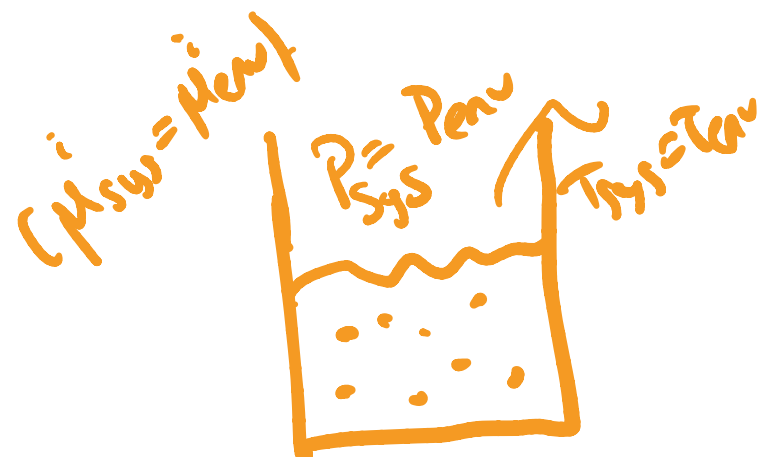


Lecture 9

[dS]
(max entropy)

Mixtures \rightarrow Phase transitions
(chemical potential)

$$E(N, V, S) \xrightarrow{-TS} A(N, V, T)$$



+PV
↓

+PV
↓

$$H(N, P, S) \xrightarrow{-TS} G(N, P, T)$$

isobaric, $dy = 0$

Legendre Transformations $A(N, V, T) = E(N, V, S) - S(\partial E / \partial S)_{N, V}$

$$A(N, V, T) = E(N, V, S) - S \left(\frac{\partial E}{\partial S} \right)_{N, V} \leftarrow T$$

1st law

$$dE = \overset{dq}{T} dS - P dV$$

\leftarrow 1st law

$$dE(N, V, S) = \left(\frac{\partial E}{\partial S} \right)_V dS + \left(\frac{\partial E}{\partial V} \right)_S dV \leftarrow \text{chain rule}$$

$$\left(\frac{\partial E}{\partial S} \right)_V = T \quad \left(\frac{\partial E}{\partial V} \right)_S = -P$$

$$G(P, T) \Rightarrow$$

$$dE = Tds - PdV$$

$$\star_2 \quad dG = \left(\frac{\partial G}{\partial P} \right)_T dP + \left(\frac{\partial G}{\partial T} \right)_P dT$$

Also know

$$G = E - TS + PV = (H - TS)$$

$$dG = dE - Tds - SdT + PdV + VdP$$

$$= \underbrace{(dE - Tds + PdV)}_{\text{b/c of 1st law}} - SdT + VdP$$

o b/c of 1st law

$$\star_1 \quad = -SdT + VdP \Rightarrow$$

$$S = - \left(\frac{\partial G}{\partial T} \right)_P$$
$$V = \left(\frac{\partial G}{\partial P} \right)_T$$

Table 5.1 Energy potentials, differentials, and derivatives

Integrated form	Differential form ^a	Energy derivative identities	Maxwell Relations
$U(S,V)$	$dU = TdS - pdV$	$\left(\frac{\partial U}{\partial S}\right)_V = T, \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
$H(S,p) = U + PV$	$dH = TdS + Vdp$	$\left(\frac{\partial H}{\partial S}\right)_p = T, \quad \left(\frac{\partial H}{\partial p}\right)_S = V$	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
$A(T,V) = U - TS$	$dA = -SdT - pdV$	$\left(\frac{\partial A}{\partial T}\right)_V = -S, \quad \left(\frac{\partial A}{\partial V}\right)_T = -p$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$
$G(T,p) = H - TS$	$dG = -SdT + Vdp$	$\left(\frac{\partial G}{\partial T}\right)_p = -S, \quad \left(\frac{\partial G}{\partial p}\right)_T = V$	$\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$

^a Differential relations are evaluated at equilibrium, and thus are equalities.

Maxwell relationship:

$$\frac{\partial}{\partial x} \left(\frac{\partial}{\partial y} f \right) = \frac{\partial}{\partial y} \left(\frac{\partial}{\partial x} f \right)$$

$$dG = \left(\frac{\partial G}{\partial P} \right)_T dP + \left(\frac{\partial G}{\partial T} \right)_P dT$$

$$= V dP - S dT$$

$$\left. \frac{\partial}{\partial T} \right|_P \left(\frac{\partial G}{\partial P} \right)_T = \left. \frac{\partial}{\partial P} \right|_T \left(\frac{\partial G}{\partial T} \right)_P$$

$$\left(\frac{\partial V}{\partial T} \right)_P = - \left(\frac{\partial S}{\partial P} \right)_T \quad \leftarrow \text{hard to measure}$$

\uparrow easy to measure

$$T = \left(\frac{\partial E}{\partial S} \right)_V \Rightarrow \frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_V$$

@ low T , $E \uparrow$ $S \uparrow$ a lot

@ high T , $E \uparrow$ $S \uparrow$ a little

$$\frac{\partial [k_B \ln \Omega]}{\partial E} = \frac{1}{T}$$

$$\frac{\partial \ln \Omega}{\partial E} = \frac{1}{k_B T} \equiv \beta$$

$$[P(E) = C e^{-E/k_B T}] \\ = e^{-\beta E}$$

Mixtures

$$\begin{aligned} N_{\text{total}} &= N_A + N_B + \dots \\ \text{Moles} &= \sum_{i=1}^k N_i \end{aligned}$$

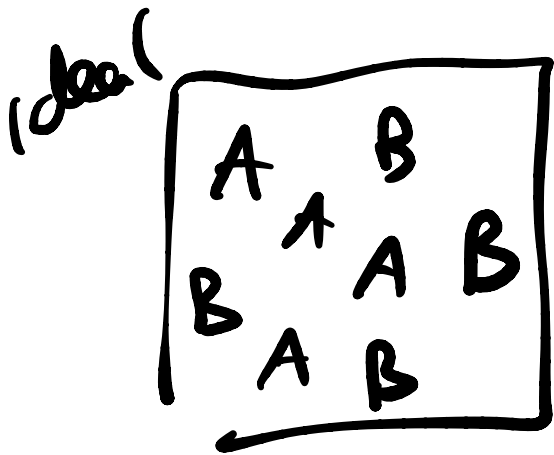
$$n_{\text{total}} = n_A + n_B + \dots$$

mole fraction

$$\chi_A = \frac{n_A}{n_{\text{total}}} \quad \chi_B = \frac{n_B}{n_{\text{total}}}$$

$$\chi_A + \chi_B = 1$$

Mixtures are not "ideal"



$$E^{ideal} = E_A^{total} + E_B^{total}$$

$$P^{ideal} = P_A^{total} + P_B^{total}$$

$$S^{ideal} = S_A^{ideal} + S_B^{ideal}$$

↓ per mole

$$E_{total} = n_A \bar{E}_A + n_B \bar{E}_B$$

but $\bar{E}_A \neq E_A^* \leftarrow \bar{E}_A$ alone

$$\bar{V}_A = V_A / n_A \text{ for a system}$$

$$\bar{V}_A^* = V_A \text{ per mol in a solution} \\ \text{with only A molecules } (\chi_A = 1)$$

$$\bar{V}_{\text{ideal}} = \chi_A \bar{V}_A^* + \chi_B \bar{V}_B^*$$

usually not true

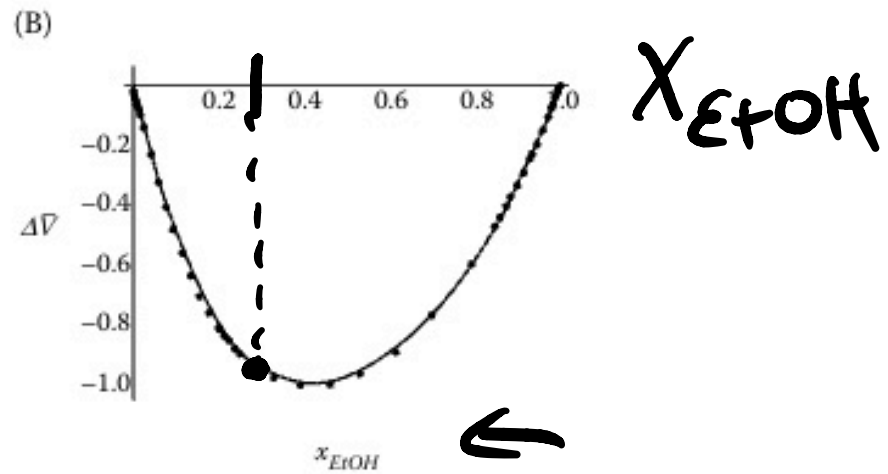
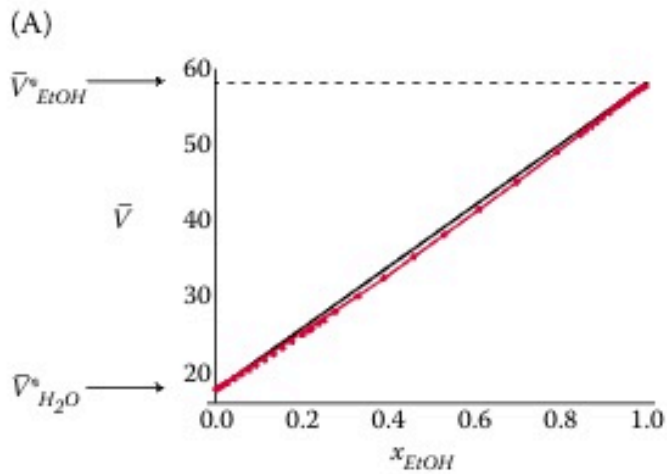


Figure 5.8 The volume of mixtures of liquid water and ethanol. (A) The total molar volume (in mL/mol, obtained by dividing the bottom line of Equation 5.60 by n_T) at different compositions. If molar volume were independent of composition ("volume ideality"), \bar{V} would be a straight line (black, Equation 5.52) connecting $\bar{V}_{H_2O}^*$ and \bar{V}_{EtOH}^* . However, mixtures of water and ethanol have a lower measured volume (red circles; the red line is a fifth order polynomial fit to the data to guide the eye). (B) The volume difference between the ideal and real mixture ($\Delta\bar{V}$). At $x_{EtOH} = 0.2$ (the mole fraction of a 50:50 volume mixture), $\Delta\bar{V}$ is about -8 mL per mole, consistent with the 3 mL contraction described in Figure 5.7C. Data are from Marsh and Richards (1980).

$$V_{H_2O}^* = 18 \text{ mL/mol}$$

$$V_{EtOH}^* = \frac{57 \text{ mL}}{\text{mol}}$$

(RT
atm)

50 mL + 50 mL of each

$$n_A = \frac{50}{18} = 2.8$$

$$n_B = \frac{50}{57} = 0.88$$

$$n_{tot} = 3.68$$

$$x_{EtOH} = 0.24$$

$$\Delta\bar{V} = -0.8 \text{ mL/mol}$$

$$\Delta V = -2.9 \text{ mL}$$

$$V(n_A, n_B) \Rightarrow dV = \left(\frac{\partial V}{\partial n_A} \right)_B dn_A + \left(\frac{\partial V}{\partial n_B} \right)_A dn_B$$

want to know volume

$$\int_0^{V^{\text{total}}} dV = \int_0^{V^{\text{total}}} \left(\quad \right)$$

a path of fixed composition

need to know $\left(\frac{dV}{dn_A} \right)_{n_B}$ ← need to measure

Chemical Potential

2 definitions:

$$\textcircled{1} \quad \mu_A = G_A / n_A = \overline{G}_A$$

$$G_{\text{total}} = \sum_{i=1}^{k \text{ things}} \mu_i n_i$$

$$\textcircled{2} \quad \mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j \neq n_i}$$

$$[\mu_i \neq \mu_i^*]$$

μ_A depends
on T, P
 $\{n_i\}$

$$G(P, T, n_1, n_2, \dots)$$

$$dG = \left(\frac{\partial G}{\partial P}\right) dP + \left(\frac{\partial G}{\partial T}\right) dT$$

$$+ \left(\frac{\partial G}{\partial n_1}\right) dn_1 + \dots$$

$$= \left(\frac{\partial G}{\partial P}\right) dP + \left(\frac{\partial G}{\partial T}\right) dT + \sum_{i=1}^k \mu_i dn_i$$

$$G = \sum_{i=1}^k \mu_i n_i$$

$$dG = \sum_{i=1}^k (\mu_i dn_i + n_i d\mu_i)$$

$$SdT - VdP + \sum_{i=1} n_i d\mu_i = 0$$

Gibbs - Duheim relation

Chemical potentials are
not independent

$$dT = 0 \quad dP = 0, \quad 2 \text{ species}$$

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