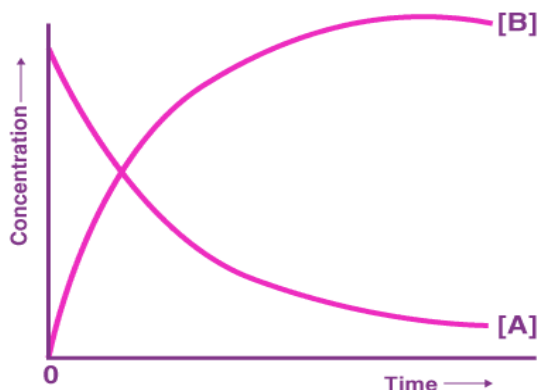


Chemical Kinetics Chemistry Questions with Solutions

Q1: What is the difference between the average rate and instantaneous rate?

Answer: Average rate is the rate measured for a long period of time. While the instantaneous rate is the rate measured for an infinitesimally small period of time.

Q2. What does the given graph represent about the nature of reaction? Which of the following expressions are in favour of the graph?



- a. $\Delta[A]/\Delta t = \Delta[B]/\Delta t$
- b. $-\Delta[B]/\Delta t = \Delta[A]/\Delta t$
- c. $-\Delta[A]/\Delta t = \Delta[B]/\Delta t$
- d. None of the above

Answer: (c.)

Explanation: The given graph represents that with the decrease in the concentration of A, the concentration of B increases. This implies that A is the reactant and B is the product of the reaction. The reaction can be represented as: $A \rightarrow B$.

Since in this reaction, A is the reactant and B is the product; the change in concentration of either of A and B with time gives the rate of the reaction.

Hence, the average rate of formation of B can be written as: $\Delta[B]/\Delta t$ (with a + sign as the concentration of B increases through the reaction).

While the average rate of consumption of A can be written as: $-\Delta[A]/\Delta t$ (with a - sign as the concentration of A decreases through the reaction)

The correct expression for the reaction curves shown in the graph is $-\Delta[A]/\Delta t = \Delta[B]/\Delta t$.

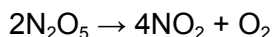
Q3. The reaction rate of a substance is directly proportional to its_____.

Answer: Active Mass

The active mass is the concentration of the reacting substance in mol l^{-1} . Hence, the rate of the reaction of the substance is directly proportional to its active mass.

Q4. In the reaction rate expression, the change in concentration of each of the reactants and products are divided by the respective stoichiometric number present in the reaction equation. Why is this division done?

Answer: To understand the above fact, we must look at the following balanced equation:



The rate of decomposition of N_2O_5 is $-\frac{d[\text{N}_2\text{O}_5]}{dt}$. The rate of formation of NO_2 and O_2 are $\frac{d[\text{NO}_2]}{dt}$ and $\frac{d[\text{O}_2]}{dt}$ respectively.

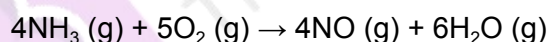
However, these rates are not equal. This is because when 2 moles of N_2O_5 decompose, 4 moles of NO_2 and 1 mole of O_2 are formed. This implies that the rate of decomposition of N_2O_5 is twice the rate of formation of O_2 and the rate of formation of NO_2 is 4 times the rate of formation of O_2 .

Hence, the rate of formation of products and the rate of decomposition of the reactants are divided by their stoichiometric coefficients in the reaction in order to get an identical value for the rate of the reaction.

Therefore, the rate of reaction in terms of each of the reactants and the products is :

$$\text{Rate of the reaction} = -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = +\frac{1}{4} \frac{d[\text{NO}_2]}{dt} = +\frac{d[\text{O}_2]}{dt}$$

Q5. Calculate the rate of the reaction in terms of the different reactants and products for the following reaction.



Given the rate of formation of NO is $3.6 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$, calculate the rate of disappearance of NH_3 and the rate of formation of H_2O .

Answer: The rate of the reaction in terms of each of the reactants and products is given as:

$$\text{Rate of Reaction} = -\frac{1}{4} \frac{d[\text{NH}_3]}{dt} = -\frac{1}{5} \frac{d[\text{O}_2]}{dt} = +\frac{1}{4} \frac{d[\text{NO}]}{dt} = +\frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt}$$

Since, the coefficients of NO and NH_3 in the balanced chemical equation are the same, both of them have the same rate of formation and disappearance respectively.

Hence, rate of formation of NO = rate of disappearance of NH_3 = $3.6 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$

$$\text{Now, the rate of reaction : } \frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt} = \frac{1}{4} \frac{d[\text{NO}]}{dt}$$

$$\text{Hence, the rate of formation of water : } \frac{d[\text{H}_2\text{O}]}{dt} = \frac{6}{4} \frac{d[\text{NO}]}{dt}$$

$$\frac{d[H_2O]}{dt} = \frac{3}{2}(3.6 \times 10^{-3}) \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\frac{d[H_2O]}{dt} = 5.4 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

Hence, the rate of formation of water is $5.4 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$.

Q6. Calculate the overall order from the given rate expressions.

- Rate = $k[A]^{1/2}[B]^{3/2}$
- Rate = $k[A]^{3/2}[B]^{-1}$

Answer: The overall orders are calculated as:

- The order w.r.t. A = $1/2$
The order w.r.t. B = $3/2$
Overall Order = $1/2 + 3/2 = 2$
- The order w.r.t. A = $3/2$
The order w.r.t. B = -1
Overall Order = $3/2 - 1 = 1/2$

Q7. The rate constants of 3 reactions are given. Identify the order of each of the given reactions.

- $k = 2.3 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$
- $k = 3.1 \times 10^{-4} \text{ s}^{-1}$
- $k = 9.3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

Answer: Since only rate constants for each reaction are given, the order of the reactions will be determined based on the units of the rate constants.

- 2nd order
- 1st order
- Zero order

Q8. What are the differences between the rate of the reaction and the reaction rate constant?

Answer: The differences between the two are:

S.No.	Rate of Reaction	Rate Constant
1.	It is the change in concentration (mol L^{-1}) of a reactant or product with time.	It is equal to the rate of the reaction when the molar concentration of each of the reactants is 1. It is a proportionality constant.
2.	The rate of reaction at any instant of time depends directly upon the concentration of reactant(s) at that	The rate constant is independent of the concentrations of the reactants. It is constant for a particular reaction at a given

	instant.	temperature.
3.	Unit is $\text{mol L}^{-1} \text{s}^{-1}$.	Unit depends on the order of the reaction.

Q9. Give an example of the reaction of the 4th order.

Answer: The dissociation of potassium chlorate to form potassium perchlorate is an example of the reaction of 4th order.



Q10. Derive the general expression of the time taken by the reactant to reduce to its nth fraction in the first order reaction.

Answer: Let us assume the initial amount of the reactant (A) = a

Hence, the nth fraction decreased from "a" in time $t = a/n$

From the first order reaction,

$$t = \frac{2.303}{k} \log \frac{[A]_o}{[A]}$$

$$t = \frac{2.303}{k} \log \frac{a}{\frac{a}{n}}$$

$$t = \frac{2.303}{k} \log n$$

Hence, the general expression of the time taken by the reactant to reduce to its nth fraction in the first order reaction is represented by $t = (2.303/k) \log n$.

Q11. The half-life period of a 1st order reaction is 60 min. What percentage of the substance will be left after 240 min?

Answer: 1 half-life period = 60 min

Number of half-lives after 240 min = $240/60 = 4$ hal-lives i.e. $n = 4$

Amount of substance left after n half-lives = $A_o/2^n$

Percentage of the amount of substance left after 4 half-lives = $A_o/2^4 \times 100 = A_o/16 \times 100 = 6.25\%$ of A.

Q12. The dissociation of N_2O_5 in CCl_4 takes place by the 1st order rate law. The table below shows the concentration of N_2O_5 measured at different times.

Time, t(s)	0	80	160	410	600	1130	1720
$[\text{N}_2\text{O}_5]$, mol/L	5.5	5.0	4.8	4.0	3.4	2.4	1.6

From the given observations, calculate k at $t = 410$ s and $t = 1130$ s.

Answer: From the first order rate law:

$$k = \frac{2.303}{t} \log \frac{[N_2O_5]_o}{[N_2O_5]}$$

Hence, at $t = 410$ s, $k = \frac{2.303}{410} \log \frac{5.5}{4.0} = 7.768 \times 10^{-4} \text{ s}^{-1}$

At $t = 1130$ s, $k = \frac{2.303}{1130} \log \frac{5.5}{2.4} = 7.341 \times 10^{-4} \text{ s}^{-1}$

So, the value of k for the given reaction at $t = 410$ s is $7.768 \times 10^{-4} \text{ s}^{-1}$ and that at $t = 1130$ s is $7.341 \times 10^{-4} \text{ s}^{-1}$.

Q13. A 1st order reaction gets 40% completed in 50 minutes. Calculate:

- (i.) the rate constant
- (ii.) the time in which the reaction will get 80% completed.

Answer: (i.) From the 1st order:

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

Where $x = (40/100)a = 0.4a$, $t = 50$ min

Hence,

$$k = \frac{2.303}{50 \text{ min}} \log \frac{a}{a-0.4a}$$

$$k = \frac{2.303}{50 \text{ min}} \log \frac{1}{0.6} = 0.010216 \text{ min}^{-1}$$

The rate constant for the reaction is $0.010216 \text{ min}^{-1}$.

(ii.) To determine $t = ?$, $x = 0.8a$

As k is constant for a given reaction, $k = 0.010216 \text{ min}^{-1}$

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

$$t = \frac{2.303}{0.010216 \text{ min}^{-1}} \log \frac{a}{a-0.8a} = 157.58 \text{ min}$$

Hence, the time in which the reaction will get 80% completed is 157.58 min.

Q14. Determine the order of a reaction whose rate constant has the same unit as the rate of the reaction.

Answer: Zero Order reaction.

Q15. A reaction is 2nd ordered w.r.t. a reactant. Determine the change in the rate of the reaction when the amount of the reactant is:

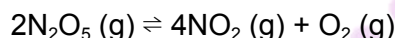
- Doubled
- Reduced to its half

Answer: For a 2nd order reaction, Rate = $k[A]^2 = ka^2$

- When $A = 2a$, Rate = $k(2a)^2 = 4.ka^2$, the reaction rate increases 4 times.
- When $A = \frac{1}{2} a$, Rate = $k(\frac{1}{2} a)^2 = \frac{1}{4}$ times, the reaction rate decreases by $\frac{1}{4}$ times.

Practise Questions on Chemical Kinetics

Q1. The given reaction is carried out in a closed vessel:



It was observed that the concentration of NO_2 increased by $2.0 \times 10^{-2} \text{ mol L}^{-1}$ within 5 seconds of the reaction. Calculate:

- the rate of the reaction.
- the rate of change of concentration of N_2O_5 .

Answer: (i.) Rate of reaction = $\frac{1}{4} \frac{d[NO_2]}{dt}$

The rate of formation of NO_2 :

$$\frac{d[NO_2]}{dt} = \frac{2.0 \times 10^{-2} \text{ mol L}^{-1}}{5 \text{ s}} = 4 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

Hence, the rate of reaction = $\frac{1}{4} \times 4 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1} = 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$

(ii.) Rate of change of concentration of $N_2O_5 = -d[N_2O_5]/dt$

From the Rate of the reaction:

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

$$\frac{d[N_2O_5]}{dt} = -\frac{1}{2} (4 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}) = 2 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

Hence, Rate of change of concentration of $N_2O_5 = 2 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$.

Q2. For $A \rightarrow \text{Products}$, $k = 2.0 \times 10^{-2} \text{ s}^{-1}$. Calculate the concentration of A after 100 s.
Given $[A]_0 = 1.0 \text{ mol L}^{-1}$

Answer: The unit of k implies that the reaction is of first order.

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

Hence,

$$2.0 \times 10^{-2} \text{ s}^{-1} = \frac{2.303}{100 \text{ s}} \log \frac{1.0 \text{ mol L}^{-1}}{[A]}$$

So,

Hence, $[A] = 0.1354 \text{ mol L}^{-1}$.

Q3. The equation followed by the composition of a hydrocarbon is:

$$k = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000 \text{ K/T}}$$

Calculate the E_a .

Answer: From the Arrhenius equation, $k = Ae^{-E_a/RT}$

Hence, $-E_a/RT = -28000 \text{ K} / T$

$$E_a = 28000 \text{ K} \times R = 28000 \text{ K} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 232.79 \text{ kJ mol}^{-1}$$

Hence, E_a is $232.79 \text{ kJ mol}^{-1}$.

Q4. A 1st order reaction gets 30% decomposed in 40 min. Calculate its $t_{1/2}$.

Answer: The 30% decomposition would mean that $x = 30\%$ of a .

Hence, $x = 0.30a$ and $t = 40 \text{ min}$

From the 1st order reaction:

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

$$k = \frac{2.303}{40 \text{ min}} \log \frac{a}{a-0.3a}$$

$$k = \frac{2.303}{40 \text{ min}} \log \frac{10}{7} = 8.918 \times 10^{-3} \text{ min}^{-1}$$

As for a 1st order reaction, $t_{1/2} = 0.693/k$

$$t_{1/2} = 0.693 / 8.918 \times 10^{-3} \text{ min}^{-1} = 77.7 \text{ min}$$

Hence, the $t_{1/2} = 77.7 \text{ min}$

Q5. The rate law for a reaction is: $\text{Rate} = k = [A][B]^{1/2}$. Can this be an elementary reaction?

Answer: For an elementary reaction, the order must be equal to the molecularity and on going ahead, molecularity must be an integral value.

In the given reaction, $\text{Order} = 1 + \frac{1}{2} = 3/2$

Here, the order of the reaction is fractional, but as the molecularity cannot be fractional. Hence, the order of this given equation cannot be equal to its molecularity. This is why the given reaction cannot be an elementary reaction.