Question

The rate constants of a reaction at 500K and 700K are $0.02\,s^{-1}$ and $0.07\,s^{-1}$ respectively. Calculate the values of E_a and A.

Answer:

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

$$\log\left(\frac{0.02}{0.07}\right) = \frac{E_a}{2.303 \times 8.314}\left(\frac{1}{700} - \frac{1}{500}\right)$$

$$\log \frac{2}{7} = -2.985 \times 10^{-5} E_a$$

$$\log 2 - \log 7 = -2.985 \times 10^{-5} E_a$$

$$0.3 - 0.85 = -2.985 \times 10^{-5} E_a$$

$$E_a = 1.84 \times 10^{4}\ J\,mol^{-1} = 18.4\ kJ\,mol^{-1}$$

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

$$\log(0.02) = \log A - \frac{1.84 \times 10^{4}}{2.303 \times 8.314 \times 500}$$

$$\log 2 - \log 100 = \log A - 1.92$$

$$0.3 - 2 = \log A - 1.92$$

$$\log A = 0.22$$

$$A = \text{antilog}(0.22) = 1.66\,s^{-1}$$

Question

The first order rate constant for the decomposition of ethyl iodide at 600K is 1.60×10^{-5} s^{-1}. Its energy of activation is 209 $kJ\,mol^{-1}$. Calculate the rate constant of the reaction at 700K.

$$C_2H_5I(g) \rightarrow C_2H_4(g) + HI(g)$$

Answer

$$\log \frac{K_1}{K_2} = \frac{E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\log\left(\frac{1.6 \times 10^{-5}}{K_2}\right) = \frac{209 \times 1000}{2.303 \times 8.314}\left(\frac{1}{700} - \frac{1}{600}\right)$$

$$\log\left(\frac{1.6 \times 10^{-5}}{K_2}\right) = -2.6$$

$$= -2 - 0.6$$

$$= -\log 100 - \log 4$$

$$= \log \frac{1}{100} + \log \frac{1}{4}$$

$$= \log \frac{1}{400}$$

$$\frac{1.6 \times 10^{-5}}{K_2} = \frac{1}{400}$$

$$K_2 = 6.4 \times 10^{-3}\ s^{-1}$$

Question

What is the effect of temperature on the rate constant of a reaction? How can this effect of temperature on rate constant be represented quantitatively?

Answer:

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

$$K = Ae^{-E_a/RT}$$

Here $e^{-E_a/RT}$ represents the fraction of molecules having energy greater than activation energy. For every 10° rise in temperature value of $e^{-E_a/RT}$ is approximately doubled ie the fraction of molecules having energy greater than activation energy are doubled. Thus for a chemical reaction the rate constant is nearly doubled with 10° rise in temperature.

ii) Take natural log on both sides of Arrhenius equation

$$\ln k = \ln Ae^{-E_a/RT} = \ln A + \ln e^{-E_a/RT} = \ln A - \frac{E_a}{RT}$$

Let k_1 be rate constant at temperature T_1 and k_2 be rate constant at temperature T_2

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \qquad \ln k_2 = \ln A - \frac{E_a}{RT_2}$$

$$\ln k_1 - \ln k_2 = \left(\ln A - \frac{E_a}{RT_1}\right) - \left(\ln A - \frac{E_a}{RT_2}\right)$$

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

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

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

Question

The rate of the chemical reaction doubles for an increase of 10K in absolute temperature from 298K. Calculate E_a.

Answer:

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

$$\log\frac{k_1}{2k_1} = \frac{E_a}{2.303 \times 8.314}\left(\frac{1}{308} - \frac{1}{298}\right)$$

$$\log \frac{1}{2} = E_a(-5.69 \times 10^{-6})$$

$$-\log 2 = -5.69 \times 10^{-6} E_a$$

$$-0.3 = -5.69 \times 10^{-6} E_a$$

$$E_a = 5.27 \times 10^{4} \text{ J mol}^{-1} = 52.7 \text{ kJ mol}^{-1}$$

Question

The activation energy for the reaction

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

is 209.5 kJ mol^{-1} at 581 K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

Answer:

The fraction of molecules having energy greater than activation energy $= e^{-E_a/RT} = e^{-209.5 \times 1000/(8.314 \times 581)}$

$$= e^{-43.37}$$

$$= 1.46 \times 10^{-19}$$

Question

The rate constant for the decomposition of hydrocarbons is 2.418×10^{-5} s^{-1} at 546 K. If the energy of activation is 179.9 kJ mol^{-1}, what will be the value of pre-exponential factor.

Answer:

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

$$\log 2.418 \times 10^{-5} = \log A - \frac{179.9 \times 1000}{2.303 \times 8.314 \times 546}$$

$$\log A - \log 2.418 \times 10^{-5} = 17.2$$

$$\log \frac{A}{2.418 \times 10^{-5}} = 17.2$$

$$\frac{A}{2.418 \times 10^{-5}} = \text{antilog}(17.2)$$

$$= 1.58 \times 10^{17}$$

$$A = 3.83 \times 10^{12}\ s^{-1}$$