Rate Equations and Temperature: Arrhenius Equation

Collision theory supposes that the **rate of a reaction depends on the rate of collision of particles that are reacting**. For a reaction to occur, the particles must collide. Since the effective collisions i.e. collisions which result in reaction are far fewer than the total number of collisions which occur (1 in 10^{11} collisions are generally effective), therefore a collision only seldom results in reaction.

Only those collisions will result in reaction, when the molecules have sufficient K.E necessary to break old bonds i.e. activation energy, those molecules possessing activation energy will be capable of taking part in chemical reaction.

From the Kinetic Theory of gases, we know that not all molecules of a gas have all the same K_E, a small fraction will have energy in excess of the average and a fraction below the average K_E.

From the Maxwell- Boltzmann distribution of velocities at different temperatures, we know that at higher temperatures the number of molecules possessing the activation energy, E_A, is increased, i.e. mathematically the probability that a molecule will possess E_A, at a temperature T is expressed in the Boltzmann factor:

$$e^{-E_A / RT}$$

E_A = activation energy, R = molar gas constant, T = temperature (K)

At any given temp. T, the proportion of molecules that have an energy equal to or greater than a certain E_A, is given by the formula: $e^{-E_A / RT}$

Refer to the Graph of Maxwell-Boltzmann Distribution of Velocities:

Note: the graph flattens i.e. the distribution is seen to flatten -.• the total area under the two curves must remain the same since the number of molecules must remain constant.

Changing the temperature alters the rate of a reaction by changing the value of the rate constant, k, and the amount that the rate constant changes depends on the magnitude of the activation energy.

When the activation energy is large, a small increase in temperature causes a very substantial increase in the number of molecules that have the required activation energy to react, leading to a relatively large increase in the rate of the reaction.

If however, the activation energy is small, the same temperature rise has a proportionally smaller effect on the number of molecules that have the required activation energy to react.

This is because there are already a large number of molecules able to react, hence a there is relatively not much of a change in the percentage of molecules with the required activation energy when the temperature is changed by a small amount.

The relationship between the activation energy and the rate constant was developed by Svante Arrhenius

Temperature has no effect on configuration, i.e. there is no change in probability of suitable configuration during a collision when the temperature is increased. Increase in temperature is only related to the number of molecules which have the E_A.

The rate of a reaction depends on the temperature:

$$\text{Rate} \propto \text{temp.}$$
$$\text{Rate} = k^{*}\ \text{temp.}$$

The rate of a reaction is directly dependent on the rate constant, k, higher the value of ‘k', the higher the reaction rate.
The rate constant, k, is independent of concentration.

Whether or not a collision will result in **reaction also depends on the configuration of the reacting molecules** i.e. the orientation of the reacting molecules.
The rate constant, k, has different values at different temps, and it will depend on :

1. the collision frequency, Z, and the correct orientation (steric factor), q.
   The product of these two factors can be put together as a constant A.
   $A = Z^{*}q$ (i.e. collision frequency x correct orientation)

A, is known as the collision number or the frequency factor, and is a characteristic of the reaction being studied, this rises sharply with temp (as shown above to be: $e^{-E_A/RT}$)

2. Also the number of molecules with $E_A = e^{-E_A/RT}$

Hence the rate constant will be dependent on the product of A and $e^{-E_A/RT}$ so that it is possible to write:

$$\text{Rate Constant,}\quad \mathbf{k = A\, e^{-E_A/RT}}$$

This is known as the **Arrhenius Equation**, first proposed by Svante Arrhenius,(1829)

e	is the base of the natural logs (2.718 ...)
E_A	is the activation energy of the reaction (J mol^{-1})
R	is the molar gas constant (8.3143 J K^{-1} mol^{-1})
T	is the absolute temperature (K)

Determining the Activation Energy Graphically

Taking natural logs of both sides of the equation:

$$\mathbf{\ln k = \ln A - \frac{E_A}{RT}}$$

This is the form of: $y = c - m x$

There are two variables in this equation, k and T.
By plotting ln k against 1/T, the slope of the straight line is given by $–E_A/R$, and a y-intercept of ln A.
Hence, if you determine the values of k at various temperatures and plot the above data, E_A can be determined from the slope and A would be the antilog of the y-intercept.

Taking log10… $\log_{10} k = \log_{10} A - \frac{E_A}{2.3R} * \frac{1}{T}$

The values of E_A and A for a reaction can also be found from the rate constants for two different temperatures:

At T_1 the rate constant is k_1 $\ln k_1 = \ln A - \frac{E_A}{RT_1}$

At T_2 the rate constant is k_2 $\ln k_2 = \ln A - \frac{E_A}{RT_2}$

$$\ln k_2 - \ln k_1 = -\frac{E_A}{RT_1} + \frac{E_A}{RT_2}$$

Therefore: $\mathbf{\ln (k_2 / k_1) = E_A / R \{ 1/T_1 - 1/T_2 \}}$

Reactions with large values of E_A, have small numerical value of the rate constant, k (because the exponent is negative), and are therefore slow.

Also for a given value of E_A, the equation shows that as the temperature increases, the value of the rate constant ,k, also increases indicating the reaction is faster as expected, because more molecules can collide.
A *small change in temperature causes a relatively large change in k,* and a change in the value of k is reflected in the rate of reaction.
The fact that most rate constants obey the Arrhenius Equation to a good approximation therefore this is evidence for collision models for theoretical reactions.

Unimolecular reactions i.e. reactions involving only one molecule are considered to occur after one molecule (as a result of numerous collisions) has acquired sufficient K_E for bond breaking to take place (i.e. has acquired E_A)

Collision theory applies to gases in its mathematical derivation.
But the number of collisions in a liquid is considerably smaller, therefore we can apply collision theory to liquids but Arrhenius Equation can not be derived satisfactorily.
Hence, there is a need to expand collision theory to liquids and solids. (Transition State theory).

Assignment: Do the problem sheet on Rate Equation and Temperature.