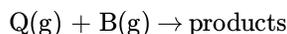


30.1: The Rate of Bimolecular Gas-Phase Reaction Can Be Estimated Using Hard-Sphere Collision Theory and an Energy-Dependent Reaction Cross Section

Collision Frequency using the Hard Sphere Model

For the bimolecular gas-phase reaction



the reaction rate is

$$\text{rate} = -\frac{d[Q]}{dt} = k[Q][B]$$

If it is assumed that every collision between Q and B particles results in products, the rate at which molecules collide is equal to the frequency of collisions per unit volume, Z_{QB} (Equation 27.6.4)

$$\text{rate} = Z_{QB} = \sigma_{QB} \langle v_r \rangle \rho_Q \rho_B \quad (30.1.1)$$

Also known as the **collision frequency**, Z_{QB} , has units of molecules per volume per time, $\text{molecules} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$. It is possible to obtain a rough estimate of the value of the rate constant, k , from the collision frequency.

Equation 30.1.1 shows the rate on a molecular scale. Generally, Z_{QB} is divided by Avogadro's number, N_0 , to obtain the collision frequency on a molar scale

$$\text{rate} = -\frac{d[Q]}{dt} = \frac{Z_{QB}}{N_0} = \frac{\sigma_{QB} \langle v_r \rangle}{N_0} \rho_Q \rho_B$$

To convert the number densities to molar concentrations, we need to realize that

$$\frac{\rho_Q}{N_0} = [Q]$$

then

$$\begin{aligned} -\frac{d[Q]}{dt} &= \frac{Z_{QB}}{N_0} = \frac{\sigma_{QB} \langle v_r \rangle}{N_0} (N_0 [Q]) (N_0 [B]) \\ -\frac{d[Q]}{dt} &= \frac{Z_{QB}}{N_0} = N_0 \sigma_{QB} \langle v_r \rangle [Q][B] \\ -\frac{d[Q]}{dt} &= \frac{Z_{QB}}{N_0} = N_0 \sigma_{QB} \sqrt{\frac{8k_B T}{\pi \mu_{QB}}} [Q][B] \end{aligned}$$

Thus

$$Z_{QB} = N_0^2 \sigma_{QB} \sqrt{\frac{8k_B T}{\pi \mu_{QB}}} [Q][B]$$

and

$$k = N_0 \sigma_{QB} \sqrt{\frac{8k_B T}{\pi \mu_{QB}}}$$

where:

- $\langle v_r \rangle$ is the mean relative speed of molecules, which is equal to $\sqrt{\frac{8k_B T}{\pi \mu_{QB}}}$
- ρ_Q and ρ_B are the number densities of Q molecules and B molecules
- N_Q and N_B are the numbers of Q molecules and B molecules

- σ_{QB} is the averaged sum of the **collision cross sections** of molecules Q and B, $\sigma_{QB} = \pi \left(\frac{d_Q + d_B}{2} \right)^2$. The collision cross section represents the collision region presented by one molecule to another. σ_{QB} is often written as πd_{QB}^2 .

The units of σ are m^2 , the units of N_0 are mole^{-1} , and the units of $\langle v_r \rangle$ are $\frac{m}{s}$. Thus, the units of k are $\frac{m^3}{\text{mole} \cdot s}$

As noted earlier, using this hard-sphere collision theory value for the rate constant is a rough estimate, mainly because the temperature dependence of k is improperly represented in the hard-sphere collision theory prediction. The next sections will describe an initial attempt to correct that error.

Successful Collisions

For a successful collision to occur, the reactant molecules must collide with enough kinetic energy to overcome the repulsions of the electron clouds and to break the existing bonds. To take the energy dependence of a successful collision into account, we will introduce a new reaction cross-section, $\sigma_r(v_r)$, which takes into account the speed of the reactants. Thus

$$k(v_r) = v_r \sigma_r(v_r)$$

The rate constant can be calculated by averaging over a distribution of all speeds, $f(v_r)$

$$k = \int_0^{\infty} k(v_r) f(v_r) dv_r = \int_0^{\infty} v_r f(v_r) dv_r \sigma_r(v_r) \quad (30.1.2)$$

From equation 27.7.4, we know that $v_r f(v_r) dv_r$ is

$$v_r f(v_r) dv_r = \left(\frac{\mu}{k_B T} \right)^{3/2} \left(\frac{2}{\pi} \right)^{1/2} v_r^3 e^{-\mu v_r^2 / 2k_B T} dv_r \quad (30.1.3)$$

Equation 30.1.3 presents the rate constant as a function of speed. If we want to compare this version of k with the common, Arrhenius form of k , the dependent variable must be changed from relative speed to relative kinetic energy, E_r . The relationship is

$$E_r = \frac{1}{2} \mu v_r^2 \text{ which rearranges to } v_r = \left(\frac{1}{2\mu E_r} \right)^{1/2}$$

Thus,

$$dv_r = \left(\frac{1}{2\mu E_r} \right)^{1/2} dE_r$$

Substituting v_r and dv_r into equation 30.1.3 gives

$$v_r f(v_r) dv_r = \left(\frac{\mu}{k_B T} \right)^{3/2} \left(\frac{2}{\pi} \right)^{1/2} \left(\frac{1}{2\mu E_r} \right)^{3/2} e^{-E_r/k_B T} \left(\frac{1}{2\mu E_r} \right)^{1/2} dE_r$$

Substituting this equation into equation 30.1.2 and simplifying gives

$$k = \left(\frac{2}{k_B T} \right)^{3/2} \left(\frac{1}{\mu \pi} \right)^{1/2} \int_0^{\infty} dE_r E_r e^{-E_r/k_B T} \sigma_r(E_r) \quad (30.1.4)$$

We can then assume that the energy dependent reaction cross section $\sigma_r(E_r)$ will include only those molecules which undergo effective collisions with a kinetic energy that is greater than or equal to a minimum sufficient energy, E_0 . Thus $\sigma_r(E_r)$ is equal to 0 if $E_r < E_0$ and is equal to σ_{QB} if $E_r \geq E_0$.

Thus,

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

$$= \langle v_r \rangle \sigma_{QB} e^{-E_r/k_B T} \left(1 + \frac{E_0}{k_B T} \right)$$

This model results in a value for k that takes into account the temperature and a minimum energy requirement to determine the fraction of successful collisions. However, it is not yet equivalent to the Arrhenius equation, in which k is proportional to $e^{-E_r/k_B T}$ and not $e^{-E_r/k_B T} \left(1 + \frac{E_0}{k_B T} \right)$.

References

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