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Chapter 8 Introduction to Chemical Kinetics

Multiple Choice Questions (M.C.Qs)

Choose the correct answer for each from the given options:

01 **Reactions with high activation energy:**
(a) are slow (b) are fast (c) are moderate (d) do not occur

02 **The change in concentration of reacting substances in a unit time is called:**
(a) rate of reaction (b) rate constant (c) rate law (d) velocity constant

03 **The addition of a catalyst to a reaction changes the:**
(a) internal energy (b) activation energy (c) threshold energy (d) Gibbs free energy

04 **Which of the following are best to explain the action of catalyst in speeding up a chemical reaction?**
(a) It increases the equilibrium constant for the reaction.
(b) It increases the kinetic energy of reacting molecules.
(c) It prevents reverse reaction from occurring.
(d) It decreases energy of activation for the reaction.

05 **Rate constant of a reaction depends upon:**
(a) temperature (b) initial concentration of reactants
(c) time of reaction (d) extent of reaction

06 **Powdered zinc reacts more rapidly with water than the chunks of metallic zinc because:**
(a) powdered zinc is more reactive.
(b) energy of activation is lowered.
(c) number of effective collision has increased.
(d) surface area of powdered zinc is much more than chunks of Zn.

07 **Combustion of gasoline occurs more rapidly in an internal combustion engine than in open air because:**
(a) number of molecules per unit volume increases.
(b) there is more collisions between the molecules.
(c) there are more effective collisions
(d) the temperature is higher in internal combustion engine than in open air. More collision among molecules. The fraction of molecules possessing activation energy increases.

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08 ***In zero order reaction the rate is independent of :***

(a) temperature of reaction *(b) concentration of reactants*
(c) concentration of products *(d) None of them*

09 **The branch of chemistry that deals with the reaction rates and reaction mechanism is called:**

(a) thermochemistry *(b) chemical kinetics* *(c) electrochemistry* *(d) physical chemistry*

10 ***Rate of a chemical reaction depends upon:***

(a) temperature *(b) concentration* *(c) surface area* *(d) all of the above*

11 ***The velocity of reaction is:***

(a) quantity of reactants consumed *(b) quantity of products formed*
(c) the rate of the reaction at a specific time
(d) equal to the rate of reaction.

12 ***Velocity of reaction is equal to:***

(a) $-\log [H^+]$ *(b)* $\frac{[A^+]\ [B^+]}{[A]\ [B]}$ *(c)* $\frac{dx}{dt}$ *(d) None of them*

13 ***During the course of chemical reaction the molar concentration of the reactants:***

(a) increases *(b) decreases* *(c) remain unchanged* *(d) None of them*

14 ***Every 10°C rise in temperature doubles the rate of chemical reaction. This increase in rate is due to:***

(a) decrease in activation energy of reaction
(b) decrease in the number of collisions between reactants molecule
(c) increase in activation energy of reactants
(d) increase in number of effective collisions.

15 ***The rate of a chemical reaction:***

(a) increases as the reaction proceeds *(b) decreases as the reaction proceeds*
(c) remain the same as the reaction proceeds *(d) many increases or decreases*

16 ***The unit of rate constant is same as the rate of reaction in the:***

(a) first order reaction *(b) zero order reaction*
(c) second order reaction *(d) third order reaction*

17 ***Rate equation gives the relation between rate of reaction and:***

(a) concentration of reactant and rate constant
(b) concentration of products and rate constant
(c) rate constant only *(d) none of them*

18 ***The unit of rate constant is:***

(a) mol / sec *(b)* $mol.dm^{-3}\ sec^{-1}$ *(c)* $dm^3.\ mol^{-1}.\ sec^{-1}$ *(d) no unit*

19 ***The reaction which proceeds at experimental measurable rate are called:***

(a) fast reaction *(b) slow reaction* *(c) activation energy* *(d) ionic reaction*

20 ***The minimum energy necessary for a reaction to take place is called:***

(a) threshold energy *(b) kinetic energy* *(c) activation energy* *(d) internal energy*

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21 ***Rate of reaction does not depend upon:***

(a) pressure *(b) concentration* *(c) temperature* *(d) catalyst*

22 $2NO + Cl_2 \longrightarrow 2NOCl$. ***The order of reaction is:***

(a) first order *(b) third order* *(c) second order* *(d) zero order*

23 ***The rate expression of the reaction:***

$2NO + O_2 \longrightarrow 2NO_2$ ***may be written as:***

(a) $Rate = [NO]^2\ [O_2]$ *(b)* $Rate = K\ \frac{[NO_2]_2}{[NO]^2\ [O_2]}$

(c) $Rate = K\ [NO]^2\ [O_2]$ *(d) None of these*

24 ***Which of the following is first order reaction?***

(a) $2NH_3 \longrightarrow N_2 + 3H_2$ *(b)* $2NO + O_2 \longrightarrow 2NO_2$

(c) $2NO_2 \longrightarrow 2NO + O_2$ *(d)* $NH_4NO_3 \longrightarrow N_2 + 2H_2O$

25 ***The sum of all exponents (power) of the reactants in the rate expression is called:***

(a) molecularity *(b) rate constant* *(c) order of reaction* *(d) None of them*

26 ***In a reaction, activation energy is equal to:***

(a) threshold energy + average energy of the molecules

(b) threshold energy - average energy of the molecules

(c) average energy of the molecules

(d) threshold energy of the molecules

27 ***Rate constant is denoted by:***

(a) dx / dt *(b)* K_c *(c)* K_f *(d)* K

28 ***A catalyst increases the rate of a chemical reaction by:***

(a) reacting with reactants *(b) reacting with products*

(c) decreasing the activation energy *(d) increasing the activation energy*

29 ***A substance which retards the rate of chemical reaction is:***

(a) inhibators *(b) auto-catalyst* *(c) activators* *(d) positive catalyst*

30 ***The reaction which have low values of activation energy are:***

(a) slow reaction *(b) fast reaction*

(c) moderate reaction *(d) none of them*

31 ***For the reaction,*** $2NO + O_2 \longrightarrow 2NO_2$, ***what happen if the concentration of*** O_2 ***is doubled?***

(a) Rate will reduced to half *(b) Rate will also double*

(c) No effect on rate *(d) Rate will increase by four times.*

32 ***Which catalyst is used to increase the rate of the following reaction?***

$2H_2O_2 \longrightarrow 2H_2O + O_2$

(a) glycerine *(b)* V_2O_5 *(c)* MnO_2 *(d) Pt*

33 ***For the conversion of*** SO_2 ***to*** SO_3, V_2O_5 ***is:***

(a) a positive catalyst *(b) a negative catalyst*

(c) an auto catalyst *(d) none of these*

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34 ***Ionic reactions of inorganic compounds are:***

(a) very slow *(b) moderate* *(c) very fast* *(d) slow*

35 ***The rate of reaction at a particular time is called:***

(a) average rate of reaction *(b) absolute rate of reaction*

(c) instantaneous rate of reaction *(d) none of them*

36 ***Larger the surface area of the reactants molecule:***

(a) lower will be the rate of reaction *(b) higher will he the rate of reaction*

(c) no change on the rate of reaction *(d) the rate may increase or decrease*

37 ***The term dx / dt in the rate expression refers to the:***

(a) increase in concentration of reactants *(b) average rate of reaction*

(c) intantaneous rate of reaction *(d) change in concentration of the reactants with respect to time*

38 ***Which of the following reactions are usually slow?***

(a) Neutralization of acid by base *(b) Explosive reactions*

(c) Organic substitution reactions *(d) Photochemical reactions*

39 ***The total number of atoms or molecules taking part in a chemical reaction is called:***

(a) molecularity *(b) order of reaction*

(c) zero order reaction *(d) none of the above*

40 ***The reaction,*** $H_2 + I_2 \longrightarrow 2HI$ ***belongs to the:***

(a) first order *(b) second order* *(c) third order* *(d) zero order*

41 ***According to the collisions theory, the rate of reaction is equal to the:***

(a) number of collisions *(b) number of effective collisions*

(c) concentration of the reactants *(d) number of collisions b / w reactants & products*

42 ***Photochemical reactions, which proceed only under the influence of light are:***

(a) zero order *(b) first order* *(c) second order* *(d) third order*

43 ***Inhibitors are also called:***

(a) positive catalysts *(b) negative catalysts*

(c) enzymes *(d) None of the above*

44 ***The word "kinetic" is a Greek word which means:***

(a) rotation *(b) motion* *(c) vibration* *(d) acceleration*

45 ***At the beginning of a reaction, the reaction rate for the reaction is:***

(a) increases & remains constant *(b) increases then decreases*

(c) decreases then increases *(d) decreases & remains constant*

46 ***The chemical reactions in which reactants require high amount of activation energy are generally:***

(a) slow *(b) instantaneous* *(c) fast* *(d) spontaneous*

47 ***Velocity of a reaction is given by:***

(a) dx / dt *(b) dt / dx* *(c) dx × dt* *(d) None of them*

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48 ***The reactions proceed only in the presence of sunlight are called:***

(a) endothermic reactions (b) exothermic reactions
(c) photochemical reactions (d) all of them

49 ***Slope of curve is equal to:***

(a) base / perpendicular (b) perpendicular / base
(c) base × perpendicular (d) All of these

50 ***The sum of average internal energy and energy of activation is called:***

(a) activated energy (b) potential energy (c) threshold energy (d) none of these

51 ***Which statement is true?***

(a) crystalline boron is much more reactive than amorphous boron
(b) amorphous boron is much more reactive than crystalline boron
(c) both have the same reacting power (d) both of them don't react at all

52 ***Rate of reaction can be determined by:***

(a) physical methods (b) chemical methods
(c) both methods (d) None of these

53 ***Which one is the fastest reaction?***

(a) Neutralization (b) Rusting of iron
(c) Hydrolysis of ester (d) None of these

54 ***In most of chemical reaction, rate of reaction become double with the rise of :***

(a) 10°C (b) 5°C (c) 20°C (d) 0°C

55 ***The velocity of a chemical reaction can maintain constant by:***

(a) maintaining a constant temperature (b) keeping the constant stirred
(c) doing both (a) & (b) (d) None of these

56 ***Which one of the following can give order of a reaction?***

(a) Balanced chemical reaction (b) Magnitude of rate constant
(c) Experimental rate law (d) Nature of reactants

57 ***A powdered solid is more reactive than its chunks due to:***

(a) higher temperature (b) higher pressure
(c) greater surface area (d) greater volume

Answer Key

1. (a)	9. (b)	17. (a)	25. (c)	33. (a)	41. (b)	49. (b)
2. (a)	10. (d)	18. (c)	26. (b)	34. (c)	42. (a)	50. (c)
3. (b)	11. (c)	19. (c)	27. (d)	35. (c)	43. (b)	51. (b)
4. (d)	12. (c)	20. (a)	28. (c)	36. (b)	44. (b)	52. (c)
5. (a)	13. (b)	21. (a)	29. (a)	37. (d)	45. (b)	53. (a)
6. (d)	14. (d)	22. (b)	30. (b)	38. (c)	46. (a)	54. (a)
7. (d)	15. (b)	23. (c)	31. (b)	39. (a)	47. (a)	55. (a)
8. (b)	16. (c)	24. (d)	32. (c)	40. (b)	48. (c)	56. (c)
						57. (c)

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Short / Detailed Answer Questions

Q.01 ***Define chemical kinetics and give examples and explanation.*** ***Karachi Board: 2008***

Ans. ***Definition:*** The study of rates of chemical reactions and the factors that affect the rates of chemical reactions is called chemical kinetics.

Examples:

(i) ***Fast reaction kinetics:*** Many reactions in aqueous solutions are so rapid that they seem to occur instantaneously. For example, a white precipitate of silver chloride is formed immediately on addition of silver nitrate solution to sodium chloride solution. It is impossible to determine their rates of reactions.

$$Ag^+NO_{3(aq)}^- + Na^+Cl^-_{(aq)} \longrightarrow Ag^+Cl^-_{(s)} + Na^+NO^-_{3(aq)}$$

(ii) ***Moderate reaction kinetics:***

Some reactions proceed at a moderate rate e.g., hydrolysis of an ester.

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

(iii) ***Slow reaction Kinetics:*** Still other reactions take a much longer time e.g., rusting of iron, the chemical weathering of stone work of building by acidic gases in the atmosphere and the fermentation of sugars.

Q.02 ***Briefly describe the mechanism of reactions.***

Ans. All reactions occur in single or a series of steps. If a reaction consists of several steps, one of the steps will be the slowest than other steps. The slowest step is called the rate determining step. The other steps will not affect the rate. Many factors influence the rate of a chemical reaction and it is important to discover the conditions under which the reaction proceeds most economically in industry.

Q.03 ***Define rate of reaction and give its graphical explanation.***

Karachi Board: 2007, 2008, 2010, 2013, 2014

Ans. ***Definition:*** The change in concentration of reactant or product per unit time is called rate of reaction.

Explanation: During a chemical reaction, reactants are converted into products. So the concentration of product increases and the concentration of reactant decreases. The situation is explained for the reactant A changing to the product B.

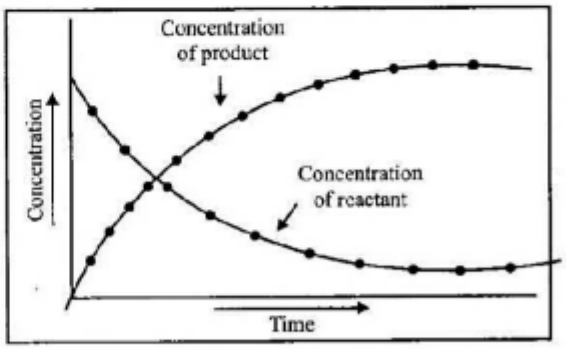

Fig 8.1 Change in the concentration of reactants and products with time for the reaction A ⟶ B

The slope of the graph for the reactant or the product shows rapid decrease in the concentration of the reactant and consequently a rapid increase in the concentration of the product. As the reaction proceeds, the slope becomes less steep indicating that the reaction is slowing down with time. Where the graph becomes a horizontal line, the reaction stops, Since at this stage all of the reactant has been consumed.

Unit of rate of reaction: $mole\,dm^{-3}\,sec^{-1}$

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Q.04 ***Define velocity of reaction.***

Ans. The rate of a chemical reaction at a particular given moment is known as velocity of the reaction.

$$\text{Velocity of a reaction} = \frac{dx}{dt}$$

where dx = very small change of concentration
dt = very small change in time.

Q.05 ***Give significance of plus and minus sign in*** $\frac{dx}{dt}$

Ans. The reaction rate $\frac{dx}{dt}$ at any instant can be expressed in the following way for a given reaction:

$$A + B \longrightarrow C + D$$

$$\text{Rate of reaction} = \frac{-dx}{dt} = \frac{\text{Amount of A or B consumed}}{\text{Time taken for change}}$$

$$\text{Rate of reaction} = \frac{+dx}{dt} = \frac{\text{Amount of C or D produced}}{\text{Time taken for change}}$$

The minus sign in the rate of reaction -dx indicates decrease in the concentration of reactants (A and B) while positive sign shows the increase in concentration of product (C and D).

Q.06 ***Describe instantaneous rate of reaction.***

Ans. ***Definition:*** The rate of change of concentration of any one of the reactants or product over a small interval of time is called instantaneous rate of reaction.

It can be determined by finding the slope of curve, at a particular time. The slope can be find out by simply drawing a tangent to the curve at that time. (See fig. 8.2)

Consider the reaction between HCl and Mg.

$$Mg_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_{2(g)}$$

The reaction is followed by measuring the volume of hydrogen as evolved at regular interval of time. The results are plotted and a rate curve is obtained.

To calculate velocity of reaction, say at 40s the tangent to the curve at 40s is shown in the graph.

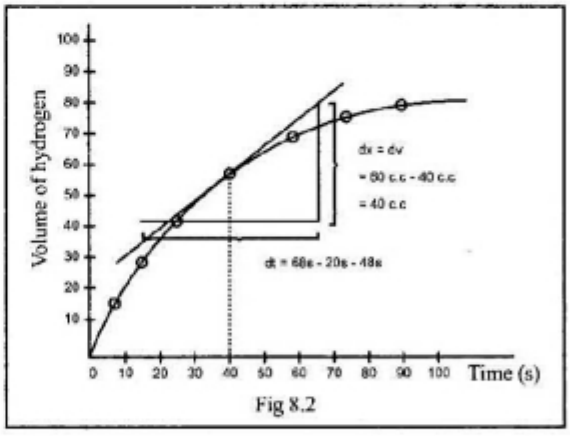

Fig 8.2

Velocity of reaction at 40s = slope of tangent

$$\text{Velocity} = \frac{dx}{dt} = \frac{dv}{dt} = \frac{40\text{cm}^3}{48\text{s}} = 0.83\ \text{cm}^3/\text{s}$$

Thus rate of production of H_2 at 40s = 0.83 cm^3/s

Q.07 ***Describe rate constant or velocity constant.*** ***Karachi Board: 2013***

Ans. According to law of mass action "Rate of a chemical reaction is directly proportional to the product of active masses or molar concentration of the reactants."

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Consider the following reaction:

$$A + B \longrightarrow C \qquad \text{(Product)}$$

Rate expression of the above reaction will be as:

$$\text{Rate} \ \alpha \ [A]\,[B]$$

$$\frac{dx}{dt} \ \alpha \ [A]\,[B]$$

$$\frac{dx}{dt} = K[A]\,[B]$$

The above equation is called rate expression. In this expression, K is called rate constant or velocity constant.

Q.08 ***Describe specific rate constant.*** ***Karachi Board: 2007, 2010***

Ans. When the molar concentration of each reactant is unity i.e 1 mole/ dm^3 then K is called specific rate constant. Consider the following reaction:

$$A + B \longrightarrow C$$

$$\text{Rate} \ \alpha \ [A]\,[B]$$

$$\frac{dx}{dt} \ \alpha \ [A]\,[B]$$

If $[A] = 1$ and $[B] = 1$, then

$$\frac{dx}{dt} = K[1]\,[1]$$

$$\therefore \quad \frac{dx}{dt} = K \qquad \text{(specific rate constant)}$$

Q.09 ***What are the characteristics of 'K' ?***

Ans. ***(i)*** It has a fixed value at a particular temperature.

(ii) Its value varies with temperature.

(iii) Its value at a particular temperature remains unchanged when the concentration of either one or of all reactants is changed.

Q.10 ***Define activation energy. Give its relation with the speed of reaction.***

Karachi Board: 2011-2014-2018-2019

Ans. ***Definition:*** The minimum amount of energy required for a reactant to reach to an excited state or activated state is called energy of activation.

"Sum of the energies (excess + average) which the colliding molecules should possess for effective collision or for reaction is called energy of activation (E_a).

It is independent of the initial and final energy contents of the reacting particles but depends upon the mechanism or path followed by the reaction and also the nature of the chemical bonds under going rupture.

The colliding molecules of the reactants possess

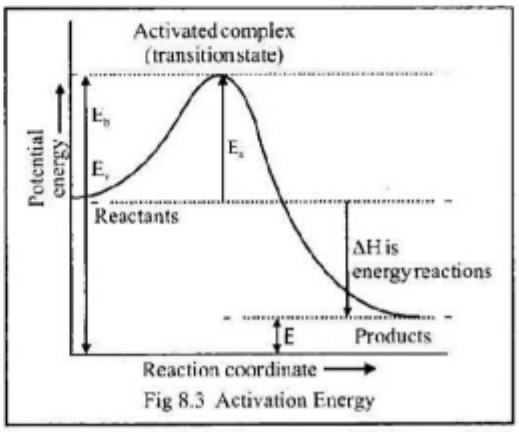

Fig 8.3 Activation Energy

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activation energy form activated complex (see fig 8.3).

Activation Energy = Threshold energy - Average internal energy

Threshold energy: Average energy + Activation energy

The speed of reaction depends upon the activation energy of molecules. The reactions which have low values of activation energy are fast reactions and those which proceed slowly or moderately have comparatively high value of energy of activation.

Q.11 ***How does temperature & a catalyst affect the activation energy?*** ***Karachi Board: 2007***

Ans. ***(i)*** ***Effect of temperature:*** Rise in temperature decreases the activation energy. As temperature increases the number of effective collisions per second also increases which increases the rate.

(ii) ***Effect of Catalyst:*** A catalyst is a substance which alters the rate of reaction by increasing or decreasing the activation energy without being consumed itself.

Q.12 ***Briefly describe the rate expression (rate law).*** ***Karachi Board: 2019***

Ans. ***Rate law:*** "The rate of a reaction is directly proportional to the product of the concentration of the reactants each raised to some power."

Consider the following reaction:

$$aA + bB \longrightarrow cC + dD$$

$$\text{Rate of reaction} \quad \alpha \quad [A]^a \times [B]^b$$

$$\text{Rate of reaction} \quad = \quad K[A]^a \times [B]^b \qquad \text{(i)}$$

where [A] and [B] are the concentration of A and B.

a and b are the exponents of concentrations of a and b. The values of a and b are determined experimentally.

K is a constant known as rate constant. Equation (i) is known as rate law or rate expression.

Advantage of rate expression: Rate law expresses the effect of concentration on the rate of reaction.

Q.13 ***Name the physical methods along with the observed physical properties for determining the rate of reaction.*** ***Karachi Board: 2007, 2012, 2017***

Ans. ***Physical Methods:*** The following physical methods are based on the measurement of physical properties of reaction mixture during the reaction.

(i) ***Refractometric method:***
Change in refractive index of the mixture of a substance is observed.

(ii) ***Spectroscopic method:***
This method is based on the absorption of ultraviolet or infrared radiations by a substance.

(iii) ***Calorimetric method:***
Change in the intensity of colour is observed.

(iv) ***Conductivity method:***
Conductivity measurement of ions are observed. The conductivity is proportional to the rate of change in concentration.

(v) ***pH method:***
Change of pH in the reaction mixture is observed.

(vi) ***Polarimetric method:***
Optically active reaction mixtures are observed if change in optical rotation of plane polarized light happens.

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Q.14 ***Describe chemical methods for the determination of rate of chemical reaction.***

Karachi Board: 2008,2017

Ans. In these methods, the concentration of reactants and products are measured by acid base titration, redox titration, gravimetrically etc. at regular time intervals.

For example, in the hydrolysis of ethyl acetate $CH_3COOC_2H_5$ in the presence of acid. The samples of reaction solutions are withdrawn at regular time intervals and the amount of acetic acid (CH_3COOH) produced at different time intervals is noted by acid base titration.

A graph is plotted between concentrations and time intervals. The slope of tangent at any point on the curve is equal to the rate of reaction.

$$\text{Rate} = \frac{dx}{dt} = \frac{dv}{dt}$$

Rate constant = rate when the molar concentration of cash reactant in 1 M.

Q.15 ***Make a list of factors which affect the rates of chemical reactions.***

Karachi Board: 2006, 2010, 2011, 2013, 2018

Ans. Following are those factors which change the number of effective collisions per second that can affect the rate of a chemical reaction.

(i) Concentration of reactants.
(ii) Nature of reactants.
(iii) Temperature.
(iv) Presence of catalyst.
(v) Surface area of reactants (heterogeneous reactions).
(vi) Radiations.

Q.16 ***How rate of reaction is affected by concentration of reactants?***

Karachi Board: 2005, 2006, 2010, 2011

Ans. If there are more number of molecules, there are more chances of collision. Thus an increase in the concentration of the reactants will result increase in reaction rate while a decrease in the concentration will have a reverse effect.

e.g., Combustion that occurs slowly in air (21 % oxygen) will occur more rapidly in pure oxygen.

The rate of chemical reaction is proportional to the molar concentration of reacting substances.

$$xA + yB \longrightarrow C$$

$$\text{Rate of reaction} \quad \alpha \quad [A]^x\ [B]^y$$

$$\frac{dx}{dt} = K[A]^x\ [B]^y$$

Rates of majority of chemical reactions are effected by concentration.

Q.17 ***How nature of reactants affect rate of reaction?***

Karachi Board: 2005, 2006, 2010, 2011, 2014

Ans. The rate of reaction depends upon the nature of reacting substances because activation energy for effective collisions is different for different reacting substance.

Consider the following two reactions in which the collision probabilities are same, Even then their rates are not equal.

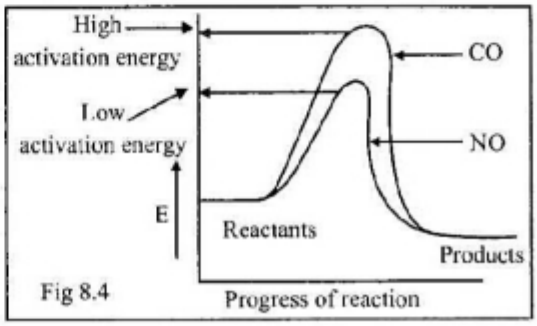

Fig 8.4

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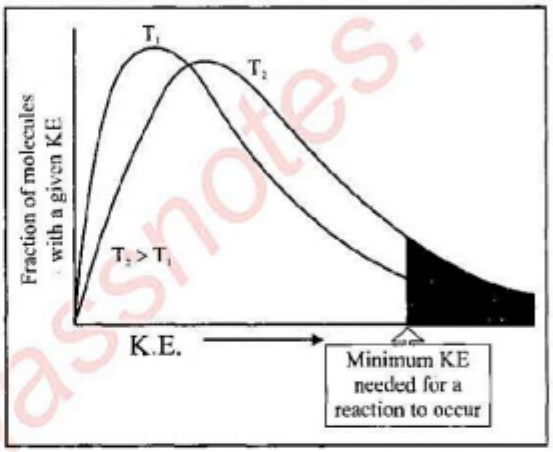
$$2NO + O_2 \longrightarrow 2NO_2 \text{ (Fast reaction)}$$
$$2CO + O_2 \longrightarrow 2CO_2 \text{ (Slow reaction)}$$

Reaction between NO and O_2 is fast while that for CO and O_2 is slow. This is because activation energy for CO is higher than that of NO. Similarly, the neutralization and double decomposition reaction are very fast as compared to these reaction in which bonds are rearranged.

Q.18 ***How rate of reaction is affected by temperature?*** ***Karachi Board: 2013, 2018***

Ans. According to collision theory the rate of a reaction is proportional to the number of collision among the reactant molecules. The rate of reaction varies with temperature. As a general rule of thumb, the rate of reaction double for every 10 K rise in temperature.



The rise in temperature raises the kinetic energy of each molecule. It is noted that the fraction of molecules possessing threshold energy or activation energy becomes doubled as a result number of effective collisions is also doubled, hence rate is doubled. The graph shows the kinetic energy of molecules at different temperatures. The shaded area shows the fraction of molecules having the threshold energies. Shaded area of T_2 is doubled of T_1.

Q.19 ***How rate of reaction is affected by a catalyst?***

Ans. ***Catalysis:*** A catalyst is a substance which alters the rate of a chemical reaction, but remains chemically unchanged at the end of reaction. The process which takes place in the presence of a catalyst is called catalysis.

Catalysts are classified as:

(i) Positive catalysts ***(ii)*** Negative catalysts
(iii) Auto catalysts ***(iv)*** Biocatalysts

Q.20 ***Describe the positive catalysts.*** ***Karachi Board: 2008, 2011***

Ans. ***(i)*** ***Positive catalysts :*** A catalysts which increases the rate of reaction by lowering the energy of activation is known as positive catalyst.

Examples: In the presence of positive catalysts, a greater fraction of total molecules will have lower energy of activation and will collide successfully in a short time to give more products by increasing the rate of reaction.

(i) $2KClO_3 \xrightarrow{Heat} 2KCl + 3O_2$ (slow reaction)

(ii) $2KClO_3 \xrightarrow[MnO_2]{Catalyst} 2KCl + 3O_2$ (fast reaction)

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Q.21 ***Describe the negative catalyst.*** ***Karachi Board: 2008***

Ans. A catalyst which retards the rate of reaction by increasing the energy of activation is known as negative catalyst or inhibitor.

Examples: Glycerine is an inhibitor for the decomposition of H_2O_2.

$$2H_2O_{2(aq)} \xrightarrow{\text{Glycerine}} 2H_2O_2 + O_2 \qquad \text{(slow with negative catalyst)}$$

Negative catalyst decreases the effective collision, hence decreases the rate of reaction.

Q.22 ***What are auto-catalyst and biocatalyst?***

Ans. ***Auto Catalyst:*** In some of the reactants a product formed acts as a catalyst. This phenomenon is called as auto catalyst.

Examples:

(i) Hydrolysis of ethyl acetate generates acetic acid which acts as catalyst for further reaction.

(ii) The reaction of oxalic acid with acidified $KMnO_4$ is slow at the beginning, but after some times, MnO_4 produced in reaction makes it faster.

$$2KMnO_4 + 3H_2SO_4 + 5(COOH)_2 \xrightarrow{Mn^{2+}} K_2SO_4 - 2MnSO_4 + 10CO_2 + 8H_2O$$

Biocatalyst (Enzyme): Enzymes are the complex protein molecules and catalyze the organic reactions in the living cells.

e.g., Glucose is converted into ethanol by the enzyme zymase present in the yeast.

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

Q.23 ***How rate of reaction is affected by surface area?*** ***Karachi Board: 2008, 2013, 2014, 2018***

Ans. In case of heterogeneous reactions in which the reacting species are in different physical states, the surface area of solid reactant plays an important role with respect to rate of reaction, greater the surface area, the higher is that rate of reaction.

e.g., $CaCO_3$ in the powder form reacts with dilute H_2SO_4 more efficiently than the big pieces of $CaCO_3$. Similarly for the same reason amorphous boron is much more reactive than crystalline boron.

Q.24 ***How rate of reaction is affected by light (radiation)?*** ***Karachi Board: 2011***

Ans. Light consists of photons having definite amount of energies depending upon their frequencies. Same chemical reaction proceed only under the influence of light. They are called photochemical reactions. The concentration of reactants does not influence rate of such reactions so they are zero order reaction.

Examples: ***(i)*** Reaction between H_2 and Cl_2

$$H_2 + Cl_2 \xrightarrow[\text{Sunlight}]{\text{Bright}} 2HCl$$

(ii) Reaction between CH_4 and Cl_2

$$CH_4 + Cl_2 \xrightarrow{\text{Sunlight}} CH_3Cl + HCl$$

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The photons strike the reactant molecules. They provide the necessary activation energy to the reactant molecules to react.

Q.25 ***Define order of reaction give its example.*** ***Karachi Board: 2004***

Ans. ***Definition:*** The sum of all the exponents of the concentration terms in the rate equation is called order of reaction.

Example: Consider the following reaction.

$$aA + bB \longrightarrow cC + dD$$

$$\text{rate of reaction} = K[A]^a \times [B]^b \quad \text{(rate equation)}$$

$$\text{order of reaction} = a + b$$

Q.26 ***Define Zero order reaction and give examples.*** ***Karachi Board: 2013***

Ans. ***Zero order reaction:*** It is the rate of reaction in which sum of all the exponents of concentration terms in the rate equation is equal to zero. Photochemical reactions are zero order reactions.

Example:

(i) $2NH_{3(g)} \longrightarrow 3H_{2(g)} + N_{2(g)}$

It is independent of the concentration of the reactant.

(ii) $H_2 + Cl_{2(g)} \xrightarrow{h\nu} 2HCl_{(g)}$

Zero order expression:

$$\frac{dx}{dt} \propto a^\circ a^\circ = 1 \qquad \frac{dx}{dt} = K$$

where K is called the rate constant for zero order reaction.

Q.27 ***Define first order reaction and give examples.***

Ans. ***First order reaction:*** It is the rate reaction in which sum of all exponent of concentration terms in the rate equation is equal to one.

Examples:

(i) $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$

Rate equation of the above reaction is given below:

$$\text{Rate of reaction} = K[N_2O_5] = 1$$

As the exponent of the concentration of N_2O_5 in one, hence the above reaction is of first order.

(ii) $C_{12}H_{22}O_{11} + H_2O \longrightarrow \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6}$

$$\text{Rate of reaction} = K[C_{12}H_{22}O_{11}] \times [H_2O] = K[C_{12}H_{22}O_{11}]$$

As the exponent of the concentration of $C_{12}H_{22}O_{11}$ is one and that of H_2O is zero, hence sum of the exponents is $1 + 0 = 1$. The above reaction is of first order.

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Q.28 ***Define second order reaction and give examples.***

Ans. ***Second order reaction:***

It is the rate of reaction in which sum of all the exponent of concentration terms in the rate equation is equal to two.

Examples:

(i) $2NO_2 \longrightarrow N_2 + 2O_2$

Rate of reaction $= K[NO_2]^2$

As the exponent of the concentration of NO_2 is two, hence the above reaction is of second order.

(ii) $H_2 - I_2 \longrightarrow 2HI$

Rate of reaction $= K[H_2]^1 \times [I_2]^1 = K[H_2]\ [I_2]$

Sum of the exponents is $1 + 1 = 2$.

The above reaction is of second order.

Q.29 ***Define third order reaction and give examples.***

Ans. ***Third order reaction:***

It is the rate of reaction in which sum of all the exponent of concentration terms in the rate equation is equal to three.

Examples:

(i) $2NO + O_2 \longrightarrow 2NO_2$

Rate equation of the above reaction is given below:

Rate of reaction $= K[NO]^2\ [O_2]^1$

As the exponent of the concentration of NO is two and that of O_2 in one, hence sum of the exponents is $2 + 1 = 3$. Thus the above reaction is of third order.

(ii) $2NO + Cl_2 \longrightarrow 2NOCl$

Rate $= K[NO]^2 \times [Cl_2]^1$

Sum of the is $2 + 1 = 3$

So, the above reaction is of this third order.

Solved Problems of Textbook

Writing Rate Expression

Example 1: ***Write rate expression for the following reactions:***

(a) $PCl_5 \longrightarrow PCl_3 + Cl_2$

(b) $2NO + O_2 \longrightarrow 2NO_2$

(C) $H_2SeO_3 + 6I^- + 4H^+ \longrightarrow Se + 3I_2 + 3H_2O$

Solution: ***Karachi Board: 2013***

(a) Rate of reaction α $[PCl_5]$

$$\frac{dx}{dt} = K[PCl_5]$$

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(b) Rate of reaction α $[NO]^2$ $[O_2]$

$$\frac{dx}{dt} = K[NO]^2 [O_2]$$

(c) Rate of reaction α $[H_2SeO_3]$ $[I^-]^6$ $[H^+]^4$

$$\frac{dx}{dt} = K[H_2SeO_3]^- [I^-]^6 [H^+]^4$$

Significance of plus and minus sign.

Example 2: ***For a chemical reaction A ⟶ B, the rate of reaction is denoted by:***

$\frac{-dA}{dt}$ ***or*** $\frac{+dB}{dt}$ ***State the significance of plus and minus signs.***

Solution:

$\frac{-dA}{dt}$ represents the rate of reaction in terms of decrease in concentration of reactant A.

$\frac{+dB}{dt}$ represents the rate of reaction in terms of decrease in concentration of reactant B.

Calculating rate of disappearance

Example 3: ***For a chemical reaction, $C_2H_{2(g)} + 2H_{2(g)} \longrightarrow C_2H_{6(g)}$, the rate of appearance of C_2H_6 is 0.25 mole / dm³.s. What is the rate of disappearance of C_2H_2 and H_2?***

Solution:

rate of disappearance of C_2H_2 = 0.25 mole / dm³.s

rate of disappearance of H_2 = 0.25 × 2 = 0.5 mole / dm³.s

Calculating rate constant.

Example 4: ***For a chemical reaction A + B ⟶ AB***
Calculate (a) Rate constant when initial concentration of both the reactants is 0.1 moles / dm³ each and rate of reaction is 3.02×10^{-4} moles / dm³
(b) Rate constant if initial concentration of A or B is doubled.

Solution:

(a) For this reaction

Rate of reaction α [A] [B]

$$\frac{dx}{dt} = K[A][B]$$

$$3.02 \times 10^{-4} \text{ mole / dm}^3\text{.s} = K(0.1 \text{ mole / dm}^3)(0.1 \text{ mole / dm}^3)$$

$$K = \frac{3.02 \times 10^{-4} \text{ mole / dm}^3\text{.s}}{(0.1 \text{ mole / dm}^3)(0.1 \text{ mole / dm}^3)} = \frac{3.02 \times 10^{-4} \text{ dm}^3}{0.1 \text{ mole .s}}$$

$$K = 3.02 \times 10^{-2} \text{ dm}^3 \text{ / mole .s.}$$

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(b) Let the concentration of " B " is doubled

As [A] = 0.1 mole / dm^3

$\therefore$ [B] = 0.1 × 2 = 0.2 mole / dm^3

Since concentration of [B] is doubled, the rate of reaction will also become double i.e.,

Ratc = $3.02 \times 10^{-4} \times 2 = 6.04 \times 10^{-4}$ mole / dm^3 .s

Now Rate = K [A] [B]

6.04×10^{-4} mole / dm^3 .s = K (0.1 mole / dm^3) (0.2 mole / dm^3)

$$K = \frac{6.04 \times 10^{-4} \text{ mole / dm}^3 \text{.s}}{(0.1 \text{ mole / dm}^3)\ (0.2 \text{ mole / dm}^3)}$$

K = 3.02×10^{2} dm^3 / mole

Calculating activation energy

Example 5: ***For a chemical reaction A ⟶ B the threshold energy of reaction is 31 K.J / mole. The average internal energy of A is 12 KJ / mole. Calculate Activation energy of A.***

Solution:

Activation energy = Threshold energy - Average internal energy

E_a = 31 KJ / mole - 12 KJ / mole

Activation energy of A = 19 KJ / mole

Predicting effect of concentration on rate

Example 6: ***The rate of a chemical reaction for the reaction :***

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

$$Rate = K[NO]^2\ [O_2]$$

What will be the effect on rate if:

(a) concentration of NO is doubled.

(b) concentration of NO is halved.

(c) concentration of O_2 is doubled.

Karachi Board: 2013

Solution:

(a) As rate α [NO]^2 hence if concentration of NO is doubled, the rate will increase by [2]^2 = 4 times.

(b) If concentration of NO is halved the rate will be decreed by [½]^2 = $\frac{1}{4}$ times.

(c) As rate α [O_2] hence if concentration of O_2 is doubled the rate will also be doubled.

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Predicting effect of concentration on rate constant

Example 7: ***For a chemical reaction at 450°C***

$$2NH_3 \longrightarrow N_2 + 3H_2$$

$$Rate = K\,[NH_3]^2$$

What will be the effect on rate constant if concentration of NH_3 is increased four times?

Solution:

Now $K = \dfrac{Rate}{[NH_3]^2}$

The value of K will remain constant for either increasing or decreasing rate with reference to the ammonia concentration. K remains constant because as concentration of NH_3 is increased four times, the rate also increases by that factor.

Determining order of reaction.

Example 8: ***A certain reaction $A + 2B \longrightarrow C + D$ gave the following data:***

Initial Concentration mole / dm³			*Initial rate of Reaction mole / dm³ s*
No.	*A*	*B*	
1	0.1	0.1	3×10^{-3}
2	0.2	0.1	6×10^{-3}
3	0.1	0.2	9×10^{-6}

What is rate law and order of reaction?

Solution:

Rate expression based on experimental data is called rate law. According to data:

(a) When concentration of A is doubled, the rate is also doubled; hence

$$Rate \ \alpha \ [A] \qquad \text{_____(1)}$$

(b) When concentration of B is doubled, rate increases by square i.e from 3×10^{-3} to 9×10^{-6} i.e $(3)^2 \times 10^{-6}$; hence

$$Rate \ \alpha \ [B]^2 \qquad \text{_____(2)}$$

(c) Now combining (1) and (2), we have

$$Rate \ \alpha \ [A]\,[B]^2$$

or $$Rate = K\,[A]\,[B]^2$$

This is rate law for the given reaction.

Now, Order of Reaction = Sum of exponents of concentration in rate law.

Order of Reaction = 1 + 2 = 3.

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Estimating value of K with change in temperature

Example 9: ***As a rule of thumb, rate constant of a reaction increases by a factor of 2 for each 10°C rise in temperature, although the actual amount of increase differs from one reaction to another.***
Consider a reaction A ⟶ B, for which at 400°C, rate constant K has a value of 3×10^{-12}. s^{-1}.
What can be the possible value of K at 450°C ?

Solution:

Temperature increases from 400°C to 450°C. Thus rise in temperature = 50°C. For each 10°C, K is more or less doubled. Hence value of K will increase 5 times i.e.

$$K = (3 \times 10^{-12} s^{-1}) \times 5$$
$$K = 15 \times 10^{-12} s^{-1}$$

Solved Problems From Past Papers

Problem 1: ***Consider the reaction A + B ⟶ C and answer the following:***
(a) Write the rate expression for the above reaction. What are the units of the rate of reaction?
(b) Will the specific rate constant (K) increases, decreases or remain unchanged if the concentration of A and B is doubled?
Karachi Board: 2010

Solution:

(a) A + B ⟶ C

rate expression:

$$\frac{dx}{dt} = K[A][B]$$

unit = mole / dm^3. sec

(b) Rate constant will not change with the increase or decrease in concentration of A and B.

Problem 2: ***For the given reaction A + B ⟶ Products, determine the order of reaction from the following data:***
Karachi Board: 2019

A (mole / dm^3)	*B (mole / dm^3)*	*Rate mole s^{-1}*
0.1	0.1	1×10^{-3}
0.2	0.1	4×10^{-3}
0.1	0.2	3×10^{-3}

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Solution:

According to above data :

(a) When concentration of A is doubled the rate increases four times hence Rate α $[A]^2$ _____ (1)

(b) When concentration of B is tripled, the rate is also tripled. Rate α [B] _____ (2)

Now combine 1 and 2, we have:

Rate α $[A]^2$ [B]

Rate = K $[A]^2$ [B]

Order of reaction = 2 + 1 = 3 **Ans.**

Problem 3: ***For the chemical reaction $F_2 + 2ClO_2 \longrightarrow 2FClO_2$, calculate the rate constant when initial concentration of F_2 is 0.1 mol / dm^3 of ClO_2 is 0.01 mol / dm^3 and the rate of reaction is 1.2×10^{-3} mol / dm^3.***

Solution: ***Karachi Board: 2008***

$$F_2 + 2ClO_2 \longrightarrow 2FClO_2$$

$$\frac{dx}{dt} = K[F_2][ClO_2]^2$$

$$1.2 \times 10^{-3} \text{ mol / dm}^3 \text{ s} = K[0.1 \text{ mol/dm}^3][0.1 \text{ mol/dm}^3]$$

$$1.2 \times 10^{-3} \text{ mol / dm}^3 \text{ s} = K[1 \times 10^{-5} \text{ mol / dm}^3]$$

$$\frac{1.2 \times 10^{-3} \text{ mol. dm}^{-3} \text{ s}^{-1}}{1 \times 10^{-5} \text{ mol dm}^{-3}} = K$$

$$K = 120 \text{ mol dm}^{-3} \text{ s}^{-1}$$ **Ans.**

Problem 4: ***Write the rate expression, find the value of rate constant and determine the order of reaction using the following date :*** ***Karachi Board: 2007***

	[NO]	$[O_2]$	Rate
(i)	0.1 M	0.1 M	2×10^{-3} mol / sec
(ii)	0.2 M	0.1 M	8×10^{-3} mol / sec
(iii)	0.1 M	0.2 M	4×10^{-3} mol / sec

Solution:

Rate expression:

$$2NO + O_2 \longrightarrow 2NO_2$$

$$\frac{dx}{dt} = K[NO]^2[O_2]$$

Rate constant

$$\frac{dx}{dt} = K[NO]^2[O_2]$$

$$8 \times 10^{-3} = K[0.2]^2[0.1]$$

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$$\frac{8 \times 10^{-3}}{[0.2]^2\ [0.1]} = K$$

$$K = \frac{8 \times 10^{-3}}{0.04 \times 0.1} = \frac{8 \times 10^{-3}}{4 \times 10^{-3}} = 2$$

Rate constant = 2 dm^3 / mol. sec

Order of reaction:

Rate = $K [NO]^2 [O_2]$

2 + 1 = 3

Order of reaction is 3.

Problem 5: ***For the decomposition of chloroethyl carbonate*** $ClCOOCH_2CH_3 \longrightarrow CO_2 + CH_3CH_2Cl$, ***$K = 1.3 \times 10^{-3}\ s^{-1}$ at 200°C. If the initial rate is $3.25 \times 10^{-4}\ Ms^{-1}$, find the initial concentration of $ClCOOCH_2CH_3$.***

Solution: ***Karachi Board: 2006***

Rate constant = $1.3 \times 10^{-3}\ s^{-1}$

Rate of reaction = $\frac{dx}{dt} = 3.25 \times 10^{-4}\ Ms^{-1}$

Initial concentration = ?

$$\frac{dx}{dt} = K [ClCOOCH_2CH_3]$$

$$3.25 \times 10^{-4}\ Ms^{-1} = 1.3 \times 10^{-3}\ s^{-1} [ClCOOCH_2CH_3]$$

$$[ClCOOCH_2CH_3] = \frac{3.25 \times 10^{-4}\ Ms^{-1}}{1.3 \times 10^{-3}\ s^{-1}} = 0.25$$

Concentration of $ClCOOCH_2CH_3$ = 0.25 M **Ans.**

Problem 6: ***For the reaction $A + B \longrightarrow AB$, find the following :***

(i) Rate constant if the initial concentration of each reactant is 0.2 mol / dm^3 & rate of reaction is 9.04×10^{-4} mol / dm^3 s. ***Karachi Board: 2005***

Data:

K = ?

[A] = 0.2 mol / dm^3 [B] = 0.2 mol / dm^3

$\frac{dx}{dt}$ = 9.04×10^{-4} mol / dm^3 s

Solution:

$$\frac{dx}{dt} = K [A]\ [B]$$

$$9.04 \times 10^{-4}\ \frac{mol}{dm^3\ s} = K [0.2\ mol / dm^3]\ [0.2\ mol / dm^3]$$

$$K = \frac{9.04 \times 10^{-4}\ mol\ dm^{-3}\ s^{-1}}{0.04\ mol^2\ dm^{-3}}$$

Result: $K = 2.0226\ mol\ dm^{-3}\ s^{-1}$

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(ii) Rate constant if the initial concentration of B is doubled in $A + B \longrightarrow AB$ solution:

$$[A] = 0.2 \text{ mol / dm}^3$$

$$[B] = 2 \times 0.2 \text{ mol / dm}^3 = 0.4 \text{ mol / dm}^3$$

$$\frac{dx}{dt} = 9.04 \times 10^{-4} \times 2 \text{ mol / dm}^3\text{. s} = 1.808 \times 10^{-3} \text{ mol/dm}^3\text{.s}$$

$$= K[A][B] = 1.808 \times 10^{-3} = K[0.2][0.4]$$

$$K = \frac{1.808 \times 10^{-3}}{0.08}$$

$$K = 2.25 \times 10^{-2} \text{ mol dm}^3\text{, s}^{-1}$$ **Ans.**

Problem 7: ***Consider reaction $A + B \longrightarrow C$ and answer the following: Will the specific rate constant (K) increase, decrease or remain unchanged if the concentration of A and B is doubled?*** *Karachi Board: 2006*

Solution:

We have $K = \frac{\frac{dx}{dt}}{[A][B]}$ _____ (1)

By given condition:

$$[A] = [2A] \; ; \; [B] = [2B]$$

Therefore, equation 1 becomes

$$\Rightarrow K' = \frac{\frac{dx}{dt}}{[A][B]} = \frac{\frac{dx}{dt}}{4[A][B]}$$

$$\Rightarrow K' = \frac{1}{4} K$$

$\therefore$ it decreases. **Ans.**

Problem 8: ***For the chemical reaction: $F_2 + 2ClO_2 \longrightarrow 2FClO_2$ Calculate the:***

(i) rate expression (ii) order of reaction

(iii) rate constant when the initial concentration of F_2 is 0.1 mole / dm^3, ClO_2 is 0.01 mole / dm^3 and the rate of reaction is 1.2×10^{-3} mole / dm^3 -sec. *Karachi Board: 2015*

Solution:

(i) According to the equation:

$$\text{Rate} = \frac{dx}{dt} \propto [F_2]$$

$$\text{Rate} = \frac{dx}{dt} \propto [ClO_2]^2$$

$$\text{Rate} \propto [F_2][ClO_2]^2$$ **Ans.**

(ii) Order of reaction $= 1 + 2 = 3^{rd}$ order

(iii) $$K = \frac{\text{Rate}}{[F_2][ClO_2]^2}$$

$$K = \frac{1.2 \times 10^{-3}}{[0.1][0.01]^2} = \frac{1.2 \times 10^{-3}}{0.00001}$$

$$K = 120 \text{ dm}^6\text{. mole}^{-2}\text{. s}^{-1}$$ **Ans.**

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Problem 9: *For the reaction:* $2N_2O_5 \longrightarrow 4NO_2 + O_2$, *calculate the rate constant when the initial concentration of* N_2O_5 *is 10.8 g/dm³ while the initial rate is* 2.96×10^{-4} *mole / dm³. sec.* ***Karachi Board: 2016***

Solution:

Concentration of $[N_2O_5]$ $= \frac{dx}{dt} = 0.1$ mole / dm³

Initial rate $= 2.96 \times 10^{-4}$ mole / dm³. sec.

K = rate constant $= ?$

Rate Expression:

$$\text{Rate} = K[N_2O_5]^2$$

$$K = \frac{\text{Rate}}{[N_2O_5]^2}$$

$$K = \frac{2.96 \times 10^{-4}}{[0.1]^2} = \frac{2.96 \times 10^{-4}}{0.01}$$

$K = 0.0296$ dm³. mol⁻¹. s⁻¹ **Ans.**

Problem 10: *The rate constant for the decomposition of* NO_2 *in the equation* $2NO_2 \longrightarrow 2NO + O_2$ *is* 1.8×10^{-3} *dm³ mol.s. What is the initial rate when the initial concentration of* NO_2 *is 0.75 M ? What is the rate constant when the initial concentration of* NO_2 *is doubled?* ***Karachi Board: 2010, 2017***

Solution:

$K = 1.8 \times 10^{-3}$ dm³ mol⁻¹ sec⁻¹

$\frac{dx}{dt} = ?$

$[NO_2] = 0.75$ M

$$2NO_2 \longrightarrow 2NO + O_2$$

$$\frac{dx}{dt} = K[2NO_2]^2$$

$$\frac{dx}{dt} = K[0.75]^2$$

$$\frac{dx}{dt} = 1.8 \times 10^{-3} \times 0.5625$$

$$\frac{dx}{dt} = 1.01 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$$

If the concentration of NO_2 is doubled:

$[NO_2] = 0.75 \times 2 = 1.5$ moles

Rate also doubled $= 0.0010125 \times 2 = 0.002025$

Now, $\frac{dx}{dt} = K[NO_2]^2$

$0.002025 = K[1.56]^2 = K[2.25]$

$$K = \frac{0.002025}{2.25} = 0.0009 = 9 \times 10^{-3}$$

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Differences

Karachi Board: 2005

S. No.	*Activation Energy*	*Threshold Energy*
1.	The minimum amount of energy in addition to the average kinetic energy which the molecule must have for effective collision is called activation energy.	The amount of energy that the molecule of a substance possess for the effective collision between them is called threshold energy.
2.	Activation energy is always smaller than threshold energy.	Threshold energy is always greater than activation energy.
3.	E_A = Threshold energy - average internal energy	T_E = Average energy + activation energy.

Karachi Board: 2007, 2005

S. No.	*Rate of Reaction*	*Reaction Rate Constant*
1.	It is defined as the rate of change of concentration of reactants or products at given instant.	It is proportionality constant. It correlate the concentration of reactants to the rate of reaction.
2.	It is denoted by $\frac{dx}{dt}$	It is denoted by K.
3.	In dx/dt , dx is very small change in concentration in a very small change of time dt.	If molar concentration of each reactant is unity then rate of reaction is equal to the rate constant.
4.	The rate of reaction is expressed in mole $dm^{-3}. s^{-1}$.	The unit of rate constant will vary according to the order of reaction.

Karachi Board: 2005

S. No.	*Positive Catalyst*	*Negative Catalyst (inhibitor)*
1.	It increases the rate of reaction.	It decreases the rate of reaction.
2.	It decreases the energy of activation.	It increases the energy of activation.
3.	Examples: MnO_2 , V_2O_5 , Pt.	Examples: Glycerine, Aniline.
4.	It increases the effective collision.	It decreases the effective collision.

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S. No.	*Order of Reaction*	*Molecularity*
1.	It is the sum of exponents of concentration as given in the rate expression.	It is that number of molecules taking part in a chemical reaction as given in a balanced chemical equation.
2.	The value of order of reaction ranges between 0-3.	The value of molecularity of reaction may be higher than 3 but can not be zero.
3.	Order of reaction can be calculated only by experiment.	It can be calculated theoretically.

S. No.	*Rate Constant*	*Specific Rate Constant*
1.	It is the ratio between the rate and concentration of reactant.	It is the ratio between the rate and concentration of reactant when concentraction is unity and temperature and pressure are specified.
2.	The proportionally constant in the rate expression is called rate constant. $\frac{dx}{dt} = K[A][B]$	The rate of reaction when the molar concentration of each reactant is in unity. $\frac{dx}{dt} = K$
3.	The rate constant may be greater than or less than the rate.	It is always equal to rate of reaction.

Scientific Reasons

Q.01 ***Rate of reaction is increased by increase in temperature.*** ***Karachi Board: 2014***

Ans. The rate of reaction are greatly influenced by the temperature at which the reaction is carried out. As Temperature increases the velocity of molecules also increases, this results in the increase of frequency of collisions, hence rate of reaction increases.

Q.02 ***In photochemical reaction, the order of reaction is zero.*** ***Karachi Board: 2013-2019***

Ans. In photochemical reaction, the concentration of reactants does not influence rate of reaction, so they are zero order reaction.

Q.03 ***Milk sours more rapidly in summer than in winter.*** ***Karachi Board: 2017-2018-2019***

Ans. Temperature has a pronounced effect on the biochemical processes. The biochemical process increases with the increase in temperature. This shows that decomposition starts with the increase in temperature. Due to this reason milk sours more rapidly in summer than in winter.

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Q.04 ***The energy of activation decreases with the increase of temperature.***

KarachiBoard: 2009

Ans. When temperature is increased, the velocity of molecules also increases which results in increase in frequency of collisions and hence less amount of energy is required to get threshold energy.

Q.05 ***A negative catalyst decreases the rate of a reaction.*** ***Karachi Board: 2008***

Ans. A negative catalyst decreases the rate of reaction not by increasing the activation energy but by binding itself with the reactive sites of the molecules, which stops the effective collisions and hence decreases the rate of a reaction.

Q.06 ***Reaction between H_2 and Cl_2 is photochemical and of zero order.***

Ans. The rates of certain chemical reactions are greatly influence by light. Absorption of light energize the reactant molecules. They provide necessary activation energy to the reactant molecules. The concentration of reactant does not influence the rate of such reactions, so they are zero order reactions. This shows that all the photochemical reactions are of zero order.

Q.07 ***A catalyst does not change the position of equilibrium but the equilibrium position reaches earlier.***

Ans. A catalyst decreases the energy of activation. It increases the rates of both forward and backward reaction with the same proportion which helps the equilibrium to establish in less time. It has no effect on the position of equilibrium.

Q.08 ***Powdered zinc reacts more vigorously with HCl than chunks of zinc.***

Karachi Board: 2016

Ans. One of the factors which affects the rate of reaction is the surface area of reactant. Greater the surface area of reactant, greater will be the rate of reaction. For the same reason, zinc in form of powder reacts more rapidly with HCl as it provides greater surface area for the reaction than the chunks of zinc.

Solution of Textbook Progress Test - 8

Q.01 ***Only some collisions between molecules are effective in producing chemical reaction. Explain why?***

Ans. It has been found that only those collision are effective in which the colliding molecules possess a minimum amount of energy called threshold energy. The molecules must acquire activation energy for effective collision.

Q.02 ***Explain the concept of activation energy and the variation of reaction rate with temperature.***

Ans. See Q 10 and 11 on page 282 and 283.

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Q.03 ***Distinguish between: (a) Rate and velocity of a reaction (b) Rate and rate constant (c) Positive catalyst and inhibitor***

Ans. See Q 3 & 4 for (a) & (b) on page 280 & 281 and see differences 2 on page 298 and for (c) see differences 3 on page 290.

Q.04 ***Give one example each for the following: (a) Rate of reaction (b) Velocity of reaction (c) Rate equation (d) Specific rate constant***

Ans. For (a) see Q 3 on page 280. (b) see Q 4 on page 281.
(c) see Q 7 on page 281. (d) see Q 8 on page 282.

Q.05 ***For the reaction*** $2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$, ***the rate equalien is*** $\frac{dx}{dt} = K[NO^2][O_2]$. ***What is the effect on the rate of the reaction when (a) the concentration of NO is reduced by one half (b) the concentration of*** O_2 ***is doubled (c) a catalyst is added to the reaction mixture.***

Ans. For (a) & (b) see example 6 on page 290.
(c) The activation energy of NO & O_2 is already low. There is no need of a catalyst. Any how it will speed up the reaction.

Q.06 ***The decomposition of formic acid is catalyzed by strong acids.***

$HCOOH_{(l)} \xrightarrow{H^+} CO_{(g)} + H_2O_{(l)}$

(a) Write its rate expression.
(b) What is the effect on its rate if the acid concentration is doubled.

Ans. (a) $\frac{dx}{dt} = K[HCOOH]$

(b) The rate of reaction will also doubled.

Q.07 ***Write a note on slow and fast reactions?***

Ans. See Q 1 on page 280.

Q.08 ***Among the factors that influences reaction rates, which are involved in each of the following:***

(i) Milk sours more rapidly in summer than in winter.
(ii) Powdered zinc reacts more rapidly with water than the chunks of metallic zinc.
(iii) Combustion of gasoline occurs more rapidly in an internal combustion engine than in open container.
(iv) Unless ignited hydrogen does not react with oxygen of the air but a stream of hydrogen passed over platinum gauze bursts into flame.

Ans. For

(i) See scientific reason- 3, on page 299.
(ii) See Q 23 on page 286.

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(iii) See Q 16 on page 284.
(iv) The strong bond of hydrogen have high activation energy. Therefore for the reaction it is ignited. Catalyst lowers the energy of activation.

Q.09 ***Make a list of factors which affect the rates of chemical reactions. Describe the way in which each factors which affects the rate of reactions. For each factor, mention whether it is specific to a certain type of reaction or whether it is general.***

Ans. See Q 15, 16, 17, 18, 19, 20, 23 & 24 on page 284, 285 and 286.

Q.10 ***Describe the rate of a chemical reaction as a change of concentration with time.***

Ans. See Q 6 on page 281.

Q.11 ***The reaction rate 'R', for reaction*** $2A + B \longrightarrow A_2B$ ***was found experimentally to be given by the expression*** $R = K[A]^2[B]$

(a) Will K increase, decrease or remain unchanged, if the concentration of A is doubled? If the concentration of B is doubled?

(b) Will R increase, decrease or remain unchanged, if the concentration of B is doubled? If the concentration of B is doubled?

Ans. (a) If the concentration of A and B doubled, rate will also increase by the factor and K will remain the same

(b) If the concentration of A is doubled the rate will increase four times and if concentration of B is doubled the rate will also be doubled.

Q.12 ***For the decomposition of ethyl chlorocarbonate (*** $ClCO_2C_2H_5$***)***
$ClCOOCH_2CH_3 \longrightarrow CO_2 + ClCH_2CH_3$. $K = 1.3 \times 10^{-3}\ s^{-1}$ ***at 200°C.***
What is the initial rate when initial concentration of $ClCOOCH_2CH_3$ ***is 0.25 M?***

Data: $K = 1.3 \times 10^{-3}\ s^{-1}$, Rate = ? $[ClCO_2CH_3] = 0.25\,M$

Solution: $ClCOOCH_2CH_3 \longrightarrow CO_2 + ClCH_2CH_3$

Formula: Rate = K [initial concentration]

Rate = $1.3 \times 10^{-3}\,[0.25]$

Ans. R = rate = $3.25 \times 10^{-4}\ Ms^{-1}$

Q.13 ***The rate constant for decomposition of nitrogen dioxide***
$2NO_{2(g)} \longrightarrow 2NO_{(g)} + O_{2(g)}$ ***is*** $1.8 \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$.
What is the initial rate when the initial concentration of NO_2 ***is 0.50 M?***

Date: K = $1.8 \times 10^3\ dm^3 mol^{-1}\ s^{-1}$

Rate = ?

$[NO_2]$ = 0.50 M

Solution: According to the reaction:

Rate = $K[NO_2]^3$

Rate = $1.8 \times 10^3 \times (0.50)^2$

Rate = $4.50 \times 10^2\ dm^3/mol\ s$

Ans. Rate = 4.5×10^2 mole s^{-1}

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Q.14 ***Following is given a date for the reaction*** $A + B \longrightarrow C$ ***. Find order of reaction?***

S. No.	Concentration Mole / dm^3		Rate of reaction
	A	B	
1.	0.1	0.1	8×10^{-4}
2.	0.2	0.1	16×10^{-4}
3.	0.1	0.2	16×10^{-4}

Ans. See problem 2 on page 292.

Q.15 ***For the reaction*** $2H_2 + O_2 \xrightarrow{Pt} 2H_2O$

Rate $= \frac{dx}{dt} = [H_2]^2 [O_2]$

Fill in the following blanks.

S. No.	Conc. of $[H_2]$	Conc. of $[O_2]$	Rate at 25°C
1.	1 mole / dm^3	1 mole / dm^3	5×10^6 mole / dm^3 . s
2.	2 mole / dm^3	1 mole / dm^3	----------
3.	1 mole / dm^3	3 mole / dm^3	----------

Ans. 1. $R = K[H_2]^2 [O_2]$

$$K = \frac{R}{[H_2]^2 [O_2]} = \frac{5 \times 10^6}{(1) \times (1)} = 5 \times 10^6 \text{ dm}^6 . \text{mol}^{-2} . \text{s}^{-1}$$

2. $R = K \times [2]^2 \times (1) = 5 \times 10^6 \times 4 = 20 \times 10^6 \text{ M s}^{-1}$

3. $R = K \times (1)^2 \times 3 = 5 \times 10^6 \times 3 = 15 \times 10^6 \text{ M s}^{-1}$

Q.16 ***Write rate expression for the following reaction:***

(i) $CH_2 = CH_2 + H_2 \longrightarrow CH_3 - CH_3$

(ii) $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$

(iii) $C_2H_4 + 7/2\ O_2 \longrightarrow 2CO_2 + 3H_2O$

Solution:

(i) $\text{Rate} \ \alpha \ [CH_2 = CH_2] [H_2]$

$\text{Rate} = K [CH_2 = CH_2] [H_2]$

(ii) $\text{Rate} \ \alpha \ [H_2] [O_2]^{1/2}$

$\text{Rate} = K [H_2] [O_2]^{1/2}$

(iii) $\text{Rate} \ \alpha \ [C_2H_6] [O_2]^{7/2}$

$\text{Rate} = K [C_2H_6] [O_2]^{7/2}$