Partial molar volume

Add 1 mol H_2O to a large quantity of water → V_m of pure H_2O is 18 ml.

Add 1 mol H_2O to a large quantity of EtOH → increase of volume is only 14 ml. Reason is packing of molecules. 14 cm^3 mol^{-1} is the partial molar volume of water in pure ethanol.

$$V_J = \left(\frac{\partial V}{\partial n}\right)_{p,T,n'}$$

The partial molar volume is the slope of the plot of the total volume as the amount of J is changed, all other parameters being kept constant. It depends on the composition.

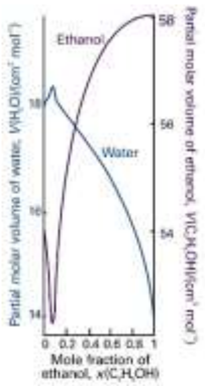
The total volume of a two-component mixture changes by

$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n_A} dn_B$$

Provided the relative composition is held constant as the amounts of A and B are increased, the final volume is

$$V = \int_0^{n_A} V_A dn_A + \int_0^{n_B} V_B dn_B = V_A \int_0^{n_A} dn_A + V_B \int_0^{n_B} dn_B = V_A n_A + V_B n_B$$

Partial molar volumes can be –ve. E.g. 1 mol $MgSO_4$ added to a large quantity of water results in a decrease in the volume by 1.4 ml.



Partial molar Gibbs energy

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'}$$

$$G = n_A\mu_A + n_B\mu_B$$

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \cdots$$

$$dG = \mu_A dn_A + \mu_B dn_B + \cdots \qquad at\ constant\ T\ and\ p$$

Also equals the $w_{add,max}$ as seen earlier.

Not just G

Since $G = U + pV - TS$

$$dU = -pdV - Vdp + SdT + TdS + dG$$

$$= -pdV - Vdp + SdT + TdS + Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \cdots$$

$$= -pdV + TdS + \mu_A dn_A + \mu_B dn_B + \cdots$$

$$dU = \mu_A dn_A + \mu_B dn_B + \cdots \qquad at\ constant\ V\ and\ S$$

$$\therefore\ \mu_J = \left(\frac{\partial U}{\partial n_J}\right)_{V,S,n'} \quad Also, \quad \mu_J = \left(\frac{\partial H}{\partial n_J}\right)_{p,S,n'} \quad and \quad \mu_J = \left(\frac{\partial A}{\partial n_J}\right)_{V,T,n'}$$

Gibbs-Duhem equation

$$dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B$$

Also we have seen, $dG = \mu_A dn_A + \mu_B dn_B$ → $n_A d\mu_A + n_B d\mu_B = 0$

In general,

$$\sum_J n_J d\mu_J = 0$$

Significance: Chemical potential of one component of a mixture cannot change independently of the chemical potentials of the other components.

In a binary mixture, $d\mu_B = -\frac{n_A}{n_B} d\mu_A$

The same line of reasoning applies to other partial molar quantities. If one increases the other must decrease.