

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

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

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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.  $\Delta G_T = \Delta H - T\Delta S$
3.  $\Delta G^0$  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*)  
 $\Delta \bar{G}_f^0(O_2(g)) \equiv 0$     $\Delta \bar{G}_f^0(C(gr)) = 0$

5.

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

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

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

**7.  $\Delta G_{\text{reaction}}$  for non-standard state concentrations, pressures**

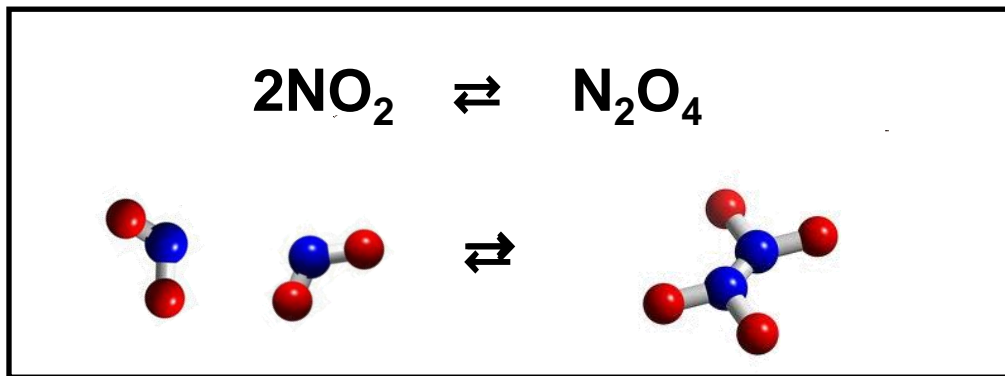
$$\Delta G_{\text{reaction}} = \Delta G^{\circ}_{\text{reaction}} + RT \ln Q$$

**8.  $K_{\text{eq}}$  and  $\Delta G^{\circ}_{\text{reaction}}$**

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

**10. Variation of  $K_{\text{eq}}$  with T**

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



*multicomponent mixture*

$n_{\text{NO}_2}$  moles  $\text{NO}_2$  ;

$n_{\text{N}_2\text{O}_4}$  moles  $\text{N}_2\text{O}_4$

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

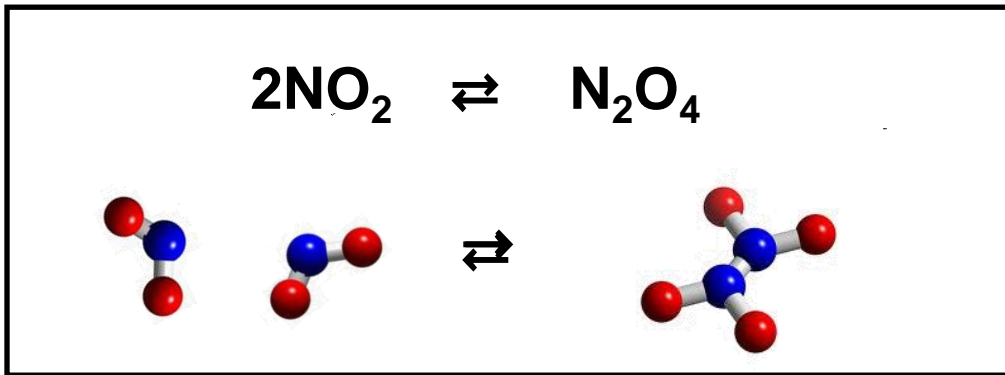
$$dG = \left( \frac{\partial G}{\partial T} \right)_{P, n_{\text{NO}_2}, n_{\text{N}_2\text{O}_4}} dT + \left( \frac{\partial G}{\partial P} \right)_{T, n_{\text{NO}_2}, n_{\text{N}_2\text{O}_4}} dP + \left( \frac{\partial G}{\partial n_{\text{NO}_2}} \right)_{T, P, n_{\text{N}_2\text{O}_4}} dn_{\text{NO}_2}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

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

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

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

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



*multicomponent mixture*

$n_{\text{NO}_2}$  moles  $\text{NO}_2$  ;

$n_{\text{N}_2\text{O}_4}$  moles  $\text{N}_2\text{O}_4$

$$\mu_{\text{NO}_2} = \left( \frac{\partial G_{(\text{NO}_2 + \text{N}_2\text{O}_4 \text{ mixture})}}{\partial n_{\text{NO}_2}} \right)_{T, P, n_{\text{N}_2\text{O}_4}}$$

*partial molar Gibbs free energy  
or chemical potential*

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

$\mu_{\text{NO}_2}$  molar Gibbs free energy of  $\text{NO}_2$  *in environment  
where other molecules are present*

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

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

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

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

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

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

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

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

$P_i = X_i P_{\text{total}}$  where  $X_i$  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:*

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

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

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

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

*for ideal gas*

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

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

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

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

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



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

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

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

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

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

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

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

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

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

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

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

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

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

for 'persnickety' units notation

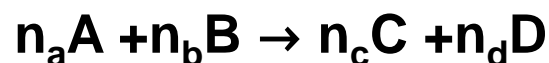
$$\underline{R} = R(\text{mol}) = [J K^{-1}]$$

$$\bar{\nu}_i = \nu_i(\text{mol}^{-1}) = [\text{unitless}]$$

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

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

reaction quotient  $Q_P = \prod_i \left( \frac{P_i}{1 \text{ bar}} \right)^{\bar{v}_i} = \frac{\prod_{q=\text{prod}} \left( \frac{P_q}{1 \text{ bar}} \right)^{\bar{n}_q}}{\prod_{r=\text{react}} \left( \frac{P_r}{1 \text{ bar}} \right)^{\bar{n}_r}}$  ***Q is UNITLESS***  
***1 bar is  $P^0$ , std state for P***



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

***'like' an equilibrium constant***

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

**HW6 prob 39**

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## 7. Q and units (persnicketyness)

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

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

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

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

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

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

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

← unitless exponent

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

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

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$$\Delta G_{\text{reaction}} = \Delta G_{\text{reaction}}^0 + \underline{RT} \ln Q$$
$$Q_P = \prod_i \left( \frac{P_i}{1 \text{ bar}} \right)^{\bar{v}_i} \quad Q_C = \prod_i \left( \frac{[i]}{1 \text{ M}} \right)^{\bar{v}_i}$$

evaluates  $\Delta G$  for **ANY** set of pressures, concentrations

$\Delta G^0$  gives free energy change for standard conditions,  
 $RT \ln Q$  corrects  $\Delta G$  for actual P's and [conc's]

at equilibrium  $\Delta G = ?$

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

at equilibrium  $\Delta G = 0$

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

$$\Delta G_{\text{reaction}}^0 = -\underline{RT} \ln Q_{\text{eq}}$$

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

$$\Delta G^0 = -\underline{RT} \ln K_{\text{eq}}$$

$$K_{\text{eq}} = e^{-\frac{\Delta G^0}{\underline{RT}}}$$

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

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

$\Delta G_{\text{reaction}} = \Delta G_{\text{reaction}}^0 + \underline{RT} \ln Q$  any concentrations for  $Q$

$Q_{\text{eq}} \equiv K_{\text{eq}}$  for equilibrium concentrations

that satisfy  $\Delta G_{\text{reaction}}^0 = -\underline{RT} \ln K_{\text{eq}}$

9.  $\Delta G_{\text{reaction}} = \Delta G^0 + \underline{RT} \ln Q$  is extensive

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

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

$$Q_2 = Q_1^2$$

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

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

$$\Delta G_2 = 2\Delta G_1^0 + \underline{RT} \ln Q_1^2 = 2(\Delta G_1^0 + \underline{RT} \ln Q_1)$$

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

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

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- $(\Delta G_{rxn})_{T,P} \Rightarrow$  reaction carried out isothermally a P
- Vary T:  $(\Delta G_{rxn})_{T1,P}$  vs  $(\Delta G_{rxn})_{T2,P}$
- Need  $\left(\frac{\partial G}{\partial T}\right)_P$  and  $\left(\frac{\partial \Delta G_{rxn}}{\partial T}\right)_P$



## 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**

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

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

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

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

---

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

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

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

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

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

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

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

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

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

---

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

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

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

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

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

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

$$T_2 > T_1$$

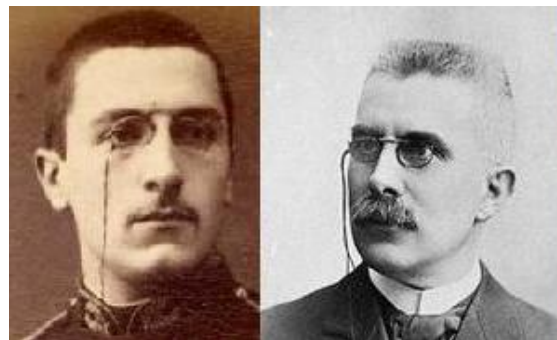
*endothermic*,  $\Delta H^0 > 0 \Rightarrow \ln \frac{K_{T_2}}{K_{T_1}} > 0 \Rightarrow K_{T_2} > K_{T_1}$

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

*Le Chatelier's Principle  
“for heat”*



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

*End of Lecture*