CHERCHER SECONDARY SCHOOL

CHEMISTRY HANDOUT AND SOLVED PROBLEMS

GRADE -11

UNIT FOUR – CHEMICAL KINETICS

Introduction

- Many chemical reactions are fast that can be over with in a fraction of second where as other may proceed slowly over a period of days, weeks months or years.
- For example Combustions of fuel/fast rxn/, reaction of Na with water /Fast rxn/ weathering of rocks/ Slow rxn/ souring of milk/ Slow rxn/
- The area of chemistry concerned that concern with the speeds/ rate/ of these chemical reaction is called Chemical kinetics.
- Besides information about the speed at which reactions occur, kinetics also explains the reaction mechanism and transition states (exactly how the reaction occurs).
- Key points of the unit

Outlines	Main concern of the outline
Reaction Rates	How we measure rates.
Rate Laws	How the rate depends on amounts of reactants.
Integrated Rate Laws	How to calculate amount left or time to reach a given amount.
Half-life	How long it takes to react 50% of reactants.
Arrhenius Equation	How rate constant changes with temperature
Mechanisms	Link between rate and molecular Scale processes.

`

RATE OF REACTION

Rates of reactions can be determined by measuring the change in concentration of either reactants or products

- as a function of time /t/.

- During the course of reaction concentration of reactants decrease with time and that of products increase.
- For the reaction A → B there are two ways of measuring rate of the reaction:
    I. the speed at which the reactants/A/ disappear
    II. the speed at which the products/ B/ appear or formed.
- In general the rate of a reaction is calculated by dividing the change in the concentrations of reactants or products by the time taken for the change to occur.
- For a simple reaction, the reaction rate can be expressed as follows A → B

Rate of rxn /r/in terms of a reactant concentration	Rate of rxn /r/in terms of product concentration
$= -\frac{\Delta[]}{\Delta} = -\frac{[]-[]}{\Delta}$ NB: [A]f < [A]i because [A] decrease with time Thus, Δ [A] = [A]f – [A]i is negative But the rate of a reaction is taken as positive quantity	$=-= \frac{\Delta[]}{\Delta} \frac{[]-[]}{\Delta}$ NB: [B]i < [B]f because [B] increase with time Thus, Δ [B] = [B]f – [B]i is positive

- The unit of rate is mol $L^{-1}s^{-1}$ or Ms^{-1}.

Reaction Rate and Stoichiometry

- The rate of reaction can be expressed either in terms of the decrease in reactant concentration over time, or in terms of the increase in product concentration with time and the rate expression can be written based on Stoichiometry.
- To generalize, consider the following reaction equation aA + b B → c C + d D The rate of reaction is given by:

$$= = \frac{1}{a}\frac{\Delta[A]}{\Delta t} = \frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

- Where r- is rate of reaction, a, b, c and d are stoichiometric coefficients.
- Example:#1 Write the rate expressions for the following reactions, in terms of the disappearance of the reactants and the appearance of the products: a. $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

Solution

- we write the rate of the reaction as follows: i.e., rate of change in concentration divided by respective stoichiometric coefficient

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

- Notice that for every 1 mole of O_2 that appears, 4 x as many moles of NO_2 will also appear. In the meantime, twice as many moles of N_2O_5will be disappearing as moles of O_2 forming.
- Example:#2 a, How is the rate of disappearance of ozone related to the rate of appearance of oxygen in the following equation? $2O_3\ (g) \rightarrow 3O_2\ (g)$ Solution

$$= = -\frac{1}{2}\frac{\Delta[3]}{\Delta} \quad \frac{1}{3}\frac{\Delta[2]}{\Delta} =$$

b. If the rate of appearance of O_2 is 6.0×10^{-5} M/s at a particular instant, what is the value of the rate of disappearance of O_3 at the same time? Solution

$$-\frac{1}{2}\frac{\Delta[3]}{\Delta} = \frac{1}{3}\frac{\Delta[2]}{\Delta}$$

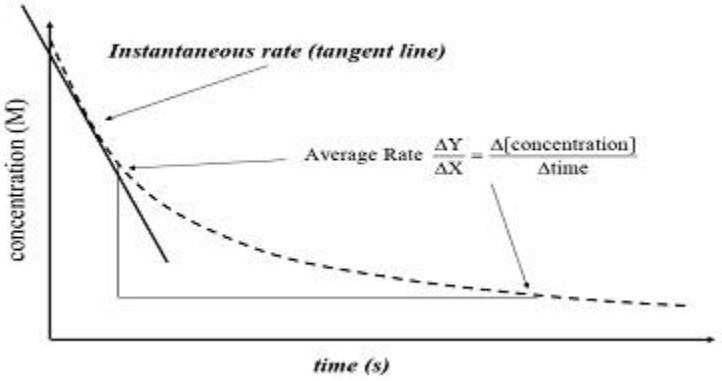
$$-\frac{\Delta[O_3]}{\Delta t} = \frac{2}{3}\frac{\Delta[O_2]}{\Delta t}$$

$\frac{\Delta[O_3]}{\Delta} = -(6.0 \times 10^{-5}\ M/s) = \underline{4.0 \times 10^{-5} M/s}$ It is correct to change the sign to positive.

Determination of Rate of Reaction

- The rate of reaction can be determined both quantitatively and qualitatively.
- Qualitatively the rate of reaction can be obtained by:-
  - Observing either the speed of disappearance of the reactants or the rate of formation of the products.
  - Observing change of colour, volume of gas evolved, amount of precipitate.
- Quantitatively by measuring change in concentration with change in time or by using formula.
- The average rate of the reaction over each interval is the change in concentration divided by the change in time - Instantaneous rate of reaction is the rate of a reaction for a given instant of time and it is calculated by drawing a

tangent to the graph at that instant of time or the slope of a line tangent to the curve at any point is the instantaneous rate at that time.



Example #1

Calculate Average Reaction Rates In a reaction between butyl chloride (C_4H_9Cl) and water, the concentration of C_4H_9Cl is 0.220*M* at the beginning of the reaction. At 4.00 s, the concentration of C_4H_9Cl is 0.100*M*. Calculate the average reaction rate over the given time period expressed as moles of C_4H_9Cl consumed per liter per second.

Solution

$t_1 = 0.00$ s
$t_2 = 4.00$ s
$[C_4H_9Cl]$ at $t_1 = 0.220M$
$[C_4H_9Cl]$ at $t_2 = 0.100M$

$$\text{Average reaction rate} = \frac{[C_4H_9Cl] \text{ at } t_2 - [C_4H_9Cl] \text{ at } t_1}{t_2 - t_1}$$ State the average reaction rate equation.

$$= -\frac{0.100M - 0.220M}{4.00\text{ s} - 0.00\text{ s}}$$ Substitute $t_2 = 4.00$ s, $t_1 = 0.00$ s, $[C_4H_9Cl]$ at $t_2 = 0.100$ *M*, and $[C_4H_9Cl]$ at $t_1 = 0.220M$.

$$= -\frac{0.100\text{ mol/L} - 0.220\text{ mol/L}}{4.00\text{ s} - 0.00\text{ s}}$$ Substitute mol/L for *M* and perform the calculations.

$$\text{Average reaction rate} = -\frac{-0.120\text{ mol/L}}{4.00\text{ s}} = 0.0300\text{ mol/(L·s)}$$

Example #2

Consider the decomposition of N2O5 to give NO2 and O2: $2N_2O_5\,(g) \rightarrow 4NO_2\,(g) + O_2\,(g)$

Solution

Time (s)	Concentration (M)		
	N_2O_5	NO_2	O_2
0	0.0200	0	0
100	0.0169	0.0063	0.0016
200	0.0142	0.0115	0.0029
300	0.0120	0.0160	0.0040
400	0.0101	0.0197	0.0049
500	0.0086	0.0229	0.0057
600	0.0072	0.0256	0.0064
700	0.0061	0.0278	0.0070

From the graph looking at t = 300 to 400 s

$$\text{Rate } O_2 = \frac{0.0009M}{100s} = 9\times10^{-6}\,Ms^{-1}$$

$$\text{Rate } NO_2 = \frac{0.0037M}{100s} = 3.7\times10^{-5}\,Ms^{-1}$$

$$\text{Rate } N_2O_5 = \frac{0.0019M}{100s} = 1.9\times10^{-5}\,Ms^{-1}$$

Why do they differ?

Recall:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

To compare the rates one must account for the ***stoichiometry.***

$$\text{Rate } O_2 = \frac{1}{1}\times9\times10^{-6}\,Ms^{-1} = 9\times10^{-6}\,Ms^{-1}$$

$$\text{Rate } NO_2 = \frac{1}{4}\times3.7\times10^{-5}\,Ms^{-1} = 9.2\times10^{-6}\,Ms^{-1}$$

$$\text{Rate } N_2O_5 = \frac{1}{2}\times1.9\times10^{-5}\,Ms^{-1} = 9.5\times10^{-6}\,Ms^{-1}$$

Now they agree!

Example #3 Based on the following chemical equation and the given data.

$[NH_3]_0$= 4.000 M, and [NH3] = 2.560 M at t = 25 s.

4 NH3(g) + 5 O2(g)→4 NO (g) + 6 H2O (g)

a. Calculate the rate of consumption of NH_3

Solution RateNH3= |Δ[NH3]| ÷ Δt ;

=(4-2.560) ÷(25-0)

Rate tNH3= <u>0.058 M•s^{-1}</u>

b. Calculate the rate of consumption of O2

Solution RateO2= (0.058 mol NH3/Ls)(5 mol O2/4 mol NH3)

= <u>0.072 M/s</u>

c. Calculate the rate of formation of H2O.

Solution Rate H2O= (0.058 mol NH3/Ls)(6 mol H2O/4 mol NH3)

= 0.087 M/s

And . . . . RateNO = RateNH3

. Exercise #1 A scientist conducts an experiment to determine the rate of the following reaction:

$N_2(g) + O_2(g) \rightarrow 2NO(g)$

If the initial concentration of N_2 was 0.500 M and the concentration of N_2 was 0.450 M after 0.100 s, what is the rate of the reaction? /Ans 0.500 M/s /

Exercise #2 HI dissociates to form I2 and H2: $2HI\ (g) \rightarrow H2(g) + I_2(g)$

If the concentration of HI changes at a rate of –0.45 M/s, what is the rate of appearance of $I_2(g)$? a. 0.90 M/s b. 1.00 M/s c. 0.45 M/s d. 0.23 M/s

FACTORS INFLUENCING THE REACTION RATES

- In general, different chemical reactions have different rates. Even a chemical reaction involving the same reactants may have different rates under different conditions.
- Change in temperature, concentration, nature of reactant, surface area and availability of a catalyst, result in changes in rate of reaction.

A. Nature of reactants

- The rate of a reaction depends on the chemical nature of the substances participating in the reaction.
- Under similar condition the rate of reaction differ simple, because of the nature of the reactant themselves. -

For example H2 react vigorously and rapidly with Cl_2 but slowly with N_2

$H_2 + Cl_2 \rightarrow 2HCl$ Fast

$3H_2 + N_2 \rightarrow 2NH_3$

B. Surface Area of Reactants

- The area of contact between the reacting species determines the rate of reaction in heterogeneous reaction.
- Because when the size of particles is minimized, contact between the atoms, ions, or molecules in the solid state maximizes with those in a different phase.
- A reaction that involves reactant which exists in different phase is referred to as a homogeneous reaction.
- For example powdered chalk react more rapidly in HCl then cube/lump/ Chalk

C. Concentration of Reactants

- When the concentration of one or more reactants increases, rate of reaction increases, because increasing the concentration produces more contacts between the reacting particles.

- In the case of reactions that involve gaseous reactants, an increase in pressure increases the concentration of the gases which leads to an increase in the rate of reaction.
- Pressure change has no effect on the rate of reaction if the reactants are either solids or liquids.

D. Temperature of reactants

- When temperature increases, rate of reaction increases, because when temperature increases overall kinetic energy of all particles of reactants increase, so more molecules will have energy greater than activation energy. So, the overall frequency of collisions increases, and thus the reaction rate increases.

E. Presence of a Catalyst

- A catalyst is a substance that changes reaction rate by providing a different reaction mechanism one with a lower activation energy, Ea
- Activation energy is which is the minimum energy needed to start a chemical reaction.
- Chemical catalysts can be either positive or negative.
- Positive Catalyst increases the rate of reaction by lowering the Activation Energy, Ea - Negative Catalyst or Inhibitors decreases the rate of reaction by increasing the value of Ea - Heterogeneous catalysts is a catalyst which has the same state with the reactants.
- Characteristics of catalyst
  - Speeds up the reaction forward and backward equally
  - Highly specific to a particular reaction
  - May even form temporary chemical bonds with the reactants
  - Recovered unchanged in original form at the end of the reaction
  - Does not alter the position of equilibrium
  - It provides an alternate mechanism by reducing activation energy
  - Does not consumed itself in the reactions

THEORIES OF REACTION RATES

- Two important theories help us to explain why different reactions occur at different rates. These are A. The collision theory and

  B. The transition-state theory.
- These two theories are distinct but in complete agreement, each emphasizing different aspects of reaction processes

A. The collision theory

- The fundamental concept of the collision theory of rate of reaction is that, in order for a reaction to occur between reacting species they must first collide (come in contact).
- The rate of reaction is directly proportional to the number of collisions per second (the frequency of collision) - But not all collisions between reacting species result in a reaction.
- The collisions that result in a reaction to form the desired products is called Effective collisions - Ineffective collisions: - are collisions that do not result in a reaction to form the desired products.
- Postulates of collision theory are summarized below.
- For a reaction to occur between reactants:
    a. The particles of the reacting substances must collide.
    b. The particles of the reacting species must have proper orientation.
    c. The particles of the reactants must collide with energy greater than or equal to the energy of activation.

- Concentration and Collision Theory

- According to the collision theory increasing the concentrations of the reacting species results in higher number of collisions per unit time, and the reaction rate is correspondingly higher.

- Temperature and Collision Theory

- As the temperature of the reacting species is raised, the average kinetic energy of the reacting particles increases considerably. This causes the particles of the reactants to collide more frequently and with greater energy. This results in an increase in reaction rate.

B. Transition State Theory/ Activated Complex Theory/

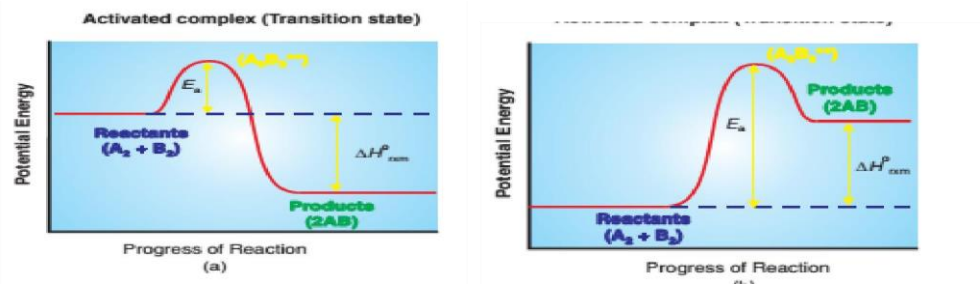
- According to transition-state theory, the collision between two reacting species results in the formation of an activated complex or transition state.
- An activated complex or transition state :- is short-lived high energy state species that is temporarily formed by the collision of reactant molecules

before they form products species can either fall to back(reactant) or form product n the activated complex, the original bonds are lengthened and weakened, and the new bonds are only

partially formed

- Let us consider the reaction: $A_2 + B_2 \rightarrow 2AB$
- The reactants, A_2 and B_2 approach each other and collide; they begin climbing up the left side of the potentialenergy hill, or barrier. If they have less energy than the energy of activation, Ea, they fail to climb the barrier and, instead, roll back down its left side. In this case, no reaction occurs.
- The formation of an activated complex in the form of an equation can be shown as,

  $A_2 + B_2 \rightarrow A_2B_2^{\ddagger} \rightarrow 2AB$ Where $A_2B_2^{\ddagger}$ is the activated complex or transition state



- According to transition-state theory, the rate of reaction depends on the rate at which reactants can climb to the top of the barrier and form an activated complex. On the other hand, the activation energy, Ea, is the energy that must be absorbed by the reactants to allow them to reach the transition state or the activated complex and cross the energy barrier.

RATE EQUATION OR RATE LAW

Order of Reaction and Rate Constant

- The rate law or rate equation is an equation which links the reaction rate with the concentrations or pressures of reactants and certain constant parameters (normally rate coefficients and partial reaction order). To determine the rate equation for a particular system, one combines the reaction rate with a mass balance for the system. - For a simple reaction,

  $A \rightarrow B$

- Where A is reactant and B is the product. The rate law or rate equation for this reaction is written as:

  Rate $\alpha[A]^x$ or Rate $= k[A]^x$

  Where- k is the rate constant and "x" is the order of the reaction

- For reactions involving more than one reactant consider the generic reaction: $A + B \rightarrow C + D$
- The rate law is: Rate = k[A]m[B]n

Where: rate = rate of reaction in M/s k= rate constant; units depend on m and n

[A] and [B] = concentration of reactants m and n = exponents

define the order or reaction with respect to reactants A and B

- A rate law must be experimentally determined
- Order of reaction; m and n usually small positive whole numbers; but could be negative, 0, or fractions
  - $[A]^m$; m = order with respect to reactant A $[B]^n$; n = order with respect to reactant B
  - m + n = overall order of the reaction
  - "m" and "n" is not necessarily stoichiometric coefficient in the balanced equation
- More about k: dependent on specific reaction and temperature
  - Large value of k means the reactant react rapidly to form product,
  - units depend on m and n (orders) can have L/M or L^2/M or S^{-1} - How does rate change dependent on order?
- A →products; rate = $k[A]^m$ if m = 1 the reaction is 1st order overall rate $\propto[A]^1$ if [A] doubles rate increases by 2^1 if m = 2 the reaction is 2nd order overall rate $\propto[A]^2$ if [A] doubles rate increases by 2^2 if m = 0 the reaction is zero order overall rate $\propto[A]^0$ if [A] doubles rate increases by 2^0 does not depend on concentration for zero order.

Change in rate with change in initial concentration/ [A]o/ for rate = k [A]m

For a reaction of	If $[A]_0$ is doubled	If $[A]_0$ is tripled
Zero-order (m = 0)	rate is unchanged	rate is unchanged
First-order (m = 1)	rate is doubled	rate is tripled
Second-order (m = 2) rate is	quadrupled (x 2^2)	rate is 9 times greater (x 3^2)

Example #1 The reaction A + 2B → C is first order in B and A. The overall order of the reaction is _____

a. first. b zero. c second d . fourth e. . third

Ans:- c because the overall reaction order is the summation of the rxn order of each species.

Example #2. For the reaction 1A + 2B + 1C →2D + 1E, the rate law is: rate =k $[B]^2[C]^1$

Which of the following statements is <u>false:</u>

a. the reaction is first order in [A] b. the reaction is second order in [B]

c. the reaction is first order in [C] d. the reaction is third order overal

Ans:- a because A has no expressed in the rate law or it has no effect on the rate of the rxn.

Example #3 For the rate law Rate = k[A][B]3/2, the order with respect to A is _____, the order with respect to B is _____, and the overall reaction order is _____.

a. 0; 3/2; 3/2 b. 1; 3/2 ; 1

c. 1; 3/2 ; 5/2 d. 1; 3/2; 7/2

e. The orders cannot be determined without a chemical reaction

Ans:- c

Determining Reaction Order: The Method of Initial Rates

Example #4 The initial rates of the reaction $2A + B \rightarrow 2C + D$ at various concentrations of A and B are given below:

[A], mol/L	[B] mol/L	Initial rate /mol/Ls^{-1}
0.01	0.20	0.10
0.02	0.20	0.20
0.01	0.40	0.40

a) What is the order of reaction with respect to A and B?

b) Write the rate law/ rate equation

c) What is the overall order of reaction?

d) What is the rate constant?

e) What will be the rate of the reaction if the concentrations of A and B are both 0.01 mol/L?

Solution a. Order of reaction with respect to each reactant can be determined as follows.

Holding the [B] constant, while the [A], doubling the rate is doubled, indicating that the reaction is first order in A

Holding the [A], constant, while the [B] doubling the rate, is x2^2 indicating that the reaction is 2nd order in B

. b. Rate =k [A], [B]^2

c. overall order = 2+1=3

d. Rate of disappearance of A =k [A], [B]^2

$$k = \frac{\text{Rate of disappearance of A}}{[A], [B]^2} = \frac{0.1 \text{ mol/Ls}^{-1}}{0.01 \text{ mol/L} \times (0.20 \text{ mol/L})^2}$$

$$K = \frac{0.1 \text{ mol/Ls}^{-1}}{0.01 \text{ mol/L} \times (0.20 \text{ mol/L})^2}$$

K= 250mol^2/L^2 /S

Example #5 Two compounds, X and Y, are known to undergo the reaction

$X + 3Y \rightarrow XY_3$

Using the experimental results in the table below:

EXPERIMENT	Initial concentration of X/moldm^{-3}	Initial concentration of Y/moldm^{-3}	Initial rate of formation of XY_3/moldm^{-3}s^{-1}
1	0.100	0.100	0.00200
2	0.100	0.200	0.00798
3	0.100	0.300	0.01805
4	0.200	0.100	0.00399
5	0.300	0.100	0.00601

Ans 2.00 mol^{-2}dm^{6}s^{-1}

The Arrhenius Equation

- Svante Arrhenius: - Observed that a mathematical relationship connects activation energy, temperature, and the rate constant. This relationship is known as the Arrhenius equation and is written as:

Arrhenius equation

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

k is the rate constant

E_a is the activation energy

T is the temperature in K

R is the ideal-gas constant (8.314 J/Kmol)

A is known the *frequency or pre–exponential factor*

In addition to carrying the units of the rate constant, "A" relates to the frequency of collisions and the orientation of a favorable collision probability

Both A and E_a are *specific to a given reaction.*

- Arrhenius discovered that most reaction-rate data obeyed an equation based on three factors:
  a. The number of collisions per unit time.
  b. The fraction of collisions that occur with the correct orientation.
  c. The fraction of the colliding molecules that have energy greater than or equal to Ea.

- By combining the equations for the values of k at two different temperaturesT1and T_2 for the same reaction, a relationship is obtained

$$l\ n\ -\left(-\right. = -\ \ O\ R\text{——} = /2.303\{-\ )$$

Examples #1

Given that Ea for the hydrolysis of sucrose is 1.08×10^3 kJ / mol, compare the rate constant of this reaction at 37°C (T1) with the rate constant of the samereaction at 27°C (T2).

Given that Ea for the hydrolysis of sucrose is 1.08×10^3 kJ /mol, compare the rate constant of this reaction at 37 ^{0}C (T1) with the rate constant of the same reaction at27 ^{0}C (T2). Solution

$T_1 = 37 + 273 = 310\ K \quad T_2 = 27 + 273 = 300\ K$

$R = 8.31\ J/K.molEa = 108 \times 10^3 = 1.08 \times 10^5\ J/mol \quad A = not\ given$

$$\ln k_1 - \ln k_2 = \left(\ln a - \frac{E_a}{RT_1}\right) - \left(\ln a - \frac{E_a}{RT_2}\right)$$

$$\ln k_1 - \ln k_2 = \ln a - \frac{E_a}{RT_1} - \ln a + \frac{E_a}{RT_2} = -\frac{E_a}{RT_1} + \frac{E_a}{RT_2}$$

$$\ln \frac{k_1}{k_2} = -\frac{E_a}{RT_1} + \frac{E_a}{RT_2} \quad (\text{since } \ln k_1 - \ln k_2 = \ln k_1 / k_2)$$

$$\ln \frac{k_1}{k_2} = -\frac{1.08 \times 10^5}{8.314 \times 310} + \frac{1.08 \times 10^5}{8.314 \times 300} = 1.396$$

$$\frac{k_1}{k_2} = 4.04$$

The reaction at 37 ^{o}C is about 4 times faster than at 27 ^{o}C.

CONCENTRATION-TIME EQUATION (INTEGRATED RATE LAW)

- A rate law tells us how the rate of reaction depends on the concentration of the reactants at a particular moment but an integrated law relates concentration to reaction time.

A. Zero Order Reaction

- Whose rate of reaction does not depend on thereactant concentration

- The rates of these zero-order reactions do not vary with increasing nor decreasing reactants concentrations. This means that the rate of the reaction is equal to the rate constant, k, of that reaction.
- A →Product Rate = $d[A]/dt = k[A]_0 = k$ = constant - Using calculus, it can be shown that

  $[A]t = -kt + [A]_o$
- Where [A]is concentration of A at t =t; [A]o is the concentration of Ais at t= 0. Now,zero-order reactions can be written as follows
- $[A]t = -Kt + [A]_0$ ... Integrated rate equation for 0thorder reaction.
- This is a linear equation with the form of y =mx + b.
- For a zero-order reaction, a plot of [A] versus-time is a straight line, whose slope is – k
- Example #1 A→C is zero order reaction. If the reaction is 30%complete after 10 min. What is the rate constant for a reaction? If the initial concentration of A was 16M Solution

  After 10min 30% of A is changed in to C. This means 70% of A remains after 10min. Thus $[A]_{10min} = 70/100 \times 16 = 11.2M$

  $[A]t = -Kt + [A]_0$

  $-[A]_{10min} = -Kt + [A]_0$

  11.2M = -k x10min +16, Then calculate for <u>k = 0.48</u>

B. First-Order Reactions

- A first-order reaction is a reaction whose rate of reaction depends on the reactant concentration raised to the first power. In a first-order of the type A → Product the rate is $\ln[A]_t = -kt + \ln[A]_0$ Integrated rate equation for 1storder reaction
- The linear equation y = mx + b, in which m is the slope of the line that is the graph of the equation. Thus, a plot of ln[A] versus t gives a straight line with a slope of k (or m).
- Example #1 a. The decomposition of H2O2is a 1st order reaction with k= 7.30 x 10-^{4}s^{-1}

  Determine the [H2O2] after1200 s of reaction if the initial concentration of H2O2 is 2.32 M

Solution ln[A]t=

$-kt + \ln[A]_0$

= - 7.30 x 10-^{4}s^{-1}x1200 s + ln[2.32 M]

= - 0.876 + 0.842M =- 0.0344M

$[A]_{1200} = e^{-0.0344} = 0.967$

b. Determine the percent H2O2 that has decomposed after 500 s of reaction.

Answer: 30.6 % decomposed

Exercise #1

Determine the rate constants for the following first-order reactions:

a. A → B, given that the concentration of A decreases to one-half its initial value in 1000s.

b. 2 A → B + C, given that $[A]_0 = 0.050$ M and that after 120 s [B] = 0.015 M.

ANS (a) $6.93 \times 10^{-4} s^{-1}$

(b) $7.6 \times 10^{-3} s^{-1}$

Second Order Reactions

- A second order reaction is a reaction whose rate depends either on the concentration of one reactant raised to the second power or on the concentrations of two different reactants, each raised to the first power. - The simpler type of reaction involves one kind of reactant molecule 2 A → Product

$$\frac{1}{[A]t} = + \frac{1}{[A]0}$$ 2

- The graph of 1[A] versus time gives a straight line with a slope of k - Example#1

The reaction: 2NOBr (g) → 2 NO (g) + Br2 (g) is a second order reaction with respect to NOBr.

k = 0.810 Ms-1 at 10 °C. If [NOBr] o= 7.5×10^{-3} M, how much NOBr will be left after a reaction time of 10 minutes?

- Solution t=10 min = 600 s
- One can solve for the amount of NOBr after 10 minutes by substituting the given data into the integrated rate law for a second-order reaction.

___= + => -=0.810600 s+] $[A]_{10} = 1.6X10^{-3}M$

[] [] [] [. ×

- In general

Reaction	Order	Differential form	Integrated form
$A \rightarrow P$	zeroth	$\frac{d[A]}{dt} = -k$	$[A] = [A]_0 - kt$
$A \rightarrow P$	first	$\frac{d[A]}{dt} = -k\,[A]$	$\ln[A] = \ln[A]_0 - kt$
$\mathbf{A \rightarrow P}$	**Second**	$\mathbf{d[A]/dt = k[A]^2}$	$\frac{1}{[A]t} = k\ t + \frac{1}{[A]0}$

THE HALF-LIFE OF A REACTION

- Half-life is the time taken for the concentration of a reactant to drop to half its original amount.
- This means that half life is the time it takes for the concentrations of A to fall from $[A]_0$ to $\frac{1}{2}[A]_0$

- Half-life of First Order Reactions

- The mathematical expression for the half-life of a first-order reaction is determined by substituting t = t½ and [A]= ½[A]o in equation

$$\log \frac{[A]_o}{[A]_t} = \frac{kt}{2.303}$$

This gives us

$$\ln \frac{[A]_o}{\frac{1}{2}[A]_o} = \frac{kt_{1/2}}{2.303} \quad \text{or} \quad \ln 2 = kt_{1/2}$$

And solving for $t_{1/2}$ gives, $\frac{\ln 2}{k} = \frac{0.693}{k}$.

From the relation, it can be noted that, for a first-order reaction, the half-life is independent of the initial concentration of A, [A]o

- Example #1 A reaction is first order in A. If the rate constant of the reaction is $6.00 \times 10^{-3} s^{-1}$, what is the half-life () of the reaction ?

a. 4.98×10^{-3}s b. 200 s c. 3.45×10^{3}s d. e. 1.73×10^{-3}s

Solution t1/2 = 0.693/k

= 0.693/$6.00 \times 10^{-3}s^{-1}$ =115.5 s

- Half-life of Second Order Reactions

- For second-order reactions, half-life depends on the initial concentration, [A]o, and the rate constant, k. For a second-order reaction, the half-life expression is given by the equation.

$$\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt \Rightarrow \frac{1}{½[A]_o} - \frac{1}{[A]_o} = kt_{½}$$

- Rearranging and solving for t½, we get the expression

$$t_{½} = \frac{1}{k[A]_o}$$

-

Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

Order	Rate Law	Concentration-Time Equation	Half-Life
0	rate = k	$[A] - [A]_0 = -kt$	$t_{½} = \frac{[A]_0}{2k}$
1	rate = k [A]	$\ln[A] - \ln[A]_0 = -kt$	$t_{½} = \frac{\text{Ln } 2}{k}$
2	rate = k $[A]^2$	$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$	$t_{½} = \frac{1}{k[A]_0}$

REACTION MECHANISM

- A mechanism:-is a collection of elementary processes (also called elementary steps or elementary reactions) that explains how the overall reactionproceeds.
- Elementary steps: -The individual reactions that make up a reactions mechanism.
- Intermediates:- A substance that is found in elementary steps but not in overall rxns
- Molecularity of a reaction: - The minimum number of reacting particles (molecules, atoms or ions) that come together or collide in a rate determining step to form product or products. - Example

a	$PCl_5 \rightarrow PCl_3 + Cl_2$	(Unimolecular)
b	$2HI \rightarrow H_2 + I_2$	(Bimolecular)
c	$2SO_2 + O_2 \rightarrow 2SO_3$	(Termolecular)
d	$NO + O_3 \rightarrow NO_2 + O_2$	(Bimolecular)
e	$2CO + O_2 \rightarrow 2CO_2$	(Termolecular)
f	$2FeCl_3 + SnCl_2 \rightarrow SnCl_2 + 2FeCl_2$	(Termolecular)

- Rate determining step: - The slowest step in the sequence of steps leading to the formation of products. In other words, the slowest step in the mechanism determines the overall rate of the reaction.
- Note: - In elementary steps, the reaction order, Molecularity and Stoichiometric Coefficient are numerically the same also they have different concepts except pseudo order reaction.
- Molecularity:- Cannot be zero, negative, fractions and infinite

Example #1 A proposed mechanism for the photodecomposition of ozone in the atmosphere is

Step 1: $O3(g) + h\nu \rightarrow O2(g) + O(g)$

Step 2: $O3(g) + O(g) \rightarrow 2\ O2(g)$

Which of the following species is an intermediate?

Solution

Sum up the two elementary steps

$O3(g) + h\nu \rightarrow O2(g) + \cancel{O(g)}$

$O3(g) + \cancel{O(g)} \rightarrow 2\ O2(g)$

Over all rxn $2O3(g) + h\nu \rightarrow 3O2(g)$

- Species such as O are called intermediates because they appear in the mechanism of the reaction (that is, the elementary steps) but not in the overall balanced equation
- Example #2 A proposed mechanism for the decomposition of ozone in the atmosphere is

Step 1: $Cl(g) + O3(g) \rightarrow ClO(g) + O2(g)$

Step 2: ClO(g) + O3(g) → Cl(g) + 2 O2(g)

Which of the following species is an intermediate?

Solution

Sum up the two elementary steps

Step 1: Cl(g) + O3(g) → ~~ClO(g)~~ + O2(g)

Step 2: ~~ClO(g)~~ + O3(g) → Cl(g) + 2 O2(g)

- Over all rxn Cl(g) + 2O3(g) → Cl(g) +3O2(g)
- Species such as ClO are called intermediates because they appear in the mechanism of the reaction (that is, the elementary steps) but not in the overall balanced equation
- Example #3 A proposed mechanism for the decomposition of ozone in the stratosphere is:

Step 1: Cl(g) + O3(g) → ClO(g) + O2(g)

Step 2: ClO(g) + O3(g) → Cl(g) + 2O2(g)

What is the molecularity of Step 1? a. zeromolecular

b. unimolecular

c. bimolecular d. termolecular e. More information is needed to answer this question.

ANS C

- Example #3 The mechanism for the reaction 2H2O2(aq) → 2H2O() + O2(g) in the presence of I–(aq) is proposed to be:

Step 1: H2O2(aq) + I– (aq) → H2O + OI–(aq) (slow)

Step 2: H2O2(aq) + OI– (aq) → H2O+ O2(g) + I–(aq) (fast)

What is the molecularity of the rate-determining step? /slowest step/

a. zeromolecular b. unimolecular c. bimolecular d. termolecular

e. More information is needed to answer this question.

ANS C

WORK SHEET

1. The initial rates of the reaction 2A + B → 2C + D at various concentrations of A and B are given below:

[A] moldm^{-3}	[B] moldm^{-3}	Initial rate /moldm^{-3}s^{-1}
0.01	0.20	0.10
0.02	0.20	0.20
0.01	0.40	0.40

a. What is the order of reaction with respect to A and B?
b. What is the overall order of reaction?
c. What is the rate constant?
d. What will be the rate of the reaction if the concentrations of A and B are both 0.01 moldm^{-3}?

- Ans a) 1 wrt A, 2 wrt B b) 3 c. 250 mol^{-2}dm^{6}s^{-1} d). 2.5 x 10^{-4} moldm^{-3}s^{-1}

2. For the reaction $PCl_3 + Cl_2 \rightarrow PCl_5$, the following data were obtained:

Experiment No.	[PCl_3]/M	[Cl_2]/M	Rate /Ms^{-1}
1	0.36	1.26	6.0 x 10^{-4}
2	0.36	0.63	1.5 x 10^{-4}
3	0.72	2.52	4.8 x 10^{-3}

Deduce the rate equation and the rate constant.

- Ans 8.3 x 10^{-3} mol^{-1}dm^{3}s^{-1}

3. Two compounds, X and Y, are known to undergo the reaction

$X + 3Y \rightarrow XY_3$

Using the experimental results in the table below:

EXPERIMENT	Initial concentration of X/moldm^{-3}	Initial concentration of Y/moldm^{-3}	Initial rate of formation of XY_3/moldm^{-3}s^{-1}
1	0.100	0.100	0.00200
2	0.100	0.200	0.00798
3	0.100	0.300	0.01805
4	0.200	0.100	0.00399
5	0.300	0.100	0.00601

Find the rate constant.

Ans rate = k[PCl_3][Cl_2]^2 k = 1.05 x 10^{-3} mol^{-2}dm^{6}s^{-1}

4. The mechanism for the reaction 2H2O2(aq) → 2H2O() + O2(g) in the presence of I–(aq) is proposed to be Step 1: H2O2(aq) + I–(aq) → H2O() + OI–(aq) (slow) Step 2: H2O2(aq) + OI–(aq) → H2O() + O2(g) + I–(aq) (fast)
What is the rate law for the overall reaction?

a. Rate = k[H2O2] d. Rate = k[H2O2][OI–]
b. Rate = k[H2O2]2 e. Rate = k[H2O2]2[I–]/[H2O]
c. Rate = k[H2O2][I⁻]

5. What percentage of a material will persist after 60 minutes if it's half life is 30 minutes?
a. 50% b. 33% c. 25% d. 12.5% e. none of the above

6. The proposed mechanism for a given chemical reaction is shown below.

Step 1: A + B ⇆ F	*(fast)*
Step 2: F+ A → C + G	*(slow)*
Step 3: G + A ⇆ C + D	*(fast)*

Which is the correct rate law?
A. Rate = k $[A]^2$ [B] C. Rate = k [A] [B] [F] [G]
B. Rate = k [A] [B] D. Rate = k $[A]^3$ [B]

✓ *ANS. A* Since the second step is the slow step, cross off the intermediate, and gather all the reactants in the first and second steps.

8. Each of the choices below gives an elementary reaction. Which one could **not**be true regarding the molecularity of individual step?
A. A + B + C → P : Trimolecular C. 2A → P : Bimolecular
B. A→ P :Unimolecular D. A + B → P :Uimolecular Ans. D

9. Which of the following statements are applicable to a balanced chemical equation of an elementary reaction?
A. Order is same as molecularity.
B. Order is less than the molecularity.
C. Order is greater than the molecularity.*Ans. A.*
D. Molecularity can never be positive value

10. The kinetics of the reaction below were studied and it was determined that the reaction rate did not change when the concentration of B was tripled. The reaction is ___ order in B:
(A + B → P)
A. First B. zero C. second D. third Asn. B.

THE END OF UNIT FOUR

Keep safe, be healthy and stay at home