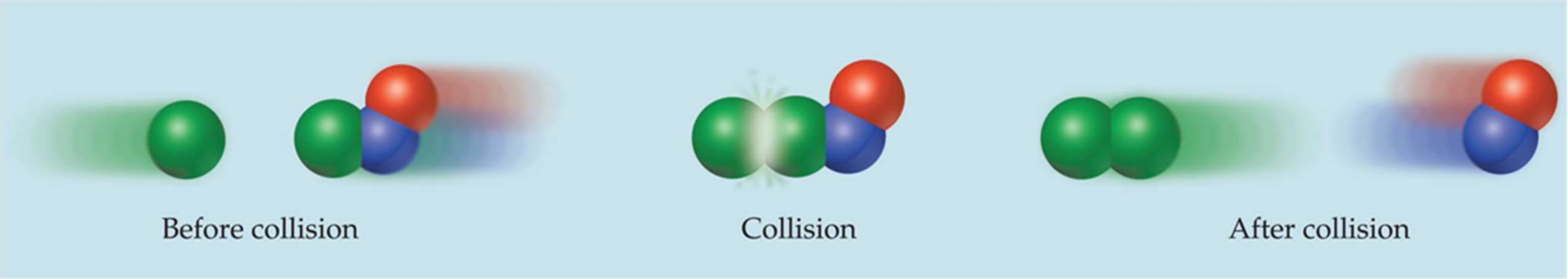
Activation Energy of a Reaction

The Collision Model

- In a chemical reaction, bonds are broken, and new bonds are formed
- Reactant molecules react upon collision between each other
- The orientation and energy during the collision are decisive in the bond breaking and formation

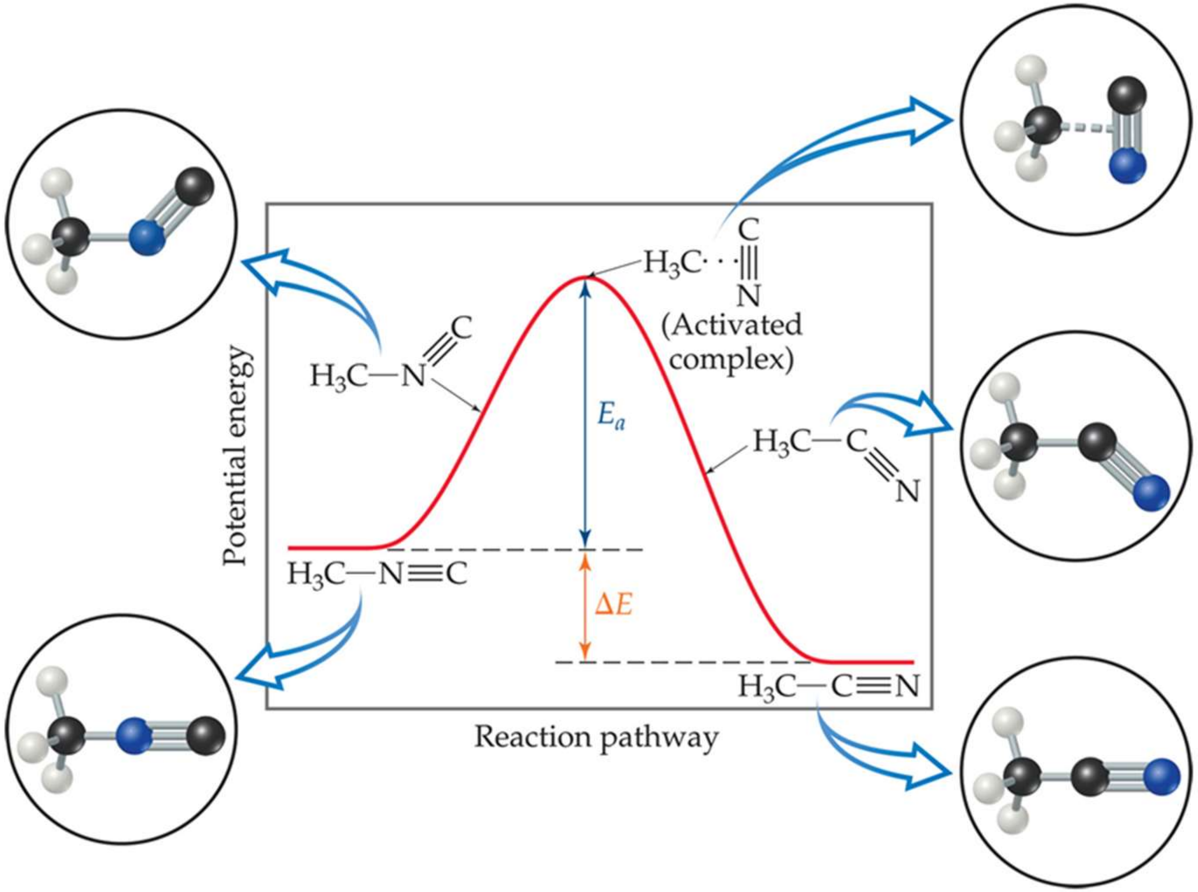


Activation Energy

- Every chemical reaction is characterized by an energy that the reactants need to overcome in order to form the products, known as activation energy, E_a
- A reaction cannot occur unless the reactant molecules possess sufficient energy to overcome the activation energy barrier

Reaction Coordinate

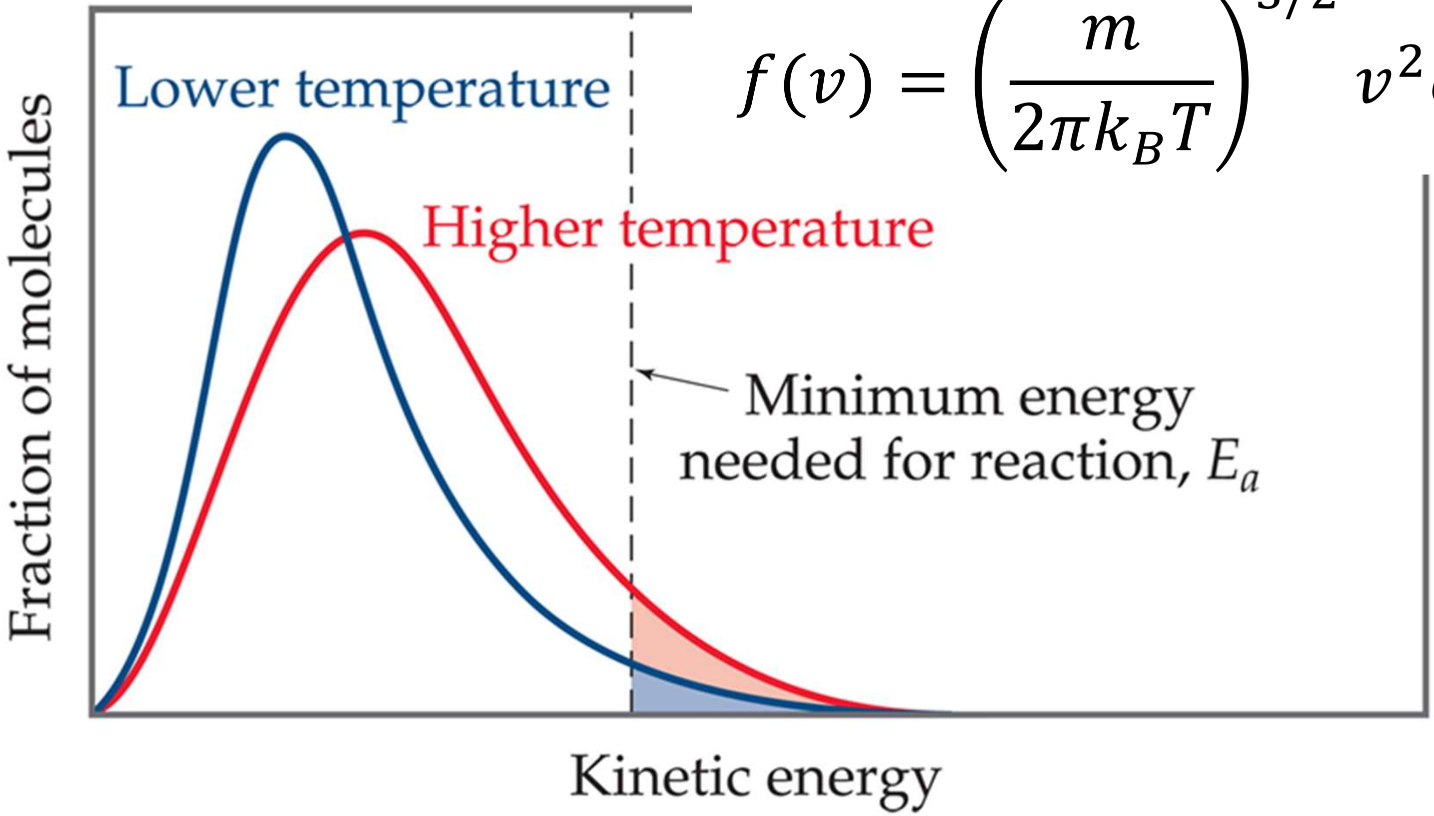
The reaction coordinate for the rearrangement of Methyl Isonitrile molecule is shown below.



- The highest point on the diagram is known as the transition state and the structure is called as the activated complex
- The energy gap between the reactants and the activated complex is the activation energy

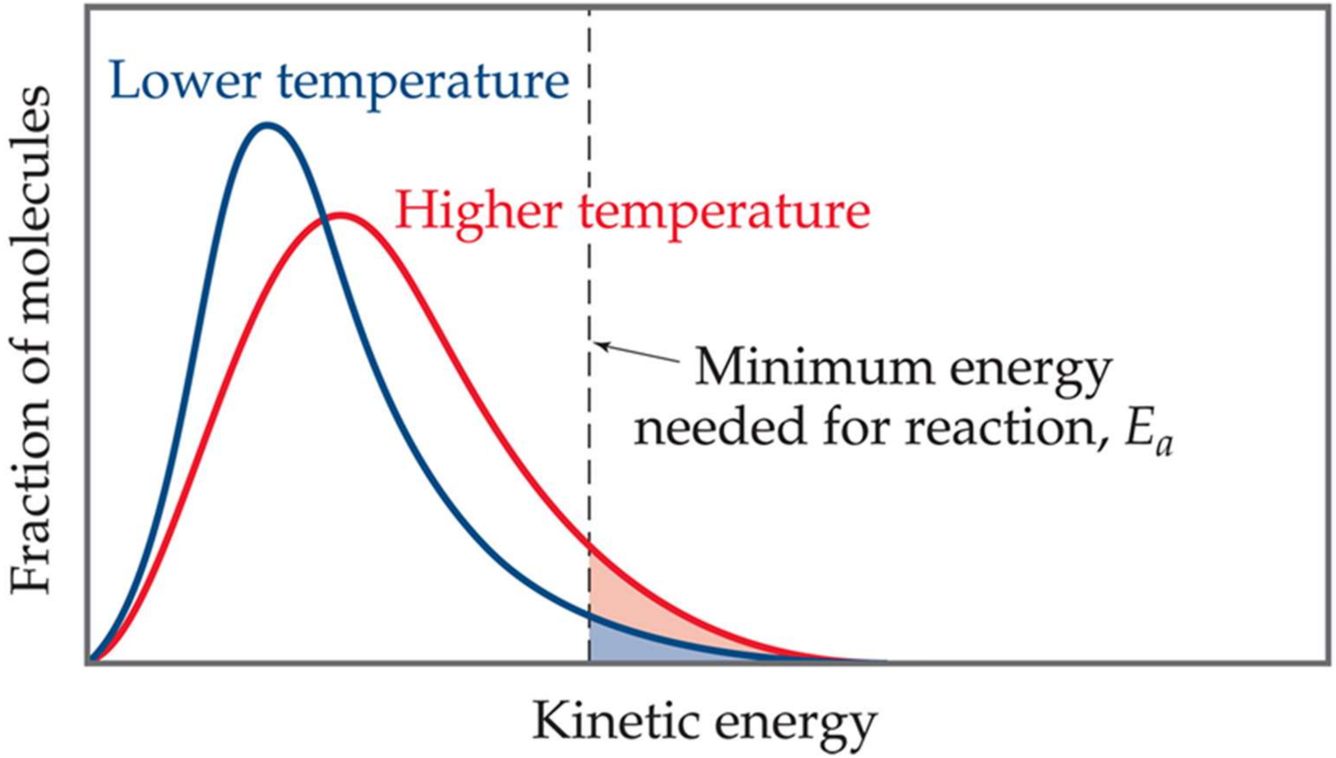
Maxwell–Boltzmann Distributions

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



- The average kinetic energy of the reactants in gaseous/liquid state is related to the temperature
- The distribution of kinetic energies of reactants are given by Maxwell–Boltzmann Distributions
- As the temperature increases, the broadening of the distribution increases. That is at higher temperature, the population of molecules with higher energy is high.

Maxwell–Boltzmann Distributions



At high temperature the fraction of molecules that can overcome the activation energy barrier is high. That is the formation of products increases.

Arrhenius Equation

Svante Arrhenius developed a mathematical relationship between rate constant of a reaction, k, and E_a

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

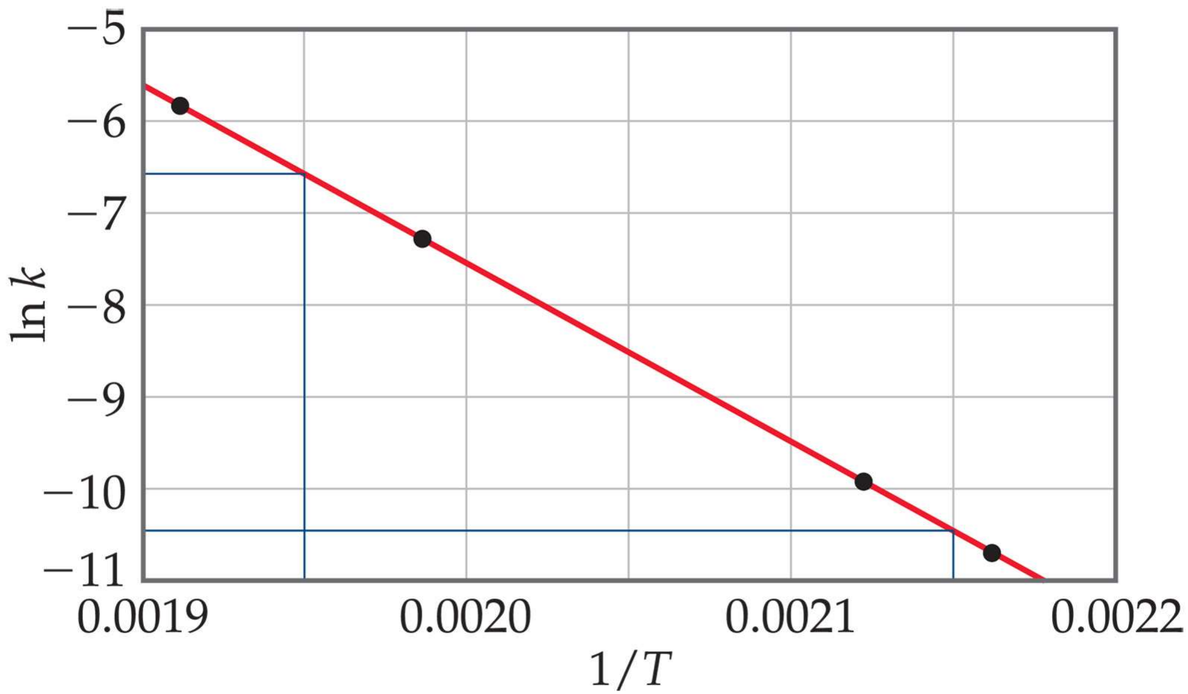
where A is the frequency factor, a number that represents the likelihood that collisions would occur with the proper orientation for reaction.

Arrhenius Equation

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

Taking the natural logarithm of both sides, the equation becomes the following and has the form of the equation for line.

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



When k is determined experimentally at several temperatures, E_a can be calculated from the slope of a plot of $\ln(k)$ vs $1/T$.

To Determine the Activation Energy of a Reaction

In this experiment we will study the reaction between potassium permanganate and dilute oxalic acid at different temperatures. The permanganate ion MnO_4^- reduces to MnO_2 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 five different temperatures and determine the activation energy for the reaction.

Experimental Protocol

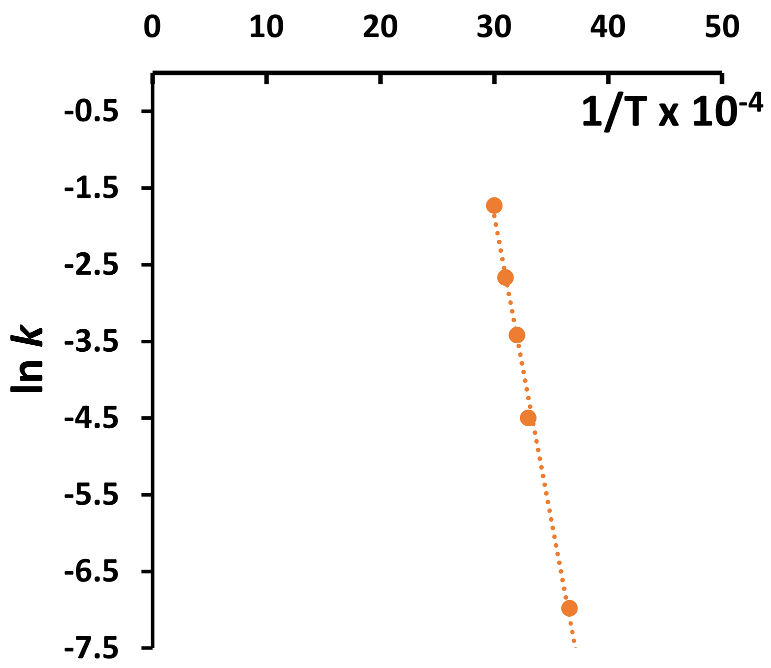
1. Using burettes, place 20 mL oxalic acid (0.5 M) in a conical flask and 10 mL KMnO4 (approximately 0.02 M) in a test tube.
2. Immerse both conical flask and test tube in a water bath to equilibrate for at least 5 minutes.
3. Mix the reactants in a conical flask and immediately start a stopwatch.
4. Swirl the reaction mixture regularly without removing it from the water bath.
5. Record the time it takes for the mixture to turn yellow/brown (indication of reduction of MnO_4^- to MnO_2).
6. Repeat the procedure with another mixture (exam same quantities) at the same temperature.
7. Repeat steps 1 to 6 for three different temperatures.
8. For the reading at 0 degree Celsius, time taken is 2160 seconds. Use this information as the fifth temperature reading in your experiment.
9. Determine the activation energy by plotting ln(k) Vs 1/T. (Temperature need to be converted to Kelvin).

Observations

[KMnO4] = 0.02M

[Oxalic Acid] = 0.5 M

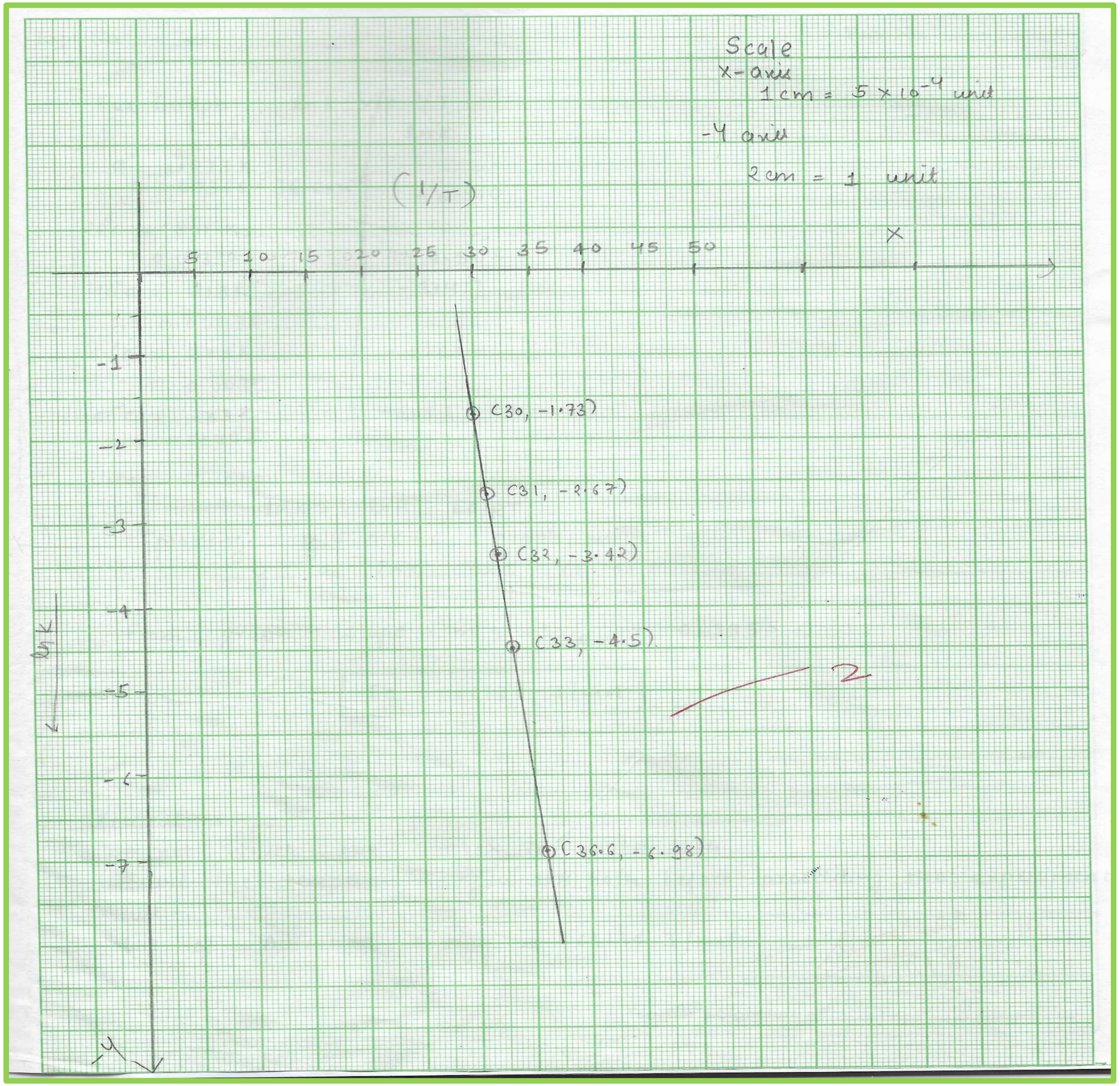
S. No.	Temp (°C)	Temp (K)	1/T (K^{-1})	Time for trial 1 (s)	Time for trial 2 (s)	Average Time (s)	Rate= $[KMnO_4]$/time	k = Rate/$[KMnO_4]$ [Oxalic]	ln (k)
1	0	273	36.6 x 10^{-4}	2155	2165	2160	0.93 x 10^{-5}	0.93 x 10^{-3}	-6.980
2	28	301	33 x 10^{-4}	183	179	181	1.105 x 10^{-4}	1.105 x 10^{-2}	-4.505
3	40	313	31.95 x 10^{-4}	61	63	61	3.28 x 10^{-4}	3.28 x 10^{-2}	-3.417
4	50	323	31 x 10^{-4}	27	31	29	6.9 x 10^{-4}	6.9 x 10^{-2}	-2.67
5	60	333	30 x 10^{-4}	11	11.53	11.26	17.76 x 10^{-4}	17.76 x 10^{-2}	-1.73



Plot of ln (k) vs 1/T

Observations

Image of a graph ln *k* vs 1/T



Observations and Calculations

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

From graph;

Slope = $-E_a$ / R = 0.7955

E_a = 66134 J/mol

Results

The rate of reduction of MnO_4^- to MnO_2 was monitored at different temperatures to determine the Activation Energy for the reaction.

Activation energy = 66.134 KJ/mol