

Arrhenius equation and collision theory

The Arrhenius equation is

$$k_2 = A \exp(-E_a / RT) \quad \dots (8)$$

and according to the collision theory, the rate constant is given by

$$k_2 = pN_A \pi \sigma_{AB}^2 \left(\frac{8kT}{\pi \mu} \right)^{1/2} \exp(-E_0 / RT) \quad \dots (9)$$

Equation (9) may be written as

$$k_2 = K \sqrt{T} \exp(-E_0 / RT) \quad \dots (10)$$

where K represent a term which is independent of temperature and is given by

$$K = pN_A \pi \sigma_{AB}^2 \left(\frac{8k}{\pi \mu} \right)^{1/2} \quad \dots (11)$$

The relation between the activation energy E_a (appeared in equation (8)) and the minimum energy E_0 (appeared in equation (10)) may be obtained through the derivation of the expression $d \ln(k / k^0) / dT$. Equation (8) gives

$$\ln(k_2 / k^0) = \ln(A / k^0) - \frac{E_0}{RT}$$

i.e.
$$\frac{d \ln(k_2 / k^0)}{dT} = \frac{E_a}{RT^2} \quad \dots (12)$$

And equation (10) gives

$$\ln(k_2 / k^0) = \ln(K / K^0) + \frac{1}{2} \ln(T / K) - \frac{E_0}{RT} \quad \dots (13)$$

i.e.
$$\frac{d \ln(k_2 / k^0)}{dT} = \frac{1}{2T} + \frac{E_0}{RT^2} \quad \dots (14)$$

Equation (12) with (14), we have

$$\frac{E_a}{RT^2} = \frac{1}{2T} + \frac{E_0}{RT^2} \quad \text{CAREER ENDEAVOUR}$$

Or,
$$E_a = \frac{RT}{2} + E_0 \quad \dots (15)$$

Thus, the activation energy E_a shows temperature dependence. Since E_0 is usually much larger than $RT/2$, the difference between the Arrhenius activation energy E_a and the minimum energy E_0 of the simple kinetic theory is not sufficient.

Substitution of equation (15) and (10), we get

$$k_2 = K \sqrt{T} \exp\left\{-\left(E_a - RT / 2\right) / RT\right\}$$

Or,
$$k_2 = K \sqrt{T} e^{1/2} \exp(-E_a / RT)$$

Comparing the above relation with the Arrhenius equation, we have

$$A = K \sqrt{T} e^{1/2}$$

i.e.
$$A = pN_A \pi \sigma_{AB}^2 \left(\frac{8k}{\pi \mu} \right)^{1/2} \sqrt{T} e^{1/2} \quad \dots (16)$$

Or,
$$A = pN_A \frac{Z_{AB}}{N_A^* N_B^*} e^{1/2} \quad \dots (17)$$

Problem: In collision theory of bimolecular gaseous reactions, the Collision frequency does not depend on

- (a) Pressure of the system (b) Number of molecules of each gas
(c) Temperature of the system (d) Reduced mass of the system

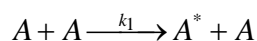
Soln. Correct option is (a)

Lindemann theory of unimolecular reaction

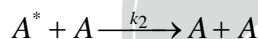
Postulates:

1. The reactive molecules acquire activation energy for making collision with another.
2. The activation molecule does not decompose immediately
3. The activated molecule may disappear by either of the following two processes
(a) decomposition (b) deactivation
4. The process of deactivation by colliding with less energetic molecule will be favoured at high pressure and the process of decomposition will be favoured at low pressure.

Step-1 : Activation process



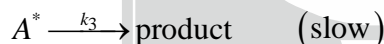
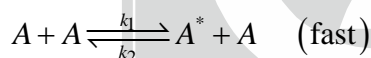
Step-2 : Deactivation process (at high pressure)



Step-3 : Deactivation process (at low pressure)



From step-1 and step-2



Therefore, the rate of reaction,

$$r = k_3 [A^*] \quad \dots (1)$$

Apply SSA, $\frac{d}{dt}[A^*] = 0$

$$k_1 [A]^2 - k_2 [A^*][A] - k_3 [A^*] = 0$$

$$k_1 [A]^2 = [A^*][k_2 [A] + k_3]$$

$$\boxed{[A^*] = \frac{k_1 [A]^2}{k_3 + k_2 [A]}}$$

From (1),

$$\boxed{r = \frac{k_1 k_3 [A]^2}{k_3 + k_2 [A]}}$$

The above equation is known as rate law expression.

Since, $[\because [A] = P_A]$

$$\boxed{r = \frac{k_1 k_3 P_A^2}{k_3 + k_2 P_A}} \quad \dots (2)$$