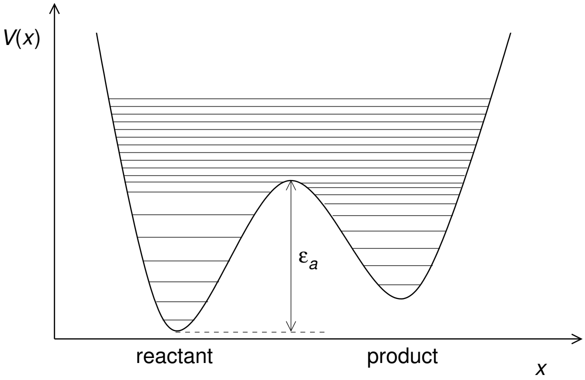
Foundations of Chemical Kinetics Lecture 3: Applications of the Boltzmann distribution

Marc R. Roussel

September 14, 2021

The Arrhenius equation



$$\text{specific rate of reaction} = (\text{probability that } \epsilon > \epsilon_a)$$
$$\times\, (\text{specific rate of crossing if } \epsilon > \epsilon_a)$$

The Arrhenius equation (continued)

- If the barrier is high enough, there will be many states below E_a, so energy can be treated approximately as a continuous variable.

$$P(\epsilon > \epsilon_a) = \frac{\int_{\epsilon_a}^{\infty} g(\epsilon)\, \exp(-\epsilon/k_B T)\, d\epsilon}{\int_0^{\infty} g(\epsilon)\, \exp(-\epsilon/k_B T)\, d\epsilon}$$

- Suppose that there is one, roughly constant, density of states below the top of the barrier and another above, i.e. that

$$g(\epsilon) = \begin{cases} g_b & \text{for} \quad \epsilon < \epsilon_a \\ g_a & \text{for} \quad \epsilon > \epsilon_a \end{cases}$$

The Arrhenius equation (continued)

- Then

$$P(\epsilon > \epsilon_a) = \frac{g_a \int_{\epsilon_a}^{\infty} \exp(-\epsilon/k_B T)\, d\epsilon}{g_b \int_0^{\epsilon_a} \exp(-\epsilon/k_B T)\, d\epsilon + g_a \int_{\epsilon_a}^{\infty} \exp(-\epsilon/k_B T)\, d\epsilon}$$

- For a high barrier, very few states above the barrier will be populated compared to the number of states in the reactant well. Thus,

$$P(\epsilon > \epsilon_a) \approx \frac{g_a \int_{\epsilon_a}^{\infty} \exp(-\epsilon/k_B T)\, d\epsilon}{g_b \int_0^{\epsilon_a} \exp(-\epsilon/k_B T)\, d\epsilon}$$

- For the same reason, we make only a small error by extending the range of integration in the denominator to infinity:

$$P(\epsilon > \epsilon_a) \approx \frac{g_a \int_{\epsilon_a}^{\infty} \exp(-\epsilon/k_B T)\, d\epsilon}{g_b \int_0^{\infty} \exp(-\epsilon/k_B T)\, d\epsilon}$$

The Arrhenius equation (continued)

$$
\begin{aligned}
P(\epsilon > \epsilon_a) &\approx \frac{g_a \int_{\epsilon_a}^{\infty} \exp(-\epsilon/k_B T)\, d\epsilon}{g_b \int_0^{\infty} \exp(-\epsilon/k_B T)\, d\epsilon} \\
&= \frac{-\, g_a k_B T \exp(-\epsilon/k_B T)\big|_{\epsilon_a}^{\infty}}{-\, g_b k_B T \exp(-\epsilon/k_B T)\big|_{0}^{\infty}} \\
&= \frac{g_a}{g_b} \exp(-\epsilon_a/k_B T) = \frac{g_a}{g_b} \exp(-E_a/RT)
\end{aligned}
$$

- Suppose that the specific rate at which molecules with sufficient energy cross the barrier is k_{cd}. Then

$$
k = k_{cd} \frac{g_a}{g_b} \exp(-E_a/RT) = A \exp(-E_a/RT)
$$

The distribution of velocities

- The Boltzmann distribution ought to apply to kinetic energy:

$$K = \frac{1}{2}mu^2 = \frac{m}{2}\left(u_x^2 + u_y^2 + u_z^2\right)$$

- Sum of terms: apply Boltzmann distribution to each term independently.

$$p(u_i)\,du_i = \frac{1}{q}\exp\left(\frac{-mu_i^2}{2k_BT}\right)\,du_i$$
$$\therefore q = \int_{-\infty}^{\infty}\exp\left(\frac{-mu_i^2}{2k_BT}\right)\,du_i$$
$$= \sqrt{2\pi k_BT/m}$$
$$\therefore p(u_i)\,du_i = \sqrt{\frac{m}{2\pi k_BT}}\exp\left(\frac{-mu_i^2}{2k_BT}\right)\,du_i$$

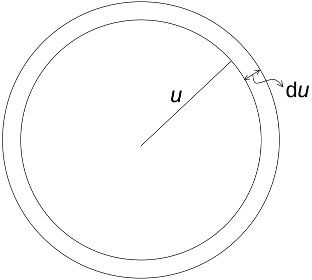
The distribution of velocities (continued)

$$\begin{aligned} p(u_x, u_y, u_z)\, du_x\, du_y\, du_z &= p(u_x)p(u_y)p(u_z)\, du_x\, du_y\, du_z \\ &= \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-m(u_x^2 + u_y^2 + u_z^2)}{2k_B T}\right) du_x\, du_y\, du_z \end{aligned}$$

This gives the probability density at a point in the velocity space, i.e. near particular values of (u_x, u_y, u_z).

The distribution of molecular speeds

- Speed u related to velocity components by $u^2 = u_x^2 + u_y^2 + u_z^2$
- The same speed is obtained at every point on a sphere satisfying this equation.
- $du_x\,du_y\,du_z$ is a volume element. Integrated over the surface of a sphere of radius u, it gives $4\pi u^2\,du$.



The distribution of molecular speeds (continued)

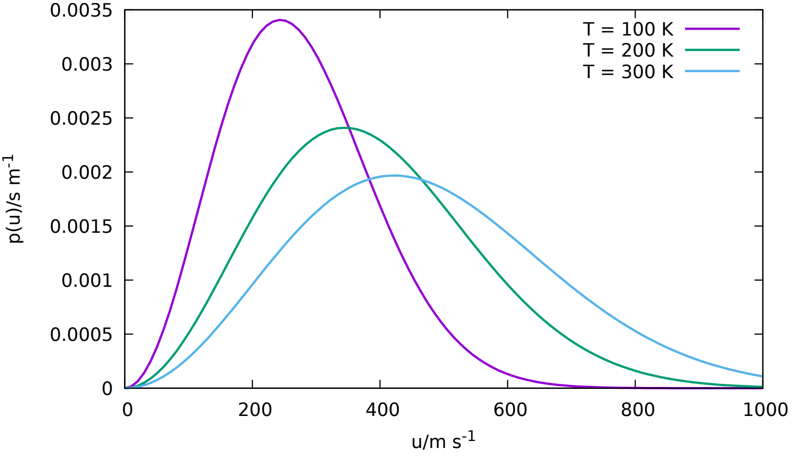
- Distribution of speeds:

$$p(u)\,du = 4\pi u^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mu^2}{2k_B T}\right)\,du$$

or

$$p(u)\,du = 4\pi u^2 \left(\frac{M}{2\pi RT}\right)^{3/2} \exp\left(\frac{-Mu^2}{2RT}\right)\,du$$

The distribution of molecular speeds



Average speed

- Given a probability density $p(x)$, the average of $f(x)$ is given by
$$\int_{\mathcal{A}} f(x)\, p(x)\, dx$$
where $\mathcal{A}$ is the region over which x is defined.
- For example, the average speed is

$$\begin{aligned}
\bar{u} &= \int_0^\infty u\, p(u)\, du \\
&= \int_0^\infty 4\pi u^3 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mu^2}{2k_B T}\right)\, du \\
&= \sqrt{\frac{8k_B T}{\pi m}}
\end{aligned}$$

Relative speeds

- We often need the relative speeds of two molecules.
- Trick: the equations for relative speed are the same as the equations for the speed of one molecule, except that the mass is replaced by the reduced mass

$$\mu = \left(m_1^{-1} + m_2^{-1}\right)^{-1}$$

- Maxwell-Boltzmann distribution of relative speeds:

$$p(u_{\text{rel}})\,du_{\text{rel}} = 4\pi u_{\text{rel}}^2 \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-\mu u^2}{2k_B T}\right)\,du_{\text{rel}}$$

- Average relative speed:

$$\bar{u}_{\text{rel}} = \sqrt{\frac{8k_B T}{\pi\mu}}$$