AP Chemistry

Kinetics

1. Predict and explain how the rate of a reaction is affected by:
   - (a) temperature changes
   - (b) concentration changes
   - (c) surface area
   - (d) use of a catalyst
2. Given experimental data (conc. vs. rate) for a given reaction,
   - (a) determine the experimental rate law
   - (b) determine the value of the specific rate constant k, and specify its units
   - (c) calculate new rates or concentrations using the rate law
3. For a given reaction, determine the relative rate of appearance of a product, or disappearance of a reactant.
4. Describe the role that the activation energy plays in the rate of a reaction. (transition state theory) (activated complex model)
5. Given appropriate graphical data, determine the order of a reactant. Use the graph to determine the value of k.
6. Apply the concept of half-life to 1st order reactions. Use graphical data to determine the half-life of a given reaction.
7. Using appropriate graphical information, determine the E_{act} for a given reaction in both the forward and reverse directions.
8. Using collision theory, predict and explain the effect on the rate of reaction related to:
   - (a) temperature changes
   - (b) concentration changes
   - (c) stearic effects
   - (d) E_{act} differences
   - (e) using a catalyst
9. Given a specific reaction and the experimental rate law, develop a simple mechanism for the reaction. Be able to justify your mechanism by showing the relationship between the slow step and the rate law.

Chemical Kinetics

Key Ideas:

Kinetics

- Chemical kinetics is the study of the speed or rate of a reaction under various conditions.

Spontaneity

- Will the given reaction happen over time? (Is the reaction spontaneous?)
- Has nothing to do with the speed of the reaction.
- A reaction may be spontaneous, but may take a million years to happen.

A mechanism is a sequence of events at the molecular level that controls the speed and outcome of the reaction.

- Slowest step controls the process.

KINETICS AND CONDITIONS

The following conditions affect the speed of a chemical process:

Concentration of reactants

- More molecules imply more collisions
- More collision ➔ faster reaction

Temperature

- Heat up the substances ➔ higher average kinetic energy
- Higher kinetic energy ➔ more speed of the molecules
- More speed ➔ more energetic collision
- More collision ➔ faster reaction

Catalysts

- Accelerate chemical reactions but are not themselves transformed
- Lowers the activation energy of the reaction ➔ more molecules have the required activation energy to have the reaction take place
- Arrange geometry of the molecules so that the collisions are more favorable.
- Biological catalysts are called enzymes
- The opposite of a catalyst is called an inhibitor.

- **Surface area of reactants**
    - more surface → more place for reaction to take place.
    - surfaces affect speed
    - solutions provide the maximum exposure for surface area

REACTION RATES

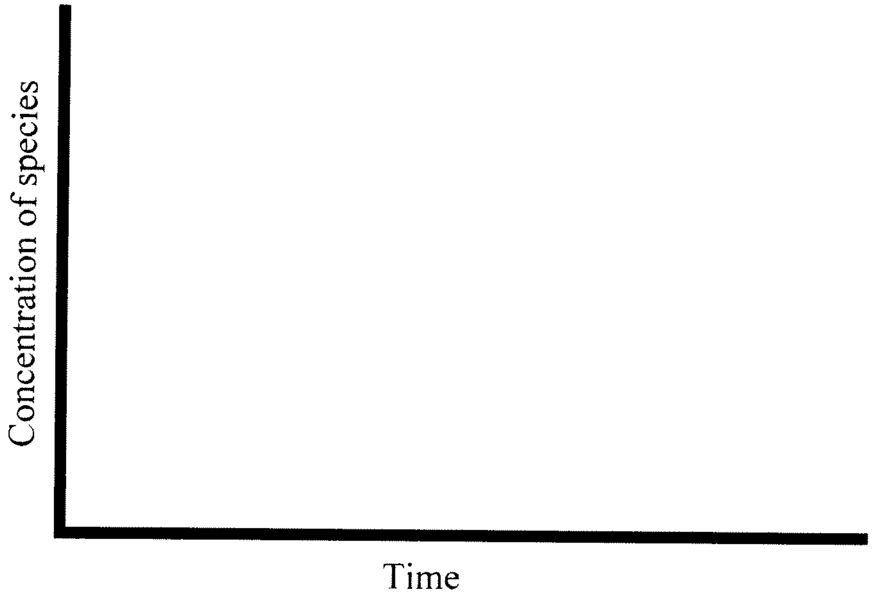
The speed of a reaction is expressed in terms of its **RATE.**

Example:

If 2 moles of PCl_3 and 1 mole of Cl_2 combine to make PCl_5 according to the equation below:

$$PCl_3 + Cl_2 \leftrightarrow PCl_5$$

draw the graph of the concentration of the species versus time.



Rate = change of concentration divided by the change of time.

$$\boxed{\text{Rate} = \frac{\Delta\,[\text{ concentration}]}{\Delta\,\text{time}}}$$

Reaction Rate

1. expressed as the change (Δ)in concentration of a reagent per unit time
2. focus either on the disappearance of reactants or the appearance of products
3. rate of change (Δ) of a reactant is always *negative*
4. rate of change (Δ) of a product is always *positive*

Instantaneous Rates

1. The rate of change at any give time.
2. Two ways to find it:
    a. Draw tangent line to the curve at that point and find the slope.
    b. For calculus students, take derivative: dy/dt

Consider the reaction $2\ H_2O_{2(g)} \rightarrow O_{2(g)} + 2\ H_2O_{(g)}$

1) Use the mole ratios to determine the relative rates.
    a) oxygen can appear only half as rapidly as the peroxide disappears (1:2 mole ratio)
    b) water forms at the same rate as hydrogen peroxide disappears (2:2 mole ratio)
2) Rate of reaction
    a) Ignore the algebraic sign on the value of the rate.
    b) Divide the rate of change in concentration of each reactant by its stoichiometric coefficient in the balanced equation.

$$\text{rate of reaction} = \frac{\Delta[\text{oxygen}]}{\Delta\ \text{time}} = \frac{-1}{2}\ \frac{\Delta[\text{peroxide}]}{\Delta\ \text{time}}$$

3) The rate of reaction is equal to
    a) the rate of change of oxygen
    b) -1/2 the rate of change of hydrogen peroxide

Method of Initial Rates

1. Initial reaction rates
    a. begin with pure reactants
    b. mix thoroughly
    c. then measure speed of reaction over time as close to time = zero as possible
    d. see Lab 18
2. Presence of products can alter results dramatically, so initial reaction rates are used.

RATE EXPRESSIONS

Key Idea: Rate expression or rate law is the relation between reaction rate and the concentrations of reactants given by a mathematical equation.

THE RATE EXPRESSION or the RATE LAW is a mathematical equation that relates the initial rates to the reactant concentrations (and/or the catalyst).

> **NOTE: The RATE LAW MUST BE DETERMINED EXPERIMENTALLY**. The stoichiometry of the reaction does not figure into the rate law.

Given the equation: $a\,A + b\,B \xrightarrow{\text{catalyst}} p\text{ Product}$

where C is the catalyst, the rate expression will *always* have the form:

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

where:

- k = rate constant
- [A] = concentration of reactant A
- [B] = concentration of reactant B
- [C] = concentration of the catalyst
- m = order of reaction for reactant A
- n = order of reaction for reactant B
- p = order of reaction for the catalyst C

Exponents can be zero, whole numbers (positive or negative) or fractions AND MUST BE DETERMINED EXPERIMENTALLY

THE RATE CONSTANT, *k*

1) temperature dependent
2) must be evaluated by experiment.

THE ORDER OF A REACTION

1) order with respect to a certain reactant is the *exponent* on its concentration term in the rate expression
2) overall order of the reaction is the sum of all the exponents on all the concentration terms in the expression
3) zero order rate {rate = $k\,[A]^0$}
   a) independent of the reactants concentration

4) first order {rate = $k\,[A]^1$}
   a) rate is directly proportional to the reactants concentration
   b) doubling [A] → doubles rate
5) second order {rate = $k\,[A]^2$}
   a) when [A] is doubled → rate is quadrupled ($[2A]^2 = 4[A]^2$)
   b) when [A] is tripled → rate is increased by a factor of 9 ($[3A]^2 = 9[A]^2$)
6) fractional orders are EXTREMELY RARE !!!
7) if order is negative:
   a) then it inhibits the reaction (slows it down)
   b) EXTREMELY RARE on AP exam!

DETERMINATION OF THE RATE EXPRESSION

Given the equation: a A + b B → x X
initial rate = $k[A]_o^m[B]_o^n$ (the little subscript Ao means original)
or simply written: rate = $k\,[A]^m[B]^n$

[A] mol/L	[B] mol/L	Initial Rate (mol/L x sec)
0.08	0.04	1.25×10^{-5}
0.04	0.04	6.25×10^{-6}
0.08	0.02	3.13×10^{-6}

First thing to do is to make sure that all of the exponents are the same on the initial rates → change them if you have to.

[A] mol/L	[B] mol/L	Initial Rate (mol/L x sec)
0.08	0.04	12.5×10^{-6}
x 2 0.04	0.04	x 2 6.25×10^{-6}
0.08	0.02	3.13×10^{-6}

How to find the order and write the rate law
1) To find the order with respect to A
   a) find two trials where A changes and B remains constant
   b) use trials one and two
   c) A doubles (2 x A) and I.R. goes up by two.
      i) Ask yourself this: $2^? = 2$
      ii) ? = 1
      iii) Order of A is 1st order.
   d) Since A is first order…
      i) triple A and the rate goes up by $3^1 = 3$
      ii) half A and the rate goes down by $(\frac{1}{2})^1 = \frac{1}{2}$

[A] mol/L		[B] mol/L		Initial Rate $molL^{-1}sec^{-1}$
0.08		0.04		12.5×10^{-6}
0.04	x 2	0.04	x 4	6.25×10^{-6}
0.08		0.02		3.13×10^{-6}

2) Find the order with respect to B
    a) find two trials where A changes and B remains constant
    b) use trials one and three
    c) B doubles (2 x B) and I.R. goes up by four.
        i) Ask yourself this: $2^{?} = 4$
        ii) ? = 2
        iii) Order of B is 2nd order
    d) Since B is second order…
        i) triple B and the rate goes up by $3^2 = 9$
        ii) half B and the rate goes down by $(½)^2 = ¼$
3) The rate law is: rate = $k\,[A][B]^2$
4) The overall order of the reaction is 2 + 1 = 3
    a) triple B triple A, then the rate goes up by $(3^2)(3^1) = (3^3) = 27$
    b) It is easier is to use the overall order $3^3 = 27$
5) To find the value of the rate constant, *k*
    a) take any trial and plug numbers in to the rate law
    b) values of the rate constant should not be different for different trials
    c) units are always:

$$\boxed{\frac{\text{liters}^{(\text{overall order} - 1)}}{\text{moles}^{(\text{overall order} - 1)} \text{ x (the unit for time)}}}$$

Solving for the value of the rate constant.

Rate = $k\,[A][B]^2$ {Using trial three}

$$3.13 \times 10^{-6} = k\,[0.08][0.02]^2 \rightarrow k = \frac{0.0978\ L^2}{mol^2 \text{ x sec}}$$

CONCENTRATION/TIME RELATIONSHIPS

If you want to know how long a reaction must proceed to reach a predetermined concentration of some reagent; then you can construct graphs or derive an equation that relates concentration to time.

FIRST ORDER REACTIONS

The initial reaction rate = $k[A]^1$. If the reaction is first order with respect to A, then the integrated rate law is

$$\boxed{\ln \frac{[A]}{[A]_o} = -kt}$$

Can also be written as $\ln [A] - \ln[A]_o = -kt$ (using your logarithm properties).

SECOND ORDER REACTION

Initial reaction rate = $k[A]^2$. If the reaction is second order with respect to A, then the integrated rate law is

$$\boxed{\frac{1}{[A]} - \frac{1}{[A]_o} = kt}$$

HALF-LIFE, $t_{1/2}$

Half-life, the time required for one half of one of the reactants to disappear. Let's develop an equation that relates k and $t_{½}$. Knowing that half-life is the time it takes for one-half of the sample to disappear, we get the following relationship:

$$[A] = 2[A]_o \quad \text{or} \quad \frac{[A]}{[A]_o} = \frac{1}{2}$$

Letting the sample sit for exactly one half life (time = $t_{½}$), then using the integrated first order rate law, we have:

$$\ln (1/2) = -kt_{½}$$

For first order reaction we then have:

$$\boxed{t_{½} = \frac{0.693}{k}}$$

For second order reaction the relationship between k and $t_{½}$ is:

$$t_{½} = \frac{1}{k[A]_o}$$

GRAPHICAL METHODS FOR DETERMINING ORDER OF REACTIONS

Taking the first order rate law and rearranging we get:

$$\ln[A] = -k\,t + \ln[A]_o$$

$$\downarrow \quad \downarrow\downarrow \quad \downarrow$$

which is the equation of a line: $y = m\,x + b$

If you graph ln[reactant] vs. time and get a straight line ➔ first order in that reactant. Also, m = $-k$ the slope of the line is *negative*.

Likewise, the second order equation is also a line:

$$1/[A] = k\,t + 1/[A]_o$$

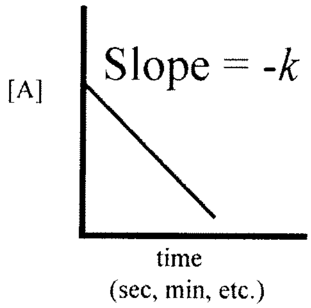
$$\downarrow \quad \downarrow\downarrow \quad \downarrow$$

$$y = m\,x + b$$

If you graph 1/[reactant] vs. time and get a straight line ➔ second order in that reactant. Slope = k the slope is *positive*.

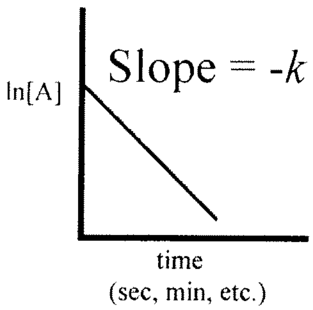
Below is a graphical reminder for zero, first, and second order reactions.

Rate = $k[A]^0$



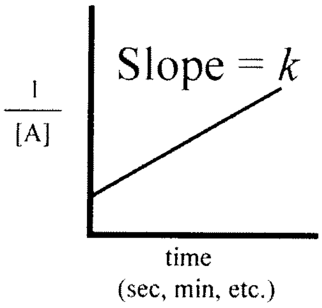
ZERO

rate = $k[A]^1$



FIRST

rate = $k\,[A]^2$



SECOND

Remember: k = |slope|

RATE CHANGES WITH TEMPERATURE

Generally reactions occur more rapidly at higher temperatures than at lower temperatures.

TRANSITION STATE THEORY

- Energy barrier must be overcome
- Activation energy, E*
  - energy a reacting molecule must absorb from its environment in order to react
  - reaction energy diagrams (see the chapter)
- Relationship between kinetics and thermodynamics
  - *endo*thermic
  - *exo*thermic
- **see graphs in the chapter**

COLLISION THEORY

- Assumes molecules must collide in order to react!
- Assumes molecules must have the correct geometry for a favorable collision
  - favorable collision = collision that produces a reaction
- Affected by
  - concentration
    - more reactants = more collisions
  - temperature
    - at higher temperatures
      - molecules move faster
      - collisions occur more frequently
      - collisions are more energetic
      - more likely to collide and produce a favorable reaction
    - more molecules have the required activation energy
  - geometry
    - must collide with correct geometry to produce a reaction
    - catalysts can help speed up a reaction by arranging the collisions in the correct geometry.

Of the three, this is the most important for the increase in temperature.

EFFECT OF TEMPERATURE ON REACTION RATE: ARRHENIUS EQUATION

$$k = \text{reaction rate constant} = Ae^{-E^*/RT}$$

Where:

- R is the 8.31×10^{-3}kJ/K x mol
- A is a constant that deals with the frequency of collisions that have the required geometry. It is called the ***frequency factor***
- $e^{-E^*/RT}$ is always less than 1 and is the fraction of molecules having the minimum energy required for reaction

This equation is used to calculate the value of activation energy given several sets of data that relates k to temperature (i.e. k has been calculated at several different temperatures).

$$k = Ae^{-E^*/RT}$$

By taking the ln of both sides, we arrive at:

$$\ln k = \ln A - (E^*/RT)$$

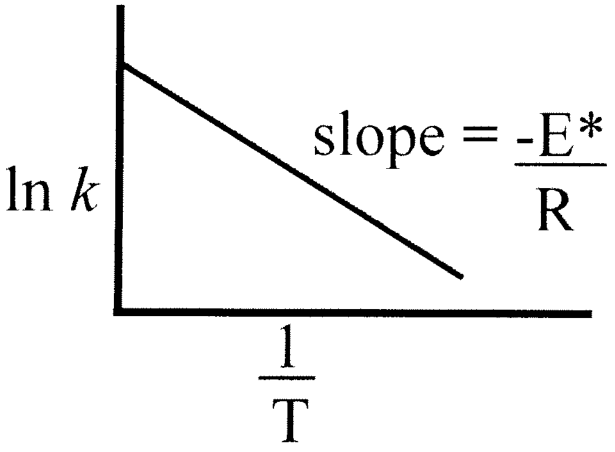
and rearranging to relate ln$k$ to 1/T, we get:

$$\underset{\substack{\Big\downarrow \\ y}}{\ln k} = \underset{\substack{\Big\downarrow \\ m}}{-\frac{E^*}{R}} \; \underset{\substack{\Big\downarrow \\ x}}{(1/T)} + \underset{\substack{\Big\downarrow \\ b}}{\ln A}$$

which is an equation of a line:

thus a graph of ln$k$ versus 1/T will have a downward sloping line with slope of -E*/R.

rule of thumb--rate doubles with every 10 K increase in temp.



REACTION MECHANISMS

The sequence of bond-making and bond-breaking steps that occurs during the conversion of reactants to products.

Must be determined by experiment!

ELEMENTARY STEPS

- molecularity
  - number of molecules that participate in an atomic rearrangement
  - three types
    - unimolecular
    - bimolecular
    - termolecular

RATE EXPRESSIONS FOR ELEMENTARY STEPS

The rate expression cannot be predicted from overall stoichiometry.

Elementary Step Reaction	**Rate Law**
Unimolecular	
[A] → Products	Rate = k [A]
Bimolecular	
[A] + [B] → Products	Rate = k [A][B]
2 [A] → Products	Rate = $k\,[A]^2$
Termolecular	
2 [A] + [B] → Products	Rate = $k\,[A]^2[B]$
[A] + [B] + [C] → Products	Rate = k [A][B][C]

THE PHYSICAL SIGNIFICANCE OF RATE EXPRESSIONS FOR ELEMENTARY STEPS

- the more molecules the more collisions → the faster the rate
- the faster the molecules are moving → the more likely they will collide → the faster the rate

MOLECULARITY AND ORDER

The molecularity of an elementary reaction and its order are the same.
THIS IS NOT TRUE OF THE OVERALL REACTION ORDER!

REACTION MECHANISMS AND RATE EXPRESSIONS

- determined by experiment
- the slowest step is the rate determining step
- reaction intermediate
  - produced in one step but consumed in another
  - can NOT be in the rate law

CATALYSTS

- Alters the mechanism so the activation energy barrier can be lowered.
- Catalysts are not altered during the reaction
  - they serve to lower the activation energy
  - speed up the reaction
- Biological catalysts are enzymes
  - proteins with specific shapes to react with specific molecules
- Heterogeneous
  - the catalyst is in a different phase than reactants
- Homogeneous
  - the catalyst is in the same phase as reactants

Example:

decomposition of hydrogen peroxide is very slow, but speeds up rapidly with light (this is why you store it in a brown bottle).

$$H_2O_2 \xrightarrow{\text{light}} H_2O_{(l)} + O_{2(g)}$$

You can also use MnO_2 – it will not be used up in the reaction

$$H_2O_2 \xrightarrow{MnO_2} H_2O_{(l)} + O_{2(g)}$$