Chemical Biology 2P03
Biophysical Chemistry

PART B
Chemical Equilibria

LECTURE B1:
Mixing Ideal Gases

Thu, 25 September 2014

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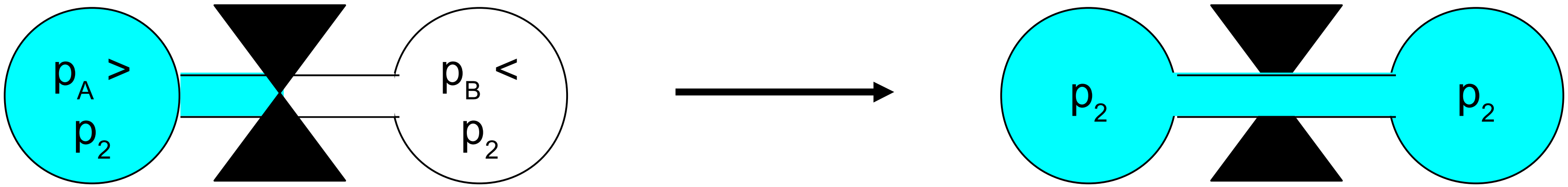
Molecular Interpretation of the 2nd Law

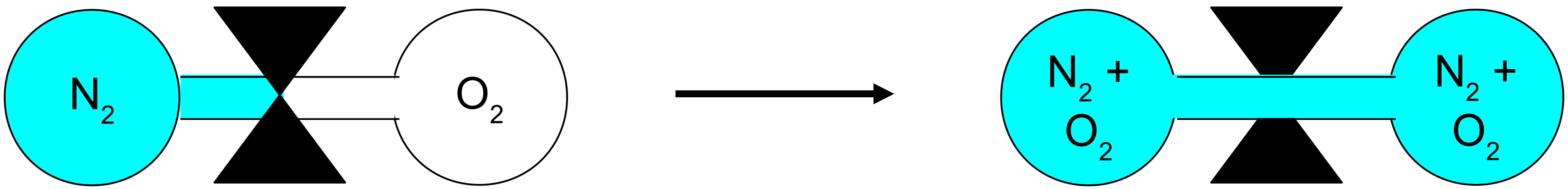
$$S = k \ln N$$

k = 1.318 x 10^{-23} J K^{-1}
N = # of microscopic states

Case A: Change in Pressure, One Component



Case B: Constant Pressure, Different Components



Entropy of Mixing

- only if mixing different species
(no ΔS for mixing with itself)

Entropy change for mixing 2 ideal gases:

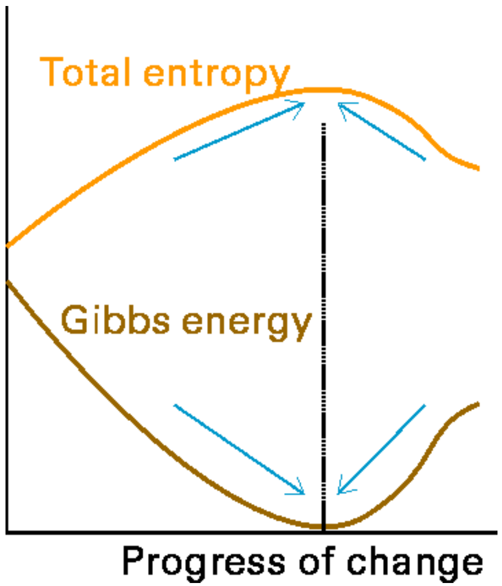
$$\Delta S_A = -n_A R \ln \frac{X_A P}{P} = -n_A R \ln X_A$$

$$\Delta S_B = -n_B R \ln \frac{X_B P}{P} = -n_B R \ln X_B$$

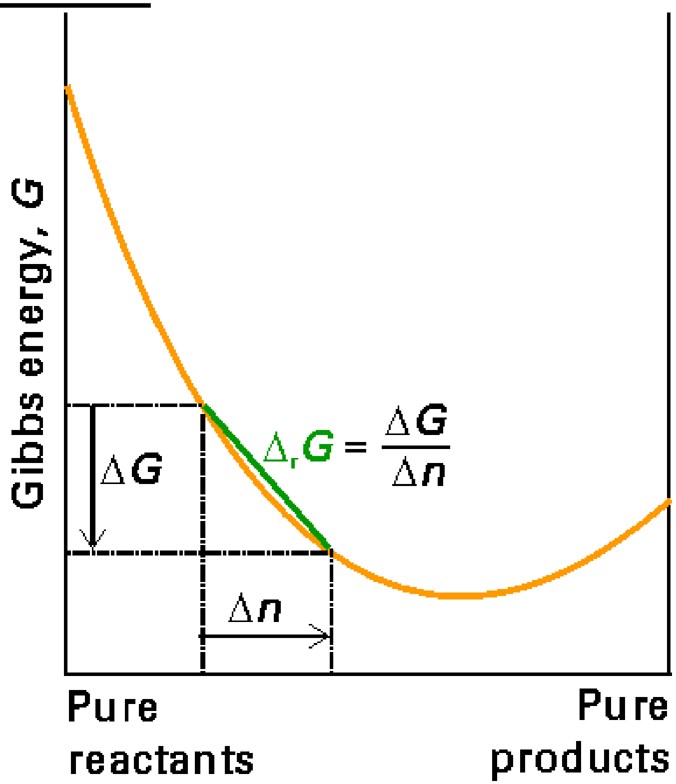
$$\Delta S_{mix} = \Delta S_A + \Delta S_B = -R\left(n_a \ln X_A + n_B \ln X_B\right)$$

Chemical Potential

"Partial Molar Gibbs Free Energy":



$$\left(\frac{\delta G}{\delta n_i}\right)_{T,P,n_{j\neq i}} = \mu_i$$



==> of central importance in understanding chemical & physical equilibria (next few weeks of the course...)

"How does the driving force towards equilibrium change if the composition of a mixture changes?"

Describing a Mixture

$$n_A A + n_B B + n_C C + n_D D$$

$$G = G(T, P, n_A, n_B, n_C, n_D)$$

$$dG = \left(\frac{\delta G}{\delta T}\right)_{P, n_A, n_B, n_C, n_D} dT + \left(\frac{\delta G}{\delta P}\right)_{T, n_A, n_B, n_C, n_D} dP + \left(\frac{\delta G}{\delta n_A}\right)_{T, P, n_B, n_C, n_D} dn_A + \ldots$$

$$\ldots + \left(\frac{\delta G}{\delta n_B}\right)_{T, P, n_A, n_C, n_D} dn_B + \left(\frac{\delta G}{\delta n_C}\right)_{T, P, n_A, n_B, n_D} dn_C + \left(\frac{\delta G}{\delta n_D}\right)_{T, P, n_A, n_B, n_C} dn_D$$

$$dG = -S\,dT + V\,dP + \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_D dn_D$$

constant T, P: $$dG = \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_D dn_D$$

adding proportional amounts:

$$\int_0^G dG = \mu_A \int_0^{n_A} dn_A + \mu_B \int_0^{n_B} dn_B + \mu_C \int_0^{n_C} dn_C + \mu_D \int_0^{n_D} dn_D$$

(Sum Rule – const. T, P) $$G = n_A \mu_A + n_B \mu_B + n_C \mu_C + n_D \mu_D$$

Describing Ideal Gas Mixtures

relationship to standard pressure:

$$G = G^0 + n\,R\,T\ln\frac{P}{1\,atm}$$

pure substance:

$$\mu = \mu^0 + R\,T\ln\frac{P}{1\,atm}$$

in a mixture:

$$\mu_A = \mu_A^0 + R\,T\ln\frac{P_A}{1\,atm}$$

e. g., Gibbs free energy of mixing

$$G_{intial} = n_A\left[\mu_A^0 + R\,T\ln\frac{P}{1\,atm}\right] + n_B\left[\mu_B^0 + R\,T\ln\frac{P}{1\,atm}\right]$$

Mixing 2 Ideal Gases...

same initial pressure P, same temperature T

$$G_{intial} = n_A \left[\mu_A^0 + RT \ln \frac{P}{1\,atm} \right] + n_B \left[\mu_B^0 + RT \ln \frac{P}{1\,atm} \right]$$

$$G_{final} = n_A \left[\mu_A^0 + RT \ln \frac{P_A}{1\,atm} \right] + n_B \left[\mu_B^0 + RT \ln \frac{P_B}{1\,atm} \right]$$

$$\Delta G_{mix} = G_{final} - G_{initial} = n_A RT \ln \frac{P_A}{P} + n_B RT \ln \frac{P_B}{P}$$

$$\Delta G_{mix} = n_A RT \ln X_A + n_B RT \ln X_B$$

previously

$$\Delta S_{mix} = -n_A R \ln X_A - n_B R \ln X_B$$

also

$$\Delta G_{mix} = -T \Delta S_{mix} \quad ; \quad \Delta U_{mix} = 0 \quad ; \quad \Delta H_{mix} = 0$$

Describing a Chemical Reaction

$$aA + bB \underset{\leftarrow}{\overset{\rightarrow}{}} cC + dD$$

$$G = G(T, P, n_A, n_B, n_C, n_D)$$

$$dG = -S\,dT + V\,dP + \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_D dn_D$$

closed system:

$$\frac{dn_A}{a} = \frac{dn_B}{b} = -\frac{dn_C}{c} = -\frac{dn_d}{d} = -d\alpha$$

(extent of rxn.)

$$dG = -S\,dT + V\,dP + \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_D dn_D$$

constant T, P:

$$dG = (c\,\mu_C + d\,\mu_D - a\,\mu_A - b\,\mu_b)\,d\alpha$$

$$dG = -[(a\,\mu_A + b\,\mu_b) - (c\,\mu_C + d\,\mu_D)]\,d\alpha$$

if spontaneous left to right:

$$dG < 0 \;\wedge\; d\alpha > 0 \;\Rightarrow\; [(a\,\mu_A + b\,\mu_b) - (c\,\mu_C + d\,\mu_D)] > 0$$

Describing Equilibrium

$$a A + b B \underset{\leftarrow}{\rightarrow} c C + d D$$

at equilibrium: $[(a \mu_A + b \mu_b) - (c \mu_C + d \mu_D)] = 0$

$$\frac{dG}{d\alpha} = c \mu_C + d \mu_D - a \mu_A - b \mu_b = \Delta G_{\text{per mole of reaction}}$$

note that this measure depends on how reaction is written...

$$C_6 H_{12} O_6 + 6 O_2 \rightarrow 6 CO_2 + 6 H_2 O$$

$$\frac{1}{6} C_6 H_{12} O_6 + O_2 \rightarrow CO_2 + H_2 O$$

also, note assumption that over dG, composition is not significantly changed

Describing Ideal Gas Reactions

relationship to standard pressure:

$$G = G^0 + nRT \ln \frac{P}{1\,atm}$$

pure substance:

$$\mu = \mu^0 + RT \ln \frac{P}{1\,atm}$$

in a mixture:

$$\mu_A = \mu_A^0 + RT \ln \frac{P_A}{1\,atm}$$

e. g., Gibbs free energy of mixing

$$G_{intial} = n_A \left[\mu_A^0 + RT \ln \frac{P}{1\,atm} \right] + n_B \left[\mu_B^0 + RT \ln \frac{P}{1\,atm} \right]$$

Describing Equilibrium

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

$$\Delta G = 2\mu_{NH_3} - \mu_{N_2} - 3\mu_{H_2}$$

$$\Delta G = 2\left[\mu^0_{NH_3} + RT\ln\frac{P_{NH_3}}{1\,atm}\right] - \left[\mu^0_{N_2} + RT\ln\frac{P_{N_2}}{1\,atm}\right] - 3\left[\mu^0_{H_2} + RT\ln\frac{P_{H_2}}{1\,atm}\right]$$

express all pressures in units of “1 atm”:

$$\Delta G = \Delta G^0 + RT\ln\frac{P^2_{NH_3}}{P_{N_2}P^3_{H_2}}$$

at equilibrium:

$$\Delta G = 0 = \Delta G^0 + RT\ln\frac{\left(P^{eq}_{NH_3}\right)^2}{\left(P^{eq}_{N_2}\right)\left(P^{eq}_{H_2}\right)^3}$$

$$\Delta G^0 = -RT\ln K \quad ; \quad K = \frac{\left(P^{eq}_{NH_3}\right)^2}{\left(P^{eq}_{N_2}\right)\left(P^{eq}_{H_2}\right)^3}$$