KEA

CHEMISTRY

CHEMICAL KINETICS

A. INTRODUCTION

- Rusting of Iron; Burning of LPG and other fuel
- Fermentation of food
- Industrial processes- Habers process , contact process etc
- Natural process- Photosynthesis
- Biological processes- Digestion and metabolism of food
- Manufacturing: Dye, drug, Caustics, explosives and many other

B. SPEEDS /RATES

- Crackers burns instantaneously
- $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$ (fast)
- Conversion of milk to curd (slow)
- Fermentation of cooked Food (slow)
- Rusting of Iron (Very Slow)

C. Chemical Kinetics

Branch of chemistry dealing with

- Rates of reactions
- Mechanisms of reactions
- Factors like T, P, concentration, catalyst, nature of reactants etc. which modify the rate of a reaction

D. Rate of Reaction

Rate of Reaction

- Average rate $\frac{\Delta x}{\Delta t}$
- Instantaneous rate: $\frac{+}{-}\ \frac{dx}{dt}$

$\frac{dx}{dt} = k[A]^n$; Where k- rate constant; n- order

$\frac{dx}{dt} = k$ When [A] = 1M; where k- specific rate

E. Rate constant (k)

Rate constant (k)

$$k = \frac{\frac{dx}{dt}}{[A]^n}$$

Zero order	kt=x	unit of k= $molL^{-1}s^{-1}$
First order	$kt=2.303\ log\frac{a}{(a-x)}$	unit of k= s^{-1}
second order reaction		unit =$mol^{-1}Ls^{-1}$

F. Molecularity

- Total number of molecules of reactants colliding at a time has shown in balanced equation
- Whole number- cannot be zero or fraction
- Reactions with molecularity of more than 3 are rare.

Order

- Sum of powers of (reactants) in the experimental rate equation
- $\frac{dx}{dt} = k[A]^{x}[B]^{y}\ [C]^{z}$; order = (x+y+z)
- Can be zero, whole number, fraction or negative

Half life period

- $t_{1/2} \alpha \frac{1}{a^{(n-1)}}$ n= order; a= initial concentration.
- First order; $t_{1/2} = \frac{0.693}{k}$; $t_{75\%} = 2t_{\frac{1}{2}}$; $t_{99\%} = 10t_{\frac{1}{2}}$;

Answer = (c)

Temperature co-efficient

$$T_c = \frac{kat(t+10)^0}{kat(t^0)}$$

- $T_c = 2$ means for every 10^0 rise in T, Rate doubles
- For most of reactions $T_c = 2$; for some cases $T_c = 3$
- $x = T_c^{\frac{T_2 - T_1}{10}}$

Answer = (c)

ARRHENIUS EQUATION

- $k = Ae^{\frac{Ea}{RT}}$
- $\log k = \log A - \frac{Ea}{2.303\, RT}$
- Greater the k lesser is E_a
- $E_a = E_T - E_R$

CHEMISTRY   Chemical Kinetics

1. If $3A \rightarrow 2B$, then the rate of reaction $+\frac{d[B]}{dt}$ is equal to

(a) $+2\frac{d[A)]}{dt}$ (b) $-\frac{1}{3}\frac{d[A]}{dt}$ (c) $-\frac{2}{3}\frac{d[A]}{dt}$ (d) $-\frac{3}{2}\frac{d[A]}{dt}$

Solution

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

$$\frac{d[B]}{dt} = -\frac{2}{3}\frac{d[A]}{dt}$$

Answer = (c)

2. For a reaction $\frac{1}{2}A \rightarrow 2B$, rate of disappearance of ‘A’ is related to the rate of appearance of ‘B’ by the expression

(a) $-\frac{d[A]}{dt} = 4\frac{d[B]}{dt}$

(b) $-\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$

(c) $-\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$

(d) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$

Solution

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

$$-\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$$

Answer is (c)

3. The rate equation for the reaction: 2A + B $\longrightarrow$ C is found to be: rate = *k*[A] [B]. The correct statement in relation to this reaction is that the

(a) Unit of *k* must be s^{-1}

(b) $t_{1/2}$ is constant

(c) Rate of formation of C is half the rate of disappearance of A

(d) Value of *k* is independent of the initial concentration of A and B

Solution

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

Answer = (c)

4. The instantaneous rate of disappearance of MnO_4^- ion in the reaction between MnO_4^- & I^- in acid medium is 4.4×10^{-3} mol dm^{-3} s^{-1}. The rate of appearance of I_2 is

a) 1.1×10^{-2} b) 4.4×10^{-3} c) 8.8×10^{-3} d) 1.32×10^{-2}

Solution:

$MnO_4^- + I^- + H^+ \longrightarrow Mn^{2+} + I_2 + H_2O$

<u>On balancing</u>

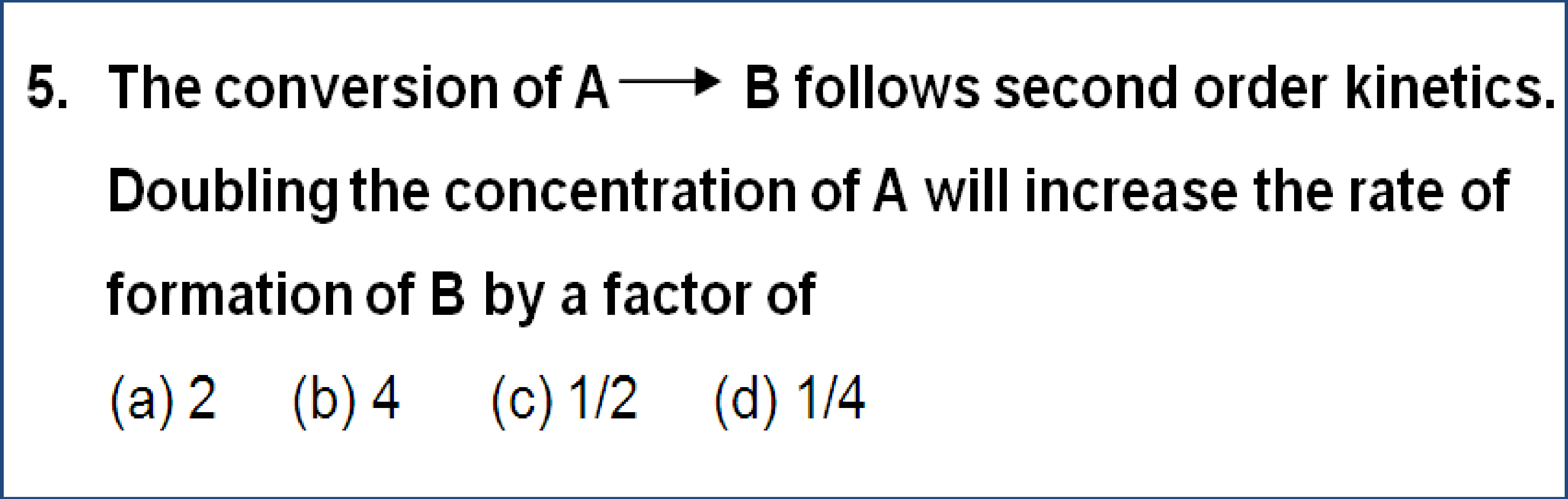
$2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$

$$-\frac{1}{2}\frac{d[\mathrm{MnO}\bar{4}]}{dt} = \frac{1}{5}\frac{d[\mathrm{I2}]}{dt}$$

$$\therefore \frac{d[\mathrm{I2}]}{dt} = -\frac{5}{2}\frac{d[\mathrm{MnO}\bar{4}]}{dt} = \frac{5}{2} X 4.4 X 10^{-3} = 1.1 X 10^{-2}$$

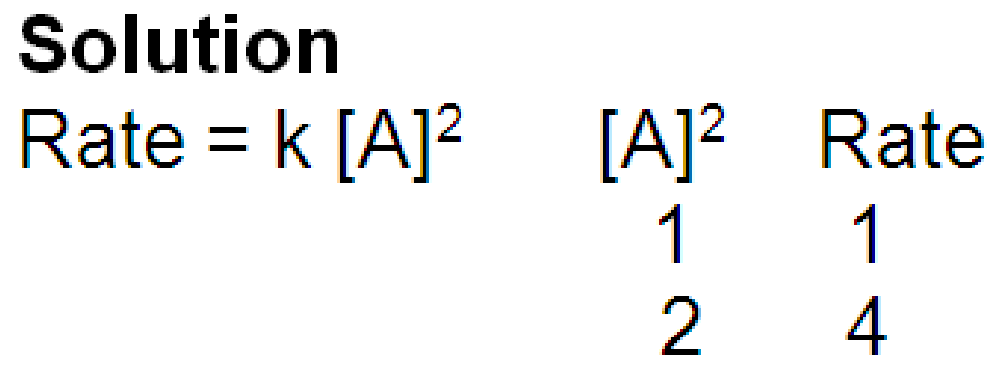
Answer = (a)

CHEMISTRY Chemical Kinetics



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

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



Solution

Rate = $k\,[A]^2$

$[A]^2$	Rate
1	1
2	4

Answer = (b)

6. **The reaction between A and B is 1st order with respect to A and Zero order with respect to B. When the rate of reaction is doubled, what is the concentration of A.**

a) 1 mol L-1 b) 2 mol L-1 c) 3 mol L-1 d) 1/2 mol L-1

Solution:

$r = k[A]^1[B]^0 \quad = 2^1 \times 2^0 = 2 \times 1 = 2.$ [A] = 2 mol L-1

Answer = (b)

CHEMISTRY Chemical Kinetics

7. A gaseous reaction is of second order with respect to a reactant. If the volume of the container is doubled, then the rate of reaction

a) increases by 2 times
b) decreases by 2 times
c) increases by 4 times
d) decreases by 4 times

Solution:

By doubling the volume the concentration of reactant decreases to half.

$[A]^2$	Rate
1^2	1
$(\frac{1}{2})^2$	$\frac{1}{4}$

$\therefore$ rate decreases by 4 times

Answer = (d)

8. Consider a reaction $aG + bH \rightarrow$ Products. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is

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

Solution

[G]	[H]	Rate	
1	1	1	
2	1	2	$2^1 \times 1^2 = 2$
2	2	8	$2^1 \times 2^2 = 8 \quad \therefore [G]^1 [H]^2 = 8$; order = 1+ 2

Answer = (d)

9. In a reaction A + B + C $\rightarrow$ D + E, the rate increases 8 times when [A] & [B] are doubled. The rate increases 4 times when [A] & [C] are doubled. The rate increases 2 times when the [B] & [C] are doubled, then Order of the reaction is

a) 4 b) 3 c) 1 d) 5

Solution

[A]	[B]	[C]	Rate		
2	2	1	8	$[A]^2\,[B]^1$	$\therefore r = k[A]^2\,[B]^1[C]^0$
2	1	2	4	$[A]^2\,[C]^0$	$= k\ 2^2\ X\ 2^1 X 1^0 = 8$
1	2	2	2	$[B]^1\,[C]^0$	order = 2+1+0 = 3

Answer
(b)

10. The conversion of a molecule X→Y follows II order kinetics. If the concentration of X is increased by three times the rate of reaction

a) Increases by 3 times
b) decreases by 3 times
c) increases by 6 times
d) increases by 9 times

Solution:

$r = k[X]^2$

$= k\,(3)^2$

$= 9k$

Answer (d)

11. A reaction that is of first order with respect to reactant A has rate constant of 6 x10^{-2} min-1, if we start with [A] = 0.5 mol L^{-1} when would [A] reach the value of 0.05 mol L^{-1}?

(a) 0.384 min (b) 0.15 min (c) 3.0 min (d) 38.4 min

Solution:

$$t = \frac{2.303}{k} \log \frac{a}{a-x} = \frac{2.303}{6X10^{-2}} \log \frac{0.5}{0.05} = 38.4\,\text{min}$$

Answer = (d)

12. The true statement regarding the Order of a reaction is

a) Order can be zero or a fraction
b) Order does not depend on Stoichiometry.
c) Order is determined only by experimental data.
d) all of these.

Solution:

All the statements are correct.

Answer = (d)

13. **The reaction X $\longrightarrow$ products follows first order kinetics. In 40 minutes the concentration of X changes from 0.1 M to 0.025 M. the rate of reaction when concentration of X is 0.01 M is: (log 4=0.6021)**

a) $1.73 \times 10^{-4} M\ min^{-1}$ b) $3.47 \times 10^{-4} M\ min^{-1}$

c) $4 \times 10^{-5} M\ min^{-1}$ d) $1.73 \times 10^{-5} M\ min^{-1}$

Solution:

$$K = \frac{2.303}{t}\log\frac{a}{(a-x)} = \frac{2.303}{40}\log\frac{0.1}{0.025} = \frac{2.303}{40}\log 4$$

$$K[A]^1 = \frac{2.303}{40} X \frac{0.6021 X 0.01}{} = 3.47 \text{ x } 10^{-4}\,\mathrm{M\,min}^{-1}$$

Answer = (b)

14. In a first order reaction A ⟶ Product, the [A] at the commencement of 20th min was 0.005 M. At the end of 20th min 10 seconds [A] was 0.0005 M. The rate constant of the reaction is

a) 0.0329 min^{-1} b) 0.329min^{-1} c) 3.29min^{-1} d) 0.0329 s^{-1}

Solution:

$$K=\frac{2.303}{t}\log\frac{a}{(a-x)}=\frac{2.303}{70}\log\frac{0.005}{0.0005}=\frac{2.303}{70}\log 10=0.0329\text{s}^{-1}$$

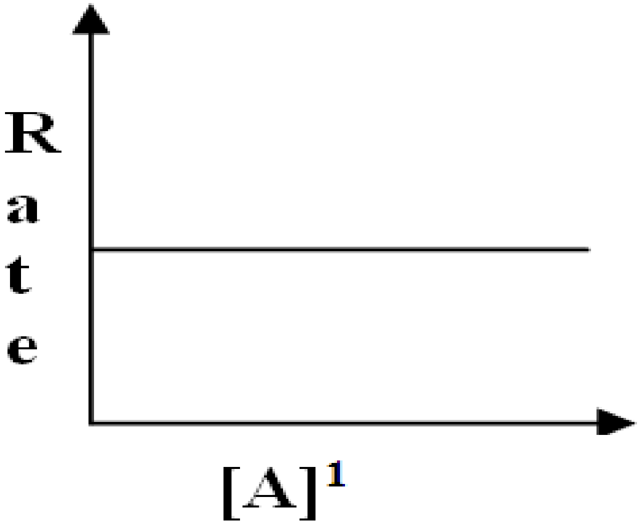
Answer = (d)

15. Reactions of molecularity more than 3 are very rare because

a) Collision of more than three molecules at a time is impossible.
b) Collision of more than three molecules at a time is less probable.
c) Collision of more than three molecules at a time is more impossible.
d) None of these.

Answer = (b)

16. The below plot represents a reaction of order



a) 0 b) 1 c) 2 d) none of these

Solution:

Since the rate is independent of the concentration of A, it is zero order

Answer = (a)

17. The half life of radioactive decay of C14 is 5730 years. An archeological artifact containing wood had only 50% of C14 found in a living tree. The age of sample in years is:

a) 5730 b) 11460 c) 2865 d) 1432.5

Solution:

It is a logical answer need not be calculated. Since the time for 50% decay is nothing but half life period. The answer is 5730 years.

Answer = (a)

18. The energies of activation for forward and reverse reactions for $A_2 + B_2 \rightleftharpoons 2AB$ are 180 and 200 kJ mol^{-1} respectively. The presence of a catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ mol^{-1}. The enthalpy change of the reaction ($A_2 + B_2 \rightarrow 2AB$) in the presence of catalyst will be (in kJ mol^{-1})

a) 120 b) 280 c) 20 d) 300

Solution

$\Delta H = E_P - E_R = 200-180 = 20\text{kJ}$

ΔH does not change in presence of a catalyst

Answer = (c)

19. Consider the reaction, $2A + B \rightarrow$ Products when Concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is

a) No unit b) $molL^{-1}s^{-1}$ c) s^{-1} d) $Lmol^{-1}s^{-1}$

Solution: Answer = (d)

$t_{1/2}$ does not change on doubling the [B]. $\therefore$ w.r.t B order = 1

when [A] is doubled r =2 $\therefore$ w.r.t A order = 1

$r= [A]^1 [B]^1$. Overall order = 1+1 = 2. $\therefore$ Unit = $Lmol^{-1}s^{-1}$

CHEMISTRY Chemical Kinetics

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

a) 46.06 minutes b) 460.6 minutes

c) 230.3 minutes d) 23.03 minutes

Solution:

$$\frac{t_{99\%}}{t_{\frac{1}{2}}} = \frac{\frac{2.303}{k}\log\frac{100}{1}}{\frac{0.693}{k}} \therefore t_{99\%} = \frac{2.303X2X6.93}{0.693}$$

$$= 46.06\,\text{min}$$

Answer = (a)

21. For a first order reaction A → P, the temperature (T) dependent rate constant (k) was found to follow the equation: $\log k = -(2000)\frac{1}{T} + 6.0$. The pre-exponential factor A and the activation energy E_a, respectively are

a) $1.0 \times 10^6 s^{-1}$ and 9.2 kJ mol^{-1}

b) 6.0 s^{-1} and 16.6 kJ mol^{-1}

c) $1.0 \times 10^6 s^{-1}$ and 16.6 kJ mol^{-1}

d) $1.0 \times 10^6 s^{-1}$ and 38.3 kJ mol^{-1}

Solution:

$$\log k = \frac{-E_a}{2.303R}\left(\frac{1}{T}\right) + \log A$$

$$\frac{-E_a}{2.303R} = -2000 \therefore E_a = 2.303 X 8.314 X 2000$$

$$E_a = 38.3 kJmol^{-1}$$

$$\log A = 6.00 \therefore A = 10^6 s^{-1}$$

Answer = (d)

22. For a first order reaction the half life period is

a) Dependent on the square of the initial concentration

b) Dependent on first power of initial concentration

c) Dependent on the square root of the initial concentration

d) Independent of initial concentration

Solution:

$t_{1/2} \alpha\ a^{(1-n)}$ for the first order reaction, n=1

$t_{1/2} \alpha\ a^{(0)}$ = constant. ∴ Independent of initial concentration

Answer = (d)

23. **If the fermentation of sugar in an enzyme solution that is initially 0.12 M the concentration of the sugar is reduced to 0.06 M in 10 h & to 0.03 M in 20 h, then, order of the reaction is**

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

Solution:

$t_{1/2}$= 10 hrs (0.12 $\xrightarrow{\text{10 hrs}}$ 0.06 $\xrightarrow{\text{10hrs}}$ 0.03 i.e.; 75% reduced)

$\therefore$ Order = 1

Answer = (b)

24. Decomposition of a compound is known to be a first order reaction. Three fourths of the compound taken is decomposed at the end of two hours. The quantity left over at the end of the next three hours will be about

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

Solution:

In a first order reaction $t_{3/4} = 2\ t_{1/2} = 2$ hrs $\therefore\ t_{1/2} = 1$ hr

Fraction left out $= \frac{a}{2^n} = \frac{1}{2^5} = \frac{1}{32}$x 100 = about 3 %

Answer = (c)

25. **An example for pseudo I order reaction is**

a) Dissociation of HI

b) Inversion of cane sugar

c) Dissociation of PCl_5

d) Decomposition of H_2O_2

Solution:

$C_{12}H_{22}O_{11}+H_2O$ (large) $\xrightarrow{H+} C_6H_{12}O_6 + C_6H_{12}O_6$

Molecularity =2 Order =1

Answer = (b)

26. The rate of decomposition increase two times when the concentration of the reaction is increased four times. The order of the reaction is

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

Solution:

$$\frac{r_2}{r_1} = \left(\frac{a_2}{a_1}\right)^n \frac{2^1}{1} = \left(\frac{4}{1}\right)^n = \left(\frac{2^{2n}}{1}\right) \therefore 2n = 1$$

$$n = \frac{1}{2}$$

Answer = (b)

27. Which of these changes with time for a first-order reaction?

A. Rate of reaction
B. Rate constant
C. Half-life

(a) A only
(b) C only
(c) A and B only
(d) B and C only

Answer = (a)

28. For the reaction $N_2O_5\ (g) \rightarrow 2NO_2\ (g) + 1/2\ O_2\ (g)$ the value of rate of disappearance of N_2O_5 is given as 6.25×10^{-3} mol L^{-1} s^{-1}. The rate of formation of NO_2 and O_2 is given respectively as:

(a) 6.25×10^{-3} mol L^{-1} s^{-1} and 3.125×10^{-3} mol L^{-1} s^{-1}

(b) 6.25×10^{-3} mol L^{-1} s^{-1} and 6.25×10^{-3} mol L^{-1} s^{-1}

(c) 6.25×10^{-3} mol L^{-1} s^{-1} and 6.25×10^{-3} mol L^{-1} s^{-1}

(d) 1.25×10^{-2} mol L^{-1} s^{-1} and 3.125×10^{-3} mol L^{-1} s^{-1}

Solution:

$$-\frac{d[N_2O_5]}{dt} = +\frac{1}{2}\frac{d[NO_2]}{dt} = +\frac{2d[O_2]}{dt}$$

$$\frac{d[NO_2]}{dt} = \frac{-2d[N_2O_5]}{dt} = 2X6.25X10^{-3} = 1.25X10^{-2}$$

$$\frac{d[O_2]}{dt} = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{2}X6.25X10^{-3} = 3.125X10^{-3}$$

Answer = (d)

29. Temperature co-efficient of a reaction is 3. How many times do the rate increase if temperature is raised from 20°C to 60° C

a) 81 b) 27 c) 9 d) 243

Solution:

$$x = \left(T_c\right)^{\frac{(T_2 - T_1)}{10}} = (3)^{\frac{60\text{-}30}{10}} = 3^{\frac{40}{10}} = 3^4 = 81$$

Answer = (a)

30. Radioactivity of a sample decreases by 90% after 10 years. What will be the half-life of the sample?

(a) 5 years

(b) 2 years

(c) 3 years

(d) 10 years

Solution:

Radio active rxns follow I order

$$\frac{t_{90\%}}{t_{1/2}} = \frac{\frac{2.303}{\lambda}\log\frac{100}{10}}{\frac{0.693}{\lambda}} \quad \therefore t_{1/2} = \frac{0.693 X 10}{2.303} = 3$$

Answer = (c)

31. The concentration of R in the reaction R → P was measured as a function of time and the following data is obtained

[R] (molar)	1.0	0.75	0.40	0.10
t (min)	0.0	0.05	0.12	0.18

The order of the reaction is

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

Solution:

$$\frac{dx}{dt} = \frac{0.25}{0.05} = 5; \frac{dx}{dt} = \frac{0.35}{0.07} = 5; \frac{dx}{dt} = \frac{0.30}{0.06} = 5$$

Rate is independent of [A] $\therefore$ order = zero

Answer = (d)

32. In a zero-order reaction for every 10° rise of temperature, the rate is doubled. If the temperature is increased from 10°C to 100°C, the rate of the reaction will become

(a) 64 times
(b) 128 times
(c) 256 times
(d) 512 times

Solution

$T_c = 2$

$$x = (T_c)^{\frac{(T_2 - T_1)}{10}} = (2)^{\frac{100-10}{10}} = 2^9 = 512$$

Answer = (d)

CHEMISTRY Chemical Kinetics

33. In the hydrolysis of an organic chloride in presence of large excess of water, $RCl + H_2O \rightarrow ROH + HCl$

(a) Molecularity and order of reaction both are 2
(b) Molecularity is 2 but order of reaction is 1
(c) Molecularity is 1 but order of reaction is 2
(d) Molecularity is 1 and order of reaction is also 1

Solution:

When $[H_2O]$ is large $r \; \alpha \; [H_2O]^{(0)}$ $\therefore \text{Molecularity} = 2, \text{ Order} = 1$

Answer = (b)

34. Half life of a reaction is found to be inversely proportional to the cube of its initial concentration. The order of reaction is

(a) 2 (b) 5 (c) 3 (d) 4

Solution:

$t_{1/2} \alpha\ a^{(1-n)}$ when n=4; $t_{1/2} = a^3$.

$\therefore$ order of the reaction is 4.

Answer = (d)

35. The number of collisions depend upon

(a) Pressure
(b) Concentration
(c) Temperature
(d) All the above

Solution:

Number of collision depends upon pressure, concentration and temperature.

Answer = (d)

36. If E_f and E_r are the activation energies of forward and reverse reactions and the reaction is known to be exothermic, then

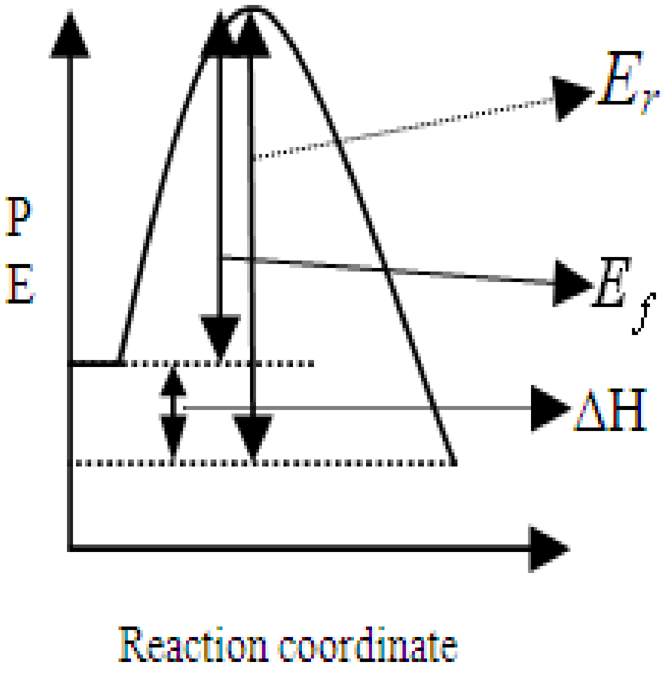
(a) $E_f > E_r$

(b) $E_f < E_r$

(c) $E_f = E_r$

(d) none of these

Solution:



For exothermic reaction $E_f = E_r - \Delta H$; $\therefore$ $E_f < E_r$

Answer = (b)

37. According to Arrhenius theory, the activation energy is

(a) The energy it should possess so that it can enter into an effective collision

(b) The energy which the molecule should possess in order to undergo reaction

(c) The energy it has to acquire further so that it can enter into a effective collision

(d) The energy gained by the molecules on colliding with another molecule

Solution:

By definition

Answer = (c)

38. Which one of the following does not represent Arrhenius equation

(a) $k = Ae^{-E/RT}$

(b) $\log_e k = \log_e A - \frac{E}{RT}$

(c) $\log_{10} k = \log_{10} A - \frac{E}{2.303\, RT}$

(d) $k = AE^{-RT}$

Solution

(d) All other are different forms of Arrhenius equation.

Answer = (d)

39. Energy of activation of a reactant is reduced by

(a)Increased temperature (b)Reduced temperature

(c)Reduced pressure (d)Increased pressure

Solution:

E_a is reduced by increasing temperature

Answer = (a)

40. The minimum energy a molecule should possess in order to enter into a fruitful collision is known as

(a)Reaction energy (b) Collision energy

(c)Activation energy (d) Threshold energy

Solution

(d) The definition of threshold energy.

Answer = (d)

41. **According to the collision theory of reaction rates, rate of reaction increases with temperature due to**

(a) Greater number of collisions
(b) Greater velocity of the reacting molecules
(c) Greater number of molecules has activation energy
(d) None of the above

Solution: The increase in temperature increases the energy of molecules and bring more effective collisions

Answer = (c)

42. For an endothermic reaction, where ΔH represents the enthalpy of the reaction in kJ/mol, the minimum value for the energy of activation will be

(a) Less than ΔH (b) Zero

(c) More than ΔH (d) Equal to ΔH

Solution: (c)

For an endothermic reaction

E_a for forward reaction $= E_a$ for backward reaction + ΔH

$\therefore \mathrm{E_f} > \Delta H$

Answer = (c)

43. The rate constant (K') of one reaction is double of the rate constant (K'') of another reaction. Then the relationship Between the corresponding activation energies of the two reactions (E_a' and E_a'') will be

(a) $E_a' > E_a''$

(b) $E_a' = E_a''$

(c) $E_a' < E_a''$

(d) $E_a' = 4E_a''$

Solution:

As $K' > K'', E_a' < E_a''$

(Greater the rate constant, lesser is the activation energy).

Answer = (c)

KEA

THANK YOU