

## CHAPTER 33

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# ELECTROLYTE SOLUTIONS – THE DEBYE-HUCKEL THEORY

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### INTRODUCTION

As a final topic on the subject of solutions, we will consider the complications that are associated with systems in which the solute molecule dissociates on solution to produce separate positively and negatively charged ions. Systems of this type include the various metal halides such as NaCl, MgCl<sub>2</sub>, carbonates nitrates or sulfates among others. These solutions, known as electrolyte solutions, present two major complications: The required maintenance of overall electrical neutrality in the solution and the energy associated with the long range Coulomb attractive force between oppositely charged ions.

### ELECTRICAL NEUTRALITY

Consider first the question of overall electrical neutrality. It can be easily shown that the energetic cost of removing a measurable number of ions of one charge (positive or negative) from a solution is prohibitively high. Consequently, for all practical purposes, we may assume a charge neutral solution, which satisfies the condition

$$\sum_i z_i n_i = 0, \quad (33.1)$$

or

$$\sum_+ z_+ n_+ = \sum_- |z_-| n_-, \quad (33.2)$$

Where  $z_i$  is the charge number of the ion, and is positive for positive ions and negative for negative ions and  $n_i = N_i / V$  is the concentration of that ionic species, ions per unit volume of the system. One consequence of this requirement is that the concentrations of the two ionic species are not independent. That is, the concentrations of  $A^+$  and  $X^-$  are not independent variables. The components of the system are thus  $AX$  and the solvent species, not  $A^+$ ,  $X^-$  and the solvent species.

We can deduce another consequence of the requirement for electrical neutrality if we carry out a thought experiment similar to that done in Chapter 4 when we determined the condition for distributive equilibrium. In this case, we look at a system of two phases, at least one of which is an electrolyte solution, having constant pressures in each phase and a constant temperature, containing a 1-1 electrolyte (e.g. NaCl). If we transfer small amounts,  $dn_+$  and  $dn_-$  of the two ionic species from one phase to the other, the Helmholtz free energy change will be

$$dF = -P^\alpha dV^\alpha - \mu_+^\alpha dn_+ - \mu_-^\alpha dn_- - P^\beta dV^\beta + \mu_+^\beta dn_+ + \mu_-^\beta dn_- \quad (33.3)$$

If the two phases are in equilibrium with respect to the electrolyte, the process considered must be reversible and  $dF$  must be equal to the work done on the system,

$$dF = -P^\alpha dV^\alpha - P^\beta dV^\beta \quad (33.4)$$

If we subtract Equation 33.4 from Equation 33.3 we have

$$(\mu_+^\beta - \mu_+^\alpha) dn_+ + (\mu_-^\beta - \mu_-^\alpha) dn_- = 0 \quad (33.5)$$

However, from the condition for electrical neutrality, we have

$$dn_+ = dn_- = dn, \quad (33.6)$$

leading to

$$(\mu_+^\beta - \mu_+^\alpha + \mu_-^\beta - \mu_-^\alpha) dn = 0 \quad (33.7)$$

or, dividing by  $dn$ ,

$$\mu_+^\alpha + \mu_-^\alpha = \mu_+^\beta + \mu_-^\beta \quad (33.8)$$

as the criterion for distributive equilibrium in systems of this type. The importance of this relation is that only the sum of the two chemical potentials is involved in defining equilibrium and consequently only this sum and not the individual chemical potentials can be determined experimentally. We will see the consequences of this later when we write expressions for the thermodynamic properties of electrolyte systems.

## ELECTROSTATIC EFFECTS

The chemical potential for any component of an ideal gas mixture (which we explicitly derived in chapter 12) is given by,

$$(\mu_j)^g = \mu_j^0 + kT \ln(P_j / P_j^0) \quad (33.9)$$

where the reference value is given at atmospheric pressure,  $P=P_{atm}$ . Similarly we showed in Chapter 19 that the chemical potential for a component in an ideal solution is given by

$$\mu_j^s = (\mu_j^o)^s + kT \ln n_j, \quad (33.10)$$

where  $n_j$  is the concentration of  $J$ ,  $n_j = N_j/V$ , where  $N_j$  is the number of particles  $J$ . (Note that the  $\mu^o$  defined here differs from that defined in Chapter 19 by the additive factor

$$-kT \ln \left( \frac{\sum_i N_i}{V} \right). \quad (33.11)$$

This change is made only because the formulation we will develop for the electrostatic energy is most conveniently expressed in terms of  $N/V$  rather than mole fraction.)

For non-ideal solutions we found, also in Chapter 19, that the effects of non-ideality could be accounted for by the introduction of an activity coefficient,  $\gamma$  that accounted for the net chemical interactions among the components of the solution, leading to

$$\mu_j^s = (\mu_j^o)^s + kT \ln n_j + kT \ln \gamma. \quad (33.12)$$

Furthermore, the non-ideality represented by  $\gamma$  was represented in our statistical treatment of solutions in Chapter 22 in terms of nearest neighbor interactions.

In case of ionic solutions (as well as ionic plasmas), even at concentrations of ions low enough that we can neglect near neighbor chemical interactions between ions, we must still deal with the Coulomb interactions between ions because of the very long range nature of these interactions. Each ion is a source of electrostatic potential,

$$\varphi_j(r) = \frac{q_j}{\epsilon r}, \quad (33.13)$$

where  $q_j$  is the ion charge,  $r$  is the distance from the ion, and  $\epsilon$  is the dielectric constant of the medium in which ions are dissolved. Unlike most of the forces, ionic forces are characterized by very slow decay with distance. By comparison with the Coulomb potential (Equation 33.13) the potential describing Van der Waals attraction decays as  $1/r^6$ . In consequence of this long-range interaction, even at low ion concentrations, the

interaction between them cannot be neglected. We will develop an expression for this interaction energy in terms of a additional activity coefficient,  $\gamma^E$ . The final complete expression for the chemical potential of an ionic species in an electrolyte solution will thus be

$$\mu_j^s = (\mu_j^o)^s + kT \ln n_j + kT \ln \gamma + kT \ln \gamma^E. \quad (33.14)$$

We will calculate this energy term using the formalism developed by Debye and Huckel, which involves first calculating the potential distribution around a single ion, then using a charging process to determine the work required to increase the charge on the ion from zero to its real value of  $ez_j$ .

## CHARGE DISTRIBUTION

Interactions of mobile ions, such as is the case in liquid solutions, leads to their rearrangement in which the positive ions tends to be surrounded by negative ions leading to lowering of the Coulomb energy. On the other hand, thermal motion of the ions tends to disperse ions at random so as to increase the entropy. The competition between energy and entropy leads to an effective screening length over which a given ion is neutralized by other ions. This length was evaluated by Debye and Huckel via the following elegant procedure.

As a starting point, ions are considered as hard spheres distributed in dielectric continuum with dielectric constant  $\epsilon$ , which for the most important medium, water, is equal to about 80. We now select an ion  $J$  with charge,  $ez_j$ , where  $e$  is the unit electronic charge, and seek the potential around this ion,  $\phi$  which will originate from the ion itself, ( $\phi$ , as given by Equation 33.13) and all other ions present in the solution. Due to spherical symmetry, the potential  $\phi$  is a function of radial distance from the center of ion  $J$ ,  $\phi = \phi_j(r)$ . It also has to satisfy the Poisson equation of electrostatics,

$$\nabla^2 \phi_j(r) = \frac{-4\pi}{\epsilon} \rho_e(r), \quad (33.15)$$

where  $\rho_e$  is the charge density. Despite the fact that all ions are constantly moving, Equation 33.14 is written for the time averaged charge distribution and in this sense the problem is electrostatic. In spherical coordinates Equation 33.15 can be rewritten as,

$$\frac{1}{r} \frac{d^2(r\phi_j(r))}{dr^2} = \frac{-4\pi}{\epsilon} \rho_e(r). \quad (33.16)$$

In order to solve the Equation 33.16 it is necessary to provide a connection between the potential and the charge distribution. This connection is given by the Boltzman distribution

$$\rho_e(r) = e \sum_i z_i n_i e^{-z_i e \phi_j(r) / kT}, \quad (33.17)$$

where the sum is over all ionic species  $i$ , with concentrations  $n_i$ . The key simplification of the Debye-Huckel (DH) theory is to expand the exponential in Equation 33.17 and keep only the first and the second term of the expansion. This approximation is justified when the temperature is high enough such that the electrostatic energy can be considered a small perturbation on thermal energy. By expanding Equation 33.17 and inserting it into Equation 33.16 we obtain,

$$\frac{1}{r} \frac{d^2(r\phi_J(r))}{dr^2} = \frac{-4\pi e}{\epsilon} \sum_i z_i n_i \left( 1 - \frac{z_i e \phi_J(r)}{kT} \right). \quad (33.18)$$

The first sum in the expansion is equal to zero due to the charge neutrality condition leading to

$$\frac{1}{r} \frac{d^2(r\phi_J(r))}{dr^2} = \kappa^2 \phi_J(r) \quad (33.19)$$

where

$$\kappa^2 = \frac{4\pi e^2}{\epsilon kT} \sum_i n_i z_i^2. \quad (33.20)$$

Equation 33.19 is a linear second order equation for  $r\phi_J(r)$ , and has a well-known solution in the form of,

$$r\phi_J(r) = Ae^{-\kappa r} + Be^{+\kappa r}. \quad (33.21)$$

In order for the solution to be physical, B has to be equal to zero ( $\phi_J(r) \rightarrow 0$  as  $r \rightarrow \infty$ ), which gives,

$$\phi_J(r) = \frac{Ae^{-\kappa r}}{r}. \quad (33.22)$$

To evaluate constant  $A$  we can use the fact that the total net charge arising from the ions surrounding ion  $J$  has to be equal to negative of charge  $z_J$ . From Equation 33.16 using  $\phi_J(r)$  given by Equation 33.22 the charge around ion  $J$  is,

$$\rho_J(r) = \frac{-\kappa^2 \epsilon A}{4\pi r} e^{-\kappa r}, \quad (33.23)$$

which integrated from the distance of the closest approach  $a$ , given by the sum of ion  $J$  and counter ion radiuses,  $a = r_J + r_{CJ}$  to infinity gives the negative of  $z_J$ .

$$-ez_J = -\kappa^2 \epsilon A \int_a^\infty r e^{-\kappa r} dr. \quad (33.24)$$

The Integral in Equation 33.24 can be evaluated by integration by parts leading to the value  $A$ ,

$$A = \frac{z_J e}{\epsilon} \frac{e^{\kappa a}}{1 + \kappa a}. \quad (33.25)$$

The final expression of the potential around ion  $J$  is thus

$$\phi_J(r) = \frac{z_J e}{\epsilon} \frac{e^{\kappa a}}{1 + \kappa a} \frac{e^{-\kappa r}}{r}. \quad (33.26)$$

Examination of Equation 33.26 reveals that  $\kappa$  is the inverse of the screening length,  $\lambda = 1/\kappa$ .  $\lambda$  is a measure of a distance over which the ion  $J$  is screened by the cloud of other ions. According to Equation 33.20 the screening length increases as the temperature increases and decreases as the concentration of ionic species increases. Large  $\lambda$  corresponds to a situation in which thermal energy is large on comparison with Coulomb energy, which is in fact assumption of the DH theory under which  $\lambda$  was calculated.

In case of water ( $\epsilon=80$ ), at room temperature and for 1-1 ionic solution, such as NaCl,  $\lambda$  in Å is given

$$\lambda = \frac{1}{\kappa} \cong \frac{3}{n_{\pm}}, \quad (33.27)$$

where  $n_{\pm}$  is the molarity of cations or anions. For  $n_{\pm}=0.01$ ,  $\lambda = 30$  Å, and we can expect DH theory to be rather accurate. For  $n_{\pm}=1$ ,  $\lambda = 3$  Å, which is of the order of the hard-core radius,  $a = r_J + r_{CJ}$ . In this case the approximation used in Equation 33.18 is not valid, and the Coulomb energy is a very strong perturbation on the thermal motion. The validity of the Debye-Huckel (DH) theory requires relatively large  $\lambda$  also for another reason. If  $\lambda$  is comparable with molecular size of water ( $\sim 3-4$  Å), then the representation of the water as continuum medium with a dielectric constant is not valid.

## ACTIVITY COEFFICIENT

We are now in a position to calculate the ionic contribution to the chemical potential,  $\gamma^E$ . For simplicity, we will assume that the solution is dilute enough that we can ignore the chemical contribution to non-ideality of the chemical potential and write

$$\mu_j = \mu_j^0 + kT \ln(\gamma^E n_j) = \mu_j^0 + kT \ln n_j + kT \ln \gamma^E. \quad (33.28)$$

In practice, as we mentioned earlier in this chapter, for ionic systems only the sum of the chemical potentials for ions and counter ions can be determined due to charge neutrality requirement. Accordingly we may write

$$\mu_j + \mu_{c_j} = \mu_j^0 + \mu_{c_j}^0 + kT \ln n_j + kT \ln n_{c_j} + kT \ln \gamma_j^E + kT \ln \gamma_{c_j}^E \quad (33.29)$$

Finally we can define a mean ionic activity coefficient,  $\gamma_{\pm} = (\gamma_j^E \gamma_{c_j}^E)^{1/2}$ , or

$$\ln \gamma_j^E + \ln \gamma_{c_j}^E = \ln \gamma_j^E \gamma_{c_j}^E = \ln \gamma_{\pm}^2. \quad (33.30)$$

This activity coefficient is associated with the excess free energy originating from the Coulomb interactions. To evaluate the excess energy associated with charge  $J$ , we can perform a so-called charging procedure. As mentioned earlier, we will start with an uncharged species  $J$  and gradually increase its charge from zero to  $ez_J$ . During the charging process the charge is equal to  $z = e\xi z_J$ , where  $\xi$  varies from 0 to one. The electrostatic work,  $W_{el}$ , associated with the charging process is equal to,

$$W_{el} = \int_0^1 d\xi \int_a^{\infty} dr 4\pi r^2 \frac{d(\xi z_J) e \rho_j(r)}{r} dr, \quad (33.31)$$

Inserting Equation 33.23 with  $A$  constant given by Equation 33.25, and  $z = \xi z_J$  instead of  $z_J$  and recognizing that this that  $W_{el}$ , is equal to the excess chemical potential,  $\mu_j^{ex} = W_{el}$  leads to

$$\mu_j^{ex} = \frac{z_j e}{2\epsilon} \frac{e^{\kappa a}}{1 + \kappa a} \int_a^{\infty} dr \int_0^1 \xi d\xi 4\pi r^2 \frac{-z_j e \kappa^2 \epsilon e^{-\kappa r}}{4\pi r r}, \quad (33.32)$$

which upon straightforward integration gives,

$$\mu_j^{ex} = -\frac{z_j^2 e^2}{2\epsilon} \frac{\kappa}{1 + \kappa a}, \quad (33.33)$$

which gives the activity coefficient,

$$\ln \gamma_j^E = \frac{\mu_j^{ex}}{kT} = -\frac{z_j^2 e^2}{2\epsilon kT} \left( \frac{\kappa}{1 + \kappa a} \right). \quad (33.34)$$

For very dilute solution, as  $\kappa \rightarrow 0$ , Equation 33.34 becomes the so-called DH limiting law,

$$\ln \gamma_j^E = -\frac{z_j^2 e^2 \kappa}{2\epsilon kT}. \quad (33.35)$$

## THERMODYNAMIC FUNCTIONS

Now that we have calculated the excess chemical potential, which, within the DH limiting law, is given by

$$\mu_j^{\text{ex}} = -\frac{z_j^2 e^2 \kappa}{2\epsilon}, \quad (33.36)$$

we can proceed to evaluate other thermodynamics functions. Here we present only excess values for the thermodynamic functions, which have to be simply added to corresponding thermodynamic functions for ideal solutions (or ideal gas) developed in previous chapters.

The excess Gibbs free energy is given by,

$$G^{\text{ex}} = \sum_i \mu_i^{\text{ex}} N_i = -\frac{e^2 \kappa}{2\epsilon} \sum_i z_i^2 N_i = -\frac{V e^2 \kappa}{2\epsilon} \sum_i z_i^2 n_i = -\frac{V \kappa^3}{8\pi} kT, \quad (33.37)$$

where  $N_i$  is the number of ions of type  $i$ , and  $n_i$  is their concentration, with the last equality following from Equation 33.20

The osmotic pressure can be evaluated starting with thermodynamics relationship,

$$\left(\frac{\partial G}{\partial V}\right)_{N,T} = \left(\frac{\partial G}{\partial P}\right)_{N,T} \left(\frac{\partial P}{\partial V}\right)_{N,T} = V \left(\frac{\partial P}{\partial V}\right)_{N,T}, \quad (33.38)$$

from which we obtain

$$\left(\frac{\partial P}{\partial V}\right)_{N,T} = \frac{1}{V} \left(\frac{\partial G}{\partial V}\right)_{N,T}. \quad (33.39)$$

By integrating Equation 33.39 over  $dV$  from infinite volume to  $V$  we obtain,

$$\int_{\infty}^V \left(\frac{\partial P}{\partial V}\right)_{N,T} dV = \int_{\infty}^V \frac{1}{V} \left(\frac{\partial G}{\partial V}\right)_{N,T} dV = P(V) - P(\infty) = P(V) \quad (33.40)$$

where the last equality is due to zero pressure in the limit of infinite volume at constant  $N$  and  $T$ . To calculate just excess pressure,  $P^{\text{ex}}$ , (over that for an ideal solution or gas), we need to insert Equation 33.37 into 33.40, yielding

$$P^{\text{ex}} = -\frac{kT}{8\pi} \int_{\infty}^V \frac{1}{V} \left(\frac{\partial(V\kappa^3)}{\partial V}\right)_{N,T} dV. \quad (33.41)$$

Moreover, since  $\kappa^3 = V^{-3/2} f(T, N)$ , we have

$$P^{ex} = -\frac{kTf(T, N)}{8\pi} \int_{\infty}^V dV \frac{1}{V} \left( \frac{\partial(V^{-1/2})}{\partial V} \right)_{N, T} = \frac{kTf(T, N)}{16\pi} \int_{\infty}^V dV \frac{1}{V^{3/2}}, \quad (33.42)$$

or, after integration,

$$P^{ex} = -\frac{kTf(T, N)V^{-3/2}}{24\pi} = -\frac{kT\kappa^3}{24\pi}. \quad (33.43)$$

As we should expect, the excess pressure is negative because the ionic interactions provide net attractive interactions. The total (osmotic) pressure is the sum on the ideal system pressure and the excess pressure,

$$P = P^{id} + P^{ex} = \frac{kT}{V} \sum_i N_i - \frac{kT\kappa^3}{24\pi}. \quad (33.44)$$

Finally we may calculate the Helmholtz excess free energy,  $F^{ex}$ , as,

$$F^{ex} = G^{ex} - P^{ex}V = -\frac{V\kappa^3}{8\pi} kT + \frac{kT\kappa^3}{24\pi} = -\frac{kT\kappa^3}{12\pi}. \quad (33.45)$$

## PROBLEMS

DH1. Using Equations 33.23 and 33.25 calculate the charge density around ion  $j$ ,  $\rho_j(r)$  in the limit of  $\kappa a \rightarrow 0$ . The net charge within the shell between  $r$  and  $r+dr$  centered at ion  $j$  is given by

$$4\pi r^2 \rho_j(r) dr.$$

Therefore the most probable location of the screening charge is where the maximum of the function  $4\pi r^2 \rho_j(r)$  is located. Find the most probable value of  $r$ , and the average value of  $r$  with the distribution  $P(r) = 4\pi r^2 \rho_j(r)$ . How do these values relate to the screening length  $\lambda = 1/\kappa$ ?

DH2. Verify Equation 33.27.

DH3. Consider a gaseous plasma ( $\epsilon=1$ ) of ionized NaCl, at high temperature  $T$ .

(a) At what sodium ion concentration,  $n_{Na}$ , will the total pressure of the gas (Equation 33.44) be equal to zero?

(b) Assuming the same concentrations, at what temperature of the NaCl plasma gas, will the screening length be the same as the screening length of NaCl water solution at  $T = 300\text{K}$ .