

Course 565/665 Lecturer Prof. Cavagnero  
 Day 4.8.04 Date 9:55 am  
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$K$  as a function of pressure

$$K = \frac{N_c^c}{N_A^a N_B^b} = \frac{\left(\frac{P_c V}{KT}\right)^c}{\left(\frac{P_A V}{KT}\right)^a \left(\frac{P_B V}{KT}\right)^b} = \frac{q_c^c}{q_A^a q_B^b} e^{-\Delta \epsilon_0 / KT}$$

$$K = \frac{P_c^c}{P_A^a P_B^b} = (KT)^{c-a-b} \frac{q_{0c}^c}{q_{0A}^a q_{0B}^b} e^{-\Delta \epsilon_0 / KT}$$

where  $q_0 \equiv \frac{q}{V}$ ,  $q'_0 = \frac{q'}{V}$

$$\mu = -KT \ln\left(\frac{q'}{N}\right)$$

$$\mu = -KT \ln\left(\frac{q'}{N}\right) = -KT \ln\left(\frac{q'_0 V}{N}\right) = -KT \ln\left(\frac{q'_0 KT}{P}\right)$$

$$P_0 \equiv q'_0 KT$$

$$\mu_0 \equiv -KT \ln P_0$$

standard chemical potential

$$\mu = \mu_0(T, q')$$

usually standard states are defined at  $T = 25^\circ\text{C}$ , specially for solvent.

$$\mu = \mu_0 + KT \ln P$$

Define  $K \equiv K_p$ .

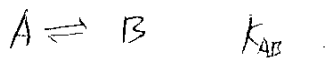
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for chem. rxn.

$$\Delta\mu = \Delta\mu_0 + kT \ln \frac{P_c^c}{P_A^a P_B^b} = \Delta\mu_0 + kT \ln K_P$$

$$\Delta\mu = c\mu_c - a\mu_a - b\mu_b ; \quad \Delta\mu_0 = c\mu_{c0} - a\mu_{a0} - b\mu_{b0}$$

How do rxns react a perturbation of equilibrium? Le Chatelier Principle



at constant T, P:  $dG = \mu_A dN_A + \mu_B dN_B$   $dN_A = -dN_B$   $N_A + N_B = N$

$$N_B \equiv N \cdot \xi \quad (\xi: \text{rxn progress parameter})$$

$$dG = (\mu_B - \mu_A) N d\xi$$

at eq.  $dG = 0$ ; towards equilibrium:  $dG = (\mu_B - \mu_A) N d\xi < 0$

$\Rightarrow \mu_B - \mu_A$  and  $d\xi$  has opposite sign.

if ① perturbation  $\uparrow \mu_B$ , then  $\mu_B - \mu_A > 0$ ,  $\Rightarrow d\xi < 0$   $B \downarrow$

② perturbation  $\downarrow \mu_B$ ,  $\mu_B - \mu_A < 0$ ,  $\Rightarrow d\xi > 0$   $B \uparrow$ .