Chemistry 4000/5000/7001, Fall 2012, Assignment 8

Due: Friday, November 30, 4:00 p.m.
Total marks: 35

1. Suppose that we want to simulate the reaction

$$2\mathrm{A} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \mathrm{B}$$

using the Gillespie algorithm.

   (a) If the mass-action rate constants have the values $k_+ = 1.4 \times 10^6\,\mathrm{L\,mol^{-1}s^{-1}}$ and $k_- = 1.0 \times 10^{-5}\,\mathrm{s^{-1}}$, and the reaction volume is 1.5 nL, what are the stochastic rate constants? [3 marks]

   (b) Suppose that at some particular point in time, $N_A = 2304$ and $N_B = 1232$. Your computer generates the following two random numbers: 0.1637 and 0.6379. Determine which reaction occurs next according to the Gillespie algorithm, and the time at which it will occur. Show all steps of the calculation. Also determine the composition after the reaction has occured. [10 marks]

2. Copper(II) ions have a mobility in water at 25 °C of $5.56 \times 10^{-8}\,\mathrm{m^2\,s^{-1}V^{-1}}$.

   (a) Calculate the diffusion coefficient of a copper(II) ion in water at this temperature. [2 marks]

   (b) The viscosity of water at 25 °C is $8.91 \times 10^{-4}\,\mathrm{Pa\,s}$. Calculate the radius of the ion. [2 marks]

   (c) The ionic radius of the copper(II) ion obtained from crystallographic data is 72 pm. Does your value agree with this one? If not, why do you think it might differ? [2 marks]

3. Typical diffusion coefficients for small molecules in water are of the order of $10^{-9}\,\mathrm{m^2s^{-1}}$.

   (a) What value of the radius does this diffusion coefficient imply? Assume that the solvent is water at 25 °C. [2 marks]

   (b) Calculate the diffusion-limited rate constant for typical neutral molecules in water at 25 °C. Report your final answer in $\mathrm{L\,mol^{-1}s^{-1}}$. [3 marks]

   (c) What would the diffusion-limited rate constant be if the two reactants were ions with charges of +1 and −2? The permittivity of water at 25 °C is $6.939 \times 10^{-10}\,\mathrm{C^2N^{-1}m^{-2}}$. [6 marks]

   (d) What if the charges were +1 and +2? [5 marks]