

Chemistry 163B Winter 2013

Lecture 15- Free Energy and Equilibrium

Chemistry 163B

Free Energy

and

Equilibrium

E&R (\approx ch 6)

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

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

1. $\Delta G < 0$ spontaneous ('natural', irreversible)
 $\Delta G = 0$ equilibrium (reversible)
 $\Delta G > 0$ spontaneous in reverse direction
2. $\Delta G_r = \Delta H - T\Delta S$
3. ΔG° all reactants and products in standard states
4. $\Delta \bar{G}_f^\circ \equiv \bar{G}_f^\circ$ Appendix A at 298.15K (reaction where reactants are elements in their most stable form and in their standard states, $P=1$ atm, $[\text{conc}]=1M$, etc)
 $\Delta \bar{G}_f^\circ(O_2(g)) = 0$ $\Delta \bar{G}_f^\circ(C(gr)) = 0$
5. $\Delta G_{\text{reaction}}^\circ = \sum_i \nu_i \Delta \bar{H}_f^\circ - T \sum_i \nu_i \bar{S}_i^\circ$
 $\Delta G_{\text{reaction}}^\circ = \Delta H_{\text{reaction}}^\circ - T \Delta S_{\text{reaction}}^\circ$

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

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goals of lecture

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

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

$2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$

multicomponent mixture
 n_{NO_2} moles NO_2 ;
 $n_{\text{N}_2\text{O}_4}$ moles N_2O_4

$G_{\text{NO}_2, \text{N}_2\text{O}_4 \text{ mixture}}(T, P, n_{\text{NO}_2}, n_{\text{N}_2\text{O}_4})$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_{\text{NO}_2}, n_{\text{N}_2\text{O}_4}} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_{\text{NO}_2}, n_{\text{N}_2\text{O}_4}} dP + \left(\frac{\partial G}{\partial n_{\text{NO}_2}}\right)_{T, P, n_{\text{N}_2\text{O}_4}} dn_{\text{NO}_2} + \left(\frac{\partial G}{\partial n_{\text{N}_2\text{O}_4}}\right)_{T, P, n_{\text{NO}_2}} dn_{\text{N}_2\text{O}_4}$$

$\mu_{\text{NO}_2} = \left(\frac{\partial G_{\text{NO}_2, \text{N}_2\text{O}_4 \text{ mixture}}}{\partial n_{\text{NO}_2}}\right)_{T, P, n_{\text{N}_2\text{O}_4}}$
partial molar Gibbs free energy
or chemical potential

more generally $G_{\text{mixture}}(T, P, n_1, \dots, n_N)$

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

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

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 n_{NO_2} moles NO_2 ;
 $n_{\text{N}_2\text{O}_4}$ moles N_2O_4

$$\mu_{\text{NO}_2} = \left(\frac{\partial G_{\text{NO}_2, \text{N}_2\text{O}_4 \text{ mixture}}}{\partial n_{\text{NO}_2}}\right)_{T, P, n_{\text{N}_2\text{O}_4}}$$
partial molar Gibbs free energy
or chemical potential

$$\bar{G}_{\text{NO}_2}$$
 molar Gibbs free energy of pure NO_2 [$\bar{G}_{\text{NO}_2} \equiv (\Delta \bar{G}_f)_{\text{NO}_2}$]

$$\mu_{\text{NO}_2}$$
 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 $\mu_i \approx \bar{G}_i$

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

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

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

7. How does $\Delta G_{\text{reaction}}$ ($\Delta\mu$) vary as the concentration of reactants and products varies?

example: 'concentration' of gas = partial pressure P_i

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

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

for ideal gas:

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

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

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

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

for ideal gas

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$RT \sum_i \nu_i \ln\left(\frac{P_i}{1 \text{ bar}}\right) = RT \ln \left[\prod_i \left(\frac{P_i}{1 \text{ bar}}\right)^{\nu_i} \right] = RT \ln Q_P$$

$$Q_P = \prod_i \left(\frac{P_i}{1 \text{ bar}}\right)^{\nu_i}$$

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

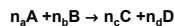
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7. $\Delta G_{\text{reaction}}$ as a function of concentration

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

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

1 bar is P^0 , std state for P



$$Q_P = \frac{\left(\frac{P_C}{1 \text{ bar}}\right)^{n_C} \left(\frac{P_D}{1 \text{ bar}}\right)^{n_D}}{\left(\frac{P_A}{1 \text{ bar}}\right)^{n_A} \left(\frac{P_B}{1 \text{ bar}}\right)^{n_B}} \quad \text{'like' an equilibrium constant}$$

for solutes in soln $Q_c = \prod_i \left(\frac{[i]}{1 M}\right)^{\nu_i} \quad Q_c = \frac{\left(\frac{[C]}{1 M}\right)^{n_C} \left(\frac{[D]}{1 M}\right)^{n_D}}{\left(\frac{[A]}{1 M}\right)^{n_A} \left(\frac{[B]}{1 M}\right)^{n_B}} \quad Q \text{ is UNITLESS}$

1 M is std state for solute 11

HW6 prob 39

7. Q and units (persnicketyness)

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

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

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

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

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

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

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

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

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

$$\Delta G_{\text{reaction}} = \Delta G_{\text{reaction}}^{\circ} + RT \ln Q$$

$$Q_p = \prod_i \left(\frac{P_i}{1 \text{ bar}} \right)^{\nu_i} \quad Q_c = \prod_i \left(\frac{[i]}{1 \text{ M}} \right)^{\nu_i}$$

evaluates ΔG for **ANY** set of pressures, concentrations

ΔG° gives free energy change for standard conditions,
 $RT \ln Q$ corrects ΔG for actual P's and [conc's]

at equilibrium $\Delta G = ?$

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

at equilibrium $\Delta G = 0$

$$0 = \Delta G_{\text{reaction}}^{\circ} + RT \ln Q_{\text{eq}}$$

$$\Delta G_{\text{reaction}}^{\circ} = -RT \ln Q_{\text{eq}}$$

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

$$\Delta G^{\circ} = -RT \ln K_{\text{eq}}$$

$$\Delta G_{\text{reaction}} = \Delta G_{\text{reaction}}^{\circ} + RT \ln Q$$

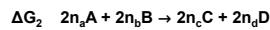
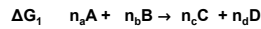
$$K_{\text{eq}} = e^{-\frac{\Delta G^{\circ}}{RT}}$$

$$Q_c = \prod_i \left(\frac{P_i}{1 \text{ bar}} \right)^{\nu_i} \quad Q_c = \prod_i \left(\frac{[i]}{1 \text{ M}} \right)^{\nu_i}$$

$\Delta G_{\text{reaction}} = \Delta G_{\text{reaction}}^{\circ} + RT \ln Q$ any concentrations for Q
 $Q_{\text{eq}} = K_{\text{eq}}$ for equilibrium concentrations
that satisfy $\Delta G_{\text{reaction}}^{\circ} = -RT \ln K_{\text{eq}}$

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



$$\Delta G_2 \text{ ?} = 2 \Delta G_1$$

$$Q_1 = \frac{\left(\frac{P_C}{1 \text{ bar}} \right)^{n_c} \left(\frac{P_D}{1 \text{ bar}} \right)^{n_d}}{\left(\frac{P_A}{1 \text{ bar}} \right)^{n_a} \left(\frac{P_B}{1 \text{ bar}} \right)^{n_b}} \quad Q_2 = \frac{\left(\frac{P_C}{1 \text{ bar}} \right)^{2n_c} \left(\frac{P_D}{1 \text{ bar}} \right)^{2n_d}}{\left(\frac{P_A}{1 \text{ bar}} \right)^{2n_a} \left(\frac{P_B}{1 \text{ bar}} \right)^{2n_b}}$$

$$Q_2 = Q_1^2$$

$$\Delta G_1 = \Delta G_1^{\circ} + RT \ln Q_1$$

$$\Delta G_2 = \Delta G_2^{\circ} + RT \ln Q_2$$

$$\Delta G_2 = 2\Delta G_1^{\circ} + RT \ln Q_1^2 = 2(\Delta G_1^{\circ} + RT \ln Q_1)$$

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

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10. variation of K_{eq} with T

• $(\Delta G_{\text{rxn}})_{T,P} \Rightarrow$ reaction carried out isothermally at P

• Vary T: $(\Delta G_{\text{rxn}})_{T1,P}$ vs $(\Delta G_{\text{rxn}})_{T2,P}$

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

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10. variation of K_{eq} with T

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

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

a few manipulations which lead to simpler final relationships

$$\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^{\circ} + RT \ln Q \quad \Delta G_{\text{rxn}}^{\circ} = -RT \ln K_{\text{eq}}$$

$$\frac{\Delta G}{T} = \frac{\Delta G^{\circ}}{T} + R \ln Q \quad \frac{\Delta G^{\circ}}{T} = -R \ln K_{\text{eq}}$$

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

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10. variation of K_{eq} with T

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

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

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

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

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10. variation of K_{eq} with T

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

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

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = +\frac{\Delta H^\circ}{RT^2}$$

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10. variation of K_{eq} with T

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = +\frac{\Delta H^\circ}{RT^2}$$

$$\int_{T_1}^{T_2} d \ln K = \int_{T_1}^{T_2} +\frac{\Delta H^\circ}{RT^2} dT$$

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

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

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10. variation of K_{eq} with T

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

$$T_2 > T_1$$

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

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

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

higher T moves equilibrium to left (reactants) reactants \rightleftharpoons 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. $\Delta G_{\text{reaction}}$ for non-standard state concentrations, pressures
 $\Delta G_{\text{reaction}} = \Delta G^\circ_{\text{reaction}} + RT \ln Q$
- ✓ 8. K_{eq} and $\Delta G^\circ_{\text{reaction}}$
- ✓ 9. $\Delta G_{\text{reaction}} = \Delta G^\circ_{\text{reaction}} + RT \ln Q$ is extensive
- ✓ 10. Variation of K_{eq} with T

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End of Lecture

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