


# Chemistry 163B Winter 2020

## Lecture 15- Free Energy and Equilibrium

Lecture 15 Chemistry 163B

Free Energy  
and  
Equilibrium  
E&R (≈ ch 6)



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

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

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.  $\Delta G^0$  all reactants and products in standard states
4.  $\Delta G_f^0 \equiv \bar{G}_f^0$  Appendix A at 298.15K (reaction where reactants are elements in their most stable form and in their standard states,  $P=1 \text{ atm}$ ,  $[\text{conc}]=1M$ , etc)  
 $\Delta \bar{G}_f^0(\text{O}_2(\text{g})) = 0$     $\Delta \bar{G}_f^0(\text{C}(\text{gr})) = 0$
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:  $\Delta G_f^0$  and  $\Delta \bar{H}_f^0$  in  $\text{kJ mol}^{-1}$  BUT  $\bar{S}^0$  in  $\text{J K}^{-1} \text{mol}^{-1}$

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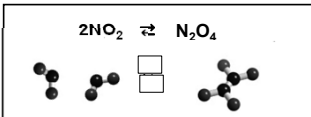
goals of lecture 15

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6. Brief hello to thermodynamics of multicomponent systems ( $n_i$ 's vary)
7.  $\Delta G_{\text{reaction}}$  for non-standard state concentrations, pressures  
 $\Delta G_{\text{reaction}} = \Delta G_{\text{reaction}}^0 + RT \ln Q$
8.  $K_{\text{eq}}$  and  $\Delta G_{\text{reaction}}^0$
9.  $\Delta G_{\text{reaction}} = \Delta G_{\text{reaction}}^0 + RT \ln Q$  is extensive
10. Variation of  $K_{\text{eq}}$  with T

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6.0 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  $\text{N}_2\text{O}_4$

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

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

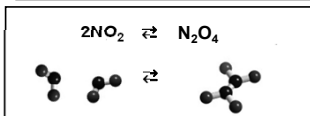
partial molar Gibbs free energy or chemical potential (of  $\text{NO}_2$ )

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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6.0 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  $\text{N}_2\text{O}_4$

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

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

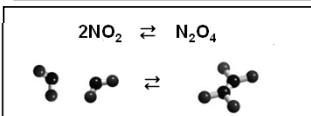
partial molar Gibbs free energy or chemical potential (of  $\text{NO}_2$ )

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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6.1 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

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

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

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

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

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

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

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

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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:

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

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

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

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

for ideal gas

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

reaction quotient  $Q_P = \prod_i \left(\frac{P_i}{1 \text{ bar}}\right)^{\nu_i} = \frac{\prod_{\text{products}} \left(\frac{P_i}{1 \text{ bar}}\right)^{\nu_i}}{\prod_{\text{reactants}} \left(\frac{P_i}{1 \text{ bar}}\right)^{\nu_i}}$   $Q$  is UNITLESS  
1 bar is  $P^{\circ}$ , std state for P

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

$Q_P = \frac{\left(\frac{P_C}{1 \text{ bar}}\right)^{\nu_c} \left(\frac{P_D}{1 \text{ bar}}\right)^{\nu_d}}{\left(\frac{P_A}{1 \text{ bar}}\right)^{\nu_a} \left(\frac{P_B}{1 \text{ bar}}\right)^{\nu_b}}$  'like' an equilibrium constant

for solutes in soln  $Q_C = \prod_i \left(\frac{[i]}{1 \text{ M}}\right)^{\nu_i}$   $Q_C = \frac{\left(\frac{[C]}{1 \text{ M}}\right)^{\nu_c} \left(\frac{[D]}{1 \text{ M}}\right)^{\nu_d}}{\left(\frac{[A]}{1 \text{ M}}\right)^{\nu_a} \left(\frac{[B]}{1 \text{ M}}\right)^{\nu_b}}$   $Q$  is UNITLESS

**HW6 prob 39** 1 M is std state for solute 12

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### 7.5 Q and units (persnicketyness)

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

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

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

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

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

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

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

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

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

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

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

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  $\Delta G = ?$

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

at equilibrium  $\Delta G = 0$

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

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

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

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

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

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

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

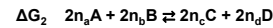
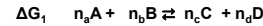
$$\Delta G_{\text{reaction}} = \Delta G_{\text{reaction}}^0 + RT \ln Q \quad \text{any concentrations for } Q$$

$Q_{eq} = K_{eq}$  for equilibrium concentrations

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

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



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

$$Q_1 = \frac{\left(\frac{P_c}{1 \text{ bar}}\right)^{n_c} \left(\frac{P_d}{1 \text{ bar}}\right)^{n_d}}{\left(\frac{P_a}{1 \text{ bar}}\right)^{n_a} \left(\frac{P_b}{1 \text{ bar}}\right)^{n_b}} \quad Q_2 = \frac{\left(\frac{P_c}{1 \text{ bar}}\right)^{2n_c} \left(\frac{P_d}{1 \text{ bar}}\right)^{2n_d}}{\left(\frac{P_a}{1 \text{ bar}}\right)^{2n_a} \left(\frac{P_b}{1 \text{ bar}}\right)^{2n_b}}$$

$$Q_2 = Q_1^2$$

$$\Delta G_1 = \Delta G_1^0 + RT \ln Q_1$$

$$\Delta G_2 = \Delta G_2^0 + RT \ln Q_2$$

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

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

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### 10.1 variation of $K_{eq}$ with T

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

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

• 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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### 10.2 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

$$\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^0 + RT \ln Q \quad \Delta G_{\text{rxn}}^0 = -RT \ln K_{eq}$$

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

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

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10.3 variation of  $K_{eq}$  with  $T$

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

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

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

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

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10.4 variation of  $K_{eq}$  with  $T$

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

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

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

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10.5 variation of  $K_{eq}$  with  $T$

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

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

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

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

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10.6 variation of  $K_{eq}$  with  $T$

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

$$T_2 > T_1$$

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"



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goals of lecture

- ✓ 6. Brief hello to thermodynamics of multicomponent systems (n's vary)
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- ✓ 8.  $K_{\text{eq}}$  and  $\Delta G^0_{\text{reaction}}$
- ✓ 9.  $\Delta G_{\text{reaction}} = \Delta G^0_{\text{reaction}} + RT \ln Q$  is extensive
- ✓ 10. Variation of  $K_{\text{eq}}$  with  $T$

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free End of Lecture 15 energy



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**persnickity**

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 **per·snick·et·y**  
/perˈsnɪkədə/  
 Learn to pronounce

**adjective** INFORMAL • NORTH AMERICAN

placing too much emphasis on trivial or minor details; fussy.  
"she's very persnickety about her food"

Similar: [fussy](#) [difficult to please](#) [difficult](#) [finicky](#) [overfastidious](#) 

• requiring a particularly precise or careful approach.

↑

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