Handin 11

**Introduction for Question 1-2:**

Consider a central ion, i, surrounded by neighbors, j. The j neighbors include all anions and cations in the solution other than ion, i. The Poisson equation for a spherical ion in solution is:

\[ \frac{1}{r} \frac{\partial^2 (r \phi_i(r))}{\partial r^2} = -\frac{\rho(r)}{\varepsilon(r)} \]  

(1)

where \( \rho(r) \) is the charge density of the ions surrounding the central ion, i, in solution. For each of these neighbor ions, j:

\[ \rho_j(r) = q_j \rho(r) = q_j \frac{N_{oj}}{V} e^{-\phi_i(r)q_j} kT \]  

(2)

where \( N_{oj}/V \) is the bulk concentration of the ion in solution. Assume that the solution has only a single electrolyte, with ion charges \( q_+ \) and \( q_- \). Then \( N_{oj} \) is correspondingly \( N_+ \) or \( N_- \). The total charge density is the sum of the charge densities for the anions and the cations:

\[ \rho(r) = \rho_+(r) + \rho_-(r) \]  

(3)

and to maintain an overall neutral solution:

\[ \frac{N_+}{V} q_+ + \frac{N_-}{V} q_- = 0 \]  

(4)

Assuming point charges and a uniform solvent dielectric gives \( \varepsilon(r) = \varepsilon_r \varepsilon_o \), which is no longer a function of distance. Expanding the Boltzmann probability in a Taylor series and keeping only the first two terms gives:

\[ e^{-\phi_i(r)q_j \frac{kT}{q_j}} \approx 1 - \frac{\phi_i(r)q_j}{kT} \]  

(5)

Define

\[ \kappa^2 = \frac{q_+^2}{\varepsilon_r \varepsilon_o kT} \left( \frac{N_+}{V} \right) + \frac{q_-^2}{\varepsilon_r \varepsilon_o kT} \left( \frac{N_-}{V} \right) \]  

(6)

**Question 1:** Show that:

\[ \frac{\partial^2 (r \phi_i(r))}{\partial r^2} = \kappa^2 (r \phi_i(r)) \]  

(7)

**Question 2:** Show that \( \phi_i(r) = \frac{C}{r} e^{-\kappa r} \) is the solution to Eq. 7, for \( C \) a constant.

**Introduction for Questions 3-5:**

The solution to Eq. 7 is the screened Coulomb potential:

\[ \phi_i(r) = \frac{C}{r} e^{-\kappa r} = q_j \frac{4 \pi \varepsilon_0}{r} e^{-\kappa r} \]  

(8)

The charges are discrete ions in solution:

\[ q_i = z_j e \]  

(9)

where \( z_i \) is the integer charge on the ion. Substituting Eq. 9 into Eq. 6 gives:
\[ \kappa^2 = \frac{e^2}{\varepsilon \varepsilon_0 k T} \left( \frac{z^+ (N^+)}{V} + \frac{z^- (N^-)}{V} \right) \]  

We can convert to more useful concentrations units by noting that \( N_i \) is the number of ions in a volume \( V \) in m\(^3\). Also, 1000 L = 1 m\(^3\), and then we can convert to molality. The general formula for converting from molarity to molality applied to a dilute solution is:

\[ m = \frac{c \text{ (1L)}}{1000 \text{mL d_{soln}}} \equiv \frac{c \text{ (1L)}}{d_{soln} \left( \frac{1000 \text{ g}}{1 \text{ kg}} \right)} \tag{2.2.8}(11) \]

Giving:

\[ m_j = \frac{N_j/N_A}{V \text{ 1000 L m}^{-3} \text{ d_{soln}}} \tag{12} \]

where \( d_{soln} \) is the density of the solution in kg L\(^{-1}\), which is equivalent to g mL\(^{-1}\). Note the L m\(^3\) units are necessary for units conversion; the m is meters not the molality. \( N_A \) is Avogadro's number. In dilute solution the solution density is well approximated by the solvent density, \( d_{soln} \equiv d_o \).

**Question 3:** Starting with Eq. 10, show that:

\[ \kappa^2 = \frac{e^2 \times 1000 \text{ L m}^{-3} d_o N_A m^o}{\varepsilon \varepsilon_0 k T} \left( \frac{2 m^+}{m^o} + \frac{2 m^-}{m^o} \right) \tag{13} \]

**Question 4:** Given the definition of ionic strength:

\[ I = \frac{1}{2} \sum_{j=1}^{s} z_j^2 \frac{m_j}{m^o} \tag{14} \]

show from Eq. 13 that:

\[ \kappa = \sqrt{\frac{2 e^2 \times 1000 \text{ L m}^{-3} d_o N_A m^o}{\varepsilon \varepsilon_0 k T} I^{1/2}} \tag{15} \]

**Question 5:** Remember that the Debye length \( r_D = 1/\kappa \). Show that for aqueous solutions of 1:1 unipositive:uninegative electrolytes at concentration \( m \) molal at 298.15 K that

\[ r_D = \frac{305 \text{ pm}}{(m/m^o)^{1/2}} \tag{16} \]

(examples of 1:1 unipositive:uninegative electrolytes include NaCl, KCl, KNO\(_3\), and NH\(_4\)Cl, but not BaSO\(_4\)). In Eq. 16 the constant is given as 305 pm; in your answer give the constant to at least four significant figures. Make sure to give your values for all the constants in Eq. 15 — in other words don’t just say the constants work out to 305 pm (a copy of a spreadsheet would work well).