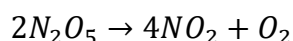


## Rate law and Rate constant

25. (b)  $R = K[A]$ ,  $1.02 \times 10^{-4} = 3.4 \times 10^{-5} [N_2O_5]$

or  $(N_2O_5) = \frac{1.02 \times 10^{-4}}{3.4 \times 10^{-5}}, K = 3$

26. (a) Rate law for the reaction



is  $r = k[N_2O_5]$  first order reaction.

27. **Solution:**

- Rate law is  $\text{Rate} = k[\text{NO}]^2[\text{O}_2]$ .
- Here, **k is the rate constant**. It depends only on **temperature** (and catalyst, if present), not on concentrations.
- Increasing the concentration of reactants affects the **rate**, but not the **rate constant**.
- To increase **k**, we need to increase **temperature**.

**Answer: (a) Increasing temperature**

28. (c) Rate constant depends on temperature only.

29. (c) According to Arrhenius concept

Rate constant  $K = A e^{-\frac{E_a}{RT}}$ , Hence rate constant depends only upon temperature of the system.

30. (d) For  $2A + B \rightarrow C$

$$\text{Rate} = K[A][B]$$

Value of rate constant  $K = A e^{-\frac{E_a}{RT}}$  here  $K$  is independent of the initial concentration of  $A$  and  $B$ .



31. (d) The specific rate constant of a first order reaction depends upon the temperature of reaction.

32. (c) Unit of  $K$  for first order reaction =  $\text{sec}^{-1}$

33. Write the rate law (second order):

$$\text{Rate} = k [A]^2$$

(or  $\text{Rate} = k [A][B]$ ; both are second order overall)

Write dimensions / units:

- Dimension of rate =  $\text{concentration} / \text{time} = \text{mol L}^{-1} \text{s}^{-1}$  (denote concentration dimension by  $C$  and time by  $T$ , so  $[\text{Rate}] = C T^{-1}$ ).
- Dimension of concentration  $[A] = \text{mol L}^{-1} = C$ .

Solve for dimension of  $k$ :

$$[k] = \frac{CT^{-1}}{C^2} = C^{-1}T^{-1}$$

$$[k] = L \text{mol}^{-1} \text{s}^{-1}$$

Conclusion / Answer: (c) Time and concentration

34. Rate law (second order):

$$\text{Rate} = k[A]^2$$

Dimensions:

- Rate:

$$[\text{Rate}] = \text{concentration} \cdot$$

$$\cdot T^{-1} = (\text{mol L}^{-1}) \text{s}^{-1}$$



- Concentration:

$$[A] = \text{mol L}^{-1}$$

**Solve for unit of k**

$$[k] = \frac{\text{mol L}^{-1} \text{s}^{-1}}{(\text{mol L}^{-1})^2}$$

$$(d) \text{ mole}^{-1} \text{ litre sec}^{-1}$$

35. (b) The rate of zero order reaction is not depend on the concentration of the reactants.

36. (c) The unit of  $K$  for zero order reaction =  $\text{mole litre}^{-1} \text{sec}^{-1}$ .

37. (c) Order of reaction is sum of the power raised on concentration terms to express rate expression.

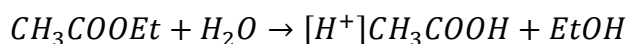
38. (a) The concentration of reactant does not change with time for zero order reaction (unit of  $K$  suggests zero order) since reactant is in excess.

39. (c)  $r = K[A]^m$  also  $2r = K[4A]^m$ ,  $\frac{1}{2} = \left(\frac{1}{4}\right)^m$

$$\therefore m = \frac{1}{2}$$

40. (b)  $K = \frac{2.303}{t} \log \frac{V_{\infty}}{V_{\infty} - V_t}$  gives constant value of  $K$ . With the given data. Hence it is 1<sup>st</sup> order.

41. Reaction:



In principle, rate depends on both ester and water concentrations:



$$\text{Rate} = k[\text{CH}_3\text{COOEt}][\text{H}_2\text{O}]$$

Since water is present in **large excess** (as solvent),  $[\text{H}_2\text{O}]$  is nearly constant.

So we can write:

$$\text{Rate} = k'[\text{CH}_3\text{COOEt}]$$

where  $k' = k[\text{H}_2\text{O}]$ .

Therefore, the reaction follows **pseudo-first order kinetics**.

**Correct Answer:** (a) First order

42. (d)  $r = K[A]^n$ ,  $100r = K[10A]^n$

$$\text{Thus } \frac{1}{100} = \left(\frac{1}{10}\right)^n \text{ or } n = 2$$

43. (a) It is a standard example of first order because in that reaction rate of reaction affected by only one concentration term.

44. (c) Inversion of cane sugar is a Pseudo unimolecular reaction.

45. (c) For 1<sup>st</sup> order reaction

$$K = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$

46. (a)  $t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{6.2 \times 10^{-4}} = 1117.7 \text{ sec.}$

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

$$\frac{0.693}{T} = \frac{2.303}{t} \log \frac{100}{100-30}$$

$$\therefore T = 58.2 \text{ min.}$$

48. (b) Order of reaction =  $\frac{3}{2} + \frac{3}{2} = \frac{3+3}{2} = \frac{6}{2} = 3$

