One Two academy | Chemical Kinetics

Maximum Mark: 25 **Chemistry** **Time: 50 minutes**

Choose the correct answer: **3 x 1 = 3**

1. The correct difference between first and second order reactions is that

   a) A first order reaction can be catalysed; a second order reaction cannot be catalysed.
   b) The half-life of a first order reaction does not depend on $[A_0]$; the half-life of a second order reaction does depend on $[A_0]$.
   c) The rate of a first order reaction does not depend on reactant concentrations; the rate of a second order reaction does depend on reactant concentrations.
   d) The rate of a first order reaction does depend on reactant concentrations; the rate of a second order reaction does not depend on reactant concentrations.
2. If 75% of a first order reaction was completed in 60 minutes, 50% of the same reaction under the same conditions would be completed in

   a) 20 minutes b) 30 minutes c) 35 minutes a) 75 minutes
3. The rate constant of a reaction is 2.3×10^{-2} lit $mol^{-1}s^{-1}$. The order of reaction is

   a) Zero Order a) First Order c) Second Order d) Third Order

Answer Any four of the following: **4 x 2 = 8**

4. Define average rate and instantaneous rate.
5. Identify the order for the following reactions

   (i) Rusting of Iron (ii) $2A + 3B \rightarrow$ products; rate = $k[A]^{1/2}[B]^2$= 2 ½
6. Describe the graphical representation of first order reaction.
7. Write a note on molecularity.
8. The rate constant for a first order reaction is 1.54×10^{-3} S^{-1} calculate its is half lifetime.

Answer any three of the following: **3 x 3 = 9**

9. Show that the in case of first order reaction the time required for the completion of 99% is twice the time required for the completion of 90% of the reaction.
10. Derive integrated rate law for a zero order, reaction: $A \rightarrow$ Product.
11. Explain pseudo first order reaction with an example.
12. Explain the effect of surface area of the reaction.

Answer the following: **1 x 5 = 5**

13. a) Derive integrated rate law for a first order reaction: $A \rightarrow$ product

(Or)

b) Explain briefly the collision theory of bimolecular reactions.

All the Best

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Answer Key attached in the next page !!!

This page is to prevent seeing answer key

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Answer Key

Choose the Correct answer:

1. - b) 2. - b) 3. – d)

Answer any four of the following:

4. **Average rate:** The average rate of a reaction is defined as the rate of change of concentration per unit time.

$$\text{Average rate} = \frac{Change\ in\ concentration}{time\ taken}$$

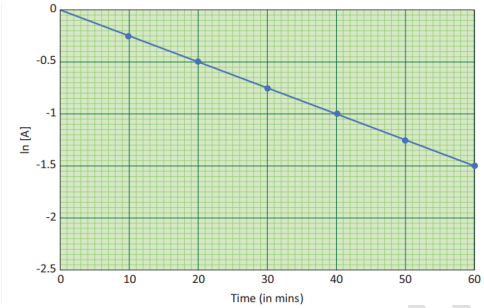
Instantaneous rate: The instantaneous rate of a reaction is defined as the decrease in concentration of any one of the product at a particular instant of time for a given temperature.

Average rate becomes instantaneous rate when $\Delta t \rightarrow 0$

5. **(i) Rusting of Iron** - First order reaction

(ii) 2A + 3B → products; rate = $k[A]^{1/2}[B]^2$= 2 ½ - Pseudo first order reaction

6. **First order reaction:**



$k = \frac{1}{t} \ln \frac{[Ao]}{[A]}$ $kt = \ln [A_o] - \ln [A]$ $\ln[A] = -kt + \ln[A_o]$ $y = -mx + C$

7. **Molecularity:** The total number of reactant species that are involved in an elementary step is called molecularity of that particular step.

Ex: $2NO + O_2 \rightarrow 2NO_2$ - This is a trimolecular reaction

8.

Solution:

We know that, $t_{1/2} = 0.693/k$

$t_{1/2} = 0.693/1.54 \times 10^{-3}\ s^{-1}$ = **450 s**

Answer any three of the following:

9. $t_{99\%} = \frac{2.303}{k1} \ln \frac{[100]}{[100-99]}$

$= \frac{2.303}{k1} \ln 100$

$t_{90\%} = \frac{2.303}{k1} \ln \frac{[100]}{[100-90]}$

$= \frac{2.303}{k1} \ln 10$

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$$\frac{t99\%}{t90\%} = \frac{log\ 100}{log\ 10} = \frac{2}{1} = 2.0$$

$\therefore t_{99\%} = 2t_{90\%}$

10. **Integrated rate law for a zero order:**

A reaction in which the rate is independent of the concentration of the reactant over a wide range of concentrations is called as zero order reactions. Such reactions are rare. Let us consider the following hypothetical zero order reaction.

$A \longrightarrow$ product

The rate law can be written as,

$Rate = k\,[A]^0$

$$\frac{-d[A]}{dt} = k\ (1) \qquad (\therefore [A]^0 = 1)$$

$$\Rightarrow \ -d[A] = k\,dt$$

Integrate the above equation between the limits of $[A_0]$ at zero time and $[A]$ at some later time 't',

$$-\int_{[A_0]}^{[A]} d[A] = k\int_0^t dt$$

$$-([A])_{[A_0]}^{[A]} = k(t)_0^t$$

$$[A_0]-[A] = kt$$

$$k = \frac{[A_0]-[A]}{t}$$

Equation (2) is in the form of a straight line $y = mx + c$

Ie., $[A] = -kt + [A_0]$

$\Rightarrow y = c + mx$

A plot of [A] Vs time gives a straight line with a slope of $-k$ and y - intercept of $[A_0]$.

11. **Pseudo first order reaction:**

- Kinetic study of a higher order reaction is difficult to follow.
- For example, in a study of a second order reaction involving two different reactants.
- The simultaneous measurement of change in the concentration of both the reactants is very difficult.
- To overcome such difficulties, A second order reaction can be altered to a first order reaction by taking one of the reactants in large excess, such reaction is called pseudo first order reaction.

12. **Effect of surface area of the reactant:**

In heterogeneous reactions, the surface areas of the solid reactants play an important role in deciding the rate. For a given mass of a reactant, when the particle size decreases surface area increases. Increase in surface area of reactant leads to more collisions per litre per second, and hence the rate of reaction is increased. For example, powdered calcium carbonate reacts much faster with dilute HCl than with the same mass of $CaCO_3$ as marble

Answer the following:

13. a) **Integrated rate law for a first order reaction:**

A reaction whose rate depends on the reactant concentration raised to the first power is called a first order reaction. Let us consider the following first order reaction,

$A \rightarrow$ product

Rate law can be expressed as

$$\text{Rate} = k\,[A]^1$$

Where, k is the first order rate constant.

$$\frac{-d[A]}{dt} = k\,[A]^1$$

$$\Rightarrow \frac{-d[A]}{[A]} = k\,dt \qquad \ldots(1)$$

Integrate the above equation between the limits of time t = 0 and time equal to t, while the concentration varies from the initial concentration $[A_o]$ to [A] at the later time.

$$\int_{[A_0]}^{[A]} \frac{-d[A]}{[A]} = k\int_0^t dt$$

$$\left(-\ln[A]\right)_{[A_0]}^{[A]} = k\,(t)_0^t$$

$$-\ln[A] - \left(-\ln[A_0]\right) = k\,(t-0)$$

$$-\ln[A] + \ln[A_0] = kt$$

$$\ln\left(\frac{[A_0]}{[A]}\right) = kt \qquad \ldots(2)$$

This equation is in natural logarithm. To convert it into usual logarithm with base 10, we have to multiply the term by 2.303.

$$2.303\log\left(\frac{[A_0]}{[A]}\right) = kt$$

$$k = \frac{2.303}{t}\log\left(\frac{[A_0]}{[A]}\right) \text{ ----- (3)}$$

(Or)

b) **Collision theory of bimolecular reactions:**

consider a bimolecular reaction between A_2 and B_2 molecules proceeds through collisions between them, then the rate would be proportional to the number of collisions per second.

Rate $\propto$ number of molecules colliding per litre per second (collision rate)

Collision rate $\propto [A_2]\,[B_2]$

Collision rate $= Z\,[A_2]\,[B_2]$

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Where, Z is a collision frequency

The collision rate in gases can be calculated from kinetic theory of gases. For a gas at room temperature (298K) and 1 atm pressure,

All collisions are not effective to lead to the reaction. In order to react, the colliding molecules must possess a minimum energy called activation energy.

Fraction of effective collisions (f) is given by the following expression $f = e^{\frac{-Ea}{RT}}$

In addition to activation energy, orientation factor (p) also necessary for reaction to take place.

Rate = p x f x collision rate

Rate = p x $e^{\frac{-Ea}{RT}}$ x Z $[A_2]$ $[B_2]$ ….(1)

As per the rate law,

Rate = k $[A_2]$ $[B_2]$ ….(2)

Comparing (1) and (2)

$\therefore \mathbf{k = pZ}e^{\frac{-Ea}{RT}}$

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