

Solutions

Solution 1:

- a) $d\xi/dt = 0.001 \text{ mol} / 0.01 \text{ s} = 0.1 \text{ mol s}^{-1}$
b) $v = (1/V) d\xi/dt = 0.1 \text{ mol s}^{-1} / 0.25 \text{ L} = 0.4 \text{ mol L}^{-1} \text{ s}^{-1}$
c) $d[\text{H}_2] / dt = -0.4 \text{ mol L}^{-1} \text{ s}^{-1}$
 $d[\text{Br}_2] / dt = -0.4 \text{ mol L}^{-1} \text{ s}^{-1}$
 $d[\text{HBr}] / dt = 0.8 \text{ mol L}^{-1} \text{ s}^{-1}$

Solution 2:

The rate law is

$$v = k[A]^a \propto p^a = \{p_0(1-f)\}^a$$

where a is the reaction order, and f the fraction reacted (so that $1-f$ is the fraction remaining). Thus

$$\frac{v_1}{v_2} = \frac{\{p_0(1-f_1)\}^a}{\{p_0(1-f_2)\}^a} = \left(\frac{1-f_1}{1-f_2}\right)^a \quad \text{and} \quad a = \frac{\ln(v_1/v_2)}{\ln\left(\frac{1-f_1}{1-f_2}\right)} = \frac{\ln(9.71/7.67)}{\ln\left(\frac{1-0.100}{1-0.200}\right)} = \boxed{2.00}$$

Solution 3:

The half life in seconds will be

$$1600 \times 325.25 \times 24 \times 60 \times 60 = 5.049 \times 10^{10} \text{ s}$$

$$k = \frac{0.693}{t_{1/2}} = 1.37 \times 10^{-11} \text{ s}^{-1}$$

the number of nuclei present in 1 g of radium is

$$\frac{6.023 \times 10^{23} \text{ mol}^{-1}}{226 \text{ g/mol}} = 2.666 \times 10^{21} \text{ g}^{-1}$$

the number of disintegration, is therefore;

$$1.37 \times 10^{-11} \text{ s}^{-1} \times 2.67 \times 10^{21} \text{ g}^{-1} = 3.66 \times 10^{10} \text{ g}^{-1} \text{ s}^{-1}$$

Solution 4:

The rate constant is given by

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad [22.31]$$

so at 24 °C it is

$$1.70 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = A \exp\left(\frac{-E_a}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times [(24 + 273) \text{ K}]}\right)$$

and at 37 °C it is

$$2.01 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = A \exp\left(\frac{-E_a}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times [(37 + 273) \text{ K}]}\right)$$

Dividing the two rate constants yields

$$\frac{1.70 \times 10^{-2}}{2.01 \times 10^{-2}} = \exp\left[\left(\frac{-E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{297 \text{ K}} - \frac{1}{310 \text{ K}}\right)\right]$$

$$\text{so } \ln\left(\frac{1.70 \times 10^{-2}}{2.01 \times 10^{-2}}\right) = \left(\frac{-E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{297 \text{ K}} - \frac{1}{310 \text{ K}}\right)$$

$$\begin{aligned} \text{and } E_a &= -\left(\frac{1}{297 \text{ K}} - \frac{1}{310 \text{ K}}\right)^{-1} \ln\left(\frac{1.70 \times 10^{-2}}{2.01 \times 10^{-2}}\right) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= 9.9 \times 10^3 \text{ J mol}^{-1} = \boxed{9.9 \text{ kJ mol}^{-1}} \end{aligned}$$

With the activation energy in hand, the prefactor can be computed from either rate constant value

$$\begin{aligned} A &= k \exp\left(\frac{E_a}{RT}\right) = (1.70 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \times \exp\left(\frac{9.9 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (297 \text{ K})}\right) \\ &= \boxed{0.94 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}} \end{aligned}$$

Here solution method is same, but the values given in question paper are different. Please substitute those values and get answer.

Solution 5:

$$\frac{\ln 2}{t^{1/2}} = A \exp^{-E_a/RT}$$

$$T = 269.5 \text{ K}$$

Substitute half – life in sec and all other values and solve for T.

Solution 6:

Number of configurations of combined system $W = W_1 W_2$

$$W = 2 \times 1040$$

$$S = k \ln W ; S_1 = k \ln W_1 ; S_2 = k \ln W_2$$

$$S = k \ln(2 \times 1040) = 92.8k = \mathbf{1.282 \times 10^{-21} \text{ J K}^{-1}}$$

$$S_1 = k \ln(1020) = \mathbf{0.637 \times 10^{-21} \text{ J K}^{-1}}$$

$$S_2 = k \ln(2 \times 1020) = \mathbf{0.645 \times 10^{-21} \text{ J K}^{-1}}$$

Solution 7:

$$\frac{n_1}{n_0} = \frac{g_1 e^{-\epsilon_1/kT}}{g_0 e^{-\epsilon_0/kT}} = 3 e^{-hcB/kT}$$

$$\frac{n_1}{n_0} = 1/e \text{ and solve for T}$$

$$T = \mathbf{7.26 \text{ K}}$$

Solution 8:

a) The ratio of populations is given by the Boltzmann factor

$$\frac{n_2}{n_1} = \exp\left(\frac{-\Delta E}{kT}\right) = e^{-25K/T} \quad \text{and} \quad \frac{n_3}{n_1} = e^{-50K/T}$$

$$\text{At } 25 \text{ K} \quad \frac{n_2}{n_1} = 0.368 \text{ and } \frac{n_3}{n_1} = \mathbf{0.135}$$

b) The molecular partition function is

$$q = \sum e^{-E_{state}/kT} = 1 + e^{-25K/T} + e^{-50K/T}$$

$$\text{At } 25 \text{ K} \quad q = \mathbf{1.503}$$

c) The molar internal energy is

$$U_m = U_m(0) - \frac{N_A}{q} \left(\frac{\partial q}{\partial \beta} \right) \text{ where } \beta = (kT)^{-1}$$

At 25 K $U_m = U_m(0) = \mathbf{88.3 \text{ J mol}^{-1}}$

Solution 9:

The relative population of states is given by Boltzmann distribution

$$\frac{n_2}{n_1} = \exp\left(\frac{-\Delta E}{kT}\right) = \exp\left(\frac{-hc\tilde{\nu}}{kT}\right) \text{ and solve for T}$$

Having 15 % of the molecules in the upper level means

$$\frac{2n_2}{n_1} = \frac{0.15}{1 - 0.15}$$

Hence T = **213 K**