

## Accurate Calculation of Collision Rates

We introduced in class the concept of collision rates as the following:

Collision rate per unit time per unit volume =  $\theta_{AB} = n_A n_B A_{col} \bar{g}$  where  $A_{col}$  is the collision area, which we could represent as  $\pi(d_A + d_B)^2/4$ , and  $\bar{g}$  is the mean relative speed. Putting these together into a rate constant  $k_{col}$  such that  $\theta_{AB} = k_{col} n_A n_B$ , we can get the expression:

$$k_{col} = \frac{\pi}{4} (d_A + d_B)^2 \left( \frac{8kT}{\pi\mu} \right)^{1/2} \quad (1)$$

In this expression,  $\mu$  is the reduced mass  $m_A m_B / (m_A + m_B)$ , and  $k$  is boltzmann's constant.

Unfortunately, the collision diameters are poorly defined in this approach, and although we can approximate them, it's best to use the correct approach from kinetic theory. This approach yields a very similar formula, but with a collision integral  $\Omega^{(1,1)*}$  which we'll discuss in the transport section of the class. The collision rate then becomes:

$$k_{col} = \left( \frac{8\pi kT}{\mu} \right)^{1/2} \sigma^2 \Omega^{(1,1)*} \quad (2)$$

which is very similar except for the terms  $\sigma$  and  $\Omega$ . These are calculated as follows:

The term  $\sigma$  is the reduced collision diameter, and is defined as  $(\sigma_A + \sigma_B)/2$  where  $\sigma_A$  and  $\sigma_B$  are the Lennard-Jones diameters for species A and B. These diameters are obtained from experimental data or calculations, and are tabulated in transport properties files. Here's an example of a few lines from such a file (from the class website):

|    |   |         |       |       |       |       |
|----|---|---------|-------|-------|-------|-------|
| O  | 0 | 80.000  | 2.750 | 0.000 | 0.000 | 0.000 |
| O2 | 1 | 107.400 | 3.458 | 0.000 | 1.600 | 3.800 |
| O3 | 2 | 180.000 | 4.100 | 0.000 | 0.000 | 2.000 |

The leftmost column is the species name, the 2<sup>nd</sup> column is 0 for monatomic, 1 for diatomic, and 2 for polyatomic species. Column 3 is the Lennard-Jones well depth for each species  $i$  ( $\epsilon_i/k$ ) in units of kelvin, such that the term  $\epsilon_i/kT$  is unitless. Column four is the Lennard-Jones collision diameters ( $\sigma_i$ ) in Angstroms. Columns 5-7 are related to polarizability, dipole moment, and relaxation constants. To first order, we can ignore them in this analysis.

The collision integral  $\Omega^{(1,1)*}$  which is easily calculated as follows:

- 1) Calculate  $\epsilon_{AB}/k$  for the collision partners using  $\epsilon_i/k$  data and the expression:

$$\frac{\epsilon_{AB}}{k} = \left( \frac{\epsilon_A}{k} \frac{\epsilon_B}{k} \right)^{1/2}$$

- 2) Invert this and multiply by the temperature T to get  $T^* = kT/\epsilon_{AB}$ .

$$3) \Omega^{(1,1)*} = 1.16145T^{*(-0.14874)} + 0.52487e^{-0.7732T^*} + 2.16178e^{-2.437887T^*}$$

Let's do an example, calculating  $k_{col}$  for O and O<sub>2</sub> at 1500 K. Note that to get collision rate, you just multiply by the two number densities of the colliding species.

First, let's calculate  $\mu$ , using O (Mwt = 16) and O<sub>2</sub> (Mwt = 32), so  $\mu = 10.67$  kg/kmol. To get this into MKS units, we divide by Avogadro **per kmol** so  $6.023e26$ , giving  $\mu = 1.77e-26$  kg.

Inserting this into equation (2), the speed term in parentheses is 5421 m/s.

For  $\sigma$ , we see  $\sigma_O = 2.75$ , and  $\sigma_{O_2} = 3.458$ , both in Angstroms, so  $\sigma_{AB} = 3.104 \text{ \AA}$ , and  $\sigma^2 = 9.635 \times 10^{-20} \text{ m}^2$ .

For the collision integral the  $\epsilon_i/k$  values are 80 and 107.4 K, so  $\epsilon_{AB}/k$  is 92.693 K, and  $T^*$  is 16.182 at 1500 K.

Plugging this into the collision integral polynomial, we get  $\Omega^{(1,1)*} = 0.76766$ .

Multiplying these together, we get:  $4.01e-16$  with units  $\text{m}^3/\text{s}$ , so that when you multiply by two number densities ( $1/\text{m}^3$ )\*( $1/\text{m}^3$ ), you get number of collisions/ $\text{m}^3/\text{s}$ . To get moles of collisions per unit area per unit time, multiply by Avogadro's number.

Note that the only real difference between the approximate approach (1) and better approach (2) is the collision integral, which here is about a 25% difference.