Slide 1

Lecture 15 Chemistry 163B

Free Energy

and

Equilibrium

E&R (≈ ch 6)

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$\Delta G_{reaction}$ and equilibrium (first pass, lecture 14)

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. **ΔG° all reactants and products in standard states**

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

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

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

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goals of lecture 15

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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6.0 molar free energy and partial molar free energy (chemical potential)

2NO₂ ⇌ N₂O₄

multicomponent mixture
n_{NO_2} moles NO_2 ;
$n_{N_2O_4}$ moles N_2O_4

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

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

$$\mu_{NO_2} = \left(\frac{\partial G_{(NO_2 + N_2O_4\ mixture)}}{\partial n_{NO_2}}\right)_{T, P, n_{N_2O_4}}$$
partial molar Gibbs free energy
or chemical potential (of NO_2)

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

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

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6.0 molar free energy and partial molar free energy (chemical potential)

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multicomponent mixture
n_{NO_2} moles NO_2 ;
$n_{N_2O_4}$ moles N_2O_4

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

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

$$\mu_{NO_2} = \left(\frac{\partial G_{(NO_2 + N_2O_4\ mixture)}}{\partial n_{NO_2}}\right)_{T, P, n_{N_2O_4}}$$
partial molar Gibbs free energy
or chemical potential (of NO_2)

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

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

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6.1 molar free energy and partial molar free energy (chemical potential)

2NO₂ ⇌ N₂O₄

multicomponent mixture
n_{NO_2} moles NO_2 ;
$n_{N_2O_4}$ moles N_2O_4

$$\mu_{NO_2} = \left(\frac{\partial \overline{G}_{(NO_2 + N_2O_4\ mixture)}}{\partial n_{NO_2}}\right)_{T, P, n_{N_2O_4}}$$
partial molar Gibbs free energy
or chemical potential

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

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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$$\mu_i \approx \bar{G}_i$$

$$\boxed{\begin{array}{c} for\ \text{now}\ \mu_i \approx \bar{G}_i \\[4pt] \Delta\mu_{reaction} \approx \Delta G_{reaction} \end{array}}$$

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

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

7. How does $\Delta G_{reaction}$ ($\Delta\mu$) 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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7.1 $\Delta G_{reaction}$ as a function of concentration

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

for ideal gas

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

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

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

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

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

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7.2 $\Delta G_{reaction}$ as a function of concentration (ideal gas)

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

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

$$\boxed{\begin{array}{c}\bar{G}_i(P_i) = \bar{G}_i^0 + RT\ln\left(\dfrac{P_i}{1\,bar}\right) \\[8pt] later\ \mu_i(P_i) = \mu_i^0 + RT\ln\left(\dfrac{P_i}{1\,bar}\right)\end{array}}$$

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7.3 $\Delta G_{reaction}$ as a function of concentration

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

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

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

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

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

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

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

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

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7.4 $\Delta G_{reaction}$ as a function of concentration

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

$$reaction\ quotient\quad Q_P = \prod_i\left(\frac{P_i}{1\,bar}\right)^{\bar{\nu}_i} = \frac{\prod_{q=prod}\left(\frac{P_q}{1\,bar}\right)^{\bar{\nu}_q}}{\prod_{r=react}\left(\frac{P_r}{1\,bar}\right)^{\bar{\nu}_r}}$$

Q is UNITLESS

1 bar is P^0, *std* state for P

$$n_a A + n_b B \rightleftarrows n_c C + n_d D$$

$$Q_P = \frac{\left(\frac{P_C}{1\,bar}\right)^{\bar{\nu}_c}\left(\frac{P_D}{1\,bar}\right)^{\bar{\nu}_d}}{\left(\frac{P_A}{1\,bar}\right)^{\bar{\nu}_a}\left(\frac{P_B}{1\,bar}\right)^{\bar{\nu}_b}}$$

'like' an equilibrium constant

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

HW6 prob 39

1 M is std state for solute   12

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7.5 Q and units (persnicketyness)

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

reaction quotient $\quad Q_P = \prod_i \left(\frac{P_i}{1\ bar}\right)^{\nu_i} \quad$ **Q is UNITLESS**

$$Q_C = \prod_i \left(\frac{[i]}{1\ M}\right)^{\nu_i}$$

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

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

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

$$\Delta G_{reaction} = \Delta G^0_{reaction} + \sum_i (\underline{R})T \ln\left(\frac{P_i}{1\ bar}\right)^{\nu_i} \quad \leftarrow \text{unitless exponent}$$

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

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7.6 $\Delta G_{reaction}$ as a function of concentration

$$\boxed{\begin{array}{c} \Delta G_{reaction} = \Delta G^0_{reaction} + RT \ln Q \\[2mm] Q_P = \prod_i \left(\frac{P_i}{1\ bar}\right)^{\nu_i} \quad Q_C = \prod_i \left(\frac{[i]}{1\ M}\right)^{\nu_i} \end{array}}$$

evaluates ΔG for ANY set of pressures, concentrations

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

at equilibrium ΔG= ?

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8. $\Delta G_{reaction}$ at equilibrium

at equilibrium ΔG= 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 $\quad Q_{eq} = constant \equiv K_{eq}$

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

$$K_{eq} = e^{-\frac{\Delta G^0}{\underline{R}T}} \qquad Q_P = \prod_i \left(\frac{P_i}{1\ bar}\right)^{\nu_i} \quad Q_C = \prod_i \left(\frac{[i]}{1\ M}\right)^{\nu_i}$$
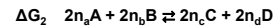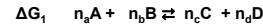
$$\boxed{\begin{array}{l} \Delta G_{reaction} = \Delta G^0_{reaction} + \underline{R}T \ln Q \quad any\ concentrations\ \text{for } Q \\[2mm] Q_{eq} \equiv K_{eq}\ \ for\ equilibrium\ \text{concentrations} \\[2mm] \qquad \text{that satisfy } \Delta G^0_{reaction} = -\underline{R}T \ln K_{eq} \end{array}}$$

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9. $\Delta G_{reaction} = \Delta G^o + RT \ln Q$ is extensive

$$\Delta G_1 \qquad n_aA + n_bB \rightleftarrows n_cC + n_dD$$
$$\Delta G_2 \qquad 2n_aA + 2n_bB \rightleftarrows 2n_cC + 2n_dD$$

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

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

$$Q_2 = Q_1^2$$

$$\Delta G_1 = \Delta G_1^0 + \underline{R}T \ln Q_1$$
$$\Delta G_2 = \Delta G_2^0 + \underline{R}T \ln Q_2$$
$$\Delta G_2 = 2\Delta G_1^0 + \underline{R}T \ln Q_1^2 = 2\left(\Delta G_1^0 + \underline{R}T \ln Q_1\right)$$
$$\Delta G_2 = 2\Delta G_1$$

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10.1 variation of K_{eq} with T

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

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

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

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10.2 variation of K_{eq} with T

$$d\overline{G} = -\overline{S}dT + \overline{V}dP$$
$$\left(\frac{\partial \overline{G}}{\partial T}\right)_P = -\overline{S} \quad but\ \text{remember } S(T)$$

a few manipulations which lead to simpler final relationships

$$\Delta G_{rxn} = \Delta G^0_{rxn} + \underline{R}T \ln Q \qquad \Delta G^0_{rxn} = -\underline{R}T \ln K_{eq}$$
$$\frac{\Delta G}{T} = \frac{\Delta G^0}{T} + \underline{R} \ln Q \qquad \frac{\Delta G^0}{T} = -\underline{R} \ln K_{eq}$$
$$\left(\frac{\partial \frac{\Delta G}{T}}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial \Delta G}{\partial T}\right)_P - \frac{\Delta G}{T^2}$$

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10.3 variation of K_{eq} with T

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

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

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

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

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10.4 variation of K_{eq} with T

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

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

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

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10.5 variation of K_{eq} with T

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

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

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

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

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10.6 variation of K_{eq} with T

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

$$T_2 > T_1$$

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

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

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

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

Le Chatelier's Principle
"for heat"

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goals of lecture

✓ **6. Brief hello to thermodynamics of multicomponent systems (n'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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free   *End of Lecture 15*   *energy*

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