30.5: A Reactive Collision Can Be Described in a Center-of-Mass Coordinate System

We will apply a center-of-mass coordinate system to the bimolecular reaction of ideal gases

$$\mathrm{B(g) + Q(g) \longrightarrow F(g) + G(g)}$$

to develop an improved model for reaction kinetics that produces theoretical values that more closely represent experimental results. In this model, the reactant molecules will travel at velocities $\vec{v}_B$ and $\vec{v}_Q$ before the collision. The product molecules will travel at velocities $\vec{v}_F$ and $\vec{v}_G$ after the collision.

The Velocity and Kinetic Energy of the Center of Mass

The center of mass of two objects must lie along a straight line drawn between the centers of the two objects. Because the two molecules are heading toward each other, the line between them will be changing in size and can be best represented with the vector, $\vec{r}$, where $\vec{r} = \vec{r}_B - \vec{r}_Q$. The pre-reaction center of mass, $\mathbf{R}$ is defined as

$$\mathbf{R} = \frac{m_B \mathbf{r}_B + m_Q \mathbf{r}_Q}{M}$$

where m_B and m_Q are the masses of the individual reactants, and M is the total mass, $m_B + m_Q$.

Velocity is $\dfrac{d\vec{r}}{dt}$, and so the velocity of the center of mass, $\vec{v}_{cm}$ is

$$\vec{v}_{cm} = \frac{m_B \vec{v}_B + m_Q \vec{v}_Q}{M}$$

The kinetic energy of the reacting system is

$$\mathrm{KE}_{react} = \frac{1}{2} m_B v_B^2 + \frac{1}{2} m_Q v_Q^2$$

This equation can be rewritten as

$$\mathrm{KE}_{react} = \frac{1}{2} M v_{cm}^2 + \frac{1}{2} \mu v_r^2 \tag{30.5.1}$$

Here, μ is the reduced mass and the realtive speed of the colliding particles is $v_r = |\vec{v}_r| = |\vec{v}_B| - |\vec{v}_Q|$. Because we are assuming we have ideal gases, $\mathrm{KE}_{\text{react}}$ is a constant for the center of mass.

The Reaction

As shown in equation 30.5.1, the kinetic energy of the moving reactants consists of two parts, one due to the relative motion of the two reactant particles, and one due to the motion of the center of mass. The energy due to the motion of the center of mass will not contribute to the reaction, as will soon be shown. Only the energy due to the relative motion of the reacting molecules $\frac{1}{2}\mu v_r^2$ will contribute to overcoming the energy barrier of the energy of the reaction. And only a fraction of that energy will contribute because the molecules are not colliding head-on. Figure 30.5.1 gives a view of the progress of the reaction at several times.

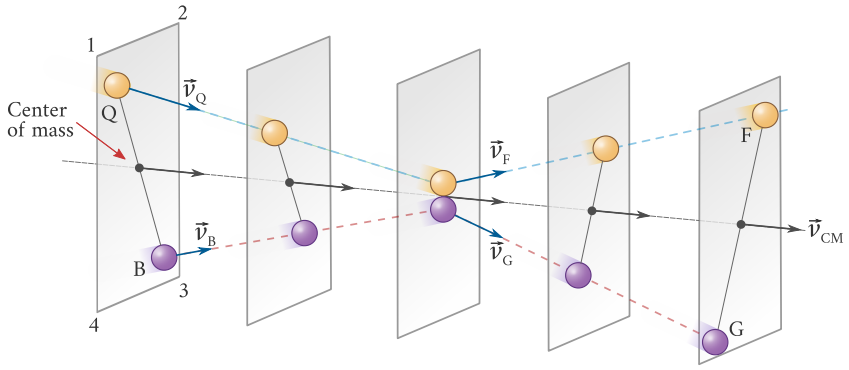

Figure 30.5.1: A diagram showing the progress of a reaction collision occurring along the path of the center of mass as time passes. The velocity of the center of mass remains constant at all times. The energy that can be contributed towards the reaction by each reactant particles is the component of its own velocity that is co-linear with the collision direction. As shown by Equation 30.5.1, this energy contribution of the reacting particles is combined in the term $\frac{1}{2}\mu v_r^2$. (CC BY-NC; Ümit Kaya via LibreTexts)

Removing the Center of Mass Term

Once F and G have formed, the post-reaction center of mass, $\mathbf{R}$ is defined as

$$\mathbf{R} = \frac{m_F\vec{r}_F + m_G\vec{r}_G}{M}$$

where m_F and m_G are the masses of the individual reactants, and M is the total mass, $m_F + m_G$. That means that the velocity of the center of mass, $\vec{v}_{cm}$ is

$$\vec{v}_{cm} = \frac{m_F\vec{v}_F + m_G\vec{v}_G}{M}$$

The kinetic energy of the reacting system is

$$\text{KE}_{react} = \frac{1}{2}m_F v_F^2 + \frac{1}{2}m_G v_G^2$$

This equation can be rewritten as

$$\text{KE}_{react} = \frac{1}{2}M v_{cm}^2 + \frac{1}{2}\mu_P v_{P_r}^2$$

Because the products have different individual masses than the reactants, the reduced mass μ_P and the relative speed v_{P_r} of the products must be denoted as having different values from those of the reactants. The total mass is conserved, however, as is $\vec{v}_{cm}$, the velocity of the center of mass. Because linear momentum must be conserved,

$$m_B\vec{v}_B + m_Q\vec{v}_Q = m_F\vec{v}_F + m_G\vec{v}_G = M\vec{v}_{cm}$$

Because mass is conserved and velocity of the center of mass is constant, the energy contribution of the motion of the center of mass is also constant, and thus does not contribute to the kinetic energy used to attain a successful reaction collision.

Estimating the Total Internal Energy

Using the center of mass model for a reaction, we have found the kinetic energy terms for the reactants, $\frac{1}{2}\mu v_r^2$, and products, $\frac{1}{2}\mu_P v_{P_r}^2$. Thus the law of conservation of energy tells us

$$E_{Reactant_{(internal)}} + \frac{1}{2}\mu v_r^2 = E_{Product_{(internal)}} + \frac{1}{2}\mu_P v_{P_r}^2$$

This relationship can be rewritten as

$$E_{Reactant_{(internal)}} + E_{Reactant_{(translational)}} = E_{Product_{(internal)}} + E_{Product_{(translational)}}$$

or

$$E_{R_{(int)}} + E_{R_{(trans)}} = E_{P_{(int)}} + E_{P_{(trans)}}$$

The velocity of the products can be defined based on the laws of conservation of energy and momentum. Unfortunately, the angle between the velocity vector of the reactants $\vec{v}_r$ and the velocity vector of the products $\vec{v}_{P_r}$ cannot be determined because products molecules can theoretically disperse from the collision in any direction.
