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Solution :- Assignment 7

Ans 1. At 400K, $t_{1/2} = \frac{0.693}{k_{400K}}$

$\Rightarrow \frac{0.693}{10 \times 60}\ sec^{-1} = 1.55 \times 10^{-3}\ sec^{-1}$

Again, $\frac{k_{420K}}{k_{400K}} = 3$

$\Rightarrow k_{420K} = 3 \times 1.55 \times 10^{-3}\ sec^{-1} = 4.65 \times 10^{-3}\ sec^{-1}$

$\Rightarrow t_{0.5} = \frac{1}{4.65 \times 10^{-3}\ sec^{-1}} \ln \frac{1}{1-0.25}$

$= 61.8\ sec.$

Ans 2. $v = \frac{dP}{dt} = k[A][B]$

let the initial concentration be $[A]_0 = A_0$, $[B]_0 = B_0$ and $[P]_0 = 0$. Then, when P is formed in concentration x, the concentration of A changes to $A_0 - 2x$ and that of B changes to $B_0 - 3x$. Therefore,

$\frac{dP}{dt} = \frac{dx}{dt} = k(A_0 - 2x)(B_0 - 3x)$ with $x = 0$ at $t = 0$

$$\int_0^t k\,dt = \int_0^x \frac{dx}{(A_0 - 2x) \times (B_0 - 3x)}$$

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$$= \int_0^x \frac{6}{(2B_0 - 3A_0)} \times \left(\frac{1}{3(A_0 - 2x} - \frac{1}{2(B_0 - 3x)} \right) dx$$

$$= \left(\frac{-1}{2B_0 - 3A_0} \right) \times \left(\int_0^x \frac{dx}{x - (1/2)A_0} - \int_0^x \frac{dx}{x - (1/3)B_0} \right)$$

$$kt = \frac{-1}{(2B_0 - 3A_0)} \times \left[\ln \left(\frac{x - 1/2\, A^0}{-1/2\, A^0} \right) - \ln \left(\frac{x - 1/3\, B_0}{-1/3\, B_0} \right) \right]$$

$$= \frac{-1}{(2B_0 - 3A_0)} \ln \left(\frac{(2x - A_0) B_0}{A_0 (3x - B_0)} \right)$$

$$= \left(\frac{1}{(3A_0 - 2B_0)} \ln \left(\frac{(2x - A_0) B_0}{A_0 (3x - B_0)} \right) \right)$$

Ans 3:- For Second order - reaction of like:

$$A + B \longrightarrow P$$

Integrated rate law is:

$$kt = \frac{1}{[B]_0 - [A]_0} \ln \frac{[A]_0 ([B]_0 - x)}{([A]_0 - x)[B]_0}$$

Here, A represents $CH_3COOC_2H_5$ & B represents NaOH.

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(a) For 10s :-

$$(0.21 dm^3 mol^{-1} s^{-1}) \times (10s) = \frac{1}{(0.030 - 0.20)\ dm^{-3} mol} \ln\left[\frac{0.20}{0.03}\left(\frac{0.03 - x}{0.20 - x}\right)\right]$$

$$2.1 dm^3 mol^{-1} = \frac{2.303}{(-0.17 mol\, dm^{-3})} \log\left(6.66\left(\frac{0.03 - x}{0.20 - x}\right)\right)$$

$$\frac{-2.1 dm^3 mol^{-1}}{13.54 dm^3 mol^{-1}} = \log\left(6.66\left(\frac{0.03 - x}{0.20 - x}\right)\right)$$

$$-0.155 = \log\left(6.66\left(\frac{0.03 - x}{0.20 - x}\right)\right)$$

$$0.699 = 6.66\left(\frac{0.03 - x}{0.20 - x}\right)$$

$$0.104 = \frac{0.03 - x}{0.20 - x}$$

$$0.104(0.20 - x) = 0.03 - x$$

$$0.0208 - 0.104x = 0.03 - x$$

$$x - 0.104x = 0.03 - 0.0208$$

$$0.896x = 0.0092$$

$$x = 0.010 mol\, dm^{-3}.$$

Conc. of ester after 10s = $0.20 mol\, dm^{-3} - 0.010 mol\, dm^{-3}$

$= 0.19 mol\, dm^{-3}$.

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(b) For 10minutes:-

$(0.21\,dm^3\,mol^{-1}s^{-1}) \times (600s) = -(13.54\,dm^3mol^{-1}) \log\left(6.66\left(\frac{0.03-x}{0.2-x}\right)\right)$

$\frac{-126\,dm^3\,mol^{-1}}{13.54\,dm^3mol^{-1}} = \log\left(6.66\left(\frac{0.03-x}{0.2-x}\right)\right)$

$-9.30 = \log\left(6.66\left(\frac{0.03-x}{0.2-x}\right)\right)$

$+5.01\times10^{-10} = 6.66\left(\frac{0.03-x}{0.2-x}\right)$

$0.75\times10^{-10} = \left(\frac{0.03-x}{0.2-x}\right)$

$(0.2-x)(0.75\times10^{-10}) = (0.03-x)$

$0.15\times10^{-10} - 0.75\times10^{-10}x = 0.03-x.$

$0.15\times10^{-10} - 0.03 = 0.75\times10^{-10}x - x$

$x \approx 0.03\,mol\,dm^{-3}.$

Conc of ester after 10minutes $= 0.20 - 0.03$

$= 0.17\,mol\,dm^{-3}$

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Ans 4:- A reaction nth-order in A has the following rate law:

$$-\frac{d[A]}{dt} = k[A]^n \quad \text{so} \quad \frac{d[A]}{[A]^n} = -k\,dt = [A]^{-n}\,d[A]$$

Integration yields

$$\frac{[A]^{1-n} - [A]_0^{1-n}}{1-n} = -kt$$

let $t_{1/3}$ be the time at which $[A] = [A]_0/3$.

$$\text{So, } -kt_{1/3} = \frac{\left(\frac{1}{3}[A]_0\right)^{1-n} - [A]_0^{1-n}}{1-n}$$

$$= [A_0]^{1-n}\left[\frac{\left(\frac{1}{3}\right)^{1-n} - 1}{1-n}\right]$$

$$\text{and } t_{1/3} = \frac{3^{n-1} - 1}{k(n-1)}\,[A]_0^{1-n}$$

Ans 5 $$\ln\frac{k_2}{k_1} = -\frac{Ea}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$-\frac{R \ln k_2/k_1}{Ea} = \frac{1}{T_2} - \frac{1}{T_1}$$

$$T_2 = \frac{1}{\frac{1}{T_1} - \frac{R \ln k_2/k_1}{Ea}}$$

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$$T_2 = \frac{1}{\frac{E_a - T_1 R \ln k_1/k_2}{E_a T_1}}$$

$$T_2 = \frac{E_a T_1}{E_a - T_1 R \ln k_2/k_1}$$

$$T_2 = \frac{(154{,}000\ J/mol) \times (290 + 273.15\ K)}{154000\ J/mol - (290 + 273.15K)(8.314\ J/mol\,k) \ln\left(\frac{3.20 \times 10^{-4} s^{-1}}{2.50 \times 10^{-4} s^{-1}}\right)}$$

$$= \frac{86795100\ J/mol.K}{152844.19\ J/mol}$$

$$= 567.40\ K.$$

Ans 6:- The first order half life is related to rate constant by:-

$$t_{1/2} = \ln 2/k \quad \text{So} \quad k = \frac{\ln 2}{t_{1/2}}$$

$$\Rightarrow k = \frac{\ln 2}{22.1y} = 0.0313y^{-1}$$

The Integrated rate law tells us

$$[^{90}Sr] = [^{90}Sr]_0 e^{-kt} \quad \text{So} \quad m = m_0 e^{-kt}$$

Where m is the mass of ^{90}Sr.

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(a) After 15 year :-

$m = (2.0\,\mu g) \times \exp(-0.0313\,y^{-1} \times 15\,y)$

$= 1.25\,\mu g$

(b) After 60 year :-

$m = (2.0\,\mu g) \times \exp(-0.0313\,y^{-1} \times 60\,y)$

$= 0.3057\,\mu g$

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