

**University of Washington**  
**Department of Chemistry**  
**Chemistry 553**  
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Lecture 4: Electrolyte Solutions: Debye-Huckel Theory

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Text Reading: McQ Ch. 15.1

Comment: Debye-Huckel Theory is NOT a general theory for electrolyte solutions. It does a good job for 1:1 electrolytes of up to 0.01m concentration. With empirical adjustment of parameters concentrations of over 0.1m can be dealt with. We will concentrate on solute-solute interactions...which dominate considerations at moderate concentrations. At infinite dilution solute-solvent interactions become important.

A. Review of Electrostatics: Poisson's Equation

- In a medium of dielectric constant  $\epsilon$ , the electrostatic potential at a point located a distance  $r$  from a charge  $zq$  located at  $r_i$  is

$$\varphi(r) = \sum_i \frac{zq_i}{\epsilon|r-r_i|} \text{ or } \varphi(r_j) = \sum_{i \neq j} \frac{zq_i}{\epsilon|r_j-r_i|} = \sum_{i \neq j} \frac{zq_i}{\epsilon r_{ij}} \quad (4.1)$$

- For a continuous charge distribution...characterized by charge density  $\rho(r)$ ,

$$\varphi(r) = \int_V \frac{\rho(r')}{\epsilon|r-r'|} d^3r' \quad (4.2)$$

- We can apply the Laplacian operator

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{1}{r} \frac{\partial^2}{\partial r^2} r \dots \text{terms in } \theta \text{ and } \phi \text{ to both sides of (4.2)}$$

$$\nabla^2 \varphi(r) = \nabla^2 \left( \int_V \frac{\rho(r')}{\epsilon|r-r'|} d^3r' \right) = -\frac{4\pi}{\epsilon} \rho(r) \quad (4.3)$$

- (4.3) is Poisson's equation, a fundamental equation of electrostatics

$$\nabla^2 \varphi(r) = -\frac{4\pi}{\epsilon} \rho(r) \quad (4.4)$$

B. The Poisson-Boltzmann Equation

- To calculate electrostatic contributions to thermodynamic properties we must determine the electrostatic potential for an electrolyte solution by solving Poisson's equation. In D-H theory an expression for an average charge density is obtained by fixing an ion  $\beta$  at the origin and determining the electrostatic potential at a point  $r$  from  $\beta$ . In actuality the expression we derive for the average charge density omits the contribution from  $\beta$  and only includes contributions from the surrounding ion "atmosphere". Of course, the solvent is treated as a continuous medium with dielectric

constant  $\epsilon$ . We call the average electrostatic potential at a distance  $r$  from  $\beta$  arising from surrounding ions  $\bar{\varphi}_\beta(r)$ . It is an average in the sense that the coordinates of the surrounding ions are averaged.

- The probability that an ion of type  $\alpha$  with charge  $qz_\alpha$  is found at  $r$  relative to a fixed  $\beta$  ion is

$$P_{\alpha\beta}(r) = \exp\left(-\frac{z_\alpha q \bar{\varphi}_\beta(r)}{kT}\right) \quad (4.5)$$

- The number of ions of type  $\alpha$  with charge  $qz_\alpha$  found at  $r$  relative to a fixed  $\beta$  ion is therefore

$$N_{\alpha\beta}(r) = P_{\alpha\beta}(r) \cdot \frac{N_\alpha}{V} = \frac{N_\alpha}{V} \exp\left(-\frac{z_\alpha q \bar{\varphi}_\beta(r)}{kT}\right) \quad (4.6)$$

- The charge density contribution from ions of type  $\alpha$  with charge  $qz_\alpha$  at  $r$  relative to a fixed  $\beta$  ion is therefore

$$\rho_\alpha(r) = \frac{qN_\alpha z_\alpha}{V} \exp\left(-\frac{z_\alpha q \bar{\varphi}_\beta(r)}{kT}\right) \quad (4.7)$$

- The total average charge density is thus

$$\bar{\rho}(r) = \sum_\alpha \rho_\alpha(r) = \sum_\alpha \frac{qN_\alpha z_\alpha}{V} \exp\left(-\frac{z_\alpha q \bar{\varphi}_\beta(r)}{kT}\right) \quad (4.8)$$

- (4.4) and (4.8) are combined to yield the Poisson-Boltzmann equation

$$\nabla^2 \bar{\varphi}_\beta(r) = -\frac{4\pi}{\epsilon} \bar{\rho}(r) = -\frac{4\pi}{\epsilon} \sum_\alpha \frac{qN_\alpha z_\alpha}{V} \exp\left(-\frac{z_\alpha q \bar{\varphi}_\beta(r)}{kT}\right) \quad (4.9)$$

- Given the fact that the problem has spherical symmetry we can write:

$$\nabla^2 \bar{\varphi}_\beta(r) = \frac{1}{r} \frac{d^2}{dr^2} (r \bar{\varphi}_\beta(r)) = -\frac{4\pi}{\epsilon} \sum_\alpha \frac{qN_\alpha z_\alpha}{V} \exp\left(-\frac{z_\alpha q \bar{\varphi}_\beta(r)}{kT}\right) \quad (4.10)$$

- (4.10) is a nonlinear second order differential equation. It can be solved analytically in special cases. In the dilute solution limit  $z_\alpha q \bar{\varphi}_\beta(r) \ll kT$ , and the exponential can be expanded in a series....

$$\exp\left(-\frac{z_\alpha q \bar{\varphi}_\beta(r)}{kT}\right) \approx 1 - \frac{z_\alpha q \bar{\varphi}_\beta(r)}{kT} \quad (4.11)$$

- Combining (4.10) and (4.11) we obtain the linearized P-B equation:

$$\nabla^2 \bar{\varphi}_\beta(r) = \frac{1}{r} \frac{d^2}{dr^2} (r \bar{\varphi}_\beta(r)) = -\frac{4\pi}{\epsilon} \sum_\alpha \frac{qN_\alpha z_\alpha}{V} \left(1 - \frac{z_\alpha q \bar{\varphi}_\beta(r)}{kT}\right) \quad (4.12)$$

- Solving the linearized P-B equation is of fundamental importance in the theory of electrolyte solutions.