OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
CHM 305 - Chemical Kinetics
Harmattan Semester Test 2023/2024 Session

Time Allowed: 30 mins

(Given: R = 8.314 $J.K^{-1}.mol^{-1}$, k_b = 1.3805 × 10^{-23} $J.K^{-1}$, h = 6.626 × 10^{-34} J.s)

Name…………………………………………………………………………………….

Dept:…………………………………………… Reg. No:………………………………..

1. (a) A first order reaction has an activation energy (E_a) of 120 kJ/mole and a pre-exponential factor (A) of 6 x 10^{12} s^{-1}. At what temperature will the reaction have a half-life ($t_{1/2}$) of 30 days?
   (b) Explain the following:
   i. the larger the decrease in entropy, smaller will be the value of Arrhenius factor.
   ii. The steric factor involved in collision theory may be interpreted in terms of $\Delta S^{\neq}$

2. Assuming $q_t = 10^8, q_r = 10,\ q_v = 1\ and\ \frac{k_bT}{h} = 10^{13}$, determine the expression for the value of rate constant for $A + B \rightarrow X^{\neq}$ in litres $mole^{-1}$ sec^{-1} if A and B are atoms.

CHM 305 Test Marking Scheme 2024

1 (a) Arrhenius Equation: $k = Ae^{\frac{-E_a}{RT}}$

First order kinetics: $k = \frac{ln2}{t_{\frac{1}{2}}}$

$t_{1/2} = 30\ days = (30 \times 24 \times 60 \times 60)s$

$= 2.592 \times 10^6$ s

$\therefore\ k = \frac{0.693}{2.592 \times 10^6} = 2.674 \times 10^{-7} s^{-1}$

Hence, from Arrhenius equation,

$2.674 \times 10^{-7} s^{-1} = 6.0\ \times 10^{12}\ s^{-1} \times e^{-120{,}000/8.314T}$

$e^{-14433.49/T} = \frac{2.674 \times 10^{-7} s^{-1}}{6.0\ \times 10^{12}\ s^{-1}} = 4.45 \times 10^{-20}$

Taking the natural log of both sides,

$$\frac{-14433.49}{T} = \ln(4.45 \times 10^{-20})$$

$T = \frac{14433.9}{29.858} = 483.4K$

(b) (i) From the TST expression,

$A = e^{(1-\Delta n)}\ \frac{k_bT}{h}\ e^{\Delta S^{\neq}/R}$

therefore $A \alpha \ell^{\frac{\Delta S^{\neq}}{R}}$

The larger the decrease in entropy, the more $\Delta S^{\neq}$ tends to –ve value. Hence, the smaller A value becomes

(ii) Comparing Arrhenius equation with Collision Theory and Transition State Theory:

$k = Ae^{\frac{-E_a}{RT}}$ (Arrhenius Equation)……..(1)

$k = PZe^{\frac{-E_a}{RT}}$ (Collision Theory)…….(2)

$k = e^{-(\Delta n-1)}\ \frac{k_bT}{h}\ e^{\Delta S^{\neq}/R}\ .e^{\frac{-E_a}{RT}}$ (TST)…….(3)

Comparing these theories, we have

$$A = PZ = e^{(1-\Delta n)}\ \frac{k_bT}{h}\ e^{\Delta S^{\neq}/R}$$

Where P = steric factor

2. For reaction $A + B \rightarrow X^{\neq}$

Since A and B are atoms, $X^{\neq}$ is a linear molecule.

Hence, $Q_A = q_t^3;\quad Q_B = q_t^3;$

$Q^{\neq} = q_t^3 q_r^2 q_v$

$$k = \frac{k_b T}{h} . \frac{Q^{\neq}}{Q_A Q_B} . e^{-E_a/RT}$$

$$k = 10^{13} . \frac{q_t^3 q_r^2 q_v}{q_t^3 q_t^3} . e^{-E_a/RT}$$

$$k = 10^{13} . \frac{(10^8)^3 (10)^2 .1}{(10^8)^3 .(10^8)^3} . e^{-E_a/RT}$$

(cm^3 $molecule^{-1}$ s^{-1})

$$k = \frac{10^{15}}{10^{24}} . e^{-E_a/RT}$$

$$= 10^{-9} e^{-E_a/RT} \quad \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

To convert the units to dm^3 $mol^{-1}s^{-1}$, we multiply the value by N_A and 10^{-3}

$$k = (10^{-9} \times 10^{-3} \times 6.023 \times 10^{23}) e^{-E_a/RT}$$

$$= 6.023 \times 10^{11} e^{-E_a/RT} \quad \text{Liters mole}^{-1}$$
sec^{-1}