

Chemical Kinetics

Previous Years' Questions Answers

- Q. 1. Define the term, 'Order of reaction' for chemical reactions.
- Q. 2. What is meant by the 'rate constant, k ' of a reaction? If the concentration is expressed in mol L^{-1} units and time in seconds, what would be the units for k (i) for a zero order reaction and (ii) for a first order reaction?
- Q. 3. A first order decomposition reaction takes 40 minutes for 30% decomposition. Calculate its $t_{1/2}$ value.
- Q. 4. (a) Derive the general form of the expression for the half-life of a first order reaction.
(b) The decomposition of NH_3 on platinum surface is a zero order reaction. What are the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$?
- Q. 5. (a) List the factors on which the rate of a chemical reaction depends.
(b) The half-life for decay of radioactive ^{14}C is 5730 years. An archaeological artefact containing wood has only 80% of the ^{14}C activity as found in living trees. Calculate the age of the artefact.
- Q. 6. (a) A reaction is of first order in A and of second order in B. Write the differential rate equation for this reaction. How will its initial rate be affected if the concentration of both A and B are together doubled?
(b) The rate constant k of a reaction increases four fold when the temperature changes from 300 K to 320 K. Calculate the activation energy for the reaction. ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
- Q. 7. Define the following terms giving an example for each:
(i) The order of a reaction
(ii) The molecularity of a reaction
- Q. 8. The rate constant for a first order reaction is 60 s^{-1} . How much time will it take to reduce the initial concentration of the reactant to 1/16th of its initial value?
- Q. 9. What is meant by a pseudo first order reaction? Give an example of a pseudo first order reaction and write the rate equation for the same.
- Q. 10. The rate constant for a first order reaction is 60 s^{-1} . How much time will it take to reduce the initial concentration of reactant to 1/10th of its value?

Ans. 1. The sum of powers of the concentration terms of the reactants in the rate law expression is called the order of reaction.

Ans. 2.

Rate constant is the rate of the reaction when the concentration of each reactant is taken as unity.

$$\therefore \text{rate} = K[A]^n$$

$$\therefore \text{General unit of } K = \left(\frac{\text{mol.}}{\text{lit.}} \right)^{1-n} \text{ s}^{-1}$$

(i) For a zero order reaction $n = 0$

$$\therefore \text{Unit of } K = \text{mol lit}^{-1} \text{ sec}^{-1}$$

(iii) For a first order reaction $n = 1$

$$\therefore \text{Unit of } K = \text{sec}^{-1}$$

Ans. 3.

For a first order reaction

$$K = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$\text{when } t = 40 \text{ minutes, } \frac{[R]_0}{[R]} = \frac{100}{100 - 30} = \frac{10}{7}$$

$$K = \frac{2.303}{40} \log \frac{10}{7} = \frac{2.303}{40} \log 1.428 = \frac{2.303}{40} \times 0.1548$$

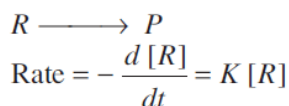
$$K = 8.91 \times 10^{-3} \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{8.91 \times 10^{-3}}$$

$$t_{1/2} = 77.78 \text{ min.}$$

Ans. 4.

(a) Consider the first order reaction



or
$$\frac{d[R]}{[R]} = -K dt$$

Integrating both the sides we get

$$\ln [R] = -Kt + C \quad \dots(i)$$

when $t = 0$, $R = [R]_0$ where $[R]_0$ is the initial concentration of the reactant.

Therefore equation (i) can be written as

$$\ln [R]_0 = -K \times 0 + C$$

$$\ln [R]_0 = C$$

Substituting the value of C in equation (i)

$$\ln [R] = -Kt + \ln [R]_0$$

$$Kt = \ln [R]_0 - \ln [R]$$

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

$$Kt = 2.303 \log \frac{[R]_0}{[R]} \quad \Rightarrow \quad t = \frac{2.303}{K} \log \frac{[R]_0}{[R]}$$

when $t = t_{1/2}$ $[R] = \frac{[R]_0}{2}$

$$\therefore t_{1/2} = \frac{2.303}{K} \log \frac{[R]_0}{\frac{[R]_0}{2}}$$

$$t_{1/2} = \frac{2.303}{K} \log 2 = \frac{2.303}{K} \times 0.3010$$

$$\therefore t_{1/2} = \frac{0.693}{K}$$



For a zero order reaction

$$\text{Rate} = K [\text{NH}_3]^0$$

$$\text{Rate} = K = 2.5 \times 10^{-4}$$

$$\text{Rate} = -\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

$$\therefore \frac{d[\text{N}_2]}{dt} = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ S}^{-1}$$

$$\frac{d[\text{H}_2]}{dt} = \frac{3d[\text{N}_2]}{dt} = 3 \times 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ S}^{-1}$$

$$\frac{d[\text{H}_2]}{dt} = 7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ S}^{-1}$$

Ans. 5.

(a) Rate of reaction depends on

(i) Concentration

(ii) Temperature

(iii) Nature of reactant

(iv) Pressure of the gaseous reactant

(v) Surface area

(vi) Catalyst

(b) $t_{1/2} = 5730$ years

$$\therefore K = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730} = 1.209 \times 10^{-4} \text{ year}^{-1}$$

$$t = \frac{2.303}{K} \log \frac{[R]_0}{[R]} = \frac{2.303}{1.2 \times 10^{-4}} \log \frac{100}{80}$$

$$t = \frac{2.303 \times 10^4}{1.2} (\log 10 - \log 8) = \frac{2.303 \times 10^4}{1.2} (1 - 3 \log 2)$$

$$t = \frac{2.303}{1.2} \times 10^4 (1 - 3 \times 0.3010) = \frac{2.303 \times 0.097 \times 10^4}{1.209}$$

$$t = 1847.7 \text{ years}$$

Ans. 6.

$$(a) \quad \text{Rate} = \frac{dx}{dt} = K [A][B]^2$$

If concentration of both A and B are doubled, then

$$\begin{aligned}\text{Rate} &= K [2A][2B]^2 \\ &= 8K [A][B]^2\end{aligned}$$

i.e., the rate of reaction becomes 8 times.

$$(b) \quad K_2 = 4K_1 \quad \text{i.e.,} \quad \frac{K_2}{K_1} = 4$$

$$T_1 = 300 \text{ K}$$

$$T_2 = 320 \text{ K}$$

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log 4 = \frac{E_a}{2.303 \times 8.314} \left(\frac{320 - 300}{300 \times 320} \right)$$

$$2 \log 2 = \frac{E_a}{19.147} \left(\frac{20}{300 \times 320} \right)$$

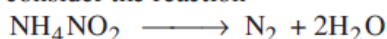
$$E_a = \frac{2 \times 0.3010 \times 19.147 \times 300 \times 320}{20} = 55327 \text{ J}$$

$$E_a = 55.327 \text{ kJ}$$

Ans. 7.

- (i) Order of reaction may be defined as the sum of powers of the concentration of the reactants in the rate law expression.

For example consider the reaction



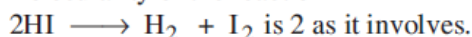
Experimentally, it is observed that the rate law for this reaction is

$$\text{Rate} = K [\text{NH}_4\text{NO}_2]$$

Hence, the order of reaction is 1.

- (ii) Molecularity of a reaction may be defined as the number of reacting species (atoms, ions or molecules) taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction.

For example molecularity of the reaction



Simultaneous collision between two HI molecules.

Ans. 8.

$$K = 60 \text{ s}^{-1}, \quad [R] = \frac{[R]_0}{16}$$

$$t = ?$$

$$t = \frac{2.303}{K} \log \frac{[R]_0}{[R]}$$

Substituting the values

$$t = \frac{2.303}{60} \log \frac{[R]_0}{\frac{[R]_0}{16}}$$

$$t = \frac{2.303}{60} \log 16 = \frac{2.303}{60} \cdot 4 \log 2$$

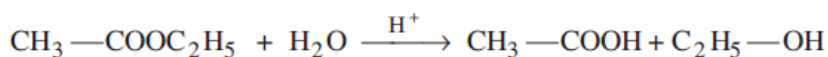
$$t = \frac{2.303}{15} \times 0.3010 = \frac{0.6932}{15}$$

$$t = 4.62 \times 10^{-2} \text{ s.}$$

Ans. 9.

A reaction which is of higher order but follows the kinetics of first order under special conditions is called a pseudo first order reaction.

Example, Acid hydrolysis of ethyl acetate.



Here, the rate law is given by expression

$$\text{Rate} = K [\text{CH}_3\text{—COOC}_2\text{H}_5]$$

The concentration of H_2O is so large that it hardly undergoes any change during the reaction, therefore, it does not appear in the rate law.

Ans. 10.

$$K = 60 \text{ s}^{-1}$$

$$t = \frac{2.303}{K} \log \frac{[R]_0}{[R]}$$

$$t = \frac{2.303}{60} \log \frac{[R]_0}{\frac{[R]_0}{10}} = \frac{2.303}{60} \log 10 = 0.038 \times 1$$

$$t = 0.038 \text{ s}$$