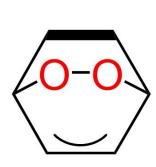
# CHEM103 General Chemistry

**Chapter 15: Chemical Equilibrium** 



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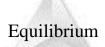
### Homeworks 13 & 14

**Homework 13** 

Due date: 28th Nov. (Mon)

**Homework 14** 

Due date: 5th Dec. (Mon)



### **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

### **Outline of Chapter 15**

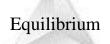
Equilibrium constant (*K*), Homogeneous equilibria, Heterogeneous equilibria

$$aA + bB \rightleftharpoons dD + eE$$

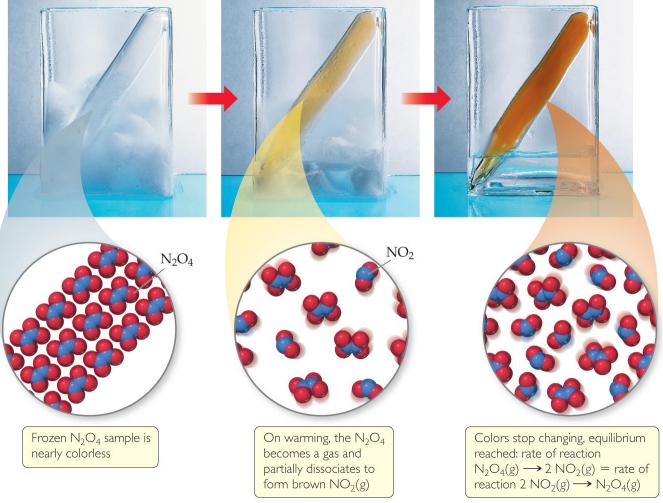
$$K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}$$

Reaction quotient (Q)

Le Châtelier's Principle (勒夏特列原理)

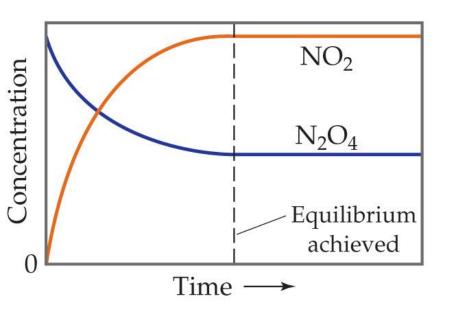


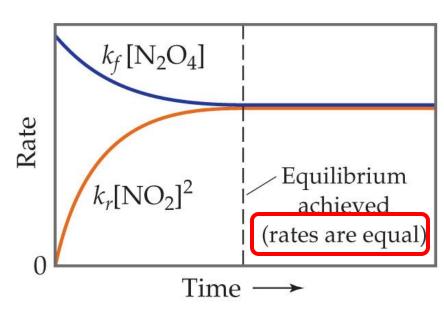
The Concept of Equilibrium



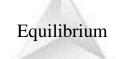
• Chemical equilibrium occurs when a forward reaction & its reverse reaction proceed at the same rate. Equilibrium is finally reached in the right picture.

### $N_2O_4(g) \longrightarrow 2NO_2(g)$





- 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.



### **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<sub>r</sub> = 
$$k_r^*[NO_2]^2$$

### **Equilibrium Constant**

At equilibrium:

Rate<sub>f</sub> = Rate<sub>r</sub>  
$$k_f[N_2O_4] = k_f[NO_2]^2$$

Rewriting this, it becomes:

$$K_{eq} = \frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$

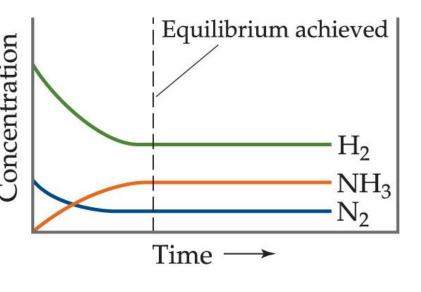
• A ratio of concentration terms equals the equilibrium constant ( $K_{eq}$ ) at that temperature (a temperature-dependent thermochemical property).

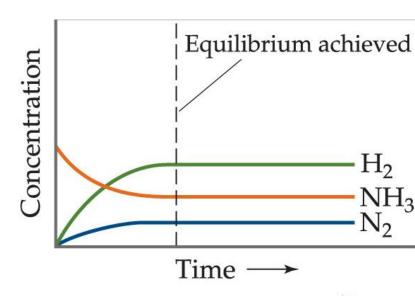
### **Another Example: The Haber Process**

$$N_2(g) + 3H_2(g) - 2NH_3(g)$$

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.

### The Equilibrium Constant

Consider the generalized reaction

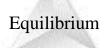
$$aA + bB \rightleftharpoons dD + eE$$

The equilibrium expression for this reaction:

$$K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b} \longleftarrow \text{products}$$
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: (D) d(D) e

$$K_p = \frac{(P_{\rm D})^d (P_{\rm E})^e}{(P_{\rm A})^a (P_{\rm B})^b}$$



## 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

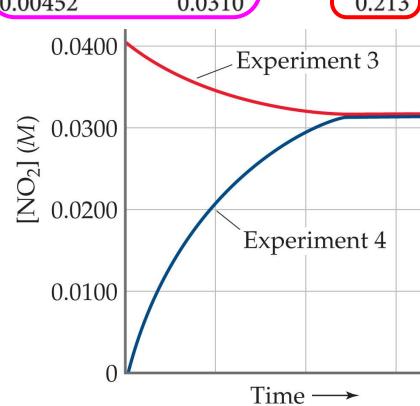
 $\Delta n = \text{(moles of gaseous product)} - \text{(moles of gaseous reactant)}$ 

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 <sub>2</sub> ] (M)	Equilibrium $[N_2O_4](M)$	Equilibrium $[NO_2]$ $(M)$	K <sub>c</sub>
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
			0.0400		

• The ratio of  $[NO_2]^2$  to  $[N_2O_4]$  ( $\rightarrow$   $K_c$ ) remains constant at this temperature no matter what the initial concentrations of  $NO_2$  and  $N_2O_4$  are.



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### 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:  $K_c = 1/K_{c*}$ 

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

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

$$2 \text{ NO}_2(g) \rightleftharpoons \text{ N}_2\text{O}_4(g)$$

$$K_{c^*} = \frac{[N_2O_4]}{[NO_2]^2} = 4.72 \text{ at } 100 \,^{\circ}\text{C}$$

### 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!

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

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

$$2 N_2O_4(g) \rightleftharpoons 4 NO_2(g)$$

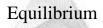
$$K_c = \frac{[NO_2]^4}{[N_2O_4]^2} = (0.212)^2 \text{ at } 100^{\circ}C_{\text{quilibrium}}$$

### **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  $(K_{c1} \& K_{c2})$ :

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

$$\begin{array}{ccc}
 & \mathbf{k}_{I} \\
\mathbf{A} & \stackrel{}{\Longrightarrow} & \mathbf{k}_{2} \\
 & \mathbf{k}_{-I}
\end{array}$$



2 NOBr(g) 
$$\Longrightarrow$$
 2 NO(g) + Br<sub>2</sub>(g)  $K_c = \frac{[NO]^2[Br_2]}{[NOBr]^2} = 0.014$ 

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

$$2 \operatorname{NOBr}(g) + \operatorname{Cl}_2(g) \rightleftharpoons 2 \operatorname{NO}(g) + 2 \operatorname{BrCl}(g)$$

$$K_c = \frac{[\text{NO}]^2[\text{BrCl}]^2}{[\text{NOBr}]^2[\text{Cl}_2]} = \frac{[\text{NO}]^2[\text{Br}_2]}{[\text{NOBr}]^2} \times \frac{[\text{BrCl}]^2}{[\text{Br}_2][\text{Cl}_2]}$$

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

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:

$$A + B \Longrightarrow C + D \quad K_1$$
  
 $C + D \Longrightarrow A + B \quad K = 1/K_1$ 

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.

$$A + B \Longrightarrow C + D \qquad K_1$$
  
 $nA + nB \Longrightarrow nC + nD \qquad K = K_1^n$ 

**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. 
$$C + F \Longrightarrow G + A \quad K_2$$

3. B + F 
$$\Longrightarrow$$
 D + G  $K_3 = (K_1)(K_2)$ 

### **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.

$$K = \left(\prod_{J} a_{J}^{\nu_{J}}\right)$$

- molalities, by replacing  $a_{\rm I}$  by  $b_{\rm I}/b^{\circ}$ , where  $b^{\circ}=1$  mol kg<sup>-1</sup>  $K = \left(\prod_{J} a_{J}^{V_{J}}\right) \quad \text{molar concentrations, by replacing } a_{J} \text{ by } [J]/c^{\Theta}, \text{ where } c^{\Theta} = 1 \text{ mol dm}^{-3}$   $\cdot \text{ partial pressures, by replacing } a_{J} \text{ by } p_{J}/p^{\Theta}, \text{ where } p^{\Theta} = 1 \text{ bar}$ 

  - 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 0.01M, its activity is 0.01M/1M = 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<sub>2</sub>(s) 
$$\longrightarrow$$
 Pb<sup>2+</sup>(aq) + 2Cl<sup>-</sup>(aq)  
 $K_c = [Pb^{2+}]^*[Cl^-]^2$ 

Equilibrium

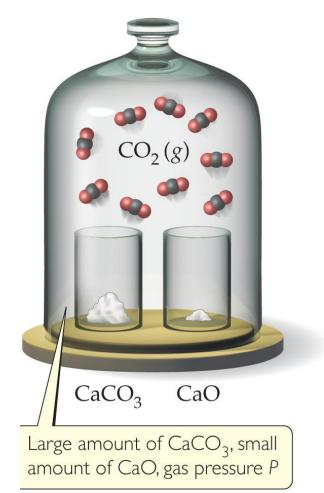
## The Decomposition of CaCO<sub>3</sub>: A Heterogeneous Equilibrium

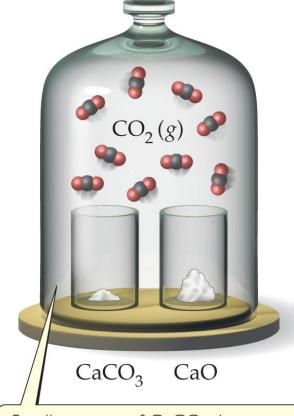
 $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ 

• 
$$K_c = [CO_2]$$

• 
$$K_p = P_{\text{CO}_2}$$

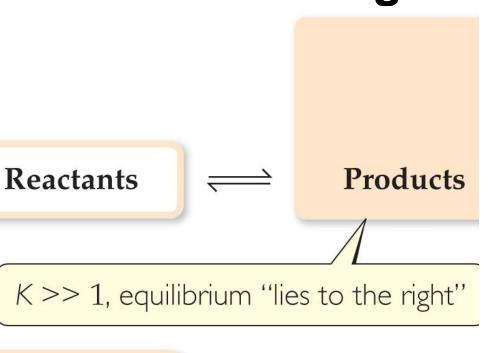
• The amount of CO<sub>2</sub> above the solid remain the same.





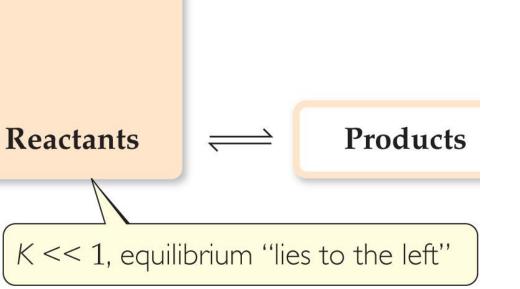
Small amount of CaCO<sub>3</sub>, large amount of CaO, gas pressure still P

### Magnitude of K



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

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



• If K<<1, the reaction favors reactants; reactants predominate at 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.



### An Example

A closed system initially containing 1.000  $\times$  10<sup>-3</sup> M H<sub>2</sub> and 2.000  $\times$  10<sup>-3</sup> M I<sub>2</sub> at 448 °C is allowed to reach equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is 1.87  $\times$  10<sup>-3</sup> M. Calculate  $K_c$  at 448 °C for the reaction.

$$H_2(g) + I_2(g) \rightleftharpoons 2 HI(g)$$

	$H_2(g)$ +	$I_2(g) =$	$\Rightarrow$ 2 HI(g)
Initial concentration (M)	$1.000 \times 10^{-3}$	$2.000 \times 10^{-3}$	0
Change in concentration ( <i>M</i> )			
Equilibrium concentration ( <i>M</i> )			$1.87 \times 10^{-3}$

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

• The change in concentration of HI is 
$$1.87 \times 10^{-3}$$
  $M$ .

Initial concentration ( $M$ )

Change in concentration ( $M$ )

Equilibrium concentration ( $M$ )

• Stoichiometry tells us [H<sub>2</sub>] and [I<sub>2</sub>] decrease by half.

(Use the balanced equation and

concentration for all reactants and products.)

 $1.000 \times 10^{-3}$ 

Initial concentration (*M*)

Change in concentration (*M*)

Equilibrium concentration (M)

concentrations to

 $H_2(g)$  +

 $2.000 \times 10^{-3}$ 

find change/equilibrium

 $I_2(g) \Longrightarrow 2 HI(g)$ 

0

 $+1.87 \times 10^{-3}$ 

 $1.87 \times 10^{-3}$ 

	112(8)	-2(8)	2111(8)
Initial concentration (M)	$1.000 \times 10^{-3}$	$2.000 \times 10^{-3}$	0
Change in concentration (M)	$-0.935 \times 10^{-3}$	$-0.935 \times 10^{-3}$	$+1.87 \times 10^{-3}$
Equilibrium concentration ( <i>M</i> )	$0.065 \times 10^{-3}$	$1.065 \times 10^{-3}$	$1.87 \times 10^{-3}$

 $H_2(g)$  +  $I_2(g)$   $\Longrightarrow$  2 HI(g)

- 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.)

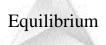


## Is a Mixture in Equilibrium? Which Way Does the Reaction Go?

- 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.

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

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



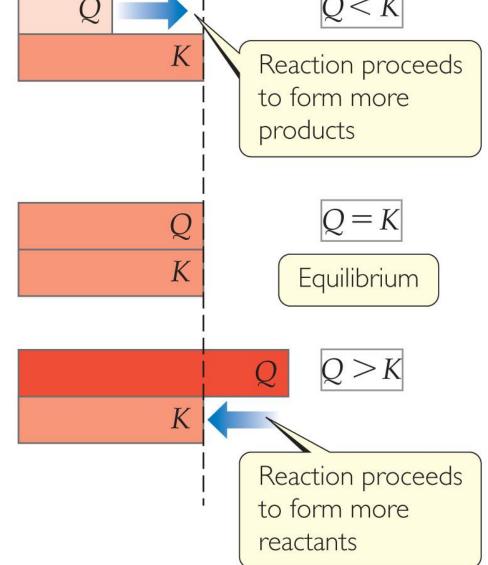
### Comparing Q and K

At equilibrium

• If Q < K, nature will make the reaction proceed to products.

Reaction proceeds to form more products

- If Q = K, the reaction is in equilibrium.
- If Q > K, nature will make the reaction proceed to 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?

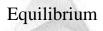
• Set up a below table & set the "change in concentration" row to be a factor of "x" based on the stoichiometry.

stolchiometry.				
	$H_2(g)$	$+$ $I_2(g)$	$\Longrightarrow$	2 HI(g)
Initial concentration ( <i>M</i> )	1.000	2.000		0
Change in concentration ( <i>M</i> )	-x	-x		+2x
Equilibrium concentration ( <i>M</i> )				

	$H_2(g) +$	$I_2(g) =$	$\implies$ 2 HI(g)
Initial concentration (M)	1.000	2.000	0
Change in concentration (M)	-x	-x	+2x
Equilibrium concentration ( <i>M</i> )	1.000 - x	2.000 - x	2x

- The equilibrium concentration = the initial concentration minus the "change in concentration".
- Set up the equilibrium constant expression:

$$K_c = \frac{[\mathrm{HI}]^2}{[\mathrm{H}_2][\mathrm{I}_2]}$$



	$H_2(g) +$	$I_2(g) =$	$\Rightarrow$ 2 HI(g)
Initial concentration (M)	1.000	2.000	0
Change in concentration ( <i>M</i> )	-x	-x	+2x
Equilibrium concentration ( <i>M</i> )	1.000 - x	2.000 - x	2 <i>x</i>

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

- 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)

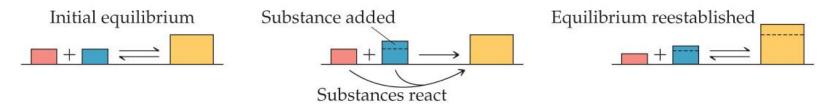
"If a system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance."

Henri-Louis Le Châtelier (1850–1936)

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.

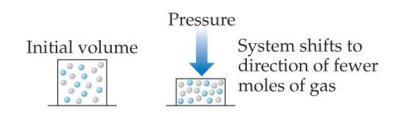
#### Concentration: adding or removing a reactant or product

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.



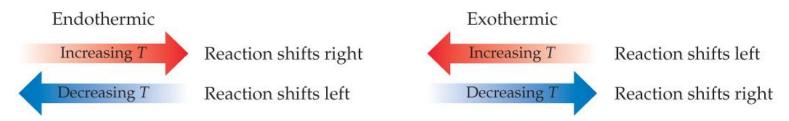
### Pressure: changing the pressure by changing the volume

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.

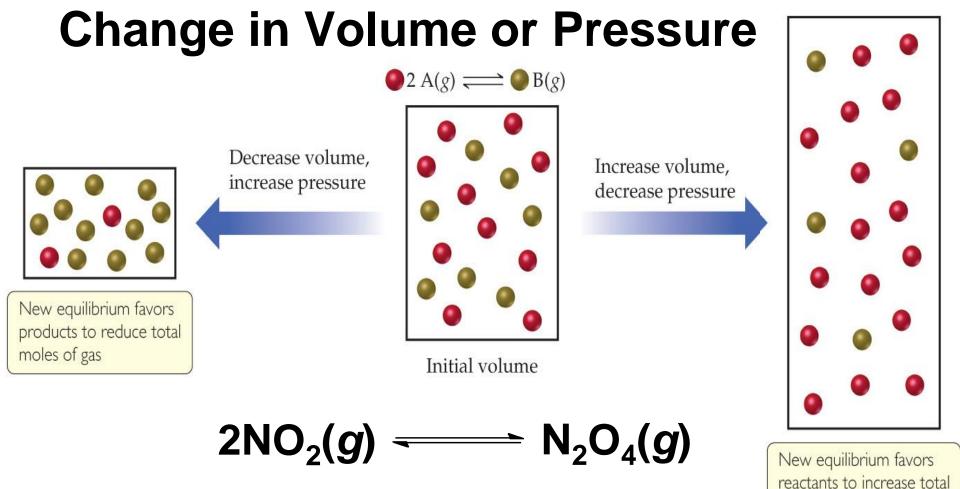


#### Temperature:

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.



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



• A change in pressure or volume of gases affects equilibrium: Higher volume or lower pressure favors the side of the equation with more moles → Equilibrium more pressure (and *vice-versa*).

moles of gas

### **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.

$$CoCl_4^{2-}(aq) + 6H_2O(I) \xrightarrow{\Delta H < 0} Co(H_2O)_6^{2+}(aq) + 4Cl^{-}(aq)$$
Blue

 $\Delta H > 0$  Pink



H <sub>2</sub> (g) + I <sub>2</sub> (g) → Some nitrogen gas is added  NaCl(s) + H <sub>2</sub> SO <sub>4</sub> (l)  Na <sub>2</sub> SO <sub>4</sub> (s) + HCl(g)n an open container  H <sub>2</sub> O(l) → H <sub>2</sub> O(g)  Water evaporates from an open container  HCN(aq) → H <sup>+</sup> (aq) + CN <sup>-</sup> (aq)  AgCl(s) → Ag <sup>+</sup> (aq) + Cl <sup>-</sup> (aq)  Some NaCl is added to the solution  No change; N <sub>2</sub> is not a component of this reaction system.  HCl gas can escape from the system, the reaction is forced to the <b>right</b> : the basis for the commercial production of HCl.  Continuous removal of water vapor forces the reaction to the <b>right</b> , so equilibrium is never achieved.  Shift to <b>right</b> ; the product [H <sup>+</sup> ][CN <sup>-</sup> ] diminishes more rapidly than does [HCN].  Some NaCl is added to the solution  Some NaCl is added to the solution  No change. Catalysts affect only the rate of a reaction; the have no effect at all on the composition of the equilibrium state.		$H_2O(g) + CO$	added to absorb H <sub>2</sub> O	a product will force any reaction to the
NaCl(s) + H <sub>2</sub> SO <sub>4</sub> (l) Reaction is carried out $\rightarrow$ Na <sub>2</sub> SO <sub>4</sub> (s) + HCl(g in an open container for the commercial production of HCl.  Water evaporates from an open container for the commercial production of HCl.  Continuous removal of water vapor forces the reaction to the <b>right</b> , so equilibrium is never achieved.  HCN(aq) $\rightarrow$ H+(aq) + CN-(aq) The solution is diluted for the right, so equilibrium is never achieved.  Shift to <b>right</b> ; the product [H+][CN-] diminishes more rapidly than does [HCN].  Some NaCl is added to the the right for the common ion effect on solubility.  Some NaCl is added to the right for the common ion of the reaction of the reaction of the reaction of the equilibrium state.			J J	
$H_2O(l) \rightarrow H_2O(g)$ from an open container the reaction to the <b>right</b> , so equilibrium is never achieved. Shift to <b>right</b> ; the product [H <sup>+</sup> ][CN <sup>-</sup> ] diminishes more rapidly than does [HCN]. Some NaCl is added to the solution Shift to <b>left</b> due to increase in [Cl <sup>-</sup> ]: the common ion effect on solubility. No change. Catalysts affect only the rate of a reaction; the have no effect at all on the composition of the equilibrium state.				reaction is forced to the <b>right:</b> the basis
$H^+(aq) + CN^-(aq)$ The solution is diluted diminishes more rapidly than does [HCN]. $AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$ Some NaCl is added to the solution Shift to <b>left</b> due to increase in [Cl <sup>-</sup> ]: the common ion effect on solubility. $N_2 + 3 H_2 \rightarrow 2 NH_3$ A catalyst is added to speed up this reaction Shift to <b>left</b> due to increase in [Cl <sup>-</sup> ]: the common ion effect on solubility. <b>No change</b> . Catalysts affect only the rate of a reaction; the have no effect at all on the composition of the equilibrium state.		$H_2O(l) \rightarrow H_2O(g)$	from an open	the reaction to the <b>right</b> , so equilibrium is
AgCl(s) $\rightarrow$ to the solution common ion effect on solubility.  Shift to left due to increase in [CI]: the common ion effect on solubility.  No change. Catalysts affect only the rate of a reaction; the have no effect at all on the composition of the equilibrium state.		` **	The solution is diluted	_
$N_2 + 3 H_2 \rightarrow 2 NH_3$ A catalyst is added to speed up this reaction of a reaction; the have no effect at all on the composition of the equilibrium state.		<b>O</b> , ,		2 3
© 2015 Pearson Education		$N_2 + 3 H_2 \rightarrow 2 NH_3$	•	of a reaction; the have no effect at all on

Change

A drying agent is

Result

Shift to the right. Continuous removal of

**System** 

 $CO_2 + H_2 \rightarrow$ 

### The Haber Process-Changes in Temperature

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

Temperature (°C)

 $K_p$ 
 $4.34 \times 10^{-3}$ 

$$1.64 \times 10^{-4}$$

450 
$$4.51 \times 10^{-5}$$

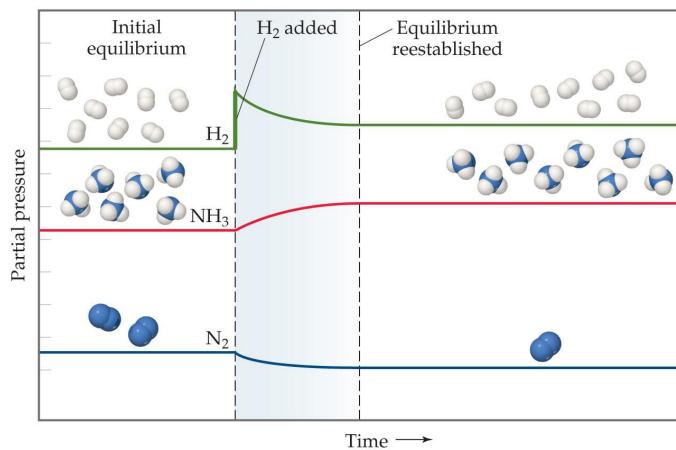
$$500$$
  $1.45 \times 10^{-5}$ 

$$5.38 \times 10^{-6}$$

600 
$$2.25 \times 10^{-6}$$
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<sub>2</sub> is added to the system, N<sub>2</sub> will be consumed & the two reagents will form more NH<sub>3</sub>.

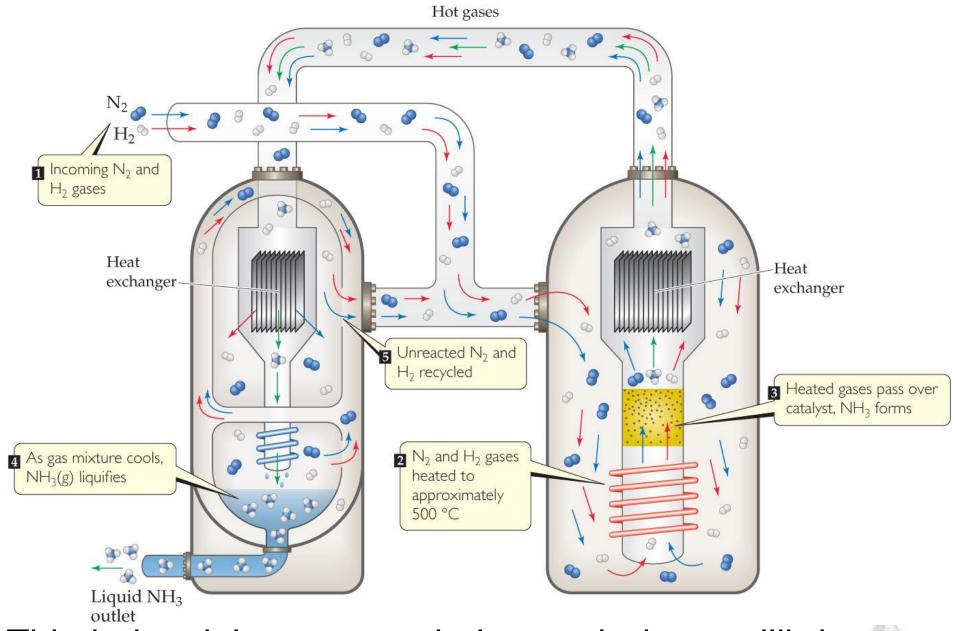
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#### **Effect of Temperature & Pressure**

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

Percent of  $NH_3$ 
increases with increasing pressure

 $A_{S_0} = A_{S_0} = A_{S_0}$ 

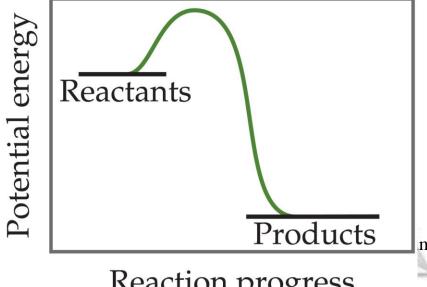


This industrial apparatus helps push the equilibrium to the right by removing NH<sub>3</sub> from the system as **a liquid**.

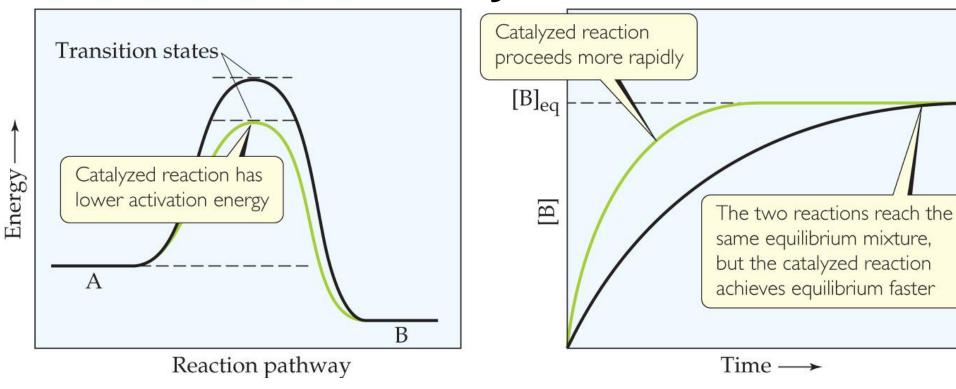
- The Haber process for producing ammonia from the elements is exothermic.
- One would think that cooling down the reactants would result in more product.
- However, the activation energy for this reaction is high!

 This is the one instance where a system in equilibrium can be affected by a catalyst by lowering the activation

energy!



#### **Catalysts**



- 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.

Write the equilibrium expression for  $K_c$  for the following reactions:

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

(b) 
$$2 \text{ NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{ NOCl}(g)$$

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

#### Solve

(a) 
$$K_c = \frac{[O_2]^3}{[O_3]^2}$$
 (b)  $K_c = \frac{[NOCl]^2}{[NO]^2[Cl_2]}$  (c)  $K_c = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$  Write the equilibrium-constant expression for the evaporation of water

Write the equilibrium-constant expression for the evaporation of water,  $H_2O(I) \rightleftharpoons H_2O(g)$ , 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. 
$$K_p = 1/P_{H_2O(g)}$$



$$HF(aq) \Longrightarrow H^{+}(aq) + F^{-}(aq)$$
  $K_{c} = 6.8 \times 10^{-4}$   
 $H_{2}C_{2}O_{4}(aq) \Longrightarrow 2 H^{+}(aq) + C_{2}O_{4}^{2-}(aq)$   $K_{c} = 3.8 \times 10^{-6}$ 

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

$$2 \text{ HF}(aq) + C_2 O_4^{2-}(aq) \Longrightarrow 2 \text{ F}^-(aq) + H_2 C_2 O_4(aq)$$

$$2 \text{ HF}(aq) \iff 2 \text{ H}^{+}(aq) + 2 \text{ F}^{-}(aq)$$

$$K_c = (6.8 \times 10^{-4})^2 = 4.6 \times 10^{-7}$$

$$2 \text{ H}^+(aq) + \text{C}_2\text{O}_4^{2-}(aq) \Longrightarrow \text{H}_2\text{C}_2\text{O}_4(aq)$$
  $K_c = \frac{1}{3.8 \times 10^{-6}} = 2.6 \times 10^5$ 

$$2 \text{ HF}(aq) \implies 2 \text{ H}^{+}(aq) + 2 \text{ F}^{-}(aq) \qquad K_{c} = 4.6 \times 10^{-7}$$

$$2 \text{ H}^{+}(aq) + C_{c} \Omega_{c}^{2-}(aq) \implies \text{H}_{c} C_{c} \Omega_{c}(aq) \qquad K_{c} = 2.5 \times 10^{5}$$

$$\frac{2 \text{ H}^{+}(aq) + \text{C}_{2}\text{O}_{4}^{2-}(aq) \iff \text{H}_{2}\text{C}_{2}\text{O}_{4}(aq)}{2 \text{ H}^{+}(aq) + \text{C}_{2}\text{O}_{4}^{2-}(aq) \iff 2 \text{ F}^{-}(aq) + \text{H}_{2}\text{C}_{2}\text{O}_{4}(aq)} \qquad K_{c} = 2.5 \times 10^{5}$$

$$\frac{2 \text{ H}^{+}(aq) + \text{C}_{2}\text{O}_{4}^{2-}(aq) \iff 2 \text{ F}^{-}(aq) + \text{H}_{2}\text{C}_{2}\text{O}_{4}(aq)}{2 \text{ F}^{-}(aq) + \text{H}_{2}\text{C}_{2}\text{O}_{4}(aq)} \qquad K_{c} = (4.6 \times 10^{-7})(2.6 \times 10^{5}) = 0.12$$

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

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

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

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  $2.0 \times 10^{-2}$  mol of HI,  $1.0 \times 10^{-2}$  mol of H<sub>2</sub>, and  $3.0 \times 10^{-2}$  of I<sub>2</sub> 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<sub>2</sub>] =  $1.0 \times 10^{-2} \text{ mol}/2.00 \text{ L} = 5.0 \times 10^{-3} M$   
[I<sub>2</sub>] =  $3.0 \times 10^{-2} \text{ mol}/2.00 \text{ L} = 1.5 \times 10^{-2} M$ 

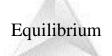
The reaction quotient is

$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.0 \times 10^{-2})^2}{(5.0 \times 10^{-3})(1.5 \times 10^{-2})} = 1.3$$

Because  $Q_c < K_c$ , the concentration of HI must increase and the concentrations of H<sub>2</sub> and I<sub>2</sub> 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  $H_2O(1) \rightleftharpoons H_2O(g)$  to the right and increases the equilibrium vapor pressure.
- B. Evaporation is an endothermic process and an increasing temperature shifts the equilibrium  $H_2O(1) \rightleftharpoons H_2O(g)$  to the right and increases the equilibrium vapor pressure.
- C. Evaporation is an exothermic process and an increasing temperature shifts the equilibrium  $H_2O(1) \rightleftarrows H_2O(g)$  to the left and increases the equilibrium vapor pressure.
- D. Evaporation is an endothermic process and an increasing temperature shifts the equilibrium  $H_2O(1) \rightleftarrows H_2O(g)$  to the left and increases the equilibrium vapor pressure.

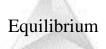


At equilibrium, the rate of the forward reaction is the rate of the reverse reaction.

- 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].

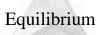


If the value of the equilibrium constant is large, then will mostly be present at equilibrium.

- 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



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.  $M^2$ .
- с. M<sup>1-</sup>.
- 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 ←→ H<sup>+</sup> + A<sup>-</sup>
[HA] = 1.65 × 10<sup>-2</sup> M and [H<sup>+</sup>] = [A<sup>-</sup>] = 5.44 × 10<sup>-4</sup>
M at equilibrium. 
$$K_c =$$
\_\_\_\_\_.

- a.  $1.79 \times 10^{-2}$
- b.  $1.79 \times 10^{-3}$
- c.  $1.79 \times 10^{-4}$
- d.  $1.79 \times 10^{-5}$

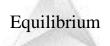
Equilibrium

$$K_P = K_C$$
 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.

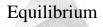


$$CO_2 + H_2 \longleftrightarrow CO + H_2O$$
  
If all species are gases and  $H_2O$  is added, the equilibrium concentration of  $CO$ 

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

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

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

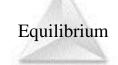


 $CO_2 + H_2 \longleftrightarrow CO + H_2O$ Increasing the temperature of this endothermic reaction will \_\_\_\_\_ [CO] at equilibrium.

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

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

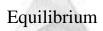
- a. increase.
- b. decrease.
- c. remain unchanged.
- d. vanish.



$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

Adding a catalyst to this reaction will cause the [CO] at equilibrium to

- a. increase.
- b. decrease.
- c. remain unchanged.
- d. cease to exist.



#### **Summary of Chapter 15**

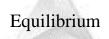
Equilibrium constant (*K*), Homogeneous equilibria, Heterogeneous equilibria

$$aA + bB \rightleftharpoons dD + eE$$

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

Reaction quotient

Le Châtelier's Principle



# Thank You for Your Attention! Any Questions?

