27.7: Rates of Gas-Phase Chemical Reactions

Now that we have a description of how often gas molecules will collide with one another, we can make an initial attempt to describe how the collision of gas molecules can lead to reactions between the molecules. This topic will be covered in much more detail in Chapter 30.

Collision Frequency, Collision Energy, and Effective Collisions

In example 27.6.1, we calculated that the number of collision between H_2 molecules at one bar and 25ºC is around $10^8 \ \dfrac{\text{moles}}{\text{dm}\cdot\text{s}}$. Consider the elementary reaction

$$\text{A} + \text{B} \longrightarrow \text{C}$$

If all of the collisions between A and B resulted in a reaction, then the rate of the reaction would be about $10^8 \ \dfrac{\text{moles}}{\text{dm}\cdot\text{s}}$. We know from experiment that most chemical reactions do not occur this quickly. It must be true, then, that not all collisions result in a reaction. It is intuitive that molecules traveling at faster speeds should be more likely to react because they have sufficient energy to overcome electronic repulsions, and to break existing bonds.

One way to approach this estimate is to use a modified version of the equation for the collision frequency with a wall. The reason for starting with this equation is that it is reasonable to assume that the faster a molecule is traveling, the more likely it is to hit the wall. If this is so, then the faster a molecule is traveling, the more likely it is to collide with other molecules so as to react.

Recall equation 26.4.1

$$z_w = \frac{1}{4}\frac{N}{V}\langle v\rangle$$

which can be rewritten for the molecular level by substituting ρ for $\dfrac{N}{V}$

$$z_w = \frac{1}{4}\rho\langle v\rangle$$

This equation was obtained by carrying out the integration

$$z_w = \frac{\rho}{4\pi}\int_0^\infty vF(v)dv\int_0^{\pi/2}\cos\theta\sin\theta d\theta\int_0^{2\pi}d\phi \tag{27.7.1}$$

which takes into account the fact that molecules will only hit the wall from one direction.

Recall from equation 27.3.1, the Maxwell-Boltzmann distribution of speeds

$$f(v) = 4\pi v^2\left(\frac{m}{2\pi k_BT}\right)^{3/2}\exp\left(\frac{-mv^2}{2k_BT}\right)$$

that $f(v)$ has a factor of v^2. Thus, equation 27.7.1 has a factor of v^3, meaning that the molecules colliding with the wall are traveling faster than the molecule in the bulk of the sample. The assumption is that the faster molecules are more likely to hit the wall in a given amount of time.

We must modify equation 27.7.1 to take into account the collision of molecules with each other, rather than with the wall. This is done by replacing the mass of a single molecule m with the reduced mass of the two colliding molecules μ. The resulting speed is the relative average speed v_r. The result of these assumptions is that the collision frequency of molecules A and B per unit volume in which the molecules collide with a relative speed between v_r and $v_r + dv_r$ is

$$dZ_{AB} = Av_r^3e^{-\mu v_r^2/2k_BT}dv_r \tag{27.7.2}$$

where A is a proportionality constant.

If we require the integral of this equation over all relative speeds to be equal to Z_{AB}, then

$$Z_{AB} = \sigma_{AB}\rho_A\rho_B\left(\frac{8k_BT}{\pi\mu}\right)^{1/2} = A\int_0^\infty v_r^3 e^{-\mu v_r^2/2k_BT} dv_r$$

$$Z_{AB} = \sigma_{AB}\rho_A\rho_B\left(\frac{8k_BT}{\pi\mu}\right)^{1/2} = 2A\left(\frac{k_BT}{\mu}\right)^2$$

Rearranging to solve for A gives

$$A = \sigma_{AB}\rho_A\rho_B\left(\frac{\mu}{k_BT}\right)^{3/2}\left(\frac{2}{\pi}\right)^{1/2} \tag{27.7.3}$$

Substituting equation 27.7.3 into equation 27.7.2 gives

$$dZ_{AB} = \sigma_{AB}\rho_A\rho_B\left(\frac{\mu}{k_BT}\right)^{3/2}\left(\frac{2}{\pi}\right)^{1/2} v_r^3 e^{-\mu v_r^2/2k_BT} dv_r$$

With this equation, we can describe the collision frequency per unit volume between A molecules and B molecules with relative speeds in the range of v_r and $v_r + dv_r$. In this equation, the portion

$$\left(\frac{\mu}{k_BT}\right)^{3/2}\left(\frac{2}{\pi}\right)^{1/2} v_r^3 e^{-\mu v_r^2/2k_BT} dv_r$$

which is $v_r f(v_r) dv_r$, is the probability that the relative speed of the molecules will fall between v_r and $v_r + dv_r$.

Contributors and Attributions

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