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Ex-36 The rate constant of forward reaction of a reaction increases by 6% when the temperature of the reaction is increased from 300 to 301 K, whereas equilibrium constant increases by 2%. Calculate the activation energy for the forward as well as backward reaction.

Sol. According to Arrhenius equation, $\log \frac{k_2}{k_1} = \frac{E_{act}}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$

If $k_1 = k$ at 300 K then at 301 K, $k_2 = k + k \frac{6}{100} = 1.06 k$

$$\therefore \log_{10} \frac{1.06 k}{k} = \frac{E_{act}}{2.303 \times 8.314} \left[\frac{301 - 300}{300 \times 301} \right]$$

$$\therefore E_{act} = \log(1.06) \cdot 2.303 \cdot 8314 \cdot 300 \cdot 301 = 43753 \text{ J/mol}$$

According to Van't Hoff equation, $\log \frac{k_2}{k_1} = \frac{\Delta H^\circ}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$

$$\text{If } k_1 = k \text{ at } 300 \text{ K, } k_2 = k + \frac{2}{100} k = 1.02 k$$

$$\log_{10} \frac{1.02K}{K} = \frac{\Delta H^\circ}{2.303 \times 8.314} \left(\frac{301 - 300}{300 \times 301} \right)$$

$$\begin{aligned} \therefore \Delta H &= (\log 1.02) 2.303 \times 8.314 \times 300 \times 301 \text{ J/mol} \\ &= 14869 \text{ J mol}^{-1} = 14.87 \text{ kJ/mol} \end{aligned}$$

Thus, reaction is endothermic.

For such a reaction, $\Delta H = E_{as} - E_{ab}$

$$\begin{aligned} \therefore E_{ab} &= E_{as} - \Delta H = 43.753 - 14.87 \text{ kJ/mol} \\ &= 28.883 \text{ kJ mol}^{-1} \end{aligned}$$

Ex. 37 Value of rate constant for a first order reaction at 500K is $1.60 \times 10^{-5} \text{ second}^{-1}$, whereas at 600K, it is

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

$$\log 1.60 \times 10^{-5} - \log 6.36 \times 10^{-3} = \frac{-E_a}{2.303 \times 8.314} \left[\frac{1}{500} - \frac{1}{600} \right]$$

$$5.241 - 3.8035 = \frac{E_a}{19.15} \cdot \frac{1}{3000}$$

$$E_a = 1.49 \times 10^5 \quad E_a = 2.5999 \times 19.15 \times 3000$$

Ex. 38.

An exothermic reaction, $X \rightarrow Y$, has an activation energy 30 kJ mol^{-1} . If energy change (ΔE) during

the reaction is -20 kJ , then the activation energy for the reverse reaction is

Soln

[A] -30 kJ [B] 20 kJ [C] 50 kJ [D] 10 kJ

$$\Delta E = E_{a(f)} - E_{a(r)} ; -20 = 30 - E ;$$

$$E_{a(r)} = 50 \text{ kJ [A] [C]}$$

Ex.39 An endothermic reaction, $A \rightarrow B$, has an activation energy of $x \text{ kJ mol}^{-1}$ of A. If energy change of the reaction is $y \text{ kJ}$, the activation energy of reverse reaction is

[A] x [B] $x-y$ [C] $x+y$ [D] $y-x$

Soln

$$\Delta E = E_{a(f)} - E_{a(r)} ; y = x - E_{a(r)} ; E_{a(r)} = x - y$$

Ex.40 Which of the following relations is correct?

[A] $k = A e^{E_a/RT}$ [B] $\ln k - \ln A = \frac{E_a}{RT}$ [C] $\ln A - \ln k = \frac{E_a}{RT}$

[D] $\ln A - \ln k = -\frac{E_a}{RT}$

Soln

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

$$\ln k = \ln A - \frac{E_a}{RT} \quad \text{or} \quad \ln A - \ln k = \frac{E_a}{RT}$$

Ex. 41 Which of the following expression give the effect of temperature on the rate constant?

[A] $\ln A = RT \ln E_a - \ln k$ [B] $\ln k = \ln A - E_a/RT$

[C] $k = A E_a/RT$ [D] None of these

Solⁿ

The effect of temperature on rate constant is quantitatively given by Arrhenius equation

$$k = A e^{-E_a/RT} \text{ or } \ln k = \ln A - E_a/RT$$

Ex. 42

The plot of $\log k$ vs $\frac{1}{T}$ helps to calculate

[A] Energy of activation [B] Rate of constant of the reaction.

[C] Order of the reaction [D] Energy of activations as well as the frequency factor.

Solⁿ

According to Arrhenius equation: $\log k = \log A -$

Plot of $\log k$ vs. $\frac{1}{T}$ is straight line $\frac{E_a}{2.303} \cdot \frac{1}{T}$

$$\text{Slope} = - \frac{E_a}{2.303 R}$$

$$\text{Intercept} = \log A$$

