Exp. 8

Aim: To determine the activation energy of reaction between potassium permanganate ($KMnO_4$) and Oxalic acid.

Apparatus Required: Burettes, test tubes, conical flasks, hot water bath, stopwatch, other general glasswares.

Chemicals Required: Oxalic acid (0.5M), $KMnO_4$ (0.02M)

Principle: In any chemical reaction, bonds are broken and new bonds are formed.

According to Collision Model, reactants react upon collision between each other. and the orientation and energy during the collision are crucial in the bond breaking and formation.

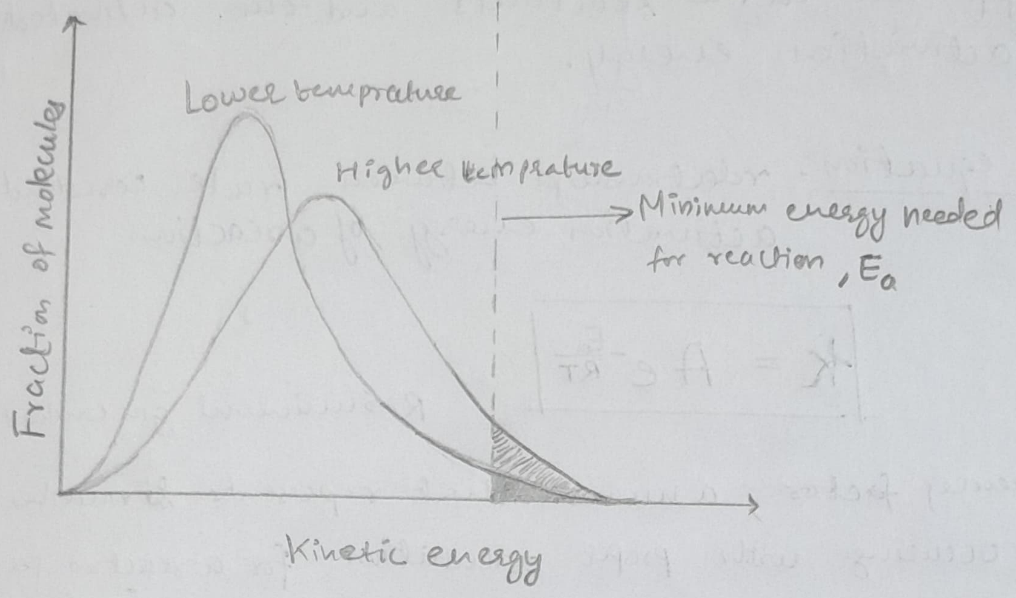
Activation Energy is characterized by that energy which the reactants need to overcome in order to form the products in a chemical reaction. It is denoted by E_a. It means that a reaction cannot occur if energy of incoming reactants is not sufficient to overcome the activation energy barrier. Activation energy can also be said as minimum energy needed for reaction to occur.

Maxwell - Boltzmann Distribution -

- The average K.E. of the reactants in gaseous / liquid state is related to the temprature.
- As the temperature increases, broadening of distribution increases i.e. at higher temprature, ~~molecules~~ fraction of molecules having higher energy ~~[illegible]~~ is high.
- Now, as the fraction of molecules having higher energy increases at high temprature, fraction of molecules that can overcome the E_a (activation energy) barrier is higher at higher temperature, so the product formation increases.

• The distribution of K.E. of reactants as given by Maxwell-Boltzmann distribution is as follow:

$$f(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_BT}} dV$$

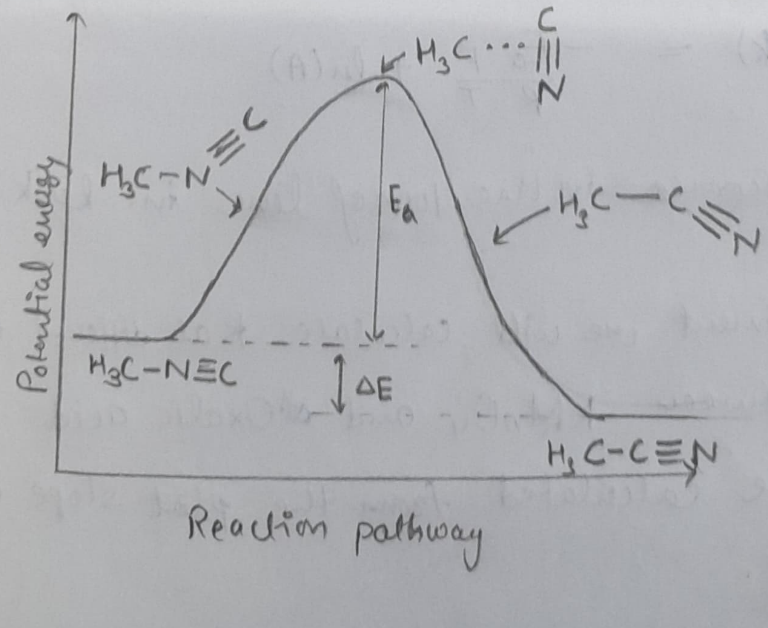


$k_B \rightarrow$ Boltzmann constant , $T \rightarrow$ Temprature , $v \rightarrow$ avg. molecular speed

$m \rightarrow$ mass of a molecule

Reaction Coordinate: where the reaction is in its pathway or progress of the reaction along pathway is known as reaction coordinate

eg. Reaction coordinate for the rearrangement of Methyl Isonitrile to molecule is – (here reaction coordinate is given by angle between CH_3 & $C \equiv N$)



- The highest point on the diagram is known as the transition state and the structure is called as the activated complex.

- Energy gap between the reactants and the activated complex is the activation energy.

Arrhenius equation: relationship between rate constant and activation energy of a reaction.

$$\boxed{k = A e^{-\frac{E_a}{RT}}}$$

R → universal gas constant

A → frequency factor, a number that represents ~~to~~ number of collisions occuring with proper orientation for a reaction per unit time.

Here by, we can understand that
if Activation energy is high, reaction will be slower, rate constant will be very low.

Here also, we can understand that Temprature ↑ Rxn rate ↑, temperature increment doesn't changes E_a.

Taking natural logarithm of both sides of Arrhenius equation, we get

$$\ln(k) = -\frac{E_a}{R}\frac{1}{T} + \ln(A)$$

→ the equation becomes in the form of line in $\ln(k)$ vs $\frac{1}{T}$

So in the experiment we will calculate k at different temperatures for reaction between $KMnO_4$ and Oxalic acid and then Ea can be calculated from the ~~plot~~ slope of plot of $\ln(k)$ vs $\frac{1}{T}$.

In the reaction MnO_4^- (permanganate ion) reduces to MnO_2 ~~and is~~ by reducing agent Oxalic acid and is detectable by the change in color from bright purple / pink to yellow-brown. We will find the rate constant for this reaction at 5 different temperatures to determine activation energy for the reaction,

Reactions:

$MnO_4^- \rightarrow MnO_2$ & Oxalic Acid $\rightarrow CO_2$

Procedure:

1) Using burettes, take 20ml oxalic acid (0.5M) in a conical flask and 10ml $KMnO_4$ (approx. 0.02M) in a test tube.

2) Immerse both conical flask and test tube in a water bath to equilibrate for at least 5 minutes

3) Mix the reactants in the conical flask and immediately start a stopwatch & do not remove flask from water bath.

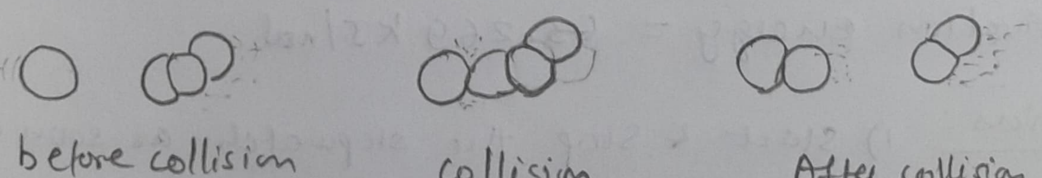
4) Swirl the mixture regularly without removing it from the water bath

5) Stop the ~~time~~ stopwatch as colour of mixture turns from purple / pink to yellow-brown (indication of reduction of MnO_4^- to MnO_2). Note the time.

6) Repeat the procedure at same and different temperatures.

7) Determine the activation energy by plotting $\ln(k)$ vs $\frac{1}{T}$ (T in K)

Collision model:



Observations and Calculations :

$[KMnO_4] = 0.02M$ [Oxalic Acid] = 0.5 M

Rate = k $[KMnO_4]$ [Oxalic Acid] = $\Delta[KMnO_4]$/time

S No.	Temp (°C)	Temp (K)	1/T (K^{-1})	Time for Trial 1 (s)	Time for Trial 2 (s)	Average time (s)	Rate = $[KMnO_4]$/time	k = Rate/$[KMnO_4]$ [Oxalic]	ln(k)
1	0	273	36.6×10^{-4}	2160	2160	2160	0.93×10^{-5}	0.93×10^{-3}	-6.980
2	28	301	33.22×10^{-4}	204	207	205.5	0.97×10^{-4}	0.97×10^{-2}	-4.63
3	40	313	31.95×10^{-4}	65	68	66.5	3×10^{-4}	3×10^{-2}	-3.50
4	50	323	30.96×10^{-4}	24	26	25	8×10^{-4}	8×10^{-2}	-2.52
5	60	333	30.03×10^{-4}	15	14	14.5	13.8×10^{-4}	13.8×10^{-2}	-1.98

$$\ln(k) = -\frac{E_a}{RT} + \ln(A)$$

From graph, (on next page)

$$\text{Slope} = -E_a/R = \frac{-(6.98 - 1.98) \times 10^4}{36.6 - 30.03} = 0.7610 \times 10^4$$

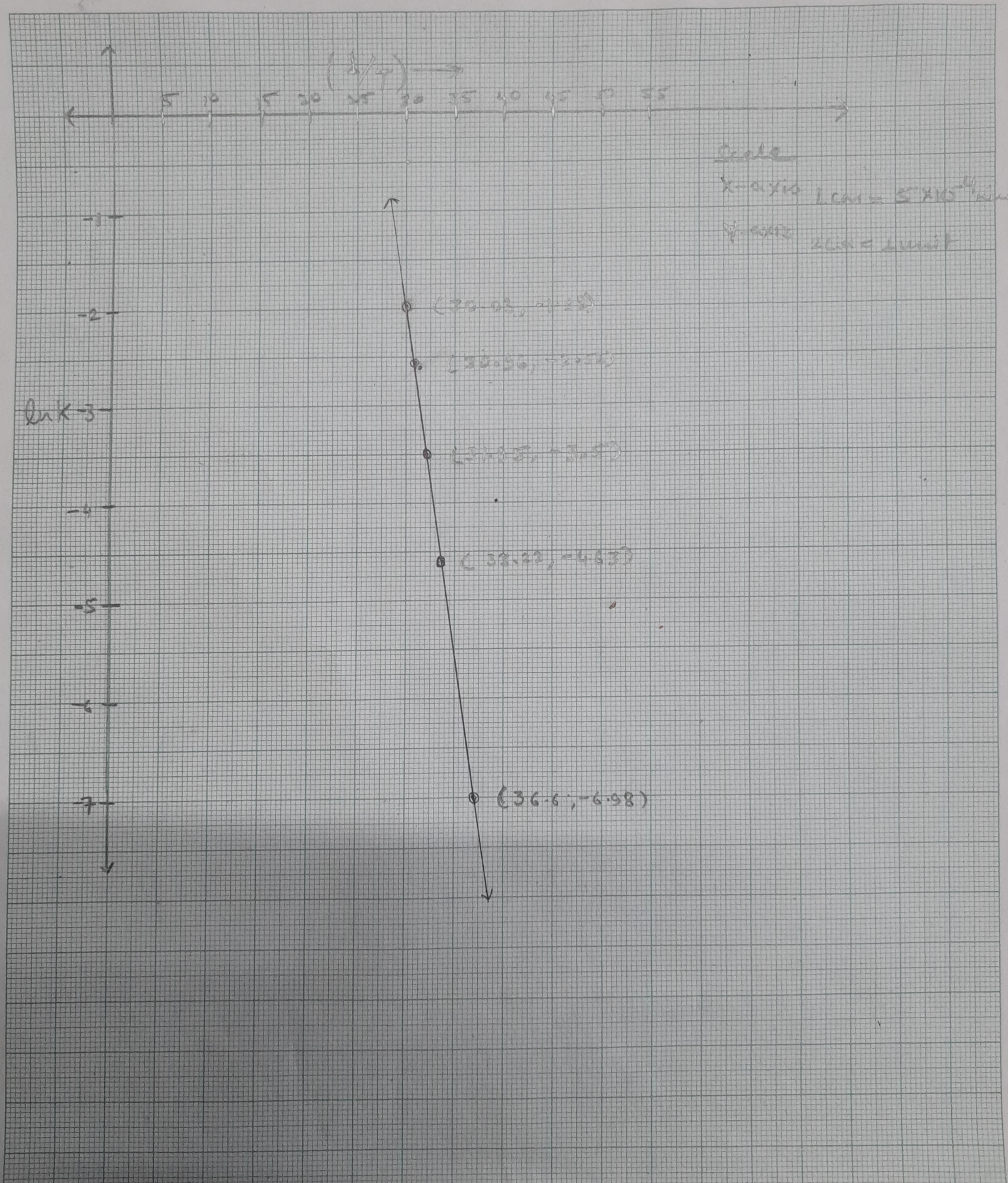
$$E_a = 0.7610 \times 10^4 \times 8.314 = 63269 \text{ J/mol} = 63.269 \text{ kJ/mol}$$

Results: 1) Rate of reduction of MnO_4^- to MnO_2 was monitored at different temperatures to determine the Activation Energy for the reaction.

2) Activation energy = 63.269 kJ/mol

Precautions: 1) Start & Stop the stopwatch as soon as you add $KMnO_4$ and as you see yellow-brown colouration respectively

2) Keep stirring the conical flask at a constant rate to ensure reaction proceeds evenly



(1/T)
5 10 15 20 25 30 35 40 45 50 55
ln K
-1 -2 -3 -4 -5 -6 -7
(32.22, -4.63)
(36.6, -6.98)
Scale
X-axis 1cm = 5×10^-4 unit
Y-axis 2cm = 1 unit