

## Rate Law and the Eyring Equation

Manjunath.R

#16/1, 8th Main Road, Shivanagar, Rajajinagar, Bangalore560010, Karnataka, India

\*Corresponding Author Email: [manjunath5496@gmail.com](mailto:manjunath5496@gmail.com)

\*Website: <http://www.myw3schools.com/>

**Abstract:** When we talk about the rate of a chemical reaction, what we mean is the rate at which reactants are converted into products. The rate of a reaction decreases as time progresses. In this article, we provide insight into the derivation of the rate of decrease of reaction velocity with time and Eyring Equation which can be applied with considerable success to a wide variety of rate processes.

**Keywords:** rate constant; reactant; activated complex; Equilibrium constant; law of mass action; rate of reaction; Eyring Equation; rate law.

The dependence of the reaction rate on the concentrations of reacting substances is given by the **Law of Mass Action**. This law states that the rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reactants at any constant temperature at any given time. For a general reaction,



The rate law can be written as:

$$v = - \frac{dC}{dt} = kC^n$$

where C express the concentration of the reactant "A", k the reaction rate constant or rate coefficient of the reaction and n the order of the reaction. As we increase the temperature the rate of reaction "v" increases. As a rough approximation, for many reactions happening at around

room temperature, the **rate of reaction** doubles for every 10°C rise in temperature.

Differentiating this expression with respect to temperature, we obtain:

$$\frac{dv}{dT} = \frac{dk}{dT} C^n + \frac{dC^n}{dT} k$$

$$\frac{dv}{dT} = \frac{dk}{dT} C^n + nC^{n-1} \frac{dC}{dT} k$$

Since  $d \ln k = \frac{dk}{k}$ . Therefore:

$$\frac{dv}{dT} = \frac{d \ln k}{dT} k C^n + nC^{n-1} \frac{dC}{dT} k$$

Each reaction rate coefficient  $k$  has a temperature dependency, which is usually given by the equation:

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

where  $E_a$  is the activation energy and  $R$  is the gas constant.

$$\frac{dv}{dT} = \frac{E_a}{RT^2} v + \frac{nv}{C} \frac{dC}{dT}$$

$$\frac{dv}{dt} = \frac{dT}{dt} \frac{E_a}{RT^2} v + \frac{nv}{C} \frac{dC}{dt}$$

**Heat capacity or thermal capacity** is a physical property of matter, defined as the amount of heat to be supplied to a given mass of a material to produce a unit change in its temperature. The heat capacity of an object, denoted by  $c$ , is given by the equation:

$$c = \frac{dQ}{dT}$$

$$\frac{dv}{dt} = \frac{dQ}{dt} \frac{E_a}{cRT^2} v + \frac{nv}{C} \frac{dC}{dt}$$

During the course of the reaction, reactant **A** is consumed to form products. Physically, it reminds us that the concentration of the reactant **A** decreases with time – which leads to a decreased reaction rate as time progresses.

$$-\frac{dv}{dt} = \left(-\frac{dQ}{dt}\right) \frac{E_a}{cRT^2} v + \frac{nv}{C} \left(-\frac{dC}{dt}\right)$$

$$-\frac{dv}{dt} = v_{\text{rate}} \frac{E_a}{cRT^2} v + \frac{nv}{C} v$$

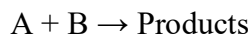
where  $v_{\text{rate}}$  is the rate of absorption of heat energy.

$$-\frac{dv}{dt} = v_{\text{rate}} \frac{E_a}{cRT^2} v + \frac{nv^2}{C}$$

### Eyring Equation:

The Eyring Equation gives a more accurate calculation of rate constants and provides insight into how a reaction progresses at the molecular level.

Consider a bimolecular reaction:



In the transition state model, the activated complex  $AB^*$  is formed:



The rate of formation of activated complex is given by:

$$v_1 = k_1 [A] [B]$$

where  $k_1$  is the rate constant of the forward reaction. The rate of dissociation of the activated complex to give back the reactants is given by:

$$v_2 = k_2 [AB^*]$$

where  $k_2$  is the rate constant of the backward reaction. Further, the ratio  $\frac{v_1}{v_2}$  yields:

$$\frac{v_1}{v_2} = \frac{k_1 [A][B]}{k_2 [AB^*]}$$

But

"Equilibrium constant is the ratio of the rate constant of the forward reaction to the rate constant of the backward reaction"

and, consequently,

$$\frac{v_1}{v_2} = K_{eq} \frac{[A][B]}{[AB^*]}$$

We may resort to thermodynamics and write for  $K_{eq}$ :

$$K_{eq} = e^{-\frac{\Delta G^0}{RT}}$$

where  $\Delta G^0$  is the standard Gibbs free energy of formation of the activated complex.

$$\frac{v_1}{v_2} = e^{-\frac{\Delta G^0}{RT}} \frac{[A][B]}{[AB^*]}$$

The rate of reaction is given by:

$$v = k [A] [B] = \kappa \frac{k_B T}{h} [AB^*]$$

where  $\kappa$  is the transmission coefficient (fraction of  $[AB^*]$  crossing forward to products),  $k_B$  is Boltzmann's constant, and  $h$  is Planck's constant.

$$\frac{v_1}{v_2} = e^{-\frac{\Delta G^0}{RT}} \kappa \frac{k_B T}{h} \frac{1}{k}$$

$$k = \kappa \frac{k_B T}{h} \frac{v_2}{v_1} e^{-\frac{\Delta G^0}{RT}}$$

#### References:

- Chemical Kinetics and Reaction Dynamics by **Santosh K. Upadhyay**.
- Chemical Kinetics: From Molecular Structure to Chemical Reactivity by **Luis Arnaut**.
- The Origin and Status of the Arrhenius Equation by **S. R. Logan**.
- Modeling of Chemical Kinetics and Reactor Design by **A. Kayode Coker**.