Study Notes on Kinetics of First Order Reaction

Kinetics of first order reaction

It is directly proportional to the concentration of a single reactant.

Let a general equation be:

$$A \longrightarrow Product$$

t = 0   a   0

t = t   a − x   x

The expression of rate of reaction can be written as:

$$\frac{dx}{dt} \propto [A]^1$$

$$\frac{dx}{dt} = k[A]^1$$

$$\frac{dx}{dt} = k(a-x)$$

$$\frac{dx}{a-x} = k\,dt$$

$$\int \frac{1}{(a-x)}dx = k\int dt + c \qquad \qquad \text{… (1)}$$

$$\ln\frac{1}{(a-x)} = kt + c \qquad \qquad \text{… (2)}$$

But initially t = 0, x = 0

$$\ln\frac{1}{(a-0)} = k\cdot 0 + c$$

$$\ln\frac{1}{a} = c$$

$$c^1 = \ln\left(\frac{1}{a}\right) \qquad \qquad \text{… (3)}$$

From equations (2) and (3):

$$\ln\frac{1}{(a-x)} = kt + \ln\left(\frac{1}{a}\right)$$

$$kt = \ln\left(\frac{1}{a-x}\right) - \ln\left(\frac{1}{a}\right)$$

$$kt = \ln\left(\frac{\left(\frac{1}{a-x}\right)}{\left(\frac{1}{a}\right)}\right)$$

$$kt = \ln\left(\frac{a}{a-x}\right)$$

$$kt = 2.303 \log \frac{a}{a-x} \qquad \text{... (4)}$$

This relation is known as rate law expression.

Half-life time for first order reactions:

For half lifetime,

$t \to t_{1/2}$; $x \to a/2$

From equation (7),

$k.t_{1/2} = 2.303 \log \dfrac{a}{a-a/2}$

$k.t_{1/2} = 2.303 \log \dfrac{2a}{a}$

$k.t_{1/2} = 2.303 \log 2$

$k.t_{1/2} = 2.303 \times 0.3010$

$k = \dfrac{0.693}{t_{1/2}}$

$t_{1/2} = \dfrac{0.693}{k}$

Unit of rate constant for first order reactions:

Unit of rate constant = $\sec^{-1}$

Graphical representation of first order reactions:

(i). When log (a − x) is plotted versus time (t):

$$kt = \ln\frac{a}{a-x} = 2.303 \log_{10}\frac{a}{(a-x)}$$
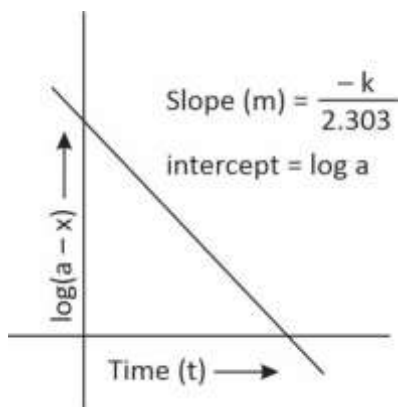
$$\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$$

2.303 log a − 2.303 log (a − x) = kt

2.303 log (a − x) = − kt + 2.303 log a

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

From, $y = mx + c$

Slope (m) = $\frac{-k}{2.303}$ and intercept (c) = log a

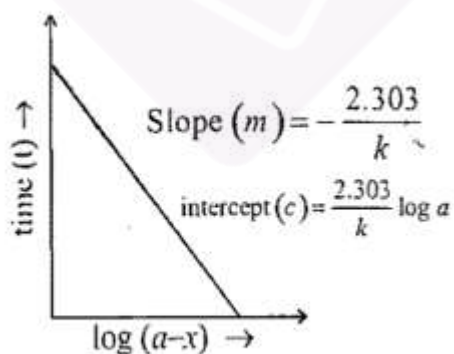(ii). When time (t) versus log (a – x)

Since from equation (7),

kt = 2.303 log a – 2.303 log (a – x)

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

$$t = \left(-\frac{2.303}{k}\right)\log(a-x) + \frac{2.303}{k}\log a$$

From y = mx + c,

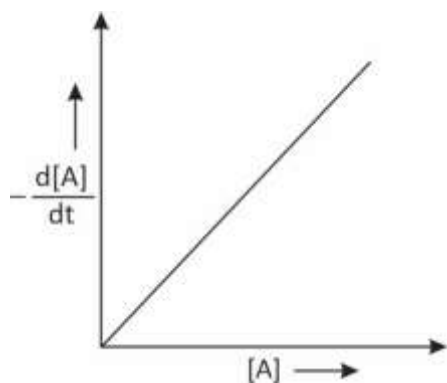Slope (m) = $-\frac{2.303}{k}$ and intercept (c) = $\frac{2.303}{k}$ log a

(iii). $-\frac{d[A]}{dt}$ versus concentration [A]:

Rate of reaction $\propto [A]^1$

$$-\frac{d[A]}{dt} = k[A] + 0$$

From y = mx + c,

Slope (m) = k and intercept (c) = 0
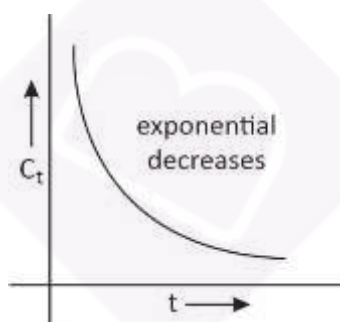

(iv). Concentration (C_t) versus time (t):

$$A \longrightarrow Product$$

t = 0 C_0 0

t = t C_t $(C_0 - C_t)$

$$kt = \ln\frac{C_0}{C_t} \Rightarrow e^{kt} = e^{\ln\left(\frac{C_0}{C_t}\right)} \Rightarrow e^{kt} = \frac{C_0}{C_t}$$

$C_0 = C_t \, e^{kt}$ or $C_t = C_0 \, e^{-kt}$

First order reaction is never completed.

Since,

$C_t = C_0 \, e^{-k.x}$ [t = ∞]

$C_t = C_0 . 0$

$C_t = 0$

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