Chapter

18

Chemical Kinetics

TYPE A : MULTIPLE CHOICE QUESTIONS

1. The rate constant of first order reaction is 3×10^{-6} per second. The initial concentration is 0.10 M. The initial rate is: ***[1998]***

(a) 3×10^{-7} mol/litre/sec
(b) 3×10^{-8} mol/litre/sec
(c) 3×10^{-5} mol/litre/sec
(d) 3×10^{-8} mol/litre/sec

2. Which of the following statement is true for the reaction, $H_2 + Br_2 \rightarrow 2HBr$. The rate law is $\frac{dx}{dt} = k[H_2][Br_2]^{1/2}$: ***[2000]***

(a) order of reaction is 1.5
(b) molecularity of the reaction is 2
(c) by increasing the concentration of Br_2 four times the rate of reaction is doubled
(d) all the above are correct.

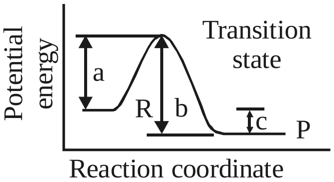
3. For the reaction :

$$H_2 + Cl_2 \xrightarrow{\text{sunlight}} 2HCl$$

the order of reaction is ***[2002]***

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

4. The potential energy diagram for a reaction $R \longrightarrow P$ is given below



$\Delta H°$ of the reaction corresponds to the energy : ***[2003]***

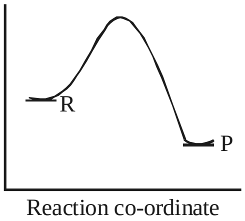
(a) a (b) b
(c) c (d) a + b

5. The rate constant k, for the reaction $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$ is $1.3 \times 10^{-2} s^{-1}$. Which equation given below describes the change of $[N_2O_5]$ with time ? $[N_2O_5]_0$ and $[N_2O_5]_t$ corrospond to concentration of N_2O_5 initially and at time t. ***[2004]***

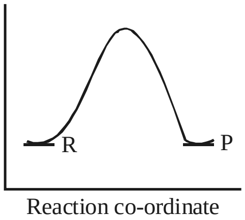
(a) $[N_2O_5]_t = [N_2O_5]_0 + kt$
(b) $[N_2O_5]_0 = [N_2O_5]_t e^{kt}$
(c) $\log [N_2O_5]_t = \log [N_2O_5]_0 + kt$
(d) $\log \frac{[N_2P_5]_0}{[N_2P_5]_t} = kt$

6. An endothermic reaction with high activation energy for the forward reaction is given by the diagram : ***[2005]***

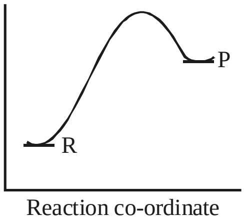
(a)



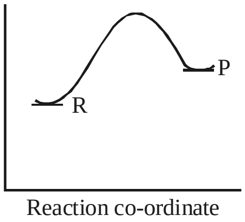
(b)



(c)



(d)



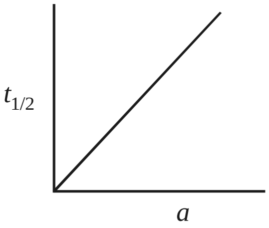
7. For reaction $aA \rightarrow xP$, when [A] = 2.2 mM, the rate was found to be 2.4 mMs^{-1}. On reducing concentration of A to half, the rate changes to 0.6 mMs^{-1}. The order of reaction with respect to A is : ***[2005]***

(a) 1.5 (b) 2.0

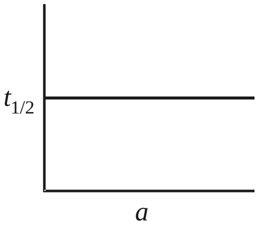
(c) 2.5 (d) 3.0

8. Which of the following graphs represent relation between initial concentration of reactants and half-life for third order reaction?

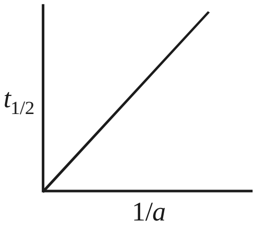
(a)



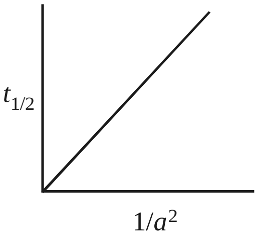
(b)



(c)



(d)



9. For the reaction,

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

the rate of reaction is : ***[2006]***

(a) $\frac{1}{2}\frac{d}{dt}[N_2O_5]$ (b) $2\frac{d}{dt}[N_2O_5]$

(c) $\frac{1}{4}\frac{d}{dt}[NO_2]$ (d) $4\frac{d}{dt}[NO_2]$

10. For a first order reaction, to obtain a positive slope, we need to plot {where [A] is the concentration of reactant A} ***[2008]***

(a) $-\log_{10}[A]$ *vs* t (b) $-\log_e[A]$ *vs* t

(c) $\log_{10}[A]$ *vs* log t (d) [A] *vs* t

11. T_{50} of first -order reaction is 10 min. Starting with 10 mol L^{-1}, rate after 20 min is ***[2008]***

(a) 0.0693 mol L^{-1} min^{-1}

(b) 0.0693×2.5 mol L^{-1} min^{-1}

(c) 0.0693×5 mol L^{-2} min^{-1}

(d) 0.0693×10 mol L^{-1} min^{-1}

12. The first order rate constant for a certain reaction increases from 1.667×10^{-6} s^{-1} at 727°C to 1.667×10^{-4} s^{-1} at 1571°C. The rate constant at 1150°C, assuming constancy of activation energy over the given temperature range is [Given : log 19.9 = 1.299] ***[2009]***

(a) 3.911×10^{-5} s^{-1} (b) 1.139×10^{-5} s^{-1}

(c) 3.318×10^{-5} s^{-1} (d) 1.193×10^{-5} s^{-1}

13. In most cases, for a rise of 10K temperature the rate constant is doubled to tripled. This is due to the reason that ***[2011]***

(a) collision frequency increases by a factor of 2 to 3.

(b) fraction of molecules possessing threshold energy increases by a factor of 2 to 3

(c) Activation energy is lowered by a factor of 2 to 3.

(d) none of these

14. The rate constant for the reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$ is $3.0 \times 10^{-4}\ s^{-1}$. If start made with 1.0 mol L^{-1} of N_2O_5, calculate the rate of formation of NO_2 at the moment of the reaction when concentration of O_2 is 0.1 mol L^{-1}.

(a) 2.7×10^{-4} mol $L^{-1}s^{-1}$ ***[2011]***

(b) 2.4×10^{-4} mol $L^{-1}s^{-1}$

(c) 4.8×10^{-4} mol $L^{-1}s^{-1}$

(d) 9.6×10^{-4} mol $L^{-1}s^{-1}$

15. A reaction which is of first order w.r.t. reactant A, has a rate constant 6 min^{-1}. If we start with [A] = 0.5 mol L^{-1}, when would [A] reach the value of 0.05 mol L^{-1} ***[2013]***

(a) 0.384 min (b) 0.15 min

(c) 3 min (d) 3.84 min

16. Half-lives of a first order and a zero order reaction are same. Then the ratio of the initial rates of first order reaction to that of the zero order reaction is ***[2014]***

(a) $\frac{1}{0.693}$ (b) 2×0.693

(c) 0.693 (d) $\frac{2}{0.693}$

17. Select the rate law that corresponds to the data shown for the following reaction $A + B \longrightarrow C$ ***[2012, 2015]***

Expt. No.	*(A)*	*(B)*	*Initial Rate*
1	0.012	0.035	0.10
2	0.024	0.070	0.80
3	0.024	0.035	0.10
4	0.012	0.070	0.80

(a) Rate = $k[B]^3$ (b) Rate = $k\,[B]^4$

(c) Rate = $k\,[A]\,[B]^3$ (d) Rate = $k\,[A]^2\,[B]^2$

18. Collision theory is used to explain how chemical species undergo a reaction. Using this theory and the kinetic molecular model, which of the following does NOT influence the rate of a chemical reaction? ***[2016]***

(a) The temperature of the system

(b) The geometry or orientation of the collision

(c) The velocity of the reactants at the point of collision

(d) All of the above influence the rate

19. For the following reaction: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$, the rate law is: Rate = $k\,[NO_2]^2$. If 0.1 mole of gaseous carbon monoxide is added at constant temperature to the reaction mixture which of the following statements is true? ***[2016]***

(a) Both k and the reaction rate remain the same

(b) Both k and the reaction rate increase

(c) Both k and the reaction rate decrease

(d) Only k increases, the reaction rate remain the same

20. Which of the following relation represents correct relation between standard electrode potential and equilibrium constant? ***[2017]***

I. $\log K = \frac{nFE^\circ}{2.303\ RT}$

II. $K = e^{\frac{nFE^\circ}{RT}}$

III. $\log K = \frac{nFE^\circ}{2.303\ RT}$

IV. $\log K = 0.4342\frac{nFE^\circ}{RT}$

Choose the correct statement(s).

(a) I, II and III are correct

(b) II and III are correct

(c) I, II and IV are correct

(d) I and IV are correct

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 21-26) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.

(c) If the Assertion is correct but Reason is incorrect.

(d) If both the Assertion and Reason are incorrect.

(e) If the Assertion is incorrect but the Reason is correct.

21. **Assertion :** According to transition state theory for the formation of an activated complex, one of the vibrational degree of freedom is converted into a translational degree of freedom.

Reason : Energy of the activated complex is higher than the energy of reactant molecules. ***[2006]***

22. **Assertion :**The order of a reaction can have fractional value.

Reason : The order of a reaction cannot be written from balanced equation of a reaction. ***[2008]***

23. **Assertion :** In rate law, unlike in the expression for equilibrium constants, the exponents for concentrations do not necessarily match the stoichiometric coefficients.

Reason : It is the mechanism and not the balanced chemical equation for the overall change that governs the reaction rate. ***[2009]***

24. **Assertion :** The rate of the reaction is the rate of change of concentration of a reactant or a product.

Reason : Rate of reaction remains constant during the course of reaction. ***[2010]***

25. **Assertion :** If the activation energy of a reaction is zero, temperature will have no effect on the rate constant. ***[2015]***

Reason : Lower the activation energy, faster is the reaction.

26. **Assertion :** The kinetics of the reaction –

$$mA + nB + pC \longrightarrow m'X + n'Y + p'Z$$

obey the rate expression as $\frac{dX}{dt} = k[A]^m[B]^n$.

Reason : The rate of the reaction does not depend upon the concentration of C.***[2011, 17]***

HINTS & SOLUTIONS

Type A : Multiple Choice Questions

1. **(a)** $\frac{dc}{dt} = k[c] = 3\times10^{-6}\times0.1$

$\frac{dc}{dt} = 3\times10^{-7}$ mol litre^{-1} sec^{-1}

2. **(d)** All the statements are correct.

Order of reaction $= 1+\frac{1}{2} = 1.5$

Molecularity $= 1 + 1 = 2$

$\frac{dx}{dt}\alpha[Br_2]^{1/2}$

So, reaction rate will be doubled if concentration of Br_2 is increased by 4 times.

3. **(a)** The order of all photochemical reactions is zero as it does not depend upon the concentration of reactants.

4. **(c)** Activation energy of forward reaction = *a*

Activation energy of backward reaction = *b*

$\therefore\ \Delta H = b - a$

Since $b > a$, therefore reaction is exothermic

5. **(d)** As the unit of rate constant is sec^{-1}, so the reaction is first order reaction. Hence

$k = \frac{1}{t} = \log\frac{a}{(a-x)}$ or $kt = \log\frac{[N_2O_5]_0}{[N_2O_5]_t}$

6. **(c)** Reactions which involve absorption of heat energy are called endothermic reactions. For such reactions.

$\Sigma H_P > \Sigma H_R$

In graphs (*c*) and (*d*), the heat of products is more than heat of reactants and thus they represent endothermic reactions. But in (*d*) only small amount of energy is absorbed (less difference between energy of reactants and products). Thus, (*c*) represents maximum activation energy.

Note : Activation energy is the excess energy that the reactant molecule must possess to cross energy barrier.

7. **(b)** When the concentration of reactant is reduced to half its initial value, the rate is reduced by $\frac{2.4}{0.6} = 4$ times

It means, rate $\propto$ [reactant]^2

So, order of reaction = 2

8. **(d)** Graph (*d*) represents graph between $t_{1/2}$ and initial concentration for 3rd order reaction :

(a) Zero order reaction

(b) 1st order reaction

(c) 2nd order reaction.

9. **(c)** Rate of reaction

$$= -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt}$$

10. **(b)** For a first order reaction the positive slope is obtained when we plot $-\log_e[A]$ vs t.

11. **(b)** Initial concentration = 10 mol L^{-1}

$\therefore$ Conc. after 20 min (two half lives) = 2.5 mol L^{-1}

Now, $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10\text{ min}}$

or 0.0693 min^{-1}

$\therefore$ rate = $k\times$ [reactant]

$= 0.0693\times2.5$ mol L^{-1} min^{-1}

12. **(c)** $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$

or $2.303\log\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]$

$$2.303\log\left[\frac{1.667\times10^{-4}}{1.667\times10^{-6}}\right] = -\frac{E_a}{R}\left[\frac{1}{1844}-\frac{1}{1000}\right]$$

$$2.303\times2 = \frac{E_a}{R}\times\frac{844}{1844\times1000} \qquad \text{........(1)}$$

$$\therefore\ \frac{E_a}{R} = \frac{4.606\times1844\times1000}{844}$$

$$2.303\log\left[\frac{k_3}{1.667\times10^{-6}}\right] = \frac{E_a}{R}\times\frac{1423-1000}{1423\times1000}$$

$$= \frac{E_a}{R}\times\frac{423}{1423\times1000} \qquad \text{........(2)}$$

Dividing equation (2) by equation (1)

$$\frac{\log\left[\frac{k_3}{1.667\times10^{-6}}\right]}{2}$$

$$= \frac{423}{1423\times1000}\times\frac{1844\times1000}{844}$$

$$\therefore \log\left[\frac{k_3}{1.667\times10^{-6}}\right]$$

$$= 2\times\frac{423\times1844}{1423\times844} = 1.299$$

On taking Antilog, $k_3 = 19.9$

∴ $k_3 = 19.9\times1.667\times10^{-6} = 3.318\times10^{-5}\ s^{-1}$

13. (b) For a 10 *K* rise in temperature, collision frequency increases merely by 1 to 2% but the number of effective collisions increases by 100 to 200%.

14. (d) Mol L^{-1} of N_2O_5 reacted = 2 × 0.1 = 0.2

$[N_2O_5]$ left = 1.0 – 0.2 = 0.8 mol L^{-1}

Rate of reaction = $k\times[N_2O_5]$

$$= 3.0\times10^{-4}\times0.8$$

$$= 2.4\times10^{-4}\ \text{mol}\ L^{-1}s^{-1}$$

Rate of formation of NO_2

$$= 4\times2.4\times10^{-4} = 9.6\times10^{-4}\ \text{mol}\ L^{-1}s^{-1}$$

15. (a) $t = \frac{2.303}{k}\log\frac{a}{a-x}$

$$= \frac{2.303}{6}\log\frac{0.5}{0.05} = 0.384\ \text{min}.$$

16. (b) For first order reaction,

$$\text{Rate} = kA_0^{'} = \frac{0.693}{t_{1/2}}.A_0$$

For zero order reaction, $\text{Rate} = kA_0^0 = \frac{A_0}{2t_{1/2}}$

Ratio in rates = 2 × 0.693

17. (a) Let the rate law be $r = k[A]^x[B]^y$

Divide (3) by (1) $\frac{0.10}{0.10} = \frac{[0.024]^x[0.035]^y}{[0.012]^x[0.035]^y}$

$\therefore 1 = [2]^x, x = 0$

Divide (2) by (3) $\frac{0.80}{0.10} = \frac{[0.024]^x[0.070]^y}{[0.024]^x[0.035]^y}$

$\therefore 8 = (2)^y, y = 3$

Hence rate equation, $R = k[A]^0[B]^3 = k[B]^3$

18. (d)

19. (a) k remains constant at constant temperature and CO does not effect the rate of reaction.

20. (c) $\Delta G = -2.303\ RT\log K$

$-nFE° = -2.303\ RT\log K$

$$\log K = \frac{nFE°}{2.303\ RT}$$

$$= 0.4342\frac{nFE°}{RT} \qquad \text{........ (i)}$$

$$\ln K = \frac{nFE°}{RT}$$

$$K = e^{\frac{nFE°}{RT}} \qquad \text{....... (ii)}$$

Type B : Assertion Reason Questions

21. (b) The formation of an activated complex takes place when vibrational degree of freedom convert into a translational degree of freedom. This statement is given by transition statement theory. Also the energy of activated complex is higher than the energy of reactant molecule is true but it is not the correct explanation of the assertion.

22. (b) The order of a reaction can have fractional value. Assertion is true.

The order of a reaction can not be written from balanced equation of a reaction because its value changes with pressure, temperature and concentration. It can only be determined experimentally. Thus the reason is also correct, but the reason is not the correct explanation of assertion.

23. (a) Rate law is always written according to the slowest step and thus the exponents for concentrations do not necessarily match the stiochiometric coefficients.

24. (c) Rate of reaction does not remain constant during the complete reaction because rate depends upon the concentration of reactants which decreases with time.

25. (b) According to Arrhenius equation, $k = Ae^{-E_a/RT}$

When $E_a = 0$, k = A.

26. (a) Rate expression $\frac{dX}{dt} = k[A]^m[B]^n$ shows that the total order of reaction is $m + n + 0 = m + n$

As the rate of reaction is independent of concentration of *C*, i.e., the order with respect to *C* is zero. This is the reason that *C* does not figure in the rate expression.