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

Due: Friday, October 5, 4:00 p.m.
Total marks: 36

1. (a) The reaction

$$K_{(g)} + Br_{2(g)} \rightarrow KBr_{(g)} + Br_{(g)}$$

has an activation energy of zero so that the rate constant is equal to the preexponential factor. At 600 K, the rate constant is approximately $10^{12}\,\mathrm{L\,mol^{-1}s^{-1}}$. Assuming that the reaction occurs at the collision-limited rate, what is the collision cross-section? What does the size of the cross-section tell us about this reaction? [12 marks]

(b) We can estimate the change in energy in this reaction from the bond energies, which are as follows:

Species	Bond dissociation energy/$\mathrm{kJ\,mol^{-1}}$
$Br_{2(g)}$	190.33
$KBr_{(g)}$	378.46

Using these data and information from part (a), sketch the reaction profile for this reaction, i.e. a graph of energy vs reaction coordinate. [6 marks]

2. The theory of reactive scattering studied in class is quite general and can be applied to a variety of rate processes. For example, it has been applied to processes involving neutron impacts with nuclei (neutron capture, induced fission, etc.).

(a) The radius of the neutron is not directly relevant in estimating the cross-section. Because of the quantum mechanical effects associated with small particles like neutrons, the de Broglie wavelength ($\lambda = h/p$) is a better estimate of the "extent" of a neutron in space. Starting from the classical expression for the kinetic energy, obtain an equation relating the momentum to the kinetic energy, and then give the de Broglie wavelength as a function of the kinetic energy of the neutron. [4 marks]

(b) Estimate the dependence of the cross-section σ_R on the kinetic energy of the neutron using the expression for the cross-section found in simple collision theory, assuming a nucleus of radius R and a neutron of effective radius equal to its de Broglie wavelength. [2 marks]

(c) Typically, $m_n \ll m_2$, where m_n is the mass of the neutron and m_2 is the mass of the nucleus. What limit does the reduced mass approach in this case? Use this limit in subsequent calculations. [2 marks]

(d) Obtain an equation for the rate constant. [4 marks]

You will likely want to use Maple for this step. To do the integral, you will need to use the `assuming` command to tell Maple that some parameters are positive. Maple will likely return an unevaluated limit. (At least it did for me.) If it does, use the `simplify()` command with the `assuming` command to get the final expression. I also applied the `expand()` function after the initial simplification, although which version is simpler is a matter of taste. Feel free to hand in your Maple worksheet with your assignment rather than transcribing the intermediate steps, but make sure to write or type the final answer.

(e) ^{10}B is used in an experimental cancer treatment called neutron capture therapy: The patient is administered a drug containing this isotope that is preferentially taken up by the tumor. The tumor is then bombarded with thermal neutrons (neutrons whose kinetic energies obey a Maxwell-Boltzmann distribution with a T similar to room temperature). The neutrons are absorbed, triggering the following nuclear reaction:

$$^{10}_{5}\mathrm{B} + ^{1}_{0}\mathrm{n} \rightarrow ^{11}_{5}\mathrm{B} \rightarrow ^{7}_{3}\mathrm{Li} + ^{4}_{2}\alpha + \gamma$$

Alpha particles are a particularly lethal form of radiation due to their mass. On the other hand, the large size prevents this radiation from getting very far, i.e. it tends to mostly damage the tumor where the drug is located and where the neutron irradiation has been applied. In this case, the lithium ion also has a large kinetic energy and acts much like an alpha particle.

Based on the theory developed above, estimate the rate constant at 37 °C for neutron capture by ^{10}B. The radius of a ^{10}B nucleus is approximately 2.7 fm. [2 marks]

If you use Maple to do this calculation, you may want to use `evalf()` to force Maple to compute a floating-point value. (Otherwise, it tends to leave π unevaluated.)

(f) The expression you developed for the rate constant behaves oddly at small and large T. Describe the odd behavior. Why does this odd behavior occur? In other words, what assumption(s) of our calculation are causing the odd behavior? [4 marks]