Chemistry 4000/5000/7001, Fall 2012, Assignment 4 Solutions

1. (a) The reduced molar mass of the reactants is

$$\begin{aligned}\mu_m &= \left(M_{\mathrm{K}}^{-1} + M_{\mathrm{Br_2}}^{-1}\right)^{-1} \\ &= \left[(39.0983)^{-1} + (159.808\,\mathrm{g/mol})^{-1}\right]^{-1} \\ &= 31.413\,\mathrm{g/mol}^{-1} \\ &\equiv 31.413 \times 10^{-3}\,\mathrm{kg/mol}.\end{aligned}$$

The relative speed at 600 K is

$$\bar{v}_r = \sqrt{\frac{8(8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}})(600\,\mathrm{K})}{\pi(31.413 \times 10^{-3}\,\mathrm{kg/mol})}} = 636\,\mathrm{m/s}.$$

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

$$A_{\mathrm{ct}} = \frac{10^{12}\,\mathrm{L\,mol^{-1}s^{-1}}}{1000\,\mathrm{L/m^3}} = 10^9\,\mathrm{m^3mol^{-1}s^{-1}}.$$

The cross-section is therefore

$$\sigma = \frac{A_{\mathrm{ct}}}{\bar{v}_r L} = 3 \times 10^{-18}\,\mathrm{m}^2.$$

This corresponds to a disk of radius $r_{AB} = \sqrt{\sigma/\pi} = 9 \times 10^{-10}$ m or 9 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 hard-sphere 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".

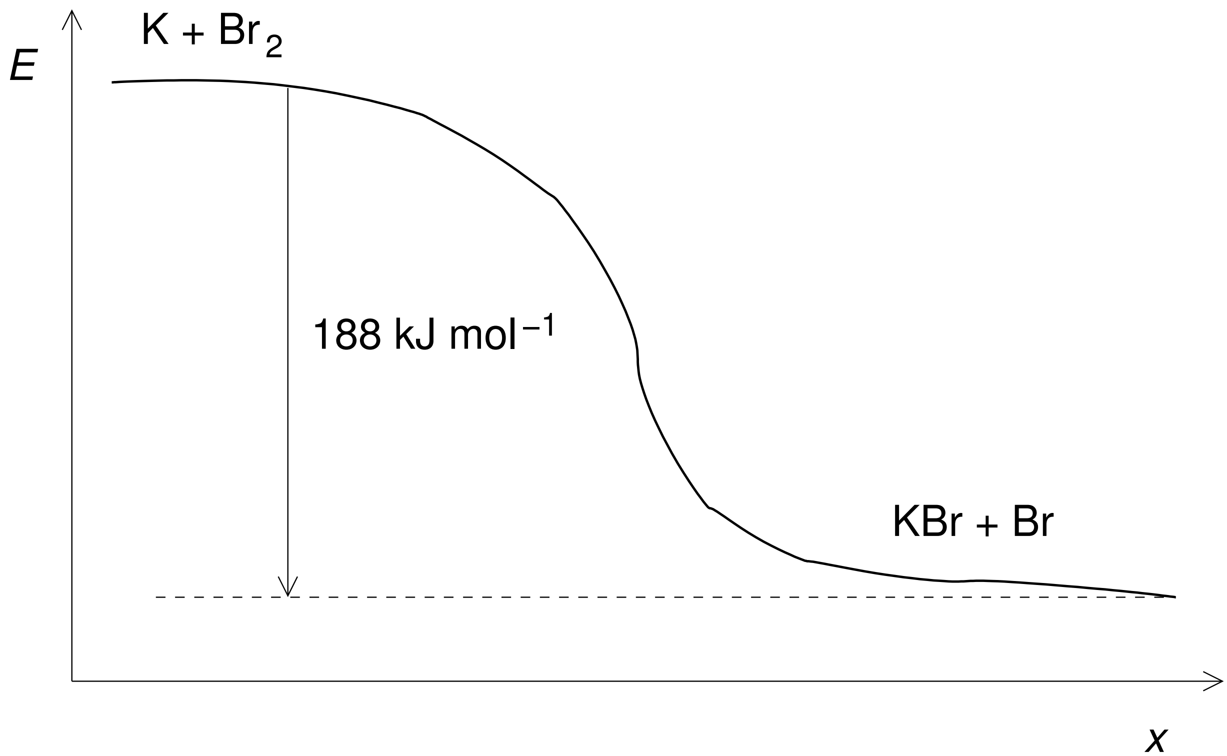

Figure 1: Reaction profile for the reaction of K with Br_2

(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.

(b) Since we need to break a bromine-bromine bond and make a K-Br bond, the change in energy is

$$\begin{aligned}\Delta U_m &= \mathrm{BDE}(\mathrm{Br_2}) - \mathrm{BDE}(\mathrm{KBr}) \\ &= 190.33 - 378.46\,\mathrm{kJ\,mol^{-1}} \\ &= -188.13\,\mathrm{kJ\,mol^{-1}}.\end{aligned}$$

We are told in part (a) that this reaction has no activation energy. Thus, it's all downhill from reactants to products. The reaction profile is sketched in figure 1

2. (a)

$$K = \frac{1}{2}mv^2$$

and

$$\begin{aligned} p &= mv \\ \therefore K &= \frac{1}{2}m\left(\frac{p}{m}\right)^2 = \frac{p^2}{2m}. \\ \therefore p &= \sqrt{2mK}. \\ \therefore \lambda &= \frac{h}{\sqrt{2mK}} \end{aligned}$$

(b) In simple collision theory, we take $\sigma = \pi R_{AB}^2$. Here, we would assume

$$R_{AB} = R + \lambda = R + \frac{h}{\sqrt{2m_n K}},$$

where m_n is the mass of the neutron. Thus,

$$\sigma_R = \pi\left(R + \frac{h}{\sqrt{2m_n K}}\right)^2.$$

(c) $\mu^{-1} = m_n^{-1} + m_2^{-1}$. Since $m_n \ll m_2$, $m_n^{-1} \gg m_2^{-1}$. Therefore $\mu^{-1} \approx m_n^{-1}$ or $\mu \approx m_n$.

(d) In processes where neutron-nucleus reactions occur, the nucleus is almost always stationary (or nearly so) and the neutron is moving at high speed. Thus, K_r is just the kinetic energy of the neutron. See my Maple worksheet for the detailed calculation. Also note that I substituted $\mu = m_n$ in the equation for the rate constant right away. The result is

$$k = 2LR^2\sqrt{\frac{2\pi k_B T}{m_n}} + \frac{2L\pi Rh}{m_n} + \frac{Lh^2}{m_n^{3/2}}\sqrt{\frac{2\pi}{k_B T}}.$$

(e) Again, I carried out the calculation in my Maple worksheet. The answer is

$$k = 1.5 \times 10^8\,\mathrm{m^3\,mol^{-1}s^{-1}}.$$

To get the units, we can analyze any of the terms in the equation for the rate constant given above. In particular, the middle term (which doesn't contain any square roots) gives

$$\begin{aligned}\frac{\mathrm{mol}^{-1}\mathrm{m\,J\,s}}{\mathrm{kg}} &= \frac{\mathrm{mol}^{-1}\mathrm{m\,(N\,m)\,s}}{\mathrm{kg}} = \frac{\mathrm{mol}^{-1}\mathrm{m\,(kg\,m^2s^{-2})\,s}}{\mathrm{kg}}\\ &= \mathrm{m^3\,mol^{-1}s^{-1}}\end{aligned}$$

(f) The rate constant becomes infinite at small and large T. Proving that this is so is not easy, but one is tempted to conclude that the divergence of the cross-section at small K is responsible for at least one of these limits. Dealing with this properly would require a study of the asymptotics of the integral defining the rate constant, which is beyond the scope of this course.