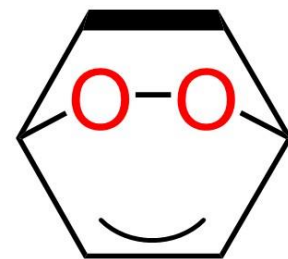# CHEM103
General Chemistry

Chapter 15: Chemical Equilibrium

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SUSTech

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Homeworks 13 & 14

Homework 13
Due date: 28th Nov. (Mon)

Homework 14
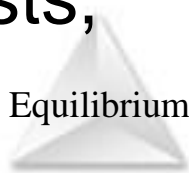### Due date: 5th Dec. (Mon)

Equilibrium

Review on Chapter 14

Rate (average/instantaneous/initial rate), rate law, rate constant, reaction order, half-life

Collision model, activation energy (barrier), transition state (activated complex), reaction coordinate diagrams, Arrhenius equation

Reaction mechanism: elementary process, intermediate, molecularity (unimolecular, bimolecular, termolecular), rate-determining step
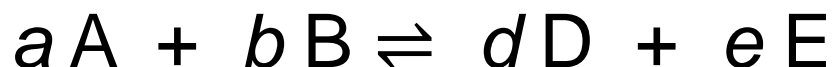
Catalyst: homogeneous/heterogeneous catalysts, enzymes

Equilibrium

Outline of Chapter 15

Equilibrium constant (*K*),
Homogeneous equilibria, Heterogeneous equilibria

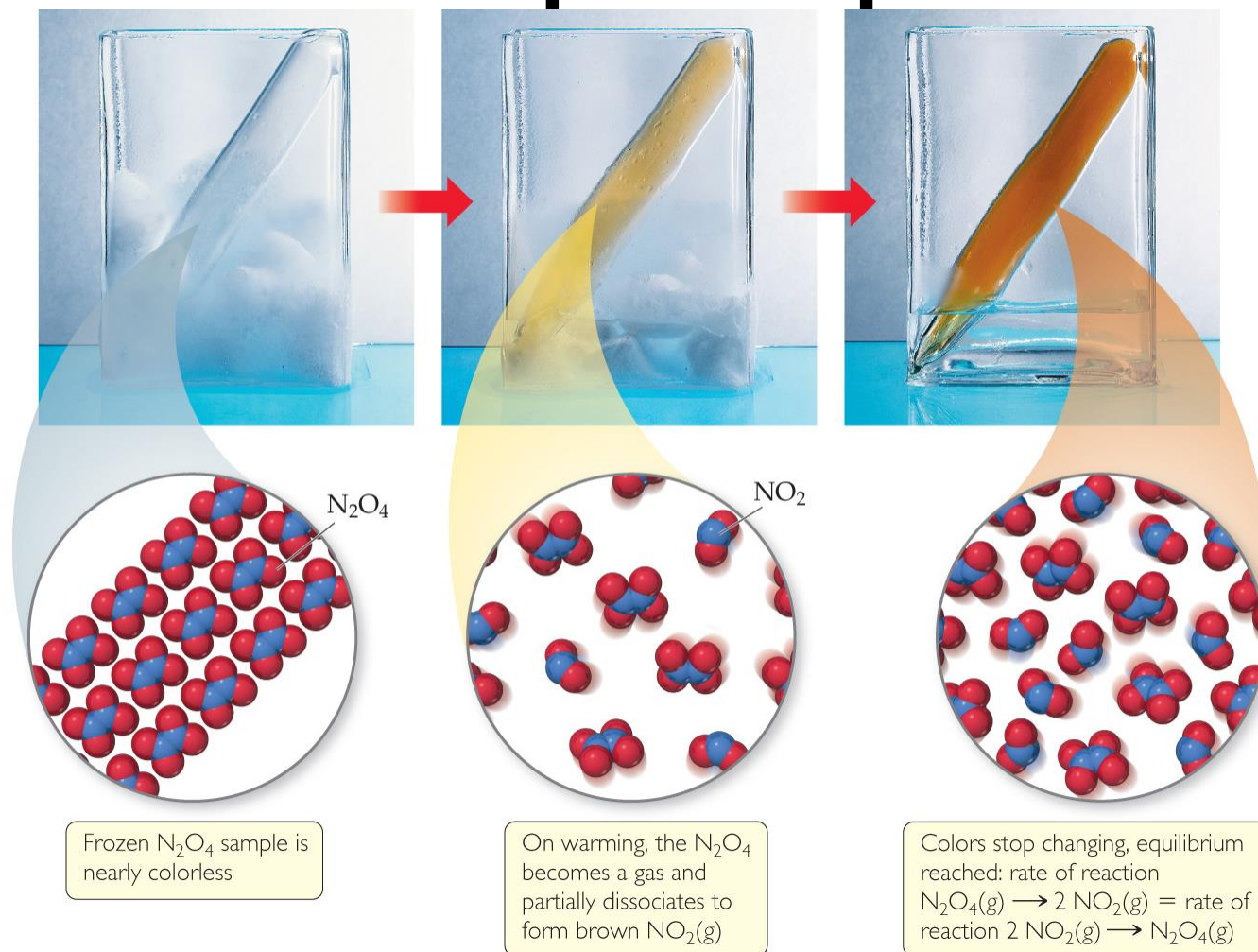$$a\,A\ +\ b\,B \rightleftharpoons\ d\,D\ +\ e\,E$$

$$K_c = \frac{[D]^d [E]^e}{[A]^a [B]^b}$$

Reaction quotient (*Q*)

Le Châtelier's Principle (勒夏特列原理)

Equilibrium

The Concept of Equilibrium

N₂O₄

NO₂

Frozen N_2O_4 sample is nearly colorless

On warming, the N_2O_4 becomes a gas and partially dissociates to form brown $NO_2(g)$

Colors stop changing, equilibrium reached: rate of reaction $N_2O_4(g) \longrightarrow 2\ NO_2(g)$ = rate of reaction $2\ NO_2(g) \longrightarrow N_2O_4(g)$

• **Chemical equilibrium** occurs when a **forward reaction & its reverse reaction** proceed at the **same rate**. Equilibrium is finally reached in the right picture.

Equilibrium

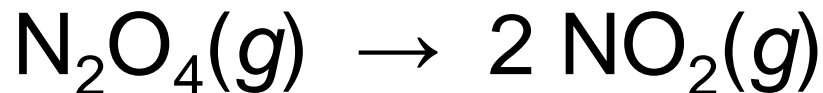$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
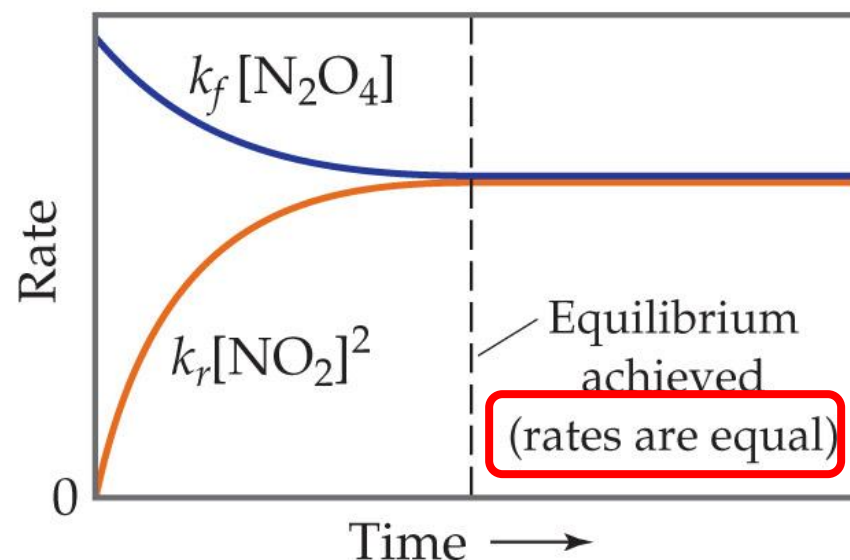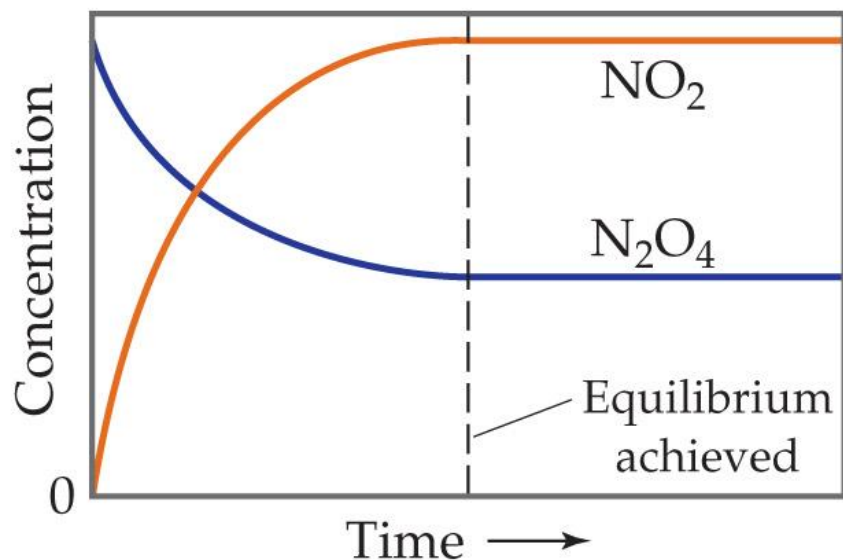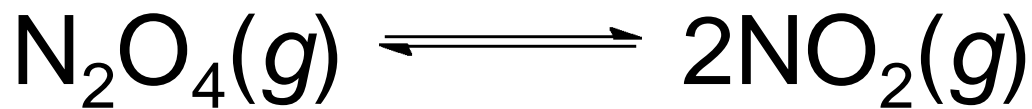
- As a system approaches equilibrium:

1. both the **forward & reverse reactions** are occurring at the **same rate**.

2. the **amount/concentration** of each **reactant** & **product** **remains** **constant**.

3. We write its equation with **a double arrow**.

Equilibrium

Comparing Rates

- For the forward reaction:

$$N_2O_4(g) \rightarrow 2\,NO_2(g)$$

- The rate law is:

$$Rate_f = k_f*[N_2O_4]$$

- For the reverse reaction:

$$2\,NO_2(g) \rightarrow N_2O_4(g)$$
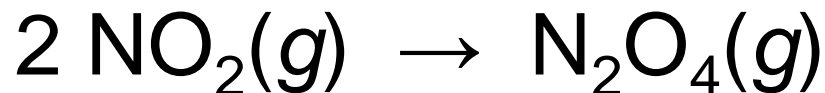
- The rate law is:

$$Rate_r = k_r*[NO_2]^2$$

Equilibrium

Equilibrium Constant

- At equilibrium:

$$\text{Rate}_f = \text{Rate}_r$$

$$k_f[\text{N}_2\text{O}_4] = k_r[\text{NO}_2]^2$$
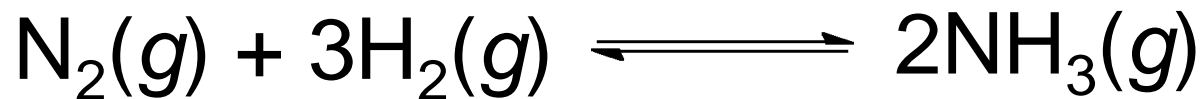
- Rewriting this, it becomes:

$$K_{eq} = \frac{k_f}{k_r} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

- A ratio of concentration terms equals the **equilibrium constant** (**K_{eq}**) at **that temperature** (a temperature-dependent thermochemical property).

Equilibrium

Another Example: The Haber Process

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

- The equilibrium constant depends on **stoichiometry**:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$
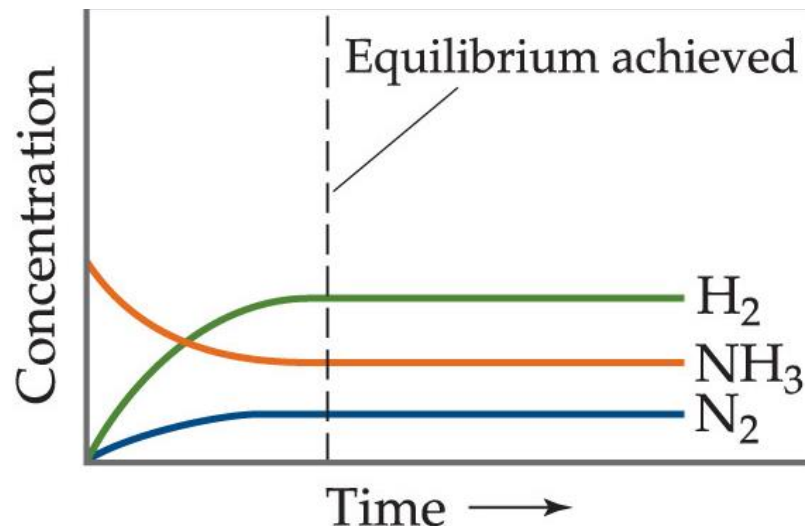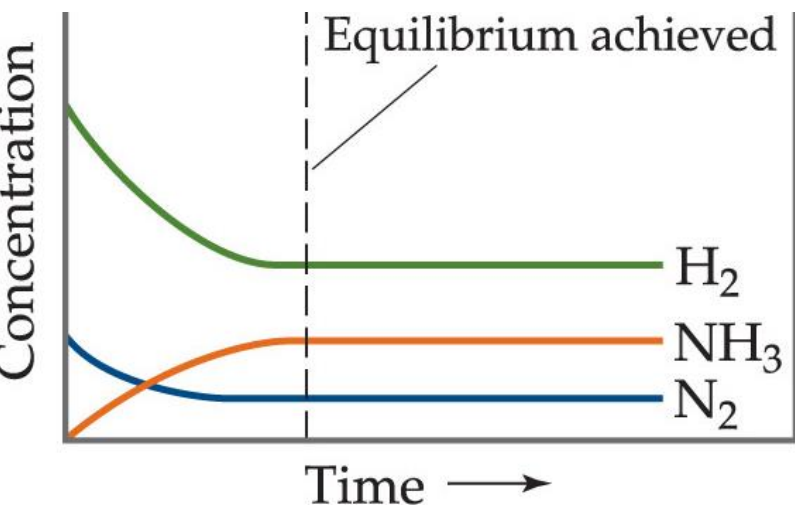
- Regardless which direction it starts, we can have the *same proportions* of all three substances at equilibrium.

Equilibrium

The Equilibrium Constant

- Consider the generalized reaction

$$a\,A\ +\ b\,B \rightleftharpoons\ d\,D\ +\ e\,E$$
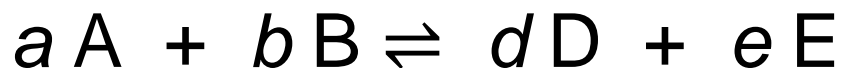
- The equilibrium expression for this reaction:

$$K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b} \quad \longleftarrow \text{ products} \atop \longleftarrow \text{ reactants}$$

- K depends **only on the stoichiometry** of the **overall reaction**, **not its mechanism** (different from rate law).

- As pressure is proportional to concentration for gases in a **closed** system, the equilibrium expression can also be written:

$$K_p = \frac{(P_D)^d(P_E)^e}{(P_A)^a(P_B)^b}$$

Equilibrium

Relationship between K_c and K_p

- For gases (the ideal gas Law):
$$PV = nRT$$

- Rearranging,
$$P = (n/V)RT$$

As (n/V) is equal to concentration, thus :

$$K_p = K_c (RT)^{\Delta n}$$

where

$$\Delta n = (\text{moles of gaseous product}) - (\text{moles of gaseous reactant})$$

Equilibrium

Table 15.1 Initial and Equilibrium Concentrations of $N_2O_4(g)$ and $NO_2(g)$ at 100 °C

Experiment	Initial $[N_2O_4]$ (M)	Initial $[NO_2]$ (M)	Equilibrium $[N_2O_4]$ (M)	Equilibrium $[NO_2]$ (M)	K_c
1	0.0	0.0200	0.00140	0.0172	0.211
2	0.0	0.0300	0.00280	0.0243	0.211
3	0.0	0.0400	0.00452	0.0310	0.213
4	0.0200	0.0	0.00452	0.0310	0.213

• The **ratio** of $[NO_2]^2$ to $[N_2O_4]$ (➡ K_c) **remains constant** at this temperature *no matter what the initial concentrations* of NO_2 and N_2O_4 are.
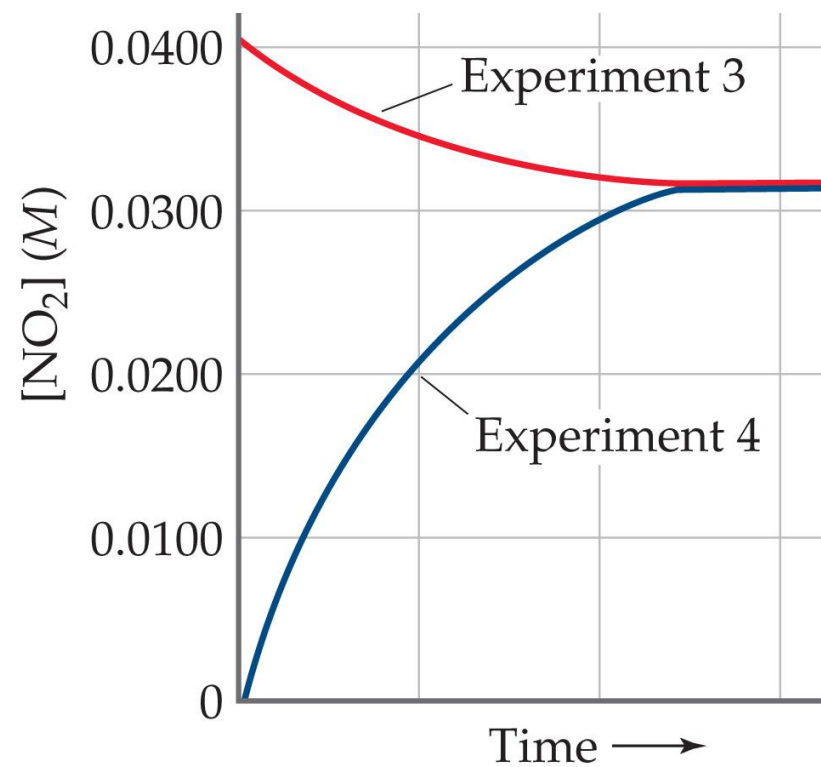
Direction of the Chemical Equation & *K*

• The equilibrium constant of a reaction in the **reverse reaction** is the **reciprocal** of the equilibrium constant of the **forward** reaction: $K_c = 1/K_{c*}$

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212 \text{ at } 100\,°C$$

$$2\,NO_2(g) \rightleftharpoons N_2O_4(g)$$
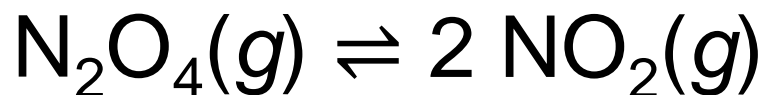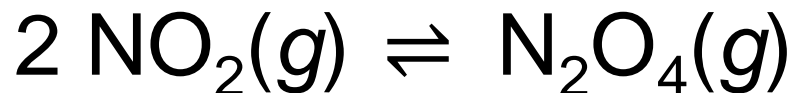
$$K_{c*} = \frac{[N_2O_4]}{[NO_2]^2} = 4.72 \text{ at } 100\,°C$$

Equilibrium

Stoichiometry & Equilibrium Constants

• When the equation is multiplied by a number (e.g. 2 in the below example), we simply raise the original equilibrium constant to that power. As the **stoichiometry** is **doubled**; the **constant** is the **squared**! *We should always write the balanced chemical reaction!*

$$N_2O_4(g) \rightleftharpoons 2\, NO_2(g)$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212 \text{ at } 100\ ^\circ C$$

$$\textbf{2}\, N_2O_4(g) \rightleftharpoons \textbf{4}\, NO_2(g)$$
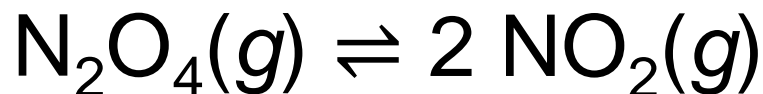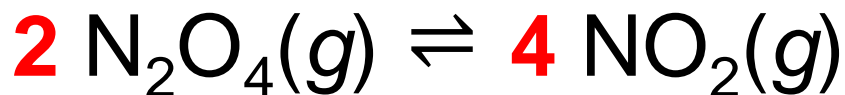
$$K_c = \frac{[NO_2]^{\textbf{4}}}{[N_2O_4]^{\textbf{2}}} = (0.212)^{\textbf{2}} \text{ at } 100\ ^\circ C$$

Equilibrium

Consecutive Equilibria

• When two or more **consecutive equilibria** occur, the equations can be **combined** to give a single equilibrium.

• The equilibrium constant of the **overall reaction** is the **product** of the constants of the **two reactions/steps** (K_{c1} & K_{c2}):

$$K_c = K_{c1} \times K_{c2}$$

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \overset{k_2}{\rightarrow} C$$

Equilibrium

$$2\,NOBr(g) \rightleftharpoons 2\,NO(g) + Br_2(g) \quad K_c = \frac{[NO]^2[Br_2]}{[NOBr]^2} = 0.014$$

$$Br_2(g) + Cl_2(g) \rightleftharpoons 2\,BrCl(g) \quad K_c = \frac{[BrCl]^2}{[Br_2][Cl_2]} = 7.2$$

$$2\,NOBr(g) + Cl_2(g) \rightleftharpoons 2\,NO(g) + 2\,BrCl(g)$$
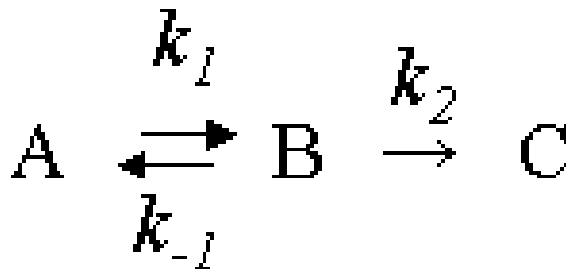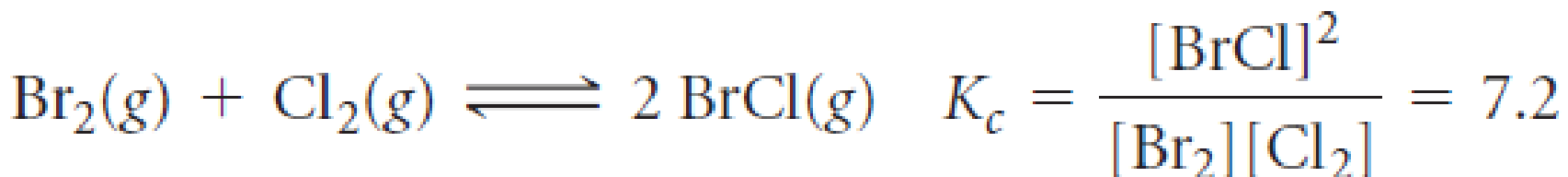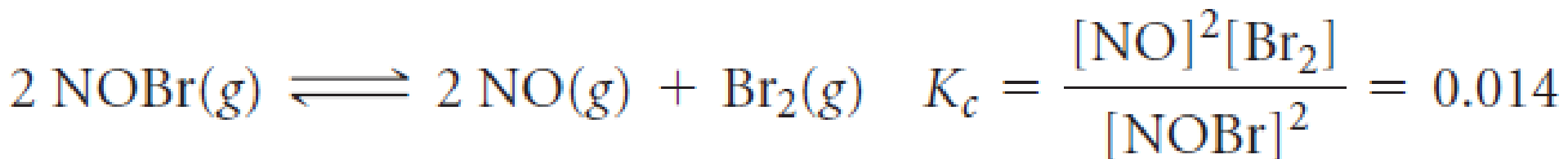
$$K_c = \frac{[NO]^2[BrCl]^2}{[NOBr]^2[Cl_2]} = \frac{[NO]^2[Br_2]}{[NOBr]^2} \times \frac{[BrCl]^2}{[Br_2][Cl_2]}$$

$$K_{c3} = (K_{c1})(K_{c2}) = (0.014)(7.2) = 0.10$$

ibrium

To summarize:

1. The equilibrium constant of a reaction in the *reverse* direction is the *inverse* (or *reciprocal*) of the equilibrium constant of the reaction in the forward direction:

$$A + B \rightleftharpoons C + D \quad K_1$$

$$C + D \rightleftharpoons A + B \quad K = 1/K_1$$
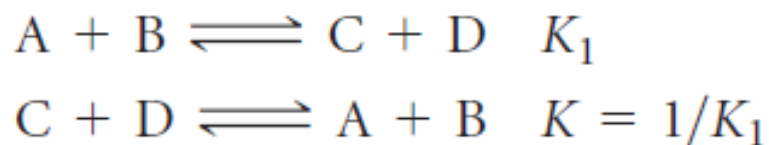
2. The equilibrium constant of a reaction that has been *multiplied* by a number is equal to the original equilibrium constant raised to a *power* equal to that number.

$$A + B \rightleftharpoons C + D \quad K_1$$

$$nA + nB \rightleftharpoons nC + nD \quad K = K_1{}^{n}$$
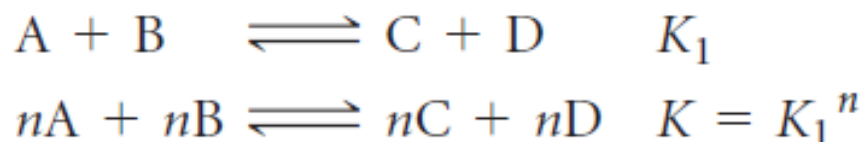
3. The equilibrium constant for a net reaction made up of *two or more reactions* is the *product* of the equilibrium constants for the individual reactions:

1. $A + B \rightleftharpoons C + D \quad K_1$
2. $C + F \rightleftharpoons G + A \quad K_2$
---
3. $B + F \rightleftharpoons D + G \quad K_3 = (K_1)(K_2)$
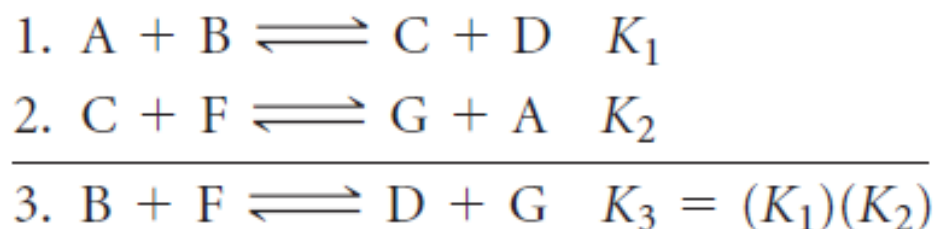
Equilibrium

Equilibrium Constants and Units

• Equilibrium constants are reported **without units**.

• Equilibrium constants derived from thermodynamic measurements are defined in terms of *activities* (*a;* 活度) rather than concentrations or partial pressures.

$$K = \left(\prod_{J} a_J^{v_J} \right)$$

• molalities, by replacing a_J by $b_J/b^{\ominus}$, where $b^{\ominus} = 1 \text{ mol kg}^{-1}$
• molar concentrations, by replacing a_J by $[J]/c^{\ominus}$, where $c^{\ominus} = 1 \text{ mol dm}^{-3}$
• partial pressures, by replacing a_I by $p_I/p^{\ominus}$, where $p^{\ominus} = 1 \text{ bar}$

• The *activity* of any substance in an ideal mixture is the **ratio** of the **concentration** or **pressure** of the substance to a **reference concentration or pressure** (1 M or 1 atm). Therefore, activities have **no unit**.

• If the concentration of a substance in an equilibrium mixture is 0.01*M*, its activity is 0.01*M*/1*M* = 0.01.

Homogeneous vs. Heterogeneous

• **Homogeneous equilibria** occur when all reactants and products are in the **same phase**.

• **Heterogeneous equilibria** occur when something in the equilibrium is in a **different phase**.

• The *activity value* used for a **pure solid or liquid** is always **1**.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

$$K_c = [Pb^{2+}]*[Cl^-]^2$$
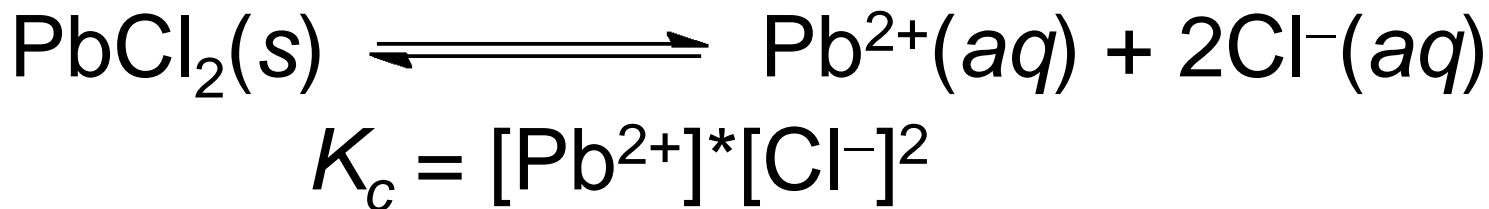
Equilibrium

The Decomposition of $CaCO_3$: A Heterogeneous Equilibrium

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

- $K_c = [CO_2]$
- $K_p = P_{CO_2}$

- The amount of CO_2 above the solid remain the same.

$CO_2(g)$

$CaCO_3$ CaO
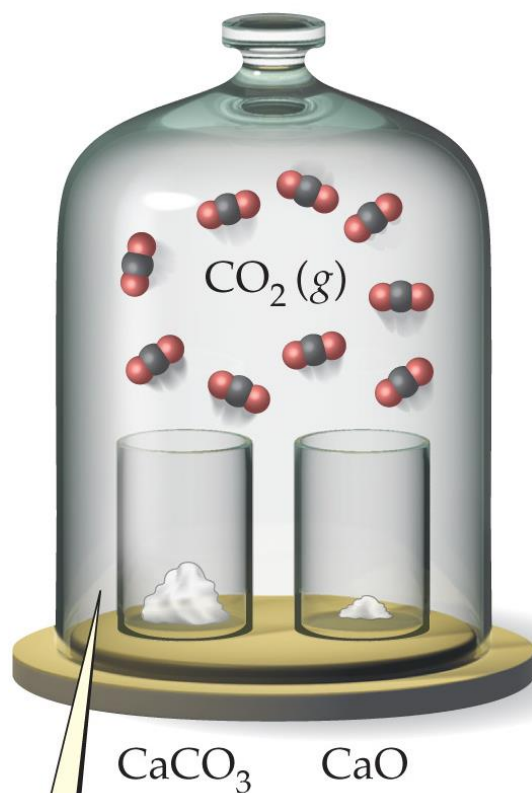
Large amount of $CaCO_3$, small amount of CaO, gas pressure P

$CO_2(g)$

$CaCO_3$ CaO
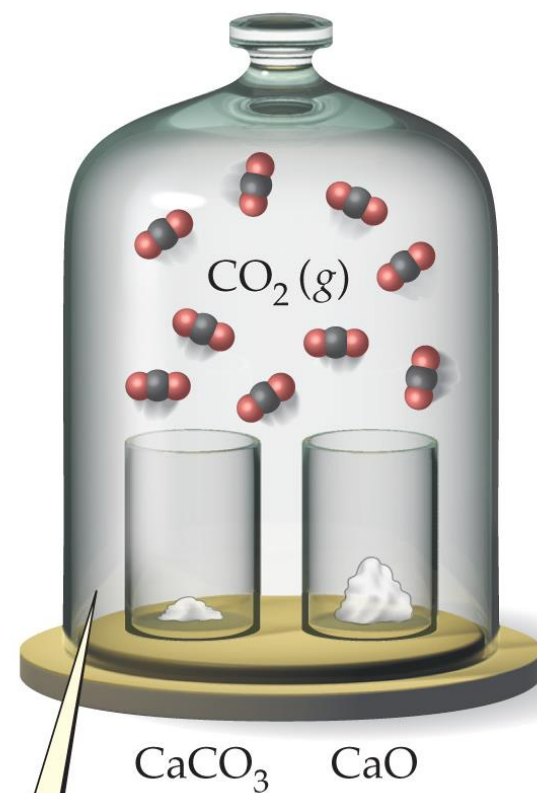
Small amount of $CaCO_3$, large amount of CaO, gas pressure still P

Magnitude of *K*

Reactants $\rightleftharpoons$ Products

$K \gg 1$, equilibrium "lies to the right"
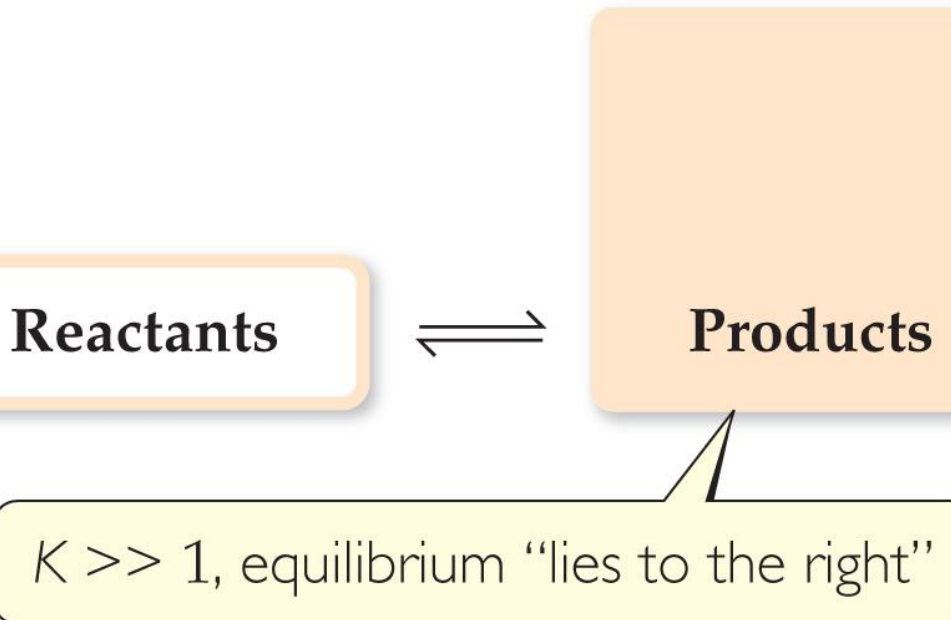
$$K_c = \frac{[\text{D}]^d[\text{E}]^e}{[\text{A}]^a[\text{B}]^b} \quad \begin{array}{l}\longleftarrow \text{ products} \\ \longleftarrow \text{ reactants}\end{array}$$

- If **K>>1**, the reaction favors products; **products predominate** at equilibrium.

Reactants $\rightleftharpoons$ Products

$K \ll 1$, equilibrium "lies to the left"
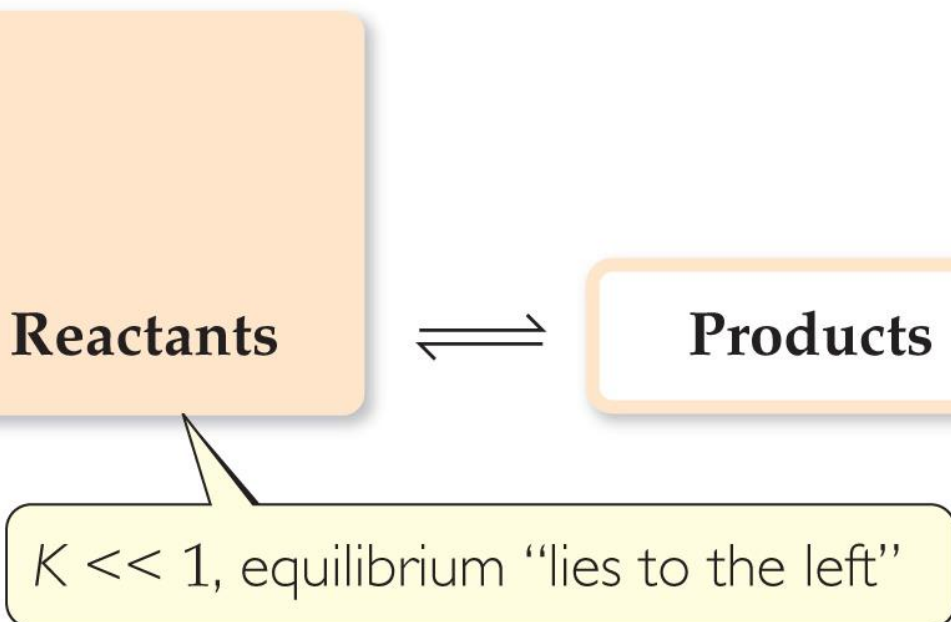
- If **K<<1**, the reaction favors reactants; **reactants predominate** at equilibrium.

Equilibrium

Calculating Equilibrium Constant

1) If any initial and equilibrium concentrations are known, **calculate the change**.

2) Use the **balanced equation and initial concentrations** to find *change/equilibrium concentration for all reactants and products*.

3) Calculate the equilibrium constant using the **equilibrium concentrations**.

Equilibrium

An Example

A closed system initially containing 1.000×10^{-3} M H_2 and 2.000×10^{-3} M I_2 at 448 °C is allowed to reach equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is 1.87×10^{-3} M. Calculate K_c at 448 °C for the reaction.
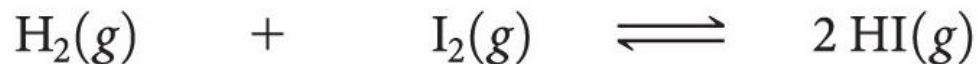
$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$
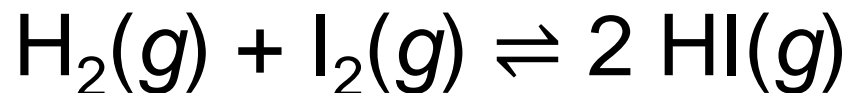
	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2\,HI(g)$
Initial concentration (M)	1.000×10^{-3}	2.000×10^{-3}	0
Change in concentration (M)			
Equilibrium concentration (M)			1.87×10^{-3}

(If any initial and equilibrium concentrations are known, calculate the change.)

Equilibrium
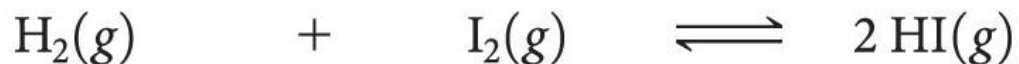
	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2\,HI(g)$
Initial concentration (M)	1.000×10^{-3}		2.000×10^{-3}		0
Change in concentration (M)					$+1.87 \times 10^{-3}$
Equilibrium concentration (M)					1.87×10^{-3}

- The change in concentration of HI is 1.87×10^{-3} *M*.

Initial concentration (M)	1.000×10^{-3}	2.000×10^{-3}	0
Change in concentration (M)	-0.935×10^{-3}	-0.935×10^{-3}	$+1.87 \times 10^{-3}$
Equilibrium concentration (M)			1.87×10^{-3}

- Stoichiometry tells us $[H_2]$ and $[I_2]$ decrease by half.

(Use the balanced equation and initial concentrations to find change/equilibrium concentration for all reactants and products.)
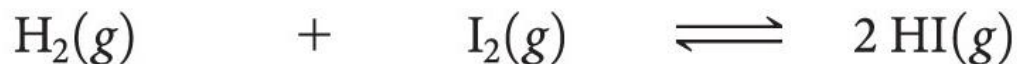
	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2\,HI(g)$
Initial concentration (M)	1.000×10^{-3}		2.000×10^{-3}		0
Change in concentration (M)	-0.935×10^{-3}		-0.935×10^{-3}		$+1.87 \times 10^{-3}$
Equilibrium concentration (M)	0.065×10^{-3}		1.065×10^{-3}		1.87×10^{-3}

- We can now calculate the equilibrium concentrations of H_2 & I_2 compounds.
- The equilibrium constant becomes:

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]}$$

$$= \frac{(1.87 \times 10^{-3})^2}{(6.5 \times 10^{-5})(1.065 \times 10^{-3})}$$

$$= 51$$

(Calculate the equilibrium constant using the equilibrium concentrations.)

Equilibrium

Is a Mixture in Equilibrium? Which Way Does the Reaction Go?

- We need to calculate the **reaction quotient**, *Q*.
- **Q** looks like the equilibrium constant (*K*), but the values used to calculate it are the **current** conditions, not necessarily those for equilibrium.
- To calculate Q, one substitutes the **initial (or current)** concentrations of reactants and products into the equilibrium expression.

$$a\,A + b\,B \rightleftharpoons d\,D + e\,E$$

$$Q_c = \frac{[D]^d [E]^e}{[A]^a [B]^b}$$

Equilibrium

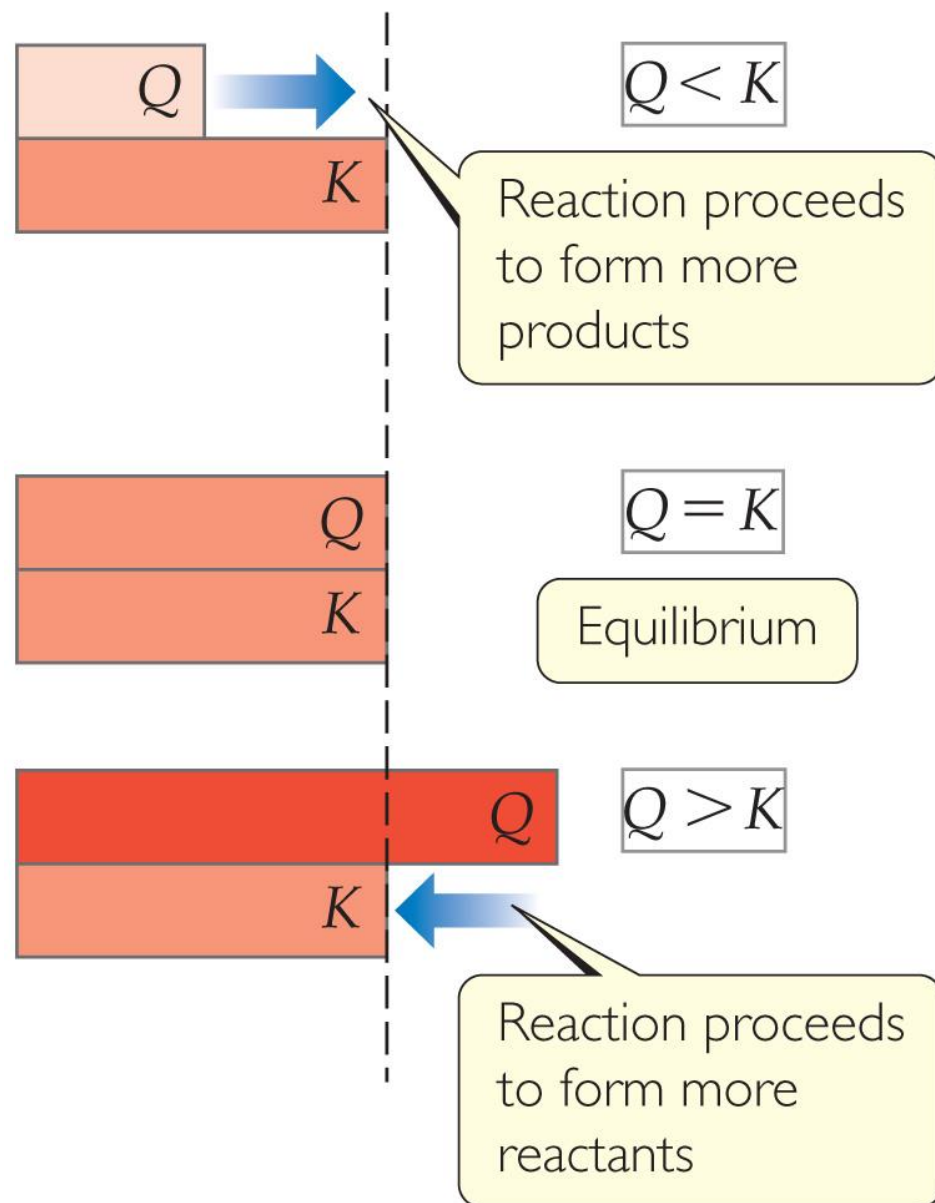# Comparing *Q* and *K*

- If **$Q < K$**, nature will make the reaction **proceed to products**.

- If **$Q = K$**, the reaction is **in equilibrium**.

- If **$Q > K$**, nature will make the reaction **proceed to reactants**.

At equilibrium

$Q < K$

Reaction proceeds to form more products

$Q = K$

Equilibrium

$Q > K$

Reaction proceeds to form more reactants

Calculating Equilibrium Concentrations

• If we know the equilibrium constant, we can *deduce equilibrium concentrations* from the known initial concentrations and changes (based on stoichiometry).

A 1.000 L flask is filled with 1.000 mol of $H_2(g)$ and 2.000 mol of $I_2(g)$ at 448 °C. Given a K_c of 50.5, what are the equilibrium concentrations of H_2, I_2, and HI?

• Set up a below table & set the "change in concentration" row to be a factor of **"x"** based on the stoichiometry.

	$H_2(g)$	$+$	$I_2(g)$	$\rightleftharpoons$	$2\,HI(g)$
Initial concentration (M)	1.000		2.000		0
Change in concentration (M)	$-x$		$-x$		$+2x$
Equilibrium concentration (M)					

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2\,HI(g)$
Initial concentration (M)	1.000	2.000	0
Change in concentration (M)	$-x$	$-x$	$+2x$
Equilibrium concentration (M)	$1.000 - x$	$2.000 - x$	$2x$

• The equilibrium concentration = the initial concentration minus the "change in concentration".

• Set up the equilibrium constant expression:

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

Equilibrium

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2\,HI(g)$
Initial concentration (M)	1.000		2.000		0
Change in concentration (M)	$-x$		$-x$		$+2x$
Equilibrium concentration (M)	$1.000 - x$		$2.000 - x$		$2x$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 50.5$$

• Solving the above equation by using the quadratic formula, we get *x* = 2.323 *or* 0.935.

• However, x *must* be 0.935.

• So $[H_2]_{eq}$ = 1.000 – 0.935 = 0.065 *M;*
$[I_2]_{eq}$ = 2.000 – 0.935 = 1.065 *M;*
$[HI]_{eq}$ = 2(0.935) = 1.87 *M*

Equilibrium

Le Châtelier's Principle (勒夏特列原理)

*"If a system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of one of the components, **the system will shift its equilibrium** position so as to **counteract the effect of the disturbance**."*

Henri-Louis Le Châtelier (1850–1936)

Equilibrium

If a system at equilibrium is disturbed by a change in **concentration, pressure,** or **temperature,** the system will shift its equilibrium position so as to counter the effect of the disturbance.

Concentration: adding or removing a reactant or product

If a substance is added to a system at equilibrium, the system reacts to consume some of the substance. If a substance is removed from a system, the system reacts to produce more of substance.

Initial equilibrium   Substance added   Equilibrium reestablished

Substances react
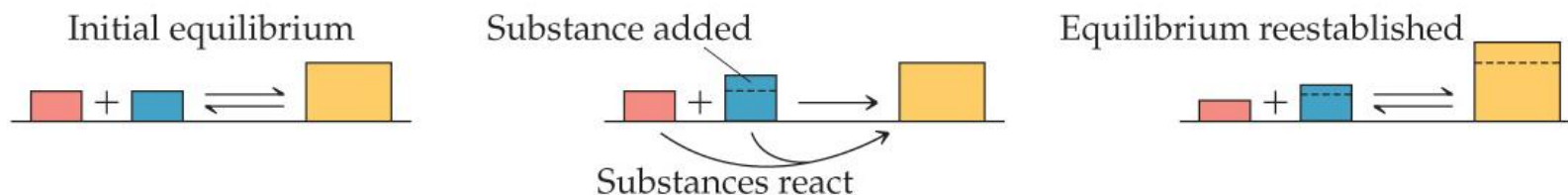
Pressure: changing the pressure by changing the volume

At constant temperature, reducing the volume of a gaseous equilibrium mixture causes the system to shift in the direction that reduces the number of moles of gas.
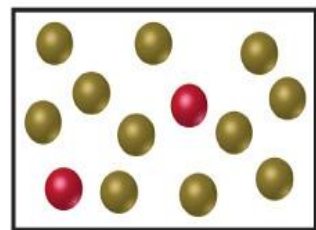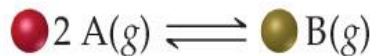
Pressure

Initial volume

System shifts to direction of fewer moles of gas

Temperature:

If the temperature of a system at equilibrium is increased, the system reacts as if we added a reactant to an endothermic reaction or a product to an exothermic reaction. The equilibrium shifts in the direction that consumes the "excess reactant," namely heat.
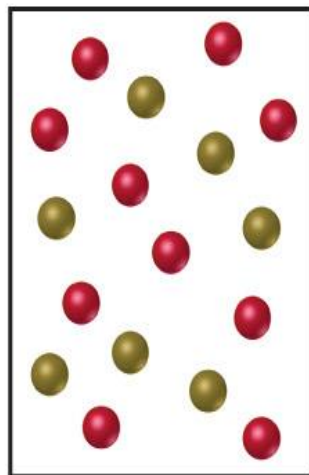
Endothermic

Increasing T   Reaction shifts right

Decreasing T   Reaction shifts left

Exothermic

Increasing T   Reaction shifts left

Decreasing T   Reaction shifts right

• Use Le Châtelier's Principle qualitatively to predict shifts in equilibrium based on **changes in conditions**.

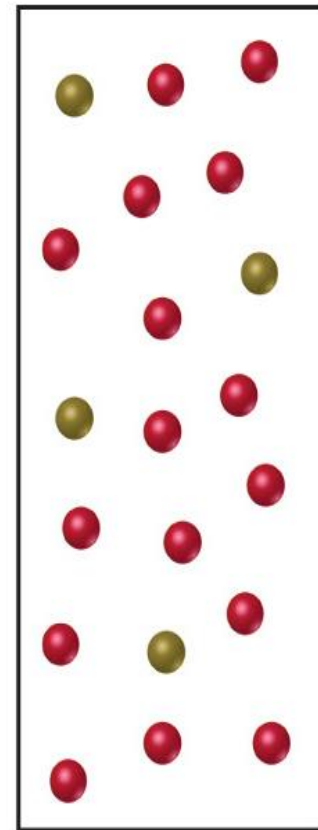Equilibrium

Change in Volume or Pressure

$2A(g) \rightleftharpoons B(g)$

Decrease volume, increase pressure

Increase volume, decrease pressure

Initial volume

New equilibrium favors products to reduce total moles of gas

New equilibrium favors reactants to increase total moles of gas
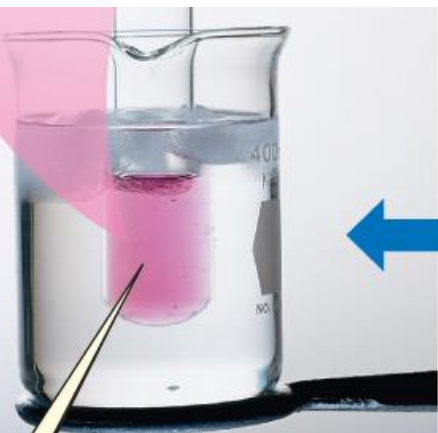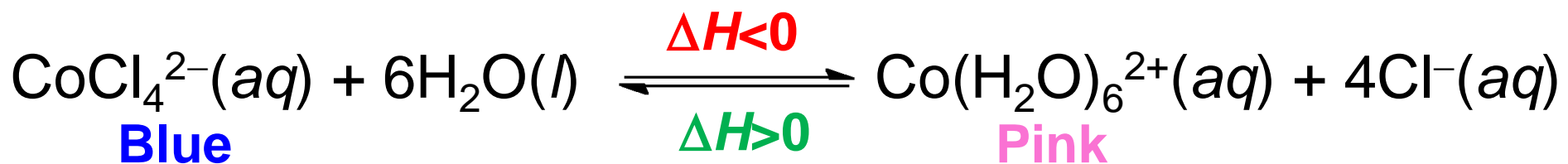
$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$
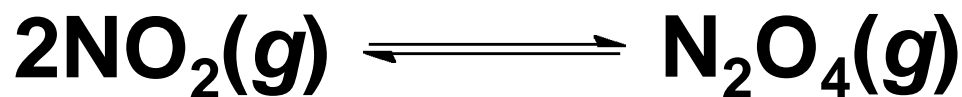
• A change in pressure or volume of gases affects equilibrium: **Higher volume or lower pressure favors** the side of the equation with **more moles** ➔ **more pressure** (and *vice-versa*).

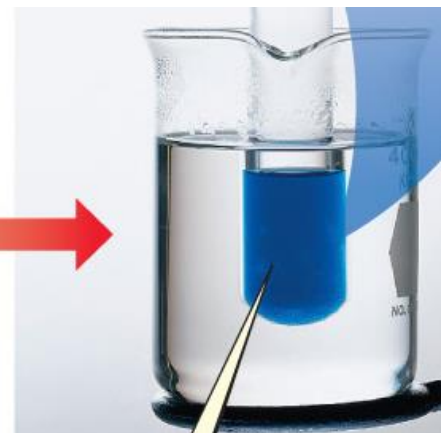Equilibrium

Change in Temperature

- Does the reaction endothermic or exothermic affect equilibrium?
- **Endothermic**: Heats acts *like* a reactant; **adding heat** drives a reaction **toward products**.
- **Exothermic**: Heat acts *like* a product; **adding heat** drives a reaction **toward reactants**.

$$CoCl_4{}^{2-}(aq) + 6H_2O(l) \underset{\Delta H>0}{\overset{\Delta H<0}{\rightleftharpoons}} Co(H_2O)_6{}^{2+}(aq) + 4Cl^-(aq)$$

Blue   **Pink**

Cool   Heat

| System	Change	Result
$CO_2 + H_2 \rightarrow$ $H_2O(g) + CO$	A drying agent is added to absorb H_2O	**Shift to the right**. Continuous removal of a product will force any reaction to the
$H_2(g) + I_2(g) \rightarrow$ $2HI(g)$	Some nitrogen gas is added	**No change**; N_2 is not a component of this reaction system.
$NaCl(s) + H_2SO_4(l)$ $\rightarrow Na_2SO_4(s) + HCl(g)$	Reaction is carried out in an open container	HCl gas can escape from the system, the reaction is forced to the **right:** the basis for the commercial production of HCl.
$H_2O(l) \rightarrow H_2O(g)$	Water evaporates from an open container	Continuous removal of water vapor forces the reaction to the **right**, so equilibrium is never achieved.
$HCN(aq) \rightarrow$ $H^+(aq) + CN^-(aq)$	The solution is diluted	Shift to **right**; the product $[H^+][CN^-]$ diminishes more rapidly than does [HCN].
$AgCl(s) \rightarrow$ $Ag^+(aq) + Cl^-(aq)$	Some NaCl is added to the solution	Shift to **left** due to increase in $[Cl^-]$: the common ion effect on solubility.
$N_2 + 3 H_2 \rightarrow 2 NH_3$	A catalyst is added to speed up this reaction	**No change**. Catalysts affect only the rate of a reaction; the have no effect at all on the composition of the equilibrium state.

The Haber Process-Changes in Temperature

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g) \qquad \Delta H = -92\ \text{kJ/mol}$$
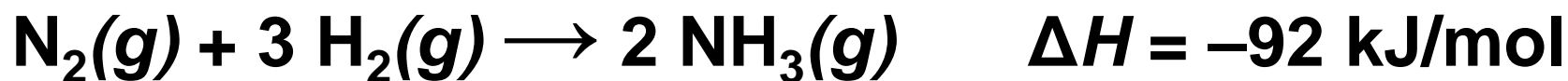
Temperature (°C)	K_p
300	4.34×10^{-3}
400	1.64×10^{-4}
450	4.51×10^{-5}
500	1.45×10^{-5}
550	5.38×10^{-6}
600	2.25×10^{-6}

Equilibrium

Change in Reactant or Product Concentration

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$
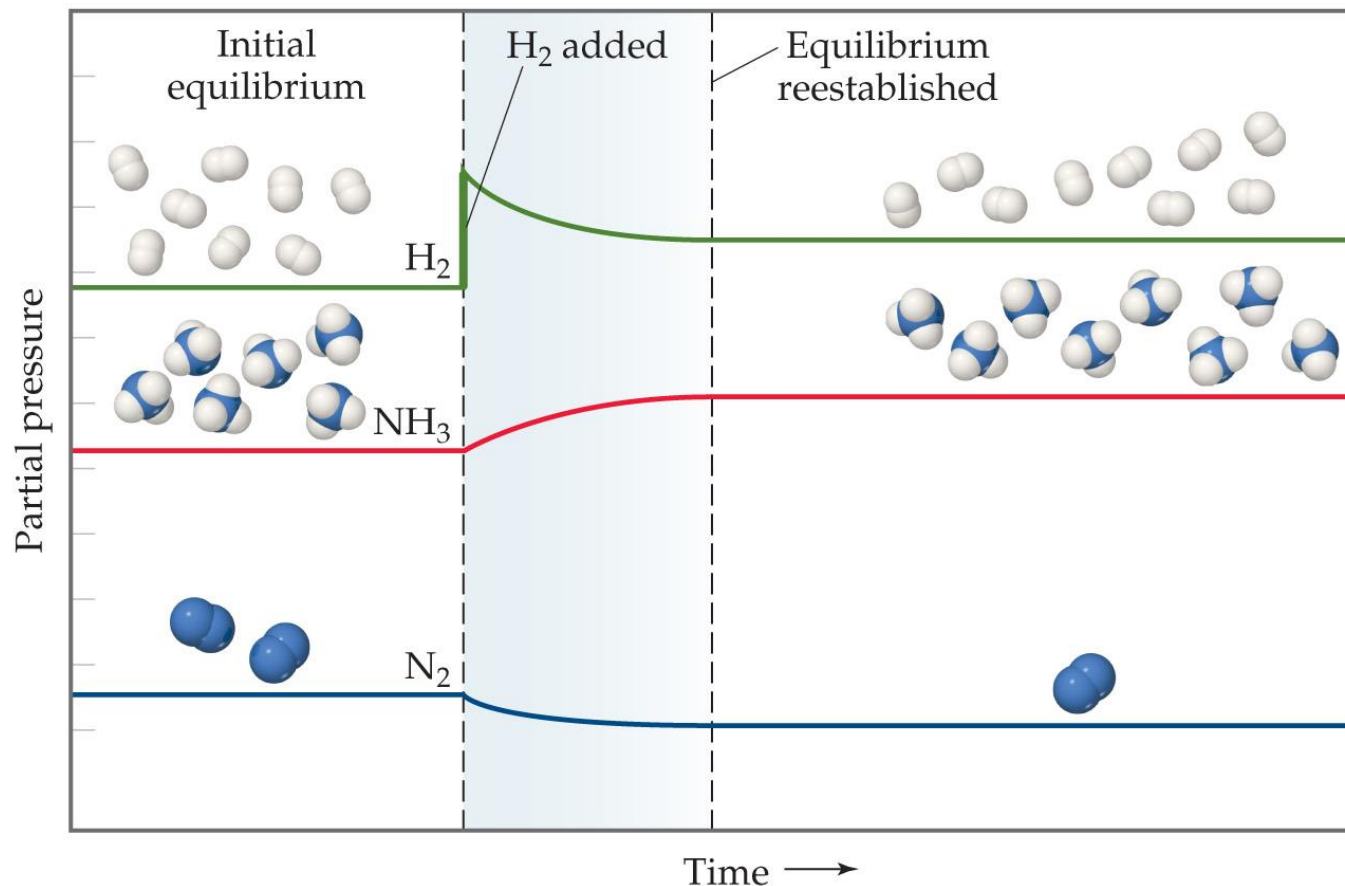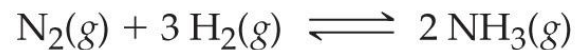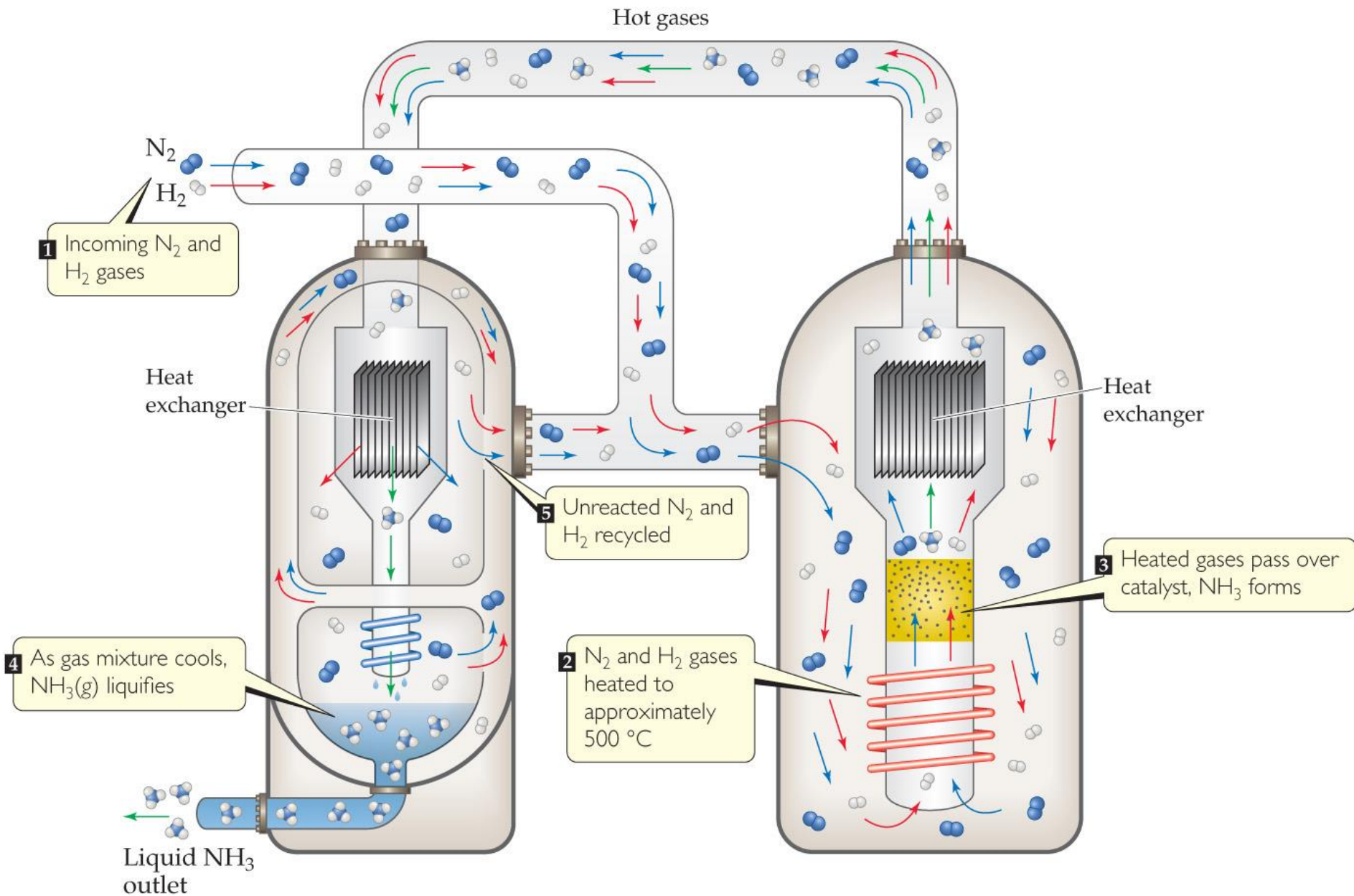

- When adding more reactant, that are used up more.
- If H_2 is added to the system, N_2 will be consumed & the two reagents will form more NH_3.

Equilibrium

Effect of Temperature & Pressure

$$N_2(g) + 3 H_2(g) \longrightarrow 2 NH_3(g) \qquad \Delta H = -92 \text{ kJ/mol}$$

Percent of NH_3 increases with increasing pressure

Percent of NH_3 decreases with increasing temperature

Percent NH_3 produced

8.8% 12.9% 16.9% 20.8%

18.9% 26.0% 32.2% 37.8%

27.4% 35.9% 42.9% 48.8%

38.7% 47.8% 54.9% 60.6%

Total pressure (atm): 200 300 400 500

Temperature (°C): 400 450 500 550

Hot gases

N$_2$

H$_2$

1 Incoming N$_2$ and H$_2$ gases

Heat exchanger

5 Unreacted N$_2$ and H$_2$ recycled

4 As gas mixture cools, NH$_3$(g) liquifies

Liquid NH$_3$ outlet

Heat exchanger

3 Heated gases pass over catalyst, NH$_3$ forms

2 N$_2$ and H$_2$ gases heated to approximately 500 °C
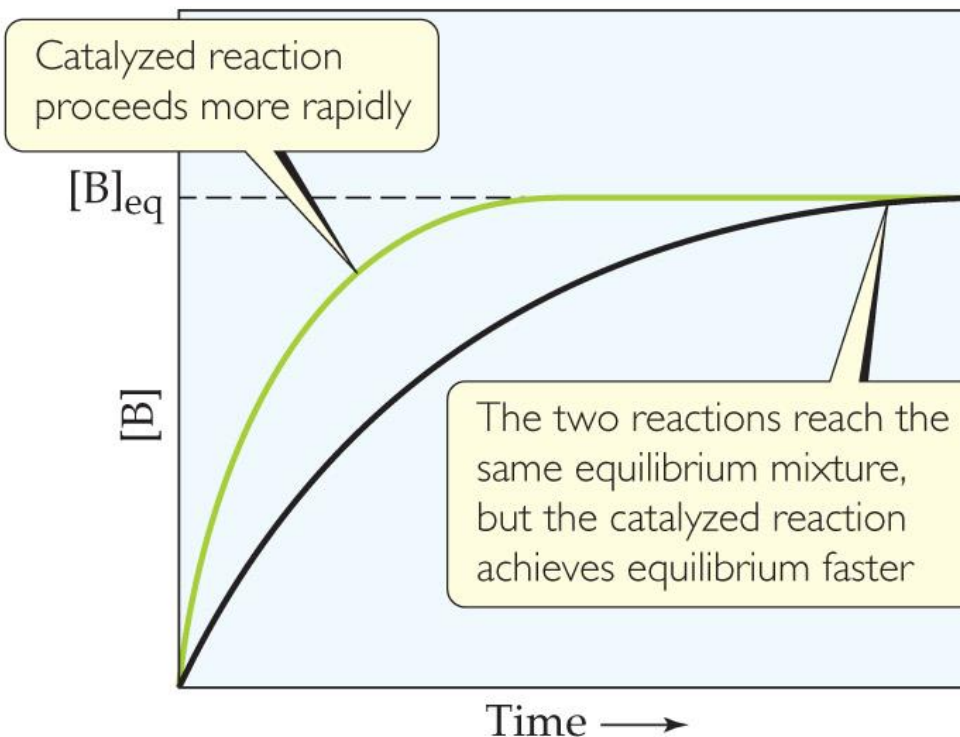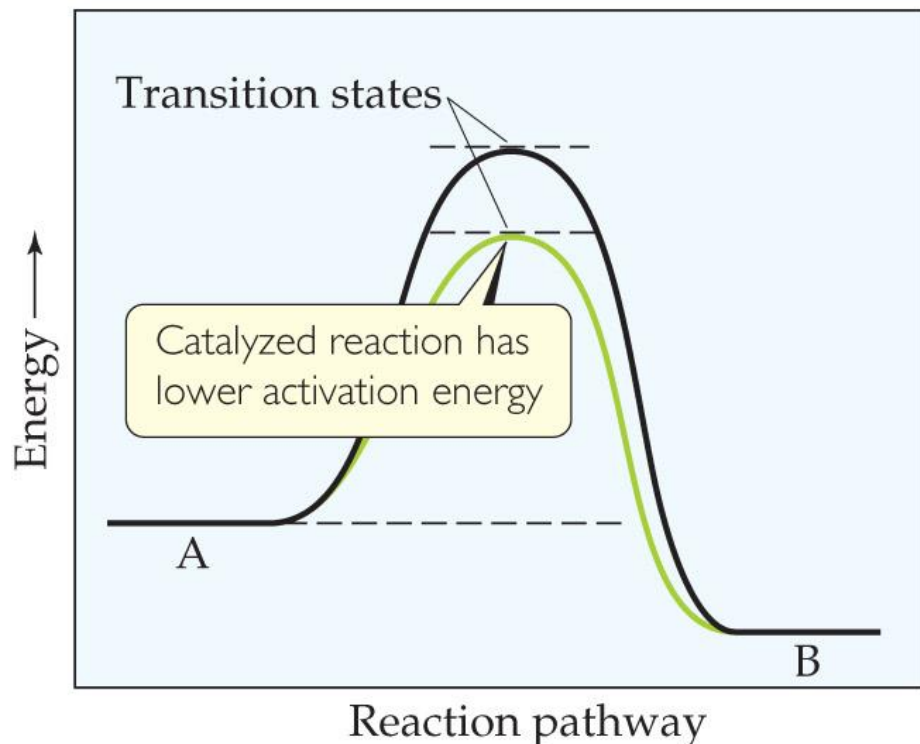
This industrial apparatus helps push the equilibrium to the right by removing NH$_3$ from the system as **a liquid**.

Equilibrium

- The Haber process for producing ammonia from the elements is exothermic.
- One would think that cooling down the reactants would result in more product.
- However, the activation energy for this reaction is high!
- This is the *one* instance where a system in equilibrium can be affected by a catalyst by lowering the activation energy!
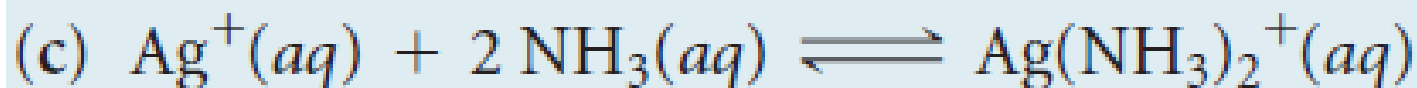

Reaction progress

Catalysts

Transition states

Energy →

Catalyzed reaction has lower activation energy

A

B

Reaction pathway

Catalyzed reaction proceeds more rapidly

$[B]_{eq}$

$[B]$

The two reactions reach the same equilibrium mixture, but the catalyzed reaction achieves equilibrium faster

Time →
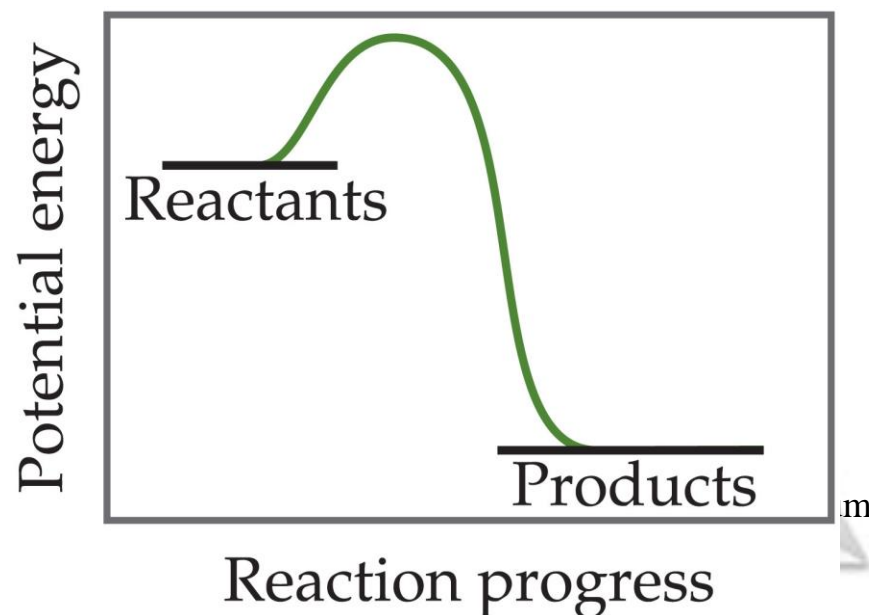
- **Catalysts increase** the **rate** of **both** the **forward & reverse reactions**.
- **Equilibrium** is achieved **faster**, but the equilibrium composition **remains unaltered**.
- Activation energy is lowered, allowing equilibrium to be established at lower temperatures.

Equilibrium

Write the equilibrium expression for K_c for the following reactions:

(a) $2\,O_3(g) \rightleftharpoons 3\,O_2(g)$

(b) $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$

(c) $Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq)$

Solve

(a) $K_c = \dfrac{[O_2]^3}{[O_3]^2}$

(b) $K_c = \dfrac{[NOCl]^2}{[NO]^2[Cl_2]}$

(c) $K_c = \dfrac{[Ag(NH_3)_2{}^+]}{[Ag^+][NH_3]^2}$

Write the equilibrium-constant expression for the evaporation of water, $H_2O(l) \rightleftharpoons H_2O(g)$, in terms of partial pressures.
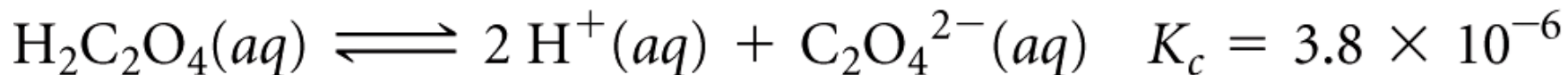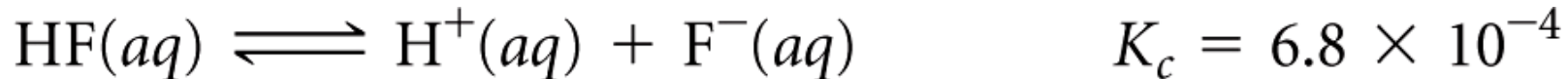
A. $K_p = 1/[H_2O(g)]$

B. $K_p = P_{H_2O(g)}$

C. $K_p = [H_2O(g)]$

D. $K_p = 1/P_{H_2O(g)}$

Equilibrium

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq) \qquad K_c = 6.8 \times 10^{-4}$$

$$H_2C_2O_4(aq) \rightleftharpoons 2\,H^+(aq) + C_2O_4{}^{2-}(aq) \qquad K_c = 3.8 \times 10^{-6}$$

On the basis of the above reactions, determine K_c for the below reaction

$$2\,HF(aq) + C_2O_4{}^{2-}(aq) \rightleftharpoons 2\,F^-(aq) + H_2C_2O_4(aq)$$

$2\,HF(aq) \rightleftharpoons 2\,H^+(aq) + 2\,F^-(aq)$ $\qquad$ $K_c = (6.8 \times 10^{-4})^2 = 4.6 \times 10^{-7}$

$2\,H^+(aq) + C_2O_4{}^{2-}(aq) \rightleftharpoons H_2C_2O_4(aq)$ $\qquad$ $K_c = \dfrac{1}{3.8 \times 10^{-6}} = 2.6 \times 10^5$

$2\,HF(aq) \rightleftharpoons 2\,H^+(aq) + 2\,F^-(aq)$ $\qquad$ $K_c = 4.6 \times 10^{-7}$

$2\,H^+(aq) + C_2O_4{}^{2-}(aq) \rightleftharpoons H_2C_2O_4(aq)$ $\qquad$ $K_c = 2.5 \times 10^5$

$2\,HF(aq) + C_2O_4{}^{2-}(aq) \rightleftharpoons 2\,F^-(aq) + H_2C_2O_4(aq)$ $\qquad$ $K_c = (4.6 \times 10^{-7})(2.6 \times 10^5) = 0.12$
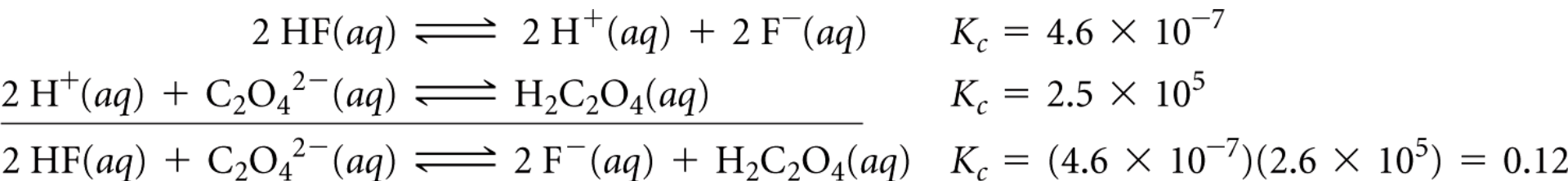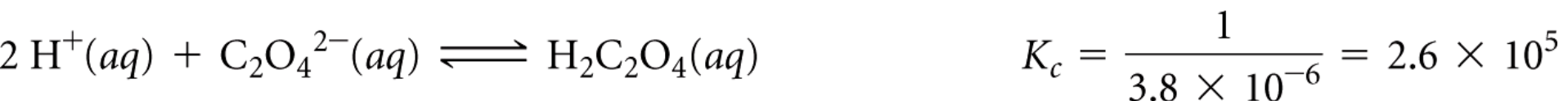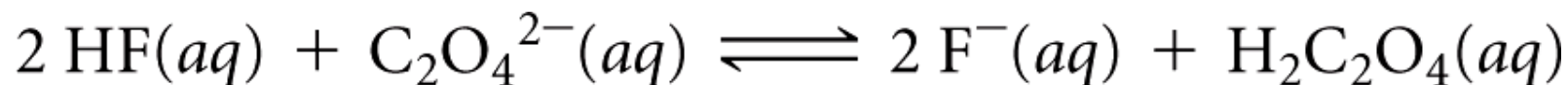
Equilibrium

Write the equilibrium-constant expression for the reaction $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

A. $K_c = [NH_4^+][OH^-]$

B. $K_c = \dfrac{[NH_4^+][OH^-]}{[NH_3]}$

C. $K_c = \dfrac{[NH_4^+][OH^-]}{[NH_3][H_2O]}$

D. $K_c = \dfrac{[NH_3][H_2O]}{[NH_4^+][OH^-]}$

Equilibrium

At 448 °C the equilibrium constant K_c for the below reaction is 50.5. Predict in which direction the reaction proceeds to reach equilibrium if we start with 2.0×10^{-2} mol of HI, 1.0×10^{-2} mol of H_2, and 3.0×10^{-2} of I_2 in a 2.00-L container.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$
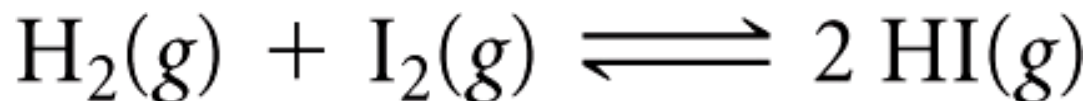
The initial concentrations are

$$[HI] = 2.0 \times 10^{-2}\,\text{mol}/2.00\,\text{L} = 1.0 \times 10^{-2}\,M$$
$$[H_2] = 1.0 \times 10^{-2}\,\text{mol}/2.00\,\text{L} = 5.0 \times 10^{-3}\,M$$
$$[I_2] = 3.0 \times 10^{-2}\,\text{mol}/2.00\,\text{L} = 1.5 \times 10^{-2}\,M$$

The reaction quotient is

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.0 \times 10^{-2})^2}{(5.0 \times 10^{-3})(1.5 \times 10^{-2})} = 1.3$$

Because $Q_c < K_c$, the concentration of HI must increase and the concentrations of H_2 and I_2 must decrease to reach equilibrium; the reaction as written proceeds left to right to attain equilibrium.

Use Le Châtelier's principle to explain why the equilibrium vapor pressure of a liquid increases with increasing temperature.

A. Evaporation is an exothermic process and an increasing temperature shifts the equilibrium $H_2O(l) \rightleftharpoons H_2O(g)$ to the right and increases the equilibrium vapor pressure.

B. Evaporation is an endothermic process and an increasing temperature shifts the equilibrium $H_2O(l) \rightleftharpoons H_2O(g)$ to the right and increases the equilibrium vapor pressure.

C. Evaporation is an exothermic process and an increasing temperature shifts the equilibrium $H_2O(l) \rightleftharpoons H_2O(g)$ to the left and increases the equilibrium vapor pressure.

D. Evaporation is an endothermic process and an increasing temperature shifts the equilibrium $H_2O(l) \rightleftharpoons H_2O(g)$ to the left and increases the equilibrium vapor pressure.

Equilibrium

At equilibrium, the rate of the forward reaction is _____ the rate of the reverse reaction.

a. equal to
b. slower than
c. faster than
d. the reverse of

The reaction quotient Q is usually represented by

a. [reactants] / [products].
b. [products] / [reactants].
c. [reactants] × [products].
d. [reactants] + [products].

Equilibrium

If the value of the equilibrium constant is large, then _____ will mostly be present at equilibrium.

a. reactants
b. products
c. catalysts
d. shrapnel

If the value of the equilibrium constant is small, then _____ will mostly be present at equilibrium.

a. reactants
b. products
c. catalysts
d. shrapnel

Equilibrium

Q = the reaction quotient; K = the equilibrium constant
At equilibrium, which is true?

a. $Q > K$
b. $Q < K$
c. $Q = K$
d. $Q^2 = K$

Equilibrium constants typically have units of

a. M.
b. M^2.
c. M^{1-}.
d. None of the above

Reaction quotients for heterogeneous equilibria do not include concentrations of

a. pure liquids.
b. pure solids.
c. Both of the above
d. Neither of the above

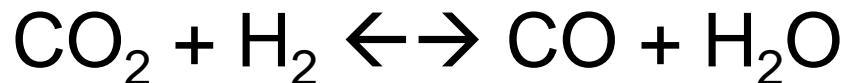$HA \leftarrow\rightarrow H^+ + A^-$
$[HA] = 1.65 \times 10^{-2}$ M and $[H^+] = [A^-] = 5.44 \times 10^{-4}$ M at equilibrium. K_c = _____.

a. 1.79×10^{-2}
b. 1.79×10^{-3}
c. 1.79×10^{-4}
d. 1.79×10^{-5}

Equilibrium

$K_P = K_C$ when
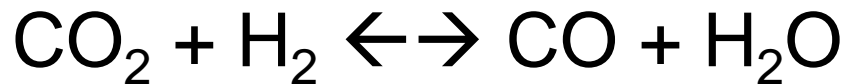
a. the reaction is at equilibrium.
b. the reaction is exothermic.
c. all of the gases present are at the same pressure.
d. the number of moles of gas on both sides of the balanced equation is the same.

$CO_2 + H_2 \longleftrightarrow CO + H_2O$
If all species are gases and H_2 is added, the concentration of CO at equilibrium will

a. increase.
b. decrease.
c. remain unchanged.
d. disappear.

Equilibrium

$CO_2 + H_2 \leftrightarrow CO + H_2O$

If all species are gases and H_2O is added, the equilibrium concentration of CO

a. will increase.
b. will decrease.
c. will remain unchanged.
d. will disappear.

$CO_2 + H_2 \leftrightarrow CO + H_2O$
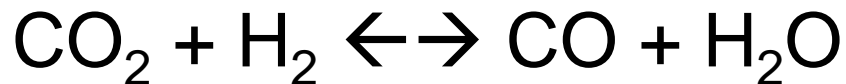
If all species are gases and CO_2 is removed, the [CO] at equilibrium will

a. increase.
b. decrease.
c. remain unchanged.
d. disappear.

Equilibrium

$CO_2 + H_2 \leftrightarrow CO + H_2O$
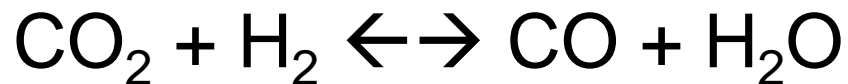
Increasing the temperature of this endothermic reaction will _____ [CO] at equilibrium.

a. increase
b. decrease
c. not change
d. eradicate

$CO_2 + H_2 \leftrightarrow CO + H_2O$
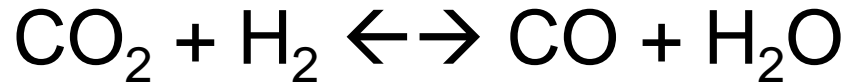
If all species are gases and the container is compressed, the amount of CO will

a. increase.
b. decrease.
c. remain unchanged.
d. vanish.

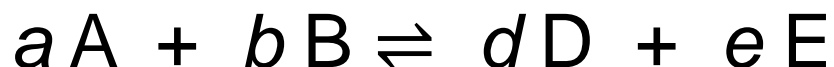Equilibrium

$CO_2 + H_2 \leftrightarrow CO + H_2O$
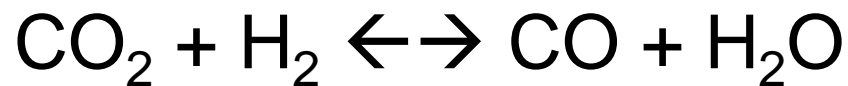
Adding a catalyst to this reaction will cause the [CO] at equilibrium to

   a. increase.

   b. decrease.

   c. remain unchanged.

   d. cease to exist.

Equilibrium

Summary of Chapter 15

Equilibrium constant (*K*),
Homogeneous equilibria, Heterogeneous equilibria

$$a\,A \ + \ b\,B \rightleftharpoons \ d\,D \ + \ e\,E$$

$$K_c = \frac{[\text{D}]^d[\text{E}]^e}{[\text{A}]^a[\text{B}]^b}$$

Reaction quotient

Le Châtelier's Principle

Equilibrium

Thank You for Your Attention!
Any Questions?

Equilibrium