

6.2.3. Numerical Problems

Problem 1: A second-order reaction, in which both the reactants have same concentration, is 20% completed in 500 seconds. How much time will it take for 60% completion?

Solution: The second-order equation when both the reactants have same concentration:

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

If $a = 100$, $c = 20$, $t = 500$ seconds.

$$k = \frac{1}{500} \times \frac{20}{100 \times (100 - 20)}$$

So,

When $a = 100$, $c = 60$, $t = ?$

$$t = \frac{1}{k} \cdot \frac{60}{100 \times 40}$$

On substituting the value of k :

$$t = \frac{500 \times 100 \times 80}{20} \times \frac{60}{100 \times 40}$$

Or

$$t = 3000 \text{ seconds.}$$

Problem 2: A first-order reaction is found to have a rate constant, $k = 5.5 \times 10^{-14} \text{ s}^{-1}$. Find the half-life of the reaction.

Solution: Half-life for a first-order reaction:

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

$$t_{1/2} = \frac{0.693}{5.5 \times 10^{-14} \text{ s}^{-1}} = 1.26 \times 10^{13} \text{ s}$$

Problem 3: Show that in a first-order reaction, time required for completion of 99.9% is 10 times of half-life of the reaction.

Solution: When reaction is completed 99.9%, $[R]_n = [R]_0 - 0.999[R]_0$:

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} = \frac{2.303}{t} \log \frac{[R]_0}{[R]_0 - 0.999[R]_0} = \frac{2.303}{t} \log 10^3$$

$$t = 6.909/k$$

For half-life of the reaction:

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

$$\frac{t}{t_{1/2}} = \frac{6.909}{k} \times \frac{k}{0.693} = 10$$

Problem 4: A prescription for a liquid aspirin preparation is called for. It is to contain 325mg/5ml or 6.5gm/100ml. The solubility of aspirin at 25°C is 0.33gm/100ml; therefore, the preparation will definitely be a suspension. The other ingredients in the prescription cause the product to have a pH of 6.0. The first-order rate constant for aspirin degradation in this solution is $4.5 \times 10^{-6} \text{ sec}^{-1}$. Calculate the zero-order rate constant. Determine the shelf-life (t_{90}) for the liquid prescription, assuming that the product is satisfactory until the time at which it has decomposed to 90% of its original concentration (i.e., 10% decomposition) at 25°C.

Solution: $k_0 = k \times [\text{Aspirin in solution}]$. Thus,

$$k_0 = (4.5 \times 10^{-6} \text{ sec}^{-1}) \times (0.33 \text{ gm}/100 \text{ ml})$$

$$k_0 = 1.5 \times 10^{-6} \text{ gm}/100 \text{ ml sec}^{-1}$$

$$t_{90} = \frac{0.10[A]_0}{k_0} = \frac{(0.10)(6.5 \text{ g}/100 \text{ ml})}{(1.5 \times 10^{-6} \text{ g}/100 \text{ ml sec}^{-1})}$$

$$= 4.3 \times 10^5 \text{ sec} = 5.0 \text{ days}$$

Problem 5: The rate constant of a reaction at 25°C is $3.46 \times 10^{-5} \text{ s}^{-1}$. Calculate Arrhenius factor if the activation energy is 103.873kJ/mol.

Solution: $k = A \exp(-E/RT)$ or $\log k = \log A - E_a/(2.303 RT)$

$$\log 3.46 \times 10^{-5} = \log A - 103.873/(2.303 \times 8.314 \times 10^{-3} \times 298)$$

$$\log A = -4.4609 + 18.2048 = + 13.7439$$

$$A = 5.5449 \times 10^{13}$$

Problem 6: The velocity constant for the decomposition of nitrous oxide is 5.16×10^4 at 1125K and 3.76×10^3 at 1085K. Calculate the activation energy for the reaction.

Solution: Activation energy may be evaluated using the equation derived from Arrhenius equation,

$$\log k_2/k_1 = \frac{E_a}{2.303R} \times \frac{(T_2 - T_1)}{T_1 T_2}$$

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Where, k_1 and k_2 are the rate constants at temperatures T_1 and T_2 .

$$\log \frac{5.16 \times 10^4}{3.76 \times 10^3} = \frac{E_a}{2.303 \times 1.99} \times \frac{1125 \times 1085}{1125 \times 1085}$$

$$1.1374 = (E_a/4.583) \times (40/1220625)$$

$$E_a = 159.1 \text{ k.cal/mol}$$

Problem 7: A reaction has a rate constant, k , given by the equation:

$$k = 1.5 \times 10^{-9} \exp\left(\frac{2.526 \times 10^3}{T}\right)$$

Calculate the energy of activation.

Solution: Comparing,

$$k = 1.5 \times 10^{-9} \exp\left(\frac{2.526 \times 10^3}{T}\right)$$

$$\text{With } k = A \exp\left(\frac{-E_a}{RT}\right)$$

$$\text{gives } \frac{E_a}{R} = 2.526 \times 10^3$$

$$E_a = 2.526 \times 10^3 \times 8.314 = 21001 \text{ J mol}^{-1} = 21 \text{ kJ/mol}$$