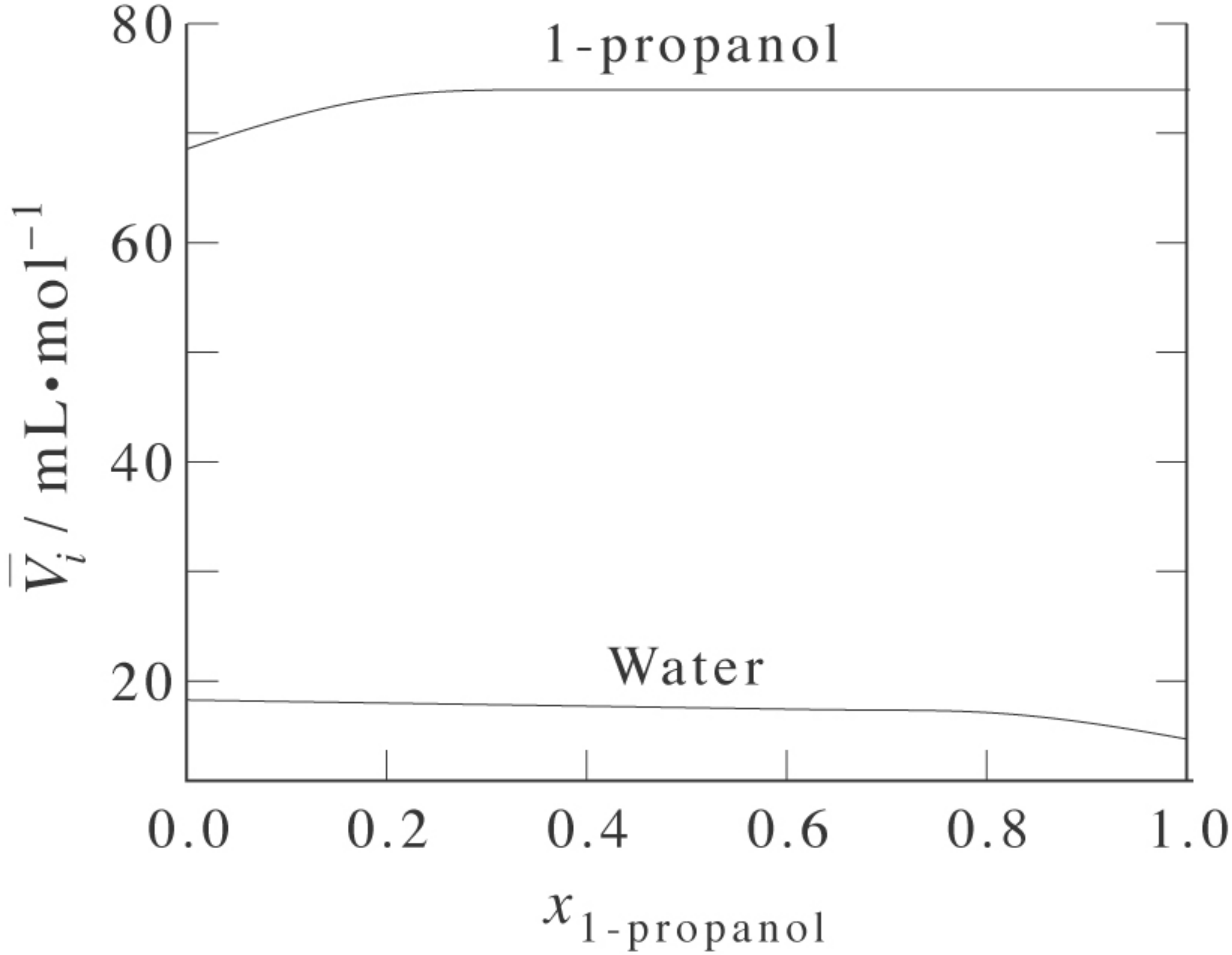
where the partial molar volume is defined as:

$$\bar{V}_j = \left(\frac{\partial V}{\partial n_j}\right)_{n_{i \neq j}, P, T}$$

for a pure substance, the partial molar volume is the volume of one mole of that substance, but $\bar{V}$ may be something different for one mole present in a mixture.

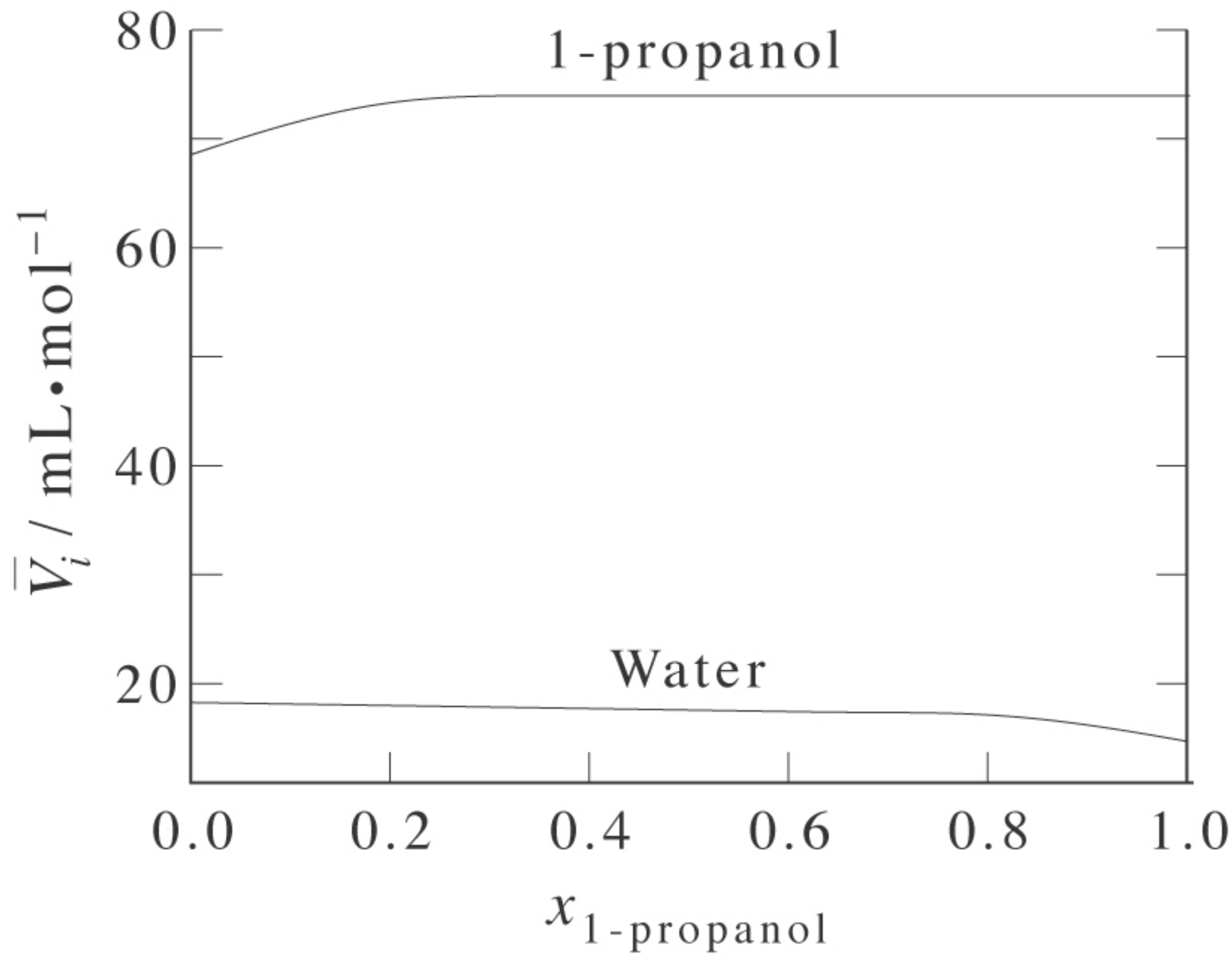
Partial Molar Volume in Solution

$$V(n_1, n_2; T, P) = \bar{V}_1 n_1 + \bar{V}_2 n_2$$



Notice how the partial molar volume for both liquids *varies* as a function of the composition of the solution

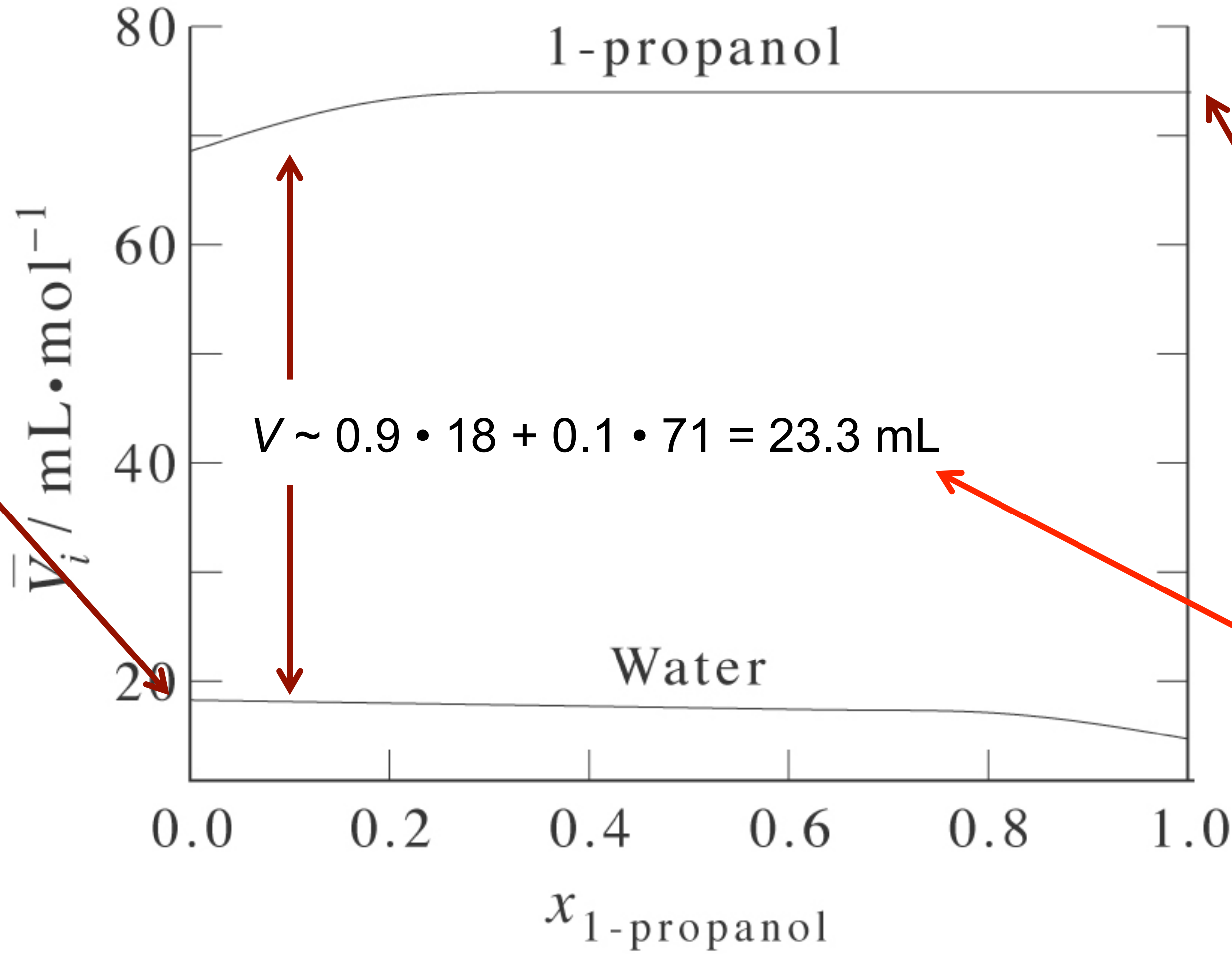
Self-assessment



Using the diagram at left, what is roughly the *total* volume of 1 mole of *n*-PrOH, 1 mole of H_2O, and of a solution of 0.1:0.9 moles *n*-PrOH:H_2O mixed together?

Self-assessment Explained

pure H_2O
~18 mL



pure *n*-PrOH
~73 mL

from pouring together 16.2 mL of H_2O and 7.3 mL of *n*-PrOH

$$V(n_1,n_2;T,P)=\bar{V}_1 n_1+\bar{V}_2 n_2$$

All Extensive Quantities Have Partial Molar Equivalents

$$G_j = \mu_j = \bar{H}_j - T\bar{S}_j$$

$$d\mu_j = -\bar{S}_j dT + \bar{V}_j dP$$

But now, let's return to:

$$dG(n_1, n_2, P, T) = \mu_1 dn_1 + \mu_2 dn_2 + VdP - SdT$$

Or, at constant *P* and *T*:

$$dG(n_1, n_2, P, T) = \mu_1 dn_1 + \mu_2 dn_2$$

Gibbs-Duhem Equation

$$dG(n_1, n_2, P, T) = \underline{\mu_1 dn_1} + \underline{\mu_2 dn_2}$$

But from Euler's theorem we know:

$$G(n_1, n_2) = n_1\mu_1 + n_2\mu_2$$

which, differentiated gives:

$$dG(n_1, n_2) = n_1 d\mu_1 + \underline{\mu_1 dn_1} + n_2 d\mu_2 + \underline{\mu_2 dn_2}$$

So that we may determine:

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

Know One Chemical Potential as a Function of Composition, Know the Other

If we divide $n_1 d\mu_1 + n_2 d\mu_2 = 0$ by (n_1 + n_2), we can write:

$$x_1 d\mu_1 + x_2 d\mu_2 = 0$$

Gibbs-Duhem Equation

(constant T and P)

Note the critical implication: if we know the variation of the chemical potential of *one* component of a mixture as a function of composition, we can determine the variation of the *other*. As we will see, this can be very useful when one is easy to measure and the other perhaps not...

Next: Multicomponent/Multiphase Equilibria