

1st Year Thermodynamic Lectures
Dr Mark R. Wormald

Solution thermodynamics :-

Lecture 1. Behaviour of ideal solutions (and solvents). Definition of ideality. Solvent in dilute solutions, colligative properties, osmotic pressure.

Lecture 2. Behaviour of non-ideal solutions (and solutes). Definition of non-ideality. Activities and activity coefficients.

Lecture 3. Behaviour of ionic solutions I. Thermodynamics of hydration. Introduction to Debye-Hückel Theory.

Lecture 4. Behaviour of ionic solutions II. Result of Debye-Hückel Theory, ionic strength. More concentrated ionic solutions.

BIBLIOGRAPHY

N.C. Price, R.A. Dwek, R.G. Ratcliffe and M.R. Wormald (2001) "Principles and Problems in Physical Biochemistry for Biochemists", pub. Oxford – *the standard Oxford 1st year biochemists text*.

E.B. Smith, "Basic Chemical Thermodynamics", pub. Oxford – *the standard Oxford 1st year chemists' text, slightly more advanced and very good*.

J. Robbins, "Ions in solution (2): an introduction to electrochemistry", pub. Oxford – *the standard 'Oxford 1st year chemists' text on electrochemistry, again slightly more advanced and very good*.

APPLICATION OF THERMODYNAMICS

As we have seen, the ideas / concepts of thermodynamics are very general, they do not depend on the nature of the system.

In order to apply thermodynamics to chemical systems we need to combine the thermodynamic equations with a model of the interactions present in the system.

If this works then the model is an *adequate description* of the system for the *properties we are interested in*.

If this does not work, then the model does not fully describe the important features and we need to refine our model.

As we shall see, the complexity of the model required depends on the property we are interested in. For example;

Osmotic pressure of
a protein solution

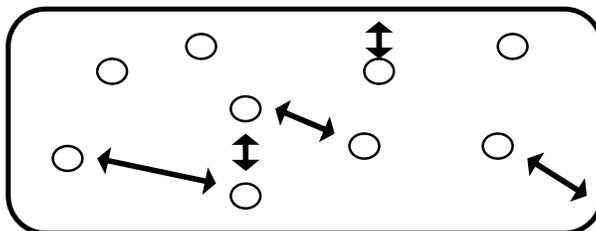
requires a very simple model

Solubility of a
protein in solution

requires a much more complex
model

AN IDEAL GAS

Physical model: The molecules in an ideal gas behave as a set of non-interacting point masses. The only interactions that occur are collisions between the molecules and the walls of the vessel. The number and force of these collisions give rise to the properties pressure and temperature.



Mathematical model:

$$PV = nRT$$

where P is pressure, V is volume, n is number of moles present, T is temperature and R is the gas constant.

Thermodynamic model:

$$G = G^\circ + RT \ln (P/P^\circ)^n$$

Derivation of G for an ideal gas:

$$G = H - TS \quad ; \quad H = U + PV \quad ; \quad \delta U = q + w \quad ; \quad T\delta S = q \quad ; \quad -P\delta V = w$$

Substituting and taking a small increment gives;

$$G = U + PV - TS \quad \Rightarrow \quad \delta G = \delta U + P\delta V + V\delta P - T\delta S - S\delta T$$

$$\delta G = q + w - w + V\delta P - q - S\delta T = V\delta P - S\delta T$$

At constant temperature, $\delta T = 0$ and so $\delta G = V\delta P$.

$$PV = nRT \quad : \quad V = nRT/P \quad \Rightarrow \quad \delta G = nRT/P \delta P$$

Integration gives

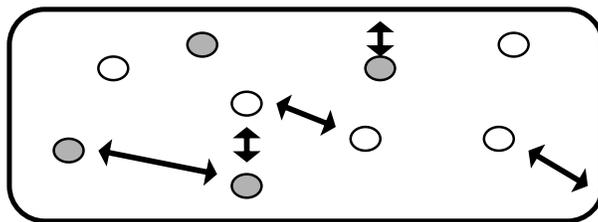
$$\int_{G^\circ}^G dG = nRT \int_{P^\circ}^P \frac{1}{P} dP$$

$$G - G^\circ = nRT (\ln(P) - \ln(P^\circ))$$

$$G = G^\circ + RT \ln\left(\frac{P}{P^\circ}\right)$$

A MIXTURE OF IDEAL GASES

Physical model: The molecules in a mixture of ideal gases behave as a set of non-interacting point masses, the only interactions that occur being collisions. One molecule cannot tell what type of neighbour it has (they do not attract or repel) and so its chemical properties are independent of the types of other species present.



Mathematical model:

$$P_i = P x_i \quad : \quad x_i = n_i/N_{\text{total}}$$

where P is total pressure, P_i is the partial pressure of component i and x_i is the mole fraction of i (number of moles of i divided by total number of moles).

[For instance, if only 25% of the molecules are of type i , then a quarter of the total collision with the vessel wall will involve i molecules and thus i molecules will contribute a quarter of the total pressure, $P_i = \frac{1}{4} P$.]

Thermodynamic model:

$$\mu_i = \mu_i^\circ + RT \ln(P_i/P^\circ)$$

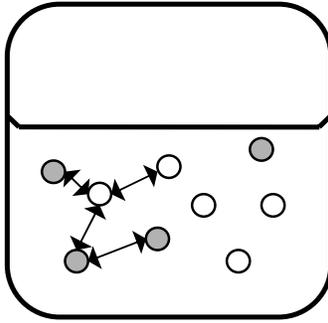
AN IDEAL SOLUTION

Physical model: The molecules in a liquid must interact (otherwise it would not be a liquid). In an ideal solution, all the molecules present interact identically. One molecule cannot tell what type of neighbour it has (they attract and repel equally) and so its chemical properties are independent of the types of other species present.

Mathematical model:

$$P_i = P_i^* x_i$$

where P_i^* is the vapour pressure of the pure liquid i , P_i is the partial vapour pressure of the component i in solution and x_i is the mole fraction of i . This is Raoult's Law.

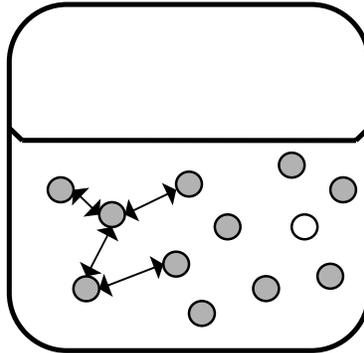


Thermodynamic model:

$$\mu_i(\text{solu}) = \mu_i^\circ(l) + RT \ln(x_i) = \mu_i^\circ(l) + RT \ln\left(\frac{[i]}{[i]^\circ}\right)$$

DILUTE SOLUTIONS

In a pure liquid (which is ideal by definition, all molecules interact identically), a solvent molecule only interacts with other solvent molecules. In a very dilute solution, a solvent molecule spends almost all the time interacting with other solvent molecules and hence behaves the same as in a pure liquid.



Adding another solute molecule;

1. decreases the concentration of the solvent slightly.
2. does not increase significantly the time that a solvent molecule spends interacting with solute molecules.

This meets the criteria for an ideal solution, i.e. the chemical properties of a given solvent molecule do not vary with composition in dilute solutions.

The chemical potential of the solvent is given by

$$\mu_{\text{solv}} = \mu_{\text{solv}}^\circ + RT \ln\left(\frac{[\text{solv}]}{[\text{solv}]^\circ}\right)$$

The presence of any solute will lower the concentration of the solvent,

$$[\text{solv}] < [\text{solv}]^\circ$$

and

$$\ln([\text{solv}]/[\text{solv}]^\circ) < 0.$$

Thus addition of solute will lower the chemical potential of the solvent, i.e. the solvent will be more stable in a dilute solution than in the pure liquid.

COLLIGATIVE PROPERTIES

These are properties of the system that depend only on the number of solute molecules present not on the type of solute molecules. There are three major colligative properties:

- Depression of freezing point.
- Elevation of boiling point.
- Solvent diffusion/osmotic pressure.

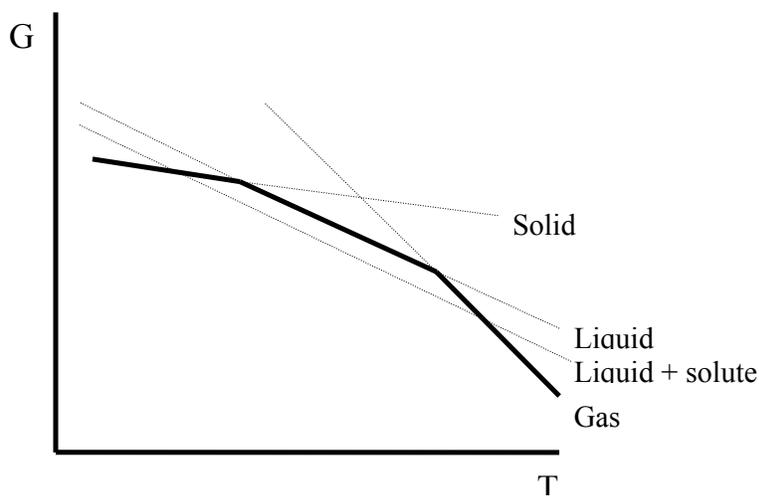
Only the third of these, osmotic pressure, is very significant in biological systems.

CHANGES IN FREEZING AND BOILING POINTS

Solid $\mu_{\text{solv}}(\text{s}) = \mu_{\text{solv}}^{\circ}(\text{s})$

Liquid $\mu_{\text{solv}}(\text{l}) = \mu_{\text{solv}}^{\circ}(\text{l}) + RT \ln([\text{solv}]/[\text{solv}]^{\circ})$

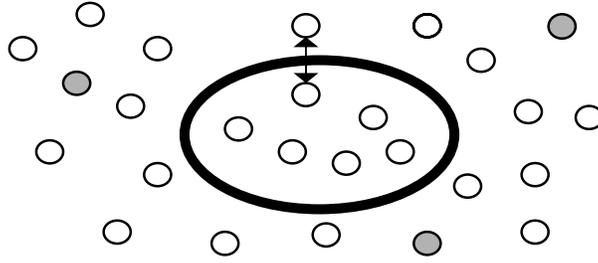
Gas $\mu_{\text{solv}}(\text{g}) = \mu_{\text{solv}}^{\circ}(\text{g}) + RT \ln(P_{\text{solv}}/P^{\circ}) = \mu_{\text{solv}}^{\circ}(\text{g})$ at 1 atms



Thus, the presence of the solute lowers the chemical potential of the solvent in the liquid phase, but does not effect the chemical potential in any other phase. The freezing point will be lowered and the boiling point raised.

OSMOTIC PRESSURE

Consider pure solvent (e.g. water) contained inside a bath of solvent + solute (e.g. water + NaCl) by a barrier permeable only to the solvent (e.g. a cell membrane).



Inside	Pure liquid	$\mu_{\text{solv}}^{\text{In}}(\text{l}) = \mu_{\text{solv}}^{\circ}(\text{l})$
Outside	Solution	$\mu_{\text{solv}}^{\text{Out}}(\text{l}) = \mu_{\text{solv}}^{\circ}(\text{l}) + RT \ln([\text{solv}]^{\text{Out}}/[\text{solv}]^{\circ})$

As $[\text{solv}]^{\text{Out}} < [\text{solv}]^{\circ}$,

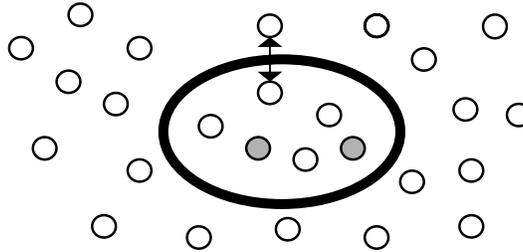
$$\mu_{\text{solv}}^{\text{In}}(\text{l}) > \mu_{\text{solv}}^{\text{Out}}(\text{l})$$

At equilibrium,

$$\mu_{\text{solv}}^{\text{In}}(\text{l}) = \mu_{\text{solv}}^{\text{Out}}(\text{l})$$

Solvent transfer will occur from in to out until $[\text{solv}]^{\text{Out}}$ the same as $[\text{solv}]^{\text{In}}$. This can never be reached, thus solvent transfer will continue until there is no solvent remaining on the inside.

Consider the reverse situation, pure solvent + solute (e.g. water + protein) contained inside a bath of solvent (e.g. water) by a barrier permeable only to the solvent (e.g. a cell membrane).



Inside	Solution	$\mu_{\text{solv}}^{\text{In}}(\text{l}) = \mu_{\text{solv}}^{\circ}(\text{l}) + RT \ln([\text{solv}]^{\text{In}}/[\text{solv}]^{\circ})$
Outside	Pure liquid	$\mu_{\text{solv}}^{\text{Out}}(\text{l}) = \mu_{\text{solv}}^{\circ}(\text{l})$

As $[\text{solv}]^{\text{In}} < [\text{solv}]^{\circ}$,

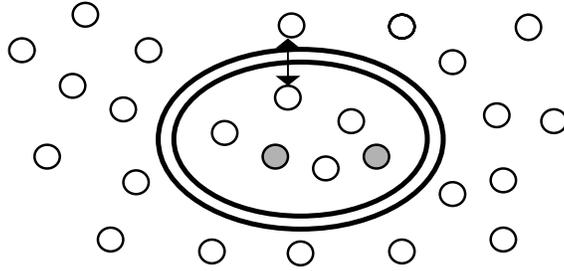
$$\mu_{\text{solv}}^{\text{In}}(\text{l}) < \mu_{\text{solv}}^{\text{Out}}(\text{l})$$

At equilibrium,

$$\mu_{\text{solv}}^{\text{In}}(\text{l}) = \mu_{\text{solv}}^{\text{Out}}(\text{l})$$

Solvent transfer will occur from out to in until $[\text{solv}]^{\text{In}} = [\text{solv}]^{\text{Out}}$. This can never be reached, thus solvent transfer will continue until there is no solvent remaining on the outside or until the membrane bursts.

If the pressure is allowed to increase inside, the pressure difference (ΔP) between inside and outside (pushing solvent out) will provide a counterbalancing force to the chemical potential difference (pushing solvent in). This requires a membrane strong enough to withstand the internal pressure (e.g. a cell wall).



The change in chemical potential with pressure is given by;

$$\left(\frac{\delta\mu_i}{\delta P}\right)_T = V_i$$

where V_i is the partial molar volume of component i .

For a pressure difference of ΔP , the change in chemical potential is then given by;

$$\delta\mu_i = V_i \Delta P$$

Thus;

Inside	Solution	$\mu_{\text{solv}}^{\text{In}}(\text{l}) = \mu_{\text{solv}}^{\circ}(\text{l}) + RT \ln([\text{solv}]^{\text{In}}/[\text{solv}]^{\circ}) + V_{\text{solv}} \Delta P$
--------	----------	--

Outside	Pure liquid	$\mu_{\text{solv}}^{\text{Out}}(\text{l}) = \mu_{\text{solv}}^{\circ}(\text{l})$
---------	-------------	--

At equilibrium;

$$\mu_{\text{solv}}^{\text{In}}(\text{l}) = \mu_{\text{solv}}^{\text{Out}}(\text{l})$$

thus;

$$\mu_{\text{solv}}^{\circ}(\text{l}) + RT \ln([\text{solv}]^{\text{In}}/[\text{solv}]^{\circ}) + V_{\text{solv}} \Delta P = \mu_{\text{solv}}^{\circ}(\text{l})$$

Rearranging gives;

$$V_{\text{solv}} \Delta P = - RT \ln([\text{solv}]^{\text{In}}/[\text{solv}]^{\circ})$$

ΔP is the osmotic pressure (sometimes represented as Π).

This equation can be simplified using;

$$[\text{solv}]^{\text{In}}/[\text{solv}]^{\circ} = x_{\text{solv}} = 1 - x_{\text{solute}} \approx 1 \quad \Rightarrow \quad \ln(x_{\text{solv}}) = - x_{\text{solute}}$$

and

$$x_{\text{solute}} / V_{\text{solv}} = [\text{solute}] \quad (\text{molarity})$$

Thus;

$$\Delta P = RT \cdot [\text{solute}]$$

NON-IDEAL SOLUTIONS

In an ideal solution, all the molecules present interact identically and thus as the composition changes the chemical properties of any given molecule do not change. This is obviously incorrect in the vast majority of cases.

SOLUTE IN DILUTE SOLUTIONS

The solvent in very dilute solutions can often be treated as ideal because most solvent molecules are surrounded by other solvent molecules.

The solute molecules are mostly surrounded by solvent molecules. At low concentrations the intermolecular interactions will remain constant, regardless of the solute concentration (until solute molecules start interacting with each other). This meets the criteria for an ideal solution, i.e. the chemical properties of a given solute molecule do not vary with composition in dilute solutions.

However, the nature of the interactions are not the same as in the pure liquid of the solute. We can deal with this by changing the standard state that we refer to.

Standard state for a solute \square solution of 1 M solute in which the only significant interactions are those between the solute and solvent molecules.

The chemical potential of an ideal solute is then still given by

$$\mu_i = \mu_i^\circ + RT \ln([i]/[i]^\circ)$$

except that

$[i]^\circ = 1 \text{ M}$ (not the concentration of the solute in the pure liquid)

μ_i° – chemical potential of the solute at 1M concentration assuming that the only interactions are those with solvent molecules (not the chemical potential of the solute in the pure liquid)

The assumption that only interactions between the solute and solvent molecules are significant is usually not valid at 1M concentration, only at much, much lower concentration. Thus μ_i° is not the chemical potential of a 1 M solution, but the chemical potential of a very dilute solution extrapolated to 1M.

NON-IDEAL SOLUTIONS

The equation

$$\mu_i = \mu_i^\circ + RT \ln([i]/[i]^\circ)$$

works at very low concentrations of solute for both the solute and the solvent (assuming that we use the correct standard state).

For higher concentrations of solute this equation does not work. There are three approaches we can use at these concentrations:

1. Model the behavior empirically (useful for extrapolating to low concentrations).
2. Introduce a fudge factor to get the equation to work.
3. Understand what is going on so that we can correctly predict behaviour (i.e. get the correct equation).

VIRIAL EQUATIONS

Many complex functions can be represented by a polynomial series such as;

$$f(x) = A + Bx + Cx^2 + Dx^3 + Ex^4 + Fx^5 + \dots$$

A, B, C, etc. are empirically determined constants, called virial coefficients. This is only a useful expansion if most of the higher order coefficients are zero.

VIRIAL EQUATION FOR GASES

The definition of an ideal gas is given by the equation $PV = nRT$. Most gases only obey this equation at low pressures. For non-ideal gases, the equation of state can be given by;

$$\frac{PV}{nRT} = 1 + B.P + C.P^2 + D.P^3 + \dots$$

VIRIAL EQUATION FOR OSMOTIC PRESSURE

For the solvent in an ideal solution, the osmotic pressure is given by

$$\Delta P = RT \times [\text{solute}]$$

For the solvent in a non-ideal solution, the osmotic pressure can be written as

$$\Delta P = RT \times ([\text{solute}] + A[\text{solute}]^2 + B[\text{solute}]^3 + \dots)$$

A, B, etc., are empirical constants that have to be found by fitting to the experimental data. Usually B, C, etc. are all assumed to be zero. In this case, a plot of $\Delta P/RT[\text{solute}]$ versus $[\text{solute}]$ should be a straight line.

CHEMICAL ACTIVITIES

$$a_i - \text{Activity} = \text{Effective concentration}$$

This is defined by the equation

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

which is deemed to hold at all concentrations.

ACTIVITY COEFFICIENTS

The activity coefficient, γ_i , is defined as;

$$\gamma_i = \frac{a_i}{[i]} = \frac{\text{Effective concentration}}{\text{Real concentration}}$$

When the activity coefficient of a component is 1, $a_i = x_i$ and the component shows ideal behaviour. Chemical potentials are then given by;

$$\mu_i = \mu_i^\circ + RT \ln \left(\gamma_i \frac{[i]}{[i]^\circ} \right)$$

All thermodynamic equations only work if we use activities, not concentrations. For example, consider the reaction



The true equilibrium constant is given by

$$K = \frac{a_{\text{ADP}} \times a_{\text{P}_i} \times a_{\text{H}^+}}{a_{\text{ATP}} \times a_{\text{H}_2\text{O}}} = \frac{g_{\text{ADP}} \times g_{\text{P}_i} \times g_{\text{H}^+}}{g_{\text{ATP}} \times g_{\text{H}_2\text{O}}} \times \frac{[\text{ADP}]_{\text{eq}} [\text{P}_i]_{\text{eq}} [\text{H}^+]_{\text{eq}}}{[\text{ATP}]_{\text{eq}} [\text{H}_2\text{O}]_{\text{eq}}}$$

The apparent equilibrium constant is given by

$$K^{\text{app}} = \frac{[\text{ADP}]_{\text{eq}} [\text{P}_i]_{\text{eq}} [\text{H}^+]_{\text{eq}}}{[\text{ATP}]_{\text{eq}} [\text{H}_2\text{O}]_{\text{eq}}}$$

K is always constant, K^{app} is not.

$$K = \frac{g_{\text{ADP}} \times g_{\text{P}_i} \times g_{\text{H}^+}}{g_{\text{ATP}} \times g_{\text{H}_2\text{O}}} \times K^{\text{app}}$$

DEMISTIFYING ACTIVITY COEFFICIENTS

The equation

$$\mu_i = \mu_i^\circ + RT \ln(\gamma_i [i]/[i]^\circ)$$

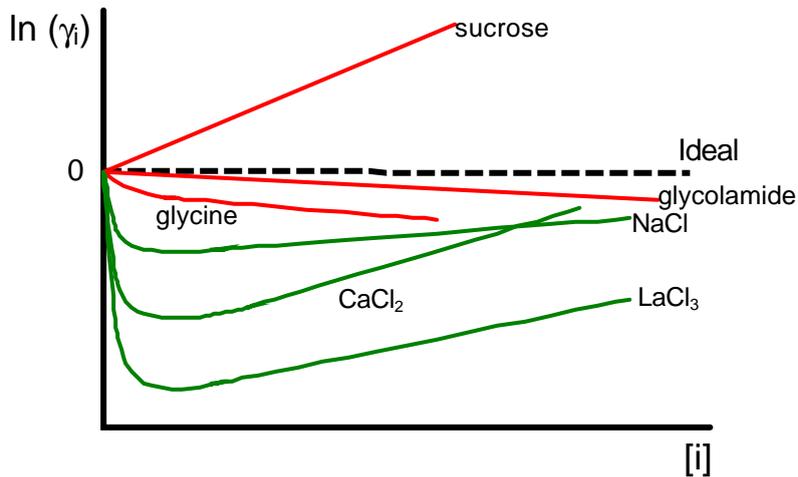
can be rewritten as

$$\mu_i = \mu_i^\circ + RT \ln([i]/[i]^\circ) + RT \ln(\gamma_i)$$

$$\mu_i = \mu_i(\text{ideal}) + RT \ln(\gamma_i)$$

Thus, $RT \ln(\gamma_i)$ is the quantitative value of the non-ideal contribution to the chemical potential.

$RT \ln(\gamma_i)$ □ measure of the ΔH and ΔS contributions of any inter-molecular interactions not included in the standard state



IONIC SOLUTIONS AT INFINITE DILUTION

Hydration shell :- layer of water molecules bound to an ion. 1st solvation shell is bound directly to the ion, 2nd hydration shell is the next layer out, etc.

Hydration number :- The hydration number is the number of water molecules on average bound to an ion. These water molecules cannot be considered as part of the bulk solvent because their properties are the not same as free water molecules.

Hydrated radii :- The effective radius of a hydrated ion is given by the sum of the ionic radius and the solvation shell. Because small ions have larger solvation shells, they have larger hydrated radii (behave in solution as though they were bigger) than large ions.

In general an ion with a smaller radius and/or higher charge will have

- more solvation shells
- a larger hydration number
- a larger hydrated radius

because they have stronger electrostatic interactions with the solvent.

Enthalpy of hydration :-

- Gain of interactions between solute ions and solvent molecules (monopole-dipole).
- Loss of interactions between solvent molecules (dipole-dipole, hydrogen bonds).

This leads to a large, negative ΔH (i.e. favourable).

Entropy of hydration :-

- Gain of entropy associated with the mixing of the solvent molecules and solute ions.
- Loss of entropy associated with the ordering of solvent molecules.
- Loss of entropy associated with the unsolvated solute ions.

This leads to a small, and usually negative ΔS (i.e. unfavourable).

Note: if ions are in a crystal then there are extra ΔH and ΔS terms to consider.

Ion	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔG (kJ mol ⁻¹)
Na ⁺	-390	-71	-367
K ⁺	-305	-34	-295
Mg ²⁺	-1891	-281	-1808
Ca ²⁺	-1561	-202	-1501
Cl ⁻	-384	-63	-365
Ar	-	-54	-

Figures include the loss of entropy associated with the gas, as well as the entropy change of the solvent. The free energy term is dominated by ΔH .

IONIC SOLUTIONS AT FINITE DILUTION

In the standard state of an ionic solute, at infinite dilution, each ion is solvated by a sphere of water molecules. This will stabilise the ions through charge-dipole interactions.

At low concentrations of an ionic solute, the solvated ions are surrounded by a cloud of oppositely charged solvated ions. This will stabilise the ions through charge-charge interactions and thus lower their chemical potential.

DEBYE-HÜCKEL THEORY

The object is to calculate the work required to take one mole of solute ions from an ideal solution to a non-ideal solution, assuming that only solute-solute electrostatic interactions are important.

Calculating the electrostatic interactions in a dynamic system is more difficult because the distances between the ions change with time.

Solution:

1. Take lots of snapshots of the system at different times.
2. Perform the calculation on each structure.
3. Average the results.

This will work as long as we take enough snapshots to represent most of the possible states of the system (in buzz words – fully explore the conformational and configurational space of the system). This is a very general approach used in most types of molecular modelling (called a Monte-Carlo calculation).

Method :-

1. Consider all ions relative to a test ion, j.
2. Take a random arrangement of all the other ions around this test ion.
3. Calculate the probability of this random arrangement occurring (using the Boltzmann equation).
4. Calculate the electrical potential at the test ion as a result of this random arrangement (using the Poisson equation).
5. Repeat steps 2-4 for all possible arrangements of ions and sum all the weighted electrical potentials.
6. Calculate the stabilisation of the test ion due to the average electrical potential.

Assumptions :-

1. The solute is present in solution as single solvated ions (there is no ion pair formation).
2. The ions are regarded as point charges.
3. Only coulombic interactions are considered.
4. The solvent is treated as a continuous medium (its molecular nature is ignored) unaffected by the presence of the ions.
5. The thermal energy of the solution is much larger than the electrostatic interactions.

All these assumptions hold in dilute solutions.

Basic equations :-

Boltzmann equation - The number of ions per unit volume, $n_i(r)$, found at a distance r from the test ion is given by;

$$n_i(r) = N_i \cdot \exp\left(\frac{-U(r)}{kT}\right)$$

where N_i is the total number of ions per unit volume, $U(r)$ is their potential energy, k is the Boltzmann constant and T is the temperature.

Poisson equation - The electrical potential at a distance r from the test ion, $\Phi(r)$, for a spherically symmetric system is given by;

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\Phi(r)}{dr} \right) = -\frac{1}{\epsilon} \rho(r)$$

where ϵ is the permittivity of the medium and $\rho(r)$ is charge density at a distance r from the test ion.

Potential energy - The potential energy, $U(r)$, of an ion i with charge $z_i e$ at a distance r from the test ion is given by;

$$U(r) = z_i \cdot e \cdot \Phi(r)$$

where e is the charge of an electron and $\Phi(r)$ is the electrical potential at a distance r from the test ion.

Charge density - The charge density (net charge per unit volume), $\rho(r)$, at a distance r from the test ion is given by;

$$\rho(r) = \sum_i n_i(r) \cdot z_i \cdot e$$

SOLUTION OF THE DEBYE-HÜCKEL THEORY

The final result of the Poisson-Boltzmann equation is the simple Debye-Hückel equation;

$$\log_{10}(\gamma_i) = -A \cdot z_i^2 \sqrt{I}$$

where A is a constant, independent of the species present in solution, given by;

$$A = \frac{e^3}{2.303(4\pi)} \sqrt{\frac{1 \text{ } \text{\AA}^3 \text{ L}}{2(\epsilon kT)^3}} \approx 0.5 \text{ (in aqueous solution)}$$

and I is the ionic strength of the solution, dependent on composition, given by;

$$\text{Ionic Strength} = I = \frac{1}{2} \sum_j [j] z_j^2$$

Mean activity coefficients :-

In practice, it is not possible to measure γ_i for a single ion as there are always counter ions present. Thus, we define a mean activity coefficient γ_{\pm} as;

$$\gamma_{\pm} = \left(\gamma_+^{z_+} \dots \gamma_-^{z_-} \dots \right)^{\frac{1}{z_+ + \dots + z_- + \dots}}$$

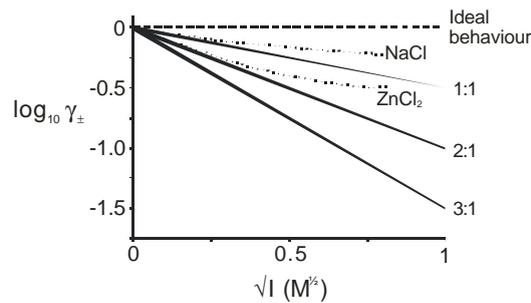
giving;

$$\log(\gamma_{\pm}) = -A |z_+| |z_-| \sqrt{I}$$

This is known as the Debye-Hückel limiting law.

1. Ions are always stabilised by the presence of other ions in solution ($\log_{10}(\gamma_i) < 0$, so $\gamma_i < 1$).
2. Higher charged ions are stabilised more than lower charged ions by other ions in solution.
3. This stabilisation depends on the concentration and charges of the other ions, not their chemical identity.
4. There should be a linear relationship between $\log_{10}(\gamma_i)$ and \sqrt{I} , the gradient of the line depending on the charges of the ions.

All these predictions are found experimentally to hold at low ionic strength, but *only* at low ionic strength.



NON-ZERO ION SIZES

One approximation of the Debye-Hückel theory is that ions are point charges. They can thus approach infinitely closely. This approximation does not matter at very high dilution where the ions are, on average, far apart, but causes errors at lower dilutions. This minimum distance of approach (a) can be included in the Debye-Hückel calculation, giving the full Debye-Hückel equation;

$$\log(\gamma_i) = -\frac{Az_1^2\sqrt{I}}{1 + Ba\sqrt{I}}$$

where B is another constant, independent of the solution, and a is the sum of the ionic radii ($r_+ + r_-$).

IONIC SOLUTIONS AT HIGHER IONIC STRENGTHS

In the standard state of an ionic solute, at infinite dilution, each ion is solvated by a sphere of water molecules. At low concentrations of an ionic solute, the ions are surrounded by a cloud of oppositely charged ions, stabilising the solution.

At high concentrations of an ionic solute, there will not be enough water molecules around to solvate all the ions present, thus there will be a destabilising effect on the solution.

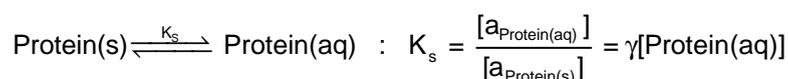
At very high concentrations of an ionic solute in water, ion pair formation ($A^+ + B^- \rightarrow AB$) becomes important, changing both the type of species present and the ionic strength of the solution.

EQUILIBRIUM CONSTANTS IN SOLUTION

$$K = \left(\frac{\prod_{\text{products}} [X_i] g_i}{\prod_{\text{reactants}} [X_i] g_i} \right) = \left(\frac{\prod_{\text{products}} g_i}{\prod_{\text{reactants}} g_i} \right) K_m$$

The true equilibrium constant, K (defined in terms of activities), is a constant, the apparent equilibrium constant, K_m (defined in terms of concentrations), is not.

“SALTING IN” AND “SALTING OUT” OF PROTEINS



K_s is a constant, thus as γ changes the actual concentration in solution, $[\text{Protein(aq)}]$, must change.

$\gamma < 1 \quad \Rightarrow$ Increased solubility Salting in

$\gamma > 1$ \Rightarrow Decreased solubility Salting out

- Proteins often have a high charge so the effect of ionic strength on γ is large.
- Different proteins have different charges and so respond to changes in ionic strength in different ways.

CHARGED MEMBRANES

The equivalent model of the Debye-Hückel theory for membranes is the Gouy-Chapman theory.

Ion concentrations close to membranes -- The electrostatic effects of a membrane are strong enough to alter the actual concentrations of ions near to the membrane. Ions of opposite charges are attracted to the membrane, ions of similar charges are repelled. These interactions can be strong enough to result in a layer of ions bound directly to the membrane surface.

Ion activities close to membranes -- The presence of the charged membrane will effect the chemical potentials of ions nearby. This is directly analogous to the Debye-Hückel theory, the membrane contributing to the effective ionic strength of the solution.