CSO202 —Atoms, Molecules & Photons

Homework – 1

- We have been focusing on the study of gas phase elementary collisional reactions. Let us go to time of Arrhenius and consider the average experimental results based on collisions.

1. Consider the following bimolecular reaction at 3000 K:

   $CO(g) + O_2(g) \rightarrow CO_2 (g) + O(g)$

   The experimentally determined Arrhenius pre-exponential factor is $A = 3.5 \times 10^9$ dm^3.mol^{-1}.s^{-1}, and the activation energy is $E_a = 213.4$ kJ.mol^{-1}. The hard-sphere collision diameter of O_2 is 360 pm and that for CO is 370 pm. Calculate the value of line-of-centers model rate constant at 3000 K and compare it with the experimental rate constant. Also compare the calculated and experimental A values.

Ans. To find the experimental value of rate constant, k_{exp}, we use the Arrhenius rate eqn:

$$k_{exp} = Ae^{-E_a/RT}$$

$$= (3.5 \times 10^9 \mathrm{dm^3.mol^{-1}.s^{-1}})\exp\left[-\frac{213400\ \mathrm{J.mol^{-1}}}{(8.315\ \mathrm{J.mol^{-1}.K^{-1}})(3000\ \mathrm{K})}\right]$$

$$= 6.7 \times 10^5\ \mathrm{dm^3.mol^{-1}.s^{-1}}$$

We can use the cross-section expression to find (look up McQuarrie Phys. Chem. Chapter 28):

$$\sigma_{AB} = \pi\left[\frac{(360 \times 10^{-12}\ \mathrm{m} + 370 \times 10^{-12}\ \mathrm{m})}{2}\right]^2 = 4.19 \times 10^{-19}\ \mathrm{m^2}$$

Similarly, the average velocity $\langle u_r \rangle$:

$$\langle u_r \rangle = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} = \left\{\frac{8(1.381 \times 10^{-23}\ \mathrm{J\cdot K^{-1}})(3000\ \mathrm{K})}{\pi\left[\frac{(28.010\ \mathrm{amu})(31.999\ \mathrm{amu})}{(60.009\ \mathrm{amu})}\right](1.661 \times 10^{-27}\ \mathrm{kg\cdot amu^{-1}})}\right\}^{1/2} = 2060\ \mathrm{m\cdot s^{-1}}$$

For head-on collision or line-of-centers model:

$$E_a = \tfrac{1}{2}k_BT + E_0 \qquad \text{and} \qquad A = \langle u_r \rangle \sigma_{AB} e^{1/2}$$

We can find E_0 using the first of these equations:

$$E_0 = E_a - \tfrac{1}{2}k_BN_AT = E_a - \tfrac{1}{2}RT$$

$$= 213400\ \mathrm{J\cdot mol^{-1}} - \tfrac{1}{2}(8.3145\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}})(3000\ \mathrm{K})$$

$$= 200.9\ \mathrm{kJ\cdot mol^{-1}}$$

Now, the theoretical value:

$$\begin{aligned} k_{\text{theor}} &= \langle u_r \rangle \sigma_{AB} e^{-E_0/k_B T} \\ &= (2060\ \text{m}\cdot\text{s}^{-1})(4.19 \times 10^{-19}\ \text{m}^2) \exp\left[-\frac{200\,900\ \text{J}\cdot\text{mol}^{-1}}{(8.314\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(3000\ \text{K})}\right] \\ &= 2.74 \times 10^{-19}\ \text{m}^3\cdot\text{molecule}^{-1}\cdot\text{s}^{-1} = 1.65 \times 10^8\ \text{dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1} \end{aligned}$$

The ratio of the theoretical rate constant to the experimental rate constant is 250. The theoretical value of A is

$$A = \langle u_r \rangle \sigma_{AB} (1000 N_A) e^{1/2} = 8.57 \times 10^{11}\ \text{dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$$

which is 250 times greater than the experimental A.

- Next, let us consider the case of a head-on collision between a moving fluoride atom [F(g)] and a stationary D_2(g) molecule. (Assume these reactants are hard spheres)

2. Calculate the total kinetic energy of the head-on collision process when F(g) is moving at a speed of 2500 m s^{-1} towards the stationary D_2(g) molecule (v=0).

$$\begin{aligned} \text{KE} &= \tfrac{1}{2} m_A u_A^2 + \tfrac{1}{2} m_B u_B^2 \\ &= \tfrac{1}{2}(18.998\ \text{amu})(1.661 \times 10^{-27}\ \text{kg}\cdot\text{amu}^{-1})(2500\ \text{m}\cdot\text{s}^{-1})^2 + 0 \\ &= 9.86 \times 10^{-20}\ \text{J} \end{aligned}$$

3. Determine the ratio of the total kinetic energy to the zero-point vibrational energy of the D_2(g) molecule given that the fundamental vibrational frequency of D_2 is 2990 cm^{-1}.

The total kinetic energy from above problem is 9.86×10^{-20} J. We know, $\tilde{\nu} = 2990$ cm^{-1}, and $G(v) = (v + \frac{1}{2})\tilde{\nu}$, so the zero-point vibrational energy is

$$G(0) = \tfrac{1}{2}(3118.4\ \text{cm}^{-1}) \left(\frac{\text{kJ}\cdot\text{mol}^{-1}}{83.60\ \text{cm}^{-1}}\right) \left(\frac{1000}{N_A}\right) = 3.10 \times 10^{-20}\ \text{J}$$

The ratio of the total kinetic energy to the zero-point vibrational energy is 3.2.

4. If the speed of the F(g) is lower, say 1540 m s^{-1}, calculate the speed of the D_2(g) molecule, so that the kinetic energy of the process remains the same as in case 1.

$$
\begin{aligned}
\mathrm{KE} &= \tfrac{1}{2}m_A u_A^2 + \tfrac{1}{2}m_B u_B^2 \\
9.86\times10^{-20}\ \mathrm{J} &= \tfrac{1}{2}(18.998\ \mathrm{amu})(1.661\times10^{-27}\ \mathrm{kg\cdot amu^{-1}})(1540\ \mathrm{m\cdot s^{-1}})^2 \\
&\quad + \tfrac{1}{2}(4.028\ \mathrm{amu})(1.661\times10^{-27}\ \mathrm{kg\cdot amu^{-1}})u_B^2 \\
6.12\times10^{-20}\ \mathrm{J} &= \tfrac{1}{2}(4.028\ \mathrm{amu})(1.661\times10^{-27}\ \mathrm{kg\cdot amu^{-1}})u_B^2 \\
u_B &= 4280\ \mathrm{m\cdot s^{-1}}
\end{aligned}
$$

5. Estimate the minimum speed of the F(g) atom so that its kinetic energy exceeds the bond dissociation energy of D_2(g). (The value of D_0 for D_2 is 435.6 kJ mol^{-1})

   [Recap: D_0 denotes the difference in energy between the ground vibrational energy of the potential energy curve and the dissociated atoms]

The dissociation energy of a $D_2(g)$ molecule is

$$\frac{435.6\ \mathrm{kJ\cdot mol^{-1}}}{N_A} = 7.23\times10^{-19}\ \mathrm{J}$$

This is the minimum energy needed by the fluorine atom. We use Equation 30.18 again:

$$
\begin{aligned}
\mathrm{KE} &= \tfrac{1}{2}m_A u_A^2 + \tfrac{1}{2}m_B u_B^2 \\
7.23\times10^{-19}\ \mathrm{J} &\le \tfrac{1}{2}(18.998\ \mathrm{amu})(1.661\times10^{-27}\ \mathrm{kg\cdot amu^{-1}})u_F^2 + 0 \\
u_F &\ge 6770\ \mathrm{m\cdot s^{-1}}
\end{aligned}
$$

The minimum speed is $6770\ \mathrm{m\cdot s^{-1}}$.