

## Pseudo-Order

- used for simplifying higher order reactions
- can typically be used when one species in a reaction mixture is used in excess (no significant change in reactant)

## Effect of Temperature on Reaction Rate

- temperature has a dramatic effect on reaction rate
- an increase of 10 degrees will double or triple the rate
- Experimental data shows that k increases exponentially as T increases. this is expressed in the Arrhenius equation

$$k = Ae^{-\frac{E_a}{RT}}$$

- R is the gas constant
- T is the temperature
- E<sub>a</sub> activation energy (J/mol)
- A is the pre-exponential/frequency factor

For a reaction to occur:

- rate of reaction is proportional to the collision frequency
- an increase in the concentration of a reactant leads to a larger number of collisions, hence increase in rate
- only a small fraction of collisions will lead to products

For collisions to be effective

- two molecules have to collide with proper orientation

the right atoms in the molecule have to collide. for  $\text{NO} + \text{NO}_3 = 2\text{NO}_2$ , the N has to collide with the O at the right angle so that a bent shape is formed

- they have to collide with sufficient energy

## Activation Energy:

- in order to be effective, collisions between particles must exceed a certain energy threshold
- when particles collide effectively, they reach an activated state
- the energy difference between the reactants and the activated state is the activation energy for the reaction
- the lower the activation energy, the faster the reaction
- activation energy is always positive
- the highest point on the activation energy curve is called the activated complex/transition state

## Exponential Factor

- and increase in temperature causes an increase in the kinetic energy of the particles

- this leads to more frequent collisions and the reaction rate increases
- at a higher temperature, the fraction of collisions with sufficient energy equal to or greater than  $E_a$  increases. reaction rate therefore increases

Exponential Factor:

$$e^{-\frac{E_a}{RT}}$$

- the fraction in the exponent is between 0 and 1

If  $E \geq E_a$  there will be a reaction, but if  $E < E_a$  no reaction will occur.

- High  $E_a$ , Low  $T$ ,  $\rightarrow 1$
- Low  $E_a$ , High  $T$ ,  $\rightarrow 0$

## Frequency Factor

- for a collision between particles to be effective, it must have both sufficient energy and the appropriate relative orientation between the reacting particles
- the  $A$  in the Arrhenius equation is the frequency factor

$$A = pz$$

- $p$  is the orientation factor
- $z$  is the collision frequency

As temperature increases to infinity,  $A \rightarrow k$  (all the molecules will be able to cross the activation barrier).

## Arrhenius Plots:

By modifying the Arrhenius equation we can get a linearized form:

$$\ln(k) = \frac{-E_a}{R} \frac{1}{T} + \ln(A)$$

## Transition State Model

- Describes how reactants become products assuming a favorable collision occurs
- Pot reaction profile or activation energy diagram

Upon collision:

- bonds in reactants stretch and become weaker
- new bonds start to form (still weak at this stage)
- the transition species is known as the transition state or the activated complex

## Nature of TS

- high energy
- short lived (unstable)
- cannot be isolated
- in equilibrium (low concentration) with reactants and products
- can proceed in either direction

# Molecularity

Elementary Reactions can be unimolecular, bimolecular or termolecular

- $A \rightarrow \text{products}$  (unimolecular)
- $A + A \rightarrow \text{products}$  (bimolecular)
- $A + B \rightarrow \text{products}$  (bimolecular)

Termolecular steps are very rare as it is unusual for 3 molecules to collide. Molecularity is the number of molecules that are involved in an elementary reaction having sufficient energy and the proper orientation to form the activated complex. The molecularity  $\in \mathbb{Z}$  and is no greater than three for elementary reactions.

## Rate Laws

Elementary Step	Molecularity	Rate Law
$A \rightarrow \text{products}$	1	$\text{Rate} = k[A]$
$A + A \rightarrow \text{products}$	2	$\text{Rate} = k[A]^2$
$A + B \rightarrow \text{products}$	2	$\text{Rate} = k[A][B]$
$A + A + A \rightarrow \text{products}$	3 (rare)	$\text{Rate} = k[A]^3$
$A + A + B \rightarrow \text{products}$	3 (rare)	$\text{Rate} = k[A]^2[B]$
$A + B + C \rightarrow \text{products}$	3 (rare)	$\text{Rate} = k[A][B][C]$

## Reaction Mechanisms

A valid mechanism must meet three criteria:

1. the elementary steps must add up to the overall balanced equation
2. the elementary steps must be reasonable
3. the mechanism must correlate with the observed rate law

A mechanism is a hypothesis - we cannot prove it correct, but if it is consistent with the data, and can be used to predict results accurately, it is a useful model for the reaction. In general, there are three types of mechanisms that you may encounter:

1. Case I - slow step followed by a fast step
2. Case II - fast step(s) followed by a slow step
3. Case III - steady state

Reaction mechanisms are theoretical concepts that show how a chemical reaction occurs

- involve elementary steps
- rate of slowest step determines overall rate

- 3 types of mechanism (slow → fast, fast → slow, steady state)

## Case III

For when both (or more) steps are the same speed ( $\frac{\Delta[\text{Intermediate}]}{\Delta t} = 0$ )

1. Find the rate law for the step that gives you products
2. Analyze the rate law, if there are intermediates you have to express it in terms of reactants or products.

## Catalysis

- a catalyst is a substance that increases the reaction rate without being consumed in the reaction
- in general, a catalyst provides an alternative reaction pathway that has a lower total activation energy than the uncatalyzed reaction
- a catalyst will speed up both forward and reverse reactions
- a catalyst does not affect  $\Delta H$  or the overall yield for a reaction
- transition metals are the most common catalysts

### Homogenous Catalysis

Catalysts that are in the same phase as reactants

### Heterogeneous Catalysts

Catalysts that are in a different phase than reactants