Topic 5I. Equilibrium Calculations

5I.1 The Extent of Reaction

5I.2 The Direction of Reaction

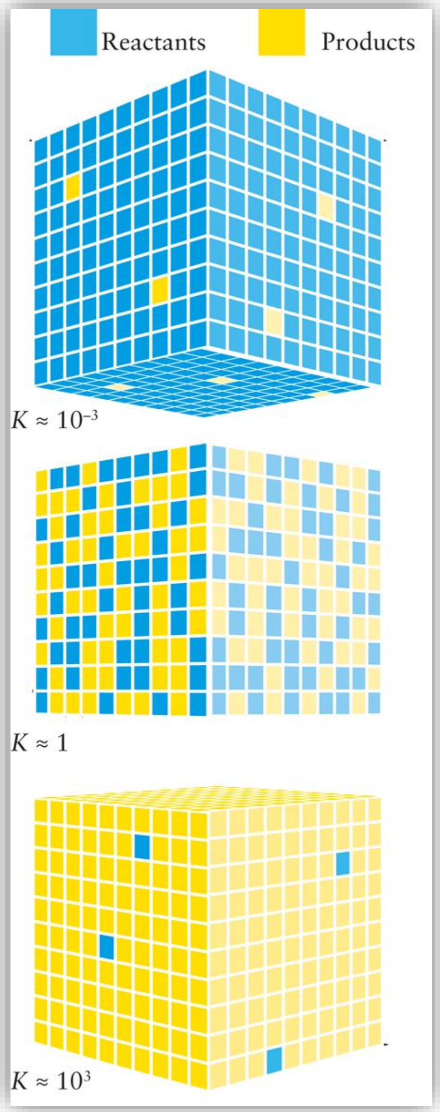
5I.3 Calculations with Equilibrium Constants

The Extent of Reaction

- The extent of reaction vs. *K*

$$\boxed{K = \frac{(a_{\mathrm{C}})^{c}(a_{\mathrm{D}})^{d}}{(a_{\mathrm{A}})^{a}(a_{\mathrm{B}})^{b}}}$$

  - 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.

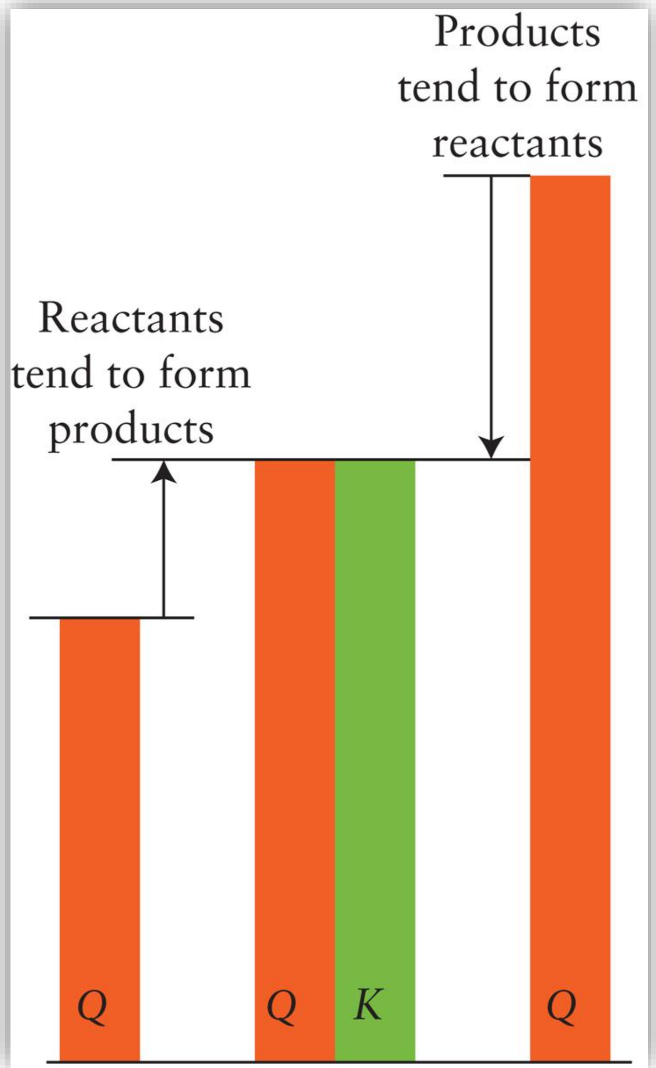

Reactants
Products
$K \approx 10^{-3}$
$K \approx 1$
$K \approx 10^{3}$

The Direction of Reaction

- *Q* vs. *K*

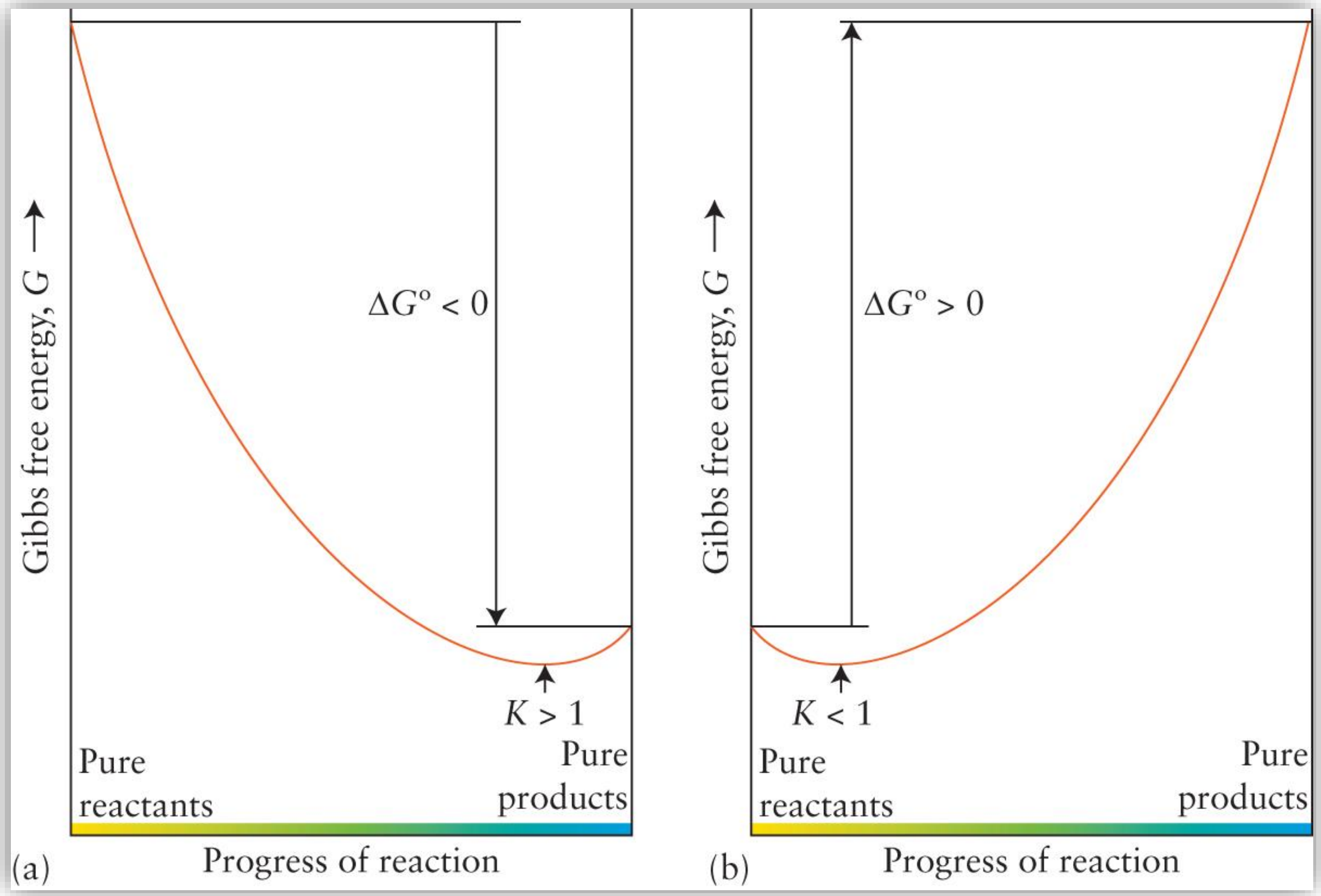
$$\boxed{Q = \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}}$$

- 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.


Products tend to form reactants
Reactants tend to form products
Q
Q
K
Q

The Direction of Reaction

- $\Delta G°$ vs. K



Calculations with Equilibrium Constants

- H_2 (g) + I_2 (g) ↔ 2HI (g) at 600 K
  - Initial concentrations: P_{H2} = 1.98 atm, P_{I2} = 1.71 atm
  - Equilibrium constant: $K_P = P_{HI}^2 / (P_{H2} \times P_{I2}) = 92.6$

What are the equilibrium pressures of the products and reactants?

	H_2	I_2	HI
Initial	1.98	1.71	0
Change	$-x$	$-x$	$2x$
Equilibrium	$1.98 - x$	$1.71 - x$	2

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

Calculations with Equilibrium Constants

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

$$\Big\downarrow$$

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

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

- Equilibrium Pressures
  - P_{H2} = 1.980 – 1.5044 = 0.4756 atm
  - P_{I2} = 1.710 – 1.5044 = 0.2056 atm

Calculations with Equilibrium Constants

- PCl_5 (g) ↔ PCl_3 (g) + Cl_2 (g)
  - Initial concentrations: 1L flask, 0.298 mol PCl_3 (g), 8.70×10^{-3} mol PCl_5 (g)
  - Final: 1 L flask, 2.00×10^{-3} mol Cl_2(g)

What are the $[PCl_5]$, $[PCl_3]$, and *K*?

	$[PCl_5]$	$[PCl_3]$	$[Cl_2]$
Initial	8.70×10^{-3} M	0.298 M	0 M
Change	$-x$	$-x$	2.0×10^{-3} M
Equilibrium	8.70×10^{-3} M $-x$	0.298 M $+x$	2.0×10^{-3} M

Calculations with Equilibrium Constants

	$[PCl_5]$	$[PCl_3]$	$[Cl_2]$
Initial	8.70×10^{-3} M	0.298 M	0 M
Change	$-x$	$-x$	2.0×10^{-3} M
Equilibrium	8.70×10^{-3} M $- x$	0.298 M $+ x$	2.0×10^{-3} M

- Equilibrium concentrations
  - $[PCl_5] = 8.70 \times 10^{-3}\ \text{M} - 2.0 \times 10^{-3}\ \text{M} = 6.70 \times 10^{-3}\ \text{M}$
  - $[PCl_3] = 0.298\ \text{M} \qquad + 2.0 \times 10^{-3}\ \text{M} = 3.00\ \text{M}$

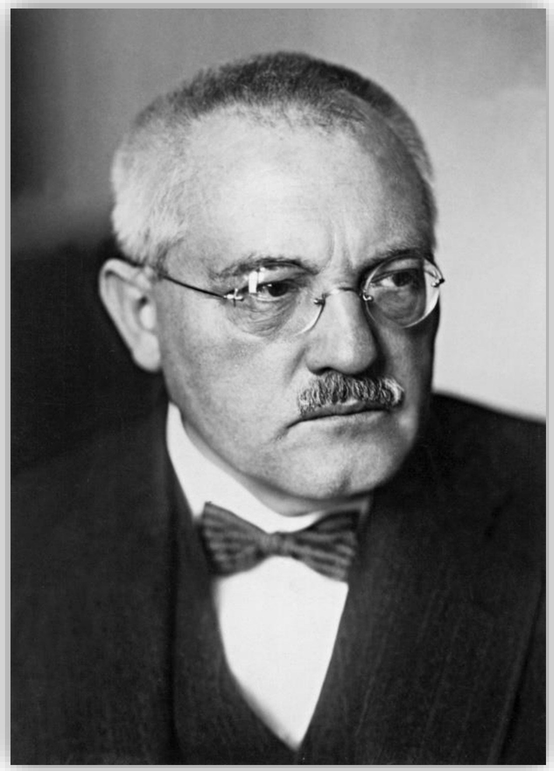
$$K = \frac{[Cl_2][PCl_3]}{[PCl_5]} = \frac{(2.00 \times 10^{-3})(0.300)}{6.7 \times 10^{-3}} = 8.96 \times 10^{-2}$$

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

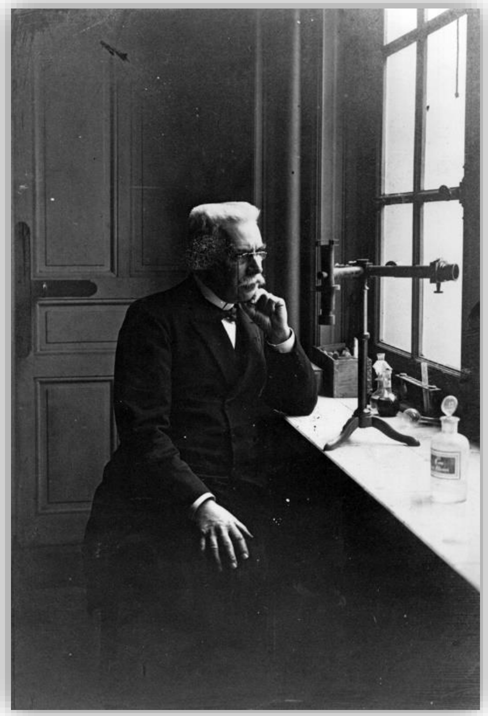
Haber–Bosch Process

- Ammonia synthesis: N_2 (g) + 3 H_2 (g) ↔ 2 NH_3 (g)
  By changing reaction conditions, product yield could be increased.



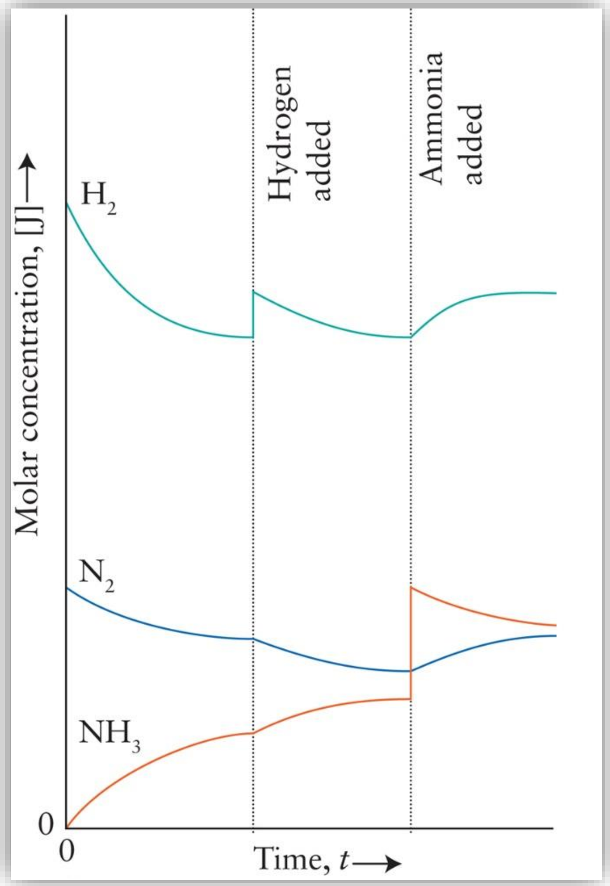
Le Chatelier's Principle

- 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

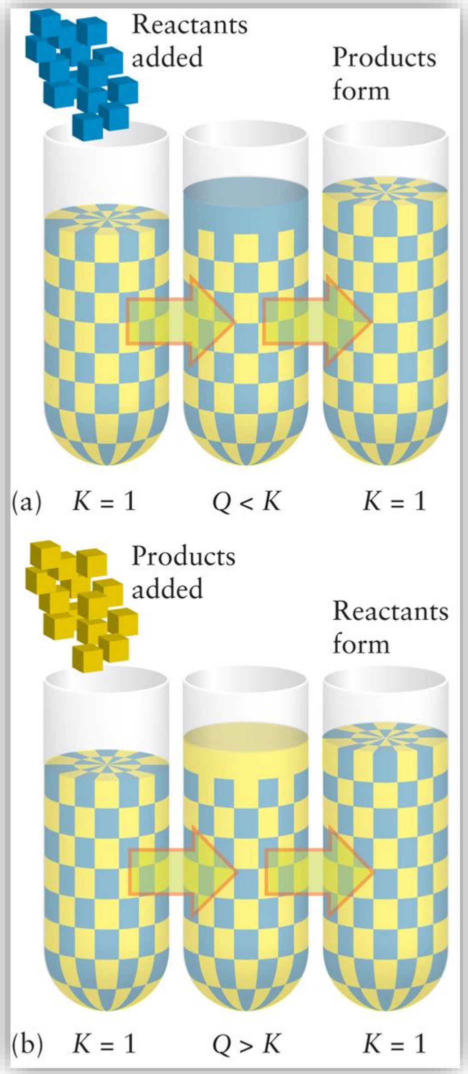
- Ammonia synthesis: N_2 (g) + 3 H_2 (g) ↔ 2 NH_3 (g)



Adding and Removing Reagents

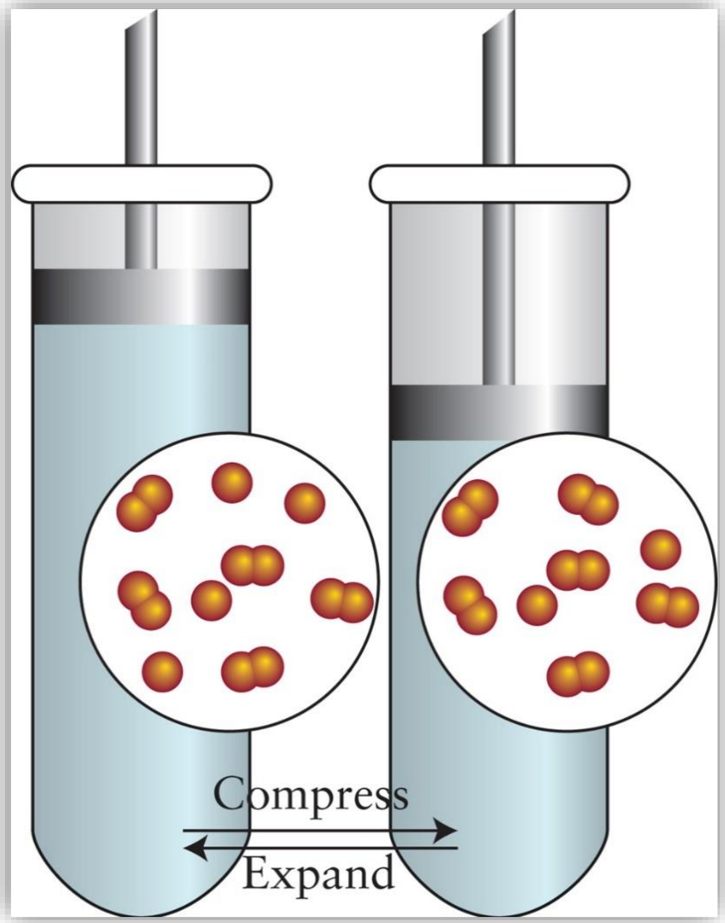
- When reactants are added to the equilibrium mixture
  - Q temporarily falls below K, $Q < K$.
  - Forming products and consuming reactants until $Q = K$ again.
  - When reactants are added to a system at equilibrium, it responds by converting reactants to products.

- 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 reactants to products.


Reactants added
Products form
(a) $K = 1$
$Q < K$
$K = 1$
Products added
Reactants form
(b) $K = 1$
$Q > K$
$K = 1$

Compressing a Reaction Mixture

- For I_2 (g) ↔ 2 I (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, I_2, because that response minimizes the increase in pressure.
- For N_2 (g) + 3 H_2 (g) ↔ 2 NH_3 (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 NO_2 (g) ↔ N_2O_4 (g)

  Equilibrium constant

$$K = \frac{P_{N_2O_4}/P^\circ}{(P_{NO_2}/P^\circ)^2}$$

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

$$K = \frac{n_{N_2O_4}RT/VP^\circ}{(n_{NO_2}RT/VP^\circ)^2} = \frac{n_{N_2O_4}}{(n_{NO_2})^2} \times \frac{P^\circ}{RT} \times V$$

Since *K* is constant at a given temperature, when *V* is reduced, the ratio $n_{N2O4}/(n_{NO2})^2$ 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

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

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

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

$$\Delta G_{r,1}{}^\circ = \Delta H_{r,1}{}^\circ - T_1\Delta S_{r,1}{}^\circ$$
$$\Delta G_{r,2}{}^\circ = \Delta H_{r,2}{}^\circ - T_2\Delta S_{r,2}{}^\circ$$

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

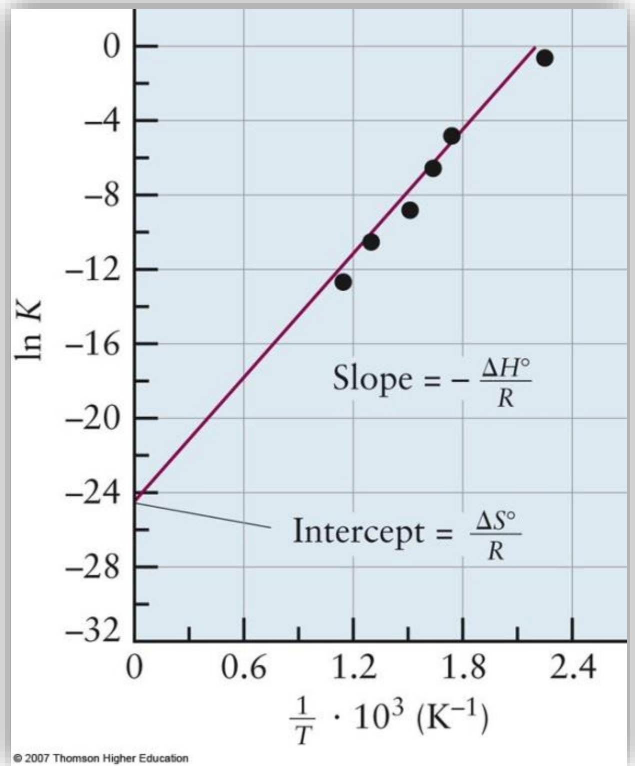
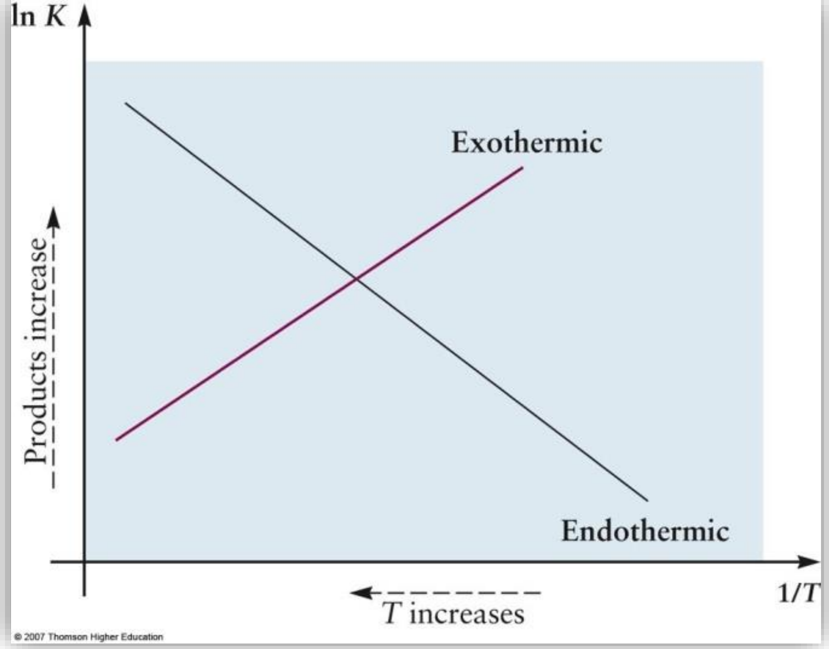
$$\ln K_1 - \ln K_2 = -\frac{\Delta H_r{}^\circ}{R}\left\{\frac{1}{T_1} - \frac{1}{T_2}\right\}$$

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

Temperature and Equilibrium

- van’t Hoff Equation

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


0
−4
−8
−12
−16
−20
−24
−28
−32
ln K
Slope = $-\frac{\Delta H^\circ}{R}$
Intercept = $\frac{\Delta S^\circ}{R}$
0
0.6
1.2
1.8
2.4
$\frac{1}{T}\cdot 10^3\ (\mathrm{K}^{-1})$
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