CHAPTER 13. CHEMICAL KINETICS

Kinetics - Study of factors that affect how fast a reaction occurs and the step-by-step processes involved in chemical reactions.

Factors that Affect Reaction Rate

A. Concentration of reactants - higher reactant concentrations increase the rate of reaction.
B. Catalyst – substance that accelerates the reaction rate without being transformed.
**C. Temperature** - higher temperatures usually increase the rate of reaction.
D. Surface area of solid - smaller particles have more surface area so the rate increases.

13.1. THE RATE OF A REACTION

Rate of reaction: The change in the amount of a reactant or product per unit time. (Analogy: speed of an automobile = ΔDistance/Δtime.)

$$\text{Average Rate} = \frac{\Delta\text{concentration}}{\Delta\text{time}}$$

[ ] = concentration

E.g. For a reaction   A $\rightarrow$ B

conc. | B / A | time
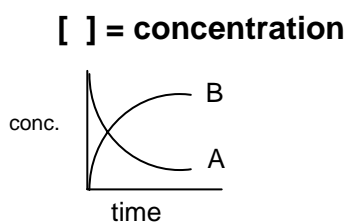
Average Rate for B =   =   ; Average Rate for A =   =

- The reaction rate is a measure of how fast a reaction occurs.
- Rate can be expressed as the rate of formation of products or the rate of disappearance of reactants.
- Reaction rate is always positive, so a (-) sign is used for reactant rate expressions. (Because the concentration of reactants decreases with time, Δ[Reactants] is a negative quantity.)
- Reaction rate decreases with time $\Rightarrow$ slope of curve decreases as reaction progresses.

Experimental Determination of Rate

We can find the rate of reaction by measuring the concentration of a reactant or product during the course of the reaction. Concentration can be obtained by different methods including titration, spectroscopy, and by taking manometer pressure readings.

Spectrometer Measurements

E.g. $Br_2 + HCO_2H \rightarrow 2Br^- + 2H^+ + CO_2$
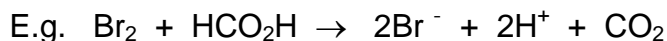
A colored species, Br_2, is consumed during this reaction, so we can use a spectrophotometer to measure the absorbance of light over a series of time intervals. (The absorbance is proportional to the concentration of Br_2.) The concentration of Br_2 vs. time can then be plotted as shown in Figure 13.5.

Example. Calculate the average rate from t = 50.0 s to 100.0 s

instantaneous rate: Rate at a specific point in time. Analogy: the speed a car is traveling when a photo radar camera snaps the picture.

To calculate instantaneous rate - draw a line tangent to the curve at a given instant in time & find the slope of the line.

Example. Instantaneous Rate at t = 200.0 s:

*Due to estimating the values used in determining the slope of the line, the value that you obtain for the instantaneous rate may differ from the instantaneous rates given in your text book.

Gas Phase Reactions

If one of the substances in the reaction mixture is a gas, manometer readings can be taken to monitor the pressure of the gas.

e.g. $2H_2O_2(aq) \rightarrow O_2(g) + 2H_2O(l)$
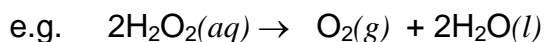
The rate of oxygen evolution can be measured with a manometer. The pressure of oxygen can then be converted to concentration by using the ideal gas law:

$PV = nRT$

Concentration can be expressed as: $\dfrac{n}{V} = \dfrac{moles}{L} = M$

By substitution: $P = MRT$ or $M = \dfrac{P}{RT}$

Reaction Rates & Stoichiometry

Consider the reaction: $2N_2O_5 \rightarrow 4NO_2 + O_2$

- For this reaction, the rate of disappearance of N_2O_5 is twice the rate of formation of O_2.
- To make the rates equal, divide rates by their stoichiometric coefficients:

$$Rate = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

Example. For the reaction, $3H_2 + N_2 \rightarrow 2NH_3$, write the rate expressions in terms of the disappearance of the reactants and the appearance of the products.

Example. For the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$, if the rate of decomposition of N_2O_5 is 4.2×10^{-7} mol/(L·s), what is the rate of appearance of (a) NO_2; (b) O_2?

13.2. THE RATE LAW

Rate law: gives relationship of the reaction rate to the rate constant and the concentrations of the reactants.

E.g. $2N_2O_5 \rightarrow 4NO_2 + O_2$ Rate = $k[N_2O_5]$
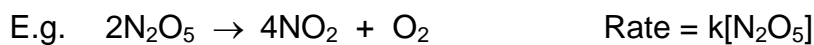
k = Rate Constant: k is a numerical constant for a reaction at a given temperature.

- k is not affected by [Reactants], but reaction rate is affected by [Reactants].

For a reaction $aA + bB \rightarrow xX$

$$\text{Rate} = k[A]^x[B]^y$$

Reaction Order: Exponent of a reactant in the rate equation.

Overall Reaction Order: Sum of all exponents in the rate equation.

- Exponents cannot be obtained by looking at the equation; they are experimentally determined values.
- Exponents are usually + whole #'s (0, 1, 2), but can be negative #'s or fractions.
- k units: $M^{-(\text{overall order} -1)}\text{time}^{-1}$

Example. For the following reaction: $2ClO_2 + F_2 \rightarrow 2FClO_2$ Rate = $k[ClO_2][F_2]$

order of ClO_2 = ___; order of F_2 = ___; Overall order = ___

Determination of Rate Law from Initial Rates Data

To determine the rate law, we observe the effect of changing the initial concentrations of the reactants on the initial rate of reaction.

Experimental Data: Initial rates (Δ[Products]/Δt after 1-2% of limiting reactant has been consumed) are usually given; there is less chance of error from competing side reactions & reversible reactions.

E.g. A reactant is 1st order if doubling [Reactant] causes the rate to double (For a first order reaction, rate is directly proportional to [Reactant]).
E.g. A reactant is 2nd Order if doubling [Reactant] causes the rate to quadruple.

➢ To find the order, x, for a specific reactant, examine what happens to the rate as the concentration of only that particular reactant changes:

$$\left(\frac{\text{conc } 2}{\text{conc } 1}\right)^x = \frac{Rate\,2}{Rate\,1}$$

➢ Repeat this process to find the orders for all of the reactants.

Example.

Experiment	[A] M	[B] M	Rate M/s
1	0.020	0.010	1.0
2	0.040	0.010	2.0
3	0.040	0.020	8.0

Order for A: ___   Order for B: ___

Rate Law:

13.3 RELATION BETWEEN REACTANT CONCENTRATION AND TIME

First Order Reactions

For a reaction, $A \rightarrow$ Products

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$$

Integrated Rate law: $\boxed{\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt}$

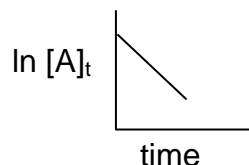$[A]_0$ = initial concentration; $[A]_t$ = concentration at time t

  $\Rightarrow$ Units for A can be g, moles, M, torr, etc

  $\Rightarrow$ A_t is always less than A_o

Rearrange: $\ln [A]_t - \ln[A]_0 = -kt$ to match straight line form of y = mx + b

$$\ln [A]_t = -kt + \ln [A]_0$$

- y intercept = $\ln [A]_0$; slope = $-k$ $\Rightarrow k = -\dfrac{\Delta \ln[A]_t}{\Delta t}$

$\ln [A]_t$

time

Note: Only for 1st order reactions will you get a straight line when plotting $\ln [A]_t$ vs. time!

Second Order Reactions

For a reaction, A $\rightarrow$ Products

Rate = $-\dfrac{\Delta [\mathbf{A}]}{\Delta \mathbf{t}} = k[A]^2$

Integrated 2nd order Equation: $\dfrac{1}{[A]_t} - \dfrac{1}{[A]_0} = kt \Rightarrow \boxed{\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}}$

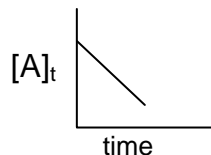- For 2nd order plot: slope = k; y-intercept = $\dfrac{1}{[A]_0}$

$\dfrac{1}{[A_t]}$
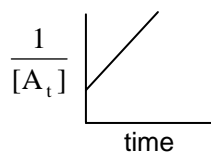
time

Note: Only for 2nd order reactions will you get a straight line when plotting $\dfrac{1}{[A]_t}$ vs. time.

Zero Order Reactions

For a reaction, A $\rightarrow$ Products: Rate = $-\dfrac{\Delta [A]}{\Delta t} = k[A]^0 = k$

Integrated 0 order law: $[A]_0 - [A]_t = kt \Rightarrow \boxed{[A]_t = -kt + [A]_0}$

- For Zero order plot: slope = -k; y-intercept = $[A]_0$

$[A]_t$

time

Note: Only for 0 order reactions will you get a straight line when plotting [A] vs. time.

Half-Life for 1st Order Reactions

$t_{1/2}$ = **Half-life**: Time that it takes for [A] to drop to 1/2 of its initial value. $[A]_t = \dfrac{1}{2}[A]_0$

Plug into the 1st order law: $\ln \dfrac{\frac{1}{2}[A]_0}{[A]_0} = -kt_{1/2} \Rightarrow \boxed{\ln \dfrac{1}{2} = -kt_{1/2}} \Rightarrow \mathbf{k \cdot t_{1/2} = 0.693}$

- $t_{1/2}$ does not depend on the initial [A] only for 1st order reactions.

Characteristics of zero, first and second order reactions

Order	Rate Law	Integrated Law	Linear graph	slope	Half-life
0	Rate = k	$[A]_t = -kt + [A]_0$	$[A]$ vs. t	-k	$t_{1/2} = \dfrac{[A]_0}{2k}$
1	Rate = k[A]	$\ln\left(\dfrac{[A]_t}{[A]_0}\right) = -kt$	$\ln [A]$ vs. t	-k	$t_{1/2} = \dfrac{0.693}{k}$
2	Rate = k[A]^2	$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$	$\dfrac{1}{[A]_t}$ vs. t	+k	$t_{1/2} = \dfrac{1}{k[A]_0}$

Graphical Method of Determining Rate Law

1) Make 3 plots: $[A]$ vs time; $\ln [A]$ vs. time; and $\dfrac{1}{[A]}$ vs. time.

2) The most linear plot gives the correct order for A; the other 2 graphs should be curves.

13.4 ACTIVATION ENERGY AND TEMPERATURE DEPENDENCE OF RATE CONSTANTS

Collision Theory: Molecules must collide with each other in order to react!

Collision frequency affects the reaction rate:
- An increase in [Reactant] results in more collisions, so the rate of reaction is faster.
- ↑T causes molecules to move faster and collide more frequently, increasing the rate.

Transition State Theory

However, only a small fraction of colliding molecules will react because:

1) the molecules must possess enough Kinetic Energy to
   A. overcome e-cloud - e-cloud repulsions
   B. transfer translational KE to vibrational energy to weaken/break reactant bonds

Molecules at a given Temperature possess a KE distribution:

Number of molecules

KE E_a

low T

high T
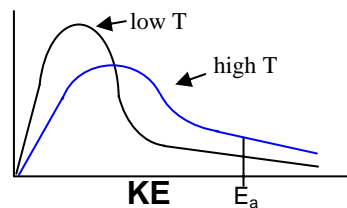
E_a, **Activation Energy** - Energy barrier that molecules have to surmount in order to react.
Energy is needed to break reactant bonds (endothermic process).
analogies: putting a golf ball over a hill or getting started on an unpleasant task

- Only a small fraction of molecules have high enough KE to initiate a reaction.
- E_a is different for each reaction – for reactions with low E_a, the reaction rate is faster and k is larger because more molecules can overcome E_a.
- At higher temperatures, a larger fraction of molecules have enough KE to surmount E_a. (This is the primary reason that the reaction rate increases rapidly as temperature rises.)

2) molecules must be properly oriented to have an effective collision.

Figure 13.17: $K + CH_3I \rightarrow KI + CH_3$

- K must collide with I in order for the reaction to occur.

Activated Complex (transition state) – a highly unstable species formed by the collision of the reactant molecules; arrangement of atoms at the top of the energy barrier.

e.g. O=N + Cl-Cl $\rightarrow$ O=N---Cl---Cl $\rightarrow$ O=N-Cl + Cl
          Reactants   Activated Complex   Products
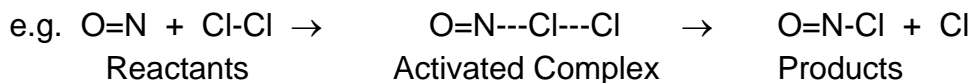
Potential energy diagram for endothermic reaction:
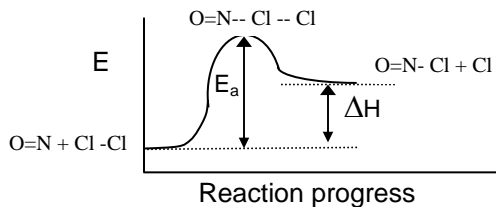

ΔH = **Heat of reaction**; this is ΔH(products) – ΔH(reactants).

The E_a shown above is the activation energy for the forward reaction, E_a(forward). This is the difference in energy between the activated complex and the reactants.

There is also an activation energy associated with the reverse process, E_a(reverse). This is the difference in energy between the activated complex and the products.

Potential energy diagram for exothermic reaction:
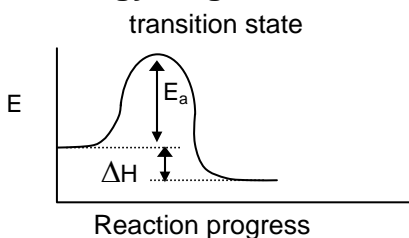
Arrhenius Equation

The Arrhenius equation gives the relationship between the rate constant and the temperature:

$$k = Ae^{-E_a/RT}$$ (e = $\ln^{-1}$ or inv ln)

R = gas constant = 8.314 J/K-mol, T = temperature in K
$e^{-E_a/RT}$ = fraction of molecules that have enough KE to react
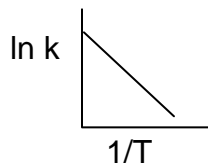A = frequency factor (relates to # of collisions that are properly oriented)

By taking the natural log of both sides and rearranging, we obtain:

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

- plot of ln k vs 1/T yields a straight line $\Rightarrow$
- slope= $\dfrac{-E_a}{R}$; y intercept = ln A

Non-graphical method:

If you have 2 sets of conditions, solve for k_1, k_2, T_1, T_2 or E_a using: $\ln\left(\dfrac{k_1}{k_2}\right) = \dfrac{E_a}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$

13.5 REACTION MECHANISMS

Many chemical reactions occur by a sequence of 2 or more steps – the specific sequence of steps is referred to as the reaction mechanism.

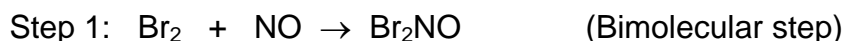Each individual event in the overall reaction is called an **elementary step**.

Molecularity: number of molecules that react in an elementary step

Unimolecular: 1 molecule $A \rightarrow$ products

Bimolecular: 2 molecules $2A \rightarrow$ products or $A + B \rightarrow$ products

Termolecular (uncommon): $3A \rightarrow$ products or $2A + B \rightarrow P$ or $A + B + C \rightarrow P$

Example. The 2 step mechanism for the overall reaction $Br_2 + 2NO \rightarrow 2BrNO$ is:

Step 1: $Br_2 + NO \rightarrow Br_2NO$ (Bimolecular step)

Step 2: $Br_2NO + NO \rightarrow 2BrNO$ (Bimolecular step)

Intermediates are short lived species that are formed during the reaction, then are subsequently consumed. Intermediates do not appear in the overall balanced equation. e.g. Br_2NO for the example above

$\Rightarrow$ For an elementary step, the rate law can be written using the stoichiometric coefficients of the reactants (molecularity = order).

E.g. Step 1 in the reaction above: Rate =

Rate determining step: the slowest step in the reaction is the rate determining step; this step limits how fast products can form. Analogy: freeway during rush hour

$\Rightarrow$ The rate law for the overall reaction is determined by the rate of this step.

Mechanisms with an Initial Slow Step

Example. The mechanism for the overall reaction $2NO_2 + F_2 \rightarrow 2NO_2F$ is proposed to be:

Step 1: $NO_2 + F_2 \rightarrow NO_2F + F$ (slow)

Step 2: $F + NO_2 \rightarrow NO_2F$ (fast)
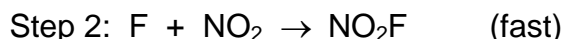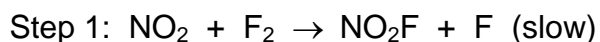
What is the Rate Law for this reaction?   **Rate =**

$\Rightarrow$ The reactants for the slow step (step 1) give us the rate law for the overall reaction.

Mechanisms with an Initial Fast Equilibrium Step

Many chemical reactions involve mechanisms with equilibrium steps:

Example. The mechanism for the reaction $Br_2 + 2NO \rightarrow 2BrNO$ occurs via two steps:

Step 1: $Br_2 + NO \rightleftarrows Br_2NO$ (fast equilibrium)

Step 2: $Br_2NO + NO \rightarrow 2BrNO$ (slow)

What is the Rate Law predicted by this mechanism?

$\Rightarrow$ From the slow step: Rate =

$\Rightarrow$ However, it is not possible to accurately measure the concentration of an intermediate so an intermediate cannot be part of an experimental rate law.

$\Rightarrow$ Since most of Br_2NO decomposes during the equilibrium reaction established in step 1, we can set up an equilibrium expression based on the rates of the forward and reverse reactions:

Rate of forward reaction = Rate of reverse reaction

$\Rightarrow$ Solve for [intermediate]:

$\Rightarrow$ Substitute in Rate law:

Experimentally you should observe the rate law: **Rate = k[NO]^2[Br$_2$]** where k = $k_2 \dfrac{k_1}{k_{-1}}$ (k is the experimentally obtained rate constant)

13.6 CATALYSIS

Catalyst: A substance that increases the rate of reaction, but is not part of the overall reaction.
- A catalyst lowers the E_a $\Rightarrow$ usually a catalyst helps weaken or break reactant bonds.
- A catalyst alters the reaction mechanism, but does not change the overall reaction.
- A catalyst may appear in the experimental rate law $\Rightarrow$ a reaction may have more than one rate law.

Catalyzed reaction: E_a is lower, but $\Delta H = \Delta H$ (products) - ΔH (reactants) is the same:
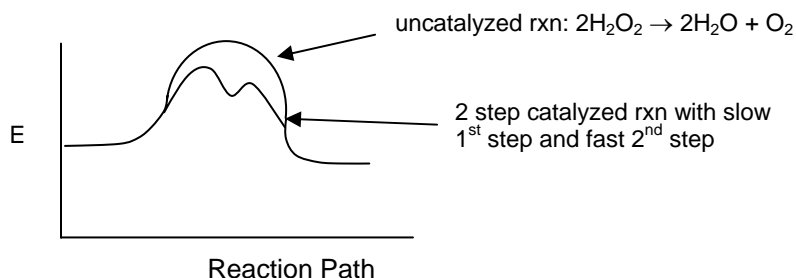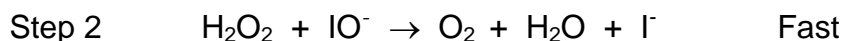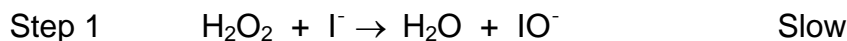

Reaction path
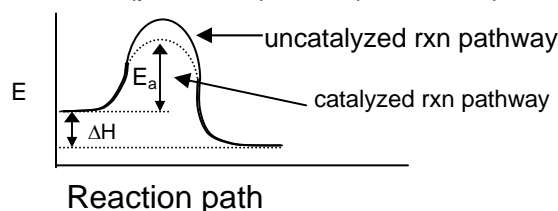
Heterogeneous – The catalyst is in a different phase than the reactants. Typically, a metal is used to provide a surface upon which reactants can adsorb and react.

E.g. Catalytic converters contain platinum metal mixed with rhodium. Pt catalyzes the oxidation of CO and unburned hydrocarbons to CO_2 and H_2O. Rh converts NO to N_2 and O_2.

Homogeneous – The catalyst is in the same phase as the reactants. The catalyst is consumed, then regenerated in a subsequent step. Homogeneous catalyst may appear in rate law.

Example. Homogeneous catalyzed decomposition of hydrogen peroxide: $2H_2O_2 \rightarrow 2H_2O + O_2$

Step 1 $H_2O_2 + I^- \rightarrow H_2O + IO^-$ Slow

Step 2 $H_2O_2 + IO^- \rightarrow O_2 + H_2O + I^-$ Fast

Reaction Path

Enzymes - Large protein molecules with one or more active sites that serve as biological catalysts in living organisms. The enzymes are compatible with specific substrate molecules.