

Paper : Physical Chemistry (III A)

Topic : Chemical Kinetics

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Effect of Temperature on Reaction Rates:-

The temperature has a significant effect on the rate of a reaction. It has been observed experimentally that an increase of temperature increases the rate of reaction and hence the rate constant. As a rule, an increase of temp. by  $10^{\circ}\text{C}$  doubles the reaction rate. The ratio of rate constants of a reaction at two different temperatures differing by  $10^{\circ}\text{C}$  is known as the temperature coefficient of the reaction. The temps. usually selected for this purpose are  $25^{\circ}\text{C}$  and  $35^{\circ}\text{C}$ . i.e.

$$\text{Temperature Coefficient} = \frac{k_{35}}{k_{25}} = 2 \text{ to } 3$$

The value of the temperature coefficient for most of the reactions is close to 2 and in some cases it approaches even 3.

For examples :

(i) Temperature coefficient for the decomposition of HBr in aqueous solution is 1.9.

(ii) Temperature coefficient for  
 $\text{CH}_3\text{I} + \text{C}_2\text{H}_5\text{ONa} \rightarrow \text{CH}_3\text{OC}_2\text{H}_5 + \text{NaI}$   
is 2.9.

(ii) For the reaction  $\text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2$ , the rate of reaction is slightly decreased as the temperature is increased and so this reaction has fractional temperature coefficient.

### Arrhenius Equation :-

In 1884, van't Hoff predicted that the value of equilibrium constant varies with temp. and that a plot of  $\log k$  versus  $1/T$  must be linear with negative slope for most of the reactions. Arrhenius, in 1889, extended his idea and proposed a mathematical relation between rate constant and absolute temperature of a reaction which is known as Arrhenius Equation. It is based on the following assumptions:

(a) All the molecules present in the system can not take part in the chemical reaction.

(b) It is only a certain number of molecules which react to yield products. Such molecules are called active molecules.

(c) Those molecules who do not take part in chemical reaction are called passive molecules.

(d) An equilibrium must exist between active and passive molecules.



(e) When temperature is raised, the equilibrium between active and passive molecules shifts towards the right. This increases the number of active molecules which may take part in chemical reaction and thus increases the reaction rate. It means passive molecules may become active by absorbing heat energy.

The Arrhenius equation is given by as

$$k = A \cdot e^{-E_a/RT} \quad \text{--- (1)}$$

where  $k$  is rate constant,  $T$  is the absolute temperature,  $R$  is the gas constant,  $E_a$  is the energy of activation for the reaction, and  $A$  is an experimentally determined quantity called the pre-exponential factor. The pre-exponential factor has the same unit as that of rate constant  $k$ . The unit of  $k$  for a first order reaction is  $s^{-1}$ , which is also the unit of frequency. Hence,  $A$  is also called the frequency factor. In the above equation,  $E_a$  and  $A$  are the Arrhenius parameters.

Calculation of  $E_a$  using Arrhenius Equation :

The Arrhenius equation

$$k = A \cdot e^{-E_a/RT}$$

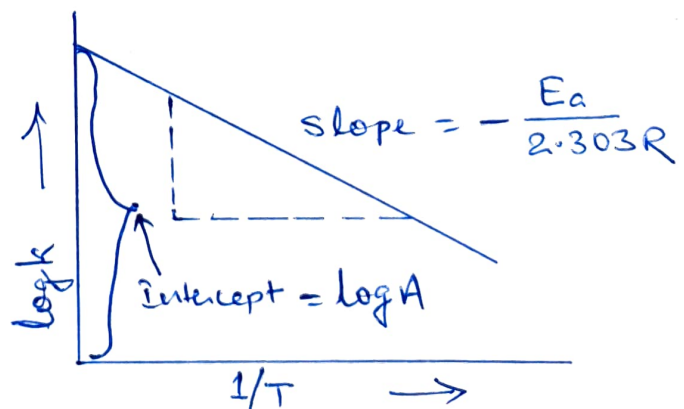
Taking log we get-

$$\ln k = \ln A - \frac{E_a}{RT} \quad \text{--- (2)}$$

$$\text{or, } \log k = -\frac{E_a}{2.303RT} + \log A \quad \text{--- (3)}$$

Comparing this equation with that of a straight line,  $y = mx + c$ , a plot of  $\log k$  versus  $1/T$  should be a straight-line with a slope  $-E_a/2.303R$  and intercept  $\log A$ .

Thus, by measuring the slope of the line, we can calculate the value of  $E_a$ . And from the intercept, we can calculate the value of  $A$ .



(04)

## Calculation of $E_a$ from the values of $k$ at two Temperatures :-

The logarithmic form of Arrhenius equation is

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

The rate constant,  $k$ , is measured at two different temperatures. If  $k_1$  is the specific rate constant at temperature  $T_1$  and  $k_2$  at another temperature  $T_2$  then from the above equation we have

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad \text{and}$$

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

On subtraction, we get-

$$\ln k_2 - \ln k_1 = \left(-\frac{E_a}{RT_2}\right) - \left(-\frac{E_a}{RT_1}\right)$$

$$\text{or, } \frac{\ln k_2}{\ln k_1} = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

$$\text{or, } \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\text{or, } \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\text{or, } \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

This is the Integrated Arrhenius Equation. Thus, knowing the rate constants at two different temperatures, the energy of activation  $E_a$  can readily be determined.

Further, when  $E_a$  and specific rate constant at one temperature are known, then specific rate constant at any other temperature can be evaluated.

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