Ionic Solutions and Electrochemistry

- Ionic Solutions are not ideal.
  - Freezing point depression due to ionic compounds dissolved in a polar solvent often observed to be larger than predicted by Raoult's Law of freezing point depression, even when dissociation is taken into account.
  - Highly concentrated aqueous solutions of ionic compounds have high density and high viscosity.
  - Solvation of ionic compounds is rarely thermoneutral.
- Svante Arrhenius (1859-1927) made a significant contribution to our understanding of the behaviour of ionic solutions (in addition to barely passing his Ph. D., coming up with the idea of Arrhenius activation energy, Arrhenius acids and bases and early theories of greenhouse gases, becoming the first Physical Chemistry professor in Sweden, founding the Stockholm Physical Society, and winning a Nobel Prize).

  - Arrhenius observed that a solution conducted electricity even though the solid or gaseous solute did not.
  - Hypothesized in his doctoral thesis that solutions contained ions.
- Properties of ionic solutions:
  - Conduct electricity
  - Charge neutrality (moles of +ve charge = moles of -ve charge).
- Coulomb's Law describes the forces between charges:

$$F = \frac{Q_1 Q_2}{4\pi\varepsilon_0\varepsilon_r r^2}$$

  where:

  - F is the force between 1 and 2 (newtons or N).
  - Q_1 is the charge on 1 (coulombs or C)
  - Q_2 is the charge on 2 (coulombs or C)
  - ε_0 is the permittivity of free space (Farad per meter or F m^{-1}: 1 F = 1 C^2 N^{-1} m$^-$1)

- ε_r is the relative permittivity (also known as the dielectric constant) which is dimensionless. For a perfect vacuum it is 1. For real substances it is > 1. For water it is 78.
- r is the separation between 1 and 2 (meters or m).

- A farad is also equivalent to a mole of unit charges.
    - A single charge is 1.602×10^{-19} coulombs.
    - Therefore 1 F = 1.602×10^{-19} C $\times$ 6.022 $\times$ 10^{23} mol^{-1} = 96485 C mol^{-1}
    - From analysis of units for the farad, it may also be shown that 1 C = 96485 J mol^{-1}.
- How far apart are ions in solution relative to the spacing in a solid crystal?
    - Consider solid NaCl with a density of 2.2 g cm^{-3}.
    - The molar mass is 58.5 g mol^{-1} giving a molar density of 3.76×10^{-2} mol cm^{-3} or 37.6 mol/L.
    - The spacing in a 1 M solution is:

$$(37.6)^{1/3} = 3.4$$

times that in the solid.

  - The spacing reduces the force by a factor of 3.4^2.
  - The nature of the solvent further reduces the force by a factor of 78 (the dielectric constant or relative permittivity).
  - Therefore the forces between the ions has been reduced by a factor of 900.

- Instead of interacting with each other directly, ions in solution interact through the electronic clouds of the solvent.
  - It is the resulting screening of the ion charges by the solvent that is represented by the dielectric constant.
- Ionic solutions are nonideal.
  - Solvents tend to be polar and orient themselves around the ionic solute.
  - Ions of opposite charge "cluster" while an ideal solution assumes that the solute species are infinitely separated.
- Consider Ba^{2+} and Cl^- which as associated as $BaCl^+$.

    - Because just coulombic attractions are involved, this situation is to be distinguished from ionic complexes involving anionic ligands.

- Such ionic complexes can form in aqueous solutions of AgI.
    - In a saturated AgI solution are present $[Ag^+] = [I^-] = 6.7 \times 10^{-9}$ M and [AgI] $= 6.0 \times 10^{-9}$ M.
    - Also present are AgI_2^- and Ag_2I^+.
- Now consider solubility of AgI in 1 M KI.
    - The "common ion" effect would predict a lower solubility of AgI than in pure water.
    - Increased solubility is observed.
    - This is due to the formation of complexes of Ag^+ and Ag_2^{2+} with I^-.
    - Ions found in the solution are: K^+, I^-, AgI_2^-, AgI_3^{2-}, AgI_4^{3-}, $Ag_2I_6^{4-}$, and $Ag_3I_8^{4-}$.
    - Not found is any appreciable Ag^+
- If AgI is dissolved in 1 M $AgNO_3$, ions formed include: Ag^+, Ag_2I^+, Ag_3I^{2+}, Ag_4I^{3+} .
    - But negligible I^- is found.

- Our discussion will continue with simple electrolytes that do not form complexes.
- We need to define chemical potential for ions solvated in water.
  - Positive and negative ions must coexist solution.
  - Therefore *mean ionic* quantities must be defined.
- Consider the general electrolyte $\mathrm{C}_{v+}\mathrm{A}_{v-}$ which dissociates into:
  - Cation C^{z+} with charge $Q_+ = z_+ e$
  - Anion A^{z-} with charge $Q_- = z_- e$

$$\mathrm{C}_{v+}\mathrm{A}_{v-} \rightarrow v_+ \ \mathrm{C}^{z+} + v_- \ \mathrm{A}^{z-}$$

- For example:

$$\mathrm{BaCl}_2 \rightarrow \mathrm{Ba}^{2+} + 2 \ \mathrm{Cl}^-$$

  has:
  - $v_+ = 1$
  - $v_- = 2$
  - $z_+ = 2$
  - $z_- =$-1

- Define the stoichiometric total of particles as $v = v_+ + v_-$
- The stoichiometric molality of each ion when the analytic molality of the solid electrolyte is m_i is:

$$m_+ = v_+ m_i, \quad m_- = v_- m_i$$

  - Therefore, in the case of $BaCl_2$, $v = 3$; $m_+ = m_i$ and $m_- = 2m_i$

- Ionic strength is defined in terms of molality:

$$I = \frac{1}{2} \sum_{j=1}^{\text{all ions}} m_j z_j^2$$

  - Therefore the ionic strength for $BaCl_2$ is:

$$I = \frac{1}{2}\left(2^2 m_i + 1^2 2m_i\right) = 3m_i$$

- Mean ionic molality is defined as:

$$m_\pm = \left[m_+^{v+} m_-^{v-}\right]^{1/v} = m_i\left(v_+^{v+} v_-^{v-}\right)^{1/v}$$

  - Therefore the mean ionic molality for $BaCl_2$ is:

$$m_\pm = \left[(m_i)(2m_i)^2\right]^{1/3} = 4^{1/3} m_i$$

- The mean ionic activity coefficient is defined as:

$$\gamma_{\pm} = \left[\gamma_{+}^{v+}\gamma_{-}^{v-}\right]^{1/v}$$

- Recall the expression for chemical potential expressed in terms of activity:

$$\mu_i(aq) = \mu_i^{\circ} + RT\ln a_i$$

where a_i is the activity of electrolyte i

$$a_i = \gamma_i m_i$$

  - The reference state m_i° is 1 mol / kg (solvent).

- Consider the ionic dissociation equilibrium:
$\mathrm{C}_{v+}\mathrm{A}_{v-}(\mathrm{aq}) \rightleftharpoons v_+\ \mathrm{C}^{z+}(\mathrm{aq}) + v_-\ \mathrm{A}^{z-}(\mathrm{aq})$
  - The equilibrium condition means that:

$$\mu_i(aq) = v_+\mu_+(aq) + v_-\mu_-(aq)$$

  - From the expression for chemical potential:

$$\mu_+(aq) = \mu_+^{\circ} + RT\ln a_+$$

$$\mu_-(aq) = \mu_-^{\circ} + RT\ln a_-$$

    may be defined, even though they cannot be measured individually.

- Therefore:

$$\mu_i(aq) = v_+\mu_+^\circ + v_-\mu_-^\circ + RT\ln\left[\gamma_+^{v+}\gamma_-^{v-}m_+^{v+}m_-^{v-}\right]$$

$$= \mu_i^\circ + RT\ln\left(\gamma_\pm m_\pm\right)^v$$

where $m_\pm \rightarrow 0$ as $\gamma_\pm \rightarrow 1$.

  - v is determined by stoichiometry
  - $m_\pm$ is controlled by experiment
  - μ_i° is the standard state which is formally defined as:

$$\mu_i^\circ = \lim_{m_\pm\rightarrow 0}\left[\mu_i - RT\ln\left(\gamma_\pm m_\pm\right)^v\right]$$

  - Therefore all variation in μ_i is due to variation in $\gamma_\pm$.

- $\gamma_\pm$ can be evaluated by calculation or extrapolated from measurement.
- Experimental approaches include:
  - Electrochemical measurements
  - Solubility measurements

  - Measurements of colligative properties
  - Measurements of solute vapour pressure
  - Measurement of distribution of solute between two immiscible solvents
  - Ultracentrifuge solid sedimentation methods.

- Consider the solubility equilibrium of an electrolyte:

  $\mathrm{C}_{v+}\mathrm{A}_{v-}(\mathrm{s}) \rightleftharpoons v_+ \ \mathrm{C}^{z+}(\mathrm{aq}) + v_- \ \mathrm{A}^{z-}(\mathrm{aq})$

- At equilibrium, the chemical potential is uniform:

$$\mu(\text{solid } C_{v+}A_{v-}) = \mu(C_{v+}A_{v-} \text{ in solution})$$
$$= \mu(\text{ions in solution})$$

  - But

$$\mu(\text{ions}) = v_+\mu_+^\circ + v_-\mu_-^\circ + RT\ln\left(\gamma_\pm m_\pm\right)^v$$
$$-\mu(\text{solid}) + \left[v_+\mu_+^\circ + v_-\mu_-^\circ\right] = -RT\ln\left(\gamma_\pm m_\pm\right)^v$$

  - Since $\mu(\text{solid}) = \mu^\circ(\text{solid})$ because the solid is in the standard state at standard pressure,

$$\Delta_r\overline{G}^\circ = -\mu(\text{solid}) + \left[v_+\mu_+^\circ + v_-\mu_-^\circ\right]$$

- Since

$$K_{eq} = (\gamma_{\pm} m_{\pm})^{v}$$

then

$$\Delta_r \overline{G}^{\circ} = -RT \ln K_{eq}$$

  - If $\Delta_r \overline{G}^{\circ}$ is known, then a measurement at some $m_{\pm}$ will give the corresponding $\gamma_{\pm}$.

- Measurements involving colligative properties must take into account nonideal chemical potentials for both the solvent and the solute.

- Consider the case of vapour pressure measurements for an insoluble solute (which many ionic electrolytes are) in a volatile solvent.

  - Measurements of vapour pressure will give the fugacity of the solvent.

  - Division of this by the fugacity of pure solvent in the reference state will give the activity of the solvent.

  - Usually the approximation that $f_i = P_i$ is valid if the vapour pressure is low at the temperature of the measurement.

- Determination of the solute activity relies on the Gibbs-Duhem equation:

$$VdP - SdT - \sum_{i=1}^{c} n_i d\mu_i = 0$$

- For a solvent, solute system at constant temperature and pressure, this becomes:

$$n_s d\mu_s + n_i d\mu_i = 0$$

Therefore at equilibrium, solvent vapour pressure measurments will determine the activity of the solute.

- There exist some ionic solutes that do have vapour pressure, such as the hydrogen halides.
  - The vapour pressure of HCl has been measured directly.
  - At equilibrium, chemical potential of HCl in the solution equals the chemical potential of HCl above the solution.

$$\mu(\mathrm{HCl(g),\ over\ solution}) = \mu(\mathrm{HCl(aq),\ in\ solution})$$

which may be rewritten as:

$$\mu^\circ(g) + RT\ln P_{HCl} =$$
$$\mu^\circ(H^+(aq)) + \mu^\circ(Cl^-(aq)) + RT\ln(\gamma_\pm m_\pm)^2$$

or

$$RT \ln \left[\frac{P_{HCl}}{(\gamma_{\pm} m_{\pm})^2} \right] = \Delta\mu^{\circ}$$

at constant T and P.

- But

  $$\Delta\mu^{\circ} = \mu^{\circ}(H^{+}) + \mu^{\circ}(Cl^{-}) - \mu^{\circ}(g)$$

  Therefore the quantity in the square brackets is equivalent to the equilibrium coefficient.

  $$K = \frac{P_{HCl}}{(\gamma_{\pm} m_{\pm})^2}$$

  - Because $\gamma_{\pm} \rightarrow 1$ as m$_{\pm} \rightarrow 0$, then as m$_{\pm} \rightarrow 0$, $P_{HCl}/m_{\pm}^2 \rightarrow K$
  - But K cannot be measured in this limit because P_{HCl} becomes too low to measure.

- Distribution between two immiscible solvents is not practical.
  - If the two solvents are immiscible then at least one of them will not support measurable amounts of electrolyte.

- The various measurements will permit the evaluation of $\gamma_\pm$ as a function of $m_\pm$
  - Some results are shown in Figures 10.2 and 10.3
- Generally $\gamma_\pm$ decreases from its value at $m_\pm = 0$ and then may either increase or continue to decrease.
  - Values of $\gamma_\pm$ that are large at high concentration indicate strong hydration of the ion.
  - Values of $\gamma_\pm$ that are moderately small at high concentration indicate transient association.
  - Values of $\gamma_\pm$ that are very small at high concentration indicate the formation of stable complex ions.

Debye Hückel Theory

- Debye Hückel theory starts with dilute solutions of simple electrolytes.
- Assume:

- The solute is completely dissociated.
- The solvent is a continuous and uniform fluid with the relative permittivity ε_r.
- Competing with the ionic forces is the Brownian motion of the solvent.
- The ion concentration is low.
- All nonideal behaviour is due to the electrostatic interaction of the ions in their final equilibrated configuration.

- These assumptions give rise to the limiting-law expression:

$$\ln \gamma_{\pm} = \frac{e^3 (2N_A \rho_s)^{1/2}}{8\pi} \left(\frac{N_A}{\varepsilon_0 \varepsilon_r RT} \right)^{3/2} z_+ z_- I^{1/2}$$

where ρ_s is the density of the solvent and I is the ionic strength.

- If water is the solvent and the temperature is 25.0° C then:

$$\frac{e^3 (2N_A \rho_s)^{1/2}}{8\pi} \left(\frac{N_A}{\varepsilon_0 \varepsilon_r RT} \right)^{3/2} z_+ z_- I^{1/2}$$

$$= 1.174 z_+ z_- (I/\text{mol kg}^{-1})^{1/2}$$

- Note that only the ionic charges are in the equation and that the chemical identity of the electrolyte is not involved.
- This means that Debye-Hückel predicts the same mean ionic activity for HCl, LiF, CsI, and NH_4NO_3.

- The Debye-Hückel limiting law works well for electrolytes that
  - Dissociate into singly charged ions and have I less than 0.07 mol kg^{-1}.
  - Dissociate into multiply charged ions and have I less than 0.001 mol kg^{-1}.
- The Debye-Hückel limiting law has been verified for solvents other than water.
- The Debye-Hückel limiting law will always predict $\gamma_{\pm} < 1$.

Derivation of the Debye Hückel Law

- Consider each of the assumptions and the equations that arise from them.

- Assumption 1: The solute is completely dissociated.

  - Consider the solute of type i at concentration c_i in mol L^{-1}. In terms of $\overline{N}_i$, the *average* number density of ions per cubic meter, this becomes:

$$\overline{N}_i^\circ = N_A \overline{n}_i$$

  where

$$\overline{n}_i = c_i (1000 \text{ L m}^{-3})$$

  - If there were no forces between ions, then the actual density of ions would be uniform. Because there are forces between ions, the number density of ions is not uniform.

  - There is a deviation $\overline{N}_i(r)$ from the uniform $\overline{N}_i^\circ$ that accounts for the nonideal behaviour of ionic solutions.

  - $\overline{N}_i(r)$ is defined with respect to a reference ion.

- A charge density function ($\rho(r)$) may be defined with respect to the distance r from the reference ion.

$$\rho(r) = \sum Q_i \overline{N}_i(r)$$

- $\overline{N}_i(r)$ is determined from statistical mechanics, taking into account the competition of thermal energy and electrostatic energy and giving the Boltzmann expression:

  $$\overline{N}_i(r) = \overline{N}_i^\circ \exp\left(-\frac{Q_i\Psi(r)}{k_B T}\right)$$

  where $\psi(r)$ is the electrostatic potential at distance r from the reference ion and is determined from classical electrostatics.

- For a spherical symmetric distribution around the reference ion this gives Poisson's equation:

  $$\frac{1}{r}\frac{d^2[r\Psi(r)]}{dr^2} = -\frac{\rho(r)}{\varepsilon}$$

  where $\varepsilon = \varepsilon_0\varepsilon_r$

- Now apply a simplification:
  - Assume that $(Q_i\Psi(r)/k_B T)$ is sufficiently small that the exponential may be replaced by the power series truncated at the first order term:

    $$\overline{N}_i(r) = \overline{N}_i^\circ \left[1 - \frac{Q_i\Psi(r)}{k_B T}\right]$$

- Substituting into the expression for $\rho(r)$ gives:

$$\rho(r) = \sum_i Q_i \overline{N}_i^\circ \left[1 - \frac{Q_i \Psi(r)}{k_B T}\right] = -\frac{\Psi(r)}{k_B T} \sum_i Q_i^2 \overline{N}_i^\circ$$

since

$$\sum_i Q_i \overline{N}_i^\circ = 0$$

due to charge balance.

- The differential equation becomes:

$$\frac{d^2[r\Psi(r)]}{dr^2} = r\rho(r) \left(\frac{\sum_i Q_i^2 \overline{N}_i^\circ}{\varepsilon k_B T}\right) = \frac{r\Psi(r)}{r_D^2}$$

where r_D is the Debye length, the distance of maximum ion density around the reference ion.

$$r_D = \frac{3.04 \mathring{A}}{(c/\text{mol L}^{-1})^{1/2}}$$

- Is the assumption that $(Q_i \Psi(r)/k_B T)$ is small justified?
  - $\Psi \cong e/4\pi\varepsilon r_D$

- $r_D \cong 10\mathring{A}$ ($c \cong 0.1$ M).
- $Q \cong e$
- $T \cong 300K$

gives $(Q_i\Psi(r)/k_BT) = 0.7$

- Therefore this approximation will be valid for concentrations under 10^{-3} M.

- With the approximation, the differential equation has exact analytical solutions of the form:

$$\Psi(r) = A\frac{\exp(-r/r_D)}{r} + B\frac{\exp(+r/r_D)}{r}$$

where the values of A and B arise from the boundary conditions.

  - One boundary condition is that the electrostatic potential asymptotically approaches zero as $r \to \infty$. It is this condition that make B zero.
  - Another boundary condition is that the smallest r that occurs is an ionic radius a. This gives:

$$\Psi(r) = \frac{Q^\circ}{4\pi\varepsilon r} + \phi$$

when $r \leq a$.

  - A third condition is that there is continuity at $r = a$ of both $\Psi(r)$ and the electric field, $-d\Psi(r)/dr$.

- The boundary conditions give:

$$A = \frac{Q^\circ \exp(a/r_D)}{4\pi\varepsilon(1 + a/r_D)}$$

and

$$\phi = -\frac{Q^\circ}{4\pi\varepsilon(1 + a/r_D)}$$

- The Debye Hückel limiting law may be shown from this by starting with the ideal situation in which there is no charge interaction, then "turning the charge on" to determine the deviation from ideality.