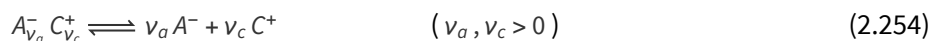


## S2.E. The Thermodynamics of Electrolytes

An **electrolyte** is a dilute solution (salt + water) in which the solute (salt) dissociates into charged ions via the reaction



where  $A^-$  &  $C^+$  are called the **anion** & **cation**, respectively.

The condition for equilibrium is [ see (2.238-9) ]

$$\mathcal{A} = -\mu_{ac} + v_a \mu_a^e + v_c \mu_c^e = 0 \quad (2.255)$$

where the **electrochemical potential**  $\mu_j^e$  is the average energy required to add 1 mole of type  $j$  (charged) ions to the system, i.e., it is the chemical potential for charged particles. For ions with valence (or charge in units of the proton charge)  $z_j$ ,

$$\mu_j^e = \mu_j + z_j F \phi \quad [ \text{See (3) of Ex.2.7 in §2.F.4.} ] \quad (2.255a)$$

where  $\phi$  is the electric potential and  $F$  is the **Faraday** (amount of charge in 1 mole of protons).

Since the salt is neutral, we have

$$v_a z_a + v_c z_c = 0 \quad (2.256)$$

Experiments show that the chemical potential of salt in aqueous solution takes the form

$$\mu_{ac}(T, P, x_{ac}) \approx \mu_{ac}^0(T, P) + RT \ln \alpha_{ac} \quad (2.257)$$

where

$$\begin{aligned} \mu_{ac}^0(T, P) &= \lim_{x_{ac} \rightarrow 1} \mu_{ac}(T, P, x_{ac}) \\ &= \text{chemical potential of pure salt.} \end{aligned}$$

The **activity**  $\alpha_{ac}$  will be defined shortly.

In the limit that the salt and water have no effect on each other, the Gibbs energy simplifies to

$$G^0(T, P, n_{ac}, n_w) = n_{ac} \mu_{ac}^0(T, P) + n_w \mu_w^0(T, P) \quad (2.258)$$

where  $\mu_w^0(T, P)$  is the chemical potential for pure water.

Hence,

$$\begin{aligned} G &= n_{ac} \mu_{ac} + n_w \mu_w && [ (2.107) \text{ of §2.F.4 used. } ] \\ &= G_0 + n_{ac} (\mu_{ac} - \mu_{ac}^0) + n_w (\mu_w - \mu_w^0) && [ (2.258) \text{ used. } ] \\ &= G_0 + n_{ac} RT \ln \alpha_{ac} + n_w (\mu_w - \mu_w^0) && [ (2.257) \text{ used. } ] \end{aligned} \quad (2.259)$$

Generalizing (2.257) to the case for ions with (2.255a) gives

$$\mu_a^e(T, P, x_{ac}) \approx \mu_a^0(T, P) + RT \ln \alpha_a + z_a F \phi \quad (2.262)$$

$$\mu_c^e(T, P, x_{ac}) \approx \mu_c^0(T, P) + RT \ln \alpha_c + z_c F \phi \quad (2.263)$$

Putting these and (2.257) into the condition for equilibrium (2.255) gives

$$\begin{aligned} \mu_{ac}^0 + RT \ln \alpha_{ac} &= v_a \mu_a^0 + v_c \mu_c^0 + RT (v_a \ln \alpha_a + v_c \ln \alpha_c) + (v_a z_a + v_c z_c) F \phi \\ &= v_a \mu_a^0 + v_c \mu_c^0 + RT (v_a \ln \alpha_a + v_c \ln \alpha_c) && [ (2.256) \text{ used. } ] \end{aligned}$$

Since this holds for arbitrary  $T$ , we have

$$\mu_{ac}^0 = v_a \mu_a^0 + v_c \mu_c^0 \quad (2.261a)$$

and

$$\ln \alpha_{ac} = \nu_a \ln \alpha_a + \nu_c \ln \alpha_c \quad (2.261)$$

$$\rightarrow \alpha_{ac} = \alpha_a^{\nu_a} \alpha_c^{\nu_c} \quad (2.260)$$

It is found experimentally that for dilute solutions,

$$\alpha_j \approx f_j c_j \quad (2.260a)$$

where  $c_j = \frac{n_j}{V}$  is the concentration and  $f_j$  is the **activity coefficient** for type  $j$  ions. Furthermore,

$$\lim_{c_j \rightarrow 0} f_j \rightarrow 1 \quad (2.260b)$$

Solutions in which

$$f_j = 1 \quad \forall j$$

are said to be **ideal**.

For ideal solutions, (2.262-3) simplify to

$$\mu_a^e(T, P, x_{ac}) \approx \mu_a^0(T, P) + RT \ln c_a + z_a F \phi \quad (2.264)$$

$$\mu_c^e(T, P, x_{ac}) \approx \mu_c^0(T, P) + RT \ln c_c + z_c F \phi \quad (2.265)$$

Changes in the Gibbs energy for a solution carrying the reaction (2.254) are given by [see (2.236)]

$$dG = -SdT + VdP + \mu_{ac} dn_{ac} + \mu_a^e dn_a + \mu_c^e dn_c + \mu_w dn_w \quad (2.266)$$

with

$$\frac{dn_{ac}}{-1} = \frac{dn_a}{\nu_a} = \frac{dn_c}{\nu_c} = d\xi$$

### Ex.2.12.

A vessel held at constant  $T$  and  $P$  is separated into two compartments, I & II, by a membrane. Each compartment contains a well-stirred dilute solution of a solute and a solvent. The membrane is permeable to the solute but not the solvent.

Compute the ratios of the concentrations of solute in the compartments for the following two cases.

- The solute is uncharged, but the solvents in the compartments are different.
- The solute is charged, and the solvents in the compartments are the same.  
But the fluids in the compartments are maintained at different electric potentials.

### Answer (a)

For uncharged solute in an ideal solution, the chemical potential is given by [see (2.257)],

$$\mu_{sj} = \mu_s^0 + RT \ln \alpha_{sj} \quad j = I, II$$

where  $c_{sj}$  the concentration of the solute in compartment  $j$  and

$$\mu_s^0 = \lim_{c_{sj} \rightarrow 1} \mu_{sj} = \text{chemical potential of pure solute}$$

The condition for equilibrium is

$$\mu_{sI} = \mu_{sII}$$

$$\rightarrow \alpha_{sI} = \alpha_{sII} \rightarrow f_I c_{sI} = f_{II} c_{sII} \quad (1)$$

i.e.,

$$\frac{c_{sI}}{c_{sII}} = \frac{f_{II}}{f_I} \quad (2)$$

The ratio  $\beta_s = \frac{c_{sI}}{c_{sII}}$  is called the **partition coefficient**.

### Answer (b)

For charged solute in an ideal solution, the chemical potential is given by [see (2.262-3)],

$$\mu_{sj} = \mu_s^0 + RT \ln \alpha_{sj} + z_s F \phi_j \quad j = I, II$$

where  $\phi_j$  is the electric potential in compartment  $j$ .

The condition for equilibrium is

$$\mu_{sI} = \mu_{sII}$$

$$\rightarrow RT \ln \alpha_{sI} + z_s F \phi_I = RT \ln \alpha_{sII} + z_s F \phi_{II} \quad (3)$$

Since the solvents are the same in both compartments, so are the activity coefficients  $f_j$ . (3) thus gives

$$RT \ln \frac{c_I}{c_{II}} = z_s F (\phi_{II} - \phi_I)$$

$$\rightarrow \frac{c_{sI}}{c_{sII}} = \exp\left(\frac{z_s F \Delta \phi}{RT}\right) \quad \Delta \phi = \phi_{II} - \phi_I \quad (3a)$$

so that solute concentration is higher where  $\phi$  is lower.

The potential difference required to maintain the concentration difference,

$$\Delta \phi = \frac{RT}{z_s F} \ln \frac{c_I}{c_{II}} \quad (4)$$

is called the **Nernst potential**.