9.15: A Reaction Cross Section Depends Upon the Impact Parameter

In the previous section, it was assumed that all collisions with sufficient energy would lead to a reaction between the Q and B particles. This is an unrealistic assumption because not all collisions occur with a proper alignment of the particles as shown in Figure $9.15.1$.

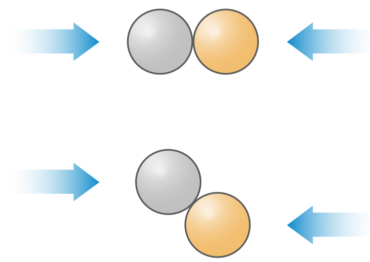

Figure 9.15.1 In the top collision, the particles collide head-on, and thus all of the kinetic energy can be used to overcome electron-electron repulsion and to break bonds. In the bottom collision, the particles collide with a glancing blow so that only part of the kinetic energy is contributed to the reaction process. With collisions involving larger, more complex molecules, there is often a specific molecular orientation required for an effective collision. (CC BY-NC; Ümit Kaya via LibreTexts)

Thus, the energy-dependent reaction cross-section,$\sigma_r(E_r)$, introduced previously is inaccurate and must be modified to take into account the inefficient collisions. One modification is to employ the *line-of-centers* (loc) model for $\sigma_r(E_r)$. This model incorporates the angle of collision relative to the line drawn between the centers of the two colliding particles, as shown in Figure $9.15.2$.

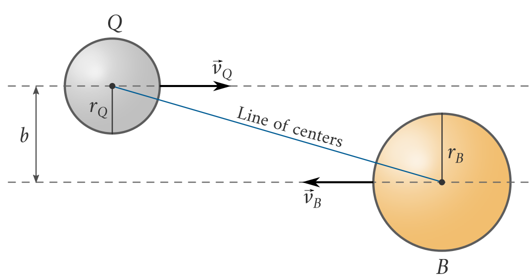

Figure 9.15.2: This figure shows the geometry of the collision between two particles. The particle velocities are $\vec{v}_Q$ and $\vec{v}_B$. The distance between the paths traveled by the two particle centers is b. (CC BY-NC; Ümit Kaya via LibreTexts)

In this model, and effective collision occurs when $E_{loc} > E_0$ where E_{loc} takes into account the fact that all particle collisions are not head-on collisions. If we define v_r as the relative velocity of approach of particles Q and B, then $v_r = \vec{v}_Q - \vec{v}_B$. The relative kinetic energy, E_r, is then $\dfrac{1}{2}\mu v_r^2$. From Figure $9.15.2$ we can see that the fraction of E_r that can be applied to the collision, (E_{loc}), is dependent upon b, the impact parameter, which is the perpendicular distance between the extrapolated paths traveled by the centers of the particles before the collision occurs. If b is 0, then $E_{loc} = E_r$, but for any other value of b, $E_{loc} < E_r$. If b is greater than the sum of the radii of Q and B, the particles will not collide, and $E_{loc} = 0$. The calculation for determining the exact relationship between the $\sigma_r(E_r)$ and E_r for this line of center model rather complicated, but the result is that $\sigma_r(E_r)$ is equal to 0 if $E_r < E_0$ and is equal to $\sigma_{QB}\left(1 - \dfrac{E_0}{E_r}\right)$ if $E_r \geq E_0$.

When compared to the simple hard-sphere collision theory, we see that

$$\sigma_r(E_r) = \sigma_{QB} \text{ if } E_r \geq E_0 \text{ (hard-sphere theory)} \tag{9.15.1}$$

$$\sigma_r(E_r) = \sigma_{QB}\left(1 - \frac{E_0}{E_r}\right) \text{ if } E_r \geq E_0 \text{ (line of centers theory)} \tag{9.15.2}$$

If we substitute Equation $9.15.2$ into Equation $30.1.4$ we get

$$\begin{aligned} k &= \left(\frac{2}{k_BT}\right)^{3/2}\left(\frac{1}{\mu\pi}\right)^{1/2}\int_{E_0}^{\infty} dE_r E_r e^{-E_r/k_BT}\sigma_{QB}\left(1-\frac{E_0}{E_r}\right) \\ &= \left(\frac{8k_BT}{\mu\pi}\right)^{1/2}\sigma_{QB}e^{-E_r/k_BT} \\ &= \langle v_r\rangle\sigma_{QB}e^{-E_r/k_BT} \end{aligned}$$

When compared to the simple hard-sphere collision theory, we see that

$$\begin{aligned} k &= \langle v_r\rangle\sigma_{QB}e^{-E_r/k_BT}\left(1+\frac{E_0}{k_BT}\right)\text{(hard-sphere theory)} \\ &= \langle v_r\rangle\sigma_{QB}e^{-E_r/k_BT}\text{(line of centers theory)} \end{aligned}$$

The line of centers theory expresses k in the same terms as the Arrhenius equation, yet experimental values of k still differ from those predicted by the line of centers model. The errors come about because $\sigma_r(E_r)$ is not accurately described by $\sigma_{QB}\left(1-\frac{E_0}{E_r}\right)$. More work needs to be done to improve the model for describing A, the Arrhenius factor.
