CHAPTER 13   CHEMICAL EQUILIBRIA

$$A \xrightarrow{K} B \qquad K = [B]/[A] \quad \text{equilibrium constant, } [\ ] \Rightarrow \text{concentration}$$

$$dG = -SdT + Vdp + \mu_A dN_A + \mu_B dN_B$$

Take T, p constant

$$dG = \mu_A dN_A + \mu_B dN_B$$

at equilibrium

$$dG = 0 = \mu_A dN_A + \mu_B dN_B \qquad N = N_A + N_B = const$$

$$dN_A = -dN_B$$

$$(\mu_A - \mu_B)dN_A = 0$$
$$\Rightarrow \mu_A = \mu_B$$

$$q' = \sum_{j=0}^{t} e^{-\varepsilon_j/kT} = e^{-\varepsilon_0/kT} + e^{-\varepsilon_1/kT} + \ldots$$

$$q = e^{\varepsilon_0/kT} q' \quad \longleftarrow \quad \text{factor out ground state}$$

$$\mu_A = -kT \ell n \frac{q'_A}{N_A}, \quad \mu_B = -kT \ell n \frac{q'_B}{N_B}$$

$$\ell n \frac{q'_A}{N_A} = \ell n \frac{q'_B}{N_B} \quad \Longrightarrow \quad \frac{q'_A}{N_A} = \frac{q'_B}{N_B}$$

$$\frac{q_A e^{-\varepsilon_{0A}/kT}}{N_A} = \frac{q_B e^{-\varepsilon_{0B}/kT}}{N_B}$$

$$K = \frac{N_B}{N_A} = \frac{q_B}{q_A} e^{-(\varepsilon_{0B} - \varepsilon_{0A})/kT}$$
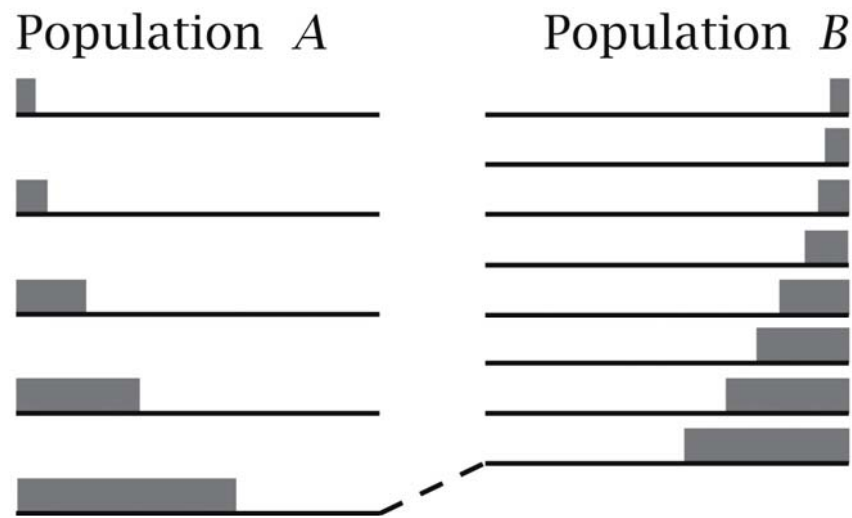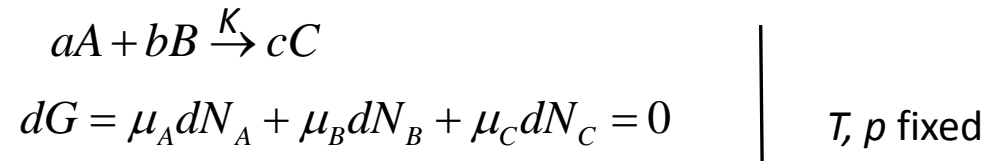
ignores interactions

Population A Population B

Figure 13.1 Molecular Driving Forces 2/e (© Garland Science 2011)

Generalize

$$aA + bB \xrightarrow{K} cC$$

$$dG = \mu_A dN_A + \mu_B dN_B + \mu_C dN_C = 0 \qquad \bigg| \qquad T, p \text{ fixed}$$

introduce a progress variable ξ

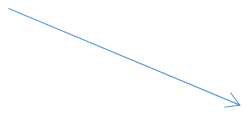$$dN_C = c\,d\xi$$

$$dN_A = -a\,d\xi$$

$$dN_B = -b\,d\xi$$
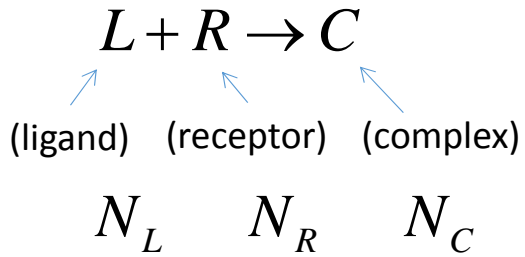
$$\left(c\mu_C - a\mu_A - b\mu_B \right) d\xi = 0$$

$$c\mu_C = a\mu_A + b\mu_B \qquad \text{at equilibrium}$$

$$c\left[-kT \ell n \frac{q'_C}{N_C} \right] = a\left[-kT \ell n \frac{q'_A}{N_A} \right] + b\left[-kT \ell n \frac{q'_B}{N_B} \right]$$

$$\Rightarrow \left(\frac{q'_C}{N_C} \right)^C = \left(\frac{q'_A}{N_A} \right)^A \left(\frac{q'_B}{N_B} \right)^B$$

$$K = \frac{N_C^c}{N_A^a N_B^b} = \frac{\left(q'_C \right)^c}{\left(q'_A \right)^a \left(q'_B \right)^b} = \frac{\left(q_C^c \right)}{\left(q_A^a \right)\left(q_B^b \right)} e^{-(c\varepsilon_{0C} - a\varepsilon_{0A} - b\varepsilon_{0B})/KT}$$

Example 13.2: Model for ligand binding

$$L + R \rightarrow C$$

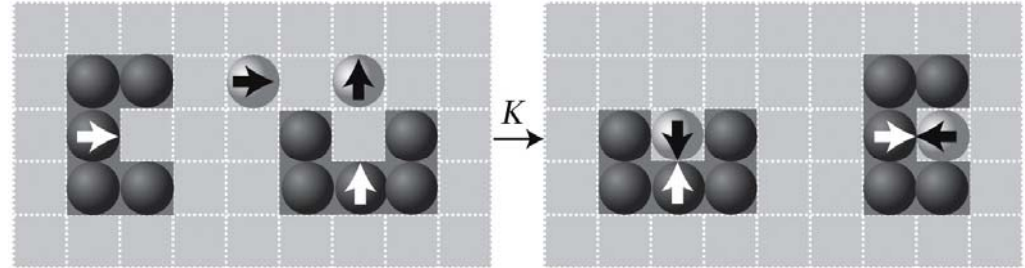(ligand)   (receptor)   (complex)

$$N_L \qquad N_R \qquad N_C$$

Figure 13.2 Molecular Driving Forces 2/e (© Garland Science 2011)

correct orientation on lattice $\rightarrow$ energy $\varepsilon_0 < 0$

V = # of lattice sites where each species can be located; Z = # of directions (2, 4, 6)

$$q_R = Vz \qquad q_L = Vz \qquad q_C = Vze^{-\varepsilon_0/kT}$$

$$K = \frac{N_C}{N_R N_L} = \frac{q_C}{q_R q_L} = \frac{e^{-\varepsilon_0/kT}}{Vz}$$

$$\ell nK = \ell n\left[\frac{e^{-\varepsilon_0/kT}}{Vz}\right]$$

$$= \frac{-\varepsilon_0}{kT} - \ell n(Vz)$$

$$\frac{d\ell nK}{dT} = \frac{\varepsilon_0}{kT^2}$$

$\Delta h \qquad -T\Delta s$

binding is weaker at higher T

A different convention for dealing with relative energies

$$\Delta \varepsilon_0 = -\Delta D \quad\bigg| \quad D = \text{dissociation energy}$$

$$H_2 + D_2 \xrightarrow{K} 2HD$$
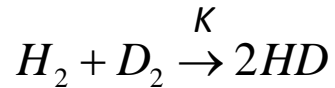
$$K = \frac{(q_{HD})^2}{q_{H_2}q_{D_2}} e^{\Delta D / kT} \quad\bigg|\quad \begin{aligned} \Delta D &= 2(435.2) \\ &\;\; -431.8 - 439.2 \\ &= 0.6 kJ\,/\,mol \end{aligned}$$

Why isn't this zero?

$$e^{\Delta D / kT} = 0.79 \text{ at } T = 300K$$

$$K = K_t K_r K_v e^{\Delta D / kT}$$

$$K_t = \frac{\left[\left(2\pi m_{HD}kT\,/\,h^2\right)^{3/2}\right]^2}{\left(2\pi m_{H_2}kT\,/\,h^2\right)^{3/2}\left(2\pi m_{D_2}kT\,/\,h^2\right)^{3/2}} = \frac{m_{HD}^3}{m_{H_2}^{3/2}m_{D_2}^{3/2}}$$

$$= \frac{3^3}{2^{3/2}4^{3/2}} = \frac{27}{2\sqrt{28}} = 1.19$$

$$K_r = \frac{\sigma_{H_2}\sigma_{D_2}}{\left(\sigma_{HD}\right)^2}\frac{I_{HD}^2}{I_{H_2}I_{D_2}}$$

$$K_r = \frac{2.2}{1^2}\frac{8}{9} = 3.56$$

$$I = \mu R^2$$

$$\mu_{H_2} = \frac{1.1}{2} = \frac{1}{2}$$

$$\mu_{D_2} = \frac{2.2}{2} = 1$$

$$\mu_{HD} = \frac{1.2}{3} = \frac{2}{3}$$

$$\frac{I_{HD}^2}{I_{D_2}I_{H_2}} = \frac{(2/3)^2}{1/2 \cdot 1} = \frac{8}{9}$$

Here I neglected R^2 as it will cancel out.

$$K_v = \frac{\left(1-e^{-hv_{HD}/kT}\right)^{-2}}{\left(1-e^{-hv_{H_2}/kT}\right)^{-1}\left(1-e^{-hv_{D_2}/kT}\right)^{-1}}$$

$$K = (1.19)(3.56)(1)(0.79) = 3.35$$

$$\quad\;\; \text{trans} \quad\;\; \text{rot} \quad\; \text{vibr} \quad\; \Delta D_e$$

Largest contribution arises from symmetry #'s in rotational term

When $\quad T \to \infty \quad K \to 4.23$

Equilibrium constants in terms of pressure

$$K = \frac{N_C^c}{N_A^a N_B^b} \quad \bigg| \quad pV = NkT, \quad N = \frac{pV}{kT}$$

$$K = \frac{(p_C V/kT)^c}{(p_A V/kT)^a (p_B V/kT)^b} = \frac{p_C^c}{p_A^a p_B^b} \left(\frac{kT}{V}\right)^{a+b-c} = \frac{q_C^c}{q_A^a q_B^b} e^{\Delta D/kT} \quad \bigg| \quad K_p = \left(\frac{V}{kT}\right)^{a+b-c} K$$

$$K_p = \frac{p_C^c}{p_A^a p_B^b} = \frac{q_C^c}{q_A^a q_B^b} \left(\frac{kT}{V}\right)^{(c-a-b)} e^{\Delta D/kT}$$

$$K_p = \frac{q_{0C}^c}{q_{0A}^a q_{0B}^b} (kT)^{c-a-b} e^{+\Delta D/kT} \quad \bigg| \quad q_0 = q/V = \text{partition function with volume removed}$$

get chemical potentials in terms of partial pressures

$$\mu = -kT \ln\left(\frac{q'}{N}\right) = -kT \ln\left(\frac{q'_0 V}{N}\right) \qquad V = \frac{NkT}{p}$$

$$\mu = -kT \ln\left(\frac{q'_0 kT}{p}\right)$$

$$\mu = +kT \ln\left(\frac{p}{p^o_{int}}\right) = \mu^o + kT \ell np \qquad p^o_{int} = q'_0 kT$$

$$\underset{}{\Big\uparrow} \quad -kT \ell n\left(q'_0 kT\right)$$

$\mu_o =$ standard state chemical potential

Example 13.4: Dissociation

$$I_2 = 2I, \qquad T = 1000K, \qquad m_I = 2.109 x 10^{-25} kg$$

$$q_{el,I} = 4 \qquad \theta_{rot} = 0.0537 K$$

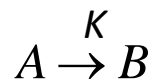$$q_{el,I_2} = 1 \qquad \theta_{vib} = 308K$$

$$\Delta D = -35.6 kcal / mol \qquad e^{\Delta D / RT} = 1.66 x 10^{-8}$$

$$K_p = 3.1 x 10^{-3} atm$$

Le Chatelier's Principle

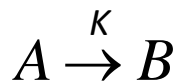$$A \xrightarrow{K} B$$

fluctuation dN_B in #B

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

move toward equilibrium $\Rightarrow$ $dG \leq 0$

so $\mu_A - \mu_B$ and $d\xi$ of opposite sign

system tends to equilibrium by moving
in a direction opposite a perturbation

K(T) at different temperatures $\rightarrow$ *S, H*

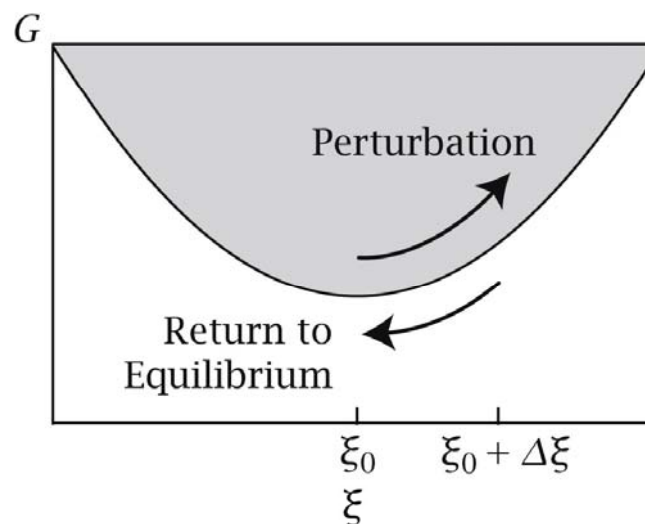$$A \xrightarrow{K} B$$

At equilibrium $\mu_A = \mu_B$

Figure 13.4 Molecular Driving Forces 2/e (© Garland Science 2011)

$$\mu_A^0 + kT\ell np_A = \mu_B^0 + kT\ell np_B$$

$$K = \left(\frac{q_B}{q_A}\right)e^{-(\varepsilon_{0B}-\varepsilon_{0A})/kT}$$

$$= \frac{p_B}{p_A}$$

$$\ell nK_p = \ell n\left(\frac{p_B}{p_A}\right) = -\frac{\left(\mu_B^o - \mu_A^o\right)}{kT} = -\frac{\Delta\mu^o}{kT}$$

The "o" meant P = 1 atm.

$$\Delta\mu^o = \Delta h^o - T\Delta s^o$$

$\Delta\mu^o$ depends only on T for ideal gas

$$\ell nK_p = -\Delta\mu^o / kT = -\frac{\Delta h^o - T\Delta s^o}{kT}$$

$$\frac{\partial \ell n K_p}{\partial T} = \frac{\Delta h^o}{kT^2}$$

assuming h^o, s^o are independent of T

$$\text{or } \frac{\partial \ell n K_p}{\partial (1/T)} = \frac{-\Delta h^o}{k}$$

van't Hoff equation

$$\ell n\left(\frac{K_p(T_2)}{K_p(T_1)}\right) = \frac{-\Delta h^o}{k}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

From integration of eq. at top assuming Δh indep. of T.

$$\Delta \mu_o = -R\ell n K_p$$

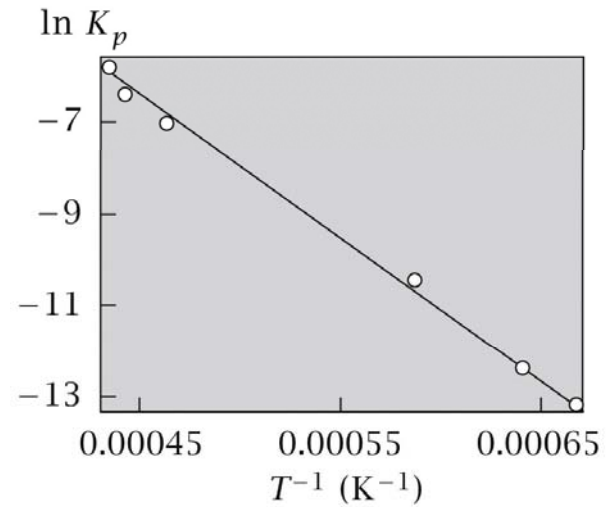$$\Delta s_0^o = \frac{\Delta h^o - \Delta \mu^o}{T}$$

Figure 13.5 Molecular Driving Forces 2/e (© Garland Science 2011)

van't Hoff plot for dissociation of water

Gibbs – Helmholtz Equation | Not restricted to gases or chem. equilibrium

$$G = H - TS$$

$$H = G + TS$$

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_p$$

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} - \frac{-1}{T^2}\left[G - T\left(\frac{\partial G}{\partial T}\right)_p\right]$$

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = -\frac{H(T)}{T^2} \quad \Bigg| \quad \text{Gibbs – Helmholtz Equation}$$

$$\left(\frac{\partial(F/T)}{\partial T}\right)_V = -\frac{U(T)}{T^2}$$

$$d\left(\frac{u}{v}\right) = \frac{v\,du - u\,dv}{v^2}$$

$$u = G, \quad v = T$$

$$d\left(\frac{G}{T}\right) = \frac{T\,dG - G\,dT}{T^2}$$

$$\frac{d}{dT}\left(\frac{G}{T}\right) = \frac{1}{T}\frac{dG}{dT} - \frac{1}{T^2}G$$

Pressure dependence of *K*

$$\ell n K_p = \frac{-\Delta\mu^o}{kT}$$

$$\frac{\partial \ell n K_p}{\partial p} = -\frac{1}{kT}\left(\frac{\partial \Delta\mu^o}{\partial p}\right) = 0 \quad \text{for ideal gas}$$

$$\left(\frac{\partial \mu}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial N}\right)_{T,p} = v$$

$$\left(\frac{\partial\left(\mu_B^o - \mu_A^o\right)}{\partial p}\right)_T = v_B^o - v_A^o = \Delta v^o$$

$$\left(\frac{\partial \ell n K_p}{\partial_\rho}\right)_T = \frac{-\Delta v^o}{kT}$$

$$\mu = kT \ell n\left(\frac{q}{N}\right)$$

$$\mu^o = -kT \ell n\left(q'_0\, kT\right)$$

$$\Delta\mu^o = \mu_B^o - \mu_A^o$$

$$\mu = \mu^o + kT \ell n\rho$$

if *B* is state of smaller volume
>*p* will shift equilibrium from *A*
toward *B*