AP Chemistry Ultimate Review Packet
Unit 5: Kinetics

Kinetics is the study of **rates of reaction**
- measures the *change in concentration* of a substance over time (M/s)
- represented by rate expressions: $\Delta[A]/\Delta t$
- rates are negative for reactants as they are being used up
- rates are positive for products as they are forming
- relative rates obey the stoichiometry of the reaction

The relationship between concentration and reaction rate is described by a **rate law**

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

- k is the rate constant
- substances A/B/C are reactants
- exponents m/n/p are typically positive integers
- exponents are **NOT** specifically the stoichiometric coefficients

Exponents in the rate law tell us about the **reaction order**
- if exponent is 0, reaction is *zero order* in that reactant
- if exponent is 1, reaction is *first order* in that reactant
- if exponent is 2, reaction is *second order* in that reactant

To get the overall reaction order we simply add up the individual reactant orders (e.g. first order in reactant A, second order in reactant B, 1 + 2 = third order)

We can determine reaction order experimentally using **initial rates data**
- run a reaction several times using different initial reactant concentrations
- examine trials where one reactant stays the same but the other has a different initial concentration,
- compare change in concentration to change in rate
    - no change in rate = zero order
    - proportional change in rate = first order (e.g. both double)
    - exponential change in rate = second order
      (e.g. concentration doubles, rate quadruples)

For example, given the following data:

trial 1: A = 1 M, B = 1 M, initial rate = 1 M/s
trial 2: A = 2 M, B = 1 M, initial rate = 2 M/s
trial 3: A = 1 M, B = 2 M, initial rate = 4 M/s
1 and 2: A doubles, B stays the same, rate doubles, *first order in A*
1 and 3: A stays the same, B doubles, rate quadruples, *second order in B*
overall: 1 + 2 = 3, reaction is *third order overall* (rate = $k[A][B]^2$)

-concentrations do not need to conveniently double, just compare proportions

We can also determine reaction order using **integrated rate laws**
- collect concentration data over the course of a chemical reaction
- plot concentration vs. time according to three equations:
    - zero order: $[A] = -kt + [A]_0$
    - first order: $\ln[A] = -kt + \ln[A]_0$
    - second order: $1/[A] = kt + 1/[A]_0$
- all of the above follow y = mx + b format (algebraic equation for a line)
- plot all three and whichever gives a **straight line plot** is the reaction order
- on a straight line plot the slope will be either k or -k

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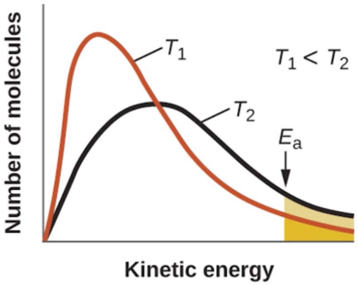
Collision Theory



Chemical reactions can be described by the postulates of **collision theory**

1. rate of reaction is proportional to rate of collisions between reactants
2. molecules must collide in a specific spatial orientation in order to react
3. collisions must occur with sufficient kinetic energy for a reaction to occur

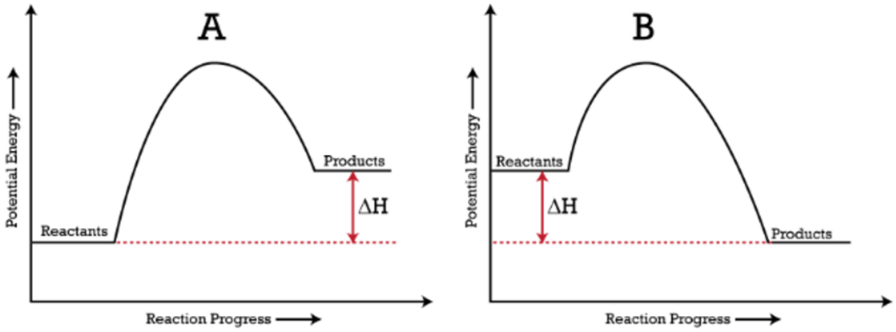
Maxwell-Boltzmann distribution shows the proportion of molecules that have sufficient kinetic energy to get over the **activation energy** (E_a) of the reaction (increases with T)

A balanced chemical equation does not tell us what is happening during a reaction.
We must examine a **reaction mechanism** to understand a chemical reaction on the molecular level:

Overall Reaction: $2O_3 \rightarrow 3O_2$
Elementary Reaction 1: $O_3 \rightarrow O_2 + O$
Elementary Reaction 2: $O + O_3 \rightarrow 2O_2$

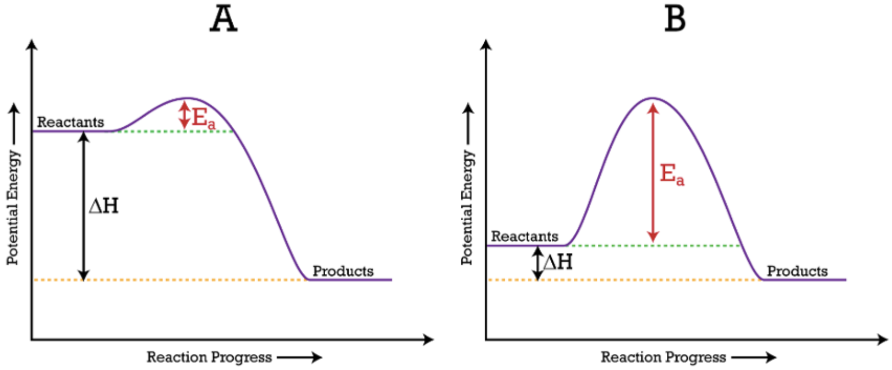
- these include multiple *elementary reactions* which can't be broken down further
- the elementary reactions add up to give the *overall reaction*
- substances not found in the overall reaction are called *intermediates*
- elementary reactions can exhibit differing **molecularity**
  - **unimolecular:** one molecule decomposes (no collision)
  - **bimolecular:** two molecules collide (most common)
  - **termolecular:** three molecules collide (quite rare)
- one elementary reaction will be the slowest or the *rate-determining step*
- if the first step is the RDS we CAN get rate law exponents from its coefficients
- if another step is the RDS we must utilize the steady-state approximation
  - makes the assumption that some intermediate has constant concentration

Energy Diagrams



Energy exchange during a reaction can be depicted visually using an **energy diagram**

- *reactants* are on the left, *products* are on the right
- distance from reactants to products is the **change in enthalpy (ΔH)**
  - products sit higher (A), reaction is **endothermic**, energy is *absorbed*
  - products sit lower (B), reaction is **exothermic**, energy is *released*
- peak of the curve is the *transition state* of the reaction



- distance from reactants to transition state is the **activation energy (E_a)**
  (minimum kinetic energy required for collision to result in reaction)
- E_a can be very small, reaction is very fast, most collisions result in reaction (A)
- E_a can be very large, reaction is very slow, few collisions result in reaction (B)

A **catalyst** is something that lowers the activation energy and thus speeds up the reaction
- catalyst is not used up stoichiometrically and promotes an *alternate pathway*

The **Arrhenius equation** relates the activation energy of a reaction to its rate constant

$$k = Ae^{-Ea/RT}$$

k = rate constant
R = gas constant (8.314 J/mol K)
T = temperature (K)
e = Euler's number (2.71828…)
A = frequency factor (fraction of molecules that surpass the activation barrier)

Nuclear Reactions

In a **chemical reaction** atoms rearrange combinations to form new substances but each atom retains a consistent identity (does not change elements)
In a **nuclear reaction** atoms can transmute from one element to another. Nuclear reactions occur when an atomic nucleus is unstable for some reason:

1. nucleus is too large (proton-proton repulsion outweighs strong nuclear force)
2. proton to neutron ratio is too high or too low (smaller atoms prefer roughly 1:1)

Nuclear decay can produce a variety of particles

proton: p^+ (atomic number = 1, mass = 1)
neutron: n^0 (atomic number = 0, mass = 1)
alpha particle: helium nucleus, 2 p^+ + 2 n^0 (atomic number = 2, mass = 4)
beta particle: electron (atomic number = -1, mass = 0)
positron: antimatter version of the electron (atomic number = 1, mass = 0)
gamma particle: high-energy photon (atomic number = 0, mass = 0)

Nuclear reactions involve *emission/absorption* of these particles and must be balanced

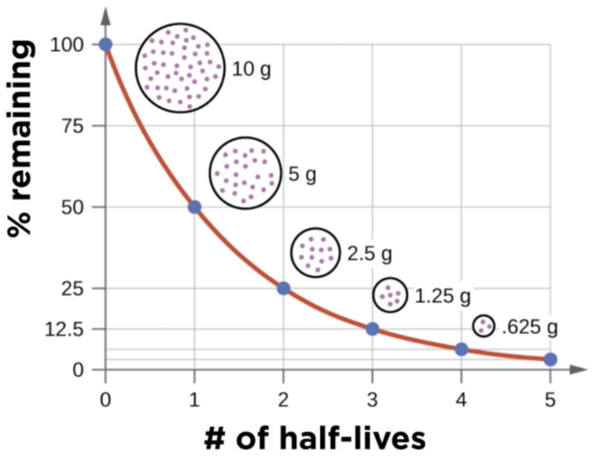
$${}^{212}_{84}\mathrm{Po} \longrightarrow {}^{208}_{82}\mathrm{Pb} + {}^{4}_{2}\mathrm{He}$$

- atomic numbers must add up to the same number on each side (84 = 82 + 2)
- mass numbers must add up to the same number on each side (212 = 208 + 4)

We can describe the time it takes for radioactive material to decay using **half-life**

- time required for sample of radioactive nuclei to be cut in half

  initial: 10 g
  1 half-life: 5 g
  2 half-lives: 2.5 g
  3 half-lives: 1.25 g
  4 half-lives 0.625 g
- it is not the case that after two half-lives have elapsed all the material is gone
- there is a logarithmic relationship (lower concentration = fewer disintegrations)
- example: carbon-14 has a half-life of 5,730 years



The half-life for a first order process is given by $\mathbf{t_{1/2} = 0.693/k}$

$t_{1/2}$ = half-life
k = rate constant