Chemistry 163B
Free Energy
and
Equilibrium
E&R ($\approx$ ch 6)

here ΔG ≡ ΔG_reaction

1. **ΔG < 0 spontaneous** *('natural', irreversible)*
   ΔG = 0 equilibrium *(reversible)*
   ΔG > 0 spontaneous in reverse direction

2. **$\Delta G_T = \Delta H - T\Delta S$**

3. **ΔG⁰ all reactants and products in standard states**

4. $\Delta \bar{G}_f^0 \equiv \bar{G}_f^0$ **Appendix A at 298.15K** *(reaction where reactants are elements in their most stable form and in their standard states, P=1 atm, [conc]=1M, etc)*

$$\Delta \bar{G}_f^0\left(O_2(g)\right) \equiv 0 \quad \Delta \bar{G}_f^0\left(C(gr)\right) = 0$$

5.
$$\Delta G_{reaction}^0 = \sum_i \nu_i \Delta \bar{H}_f^0 - T\sum_i \nu_i \bar{S}_i^0$$

$$\Delta G_{reaction}^0 = \Delta H_{reaction}^0 - T\Delta S_{reaction}^0$$

$NOTE: in\ Appendix\ A: \Delta \bar{G}_f^0\ and\ \Delta \bar{H}_f^0\ in\ $ **kJ mol⁻¹** $\ BUT\ \bar{S}^0\ in\ $ **J** $K^{-1}mol^{-1}$

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6. Brief hello to thermodynamics of multicomponent systems (n_i's vary)

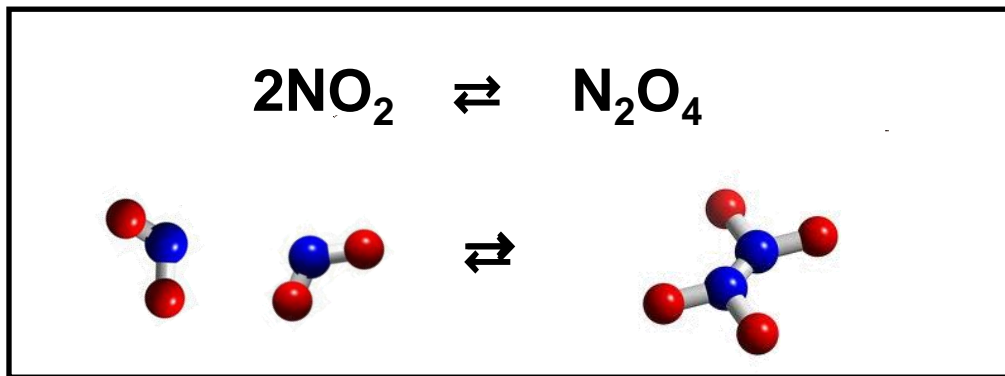**7. $\Delta G_{reaction}$ for non-standard state concentrations, pressures**
   $\Delta G_{reaction} = \Delta G^0_{reaction} + \underline{R}T \ln Q$

8. K_{eq} and $\Delta G^0_{reaction}$

9. $\Delta G_{reaction} = \Delta G^0_{reaction} + \underline{R}T \ln Q$ is extensive

10. Variation of K_{eq} with T

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6. molar free energy and partial molar free energy (chemical potential)

$$2NO_2 \quad \rightleftarrows \quad N_2O_4$$

multicomponent mixture

n_{NO_2} *moles* NO_2 ;

$n_{N_2O_4}$ *moles* N_2O_4
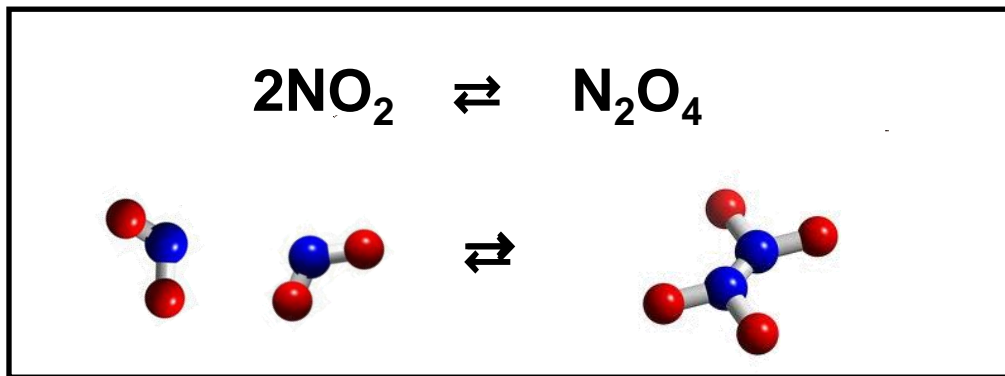

$$G_{NO_2 + N_2O_4 \text{ mixture}}(T, P, n_{NO_2}, n_{N_2O_4})$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_{NO_2}, n_{N_2O_4}} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_{NO_2}, n_{N_2O_4}} dP + \left(\frac{\partial G}{\partial n_{NO_2}}\right)_{T, P, n_{N_2O_4}} dn_{NO_2} + \left(\frac{\partial G}{\partial n_{N_2O_4}}\right)_{T, P, n_{NO_2}} dn_{N_2O_4}$$

$$\mu_{NO_2} = \left(\frac{\partial G_{(NO_2 + N_2O_4 \text{ mixture})}}{\partial n_{NO_2}}\right)_{T, P, n_{N_2O_4}}$$

partial molar Gibbs free energy *or chemical potential*

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more generally $\quad G_{mixture}(T, P, n_1, ..., n_N)$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_i} dP + \sum_{i=1}^{N} \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_{j \neq i}} dn_i = -SdT - VdP + \sum_{i=1}^{N} \mu_i dn_i$$

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multicomponent mixture

n_{NO_2} *moles* NO_2 ;

$n_{N_2O_4}$ *moles* N_2O_4

$$\mu_{NO_2} = \left(\frac{\partial G_{(NO_2 + N_2O_4 \ mixture)}}{\partial n_{NO_2}} \right)_{T,P,n_{N_2O_4}}$$

partial molar Gibbs free energy
or *chemical potential*

$\bar{G}_{NO_2}$ *molar Gibbs free energy of pure* NO_2 $\left[(\bar{G}_{NO_2} \equiv \left(\Delta\bar{G}_f \right)_{NO_2} \right]$

μ_{NO_2} *molar Gibbs free energy of* NO_2 *in environment where other molecules are present*

thermodynamics of multicomponent systems
E&R section 6.4 (later)

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$$for \; now \; \mu_i \approx \bar{G}_i$$

$$\Delta\mu_{reaction} \approx \Delta G_{reaction}$$

$$\Delta\mu_{reaction} = \sum_i \nu_i \mu_i \approx \sum_i \nu_i \bar{G}_i = \Delta G_{reaction}$$

7. How does ΔG$_{reaction}$ (Δμ) vary as the concentration of reactants and products varies?

example : *'concentration' of gas = partial pressure P_i*

$$P_i = X_i P_{total} \quad \text{where } X_i \text{ is mole fraction of species i}$$

$$d\bar{G} = -\bar{S}dT + \bar{V}dP \quad \Rightarrow \left(\frac{\partial \bar{G}}{\partial P} \right)_T = \bar{V}$$

for ideal gas:

$$P_{total} = n_{total} \frac{RT}{V}$$

$$P_i = n_i \frac{RT}{V}$$

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7. ΔG_reaction as a function of concentration

$$\left(\frac{\partial \bar{G}}{\partial P} \right)_T = \bar{V}$$

for ideal gas

$$P_{total} = n_{total} \frac{RT}{V}$$

$$P_i = n_i \frac{RT}{V}$$

$$\left(\frac{\partial \bar{G}_i}{\partial P_i} \right)_T = \bar{V}$$

$$\bar{G}_i \left(P_i \right) - \bar{G}_i \left(P_i = 1\,bar \right) = \int_{1\,bar}^{P_i} \left(\frac{\partial \bar{G}_i}{\partial P_i'} \right)_T dP_i' = \int_{1\,bar}^{P_i} \bar{V} dP_i' = \int_{1\,bar}^{P_i} \frac{RT}{P_i'} dP_i'$$

$$\bar{G}_i \left(P_i \right) - \bar{G}_i \left(P_i = 1\,bar \right) = RT\,ln\left(\frac{P_i}{1\,bar} \right)$$

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$$\bar{G}_i\left(P_i\right) - \bar{G}_i\left(P_i = 1\,bar\right) = RT\,ln\left(\frac{P_i}{1\,bar}\right)$$

$$\bar{G}_i\left(P_i\right) - \bar{G}_i^0 = RT\,ln\left(\frac{P_i}{1\,bar}\right)$$

$$\bar{G}_i\left(P_i\right) = \bar{G}_i^0 + RT\,ln\left(\frac{P_i}{1\,bar}\right)$$

$$later\ \ \mu_i\left(P_i\right) = \mu_i^0 + RT\,ln\left(\frac{P_i}{1\,bar}\right)$$

$$\bar{G}_i\left(P_i\right) = \bar{G}_i^0 + RT\,ln\left(\frac{P_i}{1\,bar}\right)$$

$$\Delta G_{reaction} = \sum_i v_i \bar{G}_i$$

$$\Delta G_{reaction} = \sum_i v_i \left(\bar{G}_i^0 + RT\,ln\left(\frac{P_i}{1\,bar}\right) \right)$$

$$\Delta G_{reaction} = \sum_i v_i \bar{G}_i^0 + \sum_i v_i RT\,ln\left(\frac{P_i}{1\,bar}\right)$$

$$\Delta G_{reaction} = \Delta G_{reaction}^0 + \sum_i v_i RT\,ln\left(\frac{P_i}{1\,bar}\right)$$

$$\underline{R}T\sum_i \bar{v}_i\,ln\left(\frac{P_i}{1\,bar}\right) = \underline{R}T\,ln\left[\prod_i \left(\frac{P_i}{1\,bar}\right)^{\bar{v}_i}\right] = \underline{R}T\,\ln Q_P$$

for 'persnickety' units notation
$$\underline{R} = R\left(mol\right) = [J\,K^{-1}]$$
$$\bar{v}_i = v_i\left(mol^{-1}\right) = [unitless]$$

$$Q_P = \prod_i \left(\frac{P_i}{1\,bar}\right)^{\bar{v}_i}$$

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7. $\Delta G_{reaction}$ as a function of concentration

$$\Delta G_{reaction} = \Delta G^0_{reaction} + \underline{R}T \ln Q_P$$

reaction quotient $Q_P = \prod_i \left(\frac{P_i}{1\ bar}\right)^{\bar{v}_i} = \dfrac{\prod_{q=prod}\left(\frac{P_q}{1\ bar}\right)^{\bar{n}_q}}{\prod_{r=react}\left(\frac{P_r}{1\ bar}\right)^{\bar{n}_r}}$ **Q is UNITLESS**

1 bar is P^0, std state for P

$$n_a A + n_b B \rightarrow n_c C + n_d D$$
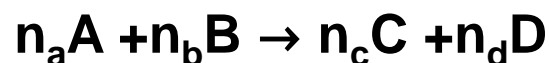
$$Q_P = \dfrac{\left(\frac{P_C}{1\ bar}\right)^{\bar{n}_c}\left(\frac{P_D}{1\ bar}\right)^{\bar{n}_d}}{\left(\frac{P_A}{1\ bar}\right)^{\bar{n}_a}\left(\frac{P_B}{1\ bar}\right)^{\bar{n}_B}}$$ *'like' an equilibrium constant*

for solutes in soln $Q_C = \prod_i \left(\frac{[i]}{1\ M}\right)^{\bar{v}_i}$ $Q_C = \dfrac{\left(\frac{[C]}{1\ M}\right)^{\bar{n}_c}\left(\frac{[D]}{1\ M}\right)^{\bar{n}_d}}{\left(\frac{[A]}{1\ M}\right)^{\bar{n}_a}\left(\frac{[B]}{1\ M}\right)^{\bar{n}_b}}$ **Q is UNITLESS**

HW7 prob 39

1 M is std state for solute 11

$$\Delta G_{reaction} = \Delta G^0_{reaction} + RT\ ln\ Q_P$$

reaction quotient $\quad Q_P = \prod_i \left(\dfrac{P_i}{1\ bar} \right)^{\bar{v}_i}$ **_Q is UNITLESS_**

$$Q_C = \prod_i \left(\dfrac{[i]}{1\ M} \right)^{\bar{v}_i}$$

$$\Delta G_{reaction} = \Delta G^0_{reaction} + \sum_i v_i RT\ ln\left(\dfrac{P_i}{1\ bar} \right)$$

$$\Delta G_{reaction} = \Delta G^0_{reaction} + \sum_i \dfrac{v_i}{1\ mol} \left(1\ mol\ R \right) T\ ln\left(\dfrac{P_i}{1\ bar} \right)$$

$$\Delta G_{reaction} = \Delta G^0_{reaction} + \sum_i \left(1\ mol\ R \right) T\ ln\left(\dfrac{P_i}{1\ bar} \right)^{\frac{v_i}{1\ mol}}$$

$$\Delta G_{reaction} = \Delta G^0_{reaction} + \sum_i \left(\underline{R} \right) T\ ln\left(\dfrac{P_i}{1\ bar} \right)^{\bar{v}_i}$$

← unitless exponent

$\left[R \times 1\ mol \right] = \left[\underline{R} \right] = J\ K^{-1}$

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7. ΔG_reaction as a function of concentration

$$\Delta G_{reaction} = \Delta G^0_{reaction} + \underline{R}T \, ln \, Q$$

$$Q_P = \prod_i \left(\frac{P_i}{1 \, bar} \right)^{\overline{v}_i} \qquad Q_C = \prod_i \left(\frac{[i]}{1 \, M} \right)^{\overline{v}_i}$$

evaluates ΔG for ANY set of pressures, concentrations

ΔG⁰ gives free energy change for standard conditions,
$\underline{R}T \, ln \, Q$ corrects ΔG for actual P's and [conc's]

at equilibrium ΔG= ?

$$\boxed{\textbf{at equilibrium } \Delta G = 0}$$

$$0 = \Delta G^0_{reaction} + \underline{R}T \ln Q_{eq}$$

$$\Delta G^0_{reaction} = -\underline{R}T \ln Q_{eq}$$

$$at\ given\ T \quad Q_{eq} = constant \equiv K_{eq}$$

$$\Delta G^0 = -\underline{R}T \ln K_{eq} \qquad \Delta G_{reaction} = \Delta G^0_{reaction} + \underline{R}T \ln Q$$

$$K_{eq} = e^{-\frac{\Delta G^0}{\underline{R}T}} \qquad Q_P = \prod_i \left(\frac{P_i}{1\ bar}\right)^{\overline{v}_i} \quad Q_C = \prod_i \left(\frac{[i]}{1\ M}\right)^{\overline{v}_i}$$

$$\boxed{\begin{aligned} \Delta G_{reaction} &= \Delta G^0_{reaction} + \underline{R}T \ln Q \quad any\ concentrations\ for\ Q \\ Q_{eq} &\equiv K_{eq}\ for\ equilibrium\ concentrations \\ &\quad that\ satisfy\ \Delta G^0_{reaction} = -\underline{R}T \ln K_{eq} \end{aligned}}$$

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$$\Delta G_1 \qquad n_a A + \ n_b B \rightarrow \ n_c C \ + n_d D$$

$$\Delta G_2 \quad 2n_a A + 2n_b B \rightarrow 2n_c C + 2n_d D$$

$$\Delta G_2 \ \ ?=? \ \ 2\Delta G_1$$

$$Q_1 = \frac{\left(P_C \Big/ 1\ bar\right)^{\bar{n}_c} \left(P_D \Big/ 1\ bar\right)^{\bar{n}_d}}{\left(P_A \Big/ 1\ bar\right)^{\bar{n}_a} \left(P_B \Big/ 1\ bar\right)^{\bar{n}_b}} \qquad Q_2 = \frac{\left(P_C \Big/ 1\ bar\right)^{2\bar{n}_c} \left(P_D \Big/ 1\ bar\right)^{2\bar{n}_d}}{\left(P_A \Big/ 1\ bar\right)^{2\bar{n}_a} \left(P_B \Big/ 1\ bar\right)^{2\bar{n}_b}}$$

$$\textcolor{red}{Q_2 = Q_1{}^2}$$

$$\Delta G_1 = \Delta G_1^0 + \underline{R}T\ ln\ Q_1$$

$$\Delta G_2 = \Delta G_2^0 + \underline{R}T\ ln\ Q_2$$

$$\Delta G_2 = 2\Delta G_1^0 + \underline{R}T\ ln\ Q_1^2 = 2\left(\Delta G_1^0 + \underline{R}T\ ln\ Q_1\right)$$

$$\Delta G_2 = 2\Delta G_1$$

- $(\Delta G_{rxn})_{T,P}$ ⇨ **reaction carried out isothermally a P**

- **Vary T:** $(\Delta G_{rxn})_{T_1,P}$ **vs** $(\Delta G_{rxn})_{T_2,P}$

- **Need** $\left(\dfrac{\partial G}{\partial T}\right)_P$ *and* $\left(\dfrac{\partial \Delta G_{rxn}}{\partial T}\right)_P$

$$d\bar{G} = -\bar{S}dT + \bar{V}dP$$

$$\left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S} \quad \textit{but \textbf{remember} S(T)}$$

a few manipulations which lead to simpler final relationships

$$\Delta G_{rxn} = \Delta G_{rxn}^0 + \underline{R}T\,\ln Q \qquad \Delta G_{rxn}^0 = -\underline{R}T\,\ln K_{eq}$$

$$\frac{\Delta G}{T} = \frac{\Delta G^0}{T} + \underline{R}\,\ln Q \qquad\qquad \frac{\Delta G^0}{T} = -\underline{R}\,\ln K_{eq}$$

$$\left(\frac{\partial \frac{\Delta G}{T}}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial \Delta G}{\partial T}\right)_P - \frac{\Delta G}{T^2}$$

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$$\left(\frac{\partial \frac{\Delta G}{T}}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial \Delta G}{\partial T}\right)_P - \frac{\Delta G}{T^2}$$

$$\left(\frac{\partial \frac{\Delta G}{T}}{\partial T}\right)_P = -\frac{\Delta S}{T} - \frac{\Delta G}{T^2}$$

$$\left(\frac{\partial \frac{\Delta G}{T}}{\partial T}\right)_P = -\frac{\Delta S}{T} - \frac{(\Delta H - T\Delta S)}{T^2}$$

$$\boxed{\left(\frac{\partial \frac{\Delta G}{T}}{\partial T}\right)_P = -\frac{\Delta H}{T^2}}$$

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$$\left(\frac{\partial \frac{\Delta G}{T}}{\partial T}\right)_P = -\frac{\Delta H}{T^2}$$

$$\left(\frac{\partial \frac{\Delta G^0}{T}}{\partial T}\right)_P = \left(\frac{\partial\left(-\underline{R}\ln K\right)}{\partial T}\right)_P = -\underline{R}\left(\frac{\partial \ln K}{\partial T}\right)_P = -\frac{\Delta H^0}{T^2}$$

$$\boxed{\left(\frac{\partial \ln K}{\partial T}\right)_P = +\frac{\Delta H^0}{\underline{R}T^2}}$$

$$\left(\frac{\partial \ln K}{\partial T} \right)_P = + \frac{\Delta H^0}{\underline{R} T^2}$$

$$\int_{T_1}^{T_2} d \ln K = \int_{T_1}^{T_2} + \frac{\Delta H^0}{\underline{R} T^2} dT$$

$$\ln K_{T_2} - \ln K_{T_1} = - \frac{\Delta H^0}{\underline{R}} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = \frac{\Delta H^0}{\underline{R}} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \left(\frac{K_{T_2}}{K_{T_1}} \right) = \frac{\Delta H^0}{\underline{R}} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln\left(\frac{K_{T_2}}{K_{T_1}}\right) = \frac{\Delta H^0}{\underline{R}}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$T_2 > T_1$$

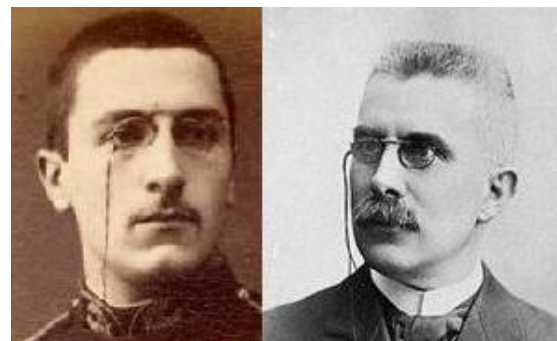*endothermic*, $\Delta H^0 > 0 \implies \ln\frac{K_{T_2}}{K_{T_1}} > 0 \implies K_{T_2} > K_{T_1}$

higher T moves equilibrium to right (products)   reactants + heat $\rightleftarrows$ products

exothermic $\Delta H^0 < 0 \implies \ln\frac{K_{T_2}}{K_{T_1}} < 0 \implies K_{T_2} < K_{T_1}$

higher T moves equilibrium to left (reactants)   reactants $\rightleftarrows$ products + heat

*Le Chatelier's Principle
"for heat"*

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✓ **6. Brief hello to thermodynamics of multicomponent systems (n's vary)**

✓ **7. $\Delta G_{reaction}$ for non-standard state concentrations, pressures**
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✓ **8. K_{eq} and $\Delta G^0_{reaction}$**

✓ **9. $\Delta G_{reaction} = \Delta G^0_{reaction} + \underline{R}T \ln Q$ is extensive**

✓ **10. Variation of K_{eq} with T**

End of Lecture