Chapter 18-Reaction Rates and Equilibrium

18.1 Rates of Reaction

Guide for Reading

Key Concepts

- How is the rate of a chemical change expressed?
- What four factors influence the rate of a chemical reaction?

Vocabulary

rate
collision theory
activation energy
activated complex
transition state
inhibitor

18.1-Reaction Rates

Working in Groups of 2 or 3, design and conduct experiments to collect data to determine the effects of the following factors on reaction rate:

1. **Temperature**
2. **Surface area**
3. **Concentration**

You will conduct your experiments when I give final approval to the 'draft' of your ***written*** procedures. I will offer guidance ONLY to advise if something is possible or not, based on what we have in stock in the lab. Your labs MUST offer some reasonable hypothesis for the effect each variable might have on reaction rate. Include 'sample' data tables in your procedure.

You will collect the appropriate quantitative/qualitative data and use it to verify or discount your hypothesis. You might wish to review the basic principles of the Particle Theory of Matter. You have a Chemistry Textbook!

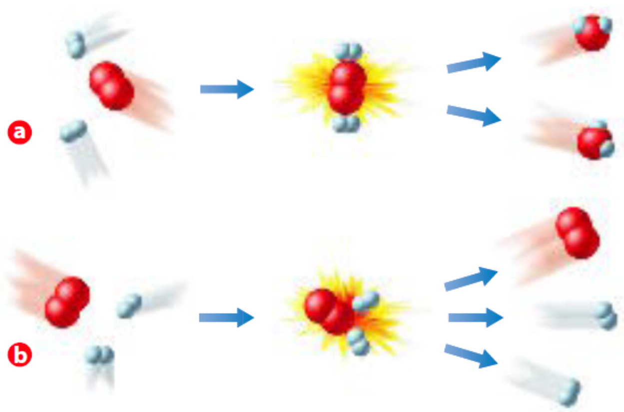
Problem
Theory
Materials
Procedure
Observations
-include data tables and graphs

Conclusions
1) Briefly explain 'collision theory'.
2) Use the collision theory to explain your results.
3) Does every collision between reacting particles lead to products?
4) How is the rate of reaction influenced by a catalyst? How do catalysts make this happen?

Due Friday, Feb. 28th
One report per group.

Collision Theory

- the rate of a chemical reaction is usually expressed as the amount of reactant changing per unit of time
- atoms, ions and molecules can react to form products when they collide with one another, provided that the colliding particles have enough kinetic energy



Effective Collision
-reactants have changed to products

Ineffective Collision
-reactants have NOT changed to products

Collision Theory (cont'd)

- the minimum amount of energy needed to make a collision 'effective' is called the activation energy

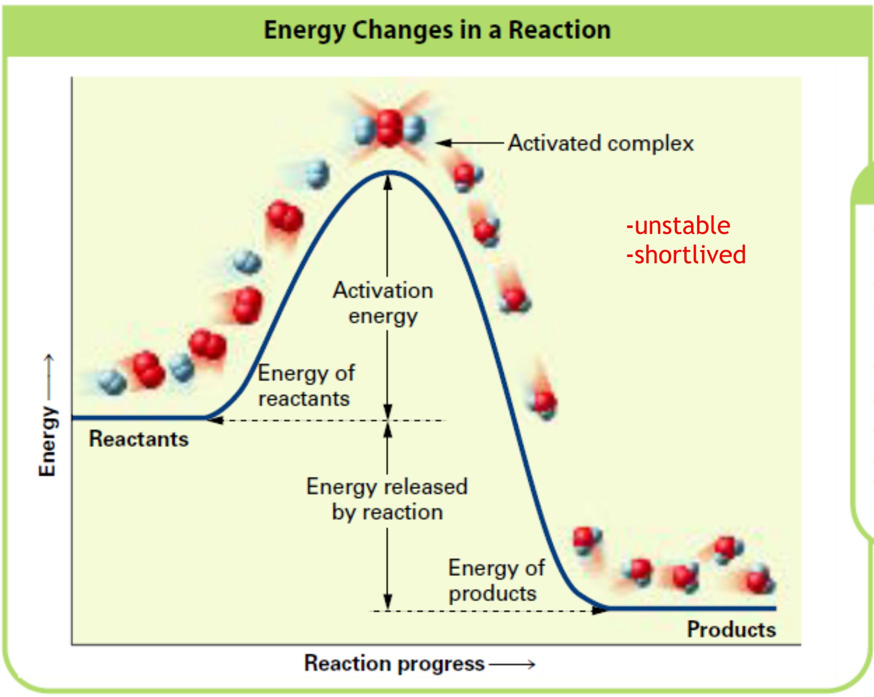


Figure 18.5 The activation-energy barrier must be crossed before reactants are converted to products.

INTERPRETING GRAPHS

a. Navigate Which are at a higher energy, the reactants or products?
b. Read Is energy absorbed or released in progressing from the reactants to the activated complex?
c. Interpret Once the activated complex is formed, will it always proceed to form products? Explain.

Factors Affecting Reaction Rates

- Temperature
- Concentration
- Particle Size (surface area)
- Catalyst

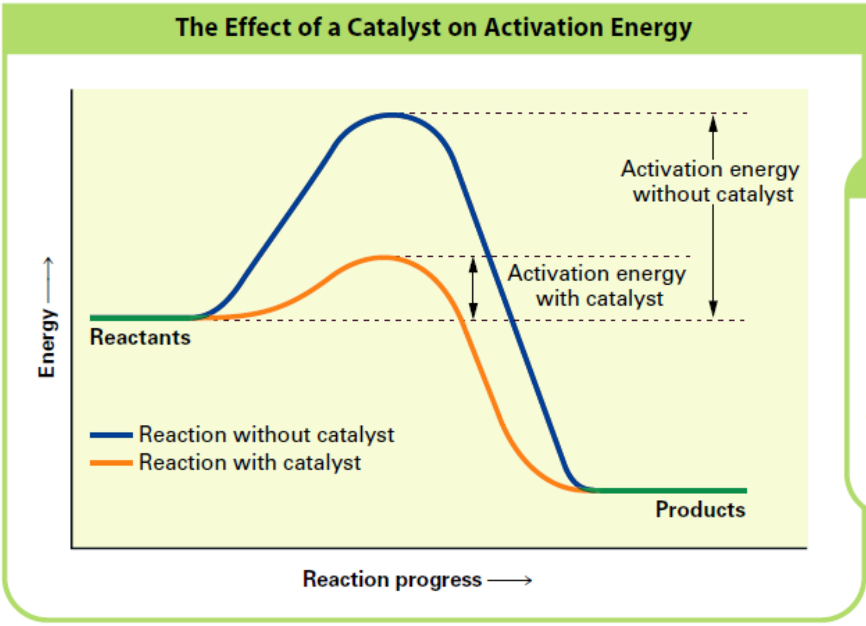


Figure 18.8 A catalyst increases the rate of a reaction by lowering the activation-energy barrier.

INTERPRETING GRAPHS

a. Navigate How does the catalyst affect the magnitude of the activation energy?
b. Read Does the catalyst change the amount of energy released in the reaction?
c. Interpret Along which of the two reaction paths are reactants converted more rapidly to products?

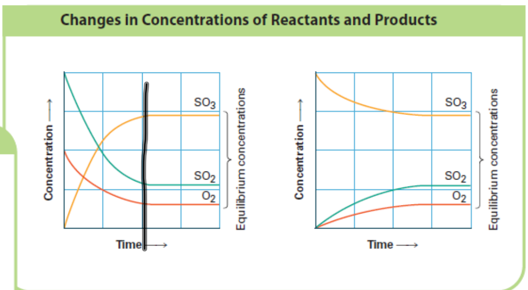
18.2-Reversible Reactions and Equilibrium p. 549

Vocabulary
- reversible reaction
- chemical equilibrium
- equilibrium position
- Le Chatelier's principle
- equlibrium constant

Consider $2SO_2 + O_2 \rightleftharpoons 2SO_3$

- the arrows indicate that the reaction can proceed in both directions
- sulphur dioxide and oxygen can combine to make sulfur trioxide and sulfur trioxide can decompose to make sulfur dioxide and oxygen
- initially, NO SO_3 is present and the 'rate' of formation is quite high
- at equlibrium, the rates level off
- NO net change occurs in the actual amounts of the components of the system

Fig 18.10-p. 550



Note: Slope = 'rate'

-the 'equilibrium position' appears to favour the production of SO_3

INTERPRETING GRAPHS

a. Navigate Where on the graphs can you find the initial concentrations of the reactants and products? The equilibrium concentrations?
b. Read Which gas is most abundant at equilibrium?
c. Interpret How do the equilibrium concentrations of O_2, SO_2, and SO_3 compare?

Factors Affecting Equilibrium-Le Chatelier's Principle

- Le Chatelier's Principle states:

when the equilibrium of a system is disturbed, the system adjusts the amounts of reactants and products to re-establish another equilibrium position.

- these stresses might include
  > changes in concentration of either reactants or products
  > changes in temperature
  > changes in pressure

Concentration

- changing the concentration of any reactant or product disturbs the equilibrium
- the system therefore reacts to minimize the effects of the change

$$\underset{<1\%}{H_2CO_3(aq)} \underset{\substack{\text{Remove } CO_2 \\ \text{Direction of shift} \rightarrow}}{\overset{\substack{\text{Add } CO_2 \\ \leftarrow \text{Direction of shift}}}{\rightleftharpoons}} \underset{>99\%}{CO_2(aq) + H_2O(l)}$$

Temperature

- increasing temperature, causes the equilibrium to shift in the direction that absorbs heat
- absorbtion of heat, reduces the applied temperature stress from the additional heat energy added.

$$2SO_2(g) + O_2(g) \underset{\substack{\text{Remove heat (cool)} \\ \text{Direction of shift} \rightarrow}}{\overset{\substack{\text{Add heat} \\ \leftarrow \text{Direction of shift}}}{\rightleftharpoons}} 2SO_3(g) + \text{heat}$$

Pressure

- a change in the pressure of a system only affects the gaseous components
- since an increase in pressure will increase the concentration of components momentarily, the equilibrium shifts in a direction that produces FEWER gas molecules

$$N_2(g) + 3H_2(g) \underset{\text{Reduce pressure} \atop \leftarrow \text{Direction of shift}}{\overset{\text{Increase pressure} \atop \text{Direction of shift} \rightarrow}{\rightleftharpoons}} 2NH_3(g)$$

CONCEPTUAL PROBLEM 18.1

Applying Le Châtelier's Principle

What effect do each of the following changes have on the equilibrium position for this reversible reaction?

$$PCl_5(g) + \text{heat} \rightleftharpoons PCl_3(g) + Cl_2(g)$$

a. addition of Cl_2

b. increase in pressure

c. removal of heat

d. removal of PCl_3 as it is formed

Practice Problem

6. How is the equilibrium position of this reaction affected by the following changes?

$$C(s) + H_2O(g) + \text{heat} \rightleftharpoons CO(g) + H_2(g)$$

a. lowering the temperature
b. increasing the pressure
c. removing hydrogen
d. adding water vapor

Equilibrium Constants

- chemists refer to equilibrium positions numerically

Consider the following general reaction expression

$$aA + bB \rightleftharpoons cC + dD$$

moles of reactants A and B

moles of products C and D

Equilibrium Constant Expression

$$K_{eq} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

If $K_{eq} > 1$, products are favoured
If $K_{eq} < 1$, reactants are favoured

SAMPLE PROBLEM 18.1

Expressing and Calculating K_{eq}

The colorless gas dinitrogen tetroxide (N_2O_4) and the dark brown gas nitrogen dioxide (NO_2) exist in equilibrium with each other.

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

A liter of a gas mixture at equilibrium at 10°C contains 0.0045 mol of N_2O_4 and 0.030 mol of NO_2. Write the expression for the equilibrium constant and calculate the equilibrium constant (K_{eq}) for the reaction.

$$\frac{(NO_2)^2}{N_2O_4} = \frac{(0.03\ mol/L)^2}{0.0045\ mol/L} = \frac{0.0009}{0.0045}$$

$$K_{eq} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

K_{eq} = = 0.2

Practice Problems p. 557

7. The reversible reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ produces ammonia, which is a fertilizer. At equilibrium, a 1-L flask contains 0.15 mol H_2, 0.25 mol N_2, and 0.10 mol NH_3. Calculate K_{eq} for the reaction.

8. For the same mixture, under the same conditions described in Problem 7, calculate K_{eq} for $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$. How is the K_{eq} for a forward reaction related to the K_{eq} for a reverse reaction?

Practice Problems p. 559

9. Suppose the following system reaches equilibrium.

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

Analysis of the equilibrium mixture in a 1-L flask gives the following results: $N_2 = 0.50$ mol, $O_2 = 0.50$ mol, and $NO = 0.020$ mol. Calculate K_{eq} for the reaction.

10. At 750°C the following reaction reaches equilibrium in a 1-L flask.

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

Analysis of the equilibrium mixture gives the following results: $H_2 = 0.053$ mol, $CO_2 = 0.053$ mol, $H_2O = 0.047$ mol, and $CO = 0.047$ mol. Calculate K_{eq} for the reaction.

Special Case Equilibrium Expressions

- by convention, equilibrium expressions ONLY include substances which can vary in concentration
- therefore,
  - > solids are never included
  - > gases and aqueous ions are always included
  - > 'pure' liquids are never included
  - > 'mixtures' of liquids are always included

Examples

a) $2 C_{(s)} + 3 H_{2(g)} \rightleftharpoons C_2H_{6(g)}$

(e) $K_{eq} = \frac{[C_2H_6]}{[H_2]^3}$

b) $Pb^{2+}_{(aq)} + 2 Br^-_{(aq)} \rightleftharpoons PbBr_{2(s)}$

$K_{eq} = \frac{1}{[Pb^{2+}][Br^-]^2}$

Equilibrium Calculations

"ICE" tables
Initial, Change, Equilibrium

EXAMPLE

1 mole of N_2O_4 is introduced into a 1L container. After equilibrium was established, only 0.8moles of N_2O_4 remained. What is the value of K_{eq} for this reaction?

ALWAYS use equilibrium concentrations for K_{eq}

Reaction

$$N_2O_4 \rightleftharpoons 2NO_2$$

	N_2O_4	$2NO_2$
Initial	1.0	0.0
Change	−0.2	+0.4
Equilibrium	0.8	+0.4

$$Keq = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.4)^2}{0.8} = 0.2$$

EXAMPLE

A 10L container is filled with 4 moles of SO_2, 2.2 moles of O_2 and 5.6 moles of SO_3. The gases react according to the following equation:

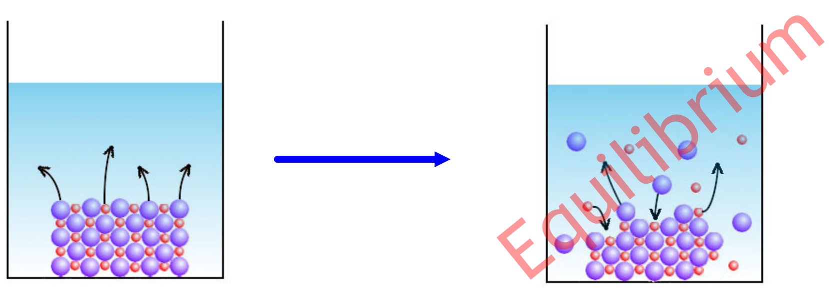
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

At equilibrium, the bulb was found to contain 2.6 moles of SO_2. Calculate the K_{eq} for this reaction.

	$2SO_2(g)$	$O_2(g)$	$2SO_3(g)$
Initial	0.4	0.22	0.56
Change	−0.14	−0.07	+0.14
Equilibrium	0.26	0.15	0.70

$$K_{eq} = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(0.70)^2}{(0.26)^2(0.15)} = 48$$

18.3-Solubility Equilibrium p. 560



Salt is initially put into the water and begins dissolving.

Eventually, the rate of dissolution will equal the rate of precipitation. The solution will be in equilibrium, but the ions wil continue to dissolve and precipitate.

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

1 mol of NaCl will produce 1 mol of Na^+ ions and 1 mol of Cl^- ions.

$$Keq = \frac{[Na^+][Cl^-]}{[NaCl]}$$ therefore $$Ksp = [Na^+][Cl^-]$$

This value NEVER changes (solid) therefore it is worked into the calculations of the solubility product.

The smaller the value of Ksp, the more insoluble the substance is.

What is the K_{sp} expression for the dissociation of $MgBr_2$

(2+) (2-)

$$MgBr_{2(s)} \rightarrow Mg^{2+}_{(aq)} + 2Br^{-}_{(aq)}$$

$$K_{sp} = [Mg^{2+}][Br^{-}]^2$$

NB: 1mol of $MgBr_2$ will dissociate to produce 1mol of Mg^{2+} and 2mol of Br^-

Table 18.1

p. 561

Solubilities of Ionic Compounds in Water

Compounds	Solubility	Exceptions
Salts of Group 1A metals and ammonia	Soluble	Some lithium compounds
Ethanoates, nitrates, chlorates, and perchlorates	Soluble	Few exceptions
Sulfates	Soluble	Compounds of Pb, Ag, Hg, Ba, Sr, and Ca
Chlorides, bromides, and iodides	Soluble	Compounds of Ag and some compounds of Hg and Pb
Sulfides and hydroxides	Most are insoluble	Alkali metal sulfides and hydroxides are soluble. Compounds of Ba, Sr, and Ca are slightly soluble.
Carbonates, phosphates, and sulfites	Insoluble	Compounds of the alkali metals and of ammonium ions

Table 18.2

Solubility Product Constants (K_{sp}) at 25°C p. 562

Salt	K_{sp}	Salt	K_{sp}	Salt	K_{sp}
Halides		**Sulfates**		**Hydroxides**	
$AgCl$	1.8×10^{-10}	$PbSO_4$	6.3×10^{-7}	$Al(OH)_3$	3.0×10^{-34}
$AgBr$	5.0×10^{-13}	$BaSO_4$	1.1×10^{-10}	$Zn(OH)_2$	3.0×10^{-16}
AgI	8.3×10^{-17}	$CaSO_4$	2.4×10^{-5}	$Ca(OH)_2$	6.5×10^{-6}
$PbCl_2$	1.7×10^{-5}	**Sulfides**		$Mg(OH)_2$	7.1×10^{-12}
$PbBr_2$	2.1×10^{-6}	NiS	4.0×10^{-20}	$Fe(OH)_2$	7.9×10^{-16}
PbI_2	7.9×10^{-9}	CuS	8.0×10^{-37}	**Carbonates**	
PbF_2	3.6×10^{-8}	Ag_2S	8.0×10^{-51}	$CaCO_3$	4.5×10^{-9}
CaF_2	3.9×10^{-11}	ZnS	3.0×10^{-23}	$SrCO_3$	9.3×10^{-10}
Chromates		FeS	8.0×10^{-19}	$ZnCO_3$	1.0×10^{-10}
$PbCrO_4$	1.8×10^{-14}	CdS	1.0×10^{-27}	Ag_2CO_3	8.1×10^{-12}
Ag_2CrO_4	1.2×10^{-12}	PbS	3.0×10^{-28}	$BaCO_3$	5.0×10^{-9}

SAMPLE PROBLEM 18.3

Finding the Ion Concentrations in a Saturated Solution

What is the concentration of lead ions and chromate ions in a saturated lead chromate solution at 25°C? ($K_{sp} = 1.8 \times 10^{-14}$)

Analyze ***List the knowns and the unknowns.***

Knowns

- $K_{sp} = 1.8 \times 10^{-14}$
- $K_{sp} = [Pb^{2+}] \times [CrO_4^{2-}]$
- $PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$

Unknowns

- $[Pb^{2+}] = ?\ M$
- $[CrO_4^{2-}] = ?\ M$

For each Pb^{2+} ion formed, one CrO_4^{2-} ion is formed.

$$K_{sp} = [Pb^{2+}][CrO_4^{2-}] = [Pb^{2+}][Pb^{2+}] = [Pb^{2+}]^2$$

$$[Pb^{2+}] = \sqrt{1.8 \times 10^{-14}}\ M$$

$$[Pb^{2+}] = 1.34 \times 10^{-7}\ M = [CrO_4^{2-}]$$

Practice Problems p. 562

17. Lead(II) sulfide (PbS) has a K_{sp} of 3.0×10^{-28}. What is the concentration of lead(II) ions in a saturated solution of PbS?

18. What is the concentration of calcium ions in a saturated calcium carbonate solution at 25°C? ($K_{sp} = 4.5 \times 10^{-9}$)

$K_{sp} = [Pb^{2+}][S^{2-}]$
$= [Pb^{2+}][Pb^{2+}]$
$= [Pb^{2+}]^2$
$[Pb^{2+}] = \sqrt{3 \times 10^{-28}}$
$[Pb^{2+}] = 1.73 \times 10^{-14}$

18. $K_{sp} = [Ca^{2+}][CO_3^{2-}] = 4.5E{-9}$
$= [Ca^{2+}][Ca^{2+}] = [Ca^{2+}]^2 = 4.5E{-9}$
$Ca^{2+} = \sqrt{4.5E{-9}}$
$Ca^{2+} = CO_3^{2-} = 6.7E{-5}\,M$

Common Ion Effect

Consider the following reaction representing the saturated solution of Lead II chromate at equilibrium:

$$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq) \quad K_{sp} = 1.8 \times 10^{-14}$$

What would happen if lead nitrate were added to the system?

- The $[Pb^{2+}]$ would increase, therefore upsetting the equilibrium.
- Le Chatelier's Principle would suggest that the 'stress' from the additional Pb^{2+} ions would cause a shift to the left, producing more PbCrO4(s)
- This $PbCrO_4$ 'precipitates' out as a visible solid.
- We can use the known K_{sp} values to predict if a substance will precipitate

Called the 'common ion effect'

If the product of the concentrations of two ions in a mixture is greater than the K_{sp} of the compound formed from the ions, a precipitate will form.

Part C Problem

Answer the following in the space provided.

8. Will a precipitate form when 0.00070 mol Na_2CO_3 is mixed with 0.0015 mol $Ba(OH)_2$ in one liter of solution? Assume that these two salts both dissolve completely. Refer to Table 18.2 in your textbook.

Table 18.2

Alkali metal hydroxides are ***SOLUBLE***
Therefore the potential ppt is the $BaCO_3$

Part C Problem

8. $[CO_3^{2-}] = 0.00070M$

$[Ba^{2+}] = 0.0015M$

$[CO_3^{2-}] \times [Ba^{2+}]$

$= (7.0 \times 10^{-4}M) \times (1.5 \times 10^{-3}M)$

$= 1.1 \times 10^{-6}$

Precipitation occurs because the ion product (1.1×10^{-6}) is greater than the K_{sp} of $BaCO_3$ (5.0×10^{-9}).