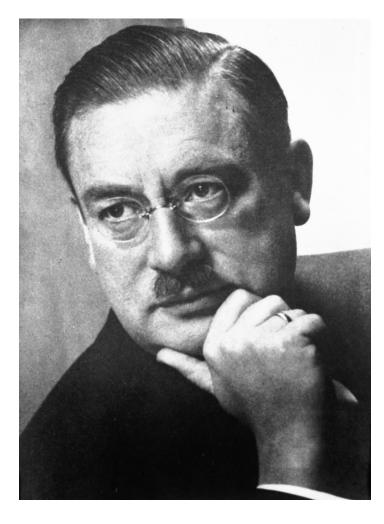
STATISTICAL MOLECULAR THERMODYNAMICS

Christopher J. Cramer

Video 11.7

Debye-Hückel Theory 1

ELECTROLYTES



How do ions distribute themselves in dilute solutions?

Let's assume
that the ions are
point charges
and the solvent
can be
represented as
a dielectric
continuum



Peter Debye

Erich Hückel

WHERE ARE THE IONS?

Consider a central ion, i. Near to i, the density of ions of opposite charge will be enriched, while the density of ions of like charge will be depleted (for simplicity, we'll consider only a single type of anion and a single type of cation). At equilibrium, we should see a Boltzmann distribution, so that the charge density (charge per unit volume) ρ at a distance r from ion i will be:

$$\rho_{i}(r) = \sum_{j=+,-} q_{j}C_{j}e^{-q_{j}\psi_{i}(r)/k_{B}T}$$

$$= electrostatic potential from ion i$$

$$= charge$$

$$= bulk number density (concentration)$$

Self-assessment

First, from intuition, what do you expect the charge density to be very, very far from ion i? Next, use the equation below to prove that.

$$\rho_i(r) = \sum_{j=+,-} q_j C_j e^{-q_j \psi_i(r)/k_B T}$$

Self-assessment Explained

Very far from ion i we would expect no charge density, i.e., no preference for positive vs. negative charge, because it is too far away to exert an influence. In the below equation, that's equivalent to $\psi = 0$.

$$\rho_{i}(r) = \sum_{j=+,-} q_{j}C_{j}e^{-q_{j}\psi_{i}(r)/k_{B}T}$$

$$= \sum_{\lim \psi \to 0} \sum_{j=+,-} q_{j}C_{j}$$
by electroneutrality
$$= 0$$

THE POISSON EQUATION

The Poisson equation fundamentally relates a charge density in a dielectric medium to an electrostatic potential. In a spherically symmetric system, the Poisson equation is

$$\frac{1}{r^{2}} \frac{d}{dr} \left[r^{2} \frac{d\psi_{i}(r)}{dr} \right] = -\frac{\rho_{i}(r)}{\varepsilon_{0} \varepsilon}$$

$$\nabla^{2} \psi$$

$$\text{dielectric constant of medium (solvent)}$$

Assuming a weak potential, so that we may truncate the exponential in the charge density, we have

$$\rho_{i}(r) = \sum_{j=+,-} q_{j} C_{j} e^{-q_{j} \psi_{i}(r)/k_{B}T} \approx \sum_{j=+,-} q_{j} C_{j} - \sum_{j=+,-} q_{j} C_{j} \frac{q_{j} \psi_{i}(r)}{k_{B}T} \\
= -\frac{\psi_{i}(r)}{k_{B}T} \sum_{j=+,-} q_{j}^{2} C_{j}$$

THE SCREENED POTENTIAL

Solution of the Poisson equation with that density leads to a general solution of the differential equation of

$$\psi_i(r) = \frac{B}{r}e^{\kappa r} + \frac{A}{r}e^{-\kappa r}$$
 where $\kappa^2 = \frac{1}{\varepsilon_0 \varepsilon k_{\rm B}T} \sum_{j=+,-} q_j^2 C_j$

For the potential to go to zero at large r, if must be true that B=0. For the potential to go to Coulomb's Law at infinite dilution ($\kappa=0$), it must be true that:

 $\begin{array}{c} \textit{number} \\ \textit{density} \\ \textit{(i.e., } c_j N_A \textit{)} \end{array}$

$$A = \frac{q_i}{4\pi\varepsilon_0\varepsilon}$$
 and thus: $\psi_i(r) = \frac{q_i e^{-\kappa r}}{4\pi\varepsilon_0\varepsilon r}$

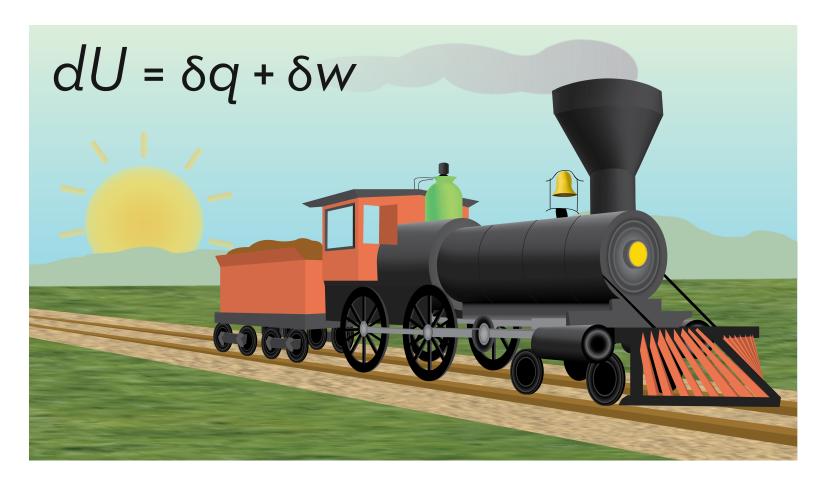
THE INVERSE DEBYE LENGTH

Note that κ has units of inverse distance. The term involving κ in the numerator of the potential indicates that the potential of ion i is increasingly "screened" with increasing ionic strength.

$$\psi_i(r) = \frac{q_i e^{-\kappa r}}{4\pi \varepsilon_0 \varepsilon r}$$

$$\kappa^2 = \frac{1}{\varepsilon_0 \varepsilon k_B T} \sum_{j=+,-} q_j^2 C_j$$

With a little calculus, one can show that κ^{-1} is the distance at which there is the highest probability of finding a counterion vs an ion of like charge around ion *i*. Note that for a given concentration of a 1:1 electrolyte (like NaCl), that distance would shrink by a factor of 2 for a 2:2 electrolyte (like CaSO₄). Thus, the counterion charge cloud "shrinks" for more highly charged species and screens them more rapidly.



Next: Debye-Hückel Theory 2