THE VILLAGE
INTERNATIONAL SCHOOL

CHEMICAL KINETICS

1. Define 'rate of a reaction'.
2. Define 'order of a reaction'.
3. Define 'activation energy' of a reaction.
4. Express the rate of the following reaction in terms of the formation of ammonia : $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
5. If the rate constant of a reaction is $k = 3 \times 10^{-4}\ s^{-1}$, then identify the order of the reaction.
6. Write the unit of rate constant for a zero order reaction.
7. Define rate constant (K).
8. For a reaction $R \rightarrow P$, half-life ($t_{1/2}$) is observed to be independent of the initial concentration of reactants. What is the order of reaction?
9. A reaction is of second order with respect to a reactant. How will the rate of reaction be affected if the concentration of this reactant is
   (i) doubled, (ii) reduced to half?
10. Define the following :
    (i) Elementary step in a reaction
    (ii) Rate of a reaction
11. A reaction is of first order in reactant A and of second order in reactant B. How is the rate of this reaction affected when (i) the concentration of B alone is increased to three times (ii) the concentrations of A as well as B are doubled?
12. The rate constant for a reaction of zero order in A is 0.0030 mol $L^{-1}\ s^{-1}$. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M?
13. Distinguish between 'rate expression' and 'rate constant' of a reaction.
14. What do you understand by the rate law and rate constant of a reaction? Identify the order of a reaction if the units of its rate constant are : (i) $L^{-1}\ mol\ s^{-1}$ (ii) $L\ mol^{-1}\ s^{-1}$
15. The thermal decomposition of HCO_2H is a first order reaction with a rate constant of $2.4 \times 10^{-3}\ s^{-1}$ at a certain temperature. Calculate how long will it take for three-fourths of initial quantity of HCO_2 H to decompose. (log 0.25 = -0.6021)
16. A reaction is of second order with respect to a reactant. How is its rate affected if the concentration of the reactant is (i) doubled (ii) reduced to half?
17. What is meant by rate of a reaction? Differentiate between average rate and instantaneous rate of a reaction .
18. (a) For a reaction $A + B \rightarrow P$, the rate law is given by, $r = k[A]^{1/2}\ [B]^2$.
    What is the order of this reaction?
    (b) A first order reaction is found to have a rate constant $k = 5.5 \times 10^{-14}\ s^{-1}$. Find the half life of the reaction.
19. Rate constant k for a first order reaction has been found to be $2.54 \times 10^{-3}\ sec^{-1}$. Calculate its 3/4th life, (log 4 = 0.6020).
20. A first order gas phase reaction : $A_2B_2(g) \rightarrow 2A(g) + 2B(g)$ at the temperature 400°C has the rate constant $k = 2.0 \times 10^{-4}\ sec^{-1}$. What percentage of A_2B_2 is decomposed on heating for 900 seconds?
21. Define the following terms :
    (a) Pseudo first order reaction.
    (b) Half life period of reaction ($t_{1/2}$).

22. Explain the following terms :

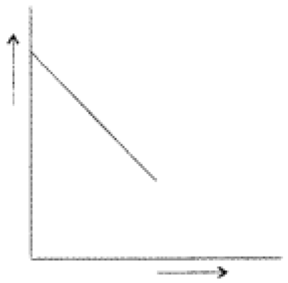
(i) Rate constant (k)

(ii) Half life period of a reaction ($t_{1/2}$)

23. For a chemical reaction R → P, the variation in the f concentration (R) vs. time (f) plot is given as

(i) Predict the order of the reaction.

(ii) What is the slope of the curve?



24. (a) For a reaction, A + B → Product, the rate law is given by, Rate = $k[A]^1[B]^2$. What is the order of the reaction?

(b) Write the unit of rate constant 'k' for the first order reaction.

25. How does a change in temperature affect the rate, of a reaction? How can this effect on the rate constant of a reaction be represented quantitatively?

26. Define each of the following :

(i) Specific rate of a reaction

(ii) Energy of activation of a reaction

27. A reaction is of second order with respect to its reactant. How will its reaction rate be affected if the concentration of the reactant is (i) doubled (ii) reduced to half?

28. For a reaction: $2NH_2(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$

Rate = k

(i) Write the order and molecularity of this reaction.

(ii) Write the unit of k.

29. For a reaction: $H_2 + Cl_2 \xrightarrow{hv} 2HCl$

Rate = k

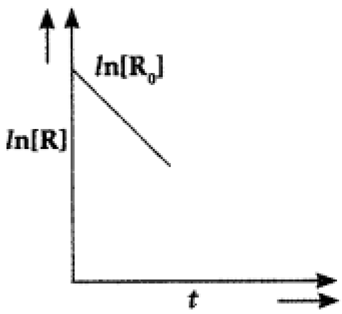
(i) Write the order and molecularity of this reaction.

(ii) Write the unit of k

30. For a chemical reaction R → P, variation in In[R] vs time (f) plot is given below:

For this reaction:

(i) Predict the order of reaction



(ii) What is the unit of rate constant (k)?

31. (a) Explain why H_2 and O_2 do not react at room temperature.
(b) Write the rate equation for the reaction $A_2 + 3B_2 \rightarrow 2C$, if the overall order of the reaction is zero.

32. Derive integrated rate equation for rate constant of a first order reaction

33. (i) What is the order of the reaction whose rate constant has same units as the rate of reaction?
(ii) For a reaction $A + H_2O \rightarrow B$; Rate $\propto$ [A],
What is the order of this reaction?

34. (a) A reaction is first order in A and second order in B.
(i) Write differential rate equation.
(ii) How is rate affected when concentration of B is tripled?
(iii) How is rate affected when concentration of both A and B is doubled?
(b) What is molecularity of a reaction?

ANSWER KEY

1. The change in the concentration of any one of the reactants or products per unit time is called rate of a reaction. Or, The rate of a chemical reaction is the change in the molar concentration of the species taking part in a reaction per unit time.
2. The sum of powers of the concentration of the reactants in the rate law expression is called the order of reaction.
3. The minimum extra amount of energy absorbed by the reactant molecules to form the activated complex is called activation energy.
   The activation energy of the reaction decreases by the use of catalyst.
4. $$\frac{-d[N_2]}{dt} = \frac{-1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$
5. S^{-1} is the unit for rate constant of first order reaction.
6. Mol L^{-1} S^{-1} is unit of rate constant for a zero order reaction.
7. Rate constant. It is defined as the rate of reaction when the concentration of reaction is taken as unity.
8. The $t_{1/2}$ of a first order reaction is independent of initial concentration of reactants.
9. Since Rate = $K[A]^2$
   For second order reaction Let [A] = a then Rate = Ka^2
   (i) If [A] = 2a then Rate = K $(2a)^2$ = 4 Ka^2
   ∴Rate of reaction becomes 4 times
   (ii) If [A] = a2 then Rate = K (a2)2=Ka24
   ∴ Rate of reaction will be 14 th .
10. **(i) Elementary step in a reaction:** Those reactions which take place in one step are called elementary reactions.
    Example : Reaction between H_2, and I_2 to form 2HI
    $H_2 + I_2 \rightarrow 2HI$
    (ii) Rate of a reaction: The change in the concentration of any one of the reactants or products per unit time is called rate of reaction.
11. r = $K[A]^1$ $[B]^2$
    (i) When concentration of B increases to 3 times, the rate of reaction becomes 9 times

r = KA(3B)^2 ∴ r = 9KAB^2 = 9 times
(ii) r = K(2A) (2B)^2 ∴ r = 8KAB^2 = 8 times

12. For a zero order reaction,

$$\text{Time, } t = \frac{1}{K}[(A)_0 - (A)]$$

$$\text{or, } t = \frac{1}{0.003}(0.10 - 0.075)$$

$$\therefore \quad \textbf{Time, } t = \frac{1}{0.003} \times \frac{0.025}{1} = \frac{25}{3} = \textbf{8.3 seconds}$$

13. **Rate expression:** The expression which expresses the rate of reaction in terms of molar concentrations of the reactants with each term raised to their power, which may or may not be same as the stoichiometric coefficient of that reactant in the balanced chemical equation.
Rate constant: The rate of reaction when the molar concentration of each reactant is taken as unity.
14. The rate of reaction is found to depend on α concentration of term of reactant A and β concentration term of reactant B
Then Rate of reaction ∝ $[A]_\alpha$ $[B]_\beta$
or Rate = K $[A]_\alpha$ $[B]_\beta$
This expression is called Rate law.
'K' in this expression is called Rate constant. Rate constant's unit :
(i) Unit = L^{-1} mol s^{-1} → Zero order reaction
(ii) Unit = L mol^{-1} s^{-1} → Second order reaction.
15. Rate = K $[A]^2$ = Ka^2
If [A] = 12a Rate = K (a2)2=14 Ka^2
∴ Rate = 1/4th (one fourth of origina rate)
The unit of rate constant is L mol^{-1} s^{-1}

According to the formula, **where** $\left[\begin{array}{l} a = 1 \\ K = 2.4 \times 10^{-3} \\ x = \frac{3}{4} = 0.75 \end{array}\right.$

$$t = \frac{2.303}{K} \log \frac{a}{a-x},$$

Putting these values in the above equation

$$t = \frac{2.303}{K} \log \frac{1}{1-0.75}$$

or $$t = \frac{2.303}{2.4 \times 10^{-3}} \log 0.25$$

or $$t = \frac{2.303}{2.4 \times 10^{-3}} \times 0.6020$$

or $$t = \frac{1.386406}{2.4 \times 10^{-3}} = 577.6$$

$\therefore$ **Time taken,** t **= 577.6 sec.**

16. As Formula, r = K[R|^2 …(Given)
    (i) R' = 2R ⇒ r = K[2R]$^{-1}$ = 4KR^{-1}
    ∴ Rate becomes 4 times than original rate
17. **Rate of reaction:** It is the change in concentration of the reactants or products in a unit time. Average rate : Average rate depends upon the change in concentration of reactants or products and the time taken for the change to occur.
    R → P

$$\text{Average rate} = -\frac{\Delta[R]}{\Delta t}$$

or $$\text{Average rate} = +\frac{\Delta[P]}{\Delta t}$$

Instantaneous rate: It is defined as the rate of change in concentration of any one of the reactant or product at a particular moment of time.

$$\underset{\Delta t \to 0}{\text{limit}} \left[\frac{-\Delta[R]}{\Delta t}\right] = \frac{-d[R]}{dt}$$

Order w.r.t. A = $\frac{1}{2}$, Order w.r.t B = 2

$\therefore$ Overall order = $\frac{1}{2} + \frac{2}{1} = \frac{5}{2}$

(*b*) For first order reaction, $t_{1/2} = \frac{0.693}{k}$

Given: $k = 5.5 \times 10^{-14}\ s^{-1}$

Thus, $t_{1/2} = \frac{0.693}{5.5 \times 10^{-14} s^{-1}}$

18. Hence $t_{1/2}$ = $\mathbf{1.26 \times 10^{13} s}$

$$t_{3/4} = \frac{2.303}{k} \log 4$$

$$= \frac{2.303}{2.54 \times 10^{-3} \text{sec}^{-1}} \times 0.6020 = 545.8 \text{ sec.}$$

$$= \mathbf{9.09 \text{ min.}}$$

19.

$$\therefore \quad k = \frac{2.303}{t} \log \frac{a}{a-x} \qquad \log \frac{100}{x} = 0.781$$

Given : $k = 2.0 \times 10^{-4} \text{ sec}^{-1}$, $t = 900$ sec

Substituting these values, we get

$$2.0 \times 10^{-4} = \frac{2.303}{900} \log \frac{a}{a-x}$$

$$\Rightarrow \quad \log \frac{a}{a-x} = \frac{2.0 \times 10^{-4} \times 900}{2.303}$$

$$\Rightarrow \quad \log \frac{a}{a-x} = 0.0781$$

$$\Rightarrow \quad \frac{a}{a-x} = \text{antilog } (0.0781) = 1.197$$

$$\Rightarrow \quad a = 1.197\, a - 1.197\, x$$

$$\Rightarrow \quad 0.197\, a = 1.197\, x$$

$$\therefore \quad \frac{x}{a} = \frac{0.197}{1.197} = 0.1645$$

$$\therefore \quad \% \text{ decomposed} = 0.1645 \times 100 = \mathbf{16.45\%}$$

20.

21. (a) Those reactions which are not truly of the first order but under certain conditions become first order reactions are called pseudo first order reaction.
(b) The time taken for half of the reaction to complete is called half life period.

22.

Order of reaction	Molecularity of reaction
(i) It is the sum of tire concentration terms on which die rate of reaction actually depends.	It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction.
(ii) It can be fractional as well as zero.	it is always a whole number.

23.

24. **(i) Rate constant (k):** It is a proportionality constant and is equal to the rate of reaction when the molar concentration of each of the reactants is unity.
(ii) Half life period of a reaction ($t_{1/2}$): The time taken for half of the reaction to complete is called half life penod.(R)t

25. (i) It is zero order reaction.
(ii) Slope of the curve = -K

26. (a) For a reaction, A + B
Rate = k $[A]^1$ $[B]^2$

This is the third order of reaction.
(b) Unit of rate constant for first order reaction is S^{-1}

27. The rate constant of a reaction increases with increase of temperature and becomes nearly double for every 10° rise in temperature.
The effect can be represented quantitatively by Arhenius equation $K = Ae^{-Ea/RT}$
Where [Ea = Activation energy of the reaction; A = Frequency factor]

28. **(i) Specific rate of a reaction:** Specific rate of reaction is the rate of reaction when the molar concentration of each of the reactants is unity.
(ii) Activation energy of a reaction: The minimum extra amount of energy absorbed by the reactant molecules so that their energy becomes equal to threshold value, is called activation energy.

29. Since Rate = $K[A]^2$
For second order reaction Let [A] = a then Rate = Ka^2
(i) If [A] = 2a then Rate = $K(2a)^2 = 4Ka^2$
∴Rate of reaction becomes 4 times
(ii) If [A] = a2 then Rate = K (a2)2=Ka24
∴ Rate of reaction will be 14 th

30. $2NH_2(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$
(i) It is a zero order reaction and its molecularity is two.
(ii) Unit of k is mol L^{-1} s^{-1}.

31. $H_2 + Cl_2 \xrightarrow{hv} 2HCl$
This reaction is zero order reaction and molecularity is two.
(ii) Unit of k = mol L^{-1} s^{-1}

32. (i) It is zero order reaction.
(ii) The unit of rate constant (k) is mol L^{-1} S^{-1}.

33. (i) H_2 and O_2 do not react at room temperature because they do not have enough activation energy to overcome the exceptionally high activation energy barrier.
(ii) $A_2 + 3B_2 \rightarrow 2C$
Rate = (dxdt) = $K[A]^0$ $[B]^0$ = K (rate constant)

34. In a first order reaction, the rate of reaction, is directly proportional to the concentration of the reactant.
Let us consider the reaction,
A → Products
The instantaneous reaction rate can be expressed as:

$$\frac{-d[A]}{dt} = K[A] \qquad [K = \text{rate constant})$$

$$\frac{-d[A]}{[A]} = Kdt \qquad \ldots(i)$$

On integrating equation (*i*)

$$-\int \frac{d[A]}{[A]} = K\int dt$$

or $$-ln[A] = Kt + I \qquad \ldots(ii)$$

where, I = Integration constant

If t = 0 and [A] = $[A]_0$, where $[A]_0$ is the initial concentration of the reactant.
Then equation (ii) becomes
$-\ln[A]_0 = I$ ……………. (iii)
Substitute the value of I in equation (ii)
$-\ln[A] = Kt - \ln[A]$
$\ln[A]_0 - \ln[A] = Kt$

35. (i) The reaction whose rate constant has same units as the rate of reaction, will have zero order of reaction.
(ii) The reaction $A + H_2O \rightarrow B$ Rate $\propto$ [A]
The order of this reaction will be pseudo first order reaction as the rate of reaction depends only on concentration of A only.

$$\ln \frac{[A]_0}{[A]} = Kt$$

$$\text{or} \quad K = \frac{1}{t} \ln \frac{[A]_0}{[A]}$$

36. $$K = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

37. (a) (i) Differential rate equation :
dxdt = rate = $K [A]^1 [B]^2$
(ii) Rate, $r_1 = K [A]^1[B]^2$ …………… (i)
When concentration of B is increased three times then
Rate, $r_2 = K [A]^1 [3B]^2$ ………..(ii)
Dividing equation (ii) by (i) we get
$r_2 = 9r_1$ rate increases by n*ne times.
(iii) When concentration of both A and B are doubled, then
$r_3 = K [2A]^1 [2B]^2$ ………….. (iii)
Dividing equation {Hi) by (t), we get
$r_3 = 8r_1$
Hence rate increases by eight times.