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Deg-I (H/S) - Chemical-Kinetics

Topics — Numerical-problem based upon order of reaction & Arrhenious-Equation

(A) Problem-based upon order of Reaction

Example:-(1) Show that in case of a first order reaction, the time required for 99.9% of the reaction to take-place is about ten-times than that required for half-life of the reaction.

Solution:—

we know that $t_{1/2}$ of first-order is expressed as

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

Time for 99.9% change is calculated as

let, $a = 100$, $x = 99.9$, $(a-x) = 0.1$

Now $K = \frac{2.303}{t} \log \frac{100}{0.1}$

$= \frac{2.303}{t} \log 10^3$

$= \frac{2.303 \times 3 \times \log 10}{t}$

$$K = \frac{6.909}{t}$$

$$t = \frac{6.909}{K}$$

By Comparing Result

$$\frac{t_{1/2}}{t} = \frac{0.693}{\cancel{K}} \times \frac{\cancel{K}}{6.909}$$

$$= \frac{1}{10}$$

$$\boxed{\therefore t = 10 \times t_{1/2}}$$

Example-(2) A first order reaction ~~takes~~ of 75% Complete in 32 minutes: Calculate its $t_{1/2}$.

let,

$t = 32$ min, $a = 100$, $x = 75$

$(a-x) = 25$

Putting the value in first order Rate expression

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

for first order

$$= \frac{2.303}{32} \log \frac{\cancel{100}^{4}}{\cancel{25}}$$

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

$$\therefore K = \frac{0.693}{K}$$

$$\frac{0.693}{K} = \frac{2.303}{32} \times \log 4$$

$\log 4 = 2\log 2 = 2 \times .3010$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{\cancel{32}_{16}} \times \cancel{2 \times 0.3010}$$

$\therefore t_{1/2} = 16$ min

Example - 3 A second order reaction in which the initial concn of both the reaction are same is 25% complete in 600 sec. How long will it take for the reaction to go to 75% completion.

Solution :- Expression for second order Reaction.

First Case

$$K = \frac{1}{t}\frac{x}{a(a-x)}$$

let $a = 100$
$x = 25$
$a-x = 75$

$$= \frac{1}{600} \times \frac{25}{100 \times 75} \quad \text{--- (1)}$$

Second Case

$$K = \frac{1}{t} \times \frac{75}{100 \times 25} \quad \text{--- (2)}$$

$a = 100$
$x = 75$
$a-x = 25$

Divide (1) by (2)

$$\frac{\cancel{K}}{\cancel{K}} = \frac{1}{600} \times \frac{\cancel{25}}{\cancel{100} \times \cancel{75}_{3}} \times \frac{t \times \cancel{100} \times \cancel{25}}{\cancel{75}_{3}}$$

$$\boxed{t = 5400 \text{ sec}}$$ Ans.

Example : 4 At 500K, the half life period of a gaseous reaction ~~is 80 kPa, the half~~ its initial pressure of 80 kPa is 350 sec. When the pressure becomes 40 kPa its half life becomes 175 sec.

Solution :- $(t_{1/2})_1 = 350$ sec, $p_1 = 80$ kPa
$(t_{1/2})_2 = 175$ sec, $p_2 = 40$ kPa

From formula $\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{P_2}{P_1}\right)^{n-1}$ $\quad \left| \; t_{1/2} \propto \frac{1}{a^{n-1}} \right.$

$$\frac{\cancel{350}^{\,2}}{175} = \left(\frac{40}{80}\right)^{n-1}$$

$$2^0 = \left(\frac{1}{2}\right)^{n-1} = 2^{1-n}$$

Thus $0 = 1-n$ $\therefore n = \text{Zero}$

It is of zero-order-Reaction.

Ⓑ Problem based on Activation-Energy.

Example: ⑤ Calculate the activation energy of a reaction whose reaction rate at 27^0C gets doubled for 10^0C rise in tempr.

Solution - $T_1 = 27+273 = 300K$
rate $= K_1$
$T_2 = 27+10+273 = 310K$
rate $= K_2$
$K_2 = 2K_1$

Putting the value in the equation

$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

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$$\log \frac{2K_1}{K_1} = \frac{Ea}{2.303 \times 8.314}\left[\frac{310-300}{300 \times 310}\right]$$

$$\log 2 = \frac{Ea}{2.303 \times 8.314} \times \frac{10}{300 \times 310}$$

$$0.30103 = \frac{Ea}{2.303 \times 8.314 \times 310 \times 30}$$

$$Ea = 53598.6\ J\ mol^{-1}$$

$$= 53.5986\ KJ\ mol^{-1}$$

Example - (6) The activation energy of a first order reaction at 300 K is 60 KJ mol^{-1}. In the presence of a Catalyst the activation energy get lowered to 50 KJ mol^{-1} at 300 K. How many times the reaction rate change in the presence of Catalyst at the same Temp.

Solution :- $K = A e^{-\frac{Ea}{RT}}$

$$K_2 = A \cdot e^{-\frac{Ea(c)}{RT}}$$

$$\log \frac{K_2}{K_1} = \frac{Ea - Ea(c)}{2.303 RT}$$

$$= \frac{6000 - 5000}{2.303 \times 8.314 \times 300}$$

$$= 1.741$$

$$\frac{K_2}{K_1} = 55.08$$

Reaction - Rate increases by 55.08 times.