

Chapter 1

Introduction

1.1. Prolegomena

Salts, that are neutral when pure, such as the table salt sodium chloride $NaCl$, can dissociate (i.e. “electrolyze”) into ions Na^{+1} and Cl^{-1} when dissolved in a strong dielectric solvents (such as water)—i.e. forming an aqueous electrolyte solution.

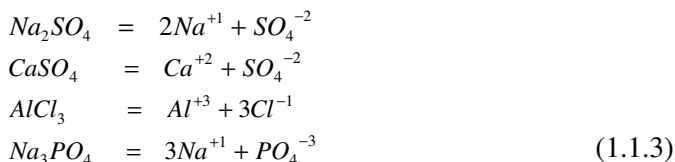


Na^{+1} and Cl^{-1} are ions that have either a positive charge (called cations) or a negative charge (anions). Cl^{-1} is a chlorine atom with one added extra electron (electron carries one negative charge, at $-1.609E-19$ Coulomb) while Na^{+} is the sodium atom which has lost an electron (thus with a positive charge: $+1.609E-19$ Coulomb). The valence is the number z of electrons lost ($+z$) or gained ($-z$). The valence of Na^{+1} is plus one (losing one electron), while that of Cl^{-1} is minus one (gaining one electron). For the salt Na_2SO_4 , sodium ion Na^{+1} has valence again of plus 1, while SO_4^{-2} has valence of minus two. Therefore we have the valence types of salts based on the resulting valences of the ions. $NaCl$ is the type 1-1 electrolyte (namely, valence 1 for cation and valence -1 for anion), while Na_2SO_4 is type 1-2 electrolyte (valence 1 for cation and valence -2 for anion). We use the symbols z_+ or z_- to denote the valences of the cation and anion, respectively. The dissociation eq. (1.1.1) is a chemical reaction. All rules for chemical reactions apply equally to the case of electrolysis. For any salt CA (C = cation and A= anion), the dissociation chemical equilibrium is written as



where ν_+ and ν_- are the stoichiometric coefficients for the cation and the anion, respectively.

In order for the salts to ionize, the solvent must have a high dielectric constant (to be defined in the following). At room temperature the relative dielectric constant D for water is about 80, and for diethylformamide 180. The higher the dielectric constant the easier it is for salts to dissociate. Salts can also dissociate as is (namely without solvents) at high temperatures, i.e., in the molten state at above 1000°C (the melting point depends on the salt). At room temperature, a dielectric solvent (or mixtures of many solvents) with high value of D is needed for dissociation. There are many salt types. We exhibit some examples below.



In the absence of an electrical field, the valences of ions z_+ , z_- and the numbers of ions ν_+ , ν_- combined will maintain the neutrality (zero net charge) of the whole solution.

$$\nu_+ z_+ + \nu_- z_- = 0 \tag{1.1.4}$$

This is called the *electroneutrality principle*, which we shall use often later. For example, the table salt, NaCl (eq. (1.1.1)), has $z_+=+1$, $z_-=-1$, $\nu_+=1$, and $\nu_- = 1$. The sum $\nu_+ z_+ + \nu_- z_- = (1)(+1) + (1)(-1) = 0$. For Na_2SO_4 , $z_+=+1$, $z_-=-2$, $\nu_+=2$, and $\nu_- = 1$. The sum $\nu_+ z_+ + \nu_- z_- = (2)(+1) + (1)(-2) = 0$. This electroneutrality applies to all valence types of salt solutions. For $MgSO_4$, a 2-2 electrolyte (valence 2 for cation Mg^{+2} and valence -2 for anion SO_4^{-2}): $z_+=+2$, $z_-=-2$, $\nu_+=1$, and $\nu_- = 1$; for $AlCl_3$ a 3-1 electrolyte (valence 3 for cation Al^{+3} and valence -1 for anion): $z_+=+3$, $z_-=-1$, $\nu_+=1$, and $\nu_- = 3$, and for Na_3PO_4 , a 1-3 electrolyte (valence 1 for cation and valence -3 for anion PO_4^{-3}): $z_+=+1$, $z_-=-3$, $\nu_+=3$, and $\nu_- = 1$. All types obey the electroneutrality rule.

Electrolyte solutions are mixtures consisting of dissociated ions in a solvent. Thus at equilibrium, the solution thermodynamic principles

apply. Namely, the free energy is at a minimum, and the chemical potentials of species balance out.

$$\mu_{CA} = \nu_+ \mu_+ + \nu_- \mu_- \quad (1.1.5)$$

where μ_+ and μ_- are the chemical potentials of the cation and anion respectively. The chemical potentials in the forward reaction are balanced by the chemical potentials in the backward reaction. A second remark is that at the equilibrium (1.1.5), the dissociation of CA is not always complete. If the dissociation is almost complete, such as $NaCl$ in water, the salt is called a *strong electrolyte*; if the extent of dissociation is limited, the salt is called a *weak electrolyte*, such as $Ca(C_2H_5COO)_2$. We can tell the dissociation strength by examining the dissociation constant (the equilibrium constant).

Since the ions are charged species, so the electrostatic principles apply. Let us first explain the units. The charge of an electron is negative and is equal to -1.60218×10^{-19} Coulomb, or in electrostatic units, -4.803×10^{-10} esu. We use the symbol e to represent the *absolute* value of the charge of one electron (i.e., $e = +1.60218 \times 10^{-19}$ Coulomb). The permittivity of vacuum is $\epsilon_0 = 111.265 \times 10^{-12}$ in units of $(\text{Coulomb})^2/(\text{Nm}^2)$. It is important to recognize that in electrostatics there are alternative units and definitions. The permittivity value above is based on the following form of *Coulomb's law*

$$\vec{F}_{12} = \frac{1}{\epsilon_m} \frac{q_1 q_2}{r^2} \vec{e}_{12} \quad (1.1.6)$$

where F_{12} is the force between two bodies 1 and 2 of charges q_1 and q_2 Coulombs, separated by a distance r_{12} , while e_{12} is the unit vector from charge 1 to charge 2. ϵ_m is called the *permittivity*, i.e., the proportionality constant. In different media (air, water, vacuum, or oil) where the two charges are immersed, the permittivity will have different values. The force can be expressed in Newton, charges in Coulomb, and distance in meter. However, alternative definition of the permittivity in Coulomb's law has been used (e.g. adding a factor 4π , to account for the spherical solid angle).

$$\vec{F}_{12} = \frac{1}{4\pi\epsilon_m^+} \frac{q_1 q_2}{r^2} \vec{e}_{12} \quad (1.1.7)$$

This definition gives a permittivity (with superscript +) of vacuum $\epsilon_0^+ = 111.265 \times 10^{-12} / 4\pi = 8.85419 \times 10^{-12}$ (Coulomb²)/(Nm²). It is always a good practice to verify which of the definitions of the permittivity is used at the beginning of any calculation.

In addition to the permittivity, a relative dielectric constant D is also used to characterize the dielectric medium. This relative dielectric constant is the ratio of the permittivity ϵ_m of the medium at hand to the permittivity ϵ_0 in vacuum

$$D \equiv \frac{\epsilon_m}{\epsilon_0} \quad (1.1.8)$$

Thus D is a ratio and is dimensionless. For vacuum, $D = 1$. The permittivity of air is almost the same as vacuum, $D_{\text{air}} \sim 1$. Given the value of the relative dielectric constant D , we can always recover the actual permittivity by $\epsilon_m = (D \epsilon_0)$. One can find the relative dielectric constants in many handbooks (such as the CRC Handbook on physical chemistry.¹⁰⁷ See also Appendix III). The relative dielectric constant is a function of temperature. For example, water has $D = 80.176$ (at 20°C), 78.358 (at 25°C), and 76.581 (at 30°C). On the other hand, for methanol $D = 33$ (at 25°C), ethanol $D = 24.3$ (at 25°C) and ammonia $D = 17$ (at 20°C). To obtain the permittivity of water at 20°C, $\epsilon_{\text{water}} = D_{\text{water}} \epsilon_0 = 80.176 \times 111.265 \times 10^{-12} = 8920.78 \times 10^{-12}$ (Coulomb²)/(Nm²).

Older literature uses the terms permittivity or dielectric constant, interchangeably. Thus when "dielectric constant" was mentioned, it could mean the *relative dielectric constant*, D , or the permittivity ϵ_m . Furthermore, the word dielectric constant was also used either for the *permittivity* ϵ_m^+ or ϵ_m , one with, the other without the factor 4π . We need to exercise caution when reading the literature.

1.2. Concentration Units

When salts are dissolved in water, its concentration is expressed (in the electrolyte solution literature) by at least three different unit systems: (i) the practical units (*molality*), (ii) the rational units (*mole fractions*), and (iii) the molar units (*molarity*). Mole fractions are easy to understand.

However, for the convenience in experimental work in physical chemistry, the practical units have been devised.

Practical Unit-- Molality, M : In the laboratory, one can easily measure 1000 g (1 kg) of pure water, then measure 58.4428g of sodium chloride (molecular weights: Na 22.9898+ Cl 35.453) After mixing the resulting a salt solution is called *1 molal* (or 1.0M). Thus molality M scale is defined as

$$M = \frac{n_s}{Wt\ kg\ H_2O} = \frac{no.\ of\ gmoles\ of\ salt}{No.\ of\ kg\ H_2O} \quad (1.2.1)$$

Molar Units-- Molarity, c : On the other hand, if one puts emphasis on the volume produced, one would weigh 58.4428g of table salt in a graduate, and pour in water until the total volume (salt+water) reaches 1000 cc. (For a graduate with smaller volume, one can do it proportionally: e.g. 5.84428g salt for a 100 cc graduate). This mixture is at *1 molar*. Note that the final volume one liter is for a mixture of both salt and water (not just for pure water at 1000 g). Thus

$$c = \frac{n_s}{liter} = \frac{no.\ of\ gmoles\ of\ salt}{liter\ solution\ (water + salt)} \quad (1.2.2)$$

For low concentrations of salt, one liter of solution and 1000 g of pure water are similar in weight, thus $M \approx c$. But their difference becomes large at high salt concentrations. The conversion between the two units is given by:

Basis = 1000g of pure water

$$c = M \left(\frac{1000d_m}{n_s W_s + 1000} \right) \quad (1.2.3)$$

and

$$M = c \left(\frac{n_s W_s + 1000}{1000d_m} \right) \quad (1.2.4)$$

where d_m is the density (in kg/liter) of the salt solution at the given molarity

$$d_m = (Wt_{solu}, \text{ total weight of solution, kg}) / (V_{solu}, \text{ volume of solution, liter})$$

(Note: total weight of the solution $Wt_{solu} = (n_s W_s + 1000)g / 1000$), in kg)

$$d_m = \frac{n_s W_s + 1000}{1000 V_{solu} (\text{liter})} \quad (1.2.5)$$

where n_s = number of gmoles of the salt, and W_s = molecular weight of the salt (in g/gmol, e.g. $W_s = 58.4428g / \text{gmol}$ for $NaCl$), and V_{solu} = volume (in liter) of the solution (i.e., mixture). In dilute salt solutions, $n_s \sim 0$, thus $d_m \sim d_0$ = the density of pure water which is around 1 kg/liter. Thus $c \approx M$. In case the solvent is not water (for example, ethanol), we apply the same procedure, we shall have 1000 g (1 kg) of ethanol instead of water. In many electrolyte solution studied, water is the only solvent. So we shall implicitly assume that the solution is aqueous, unless otherwise specified.

Rational units: mole fractions, x_i :

The mole fraction is defined as usual. There are two pictures (or scales) for electrolyte solutions: the McMillan-Mayer (MM) scale (solvent-implicit scale) and the Lewis-Randall (LR) scale (solvent-explicit scale). In the MM scale, the solvent (water) molecules are absent ("removed"). In the LR scale all molecules are present, including the solvent water. (Details to be explained in Chapter 4).

McMillan-Mayer scale (solvent-implicit)

The mole fractions are based on the ions (cations and anions) present without participation of the water molecules. The number of moles of ions are n_i ($i = Na^+, Cl^-, Mg^{+2}, SO_4^{-2}$, etc.)

$$x_i = \frac{n_i}{\sum_{j=\text{all ions}} n_j} \quad (1.2.6)$$

Lewis-Randall scale (solvent-explicit)

In this scale, the solvent molecules are restored with moles = n_0 . The mole fractions x_α' are defined as

$$x_\alpha' = \frac{n_\alpha}{n_0 + \sum_{j=\text{all ions}} n_j} \quad (1.2.7)$$

α is one of the ion species and can be the solvent species. The conversion from molality and molarity to mole fraction is simple.

[Example 1.1]: Given 125g of NaCl salt, dissolve it in 2 kg of water. The density of the solution (mixture) is 1.072 kg/liter at 25°C. Find the salt concentration in molality, molarity, and mole fraction.

Answer: First we find n_s the number of gmoles of salt,

$$n_s = 125 \text{ g} / (58.4428 \text{ g/gmole}) = 2.139 \text{ gmoles}$$

Thus the molality M

$$M = n_s / 2 \text{ kg water} = 2.139/2 = 1.0695 \text{ molal.}$$

And from (1.2.3)

$$c = M \cdot (1000 d_m) / (n_s W_s + 1000) = \\ = 1.0695 (1000 \times 1.072) / (2.139 \times 58.4428 + 1000) = 1.079 \text{ molar.}$$

In the MM picture

$$x_{Na^+} = 2.139 / (2.139 + 2.319) = 0.50$$

So is

$$x_{Cl^-} = 2.139 / (2.139 + 2.319) = 0.50$$

In the LR picture

$$x'_{Na^+} = 2.139 / (2.139 + 2.319 + 2000/18) = 0.020 \\ x'_{Cl^-} = 2.139 / (2.139 + 2.319 + 2000/18) = 0.020 \\ x'_{water} = (2000/18) / (2.139 + 2.319 + 2000/18) = 0.96$$

At higher salt concentration, say 585g of $NaCl$, the molality would be 5.00 molal. The density of solution is 1.166 g/cc at 25°C (from handbook⁶⁶). The molarity would be

$$5((1000 \times 1.166)/(5 \times 58.4428 + 1000)) = 4.51 \text{ molar.}$$

This value is very different from the molality of 5M (by -10%).

□

[Example 1.2] The argon-argon interaction potential u_{AA} can be represented by dispersion force as in the Lennard-Jones potential. The size parameter $\sigma = 3.405 \text{ \AA}$, and the energy parameter $\epsilon = 0.1654E-20 \text{ J}$. Compared to the Coulomb potential for $NaCl$ solution in water, what is the ratio of the two energies? (The temperature is at 20°C).

Answer: The minimum energy $-\epsilon$ in the argon potential is at $r_{min} = 3.822 \text{ \AA}$. We use this value in calculating the ion-ion interaction from the Coulomb potential

$$u_{12} = \frac{1}{\epsilon_m} \frac{q_1 q_2}{r} = \frac{1}{(80.176)(111.2E-12)} \frac{(1.602E-19)^2}{(3.822E-10)} = (0.753E-20)J$$

Note that the relative dielectric constant D of water is 80.176 at 20°C, and the permittivity is 111.265×10^{-12} . Thus the ratio is

$$u_{12}/u_{AA} = (0.753E-20)/(0.1654E-20) = 4.6$$

The electrostatic energy at the same distance is 4.6 times stronger than the Lennard-Jones energy. In the case of a 2-2 electrolyte solution (e.g., $MgSO_4$), the valences are +2 and -2, ($q_1 = 2e$, and $q_2 = -2e$), the energy ratio is $4.6 \times 4 = 18.4$, eighteen times stronger. When these ions are in air, the relative dielectric constant D of air is ~ 1 , the forces are 80 times stronger: $80.176 \times 4.6 = 369$ times for 1-1 electrolytes, and $80.176 \times 18.4 = 1475$ times for 2-2 electrolytes. This shows that the electrostatic forces are very strong, hundred and thousand times stronger than the dispersion forces. This also explains the statement made earlier that we need strong dielectric solvents to enable dissociation of ions. Only when the permittivity is large ($D \sim 70 \rightarrow 100$), the interatomic force between the cation and the anion is weakened. This reduction of the attraction force enables the salt to dissociate into ions. Water ($D=80$) is a good solvent,

thus many salt species can ionize in it. At room temperature $T = 293.15\text{K}$, the thermal fluctuation energy is proportional to $\sim kT$:

$$kT = (1.38054 \text{ E-23 J/K}) (293.15 \text{ K}) = 0.4 \text{ E-20 Joule}$$

The thermal agitations are of the same order of the Coulomb attraction (0.75 E-20 J). Thus salt can ionize in water. Ethanol ($D = 24.3$) is a weaker dielectric. Salts do not dissociate completely in ethanol. In air ($D = 1$), the electrostatic forces are so strong, that at room temperature, salts rarely separate into ions.

□

Exercises:

- 1.1. Show, by your own reasoning, the conversion formulas from molarity c to molality M . (a) Take a basis of 1000 g of water. (b) Take at basis 1 liter of solution.
- 1.2. Given the density of aqueous solution of $\text{KCl} = 1.1575 \text{ kg/liter}$ at 3.9618 M (10°C), find the molality, c .
- 1.3. Find the force F in Newton between two charged bodies with $q_1 = 2$ Coulomb, and $q_2 = 3.5$ Coulomb in a dielectric medium of relative dielectric constant $D = 2.8$. The distance between the two bodies is 0.75 meter.
- 1.4. What ions are formed when you dissolve the salts NH_4I , Na_2S , NaNO_3 , and LiBr in water? What are the valence types of these salts?
- 1.5. Find the molarity and mole fractions of salt CuSO_4 in water at 15°C . (a) 1.005M (density = 1.1573 g/cc). (b) 1.265M (density = 1.1965 g/cc). Find both x_i and x_i' .