

# Topic 5I. Equilibrium Calculations

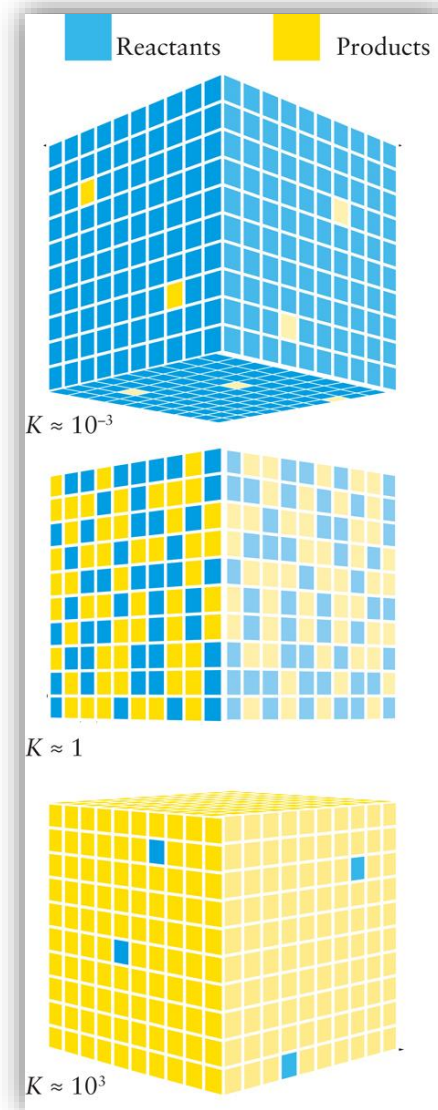
- 5I.1 The Extent of Reaction
- 5I.2 The Direction of Reaction
- 5I.3 Calculations with Equilibrium Constants

# The Extent of Reaction

- The extent of reaction vs.  $K$

$$K = \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}$$

- **Large  $K$**  (larger than about  $10^3$ ): equilibrium favors the products.
- **Intermediate  $K$**  (approximately in the range  $10^{-3}$  to  $10^3$ ): neither reactants nor products are strongly favored at equilibrium.
- **Small  $K$**  (smaller than about  $10^{-3}$ ): equilibrium favors the reactants.

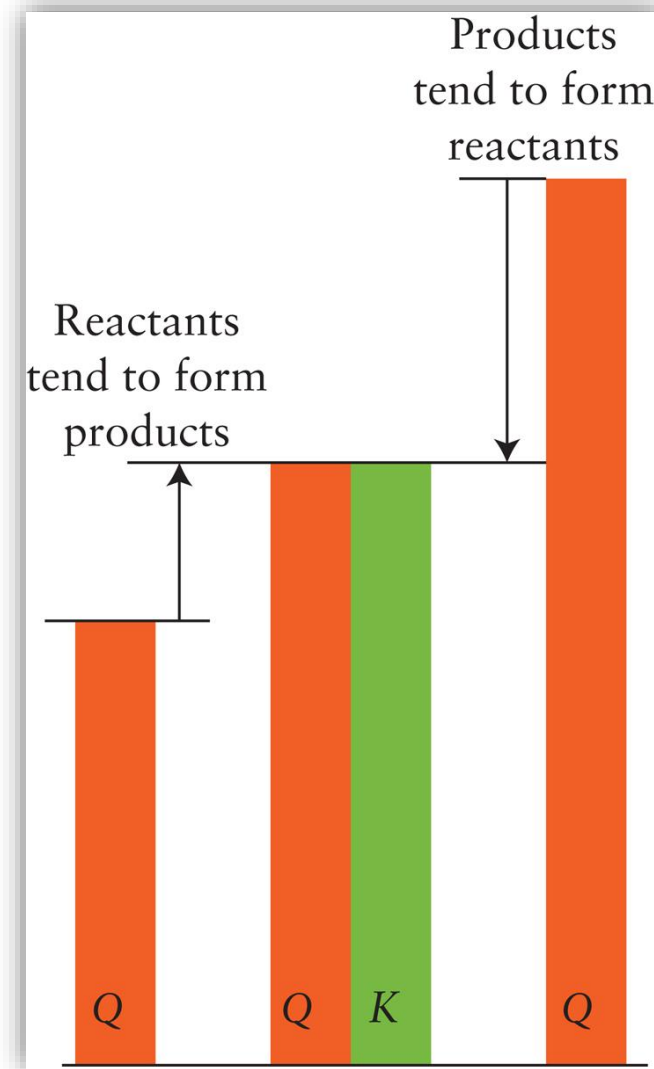


# The Direction of Reaction

## ■ $Q$ vs. $K$

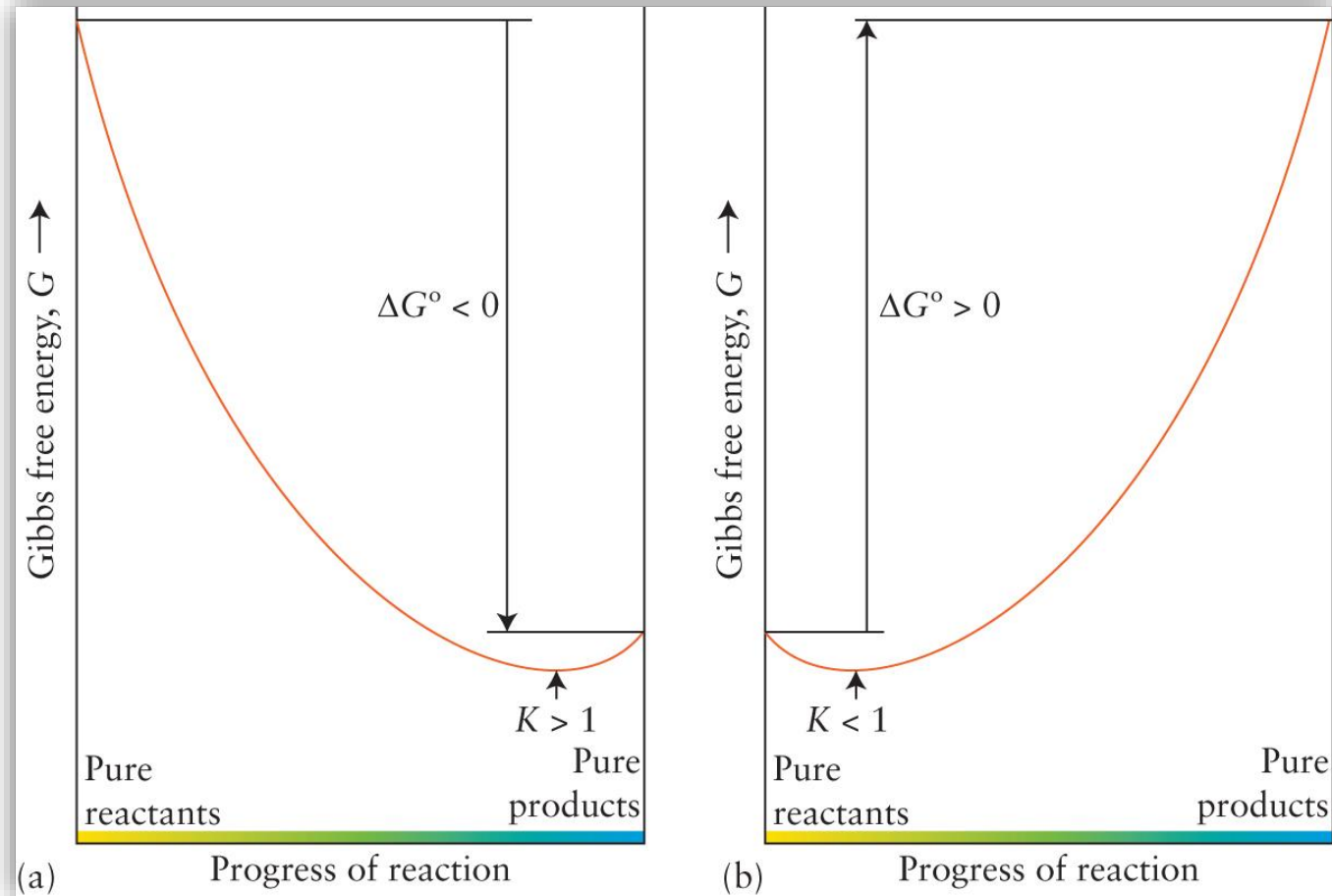
$$Q = \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}$$

- If  $Q < K$ , the concentrations or partial pressures of the products are too low relative to those of the reactants for equilibrium. Hence, the reaction has a tendency to proceed toward products.
- If  $Q = K$ , the mixture has its equilibrium composition and has no tendency to change in either direction.
- If  $Q > K$ , the reverse reaction is spontaneous and the products tend to decompose into the reactants.



# The Direction of Reaction

- $\Delta G^\circ$  vs.  $K$



# Calculations with Equilibrium Constants

- $\text{H}_2 (\text{g}) + \text{I}_2 (\text{g}) \leftrightarrow 2\text{HI} (\text{g})$  at 600 K
  - Initial concentrations:  $P_{\text{H}_2} = 1.98 \text{ atm}$ ,  $P_{\text{I}_2} = 1.71 \text{ atm}$
  - Equilibrium constant:  $K_p = P_{\text{HI}}^2 / (P_{\text{H}_2} \times P_{\text{I}_2}) = 92.6$

What are the equilibrium pressures of the products and reactants?

	$\text{H}_2$	$\text{I}_2$	$\text{HI}$
Initial	1.98	1.71	0
Change	$-x$	$-x$	$2x$
Equilibrium	$1.98 - x$	$1.71 - x$	$2x$

$$K_p = \frac{(2x)^2}{(1.98 - x)(1.71 - x)} = 92.6$$

# Calculations with Equilibrium Constants

$$K_p = \frac{(2x)^2}{(1.98-x)(1.71-x)} = 92.6$$



$$88.6x^2 - 341.694x + 313.525 = 0$$

$$x = 1.5044 \quad \text{or} \quad 2.3522 \text{ atm}$$

## ■ Equilibrium Pressures

- $P_{\text{H}_2} = 1.980 - 1.5044 = 0.4756 \text{ atm}$
- $P_{\text{I}_2} = 1.710 - 1.5044 = 0.2056 \text{ atm}$

# Calculations with Equilibrium Constants

- $\text{PCl}_5 (\text{g}) \leftrightarrow \text{PCl}_3 (\text{g}) + \text{Cl}_2 (\text{g})$ 
  - Initial concentrations: 1 L flask, 0.298 mol  $\text{PCl}_3 (\text{g})$ ,  $8.70 \times 10^{-3}$  mol  $\text{PCl}_5 (\text{g})$
  - Final: 1 L flask,  $2.00 \times 10^{-3}$  mol  $\text{Cl}_2 (\text{g})$

What are the  $[\text{PCl}_5]$ ,  $[\text{PCl}_3]$ , and  $K$ ?

	$[\text{PCl}_5]$	$[\text{PCl}_3]$	$[\text{Cl}_2]$
Initial	$8.70 \times 10^{-3} \text{ M}$	0.298 M	0 M
Change	$-x$	$+x$	$2.0 \times 10^{-3} \text{ M}$
Equilibrium	$8.70 \times 10^{-3} \text{ M} - x$	$0.298 \text{ M} + x$	$2.0 \times 10^{-3} \text{ M}$

# Calculations with Equilibrium Constants

	[PCl <sub>5</sub> ]	[PCl <sub>3</sub> ]	[Cl <sub>2</sub> ]
Initial	8.70 x 10 <sup>-3</sup> M	0.298 M	0 M
Change	- x	+ x	2.0 x 10 <sup>-3</sup> M
Equilibrium	8.70 x 10 <sup>-3</sup> M - x	0.298 M + x	2.0 x 10 <sup>-3</sup> M

- Equilibrium concentrations

- [PCl<sub>5</sub>] = 8.70 x 10<sup>-3</sup> M - 2.0 x 10<sup>-3</sup> M = 6.70 x 10<sup>-3</sup> M
- [PCl<sub>3</sub>] = 0.298 M + 2.0 x 10<sup>-3</sup> M = 0.30 M

$$K = \frac{[\text{Cl}_2][\text{PCl}_3]}{[\text{PCl}_5]} = \frac{(2.00 \times 10^{-3})(0.300)}{6.7 \times 10^{-3}} = 8.96 \times 10^{-2}$$

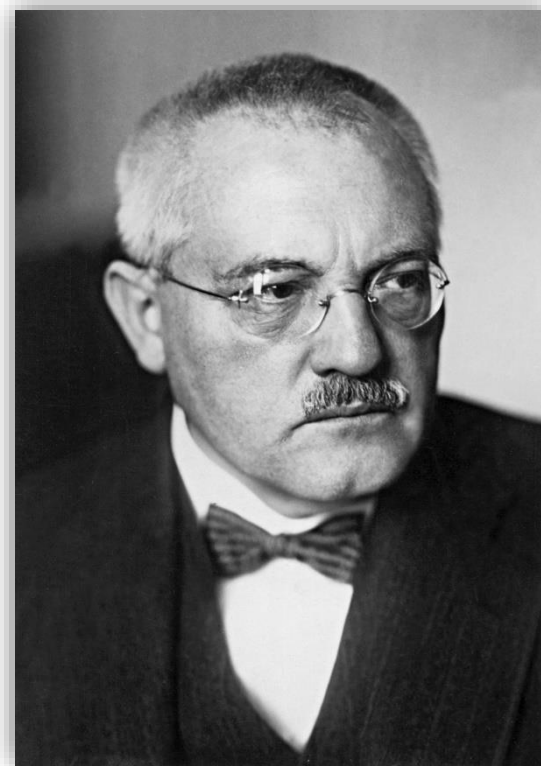


# Topic 5J. The Response of Equilibria to Changes in Conditions

- 5J.1 Adding and Removing Reagents
- 5J.2 Compressing a Reaction Mixture
- 5J.3 Temperature and Equilibrium

# Haber–Bosch Process

- Ammonia synthesis:  $\text{N}_2 (\text{g}) + 3 \text{H}_2 (\text{g}) \leftrightarrow 2 \text{NH}_3 (\text{g})$   
By changing reaction conditions, product yield could be increased.

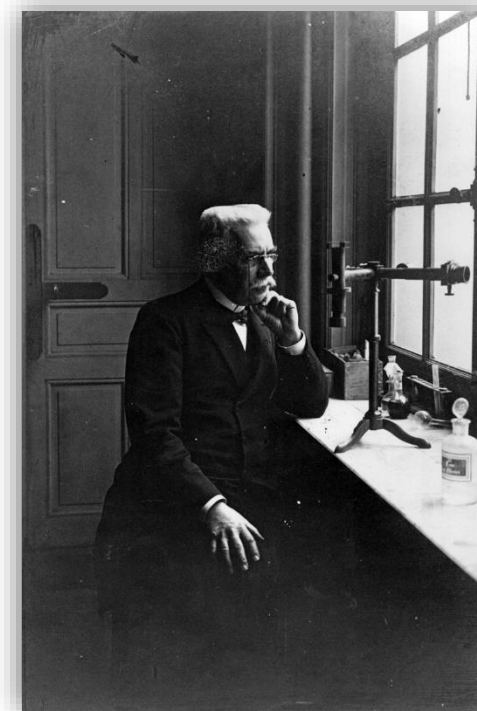


# Le Chatelier's Principle

- **Le Chatelier's principle**

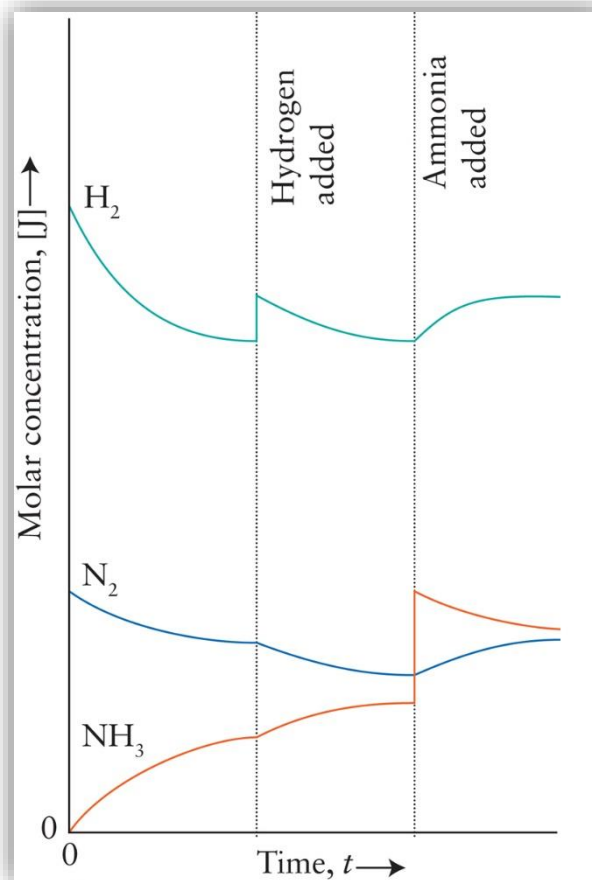
When a stress is applied to a system in dynamic equilibrium, the equilibrium tends to adjust to minimize the effect of the stress.

- Note: this is not a new principle or discovery. Le Chatelier's principle is already contained in the equilibrium expression. Le Chatelier's principle laid a foundation for chemical equilibrium theory, actually.



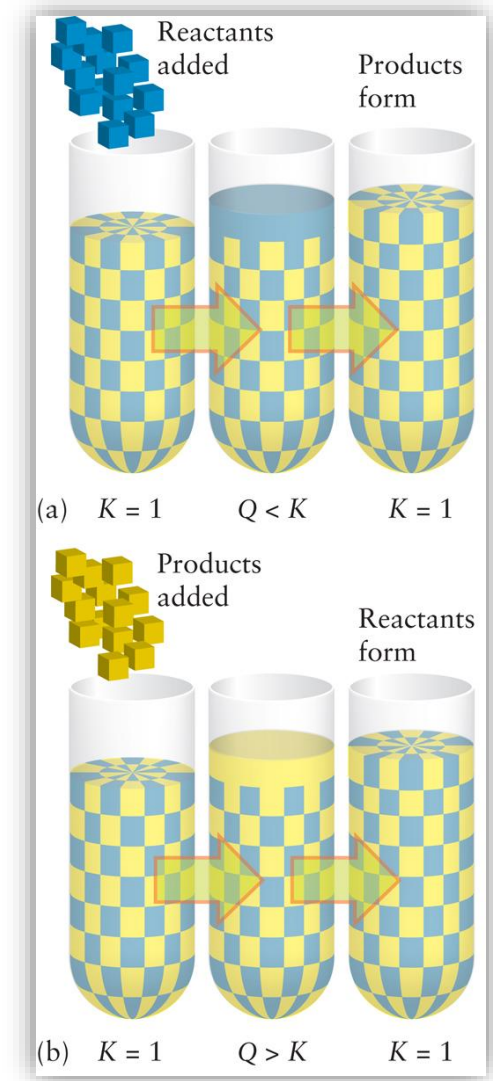
# Adding and Removing Reagents

- Ammonia synthesis:  $\text{N}_2 (\text{g}) + 3 \text{H}_2 (\text{g}) \leftrightarrow 2 \text{NH}_3 (\text{g})$



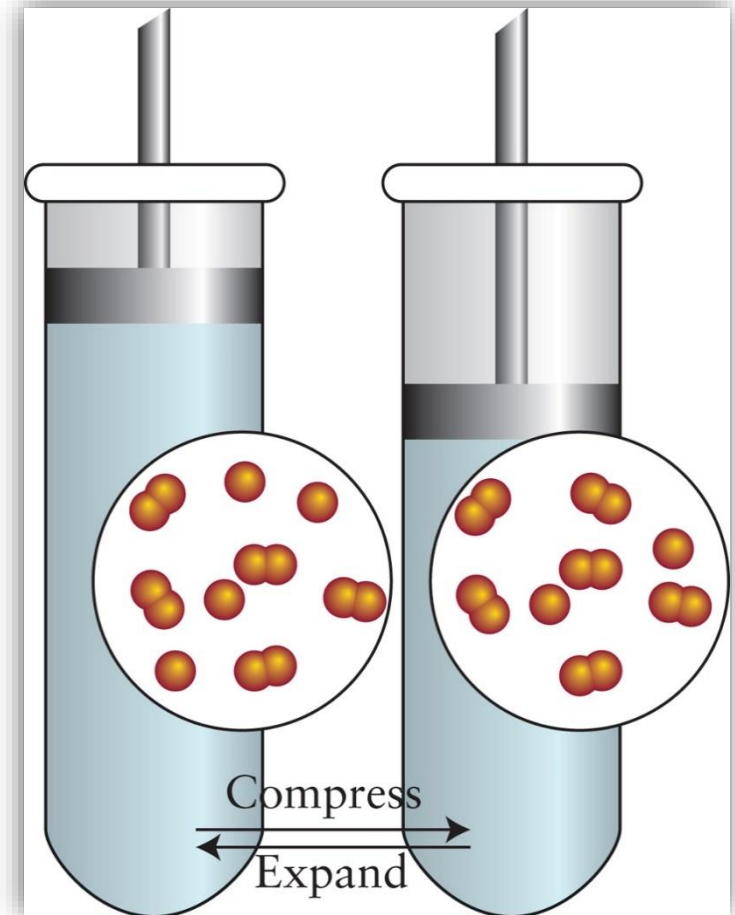
# Adding and Removing Reagents

- When reactants are added to the equilibrium mixture
  - $Q$  temporarily falls below  $K$ ,  $Q < K$ .
  - Forming products and consuming reactants until  $Q = K$  again.
  - When reactants are added to a system at equilibrium, it responds by converting reactants to products.
- When products are added to the equilibrium mixture
  - $Q$  temporarily rises above  $K$ ,  $Q > K$ .
  - Forming reactants and consuming products until  $Q = K$  again.
  - When reactants are added to a system at equilibrium, it responds by converting products to reactants.



# Compressing a Reaction Mixture

- For  $\text{I}_2 (\text{g}) \leftrightarrow 2 \text{I} (\text{g})$ ,
  - The forward reaction increases the number of particles in the container and hence the total pressure of the system.
  - The reverse reaction decreases it.
- When the mixture is compressed
  - The equilibrium composition will tend to shift in favor of the reactant,  $\text{I}_2$ , because that response minimizes the increase in pressure.
- For  $\text{N}_2 (\text{g}) + 3 \text{H}_2 (\text{g}) \leftrightarrow 2 \text{NH}_3 (\text{g})$ 
  - Increasing pressure favors the forward reaction.
  - Hence, ammonia synthesis is carried out under 250 atm.





# Compressing a Reaction Mixture



# Compressing a Reaction Mixture

- Quantitative expression: for  $2 \text{NO}_2 (\text{g}) \leftrightarrow \text{N}_2\text{O}_4 (\text{g})$

Equilibrium constant

$$K = \frac{P_{\text{N}_2\text{O}_4}/P^\circ}{(P_{\text{NO}_2}/P^\circ)^2}$$

If  $P$  is replaced with  $nRT/V$

$$K = \frac{n_{\text{N}_2\text{O}_4}RT/VP^\circ}{(n_{\text{NO}_2}RT/VP^\circ)^2} = \frac{n_{\text{N}_2\text{O}_4}}{(n_{\text{NO}_2})^2} \times \frac{P^\circ}{RT} \times V$$

Since  $K$  is constant at a given temperature, when  $V$  is reduced, the ratio  $n_{\text{N}_2\text{O}_4}/(n_{\text{NO}_2})^2$  must increase.



# Temperature and Equilibrium

- If the temperature is raised
  - For **exothermic** reaction, the **reactants are favored**. ( $K$  decreases)
  - For **endothermic** reaction, the **products are favored**. ( $K$  increases)
- Change in temperature changes the equilibrium constant.  
(Changes in pressure and volume change the equilibrium. However, these won't change the equilibrium constant.)
- Equilibrium constant is a function of temperature.

# Temperature and Equilibrium

- van't Hoff Equation

$$\Delta G_{r,1}^{\circ} = -RT_1 \ln K_1$$

$$\Delta G_{r,2}^{\circ} = -RT_2 \ln K_2$$

$$\ln K_1 = -\frac{\Delta G_{r,1}^{\circ}}{RT_1} \quad \ln K_2 = -\frac{\Delta G_{r,2}^{\circ}}{RT_2}$$

$$\ln K_1 - \ln K_2 = -\frac{1}{R} \left\{ \frac{\Delta G_{r,1}^{\circ}}{T_1} - \frac{\Delta G_{r,2}^{\circ}}{T_2} \right\}$$

$$\Delta G_{r,1}^{\circ} = \Delta H_{r,1}^{\circ} - T_1 \Delta S_{r,1}^{\circ}$$

$$\Delta G_{r,2}^{\circ} = \Delta H_{r,2}^{\circ} - T_2 \Delta S_{r,2}^{\circ}$$

$$\begin{aligned} \ln K_1 - \ln K_2 &= -\frac{1}{R} \times \\ &\quad \left\{ \overbrace{\frac{\Delta H_{r,1}^{\circ} - T_1 \Delta S_{r,1}^{\circ}}{T_1}}^{\Delta G_{r,1}^{\circ}} - \overbrace{\frac{\Delta H_{r,2}^{\circ} - T_2 \Delta S_{r,2}^{\circ}}{T_2}}^{\Delta G_{r,2}^{\circ}} \right\} \\ &= -\frac{1}{R} \left\{ \frac{\Delta H_{r,1}^{\circ}}{T_1} - \frac{\Delta H_{r,2}^{\circ}}{T_2} - \Delta S_{r,1}^{\circ} + \Delta S_{r,2}^{\circ} \right\} \end{aligned}$$

$$\ln K_1 - \ln K_2 = -\frac{\Delta H_r^{\circ}}{R} \left\{ \frac{1}{T_1} - \frac{1}{T_2} \right\}$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H_r^{\circ}}{R} \left\{ \frac{1}{T_1} - \frac{1}{T_2} \right\}$$

# Temperature and Equilibrium

- van't Hoff Equation

$$\ln \frac{K_2}{K_1} = \frac{\Delta H_r^\circ}{R} \left\{ \frac{1}{T_1} - \frac{1}{T_2} \right\}$$

