

Question

The decomposition of hydrocarbon follows the equation

$$k = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000 \text{ K}/T}$$

Calculate E_a .

Answer:

By Arrhenius equation rate constant k is related to activation energy (E_a) and temperature T as:

$$k = A e^{-E_a/RT}$$

Comparing with given equation

$$\frac{E_a}{R} = 28000$$

$$E_a = 28000R$$

$$= 28000 \times 8.314 = 232792 \text{ J mol}^{-1} = 232.792 \text{ kJ mol}^{-1}$$

Question:

The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

$$\log k = 14.34 - 1.25 \times 10^4 \frac{\text{K}}{T}$$

Calculate E_a for this reaction and at what temperature will its half-period be 256 minutes?

Answer:

$$i) \log k = \log A - \frac{E_a}{2.303RT}$$

Comparing with given equation

$$\frac{E_a}{2.303R} = 1.25 \times 10^4$$

$$E_a = 1.25 \times 10^4 \times 2.303R = 1.25 \times 10^4 \times 2.303 \times 8.314$$

$$= 239235.25 \text{ J mol}^{-1}$$

$$= 239.235 \text{ kJ mol}^{-1}$$

(ii) For first order reaction

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

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{256} = 2.7 \times 10^{-3} \text{ min}^{-1}$$

$$= 2.7 \times 10^{-3} (60\text{s})^{-1}$$

$$= 4.5 \times 10^{-5} \text{ s}^{-1}$$

Put this value of k in equation given in question

$$\log k = 14.34 - \frac{1.25 \times 10^4}{T}$$

$$\log (4.5 \times 10^{-5}) = 14.34 - \frac{1.25 \times 10^4}{T}$$

$$\log (9 \times 5 \times 10^{-6}) = 14.34 - \frac{1.25 \times 10^4}{T}$$

$$\log (3^2 \times 5 \times 10^{-6}) = 14.34 - \frac{1.25 \times 10^4}{T}$$

$$= \log 3^2 + \log 5 + \log 10^{-6} = 14.34 - \frac{1.25 \times 10^4}{T}$$

$$= 2 \times 0.48 + 0.7 + (-6) = 14.34 - \frac{1.25 \times 10^4}{T}$$

$$-4.34 = 14.34 - \frac{1.25 \times 10^4}{T}$$

$$-18.68 = -\frac{1.25 \times 10^4}{T}$$

$$T = \frac{1.25 \times 10^4}{18.68} = 669.16 \text{ K}$$

Question

The decomposition of A into product has value of k as $4.5 \times 10^3 \text{ s}^{-1}$ at 10°C and energy of activation 60 kJ mol^{-1} .

At what temperature would k be $1.5 \times 10^4 \text{ s}^{-1}$?

Answer:

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Answer:

$$\log \frac{k_1}{k_2} = \frac{E_a}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\log \frac{4.5 \times 10^3}{1.5 \times 10^4} = \frac{60 \times 1000}{2.303(8.314)} \left(\frac{1}{T_2} - \frac{1}{283} \right)$$

$$\log \frac{3}{10} = 3133.63 \left(\frac{1}{T_2} - \frac{1}{283} \right)$$

$$\log 3 - \log 10 = 3133.63 \left(\frac{1}{T_2} - \frac{1}{283} \right)$$

$$0.48 - 1 = 3133.63 \left(\frac{1}{T_2} - \frac{1}{283} \right)$$

$$T_2 = 297K$$

Question

The time required for 10% completion of a first order reaction at 298K is equal to that required for its 25% completion at 308K. If the value of A is $4 \times 10^{10} \text{ s}^{-1}$.

Calculate E_a .

Answer:

For first order reaction

$$k = \frac{2.303}{t} \log \frac{a_0}{a_t}$$

At 298K

When reaction is 10% complete, 90% reactants remain.

$$a_t = \frac{90}{100} a_0, \quad \frac{a_0}{a_t} = \frac{10}{9}$$

$$k_{298} = \frac{2.303}{t_{90\%}} \log \frac{10}{9}$$

$$t_{90\%} = \frac{2.303}{k_{298}} \log \frac{10}{9} - I$$

At 308K

When reaction is 25% complete, 75% reactants remain.

$$\text{i.e. } a_t = \frac{75}{100} a_0, \quad \frac{a_0}{a_t} = \frac{4}{3}$$

$$k_{308} = \frac{2.303}{t_{75\%}} \log \frac{4}{3}$$

$$t_{75\%} = \frac{2.303}{k_{308}} \log \frac{4}{3} \quad \text{--- II}$$

Equate I and II

$$\frac{2.303}{k_{298}} \log \frac{10}{9} = \frac{2.303}{k_{308}} \log \frac{4}{3}$$

$$\frac{k_{308}}{k_{298}} = \frac{\log \frac{4}{3}}{\log \frac{10}{9}}$$

$$= \frac{\log 4 - \log 3}{\log 10 - \log 9}$$

$$= \frac{0.6 - 0.48}{1 - 0.96}$$

$$= 3$$

$$\log \frac{k_{308}}{k_{298}} = \log 3$$

$$\frac{E_a}{2.303R} \left(\frac{1}{298} - \frac{1}{308} \right) = 0.48$$

$$E_a = 84355.3 \text{ J mol}^{-1}$$

$$= 84.36 \text{ kJ mol}^{-1}$$

Question

The rate of a reaction quadruples when the temperature changes from 293K to 313K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

Answer:

$$\log \frac{k_1}{k_2} = \frac{E_a}{2-303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\log \frac{k_1}{4k_1} = \frac{E_a}{2-303 \times 8-314} \left(\frac{1}{312} - \frac{1}{293} \right)$$

$$\log \frac{1}{4} = E_a (-1.14 \times 10^{-5})$$

$$-\log 4 = E_a (-1.14 \times 10^{-5})$$

$$-\log 2^2 = E_a (-1.14 \times 10^{-5})$$

$$-2 \log 2 = E_a (-1.14 \times 10^{-5})$$

$$-2(0.3) = E_a (-1.14 \times 10^{-5})$$

$$-0.6 = E_a (-1.14 \times 10^{-5})$$

$$E_a = 5.26 \times 10^4 \text{ J mol}^{-1} = 52.6 \text{ kJ mol}^{-1}$$