CSO202—Atoms, Molecules & Photons

Homework – 1

- We have been focusing on the study of gas-phase elementary collisional reactions. Let us go to the 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 × 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 rate constant value at 3000 K considering the model that collision is along the line where the center of mass of the individual atoms collides and compare it with the experimental rate constant. Also, compare the calculated and experimental A values.

- 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).

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}.

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 Problem 2.

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]