

### Question

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

Answer:

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

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

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

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

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

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

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

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

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

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

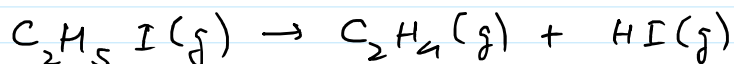
$$\log A = 0.22$$

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

### Question

The first order rate constant for the decomposition of

ethyl iodide at 600K is  $1.60 \times 10^{-5} \text{ s}^{-1}$ . Its energy of activation is  $209 \text{ kJ mol}^{-1}$ . Calculate the rate constant of the reaction at 700K.



Answer

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

$$\log \left( \frac{1.6 \times 10^{-5}}{k_2} \right) = \frac{209 \times 1000}{2.303 \times 8.314} \left( \frac{1}{700} - \frac{1}{600} \right)$$

$$\log \left( \frac{1.6 \times 10^{-5}}{k_2} \right) = -2.6$$

$$= -2 - 0.6$$

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

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

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

$$\frac{1.6 \times 10^{-5}}{k_2} = \frac{1}{400}$$

$$k_2 = 6.4 \times 10^{-3} \text{ s}^{-1}$$

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:

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

Here  $e^{-E_a/RT}$  represents the fraction of molecules having

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

ii) Take natural log on both sides of Arrhenius equation

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

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

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

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

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

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

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

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

Question

The rate of the chemical reaction doubles for an increase of  $10\text{K}$  in absolute temperature from  $298\text{K}$ .

Calculate  $E_a$ .

Answer:

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

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

..

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

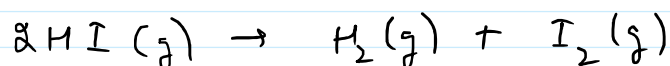
$$-\log 2 = -5.69 \times 10^{-6} E_a$$

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

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

Question

The activation energy for the reaction



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

Answer:

$$\begin{aligned} \text{The fraction of molecules having energy greater than} \\ \text{activation energy} &= e^{-E_a/RT} = e^{-209.5 \times 1000 / (8.314 \times 581)} \\ &= e^{-43.37} \\ &= 1.46 \times 10^{-19} \end{aligned}$$

Question

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

Answer:

$$\begin{aligned} \log k &= \log A - \frac{E_a}{2.303 RT} \\ \log 2.418 \times 10^{-5} &= \log A - \frac{179.9 \times 1000}{2.303 \times 8.314 \times 546} \end{aligned}$$

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

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

$$\frac{A}{2.418 \times 10^{-5}} = \text{antilog}(17.5)$$
$$= 1.58 \times 10^{17}$$

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