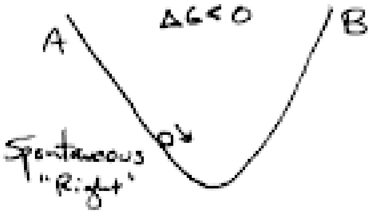
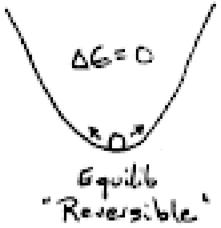
$A \rightleftarrows B$

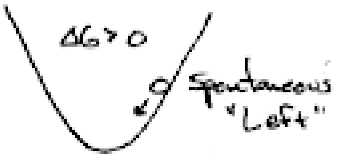
ΔG tells about the equilibrium distribution at constant P, T



"Partial Molar Gibbs Free Energy"



If K=1, then at equilibrium
[A]=[B]



Q: What happens if we add a little "A" to the system?

A: Balance is thrown off, [A] ≠ [B]

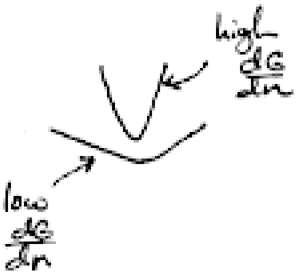
So a reaction occurs to re-establish [A]=[B]

Some A converts (spontaneously) to B,

so ΔG must be negative! ⇐ But you said....

ΔG depends on the amounts of A and B

Partial Molar ⇒ $\frac{dG}{dn}$ = How G depends on # moles



Lawyers

How G depends on # moles of A = $\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{\underbrace{T, P, n_j \neq n_A}_{\text{Constant all of this}}}$ = Chemical Potential

$$G = G(T, P, n_A, n_B, \dots)$$

$$\partial G = \left(\frac{\partial G}{\partial T}\right)_{P,n_A,n_B} \partial T + \left(\frac{\partial G}{\partial P}\right)_{T,n_A,n_B} \partial P$$

$$+ \left(\frac{\partial G}{\partial n_A}\right)_{P,T,n_B} \partial n_A + \left(\frac{\partial G}{\partial n_B}\right)_{P,T,n_A}$$

$$= -S\partial T + V\partial P + \mu_A \partial n_A + \mu_B \partial n_B$$

<u>At constant T and P</u>

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

<u>More generally</u>

$$= \sum \mu_i \, \partial n_i \quad \text{all chemical species}$$

$$aA + bB \rightleftharpoons cC + dD$$

$$\partial G_{T,P} = \mu_A \partial n_A + \mu_B \partial n_B + \mu_C \partial n_C + \mu_D \partial n_D$$

$$\int_0^G dG = \mu_A \int_0^{n_A} dn_A + \cdots$$

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

→ In a <u>closed</u> system (conservation of mass)

$$\frac{\partial n_A}{a} = \frac{\partial n_B}{b} = \frac{-\partial n_C}{c} = \frac{-\partial n_D}{d}$$

$$3A + B \rightleftharpoons 6C + D$$

3 A's (deplete) yield 1 D (add) ⇒ $\frac{\partial n_A}{3} = \frac{-\partial n_D}{1}$ // $\frac{-3}{3} = \frac{-1}{1}$

<u>Skip</u> dependence of G on partial pressures (pp 125-126)

The book then develops the EQUILIBRIUM CONSTANT using the simplicity of ideal gases.
It then moves on to <u>solutions</u> and activities (equivalent of P, for gases, but no more PV=nRT ☺).

Activities can then be approximated by Concentration
OK at <u>dilute</u> solute. See p. <u>137</u>.

We skipped P-dependence of G, but the result was $G(P_2) - G(P_1) = nRT \ln P_2/P_1$

Define P_1 as our standard (reference) state

$$G - G^\circ = nRT \ln\left(\frac{P}{1\,\text{atm}}\right)$$

$$\frac{\partial G}{\partial n_A} - \frac{\partial G^\circ}{\partial n_A} = RT \ln\left(\frac{P_A}{1\,\text{atm}}\right)$$

$\frac{\partial n}{\partial n}$ goes to 1

$$\mu_A - \mu_A^\circ = RT \ln\left(\frac{P_A}{1\,\text{atm}}\right)$$

Actual pressure

reference pressure

From before:

$$G = n_A\mu_A + n_B\mu_B + n_C\mu_C + n_D\mu_D$$

OR $$G_{PROD} = n_C\mu_C + n_D\mu_D$$

$$G_{REACTANTS} = n_A\mu_A + n_B\mu_B$$

$$\Delta G = G_{PROD} - G_{REACT} = n_C\mu_C + n_D\mu_D - n_A\mu_A - n_B\mu_B$$

↙

$$\Delta G = n_C(\mu_C^\circ + RT\ln C_C) + n_D(\mu_D^\circ + RT\ln C_D)$$
$$+ -n_A(\mu_A^\circ + RT\ln C_A) - n_B(\mu_B^\circ + RT\ln C_B)$$

Aside

[Note that we've set a reference to 1.0]
(was 1 atm)

This explains a common question:

Q: If C_B is units of moles/liter, what does $\ln C_B$ mean? Why does it not have units

A: It's really $\ln \frac{C_B}{C_B^{REF}}$ ← But we set this to 1.0 M

Now the ratio C_B/C_B^{REF} is unit-less.

$$\Delta G = \underbrace{n_C\mu_C^\circ + n_D\mu_D^\circ - n_A\mu_A^\circ - n_B\mu_B^\circ}_{} + RT[n_C\ln C_C + n_D\ln C_D - n_A\ln C_A - n_B\ln C_B$$

$$\Delta G = \Delta G^\circ + RT\ln\frac{C_C^{n_C}\,C_D^{n_D}}{C_A^{n_A}\,C_B^{n_B}}$$

And at equilibrium, $\Delta G = 0$

$$\therefore \quad \Delta G^{\circ} = -RT \ln \frac{C_C^{n_C} \, C_D^{n_D}}{C_A^{n_A} \, C_B^{n_B}}$$

$$= -RT \ln K_{eq}$$

where $K_{eq} = \dfrac{C_C^{n_C} \, C_D^{n_D}}{C_A^{n_A} \, C_B^{n_B}} = e^{-\Delta G^{\circ}/RT}$

We're now (QUICKLY) up to p. 144