UNIT-9 CHEMICAL KINETICS

Important Points

ñ **Chemical Kinetics :** The branch of chemistry which deals with the study of the rate of reaction and the factor affecting them.

Kinetics - Greek word 'kinesis' = movement

ñ classification of reaction on the basis of rates:

- Very fast reaction : ionic reactions (10-9 sec)
- very slow reaction : rusting of iron, radiation from uranium.
- Slow reaction : reaction by combining dinitrogen and dihydrogen under certainconditions.

ñ **Factors Affecting rates of Reaction:**

(i) The state of substance and the area of surface

(ii) concentration of solution.　　(iii) temperature of system.

(iv) Pressure of system　　　　(v) Effect of catalyst

(vi) Presence of light

(If there is any impurity which tries to decrease the rate of reaction then it is calledcatalytic poison)

ñ **Rate of Reaction :**

The rate of reaction is the change in the concentration of any one of the reactants or products per unit time.

Average rate of reaction

$$r_{av} = -\frac{D[R]}{Dt} = +\frac{D[P]}{Dt}$$

Instantaneous Rate of Reaction

$$r_{inst} = -\frac{d[R]}{dt} = +\frac{d[P]}{dt} \text{ as } Dt \, ® \, 0$$

Rate of reaction is always positive. The minus sign is used simply to show that the concentration of the reactant is decreasing.
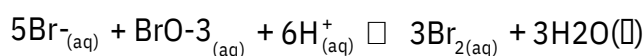
ñ **Rate determination :**

In the reactions the stoichiometric coefficients may be different. Rate of reaction can be determined but the determination must be consistent. In chemical kinetics, the following method is accepted.

$$\text{Rate} = -\frac{1}{V_R}\left[\frac{d[R]}{dt}\right] = +\frac{1}{v_p}\left[\frac{d[P]}{dt}\right]$$

- For any reation $n_1A + n_2B \, ® \, n_3C + n_4D$

$$\text{Rate} = -\frac{1}{n_1}\frac{d[A]}{dt} = -\frac{1}{n_2}\frac{d[B]}{dt} = \frac{1}{n_3}\frac{d[C]}{dt} = \frac{1}{n_4}\frac{d[D]}{dt}$$

$$5Br^-_{(aq)} + BrO\text{-}3_{(aq)} + 6H^+_{(aq)} \, \square \, 3Br_{2(aq)} + 3H2O(l)$$

$$\text{Rate} = -\frac{1}{5}\frac{d\left[Br^-\right]}{dt} = -\frac{d\left[BrO_3^-\right]}{dt} = -\frac{1}{6}\frac{d\left[H^+\right]}{dt} = +\frac{1}{3}\frac{d[Br]2}{dt}$$

- In aqueous solution, there is negligible change in concentration of water and so the change in its concentration is not expressed.

ñ **Rate Law :**
- The presentation of the rate of reaction with reference of concentration of reactants is called rate law.
- This rate law in the wide range of concentration of reactants or products is studied and the law that is established is called 'differential rate equation' or 'Rate expression'. Viz

$$H_{2(g)} + I_{2(g)} \square\ 2HI_{(g)} \qquad\qquad Rate = K[H_2][I_2]$$

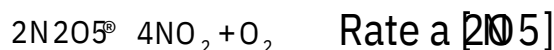ñ **Rate constant and order of Reaction :**
- In most of the reaction carried out, the simple rate equation can be obtained in which rate is proportional to exponents of the concentration of reactant. The exponent is called order of reaction.

$$H_2 + I_2 \ ^{\circledR}\ 2HI \qquad Rate\ \alpha\ [H_2]\ [I_2]$$

$$\backslash Rate = k\ [H_2][I_2]$$

$$H_2 + Br_2 \ ^{\circledR}\ 2HBr \qquad Rate\ \alpha\ [H_2][Br_2]^{1/2}$$

$$\backslash Rate = K[H_2][Br_2]^{1/2}$$

$$2N_2O_5 \ ^{\circledR}\ 4NO_2 + O_2 \qquad Rate\ \alpha\ [N_2O_5]$$

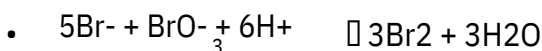$$\backslash Rate = K[N_2O_5]$$

- Where K is rate constant and it is called specific rate constant when concentration of reactant is 1 M. At that time reaction rate = rate constant.
- It is necessary to note that the order of reaction has no relation with the stoichiometric cofficient of reactant.
- For the reaction n1A + n2B $\square$ n3C + n4D
  - Rate = k [A]x[B]y
  - Order of reaction with reference to reactant A is x and with that of reactant B is y. Hence total order of reaction = x + y. Thus the total order of reaction is equal to the sum of exponents of concentration of all reactants.
  - 5Br- + BrO-$_3$ + 6H+ $\square$ 3Br2 + 3H2O
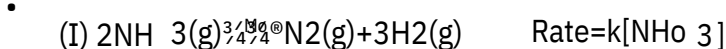 - Rate = K [Br-][BrO-$_3$][H+]2
  - Order of reaction = 1 + 1 + 2 = 4
  - The total order of reaction can be positive, zero or even a fraction
  - Examples of different order.
  - (I) 2NH$_{3(g)}$ $\xrightarrow{3/4\ 3/4\ ^{\circledR}}$ N2(g)+3H2(g) \qquad Rate=k[NHo$_3$]
  - (ii) H2O2 $^{\circledR}$ H2O+O $\frac{1}{2}$ $_2$ \qquad Rate=k[H2O]

- (iii) $2NO_2 + F_2 \,^{\circledR}\, 2NO_2F$ — $Rate = k[NO_2][F_2]$

- (iv) $2NO + O_2 \,^{\circledR}\, 2NO_2$ — $Rate = k[NO]^2[O_2]$

- (v) $CH_3CHO \,^{\circledR}\, CH_4 + CO$ — $Rate = k[CH_3CHO]^{1.5}$

- (vi) $CO + Cl_2 \,^{\circledR}\, COCl_2$ — $Rate = k[CO]^2[Cl_2]^{1.5}$

ñ   Unit of Rate constant

$$Rate = \frac{dx}{dt} = k\,(con)^n$$

$$\backslash\ K = \frac{dx}{dt} \times \frac{1}{(conc)^n} = \frac{conc}{time} \times \frac{1}{(conc)^n}$$

Order of reaction	Unit of K	
0 1 2 n	M s-1	Mole litre-1 time-1
Molecularity :	s-1	time-1
	M-1 S-1	litre mole-1 time-1
	M1-n S-1	litre1-n molen-1 time-1

ñ

- The number of atoms, ions or molecules of the reactant that take part in the reaction and which experience collision with each other so that the reaction results, it is called molecularity

- Hence, the orders of reactions and molecularities of bimolecular, trimolecular and elementary reaction are same.

- The possibility of collision of three or more molecules with one another and to result in the reaction is less.

ñ   The molecularity more than three is not seen.

Molecularity	Order of the reaction
It is equal to the sum of the number of reactant particles taking part in a single step reaction	It is equal to the exponents of the molar concentration of the reactants in the experimentally determined rate equation.
It is always a whole number	It can be fractional
It cannot be zero	It can be zero
Molecularity applies to one step reaction or a single step of reaction which involves several steps for its completion. The molecularity of an overall complex or multistep reaction has no significance or meaning.	Order of reaction applies to a reaction as a wholes, irrespective of the intermediate steps involved for its completion.
It can be obtained from simple balanced equation for the single step reactions.	It cannot be obtained from a simple balanced equation. It is obtained only from experimentally determined rate equation.
It does not help in elucidation of reaction mechanism	It is helpful in the elucidation of reaction mechanism

ñ **Zero order reaction :**

- The rate of the reaction is proportional to zero exponent of the concentration of reactant.

$$-\frac{d[R]}{dt} = k[\ ]^0 R \qquad \backslash [R] = k.t + [R]_o$$

- Graph of [R] versus t then straight line.
  Slope = - k and intercept = [R]o

ñ **First order reaction :**

- The rate of the reaction is proportional to exponent one of concentration of reactant.

$$-\frac{d[R]}{dt} = k[R] \qquad\qquad kt = \ln\frac{[R]o}{[R]}$$

$$[R] = [R]_o .e^{-kt}$$

$$\log[R]_t = -\frac{K}{2.303}.t + \log[R]_o$$

- Graph of log[R] t versus t then straight line.

$$\text{Slope} = -\frac{K}{2.303} \quad \text{and intercept} = \log[R]_o$$

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

ñ **Pseudo – unimolecular or Pseudo first order reaction :**

- Those reaction which are not truly of the first order but under certain conditions become reactions of the first order. Examples : (i) Hydrolysis of ethyl acetate. (ii) Hydrolysis of cane sugar.

ñ **Determination of order of reaction :**

Methods :   (i)   Intial rate method
             (ii)   Integrated rate equation method or Graphical method
             (iii) Half life method
             (iv)   Ostwald's isolation method

ñ **Ostwald's Isolation method :**

- In certain reaction there is involvement of more than one reactants. In this method, the concentration of other reactants in comparison to one reactant is taken in very large proportion. The reaction rate will be indicative with respect to reactant with less concentration because the concentration of other reactants remain almost constant.

ñ **Half life method :**

- The time taken for half of the reaction to complete.
- It is very simple method.

- For zero order reaction $t_{1/2} \propto [R]_0$

- first order reaction $t_{1/2}$ is independent of initial concentration

- second order reaction $t_{1/2} \propto \left[R_0\right]^{1}$

- nth order reaction

$$t_{1/2} \propto \left[R_0\right]^{1-n} \text{ or } t_{1/2} \propto \frac{1}{[R]_0^{n-1}}$$

ñ **Arrhenius equation :**

$$K = A.e^{-Ea/RT} \qquad \backslash\!\!> \ln k = \ln A - \frac{Ea}{RT}$$

$$\log k = \log A - \frac{Ea}{2.303R} \cdot \frac{1}{T}$$

Graph of $\log K$ versus $\dfrac{1}{T}$ = straight line

$$\text{Slope} = - \frac{Ea}{2.303R}$$

$$\log \frac{K_2}{K_1} = \frac{Ea}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2}\right] = \frac{Ea.DT}{2.303\ R.\ T_1.T_2}$$

ñ **Threshold energy :**
- Arrhenius equation shows that rate constant increases exponentially with temperature.
- Increasing temperature from 300 to 310 K, the Kinetic energy increases only by 3% because it is proportional to temperature.
- The reaction rates have almost doubled by increase in temperature by 10 K.
- The explanation for this can be given that there must be some pushing energy or threshold energy required for the reaction of molecules.

ñ **Arrhenius factors :**

ñ $Ea = N_A.E^*$ 　where Ea = Activation energy
　　　　　　　　　　N_a = Avogadro number
　　　　　　　　　　E^* = Kinetic energy
$K = Ae^{-Ea/RT}$　where A = pre-exponential factor or frequency factor
　　　　　　　　　　Ea = Energy of activation
　　　　Both A & Ea= Arrhenius factors

ñ **Theory of collision :**
- Max Trauz and William Lewis (1916-18) = Theory of collision.
- In Chemical reaction, the number of collision per second per unit volume is called collision frequency (z).

- For biomolecular reaction A + B ® Products

- Rate = Z_{AB} . e-Ea/RT

- Rate = P .Z_{AB} . e-Ea/RT

- Z_{AB} = collision frequency of A and B whose energy is equal to or more than activation en er gy.

- P = Probability factor OR steric factor

- Those collision in which molecules collide with sufficient kinetic energy (threshold energy) and proper direction, resulting into products. Such collision are called effective OR fruitful collision.

ñ Endothermic reaction and Exothermic reaction.

- Minimum potential energy of reactants is less than that of products then the reaction will be the endothermic.

- Minimum potential energy of reactants is more than that of products then the reaction will be exothermic.

- Endothermic reation : DH = Hp-Hr = +ve

    - DH = Ea-Ear = +ve when Ea > Ear

- Exothermic reaction : DH = Hp-Hr = -ve

    - DH = Ea-Ear = -ve when Ea < Ear

- Where Ea = activation energy of forward reaction

    Ear = activation energy of reverse reaction

ñ Effect of catalyst :

- The main function of catalyst is decrease the activation energy, bring energy barrier down and increases the rate of reaction.

- Equilibrium constant (K) is not changed.

- Rate of reaction increases.

1. Rate of reation is defined as
(a) decrease in the concentration of a reactant
(b) increase in the concentration of a product
(c) change in the concentration of any one of the reactants or products per unit time.
(d) all the above three are correct

2. 2A + B ® 3C for the reaction instant rate of reaction is...

(a) $+ \dfrac{1}{2}\dfrac{d[A]}{dt} = +\dfrac{[\ ]}{d\ B} + \dfrac{1}{3}\dfrac{d[C]}{dt}$

(b) $- \dfrac{1}{2}\dfrac{d[A]}{dt} = -\dfrac{d[B]}{dt} + \dfrac{1}{3}\dfrac{d[C]}{dt}$

(c) $+ 2\dfrac{d[A]}{dt} = +\dfrac{[\ ]}{dt} = +3\dfrac{[\ ]}{d\ C}$

(d) $- \dfrac{2d[A]}{dt} = -\dfrac{[\ ]}{d\ B} + 3\dfrac{[\ ]}{d\ C}$

3. The rate of reaction of spontaneous reaction is generally very slow. This is due to the fact that..
(a) the equilibrium constant of the reaction is < 1
(b) the activation energy of the reaction is large
(c) the reaction are exothermic
(d) the reaction are endothermic

4. $N_2 + 3H_2 \rightleftharpoons 2NH_3$ For the reaction the rate of change of concentration for hydrogen is -0.3 x 10-4Ms-1. The rate of change of concentration of ammonia is ...
(a) 0.2 ´ 10-4   (b) -0.2 ´ 10-4   (c) 0.1 ´ 10-4   (d) 0.3 ´ 10-4

5. For the reaction of 4A + B ® 2C + D. Which of the following statement is not correct ?
(a) The rate of formation of C and D are equal
(b) The rate of formation of D is one half the rate of consumption of A
(c) The rate of appearance of C is one half the rate of disappearance of B
(d) The rate of disappearance of B is one fourth of the rate of disappearance of A

6. _____ does not affect the rate of reaction.
(a) size of the vessel
(b) amount of the reactants
(c) physical state of reactants
(d) DH of reaction

7. In the reaction N2O4(g) ® 2NO2(g) the pressure of N2O4 falls from 0.5 atm to 0.32 atm is 30 minutes, the rate of appearance of NO2(g) is
(a) 0.012 atm min-1   (b) 0.024 atm min-1   (c) 0.006 atm min-1   (d) 0.003 atm min-1

8. In the reaction K1 and K2 are the velocity constants for the forward and backward reaction respectively. The equilibrium constant is

(a) $K = \dfrac{K_1}{K_2}$ (b) K=K 1 ´ K 2   (c) $K = \dfrac{K_2}{K_1}$ (d) none of the above

9. For the reaction A + B + C ® Products, Rate = K[A]2[B]3[C]$^{1/}$. The order of reaction is

(a) 3   (b) 1   (c) $\dfrac{5}{6}$ (d) $\dfrac{11}{6}$

10. For a reaction pA + qB ® Products. Rate = K[A]m[B]n. Then
(a) (p+q) = (m+n)
(b) (p+q) ¹ (m+n)
(c) (p+q) > (m+n)
(d) (p+q) = (m+n) or (p+q) ¹ (m+n)

11. A + 2B ® C + D For a reaction from following data correct rat law =

	Mole (A)	liter-1 (B)	mole lite-1 min-1
1	0.1	0.1	6.0×10^{-3}
2	0.3	0.2	7.2×10^{-2}
3	0.3	0.4	2.88×10^{-1}
4	0.4	0.1	2.4×10^{-2}

(a) Rate = K $[A]^2[B]$
(b) Rate = K $[A]^2[B]^2$
(c) Rate = K $[A][B]^2$
(d) Rate = K $[A][B]$

12. In the reaction A + B ® Products, the doubling of [A], increases the reaction rate to four times, but doubling of [B] has no effect on the reaction rate. The rate expression is ….

(a) Rate = K $[A]^2$ (b) Rate = K $[A]$ (c) Rate = K $[A]^2[B]^2$ (d) Rate = K $[A][B]$

13. A zero order reaction is one whose rate is independent of ….

(a) Reaction vessel volume
(b) Concentration of reactants
(c) temperature
(d) pressure of light

14. The rate constant of a reaction changes when …

(a) pressure is changed
(b) concentration of reactants changed
(c) temperature is changed
(d) a catalyst is added

15. Which of the following is a reaction of zero order ?

(a) $H_2 + Cl_2 \overset{\frac{3}{4}h\frac{3}{4}J}{\longrightarrow}$ ®2HCl
(b) $2N_2O_5 ® 4NO_2 + O_2$
(c) 2HI®H $_{2}+I_2$
(d) $H_2 + Br_2 ® 2HBr$

16. Which of the following is a reaction of fractional order ?

(a) $2N_2O_5 ® 4NO_2 + O_2$
(b) $2NO_2 + F_2 ® 2NO_2F$
(c) H $_2$ + Br2 ®2HBr
(d) 2NO+O2®2NO $_{2}$

17. A reaction involving two different reactants can never be a ….

(a) bimolecular reaction
(b) Unimolecular reaction
(c) first order reaction
(d) second order reaction

18. For a reaction 3A hProducts, the order of reaction

(a) 3
(b) 1, 2 or 3
(c) zero
(d) any value between 1 and 3

19. When concentration of reactant is increased eighteen times the rate becomes two times, the rate of reaction is

(a) 1   (b) $1\frac{1}{2}$ (c) $\frac{1}{3}$ (d) $\frac{1}{4}$

20. The rate determining step in a reaction is A + 2B ® C. Doubling the concentration of B would make the reaction rate...

(a) two times   (b) same rate   (c) four times   (d) $\frac{1}{4}$ times

21. The rate law of a reaction is rate = K [A]2[B]. On doubling the concentration of both A and B the rate X will become ...

(a) x3   (b) 8x   (c) 4x2   (d) 9x

22. For the reaction $CHCOCH_3$ + I2 + H® Products, the rate is governed by, rate = K[CH 3COCH3] [H]: The rate order of iodine is = _____.

(a) 3   (b) 2   (c) 1   (d) 0

23. If the order of reaction is zero. It means that

(a) rate of reaction is independent of temperature

(b) rate of reaction is independent of the concentration of the reacting species

(c) the rate of formation of activated complex is zero

(d) the rate of decomposition of activated complex is zero

24. The reactions of higher order are rare because

(a) many bady collisions involve very high activation energy

(b) many bady collisions have a low probability

(c) many bady collisions are not energetically favoured

(d) many bady collisions can take place only in the gaseous phase.

25. 2A +2B ® D + E For the reaction following mechanism has been proposed.

A + 2B ® 2C +D (slow)   A + 2C ® E (Fast)

The rate law expression for the reaction is

(a) rate = K [A]2[B]2   (b) rate = K [A]2[B]2[C]

(c) rate = K [A][B]2   (d) rate = K [A][B]

26. A 2 + B2® 2 AB reaction follow the mechanism as given below

(i) A 2 ® 2A (fast)

(ii) A + B 2® AB + B (slow)

(iii) A + B ® AB (fast) the order of overall reaction is

(a) 1.5   (b) 2   (c) 0   (d) 1

27. In the sequence of reaction A¾K¾1®, B¾K¾2®, C¾K¾3® then the rate of determining step of reaction is

(a) A ® B   (b) B ® C   (c) C ® D   (d) A ® D

28. For the reaction 2A + B ® Products, reaction rate = K [A][B]2. Concentration of A is doubled and that of B is halved the rate of reaction will be ...

(a) doubled   (b) halved   (c) unaffected   (d) four times

29. In one reaction concentration of reaction A is incereased by 16 times, the rate increases only two times. The order of the reaction would be ...

(a) 2   (b) 4   (c) $1/2$ (d) $1/4$

30. In the reaction A ® B. When the concentration of A is changed from 0.1 M to 1 M, the rate of reaction increases by a factor of 100. The order of reaction with respect to A is ....

(a) 10   (b) 1   (c) 2   (d) 3

31. For the reaction of A + B ® C + D, doubling the concentration of both the reactants increases the reaction rate by 8 times and doubling the initial concentration of only B simply doubles the reaction rate. The rate law for the reaction is

(a) r = K [A][B]2   (b) r = K [A][B]   (c) r = K [A]½[B]   (d) r = K [A]2[B]

32. The unit of rate constant for a zero order reaction is ...

(a) litre sec-1   (b) litre mole-1 sec-1   (c) mole litre-1 sec-1   (d) mole sec-1

33. The rate constant of a reaction has same units as the rate of reaction. The reaction is of ...

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

34. The rate constant of reaction is 3 ´ 10-3 bar-1 sec-1. The order of reaction is ...

(a) 1   (b) 2   (c) 3   (d) 0

35. The dimensions of the rate constant of a third order reaction involve.

(a) only time   (b) time and concentration

(c) time and square of concentration   (d) only concentration

36. The rate constant of reaction is 5 ´ 10-2 litre3 mole-3 minite-1. The order of reaction is...

(a) 1   (b) 2   (c) 3   (d) 4

37. Which of the following statements is incorrect about the molecularity of a reaction ?

(a) Molecularity of a reaction is the number of molecules in the slowest step.

(b) Molecularity of a reaction is the number of molecules of the reaction present in the balanced equation.

(c) There is no difference between order and molecularity of a reaction.

(d) Molecularity is always a positive whole number.

38. For a single step reaction A + 2B ® Products, the molecularity is

(a) zero   (b) 1   (c) 2   (d) 3

39. Which of the following statement is false ?

(a) For a zero order reaction, the rate changes with temperature.

(b) Both order and molecularity of a reaction are always the same.

(c) Active mass of 128 g of HI present in a two litre flask is 0.5.

(d) For the first order reaction, the rate of reaction halved as the concentration of a reactant halved.

40. If 'a' is the initial concentration of the reactant, the time taken for completion of the reaction, it if is of zero order, will be

(a) $K/2a$ (b) $a/2k$ (c) a/k (d) k/a

41. The reaction 2O3 ® 3O2 proceeds in two steps as follows.

(i) O 3 ⇌ O2 + O (fast)   (ii) O + O3 ® 2O2 (slow)

The rate law expression should be...

(a) r = K[O]2 3   (b) r = K[O2 3][O2]$^{-1}$ (c) r = K[O3][O2]   (d) r = K[O3][O2]$^{-1}$

42. For reaction of zero order is ...

(a) $K = [A_0]/t$ (b) $Kt = [A] - [A_0]$ (c) $Kt = [A] - [A_0]$ (d) $K = \dfrac{2.303}{t} \ln \dfrac{[A_0]}{[A]}$

43. For reaction first order is ...

(a) $t = K\,2.303\log\dfrac{[A]}{[A]_0}$

(b) $K = \dfrac{2.303}{t}\log\dfrac{[A]}{[A]_0}$

(c) $[A] = [A]_0 \cdot e^{-Kt}$

(d) $K = \dfrac{2.303}{t}\log\dfrac{a}{a+x}$

44. For the reaction Zero order

(a) $t_{1/2} \, a\, C_0^2$
(b) $t_{1/2}\, a\, \sqrt{C_0}$
(c) $t_{1/2}\, a\, C_0^{-1}$
(d) $t_{1/2}\, a\, C_0$

45. For reaction first order

(a) $t_{1/2} = \dfrac{0.693}{k}$
(b) $t_{1/2} = \dfrac{0.693}{C_0}$
(c) $t_{1/2}\, a\, \dfrac{0.693}{k}$
(d) $t_{1/2}\, a\, \dfrac{0.693}{C_0}$

46. Which of the following represents the expression for ¾th life of a first order reaction

(a) $\dfrac{k}{2.303}\log\dfrac{4}{3}$
(b) $\dfrac{2.303}{k}\log\dfrac{3}{4}$
(c) $\dfrac{2.303}{k}\log 4$
(d) $\dfrac{2.303}{k}\log 3$

47. If initial concentration is doubled, the time for half reaction is also doubled. The order of reaction is ...

(a) First
(b) Second
(c) Third
(d) Zero

48. If a is the initial concentration of the reactant, the half life period of the reaction of the nth order is proportional to ...

(a) a^{n+1}
(b) a^{1-n}
(c) a^n
(d) a^{n-1}

49. For the first order reaction, half life is 14 s. The time required for the initial concentration to reduce to 1/8th of its value is ...

(a) 28 s
(b) 42 s
(c) $(14)^2$ s
(d) $(14)^3$ s

50. In the first order reaction the concentration of the reactants is reduced to 25% in one hour. The half life period of the reaction is ...

(a) 120 min
(b) 4 hr
(c) 30 min
(d) 15 min

51. For the First order reaction with half life is 150 seconds, the time taken for the concentration of the reactant to fall from m/10 to m/100 will be approximately

(a) 600 s
(b) 900 s
(c) 500 s
(d) 1500 s

52. The half life period of a first order reaction is 15 minutes. The amount of substance left after one hour will be ...

(a) $\dfrac{1}{2}$
(b) $\dfrac{1}{4}$
(c) $\dfrac{1}{8}$
(d) $\dfrac{1}{16}$

53. For the reaction $N_2O_5 \circledR 2NO_2 + \tfrac{1}{2}O_2$ $t_{1/2} = 24$ hrs. starting with 10 g of N_2O_5 how many grams of N_2O_5 will remain after a period of 96 hours ?

(a) 0.63 g
(b) 0.5 g
(c) 1.77 g
(d) 1.25 g

54. In the first order reaction 75% of reactant disappeared in 1.386 h. Calculate the rate constant of reaction.

(a) 3.6×10^{-3} S^{-1}
(b) 2.8×10^{-4} S^{-1}
(c) 17.2×10^{-3} S^{-1}
(d) 1.8×10^{-3} S^{-1}

55. The minimum amount of energy required for the reacting molecules to undergo reaction is called:
(a) potential energy   (b) internal energy   (c) activation energy   (d) threshold energy

56. Increase in the concentration of the reactants leads to the change in
(a) heat of reaction   (b) threshold energy   (c) collision energy   (d) activation energy

57. Energy of activation of an exothermic reaction is
(a) zero   (b) negative
(c) positive   (d) can not be predicated

58. The chemical reactions in which reactants require high amount of activation energy are generally .. ..
(a) slow   (b) fast   (c) instantaneous   (d) spontaneous

59. The rate of reaction increases with increase of temperature because ...
(a) an increase in the number of activated molecules
(b) an increase in the number of collisions
(c) lowering of threshold energy
(d) activation energy is lowered

60. The activation energy of reaction is equal to
(a) Threshold energy + Energy of the products
(b) Threshold energy - Energy of the reactants
(c) Threshold energy + Energy of the reactants
(d) Threshold energy - Energy of the products

61. Collision theory is most satisfactory for _____ reaction.
(a) First order   (b) second order   (c) Bimolecular   (d) Any

62. If E_f and E_r are the activation energies of the forward and reverse reactions and the reaction is known to be exothermic then
(a) $E_f < E_r$ (b) $E_f > E_r$ (c) $E_f >>> E_r$ (d) $E_f = E_r$

63. Which of the following does not affect the rate of reaction ?
(a) size of the vessel   (b) physical state of reactants
(c) amount of the reactants   (d) DH of reaction

64. For a an endothermic reaction, DH represents the enthalpy of reaction. The minimum value for the energy of activation will be ...
(a) equal to DH   (b) zero   (c) more than DH   (d) less than DH

65. For an endothermic reaction A ® B. An activation energy of 15 Kcal mole-1 and the enthalpy change of reaction is 5 Kcal mole-1. The activation energy for the reaction B ® A is
(a) 10 Kcal mole-1   (b) 20 Kcal mole-1   (c) 15 Kcal mole-1   (d) zero

66. For an exothermic reaction an activation energy of 70 KJ mole-1 and the enthalpy change of reaction is 30 KJ mole-1. The activation energy for the reverse reaction is ...
(a) 70 KJ mole-1   (b) 30 KJ mole-1   (c) 40 KJ mole-1   (d) 100 KJ mole-1

67. The rate constant of the reaction increases by ...
(a) increasing the temperature   (b) increasing the concentration of reactants
(c) carrying out the reaction for longer period   (d) adding catalyst

68. Which of the following is the expression for Arrhenius equation ?

(a) $\ln\frac{k_2}{k_1} = \frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

(b) $\ln k = \ln A - \frac{Ea}{RT}$

(c) $k = A.e^{-Ea/RT}$

(d) All the above

69. The Plot of log K vs $\frac{1}{T}$ helps to calculate
(a) Activation energy
(b) Rate constant
(c) Reaction order
(d) Activation energy and frequency factor

70. At 290 K velocity constant of a reaction was found to be 3.2×10^{-3}. At 300 K, it will be
(a) 1.6×10^{-3} (b) 6.4×10^{-3} (c) 3.2×10^{-4} (d) 3.2×10^{-2}

71. The increase in reaction rate as a result of temperature rise from 10 K to 100 K is ...
(a) 512   (b) 614   (c) 400   (d) 112

72. At 300 K rate constant is $0.0231\ min^{-1}$, for a reaction. Bt at 320 K rate constant is $0.0693\ min^{-1}$. The activation energy of the reaction is
(a) 84 KJ mole-1   (b) 34.84 KJ mole-1   (c) 43.84 KJ mole-1   (d) 30 KJ mole-1

73. The activation energy of a reaction is 9 Kcal mole-1. The increase in the rate constant when its temperature is raised from 295 to 300 K is approximately
(a) 1.289 times   (b) 12.89 times   (c) 0.1289 times   (d) 25%

74. A reactant A forms two products.

(i) $A \xrightarrow{k_1} B$ activation energy E_1

(ii) $A \xrightarrow{k_2} C$ activation energy E_2

If $E_2 = 2E_1$ then K1, and K2 are related as

(a) $K_2 = K_1.e^{E_1/RT}$ (b) $K_2 = K_1.e^{E_2/RT}$ (c) $K_1 = AK_2.e^{E_1/RT}$ (d) $K_1 = 2K_2.e^{E_2/RT}$

75. The activation energys of two reaction are E_1 and E_2 ($E_1 > E_2$). If the temperature of the system is increased from T_1 to T_2, the rate constant of the reaction changes from K1 to K21 in the first reaction and K2 to K12 in second reaction, predict which of the following expression is correct?

(a) $\frac{k_1}{k_1} > \frac{k_2}{k_2}$ (b) $\frac{k_1}{k_1} < \frac{k_2}{k_2}$ (c) $\frac{k_1}{k_1} = \frac{k2}{k12}$ (d) $\frac{k_1^1}{k_1} = \frac{k_2^1}{k_2} = 0$

76. The rate of reaction $2x + y \rightarrow$ Products. Rate $= K[x]^2[y]$. If x is present in large excess, the order of the reaction is
(a) 3   (b) 2   (c) 1   (d) 0

77. $CH_3COOEt + H_2O \xrightarrow{H^+} CH_3COOH + Et\ OH$. Order of reaction is ...
(a) 0   (b) 1   (c) 2   (d) 3

78. In which of the following cases, does the reaction go farthest to completion ?
(a) K = 100   (b) K = 10-2   (c) K = 10   (d) K = 1

79. The activation energy of a reaction is zero. The rate constant of the reaction ...

    (a) increase with increase of temperature   (b) decrease with increase of temperature

    (c) decrease with decrease of temperature   (d) is nearly independent of temperature

80. Which of the following is the fast reaction ?

    (a) $H_2 + Cl_2 \rightarrow 2HCl$

    (b) $NO_2 + CO \rightarrow NO + CO_2$

    (c) $CH_3CHO \rightarrow CH_4 + CO$

    (d) $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

81. Oxidation of oxalic acid by acidified $KMnO_4$ is an example of autocatalysis. It is due to which of the following ?

    (a) SO_4^{2-} (b) MnO_4^{-} (c) Mn^{2+} (d) K^+

82. What will be the order of the reaction if doubling the concentration of a reactant increases the rate by a factor of 4 and trebling the concentration of the reactant by a factor of 9 ?

    (a) 1   (b) 2   (c) 3   (d) 0

83. If the half time for a particular reaction is found to be constant and independent of the initial concentration of the reactants then reaction is of ...

    (a) 1   (b) 2   (c) 3   (d) 0

84. The rate of reaction $A + B + C \rightarrow$ Products is given by $r = K[A][B]_0[C]$. If A is taken in large excess, the order of the reaction would be

    (a) 0   (b) 1   (c) 2   (d) nil

85. Rate of chemical reaction can be kept constant...

    (a) by stirring the components   (b) by keeping the temperature constant

    (c) both of the above   (d) none of the above

86. The one which is unimolecular reaction is

    (a) $HI \rightarrow H + \frac{1}{2}I_2$ (b) $NO_2 \rightarrow NO + \frac{1}{2}O_2$

    (c) $H_2 + Cl_2 \rightarrow 2HCl$ (d) $PCl_3 + Cl_2 \rightarrow PCl_5$

87. For the reaction $H_2(g) + Br_2(g) \rightarrow 2HBr$ (g) the experimental data suggests, rate $= K[H_2][Br_2]^{1/2}$ The molecularity and order of reaction respectively for the reaction is

    (a) 2, 2   (b) 2, 1½   (c) 1½, 2   (d) 1½, 1½

88. The rate of reaction for $Cl_3C\,CHO + NO \rightarrow CHCl_3 + NO + CO$ is given by equation, rate $= K[Cl_3C\,CHO][NO]$. If concentration is expressed in mole litre, the unit of K are

    (a) litre^2 mole^{-2} sec^{-1} (b) mole litre^{-1} sec^{-1} (c) litre mole^{-1} sec^{-1} (d) sec^{-1}

89. For a reaction $2A + B \rightarrow$ Products, the active mass of B is kept constant and that of A is doubled. The rate of reaction will then

    (a) increase two times   (b) increase four times

    (c) decrease two times   (d) decrease four times

90. The conversion of $A \rightarrow B$ follows second order kinetics. Doubling the concentration of A will increase the rate of formation B by a factor of

    (a) ¼   (b) 2   (c) ½   (d) 4

91. Ethyl acetate is hydrolysed in alkaline medium, its order of a reaction and molecularity are respectively

(a) 1, 1   (b) 1, 2   (c) 2, 1   (d) 2, 2

92. According to the Arrhenius equation a straight line is to be obtained by plotting the logarithm of the rate constant of a reaction against ...

(a) T   (b) log T   (c) 1/T   (d) log 1/T

93. The given reaction $2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$ is an example of _____ reaction

(a) first order   (b) second order   (c) third order   (d) none of these

94. In the reverable reaction $2NO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_4$, the rate of disappearance of NO_2 is equal to

(a) $\dfrac{2K_1}{K_2}[NO_2]^2$ (b) $2k_1[NO_2] - 2k_2[N_2O_4]$

(c) $2k_1[NO_2]^2 - k_2[N_2O_4]$ (d) $(2k_1 - k_2)[NO_2]$

95. If concentration of reactants is increased by 'x', then rate constant K becomes ..

(a) $\ln \dfrac{k}{x}$ (b) $\dfrac{k}{x}$ (c) k+x   (d) k

96. The rate constant is given by equation $K = p.z.e^{-Ea/RT}$ which factor should register a decrease for the reaction to proceed more rapidly ?

(a) E   (b) T   (c) Z   (d) P

97. For the reaction $A + B \overset{k}{\rightarrow} C$. the unit of rate constant is

(a) sec-1   (b) sec-1 mole L-1   (c) sec-1 mole-1 L   (d) sec-1 mole-2 L2

98. The rate of the gaseous reaction is equal to K[A][B]. The volume of the vessel is suddenly reduced to one forth of the initial volume. The rate of reaction would be ...

(a) $\dfrac{1}{16}$ (b) $\dfrac{16}{1}$ (c) $\dfrac{1}{8}$ (d) $\dfrac{8}{1}$

99. For reaction $Y_2 + 2Z \rightarrow$ Product, rate controlling step is $Y + \frac{1}{2} Z \rightarrow Q$. If the concentration of Z is doubled, the rate of reaction will be

(a) remain the same   (b) become four times

(c) become 1.414 times   (d) become double

100. The rate law for a reaction given by Rate = K[A]n[B]m. On doubling the concentration of A and halving the concentration of B, the ratio of the new rate of the earlier rate of the reaction will be as

(a) m+n

(b) n-m   (c) 2(n-m)   (d) $2^{(m+n)}$

101. The time for half lif of a certain reaction A $\rightarrow$ Products, is one hour. When the initial concentration of the reactant A is 2 mol L-1 how much time does it take for its concentration to come from 0.50 to 0.25 mole L-1 if it is a zero order reaction ?

(a) 0.25 h   (b) 1 h   (c) 4 h   (d) 0.5 h

102. For a first order reaction A → Products, the concentration of A changes from 0.1 M to 0.025 M in 40 minutes. The rate of reaction when the concentration of A is 0.01 M is

(a) 1.73×10^{-4} M min^{-1} (b) 1.73×10^{-5} M min^{-1}
(c) 3.47×10^{-4} M min^{-1} (d) 3.47×10^{-5} M min^{-1}

103. In the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$, initial pressure is 500 atm and rate constant K is 3.38×10^{-5} sec^{-1}. After 10 minutes the final pressure of N_2O_5 is

(a) 490 atm (b) 250 atm (c) 480 atm (d) 420 atm

104. The half life period of a first order reaction is 6.93 minutes. The time required for the completion of 99% of chemical reaction will be

(a) 230.3 min (b) 23.03 min (c) 46.06 min (d) 460.6 min

105. The rate constants K_1 and K_2 for two different reactions are $10.e^{16-2000/T}$ and $10.e^{15-1000/T}$ respectively. The temperature at which K1 = K2 is

(a) 1000 K (b) $\frac{2000}{2.303}k$ (c) 2000 K (d) $\frac{1000}{2.303}k$

ANSWER KEY

1	c	2	a	5	c	76	c	10	a
2	b	6	c	1	d	77	b	1	c
3	b	2	b	5	a	78	a	10	a
4	a	7	d	2	b	79	d	2	c
5	c	2	c	5	d	80	d	10	d
6	d	8	d	3	c	81	c	3	
7	a	2	c	5	c	82	b	10	
8	a	9	d	4	a	83	a	4	
9	d	3	b	5	a	84	b	10	
10	d	0	c	5	b	85	d	5	
11	c	3	d	5	c	86	b		
12	a	1	c	6	a	87	b		
13	b	3	d	5	d	88	c		
14	c	2	b	7	c	89	b		
15	a	3	c	5	a	90	d		
16	c	3	b	8	d	91	d		
17	b	3	b	5	a	92	c		
18	d	4	c	9	d	93	c		
19	c	3	d	6	d	94	b		
20	c	5	a	0	b	95	d		
21	b	3	c	6	a	96	a		
22	d	6	d	1	c	97	c		
23	b	3	b	6	a	98	b		
24	b	7	b	2	c	99	c		
25	c	3	c	6	a	100	c		
		8		3					
		3		6					
		9		4					
		4		6					
		0		5					
		4		6					

Hints

1. Defination of the rate of reaction

2. $$-\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = +\frac{1}{3}\frac{d[C]}{dt}$$

3. the activation energy of the reaction is large

4. 0.2×10^{-4}

    $$\frac{d[H_2]}{dt} = -0.3 \,10\, Ms^{-1} \quad \text{But} \quad Rate = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

    Hence $$\frac{d[NH_3]}{dt} = -\frac{2}{3}\frac{d[H_2]}{dt} = -\frac{2}{3}(-0.3 \times 10^{-4}) = 0.2 \times 10^{-4}$$

5. $$\backslash -\frac{1}{4}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = +\frac{1}{2}\frac{d[C]}{dt} = +\frac{d[D]}{dt}$$

    ΔH of reaction

6. 0.012 atm min^{-1}

    $$-\frac{d[N_2O_4]}{dt} = +\frac{1}{2}\frac{d[NO_2]}{dt}$$

7. $$-\frac{(0.32-0.50)}{30} = 0.006 = \frac{1}{2}\frac{d[NO_2]}{dt} \qquad \backslash \frac{d[NO_2]}{dt} = 0.012 \text{ atm min}^{-1}$$

8. $K = K_1/K_2$

9. $\frac{1}{6}$ $Rate = k[A]^{\frac{1}{2}}[A]^{\frac{1}{3}}[]1c$ $\backslash$ Order of reaction $= \frac{1}{2}+\frac{1}{3}+\frac{1}{1} = \frac{11}{6}$

10. $(p+q) = (m+n)$ or $(p+q) \neq (m+n)$

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

    Keeping [B] constant, [A] is made a 4 times, rate also become 4 times. Hence rate α [A]

    Keeping [A] constant, [B] is doubled, rate becomes 4 times. Hence rate α [B]^2

    $\backslash$ rate = $K[A][B]^2$

12. rate = $K[A]^2$

    [A] doubling, rate becomes four time. Hence rate α [A]^2

    [B] doubling, no effect on the rate. Hence rate α [B]^0

    $\backslash$ rate = $K[A]^2[B]^0$

13. concentration of reactants

    temperature is changed

14. $H_2 + Cl_2 \xrightarrow{hv} 2HCl$

15. $H_2 + Br_2 \longrightarrow 2HBr$

16.
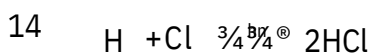
17. Unimolecular reaction
any value between 1 and 3

18.
19. $\frac{1}{3}$ $\frac{k2}{k1} = \left[\frac{A}{2}\right]^n$ Or $2 = (8)n \backslash n = \frac{1}{3}$

20. four times rate $\propto [A][B]$

$8x$ $V1 = k[A][2B] = x$ $V2 = k[2A]^?[2B] \backslash V2 = 8x$

21. OO \No I_2 in the rate law equation.
rate of zero order reaction is independent of the concentration of the reacting species
many bady collisions have a low probability

22. rate = K [A][B]2   Rate of reaction for slowest step

1.5 From slowest step rate $= k[A][B]2$

23. From 1st eq. $Keq = \frac{[A]2}{[A_2]}$ $[A] = keq2.[A_2]^{\frac{1}{2}}$

24. rate = $K[B]keq2 \times [A]2 = k \times keq2^{\frac{1}{2}}$ $[A2]^{\frac{1}{2}}[B2] = K1[A2]2[B2]^{\frac{1}{2}}$

27. C ® D is lowest

28. halved   rate '$= k[A][B]2$ rate '$= k[A]\left[\frac{B}{2}\right]^2$

$= \frac{1}{2}k[A][B]2$

$\backslash x'' = \frac{1}{2}x'$

29. ¼   (1)$r = k[2A]^n$ (2)$2r = k[16A]^n$

$2r = KA[\ ]^n16n$

$\frac{2r}{r} = \frac{KA[\ ]^n 6n}{K A[\ ]}$ $\backslash 2 = 16n \backslash n = \frac{1}{4}$

30. 2   cocentration increased = 10 times
rate increased = 102 times
\ Order = 2

31. $r = K[A]2[B]$ (i)$r = k[A]^x[B]^y$ (ii)$8r = k[2A]^x[2B]y$ (iii)$2r = k[A]^x[2B]y$

(iii) ¸ (i) @$2^y = 2 \backslash y$ 1

(ii) ¸ (i) @$2^x = 4 \backslash x = 2$

32. mole litre^{-1} sec^{-1} $\text{rate} = K[R]^n$, $\dfrac{\text{rate}}{[R]^n} = \dfrac{M/s}{M^n}$ $n = 0$

$K = M^{1-n} S^{-1} \backslash$ $K = \dfrac{M}{S}$

33. zero order $K = \dfrac{\text{rate}}{[R]^n}$ $K = \text{rate}$, when $n = 0$

34. 2 $K = \dfrac{\text{rate}}{[R]^n} = \dfrac{\text{bar}/s}{\text{bar}^n}$ when $n = 2$ $k = \text{bar}^{-1} S^{-1}$

35. time and square of concentration

$K = \dfrac{\text{rate}}{[R]^n} = \dfrac{M/S}{M^n} = M^{1-n} S^{-1}$ when $n = 3$ $k = \text{litre}^3 \text{ mole}^{-1} \text{ min}^{-1}$

36. 4 $K = \dfrac{\text{rate}}{[R]^n} = \dfrac{M/S}{M^n} = M^{1-n} S^{-1}$ when $n = 4$ $k = \text{liter}^3 \text{ mole}^3 \text{ min}^{-1}$

37. There is no difference between order and molecularity of a reaction.
3

38. Both order and molecularity of a reaction are always the same.

39. $\dfrac{a}{k}$ For Zero order reaction $t = \dfrac{1}{k}\{[A]_o - [A]\}$ But $[A] = a$

And when reaction complete $[A] = 0$ $t = \dfrac{a}{k}$

41. $r = k[O_3]^2[O_2^{-1}]$ From Slowest step $r = k[O][O_3]$

From eq (i) $keq = \dfrac{[O_2][O]}{[O_3]}$

$\backslash [O] = Keq[O_3]/[O_2]$

$\backslash r = k[O_3]Keq[O_3]/[O_2] = K[O_3]^2[O_2]^{-1}$

42. $Kt = [Ao] - [A]$

$[A] = [A]_o e^{-kt}$

43. $t_{1/2} a C_o$

45.

44. $t_{1/2} = \dfrac{0.693}{k}$

46. $\dfrac{2.303}{k} \log 4$ $t_{3/4} = \dfrac{2.303}{k} \log \dfrac{ao}{ao - ao \cdot \frac{3}{4}} = \dfrac{2.303}{k} \log \dfrac{ao}{\frac{ao}{4}}$

47. Zero For Zero order reaction $t_{1/2} \alpha C_0$

a^{1-n} $t_{1/2} \alpha a^{1-n}$

48.
49. 42 S $\qquad Ao \xrightarrow{3/4 \cdot 1/2} \dfrac{Ao}{2} \xrightarrow{3/4 \cdot 1/2} \dfrac{Ao}{4} \xrightarrow[t1]{3/4 \cdot 1/2} 2 \dfrac{Ao}{8}$ \ $3 \times t_{1/2}$

50. 30 min $100\% \xrightarrow{1/2} 50 \xrightarrow{1/2} 25\% \setminus T = 2t_{1/2} \setminus t_{1/2} = \dfrac{T}{2}$

51. 500S $\dfrac{M}{10} \xrightarrow{1/4} \dfrac{M}{20} \xrightarrow{1/2} \dfrac{M}{40} \xrightarrow{1/4} \dfrac{M}{80} \xrightarrow{1/2} \dfrac{M}{180}$

$\setminus T @ 3 \ t_{1/2}$ to $4 \ t_{1/2} @ 450$ to $600 S$

52. $\dfrac{1}{16}$ After $n + t_{1/2}$ amount left $= \dfrac{a}{2n}$

$T = n \times t_{1/2}$ $n = \dfrac{6}{0} = 4$ \ Amount left $= \dfrac{1}{2a} = \dfrac{1}{16}$

53. 0.63 g $T = n \times t_{1/2}$ $n = \dfrac{9}{6} = 4$ \ Amount left $= \dfrac{a}{2n} = \dfrac{10}{24} = \dfrac{10}{16} = 0.63$

54. $2.8 \times 10^{-4} S^{-1}$ $K = \dfrac{2.303}{1.386 \times 60 \times 60} \log \dfrac{a}{a - 0.75a} = 2.8 \times 10^{-4} S^{-1}$

55. threshould energy.

56. Collision frequency
Positive Activation energy is always Positive

57. Slow
an increase in the number of activated molecules.

58. Threshold Energy – Energy of the reactants
Bimolecular

59. Ef < Er
DH of reaction

60. more than DH

61. lo Kcal mole-1 DH=Ea-Ear\+5=15-Ear\Ear=10

62. 100 Kj mole-1 DH=Ea-Ear-30=70-Ear\Ear=100
increasing the temperature.

63. All the above
Activation energy and frequency factor.

64. 3.2×10^{-4} 10k rise, the velocity constant becomes nearly double.
512 Increases of temperature n $\times$ 10

65. Increases reaction rate = 29
DT = 100–10=90=9 $\times$ 10 \ n=9

66. \ Increases reaction rate = 29 = 512

72. 43.84 Kj mole $^{-1}$ $\log \dfrac{K_2}{K_1} = \dfrac{Ea}{2.303R}\left(\dfrac{T2-T1}{T1T2}\right)$

$\log \dfrac{0.069}{0.023} = \dfrac{Ea}{2.303 \times 8.3}\left(\dfrac{320-300}{300 \times 320}\right)$

$\log 3 = \dfrac{Ea}{1.901}\left(\dfrac{20}{96000}\right)$ $Ea = 43.84$

73. 1.289 times $\log \dfrac{K_2}{K_1} = \dfrac{Ea.DT}{2.303RT2T1} = \dfrac{9000 \times 5}{2.303 \times 2 \times 300 \times 295} = 0.1104$

$\log \dfrac{K_2}{K_1} = 0.1104$ $\dfrac{K_2}{K_1} = 1.289$ $K2 = K1 \times 1.289$

74. $K1 = K2$ $A.e^{E1/RT}$ $K1 = A1.e^{-E1/RT}$ $K2 = A2.e^{-E2/RT}$

$\dfrac{K1}{K2} = \dfrac{A_1}{A2} \times e^{(E_2-E_1)/RT} = A.e^{(2E1-E_1)/RT} = A.e^{E1/RT}$

$\therefore K1 = K2 .A.e^{E1/RT}$

75. $\dfrac{K1_1}{K1} > \dfrac{K1}{K2}$ $\log \dfrac{K^1_1}{K1} = \dfrac{E1}{2.303R}\left[\dfrac{T2-T1}{T1T2}\right]$ $\log \dfrac{K^1_2}{K2} = \dfrac{E2}{2.303R}\left[\dfrac{T2-T1}{T1T2}\right]$
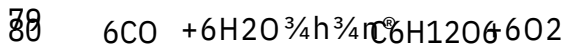
Since $E1 > E2$

$\therefore \log \dfrac{K^1_1}{K1} > \log \dfrac{K^1_2}{K2} > 1$ OR $\dfrac{K_1}{1} > \dfrac{K1}{K2}$

76. 1 The rate is not depend upon the reactant present in excess

77. $K = 100$ $\dfrac{K_1}{1}$ is nearly independent of temperature.

78. $Ea = 0 \quad \therefore K = A.e^{-Ea/RT} = A.e^o = A$

79.
80. $6CO_2 + 6H_2O \xrightarrow{h\nu}[Mn^{2+}] C_6H_{12}O_6 + 6O_2$

81. $2n = 4$ 1 $3n = 9$ $n = 2$ 1 none of the above

82.

83.

84.

85.

86. $N_2O_5 \to N_2O_4 + \frac{1}{2}O_2$

$2, 1\frac{1}{2}$

87. litre mole^{-1} sec^{-1}

increase four times

4 Rate$=K[A]_2$ rate$=K[2A]_2=4.K[A]2$

88. $2, 2$ $CH_3COOC_2H_5 + NaOH \to CH_3COONa + C_2H_5OH$

89. $\frac{1}{\sqrt{T}}$

third order

90. $2K_1[NO_2]^2 - 2K_2[N_2O_4]$ For $2NO_2 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} N_2O_4$
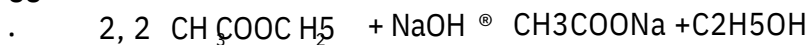
91. $Rate = -\frac{1}{2}\frac{d[NO_2]}{dt} = K_1[NO_2]^2 - K_2[N_2O_4]$

$\backslash rate = \frac{-d[NO_2]}{dt} = 2K_1[NO_2]^2 - 2K_2[N_2O_4]$

92.

95: K

E

93. Sec^{-1} mole^{-1} L \ Second order reaction

98. $\frac{16}{1}$ Volume of the vessel is reduced to one foreth

Concentration bocomes 4 ttimes

99. become 1.414 times   Rate$=KY[Z]^{1/2}$

$\backslash NewRate = 2.K[Y][2Z]^{1/2} = 1.414 \, K[Y][Z]^{1/2}$

100. $2(n-m)$ $r^1 = ka^n b^m$ $r^{11} = k(2a)^n \left(\frac{b}{2}\right)^m$

$\frac{r^{11}}{r^1} = \frac{2^n a^n b^m 2^{-m}}{a^n b^m} = 2^n.2^{-m} = 2^{(n-m)}$

101. 0.25 h For Zero order reaction $K = \frac{[A]_0}{2t_{1/2}} = \frac{2}{2 \times 1} = 1 \, molL^{-1} hr^{-1}$

$t = \frac{[A]_0 - [A]}{K} = \frac{0.50 - 0.25}{1} = 0.25 hr$