# Chemistry 163B
# Free Energy
# and
# Equilibrium
# E&R (≈ ch 6)

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## $\Delta G_{reaction}$ and equilibrium (first pass)

here $\Delta G \equiv \Delta G_{reaction}$

1. $\Delta G < 0$ spontaneous *('natural', irreversible)*
   $\Delta G = 0$ equilibrium *(reversible)*
   $\Delta G > 0$ spontaneous in reverse direction
2. $\Delta G_T = \Delta H - T\Delta S$
3. $\Delta G^o$ 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)*
   $\Delta \bar{G}_f^0(O_2(g)) \equiv 0 \quad \Delta \bar{G}_f^0(C(gr)) = 0$
5. $$\Delta G^0_{reaction} = \sum_i \nu_i \Delta \bar{H}_f^0 - T\sum_i \nu_i \bar{S}_i^0$$
   $$\Delta G^0_{reaction} = \Delta H^0_{reaction} - T\Delta S^0_{reaction}$$

*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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## goals of lecture

6. Brief hello to thermodynamics of multicomponent systems ($n_i$'s vary)
7. $\Delta G_{reaction}$ for non-standard state concentrations, pressures
   $\Delta G_{reaction} = \Delta G^o_{reaction} + \underline{R}T \ln Q$
8. $K_{eq}$ and $\Delta G^o_{reaction}$
9. $\Delta G_{reaction} = \Delta G^o_{reaction} + \underline{R}T \ln Q$ is extensive
10. Variation of $K_{eq}$ with T

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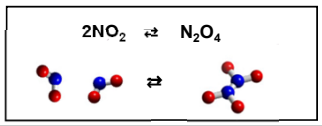
## 6. molar free energy and partial molar free energy (chemical potential)




*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*

*more generally* $G_{mixture}(T,P,n_1,\ldots,n_N)$

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

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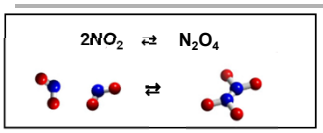
## 6'. molar free energy and partial molar free energy (chemical potential)




*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* $NO_2$ $\left[(\bar{G}_{NO_2} \equiv (\Delta \bar{G}_f)_{NO_2}\right]$

$\mu_{NO_2}$ *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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## $\mu_i \approx \bar{G}_i$

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

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

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

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

**7. How does $\Delta G_{reaction}$ (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. $\Delta G_{reaction}$ 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. $\Delta G_{reaction}$ as a function of concentration (ideal gas)

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

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

$$\boxed{\begin{aligned} \bar{G}_i(P_i) &= \bar{G}_i^0 + RT\,ln\left(\frac{P_i}{1\,bar}\right) \\ \text{later } \mu_i(P_i) &= \mu_i^0 + RT\,ln\left(\frac{P_i}{1\,bar}\right) \end{aligned}}$$

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

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

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

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

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

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

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

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

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

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

$$\boxed{\begin{aligned} &\Delta G_{reaction} = \Delta G^0_{reaction} + \underline{R}T\ ln\,Q_P \\ &\text{reaction quotient} \quad Q_P = \prod_i\left(\frac{P_i}{1\,bar}\right)^{\bar{\nu}_i} = \frac{\prod_{q=prod}\left(\frac{P_q}{1\,bar}\right)^{\bar{\nu}_q}}{\prod_{r=react}\left(\frac{P_r}{1\,bar}\right)^{\bar{\nu}_r}} \quad Q \text{ is UNITLESS} \\ &\qquad\qquad 1\,bar \text{ is } P^o\text{, std state for } P \end{aligned}}$$

$$n_aA + n_bB \rightarrow n_cC + n_dD$$

$$Q_P = \frac{\left(\frac{P_C}{1\,bar}\right)^{\bar{\nu}_c}\left(\frac{P_D}{1\,bar}\right)^{\bar{\nu}_d}}{\left(\frac{P_A}{1\,bar}\right)^{\bar{\nu}_a}\left(\frac{P_B}{1\,bar}\right)^{\bar{\nu}_b}} \quad \text{'like' an equilibrium constant}$$

*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

*HW7 prob 39* $\quad$ *1 M is std state for solute*

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### 7. Q and units (persnicketyness)

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

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

$$Q_C = \prod_i\left(\frac{[i]}{1\,M}\right)^{\bar{\nu}_i}$$

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

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

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

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

unitless exponent

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

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

$$\Delta G_{reaction} = \Delta G^0_{reaction} + \underline{R}T \ln Q$$
$$Q_p = \prod_i \left(\frac{P_i}{1\ bar}\right)^{\bar{\nu}_i} \quad Q_c = \prod_i \left(\frac{[i]}{1\ M}\right)^{\bar{\nu}_i}$$

evaluates ΔG for ANY set of pressures, concentrations

$\Delta G^o$ 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

$$0 = \Delta G^0_{reaction} + \underline{R}T \ln Q_{eq}$$
$$\Delta G^0_{reaction} = -\underline{R}T \ln Q_{eq}$$
$$at\ given\ T \quad Q_{eq} = constant \equiv K_{eq}$$

$$\Delta G^0 = -\underline{R}T \ln K_{eq}$$
$$K_{eq} = e^{-\frac{\Delta G^0}{\underline{R}T}}$$

$$\Delta G_{reaction} = \Delta G^0_{reaction} + \underline{R}T \ln Q$$
$$Q_p = \prod_i \left(\frac{P_i}{1\ bar}\right)^{\bar{\nu}_i} \quad Q_c = \prod_i \left(\frac{[i]}{1\ M}\right)^{\bar{\nu}_i}$$

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

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

$\Delta G_1$ $n_aA + n_bB \rightarrow n_cC + n_dD$

$\Delta G_2$ $2n_aA + 2n_bB \rightarrow 2n_cC + 2n_dD$

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

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

$$Q_2 = Q_1^2$$

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

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### 10. variation of $K_{eq}$ with T

- $(\Delta G_{rxn})_{T,P}$ ⇨ reaction carried out isothermally a P
- Vary T: $(\Delta G_{rxn})_{T_1,P}$ vs $(\Delta G_{rxn})_{T_2,P}$
- Need $\left(\frac{\partial G}{\partial T}\right)_P$ *and* $\left(\frac{\partial \Delta G_{rxn}}{\partial T}\right)_P$

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### 10. variation of $K_{eq}$ with T

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

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. 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. 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. 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. 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 $\Delta G_{reaction} = \Delta G^o_{reaction} + \underline{R}T \ln Q$
- ✓ 8. $K_{eq}$ and $\Delta G^o_{reaction}$
- ✓ 9. $\Delta G_{reaction} = \Delta G^o_{reaction} + \underline{R}T \ln Q$ is extensive
- ✓ 10. Variation of $K_{eq}$ with T

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*End of Lecture*

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