

11.B.6. The Rate of Reaction

In order for a reaction



to proceed, we need

1. A & B collide with each other.
2. $\mathcal{K}_{AB} > \epsilon$ (11.40)

where

$$\begin{aligned} \mathcal{K}_{AB} &= \text{relative kinetic energy in the CM frame of particles } A \text{ \& } B \\ &= \frac{1}{2} \mu_{AB} v_r^2 = \frac{1}{2} \frac{m_A m_B}{M_{AB}} (\mathbf{v}_A - \mathbf{v}_B)^2 \end{aligned} \quad (11.40b)$$

$$M_{AB} = M_A + M_B$$

ϵ = activation energy of the reaction [see Fig.11.4].

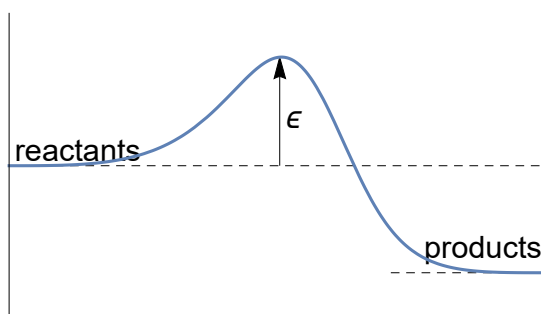


Fig.11.4. Energy barrier of height ϵ that reactants must overall to become products.

Assuming Maxwell-Boltzmann distribution, the probability density for \mathbf{V}_{CM} & \mathbf{v}_r is [see (11.3)]

$$P(\mathbf{V}_{CM}, \mathbf{v}_r) = \left(\frac{\beta M_{AB}}{2\pi} \right)^{3/2} \left(\frac{\beta \mu_{AB}}{2\pi} \right)^{3/2} \exp \left[-\frac{1}{2} \beta (M_{AB} V_{CM}^2 + \mu_{AB} v_r^2) \right] \quad (11.41)$$

Integrating over \mathbf{V}_{CM} gives

$$P(\mathbf{v}_r) = \left(\frac{\beta \mu_{AB}}{2\pi} \right)^{3/2} \exp \left(-\frac{1}{2} \beta \mu_{AB} v_r^2 \right) \quad (11.42)$$

Putting (11.40b) into (10.40) gives

$$v_r > \sqrt{\frac{2\epsilon}{\mu_{AB}}} \quad (11.42a)$$

so that (11.42) gives

$$\begin{aligned} P \left(v_r > \sqrt{\frac{2\epsilon}{\mu_{AB}}} \right) &= \left(\frac{\beta \mu_{AB}}{2\pi} \right)^{3/2} 4\pi \int_{\sqrt{2\epsilon/\mu_{AB}}}^{\infty} d v_r v_r^2 \exp \left(-\frac{1}{2} \beta \mu_{AB} v_r^2 \right) \\ &= f(\beta, \epsilon) e^{-\beta \epsilon} \end{aligned} \quad (11.43)$$

where [see *Mathematica* code below]

$$f(\beta, \epsilon) = \frac{1}{\sqrt{\pi}} \left[2\sqrt{\beta\epsilon} + e^{\beta\epsilon} \sqrt{\pi} \operatorname{erfc}(\sqrt{\beta\epsilon}) \right] \quad (11.43a)$$

and erfc is the complementary error function.

----- *Mathematica code* -----

$$\text{Assuming}[\beta > 0 \ \&\& \ \mu > 0, \left(\frac{\beta \mu}{2 \pi} \right)^{3/2} 4 \pi \int_{\sqrt{2 \epsilon / \mu}}^{\infty} v^2 e^{-\beta \mu v^2 / 2} dv]$$

$$\frac{e^{-\beta \epsilon} \left(2 \sqrt{\beta \epsilon} + e^{\beta \epsilon} \sqrt{\pi} \operatorname{Erfc}[\sqrt{\beta \epsilon}] \right)}{\sqrt{\pi}}$$

Let v_{AB} be the collision frequency between particles A & B, then the

rate of reaction \equiv average number of reactions per unit time per unit volume

can be written as

$$\dot{N}_R = v_{AB} K(\beta, \epsilon) e^{-\beta\epsilon} \quad (11.44)$$

where $K(\beta\epsilon)$ is $f(\beta, \epsilon)$ multiplied by a geometry factor dependent on the size & shape of the particles.

Using (11.15), (11.44) becomes

$$\begin{aligned} \dot{N}_R &= n_A n_B \pi d_{AB}^2 \sqrt{\frac{8}{\pi \beta \mu_{AB}}} K(\beta, \epsilon) e^{-\beta\epsilon} \\ &= n_A n_B d_{AB}^2 K'(\beta, \epsilon, \mu_{AB}) e^{-\beta\epsilon} \\ &= n_A n_B k_{AB} \end{aligned} \quad (11.44a)$$

where

$$\begin{aligned} K'(\beta, \epsilon, \mu_{AB}) &= \sqrt{\frac{8 \pi}{\beta \mu_{AB}}} K(\beta, \epsilon) \\ k_{AB} &= d_{AB}^2 K'(\beta, \epsilon, \mu_{AB}) e^{-\beta\epsilon} = \text{rate constant} \end{aligned} \quad (11.44b)$$

In view of (11.40a), we can also write (11.44a) as a **rate equation**

$$\begin{aligned} \frac{dn_A}{dt} &= -n_A n_B k_{AB} \\ &= \frac{dn_B}{dt} = -\frac{dn_C}{dt} = -\frac{dn_D}{dt} \end{aligned} \quad (11.45)$$

Comment: the foregoing results were derived under the implicit assumption that we are dealing with ideal gases. However, by treating them as phenomenological models, these results are often applied to other states of matter such as solutions and solutes.

For a more general reaction [see §S2.D]



(11.45) is easily generalized to

$$\frac{dn_A}{dt} = -k_1 n_A^{|v_A|} n_B^{|v_B|} + k_2 n_C^{v_C} n_D^{v_D} \quad (11.47)$$

Another generalization is to increase the number of reactions.

For example, the process



is a simple spontaneous decay, or molecular dissociation, and does not involve collisions.

We can introduce collision effects by breaking it up into two steps. The first is a reversible process in which a particle A is raised to an excited state A^* by collision and vice versa



The second is the irreversible decay of A^* into the final product particles



Since A^* is less stable than A , the collision-assisted process may well be more productive than the direct-decay one.

The corresponding rate equations for (10.48-9) are

$$\frac{dn_A}{dt} = -k_1 n_A^2 + k_2 n_A n_{A^*} \quad (11.50)$$

$$\frac{dn_{A^*}}{dt} = k_1 n_A^2 - k_2 n_A n_{A^*} - k_3 n_{A^*} \quad (11.51)$$

$$\begin{aligned} \frac{dn_B}{dt} &= k_3 n_{A^*} & (11.52) \\ &= \frac{dn_C}{dt} \end{aligned}$$

If (11.48a) is an on-going process, n_A will keep on decreasing so that

$$\frac{dn_A}{dt} < 0 \quad \frac{dn_B}{dt} = \frac{dn_C}{dt} > 0$$

(11.50) then gives

$$k_1 n_A > k_2 n_{A^*}$$

If (11.48a) reaches a steady state, the number of A^* should attain an equilibrium value so that

$$\frac{dn_{A^*}}{dt} \approx 0$$

(10.51) thus gives

$$n_{A^*} = \frac{k_1 n_A^2}{k_2 n_A + k_3} \quad (11.53)$$

so that (11.52) becomes

$$\frac{dn_B}{dt} = k_3 \frac{k_1 n_A^2}{k_2 n_A + k_3} \quad (11.54)$$

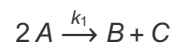
For fast A^* decay,

$$k_3 \gg k_2 n_A$$

and (11.54) simplifies to

$$\frac{dn_B}{dt} = k_1 n_A^2$$

which can be ascribed to the collision process



For slow A^* decay,

$$k_3 \ll k_2 n_A$$

and (11.54) simplifies to

$$\frac{dn_B}{dt} = \frac{k_3 k_1}{k_2} n_A$$

which can be scribed to the direct-decay process

