

## Reaction Kinetics

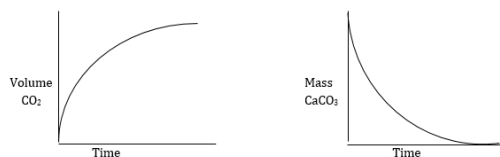
AP Chemistry 30

### Reaction Rate

- **Rate:** measure of how frequently particles are changing from reactants to products
- Measured as **decrease in concentration of reactants per unit time** or an **increase in concentration of products per unit time**.
- Units: mol/L·s, g/s, L/s, etc.

### Sample Reaction Rates

- Each of these changes could be graphed, and would look like this:



## Chemical Reactions

- **Chemical reaction:** process in which chemical species react to form new substances
- Reactants change into products
- Ability to meet criteria for successful reaction determines rate of reaction

### Reaction Rate



- Rate can be determined by:
  - Volume change (since a gas is produced):
 
$$\text{rate} = \frac{\Delta V}{t}$$
  - Mass change (as solid  $\text{CaCO}_3$  reacts):
 
$$\text{rate} = \frac{\Delta m}{t}$$
  - Concentration change (of HCl or  $\text{CaCl}_2$ ):
 
$$\text{rate} = \frac{\Delta[\text{HCl}]}{t} \text{ or } \text{rate} = \frac{\Delta[\text{CaCl}_2]}{t}$$

### Reaction Rates

- All reactions begin rapidly, then slow down, due to availability of reactant particles
- To determine the **instantaneous rate:** find slope of tangent on graph
- To determine **average rate:** find slope between two points

## Review: Particle Theory

- All matter is made of particles (atoms, molecules and ions).
- Particles have empty space between them and are constantly in motion.
- As energy is added to particles, they move faster and spread further apart.

## Collision Theory

What needs to happen for reactant particles to start reacting?

This is explained by collision theory.

Reactant particles need:

- To collide (hit each other)
- To be in the correct orientation (collide in the correct way)
- To have enough energy for the bonds to break (kinetic energy – need to be going fast enough)

## Collision Theory

What happens when reactant particles successfully collide?

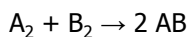
- Particles bond together in very unstable (high potential energy) transition state called the activated complex (AC)
- The particles in the AC are very weakly bonded, which makes it extremely easy to break apart

## Collision Theory

How are products formed?

- AC breaks apart into either products or reactants – each option is equally likely to occur
- Considered a transition state – cannot stay in this form (too unstable)

## Collision Theory Diagram

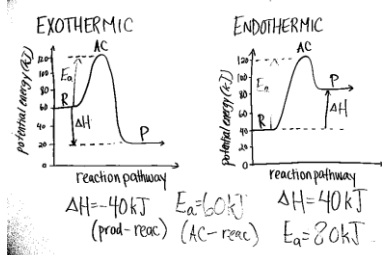


## Activation Energy

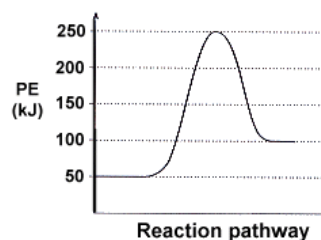
- **Activation energy:** minimum amount of energy needed for reactant particles to form the activated complex
- AC is a high energy state – absorbs free energy from system to form
- Reactions with high AE will have fewer successful collisions – very slow or very few products

## Energy Diagrams

- Energy diagrams can be used to model the energy level in the system for a chemical process.



## Example 1: Energy Diagram



## Example 2: Energy Diagram

Sketch an energy diagram in which the reactants start at 40 kJ,  $\Delta H$  is  $-20 \text{ kJ}$  and the activation energy is  $60 \text{ kJ}$ .

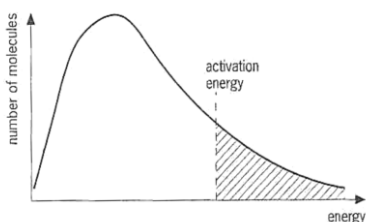


## Maxwell-Boltzmann Distribution Curve

- Shows **number of particles** in a system based on their **kinetic energy**
- Temperature is an average of the kinetic energy of the particles, some lower and some higher than average
- When temperature is changed, so is shape of graph

## Maxwell-Boltzmann Distribution Curve

- Note that energy value never touches y-axis; molecules cannot have zero energy!



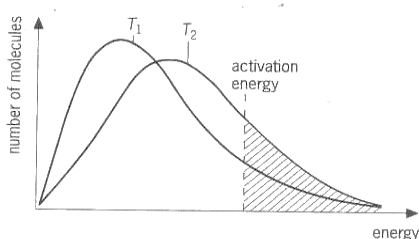
## Rate-Determining Factors

### Temperature

- Higher temperatures increase reaction rate.
- Increases kinetic energy of the particles in the system – more particles have enough energy to react
- More molecular motion = more collisions

## Rate-Determining Factors

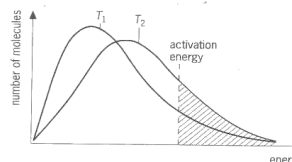
### Temperature



## Example: Rate-Determining Factors

What would happen to the reaction rate if the temperature was:

- Increased to a higher temperature than  $T_2$ ?
- Decreased to a lower temperature than  $T_1$ ?

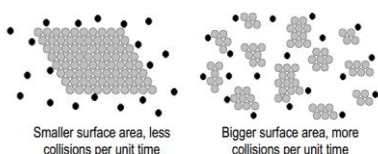


## Rate-Determining Factors

### Surface Area

More surface area increases reaction rate.

- More access between reactant particles = more collisions



## Rate-Determining Factors

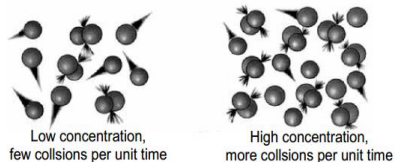
### Concentration

Higher concentration increases reaction rate

- More reactant particles = more collisions

## Rate-Determining Factors

### Concentration



## Rate-Determining Factors

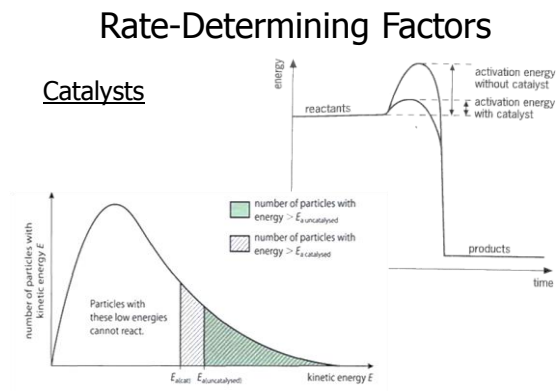
### Catalysts

- **Catalyst:** a substance that increases the rate of a reaction without being consumed by the reaction
- **Inhibitor:** opposite of a catalyst; slows down reaction rate without being consumed

## Rate-Determining Factors

### Catalysts

- Lowers the activation energy of the reaction; more reactant molecules have enough energy to react



## Rate-Determining Factors

### In General

- Anything that increases the number of collisions will increase the rate of the reaction
- By increasing the number of collisions between reactant molecules, there is more chance of having successful collisions that result in the formation of the products

## Rate Laws

- **Rate law:** mathematical expression that relates concentration of reactants to rate
- General form:

$$\text{rate} = k[A]^m[B]^n[C]^p\dots$$

where:

k is a **specific rate constant**

[A], [B]... are molar concentrations of reactants  
m, n, p... are exponents, usually positive integers

## Rate Laws

- Rate constant depends on temperature and surface area of reactants, but will not change with concentration
- Rate law must be determined experimentally

## Reaction Order

- Reaction order of a reactant is its exponent in rate equation - describes how rate is affected by that reactant.
- Overall reaction order is sum of all exponents in the rate equation
- For the general reaction rate:

$$\text{Rate} = k[A]^m[B]^n,$$

the rate order is  $m + n$ .

## Reaction Order

- **Zero order:** reactant concentration has no effect on rate, rate = k
- **First order:** rate is directly proportional to reactant concentration, rate = k[A]  
– Example: nuclear decay
- **Second order:** rate is quadrupled with [reactant] is doubled, rate = k[A]<sup>2</sup> or =k[A][B]

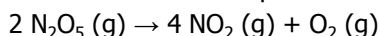
### Example: Differential Rate Law

Use the data to determine the exponents m and n in the general reaction rate law. What order is the reaction with respect to A, B and overall?

Initial Rates for aA + bB → products			
Trial	Initial [A] (mol/L)	Initial [B] (mol/L)	Initial Rate (mol/L.s)
1	0.100	0.100	2.00 × 10 <sup>-3</sup>
2	0.200	0.100	4.00 × 10 <sup>-3</sup>
3	0.200	0.200	16.0 × 10 <sup>-3</sup>

### Example: Integrated Rate Laws

The decomposition of N<sub>2</sub>O<sub>5</sub> in the gas phase was studied at constant temperature.



Time (s)	[N <sub>2</sub> O <sub>5</sub> ]
0	0.1000
50	0.0707
100	0.0500
200	0.0250
300	0.0125
400	0.00625

## Types of Rate Laws

- **Differential rate law:** determined using initial rate and initial reactant concentration data (before stuff gets “messy”)
- **Integrated rate law:** determined from concentration and time data, using graphical methods

## Integrated Rate Laws

- Work with data to get a linear concentration-time graph
- Three options:

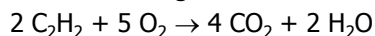
Graph	Order	Formula
[A] vs t	Zero	[A] = -kt + [A <sub>0</sub> ]
ln[A] vs t	First	ln[A] = -kt + ln[A <sub>0</sub> ]
1/[A]	Second	1/[A] = kt + 1/[A <sub>0</sub> ]

### Example, continued...

- Determine the rate law and calculate the value of k.
- Determine [N<sub>2</sub>O<sub>5</sub>] at 250 s. Does this make sense?
- Determine [N<sub>2</sub>O<sub>5</sub>] at 600 s. Does this make sense?

## Thinking Activity

Consider the following reaction:



## How Reactions Really Happen

- More complex reactions actually undergo a series of simple reactions, simultaneously
- Different particles that are not products or reactants are in existence for a brief period of time – **reaction intermediates**
- “Best guesses” – determined experimentally and must agree stoichiometrically and with rate law

## Elementary Steps

- **Elementary step:** simple reaction occurring for one or two particles

Elementary Step	Molecularity	Rate Expression
A → products	Unimolecular	rate = k[A]
A + B → products	Bimolecular	rate = k[A][B]
A + A → products	Bimolecular	rate = k[A] <sup>2</sup>
2A + B → products	Termolecular (rare)	rate = k[A] <sup>2</sup> [B]

## Elementary Steps

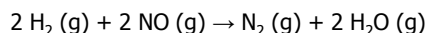
- For an elementary step, the rate law can be written from its molecularity – not true for overall reaction
- i.e. coefficients in reaction translate to exponents in rate law

## Reaction Mechanisms

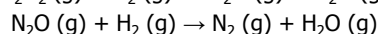
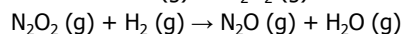
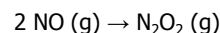
- Each reaction step has a different reaction rate, depending on the complexity of the molecules and how much energy they have
- Slowest step is **rate-determining step**, because it sets the pace of the whole reaction

## Example: Reaction Mechanism

For this reaction:

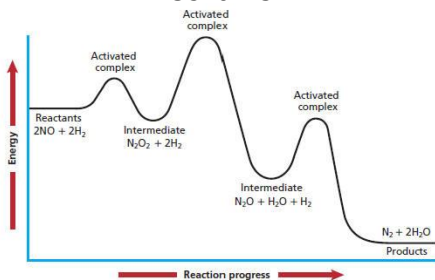


One possible mechanism is:



- Determine molecularity and rate law for each step.
- Show how the sum of these steps yield the net reaction.

## Energy Diagram for Reaction Mechanism

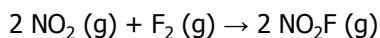


## Rate-Determining Step

- Dictates overall rate of reaction
- Rate law of slowest step is identical to experimental rate law

## Example: Rate-Determining Step

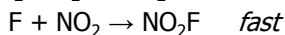
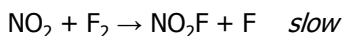
For this reaction:



The experimentally determined rate law is:

$$\text{rate} = k[\text{NO}_2][\text{F}_2]$$

A suggested mechanism is:



Is this a valid mechanism?

## Catalysts and Intermediates

- Catalysts are used early in reaction mechanism (reactant) and regenerate (product) in a later step
- Intermediates are produced early in the reaction (product) and are used up (reactant) in a subsequent step
- Both will **not** appear in the net reaction

## Example: Catalysts/Intermediates

Determine all intermediates, catalysts and the net reaction:

Step 1:	$\text{A}_2 (\text{g}) \rightarrow 2 \text{A}(\text{g})$
Step 2:	$2 \text{A}(\text{g}) + 2 \text{B} (\text{g}) \rightarrow 2 \text{AB}(\text{g})$
Step 3:	$2 \text{AB}(\text{g}) + \text{C}_2(\text{g}) \rightarrow 2 \text{ABC}(\text{g})$
Step 4:	$2 \text{ABC}(\text{g}) \rightarrow 2 \text{AC}(\text{g}) + 2 \text{B}(\text{g})$