Sapna Gupta

Kinetics (7) - Activation Energy (1)

(1) Rate constant for 1^{st} order decomposition of a reaction $A \rightarrow B$ are $k = 4.75 \times 10^{-4}$/s at 293 K and $k = 1.63 \times 10^{-3}$/s at 303 K. What is the activation energy of the reaction?

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$\boxed{T = K}$

Ans

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

$$\ln \frac{1.63 \times 10^{-3}/\cancel{s}}{4.75 \times 10^{-4}/\cancel{s}} = \frac{E_a}{\frac{8.3145}{1000} \text{ J/mol}\cancel{K}}\left(\frac{1}{293} - \frac{1}{303}\right)\cancel{K}$$

$$1.233 = E_a \times (120.3) \times (1.13 \times 10^{-4})$$

$$\rightarrow E_a = \frac{1.233}{120.3 \times 1.13 \times 10^{-4}} = \boxed{91 \text{ kJ/mol}}$$

(2) Decomposition of DTBP is 1^{st} order with half life of 320 mins at 135°C and 100 mins at 145°C. Calculate the activation energy for this reaction: $k = ?$

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

Ans

$$k_1 = \frac{0.693}{320 \text{ mins}} = 2.17 \times 10^{-3}/\text{min} \qquad k_2 = \frac{0.693}{100 \text{ mins}} = 6.93 \times 10^{-3}/\text{min}$$

$$T_1 = 135 + 273 = 408 \text{ K}, \quad T_2 = 145 + 273 = 418 \text{ K}$$

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

$$\ln \frac{6.93 \times 10^{-3}/\text{min}}{2.17 \times 10^{-3}/\text{min}} = \frac{E_a}{\frac{8.314}{1000} \text{ J/mol}\cancel{K}}\left[\frac{1}{408} - \frac{1}{418}\right]\cancel{K}$$

$$1.16 = E_a \times 120.3 \text{ mol/kJ} \times 5.86 \times 10^{-5}$$

$$\boxed{E_a = 165 \text{ kJ/mol}}$$