

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:

$$\frac{1}{r} \frac{\partial^2 (r \phi_i(r))}{\partial r^2} = -\frac{\rho(r)}{\epsilon(r)} \quad (1)$$

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

$$\rho_j(r) = q_j p(r) = q_j \frac{N_{oj}}{V} e^{-\frac{\phi_i(r)q_j}{kT}} \quad (2)$$

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:

$$\rho(r) = \rho_+(r) + \rho_-(r) \quad (3)$$

and to maintain an overall neutral solution:

$$\frac{N_+}{V} q_+ + \frac{N_-}{V} q_- = 0 \quad (4)$$

Assuming point charges and a uniform solvent dielectric gives $\epsilon(r) = \epsilon_r \epsilon_0$, which is no longer a function of distance. Expanding the Boltzmann probability in a Taylor series and keeping only the first two terms gives:

$$e^{-\frac{\phi_i(r)q_j}{kT}} \approx 1 - \frac{\phi_i(r)q_j}{kT} \quad (5)$$

Define

$$\kappa^2 = \frac{q_+^2}{\epsilon_r \epsilon_0 kT} \left(\frac{N_+}{V} \right) + \frac{q_-^2}{\epsilon_r \epsilon_0 kT} \left(\frac{N_-}{V} \right) \quad (6)$$

Question 1: Show that:

$$\frac{\partial^2 (r \phi_i(r))}{\partial r^2} = \kappa^2 (r \phi_i(r)) \quad (7)$$

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:

$$\phi_i(r) = \frac{C}{r} e^{-\kappa r} = \frac{q_j}{4\pi\epsilon_r\epsilon_0 r} e^{-\kappa r} \quad (8)$$

The charges are discrete ions in solution:

$$q_j = z_j e \quad (9)$$

where z_i is the integer charge on the ion. Substituting Eq. 9 into Eq. 6 gives:

$$\kappa^2 = \frac{e^2}{\epsilon_r \epsilon_0 kT} \left(z_+^2 \left(\frac{N_+}{V} \right) + z_-^2 \left(\frac{N_-}{V} \right) \right) \quad (10)$$

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

$$m = \frac{c \text{ (1L)}}{1000 \text{ mL } d_{\text{soln}} - c \text{ (1L)} \mathcal{M}_B} \cong \frac{c}{d_{\text{soln}}} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) \left(\frac{1000 \text{ g}}{1 \text{ kg}} \right) \quad (2.2.8)(11)$$

Giving:

$$m_j = \frac{N_j / N_A}{V \cdot 1000 \text{ L } \text{m}^{-3} d_{\text{soln}}} \quad (12)$$

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, $d_{\text{soln}} \cong d_o$.

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

$$\kappa^2 = \frac{e^2 \cdot 1000 \text{ L } \text{m}^{-3} d_o N_A \text{ m}^\circ}{\epsilon_r \epsilon_0 kT} \left(z_+^2 \frac{m_+}{\text{m}^\circ} + z_-^2 \frac{m_-}{\text{m}^\circ} \right) \quad (13)$$

Question 4: Given the definition of ionic strength:

$$I = \frac{1}{2} \sum_{j=1}^s z_j^2 \frac{m_j}{\text{m}^\circ} \quad (14)$$

show from Eq. 13 that:

$$\kappa = \sqrt{\frac{2 e^2 \cdot 1000 \text{ L } \text{m}^{-3} d_o N_A \text{ m}^\circ}{\epsilon_r \epsilon_0 kT}} I^{1/2} \quad (15)$$

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

$$r_D = \frac{305 \text{ pm}}{(m/m^\circ)^{1/2}} \quad (16)$$

(examples of 1:1 unipositive:uninegative electrolytes include NaCl , KCl , KNO_3 , and NH_4Cl , 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).