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Deg - I(H) - Chemical Kinetics
Topics — Kinetics of hydrolysis of ethyl-Acetate in acidic-Medium & Zero-order-Reaction

Hydrolysis of Ester (ethyl-Acetate) in acidic-medium

Ethyl Acetate hydrolyse as

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

The amount of CH_3COOH can be Calculated by titration against standard NaOH solution. But being an acid-Catalysed reaction, the acid present might also act as a Catalyst also react with NaOH solution. Hence for the same volume of reaction mixture with-drawn at different-time

Experimental - Observation -

Volume of NaOH Soln used initially at Zero-time (V_0) & Amount of acid used in Catalyst only (CH_3COOH) = a

Again

Volume of NaOH solution used at any instant of time (V_t) $\propto$ Amount of acid present as Catalyst + CH_3COOH formed — (2)

Combining above with statement (1)

Amount of CH_3COOH produced at any instant of time $\} \propto (V_t - V_0)$ — (3)

We see from Reaction that Amount of CH_3COOH produced is the amount of CH_3COONa react (x)

Hence $(V_t - V_0) \propto x$ — (4)

Volume of NaOH solution used after the reaction has taken place for a long time or infinite time (V_∞) $\} \propto$ Amount of acid present as Catalyst + Maximum amount of CH_3COOH produced — (5)

Maximum Amount of CH_3COOH produced $\propto (V_\infty - V_0)$ — (6)

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But the maximum amount of CH_3COOH produced } ∝ Initial conc. of $CH_3COOC_2H_5$ (a)

Thus $(V_\infty - V_0) \propto a$

Eqn (iv) & (vi)

$$(a-x) \propto (V_\infty - V_0) \quad (V_t - V_0)$$

$$\text{or, } (a-x) \propto (V_\infty - V_t) \quad \text{—(7)}$$

Putting the value of a & (a-x) in first order rate expression

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

$$\text{or, } \boxed{K = \frac{2.303}{t}\log\frac{(V_\infty - V_0)}{(V_\infty - V_t)}}$$

Zero-Order Reaction:-

Those reaction in which rate of reaction is independent upon the concentration of the reactant. Its rate is proportional to the zero power of the concentration of reaction.

For the reaction

A ⟶ Product.

Its rate is expressed.

$$\frac{dx}{dt} = K[A]^0 = K(a)^0 = K$$

Where initial concⁿ of A = a

Thus $dx = K \cdot dt$

Upon Integrating $\int dx = K \int dt$

$x = Kt + C$ | C = Integ. const.

When $t = 0$, $x = 0$

Thus $c = 0$

Hence $\boxed{x = Kt}$

Characteristics of Zero order Rxn.

(a) Unit of K, $K = \frac{dx}{dt}$ = mol/lit Time⁻¹

(b) Half-life Period:- When $t = t_{1/2}$, $x = a/2$

$$t = \frac{x}{K}$$

$$t_{1/2} = \frac{a}{2K}$$

half life ∝ Initial conc.

(c) Example of zero order Rxn

(a) Photo-Chemical Reaction ($H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$)

(b) $2NH_3 \xrightarrow{Mo} N_2 + 3H_2$ (c) $HI \xrightarrow{Au} \frac{1}{2}H_2 + \frac{1}{2}I_2$