

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- Boltzmaan distribution of velocities at different temperatures, we know that at higher temperatures the number of molecules possessing the E, is increased, i.e. mathematically the probability that a molecule will possess E, 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, 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

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.

Temperature has no effect on configuration, i.e. there is no change in probability of suitable configuration during a collision when the temp. 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:

$$\begin{aligned} \text{Rate} &\propto \text{temp.} \\ \text{Rate} &= k^* \text{temp.} \end{aligned}$$

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.

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 .
 $A = Z \cdot q$ (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:

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

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 ($8.3143 \text{ JK}^{-1} \text{ mol}^{-1}$)
- T is the absolute temperature (K)

Taking natural logs of both sides of the equation:

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

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 \log_{10} ...

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

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

Reactions with large values of E_A , have small 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