Chemistry 2710 Spring 2001 Assignment 5 Solutions

1. [The following is a sample answer only. Many other approaches to answering this question are equally valid.]

   In the pressure jump method, a change in pressure causes a change in the equilibrium constant. By following the return of the system back to equilibrium, we get a relaxation time which can be related to the rate constants. Word count: 228

   One of the better ways to create a pressure jump is to use the rupture-disk method. In this method, the reaction vessel is pressurized. A sudden drop in pressure results when the disk is broken. Pressure changes of 50 atm or more can be obtained in $\sim 60\,\mu$s by this method. This method has two advantages: First, it is very fast. Second, the final pressure is 1 atm so that the data can be combined with other data obtained at 1 atm. However, only very small changes in the equilibrium constant are obtained (of order a few percent) which means that the detection method used must be very sensitive.

   The relaxation time is measured by following the exponential decay of one of the species back to equilibrium. The data treatment then depends on the mechanism. Suppose that we have a simple reversible first-order reaction ($A \rightleftharpoons B$). Then the relaxation time is related to k_+ and k_- by $\tau = (k_+ + k_-)^{-1}$. The equilibrium constant for the reaction is $K = k_+/k_-$. If we know both K and τ, we can calculate k_+ and k_-.

2. Define a small disturbance from equilibrium δb by

   $$b = b_{\text{eq}} + \delta b.$$

   By stoichiometry,

   $$a = a_{\text{eq}} - 2\delta b.$$

   The rate equation for b is

   $$\frac{db}{dt} = k_{ab}a^2 - k_{ba}b.$$

   Note that

   $$\frac{db}{dt} = \frac{d}{dt}(b_{\text{eq}} + \delta b) = \frac{d(\delta b)}{dt}.$$

$$\begin{aligned} \therefore \frac{d(\delta b)}{dt} &= k_{ab}(a_{\rm eq} - 2\delta b)^2 - k_{ba}(b_{\rm eq} + \delta b) \\ &= k_{ab}a_{\rm eq}^2 - k_{ba}b_{\rm eq} - \delta b\left(4k_{ab}a_{\rm eq} + k_{ba}\right) + 4k_{ab}(\delta b)^2. \end{aligned}$$

At equilibrium $db/dt = k_{ab}a_{\rm eq}^2 - k_{ba}b_{\rm eq} = 0$. Also, since only small displacements are considered, $(\delta b)^2$ is very small, so we neglect the last term in the differential equation. We get

$$\frac{d(\delta b)}{dt} = -\delta b\left(4k_{ab}a_{\rm eq} + k_{ba}\right).$$

The relaxation time is the inverse of the quantity which behaves like the rate constant for this first-order process:

$$\tau = \left(4k_{ab}a_{\rm eq} + k_{ba}\right)^{-1}.$$

3. The (average) mass of a potassium atom is

$$m_{\rm K} = \frac{39.098\,{\rm g/mol}}{6.022\,142\times10^{23}\,{\rm mol}^{-1}} = 6.4924\times10^{-23}\,{\rm g} \equiv 6.4924\times10^{-26}\,{\rm kg}.$$

Similarly, the mass of a bromine molecule is

$$m_{\rm Br_2} = 2.6537\times10^{-25}\,{\rm kg}.$$

The reduced mass of the reactants is

$$\mu = \left(m_{\rm K}^{-1} + m_{\rm Br_2}^{-1}\right)^{-1} = 5.2162\times10^{-26}\,{\rm kg}.$$

The relative speed at 600 K is

$$\bar{v_r} = \sqrt{\frac{8(1.380\,658\times10^{-23}\,{\rm J/K})(600\,{\rm K})}{\pi(5.2162\times10^{-26}\,{\rm kg})}} = 636\,{\rm m/s}.$$

To use the equation relating the cross-section to the preexponential factor, we must convert the preexponential factor to SI units:

$$k_\infty = \frac{10^{12}\,{\rm L\,mol^{-1}s^{-1}}}{1000\,{\rm L/m^3}} = 10^9\,{\rm m^3mol^{-1}s^{-1}}.$$

The cross-section is therefore

$$\sigma = \frac{k_\infty}{\bar{v}_r N_A} = 2.61 \times 10^{-18}\,\mathrm{m}^2.$$

This corresponds to a disk of radius $r_{AB} = \sqrt{\sigma/\pi} = 9.12 \times 10^{-10}\,\mathrm{m}$ or 9.12 Å. This is a very large radius. For comparison, the radius of a potassium atom is 2.20 Å. The bond length in the bromine molecule is 2.29 Å. If we add these together, we get an r_{AB} which is less than *half* of the value computed from the cross-section. The cross-section calculated here is therefore not due to a simple collisional process. In fact, the large difference in electronegativity of K and Br leads to a transfer of charge from the atom to the molecule at large distances. The cation (K^+) and anion (Br_2^-) are then attracted to each other by electrostatic forces, which enhances the rate of reaction. This process is called "harpooning". (The potassium atom is imagined to use its electron as a harpoon which it uses to reel in the bromine molecule.) The r_{AB} calculated from the cross-section corresponds to the mean distance at which this harpooning process occurs.