

Solutions

A Chem1 Reference Text
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1 Solutions

Solutions are homogeneous (single-phase) mixtures of two or more components. They are extremely important in Chemistry because they allow intimate and varied encounters between molecules of different kinds, a condition that is essential for rapid chemical reactions to occur. Several more explicit reasons can be cited for devoting a significant amount of time to the subject of solutions:

1. For the reason stated above, most chemical reactions that are carried out in the laboratory and in industry, and that occur in living organisms, take place in solution.
2. Solutions are so common; very few pure substances are found in nature.
3. Solutions provide a convenient and accurate means of introducing known small amounts of a substance to a reaction system. Advantage is taken of this in the process of *titration*, for example.
4. The physical properties of solutions are sensitively influenced by the balance between the intermolecular forces of like and unlike (solvent and solute) molecules. The physical properties of solutions thus serve as useful experimental probes of these intermolecular forces.

That these intermolecular forces can have dramatic effects is made readily apparent by a simple example. At 0°C and 1 atm pressure, one litre of water will dissolve 1300 litres of ammonia gas; this corresponds to a solubility of 58 mol L⁻¹. Now if 58 mol of an ideal gas were compressed so that it would fit into the same 1-liter volume (but without the water), a *very* high pressure would be required. (You should be able to estimate this pressure; try it!).

If we actually attempt to compress pure NH₃ gas to the same degree, it would liquify, and the vapor pressure of the liquid would be about 9 atm. In other words, the escaping tendency of NH₃ molecules from H₂O is only about 1/9th of what it is from liquid NH₃. One way of interpreting this is that the strong intermolecular (dipole-dipole) attractions between NH₃ and the solvent H₂O give rise to a force that has the effect of a “negative pressure” of 9 atm.

2 Types of solutions

We usually think of a solution as a liquid; a mixture of a gas, liquid, or solid *solute* in a liquid *solvent*. Actually, solutions can exist as gases and solids as well. Gaseous mixtures don't require any special consideration beyond what you learned about Dalton's Law earlier in the course. Solid solutions are very common; most natural minerals and many alloys are solid solutions.

Everyone knows that “oil and water don't mix”. Actually, this is not strictly correct, since all substances have at least a slight tendency to dissolve in each other. This raises two important and related questions: why do solutions tend to form in the first place, and what factors limit their mutual solubilities?

You may recall that in the earlier unit on phase equilibria, we pointed out that aggregations of molecules that are more *disordered* tend to be the ones that are favored at higher temperature,

solute	solvent	energy to disperse solute	energy to introduce into solvent	increase in randomness
gas	gas	nil	nil	large
liquid or solid	gas	large	nil	large
gas	liquid	nil	varies	negative
gas	solid	nil	endothermic	negative
liquid	liquid	variable	variable	moderate
ionic solid	polar liquid	large	exothermic	small
molecular solid	polar liquid	moderate	moderate	moderate
molecular solid	nonpolar liquid	moderate	small	moderate
ionic or covalent solid	nonpolar liquid	large	small	small

Table 1: Energetics of solution formation

whereas those that possess the *lowest potential energy* are favored at lower temperatures. This is a general principle that applies throughout the world of matter; the stable form at any given temperature will always be that which leads to the best balance between low potential energy and high molecular disorder.

To see how these considerations are applied to solutions, think about the individual steps that must be carried out when a solute is dissolved in a solvent:

1. **The solute must be *dispersed***; that is, its molecular units must be pulled apart. This *requires* energy, and so this step always works *against* solution formation.
2. **The solute must be introduced into the solvent.** Whether this is energetically favorable or unfavorable depends on the nature of the solute and solvent. If the solute is A and the solvent is B, then what is important is the strength of the attractive forces between A-A and B-B molecules, compared to those between A-B pairs; if the latter are greater, then the potential energy will be lower when the substances are mixed and solution formation will be favored.

If the sum of these two steps is exothermic, this will favor solution formation, but there is one other factor to consider: Would the formation of a solution lead to an increase or a decrease in *disorder* on the molecular scale? The answer varies from case to case; mixing of different kinds of molecules always creates disorder, and substantially increasing the volume they occupy (as when a solid dissolves in a liquid) can have a very large effect. Higher temperatures generally favor processes in which disorder is created, but tend to work against those in which disorder is lost.

The qualitative assessments of these three factors for various kinds of solute-solvent combinations are given in Table 2. We will explore several of these systems in more detail.

solute	formula	solubility, mol L ⁻¹ atm ⁻¹
ammonia	NH ₃	57
carbon dioxide	CO ₂	0.0308
methane	CH ₄	.00129
nitrogen	N ₂	0.000661
oxygen	O ₂	.00126
sulfur dioxide	SO ₂	1.25

Table 2: Solubility of several gases in water at 25 °C.

2.1 Gaseous solutions

Since the energy associated with the mixing of two gases is negligible, the tendency to greater disorder dominates at all temperatures, and gases are miscible in all proportions. When the solute is a solid, “dissolving” it in a gas is formally equivalent to sublimation. The energy required to remove the molecules from their neighbors is generally too great to be compensated by the greater disorder in the vapor phase, so solids tend to have relatively low vapor pressures. The same is true of liquids at temperatures well below their boiling points.

2.2 Solutions of gases in liquids

When a gas dissolves in a liquid, the confinement of the gas in the much smaller volume of the liquid causes a loss in molecular disorder that is not usually compensated by the presence of two kinds of molecules in the liquid phase. Such processes are not favored unless there are strong compensating factors; gases therefore tend to be only slightly soluble in liquids.

Still, there is always some solubility, as is shown in Table 2.2 for several common gases in water. The greatest solubilities occur when the gas reacts chemically with the solvent (a “compensating factor”), as happens, for example, with CO₂, HCl, SO₂, and especially NH₃ in water. In these cases, the fall in potential energy associated with the reaction helps overcome the unfavorable randomness effect.

One important consequence of the reduction in disorder when a gas dissolves in a liquid is that the solubility of a gas *decreases* at higher temperatures; this is in contrast to most other situations, where a rise in temperature usually leads to increased solubility.

The temperature dependence of the solubility of oxygen in water is an important consideration for the well-being of aquatic life; thermal pollution of natural waters (due to the influx of cooling water from power plants) has been known to reduce the dissolved oxygen concentration to levels low enough to kill fish. The advent of summer temperatures in a river can have the same effect if the oxygen concentration has already been partially depleted by reaction with organic pollutants.

2.3 Solutions of liquids in liquids

Whereas all gases will mix to form solutions regardless of the proportions, liquids are much more fussy. Some liquids, such as ethyl alcohol and water, are miscible in all proportions. Others, like the proverbial “oil and water”, are not; each liquid has only a limited solubility in the other, and once either of these limits is exceeded, the mixture separates into two phases.

The reason for this variability is apparent from Table 2. Mixing of two liquids can be exothermic, endothermic, or without thermal effect, depending on the particular substances. Whatever the case, the energy factors are not usually very large, but neither is the increase in randomness; the two factors are frequently sufficiently balanced to produce limited miscibility.

A useful general rule is that liquids are completely miscible when their intermolecular forces are very similar in nature; “like dissolves like”. Thus water is miscible with other liquids that can engage in hydrogen bonding, whereas a hydrocarbon liquid in which London or dispersion forces are the only significant intermolecular effect will only be completely miscible with similar kinds of liquids.

Substances such as the alcohols, $\text{CH}_3(\text{CH}_2)_n\text{OH}$, which are hydrogen-bonding (and thus hydrophilic) at one end and hydrophobic at the other, tend to be at least partially miscible with both kinds of solvents. If n is large, the hydrocarbon properties dominate and the alcohol has only a limited solubility in water. Very small values of n allow the $-\text{OH}$ group to dominate, so miscibility in water increases and becomes unlimited in ethanol ($n = 1$) and methanol ($n = 0$), but miscibility with hydrocarbons decreases owing to the energy required to break alcohol-alcohol hydrogen bonds when the nonpolar liquid is added.

These considerations have become quite important in the development of alternative automotive fuels based on mixing these alcohols with gasoline. At ordinary temperatures the increased randomness of the mixture is great enough that the unfavorable energy factor is entirely overcome, and the mixture is completely miscible. At low temperatures, the randomness factor becomes less predominant, and the fuel mixture may separate into two phases, presenting severe problems to the fuel filter and carburetor.

2.4 Solutions of molecular solids in liquids

The stronger intermolecular forces in solids require more input of energy in order to disperse the molecular units into a liquid solution, but there is also a considerable increase in disorder that can more than compensate if the intermolecular forces are not too strong, and if the solvent has no strong hydrogen bonds that must be broken in order to introduce the solute into the liquid.

For example, at 25°C and 1 atm pressure, 20 g of iodine crystals will dissolve in 100 ml of ethyl alcohol, but the same quantity of water will dissolve only 0.30 g of iodine.

As the molecular weight of the solid increases, the intermolecular forces holding the solid together also increase, and solubilities tend to fall off; thus the solid linear hydrocarbons $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$ ($n > 20$) show diminishing solubilities in hydrocarbon liquids.

2.5 Solutions of ionic solids in water

Since the coulombic forces that bind ions and highly polar molecules into solids are quite strong, we might expect these solids to be insoluble in just about any solvent. Ionic solids are insoluble

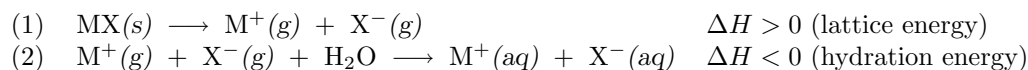
substance	LiF	NaI	KBr	CsI	LiCl	NaCl	KCl	AgCl
lattice energy (kJ)	1021	682	669	586	846	778	707	910
hydration energy (kJ)	1017	686	649	552	884	774	690	844
heat of solution (kJ)	+3	-4	+20	+34	-38	+4	+17	+66

Table 3: Energy terms associated with the dissolution of some ionic solids

in most non-aqueous solvents, but the high solubility of some (including NaCl) in water suggests the need for some further explanation.

The key factor here turns out to be the interaction of the ions with the solvent. The electrically-charged ions exert a strong coulombic attraction on the end of the water molecule that has the opposite partial charge. As a consequence, ions in solution are always *hydrated*; that is, they are quite tightly bound to water molecules through ion-dipole interaction. The number of water molecules contained in the *primary hydration shell* varies with the radius and charge of the ion.

The dissolution of an ionic solid in water can be thought of as a sequence of two steps:



The first reaction is endothermic, but the second is exothermic; whether the overall dissolution process is energetically favorable or unfavorable depends on the actual number of kilojoules associated with the two processes.

As you can see from the examples in Table 3, the net energy (the heat of solution) is the sum of two quantities having large magnitudes and opposite signs; the sign of the result is therefore rather hard to predict.

The balance between the lattice energy and hydration energy is a major factor in determining the solubility of an ionic crystal in water, but there is another factor to consider as well. We generally assume that there is a rather large increase in disorder when a solid is dispersed into the liquid phase. However, in the case of ionic solids, each ion ends up surrounded by a shell

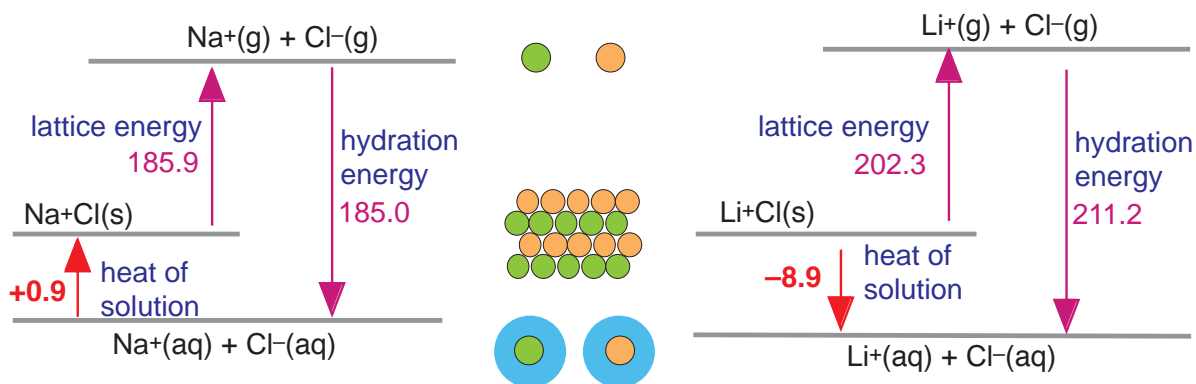


Figure 1: Energetics of dissolution of ionic solids.

of oriented water molecules. The ions themselves have become more disordered, but the water molecules are now more ordered than before. In some cases the latter effect predominates, and dissolution of the salt leads to a net increase in order. Recall that any process in which the net disorder diminishes becomes less probable as the temperature increases; this explains why the solubilities of some salts *decrease* with temperature.

3 Methods of expressing the concentration of a solution

Concentration is a general term referring to the quantity of solute used to prepare a given amount of solution. Various ways of expressing concentration are in use; the choice is usually a matter of convenience in a particular application.

3.1 “Parts-per” concentration

One common method of expressing the concentration is based on the quantity of solute in a fixed quantity of solution. The “quantities” referred to here can be expressed in weight, in volume, or both (the weight of solute in a given volume of solution.) In order to distinguish among these possibilities, the abbreviations (w/w), (v/v) and (w/v) are used.

In commerce, medicine, and other applied fields of Chemistry, (w/w) measure is often used, and is commonly expressed as *weight-percent concentration*, or simply “percent concentration”. For example, a solution containing 5 g of NaCl and 95 g of H₂O is a 5% solution of NaCl.

Problem Example 1

Find the percent (w/w) concentration of a solution containing 4.5 g of sucrose in 90 mL of water.

Solution: 90 mL of water has a mass of 90 g, so the concentration will be

$$\frac{4.5 \text{ g}}{94.5 \text{ g}} \times 100\% = 4.8\% \text{ (w/w) sucrose}$$

Percent means “parts per 100”; we can also use parts per thousand (ppt) for expressing concentrations in grams of solute per kilogram of solution. For more dilute solutions, parts per million (ppm) and parts per billion (10⁹; ppb) are used. These terms are widely employed to express the amounts of trace pollutants in the environment.

Problem Example 2

Describe how you would prepare 30 g of a 20 percent (w/w) solution of KCl in water.

Solution: The weight of potassium chloride required is 20% of the total weight of the solution, or $0.2 \times 30 \text{ g} = 6.0 \text{ g}$ of KCl. The remainder of the solution ($30 - 6 = 24$) g consists of water. Thus you would dissolve 6.0 g of KCl in 24 g of water.

3.2 Weight/volume and volume/volume basis

It is sometimes convenient to base concentration on a fixed volume, either of the solution itself, or of the solvent alone. In most instances, a “5% by volume” solution of a solid will mean 5 g of the solute dissolved in 100 ml of the *solvent*.

Problem Example 3

Fish, like all animals, need a supply of oxygen, which they obtain from oxygen dissolved in the water. The minimum oxygen concentration needed to support most fish is around 5 ppm (w/v). How many moles of O₂ per liter of water does this correspond to?

Solution: 5 ppm (w/v) means 5 grams of oxygen in one million mL (1000 L) of water, or 5 mg per liter. This is equivalent to

$$\frac{0.005 \text{ g}}{32.0 \text{ g mol}^{-1}} = 1.6 \times 10^{-4} \text{ mol}$$

If the solute is itself a liquid, volume/volume measure usually refers to the volume of solute contained in a fixed volume of *solution*. The “proof” of an alcoholic beverage is the (v/v)-percent, multiplied by two; thus a 100-proof vodka has the same alcohol concentration as a solution made by adding sufficient water to 50 ml of alcohol to give 100 ml of solution. (Since volumes of mixed substances are not strictly additive, the amount of water will be very slightly less than 50 ml).

These kinds of concentration measure are mostly used in commercial and industrial applications.

3.3 Molarity: mole/volume basis

This is the method most used by chemists to express concentration. Molar concentration (molarity) is the number of moles of solute per liter of *solution*. The important point to remember is that the volume of the solution is different from the volume of the solvent; the latter quantity can be found from the molarity only if the densities of both the solution and of the pure solvent are known. Similarly, calculation of the weight-percentage concentration from the molarity requires density information; you are expected to be able to carry out these kinds of calculations, which are covered in most texts.

Problem Example 4

How would you make 120 mL of a 0.10 M solution of potassium hydroxide in water?

Solution: The amount of KOH required is (0.120 L) × (0.10 mol L⁻¹) = 0.012 mol. The molar mass of KOH is 56.1 g, so the weight of KOH required is .012 mol × 56.1 gmol⁻¹ = 0.67 g. We would dissolve this weight of KOH in a volume of water that is *less than* 120 mL, and then add sufficient water to bring the total volume up to 120 mL. (Remember: molarity is defined in terms of the volume of the *solution*, not of the *solvent*.)

Problem Example 5

Calculate the molarity of a 60-% (w/w) solution of ethanol ($\text{C}_2\text{H}_5\text{OH}$) in water whose density is 0.8937 g mL^{-1} .

Solution: One liter of this solution has a mass of 893.7 g, of which $(0.60 \times 893.7 \text{ g}) = 536.2 \text{ g}$ consists of ethanol. The molecular weight of $\text{C}_2\text{H}_5\text{OH}$ is 46.0, so the number of moles of ethanol present in one litre (that is, the molarity) will be

$$\frac{(536.2 \text{ g}) \div 46.0 \text{ g mol}^{-1}}{1\text{L}} = \underline{11.6 \text{ mol L}^{-1}}$$

Although molar concentration is widely employed, it suffers from one serious defect: since volumes are temperature-dependent (substances expand on heating), so are molarities; a 0.100 M solution at 0°C will have another concentration at 50°C . For this reason, molarity is not the preferred concentration measure in applications where physical properties of solutions and the effect of temperature on these properties is of importance.

3.4 Mole fraction: mole/mole basis

This is the most fundamental of all methods of concentration measure, since it makes no assumptions at all about volumes. The mole fraction of substance i in a mixture is defined as

$$\chi_i = \frac{n_i}{\sum_j n_j}$$

in which n_j is the number of moles of substance j , and the summation is over all substances in the solution. Mole fractions run from zero (substance not present) to unity (the pure substance).

Problem Example 6

What fraction of the molecules in a 60-% (w/w) solution of ethanol in water consist of H_2O ?

Solution: From the previous problem, we know that one liter of this solution contains 536.2 g (11.6 mol) of $\text{C}_2\text{H}_5\text{OH}$. The number of moles of H_2O is $(893.7 - 536.2) \text{ g} \div 18.0 \text{ g mol}^{-1} = 19.9 \text{ mol}$. The mole fraction of water is thus

$$\frac{19.9}{19.9 + 11.6} = \underline{0.63}$$

Thus 63% of the molecules in this solution consist of water, and 37% are ethanol.

3.5 Molality: mole/weight basis

A 1-molal solution contains one mole of solute per 1 kg of *solvent*. Molality is a hybrid concentration unit, retaining the convenience of mole measure for the solute, but expressing it in relation to a temperature-independent mass rather than a volume. Molality, like mole fraction, is used in applications dealing with certain physical properties of solutions; we will see some of these in the next section.

Problem Example 7

Calculate the molality of a 60-% (w/w) solution of ethanol in water.

Solution: From the above problems, we know that one liter of this solution contains 11.6 mol of ethanol in $(893.7 - 536.2) = 357.5$ g of water. The molarity of ethanol in the solution is therefore $(11.6 \text{ mol}) \div (0.3575 \text{ kg}) = \underline{32.4 \text{ mol kg}^{-1}}$.

4 Colligative properties: escaping tendency of the solvent

We are accustomed to describing a solution in terms of the concentration of the one or more *solutes*. However, many of the important physical properties of a solution depend more directly on the concentration of the *solvent*. These properties include the vapor pressure, the freezing point, the boiling point, and the osmotic pressure. Because they are tied together (Latin, *co ligare*) in this way, they are referred to as the *colligative properties* of solutions.

Let us first restrict ourselves to solutions in which the solute is *non-volatile*; that is, it does not make a significant contribution to the overall vapor pressure of the solution. Solutions of salt or sugar in water fulfill this condition exactly. Other solutes that do have measurable vapor pressures, such as iodine or ethylene glycol antifreeze, can often be considered nonvolatile in comparison to the solvent at the same temperature. Solutions in which both components possess significant vapor pressures, such as alcohol in water, will be treated in another section.

4.1 Vapor pressure of solutions: Raoult's law

The colligative properties really depend on the escaping tendency of solvent molecules from the liquid phase. You will recall that the vapor pressure is a direct measure of escaping tendency, so we can use these terms more or less interchangeably.

The tendency of molecules to escape from a liquid phase into the gas phase depends in part on how much of an increase in *disorder* can be achieved by doing so. Evaporation of solvent molecules from the liquid always leads to a large increase in disorder because of the greater volume occupied by the molecules in the gaseous state. But if the liquid solvent is initially "diluted" with solute, the *increase* in disorder on entering the gas phase will be less. There will accordingly be less tendency for the solvent molecules to enter the gas phase, and so the vapor pressure of the solution diminishes as the concentration of solute increases and that of solvent decreases.

If we add sufficient nonvolatile solute to a liquid to end up with 50% solute and 50% solvent molecules, the escaping tendency of the solvent, and thus its vapor pressure, will be reduced by 50%. This linear relation between the mole fraction concentration of the solvent and its vapor pressure is expressed by *Raoult's law* (1886):

$$P = P^\circ X \tag{1}$$

in which P° is the vapor pressure of the pure solvent and X is its mole fraction in the solution. (From the definition of mole fraction, you should understand that $X_{\text{solvent}} = 1 - X_{\text{solute}}$.)

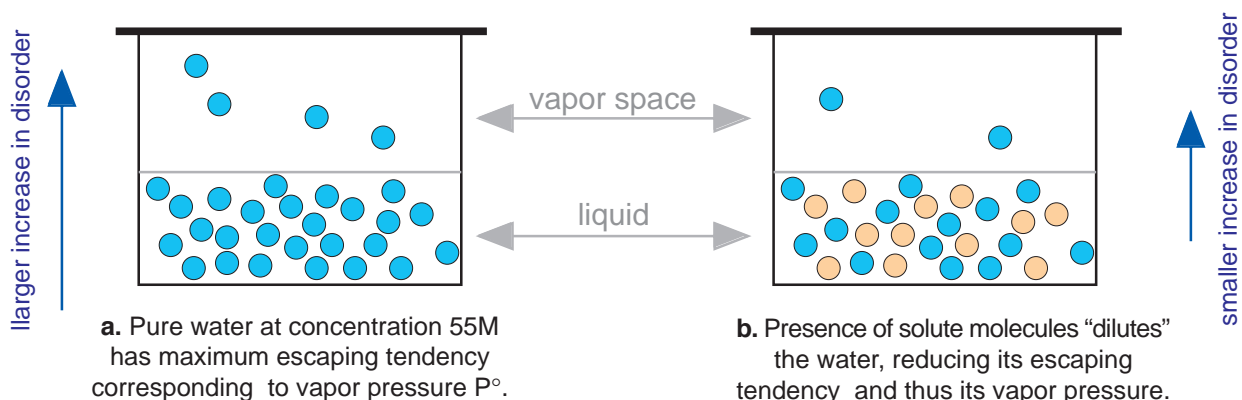


Figure 2: Escaping tendency and Raoult's Law.

The number 55.5 ($= 1000 \div 18$) is a useful one to remember if you are dealing a lot with aqueous solutions; this represents the concentration of water in pure water. (Strictly speaking, this is the molal concentration of H_2O ; it is only the molar concentration at temperatures around 4°C , where the density of water is closest to 1.000 g cm^{-3} .)

Problem Example 8

Estimate the vapor pressure of a 40 percent (W/W) solution of ordinary cane sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$, MW = 342 g mol^{-1}) in water. The vapor pressure of pure water at the same temperature is 26.0 torr.

Solution: 100 g of solution contains $40 \div 342 = 0.12$ mol of sugar and $60 \div 18 = 3.3$ mol of water. The mole fraction of water in the solution is

$$\frac{3.3}{.12 + 3.3} = 0.96$$

and its vapor pressure will be $0.96 \times 26.0 \text{ torr} = \underline{25.1 \text{ torr}}$.

Since the sum of all mole fractions in a mixture must be unity, it follows that the more moles of solute, the smaller will be the mole fraction of the solvent. Also, if the solute is a salt that dissociates into ions, then the proportion of solvent molecules will be even smaller. For example, a solution made up by dissolving 1 mole of $\text{CaCl}_2(s)$ in 12 mol of water will have a water mole fraction of 0.8 if the CaCl_2 is totally dissociated into its ions.

4.2 Boiling point elevation

If addition of a nonvolatile solute lowers the vapor pressure of the solution, then the temperature must be raised to restore the vapor pressure to the value corresponding to the pure solvent. In particular, the temperature at which the vapor pressure is 1 atm will be higher; the boiling point will be raised.

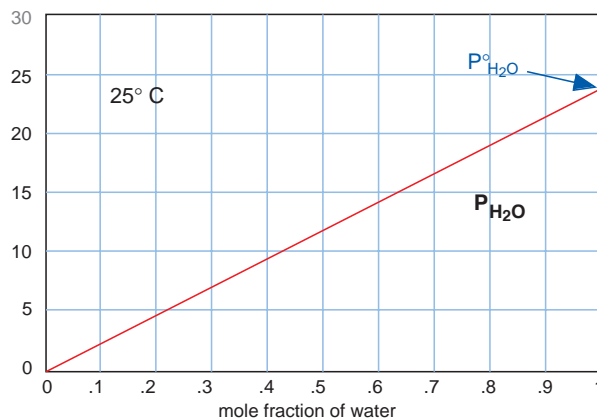


Figure 3: Vapor pressure of water as a function of its mole fraction

The relation between the boiling point of the solution and the mole fraction of the solvent is rather complicated, but for dilute solutions the elevation of the boiling point is directly proportional to the molal concentration of the *solute*:

$$\Delta_B = K_B \times \frac{\text{moles of solute}}{\text{kg of solution}} \quad (2)$$

The proportionality constant K_B , known as the *boiling point elevation constant*, is a property of the *solvent*, since it is the solvent's vapor pressure and the temperature dependence of the vapor pressure that determine the sensitivity of the boiling point to the solvent mole fraction. The only role the solute plays here is to dilute the solvent. (Note that the molality of the solute must take any dissociation into account; thus a solution containing 1 mol kg^{-1} of CaCl_2) is 1 molal in Ca^{2+} and 2 molal in Cl^- , so its total molality is 3 mol kg^{-1} .)

Problem Example 9

Estimate the boiling point of the sugar solution in the preceding problem example, given that the molal boiling point elevation constant for water is $0.514 \text{ K mol}^{-1} \text{ kg}^{-1}$.

Solution: The molality of the solution is $(0.12 \text{ mol}) \div (0.100 \text{ kg}) = 1.2 \text{ m}$, so the boiling point will be raised by

$$(0.514 \text{ K mol}^{-1} \text{ kg}) \times (1.2 \text{ mol kg}^{-1}) = 0.62 \text{ K}$$

so the boiling point will be 100.6 °C.

4.3 Freezing point depression

The freezing point is the temperature at which solid and liquid can simultaneously coexist, meaning that the escaping tendencies of molecules from the two phases is the same. Suppose now that we dilute the solvent by adding some solute. The escaping tendency of solvent molecules from the liquid phase is now reduced owing to their increased disorder in the solution, but in

the solid nothing has changed and the escaping tendency of solvent molecules from this phase remains the same. This means that there will be a net movement of solvent molecules from the solid phase to the liquid; the solid melts. In order to keep the solid from melting, the escaping tendency of molecules from the solid must be reduced. This can be accomplished by reducing the temperature; this lowers the escaping tendency of molecules from both phases, but it affects those in the solid more than those in the liquid, so we eventually reach the new, lower freezing point where the two quantities are again in exact balance and both phases can coexist.

If you prefer to think in terms of vapor pressures, you can use the same argument if you bear in mind that the vapor pressures of the solid and liquid must be the same at the freezing point. Dilution of the liquid (the solvent) by the nonvolatile solute reduces the vapor pressure of the solvent according to Raoult's law, thus reducing the temperature at which the vapor pressures of the liquid and frozen forms of the solution will be equal.

The use of salt to de-ice roads is a common application of this principle. The solution formed when some of the salt dissolves in the moist ice reduces the freezing point of the ice. If the freezing point falls below the ambient temperature, the ice melts. In very cold weather, the ambient temperature may be below that of the salt solution, and the salt will have no effect.

Automotive radiator antifreezes are mostly based on ethylene glycol, (CH₂OH)₂. Owing to the strong hydrogen-bonding properties of this double alcohol, this substance is miscible with water in all proportions, and contributes only a very small vapor pressure of its own. Besides lowering the freezing point, antifreeze also raises the boiling point, increasing the operating range of the cooling system.

As with boiling point elevation, in dilute solutions there is a simple linear relation between the freezing point depression and the molality of the solute:

$$\Delta_F = K_F \times \frac{\text{moles of solute}}{\text{kg of solution}} \quad (3)$$

For water, $K_F = -1.86 \text{ K L}^{-1} \text{ mol}$.

Problem Example 10

Estimate the freezing point of an antifreeze mixture is made up by combining one volume of ethylene glycol (MW = 62, density 1.11 g cm⁻³) with two volumes of water.

Solution: Assume that we use 1 L of glycol and 2 L of water (the actual volumes do not matter as long as their ratios are as given.) The mass of the glycol will be 1.10 kg and that of the water will be 2.0 kg, so the total mass of the solution is 3.11 kg. We then have:

$$\begin{aligned} \text{number of moles of glycol:} & \quad \frac{1110 \text{ g}}{62 \text{ g mol}^{-1}} = 17.9 \text{ mol} \\ \text{molality of glycol:} & \quad (17.9 \text{ mol}) \div (3.11 \text{ kg}) = 5.76 \text{ mol kg}^{-1} \\ \text{freezing point depression:} & \quad (K_F = -1.86 \text{ K kg}^{-1} \text{ mol}) \times (5.76 \text{ mol kg}^{-1}) = -10.7 \text{ K} \end{aligned}$$

so the solution will freeze at about -11 °C.

Any ionic species formed by dissociation will also contribute to freezing point depression. This can serve as a useful means of determining the fraction of a solute that is dissociated.

Problem Example 11

An aqueous solution of nitrous acid (HNO_2 , MW = 47) freezes at -0.198°C . If the solution was prepared by adding 0.100 mole of the acid to 1000 g of water, what percentage of the HNO_2 is dissociated in the solution?

Solution: The molality of the solution is $\Delta_F \div K_F = (-.198\text{K}) \div (-1.86 \text{ K kg}^{-1} \text{ mol}) = 0.106 \text{ mol kg}^{-1}$; this is the total number of moles of species present after the dissociation reaction $\text{HNO}_2 \longrightarrow \text{H}^+ + \text{NO}_2^+$ has occurred. If we let $x = [\text{H}^+] = [\text{NO}_2^+]$, then $[\text{HNO}_2] = 0.100 - x$ and by stoichiometry, $.106 - x = 2x$ and $x = .0355$. The fraction of HNO_2 that is dissociated is $.0355 \div .100 = .355$, corresponding to 35.5% dissociation of the acid.

4.4 Colligative properties and molecular weight determinations

The expressions for boiling point elevation and freezing point depression shown in the preceding two equations are in terms of molality of the solute. If the mass of solute that leads to a given change in boiling point or freezing point is known, then the molecular weight of the solute can be calculated. The same information can be obtained from measurement of the other two colligative properties, vapor pressure lowering and osmotic pressure (discussed below).

If the solute is a substance that is partly dissociated into ions, then the degree of dissociation can be calculated if the molecular weight of the undissociated solute is known. This is another example of the use of a property of bulk matter, such as the freezing point, to measure a microscopic property having to do with individual molecular units.

5 Solutions of volatile substances

When both the solute and the solvent are volatile, both substances will contribute to the total vapor pressure of the solution. If the solution is *ideal*, the relative contributions will be proportional to the mole fractions. The concept of the ideal solution is somewhat different from that of the ideal gas, in which intermolecular interactions are totally absent. In an ideal solution, the interactions are there, but they are all the same; A–A and B–B attractions are the same as A–B attractions. This is the case only when the solvent and solute are chemically and structurally very similar.

5.1 Solutions of volatile liquids

If two volatile liquids form an ideal solution, each will make a contribution to the overall vapor pressure that is directly proportional to the vapor pressure of the pure liquid and to its mole fraction in the solution. This is just Raoult's law again, and it also provides an operational definition for an ideal solution: *an ideal solution is one that follows Raoult's law.*

Fig. 4 shows this proportionality for a solution of benzene and toluene at 60°C . The near-ideal behavior of this solution is shown by the straightness of the three lines.

In non-ideal solutions, two kinds of things can happen. If A–B attractions are less strong than attractions between like molecules, one or both of the species will tend to be squeezed out

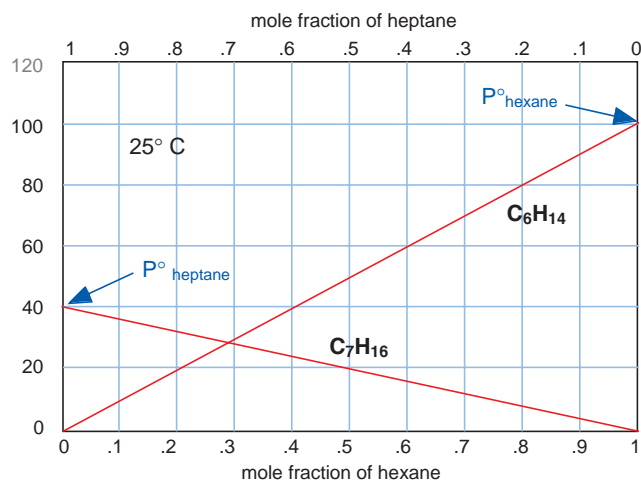


Figure 4: Raoult's Law plots for hexane-heptane mixtures.

of the solution, which will have a higher vapor pressure than would otherwise be the case. An example is seen in Fig. 5b, which illustrates a positive deviation from Raoult's law. Fig. 5a shows the opposite situation, in which unlike molecules attract each other more strongly than like molecules.

The degree to which non-ideal solutions deviate from Raoult's law varies with composition in a non-uniform way. It is always true, however, that as the mole fraction of either component approaches unity, the behavior of the solution approaches ideality. This is a simple consequence of the fact that at these limits, each molecule is surrounded mainly by its own kind, and its escaping tendency will be little influenced by its interactions with the other kind of molecule. Raoult's law is therefore a *limiting* law:

$$P_i = \lim_{X_i \rightarrow 1} P^\circ X_i \quad (4)$$

it gives the partial pressure of a substance in equilibrium with the solution more and more closely as the mole fraction of that substance approaches unity.

5.2 Distillation

In an ideal solution of two volatile liquids, the vapor will always be enriched in the more volatile component. That is, the mole fraction and partial pressure of the more volatile substance will be higher in the vapor phase than in the liquid phase. This follows very simply from the application of Raoult's law, and it serves as the basis of the separation of two volatile liquids by distillation.

Consider, for example, a solution composed of equal amounts (mole fractions = 0.5) of liquids A and B, whose vapor pressures are 300 and 400 torr. If A and B form an ideal solution, the mole fraction of B (the more volatile substance) in the vapor will be $400 \div 700 = .57$; the vapor is now richer in B. If this vapor is condensed, the resulting liquid will also be enriched in B. By repeating this process a number of times, B can be recovered from the solution in any degree of purity desired.

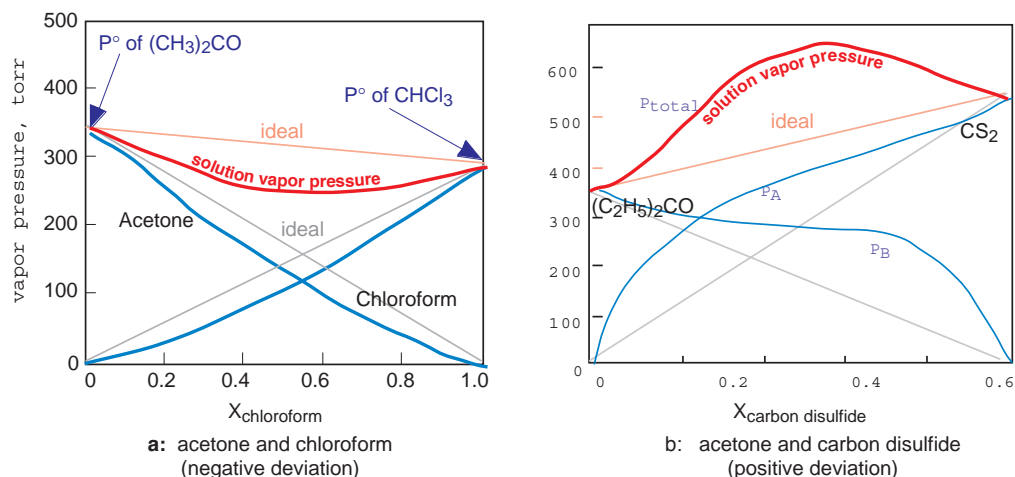


Figure 5: Positive and negative deviations from Raoult's law.

Problem Example 12

Benzene and toluene form a nearly ideal solution (i.e., one that obeys Raoult's law.) At 80 °C, the vapor pressure of pure benzene (MW = 78.1) is 753 torr and that of toluene (MW = 92.1) is 290 torr. The following questions refer to a solution that contains *equal weights* of the two liquids.

1. Calculate the partial pressure of each solution that would be in equilibrium with the solution at 80 °C.
2. At what atmospheric pressure will this solution boil at 80 °C?
3. What will be the composition of the liquid that condenses when this vapor is cooled?

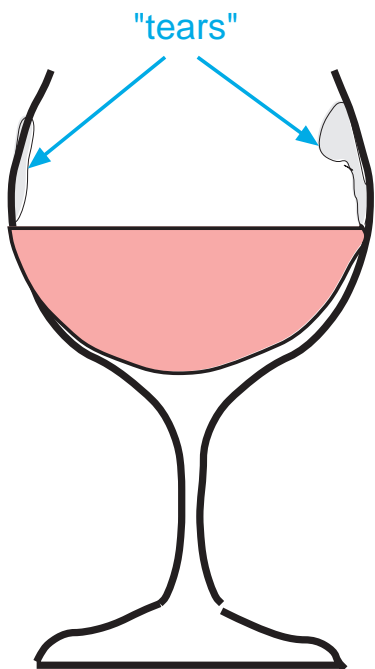
Solution: For simplicity, assume that the solution contains 100 g of each substance. The moles of each solute will be $m_B = 100 \div 78.1 = 1.28$ and $m_T = 100 \div 92.1 = 1.09$. The mole fraction of benzene is $1.28 \div (1.28 + 1.09) = 0.54$ and that of toluene is $1.00 - 0.54 = 0.46$ (why?)

The solution will boil when the atmospheric pressure is the same as the total vapor pressure of the solution, which by Dalton's and Raoult's laws is

$$P_{total} = P_B + P_T = X_B P_B^\circ + X_T P_T^\circ = \underbrace{(.54 \times 753 \text{ torr})}_{406 \text{ torr}} + \underbrace{(.46 \times 290 \text{ torr})}_{133 \text{ torr}} = \underline{540 \text{ torr}}.$$

The composition of the condensed liquid (the distillate) will be $X_B = 406 \div 540 = 0.75$ and $X_T = 0.25$. Notice that the distillate will be enriched in the more volatile component, compared to the original liquid.

Some solutions are so non-ideal that complete separation by distillation is not possible. Such solutions form *constant-boiling* mixtures in which the compositions of the liquid and vapor are the same, so that no further fractionation is possible. This is a very common behavior. For example, ethyl alcohol can be distilled from a mixture of alcohol and water until the composition reaches



Why do “tears” form inside a wine glass? You have undoubtedly noticed this; pour some wine into a glass, and after a few minutes, droplets of clear liquid can be seen forming on the inside walls of the glass about a centimeter above the level of the wine. This happens even when the wine and the glass are at room temperature, so it has nothing to do with condensation.

The explanation involves Raoult's law, hydrogen bonding, adsorption, and surface tension, so this phenomenon makes a good review of much you have learned about liquids and solutions.

First, remember that both water and alcohol are hydrogen-bonding liquids, and as such, they are both strongly attracted to the oxygen atoms and -OH groups on the surface of the glass. This causes the liquid film to creep up the walls of the glass, forming a meniscus. Alcohol, the more volatile of the two liquids, vaporizes more readily, causing the upper (and thinnest) part of the liquid film to become enriched in water, raising the meniscus even higher. Because of its stronger hydrogen bonding, water has a larger surface tension than alcohol, so as the alcohol evaporates, the surface tension of the upper part of the liquid film increases. This causes the surface to contract into a sphere-like shape which gets distorted by gravity into a “tear”, which eventually grows so large that gravity wins out over adsorption, and the drop falls back into the liquid, soon to be replaced by another.

about 95% alcohol, at which time a constant-boiling mixture is formed. Some other method must be employed to remove the remaining water.

5.3 Solutions of gases in liquids: Henry's law

A gas dissolved in a liquid will be in equilibrium with the same gas in the vapor phase. This means that the solubility of the gas in the liquid will vary with the partial pressure of the gas in the vapor. When you open a bottle or can containing a carbonated beverage, the partial pressure of CO₂ is greatly reduced. This reduces the equilibrium concentration of CO₂ in the liquid, and the excess gas leaves the solution in the form of bubbles.

Ideally, the concentration of the gas in the liquid will be directly proportional to the partial pressure in the vapor. However, gases, by their very nature, do not form ideal solutions with most liquids. This simple proportionality, known as *Henry's law*, holds strictly only in the limit of zero concentration of the dissolved gas:

$$C = \lim_{P \rightarrow 0} kP \quad (5)$$

P here is the partial pressure of the gas in the vapor phase, and C is its concentration in the solution. The proportionality constant k is the *Henry's law constant*; its units depend on the concentration units used. Most gases are so sparingly soluble in most liquids that Henry's law is often applicable over the entire range of gas pressures normally encountered. Some representative Henry's law constants are given in Table 2.2 on page 4.

Considerable attention must be given to factors involving the solubility of atmospheric gases in the blood when humans are exposed to abnormally high pressures, as in diving, for example. Under the high pressure required to force air into the lungs when one is deeply submerged, both oxygen and nitrogen become more soluble in the blood. The higher oxygen concentration can be toxic, producing a condition known as oxygen narcosis. The additional nitrogen concentration causes no ill effects until the diver returns to the surface, at which time the nitrogen (and a lesser amount of oxygen) form bubbles in the blood that can lead to painful and fatal consequences. To prevent these effects, most of the nitrogen and some of the oxygen in the breathing mixture is replaced with helium. This gas has a very small Henry's law constant, so does not tend to dissolve readily in the blood.

Problem Example 13

The solubility of oxygen gas at 1 atm pressure in pure water at 25 °C is 0.043 g L⁻¹. Find the concentration of O₂ in water exposed to the air at the same temperature.

Solution: The partial pressure of O₂ in the air is about 0.21 atm, and thus its mole fraction in the air is 0.21. Substituting into Eq 5 yields

$$C = (.043 \text{ g L}^{-1})(0.21) = 0.0090 \text{ g L}^{-1}$$

5.4 Raoult's law and Henry's law

It is easy for beginners to get these two laws confused, since they both refer to solutions and have similar forms. Bear in mind that

- Raoult's law applies to the liquid *solvent*; it expresses the escaping tendency of molecules from the liquid when they are surrounded by other molecules of identical kind;
- Henry's law applies to the *solute*, and this can be any volatile substance— not necessarily a gas. This law expresses the escaping tendency of a solute molecule from an environment composed of solvent molecules. The magnitude of the Henry's law constant is therefore a measure of the degree of attraction between unlike molecules.
- The "Raoult's law constant" is merely P° , the vapor pressure (escaping tendency) of molecules from a liquid composed of their own kind. Thus P° amounts to an indirect measure of the attractive force between *like* molecules.
- In a solution composed of significant amounts of substances whose intermolecular interactions are different, the escaping tendency of any given molecule will depend on its local environment. Since this will change with concentration, the solution will usually not follow either law except near the limiting mole fractions of 0 or 1.

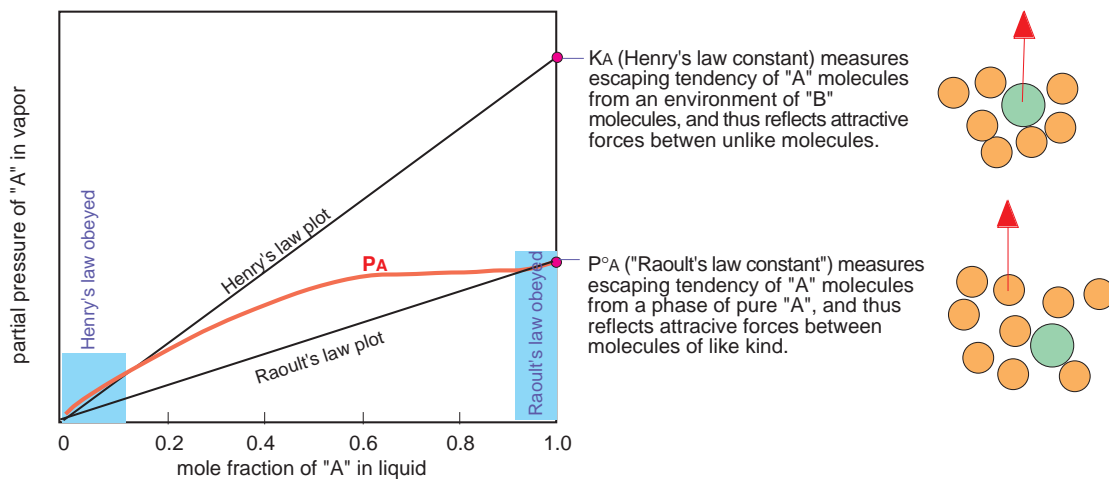


Figure 6: Comparison of Raoult's law and Henry's law.

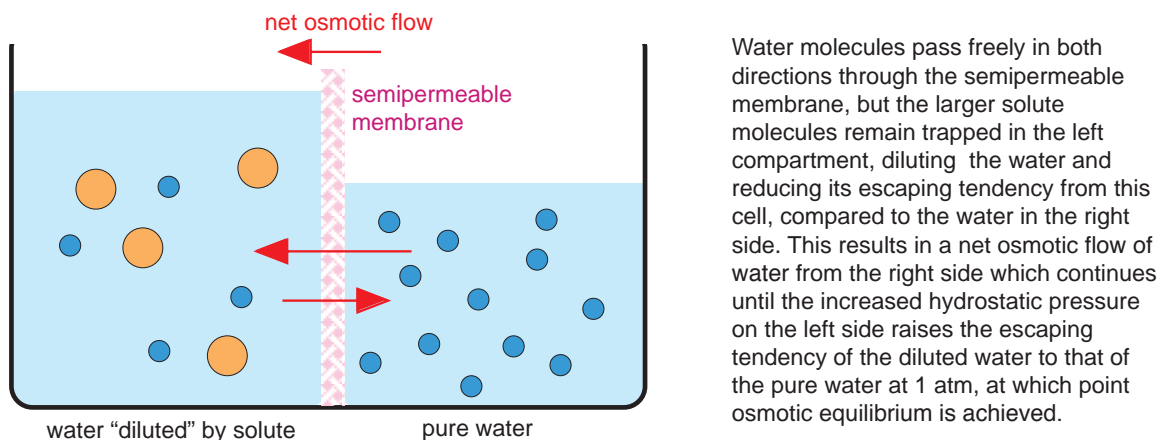


Figure 7: Osmotic flow through a semipermeable membrane.

6 Osmosis and osmotic pressure

Osmosis is the process in which a liquid passes through a membrane whose pores permit the passage of solvent molecules but are too small for the larger solute molecules to pass through. Fig. 7 shows a simple osmotic cell. Both compartments contain water, but the one on the left also contains a solute whose molecules are too large to pass through the membrane. Many artificial and natural substances are capable of acting as *semi-permeable membranes*. The walls of most plant and animal cells fall into this category.

If the cell is set up so that the liquid level is initially the same in both compartments, you will soon notice that the liquid rises in the left compartment and falls in the right side, indicating that water molecules from the right compartment are migrating through the semipermeable membrane and into the left compartment. This migration of the solvent is known as *osmotic flow*, or simply "osmosis".

What is the force that drives the molecules through the membrane? This is a misleading question, because there is no real “force” in the physical sense. It is a consequence of simple statistics that the randomly directed motions of a collection of molecules will cause more to leave a region of high concentration than return to it; the escaping tendency of a substance from a phase increases with its concentration in the phase.

6.1 Diffusion and osmotic flow

Suppose you drop a lump of sugar into a cup of tea, without stirring. Initially there will be a very high concentration of dissolved sugar at the bottom of the cup, and a very low concentration near the top. Since the molecules are in random motion, there will be more sugar molecules moving from the high concentration region to the low concentration region than in the opposite direction. The motion of a substance from a region of high concentration to one of low concentration is known as *diffusion*. We can say that the “driving force” for diffusion is a concentration gradient, or that it is the difference in escaping tendency of the substance in the two parts of the solution, but you must clearly understand that there is really no special force on the individual molecules; diffusion is purely a consequence of statistics.

Now take two solutions of differing *solvent* concentration, and separate them by a semipermeable membrane. Being semipermeable, the membrane is essentially invisible to the solvent molecules, so they diffuse from the high concentration region to the low concentration region just as before. This flow of solvent constitutes *osmotic flow*, or *osmosis*.

In the absence of the semipermeable membrane, diffusion will continue until the concentrations of all substances are uniform throughout the phase. With the semipermeable membrane in place, and if one compartment contains the pure solvent, this can never happen; no matter how much liquid flows through the membrane, the solvent in the right side will always be more concentrated than that in the left side. Osmosis will continue indefinitely until we run out of solvent, or something else stops it.

6.2 Osmotic pressure

One way to stop osmosis is to raise the hydrostatic pressure on the solution side of the membrane. This pressure squeezes the solvent molecules closer together, raising their escaping tendency from the phase. If we apply enough pressure (or let the pressure build up by osmotic flow of liquid into an enclosed region), the escaping tendency of solvent molecules from the solution will eventually rise to that of the molecules in the pure solvent, and osmotic flow will cease. The pressure required to achieve osmotic equilibrium is known as the *osmotic pressure*. Note that the osmotic pressure is the pressure required to *stop* osmosis, *not* to sustain it.

Caution! It is common usage to say that a solution “has” an osmotic pressure of x atm. It is important to understand that this means nothing more than that a pressure of this value must be applied to the solution in order to prevent flow of pure solvent into this solution through a semipermeable membrane separating the two liquids.

• Effects of temperature and concentration on osmotic pressure

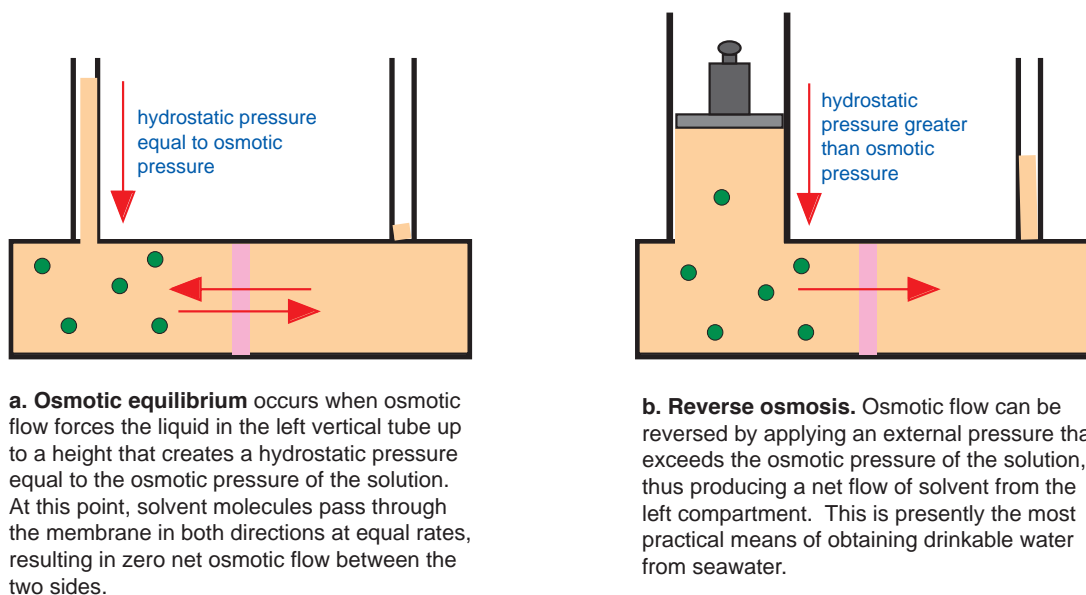


Figure 8: Osmotic equilibrium and reverse osmosis.

6.3 Effects of temperature and concentration on osmotic pressure

Osmotic pressure is the hydrostatic pressure required for a solution to achieve osmotic equilibrium with a more dilute solution. For dilute solutions, this pressure will be directly proportional to the difference in the solvent concentrations in the two solutions. If the “more dilute solution” is the pure solvent, then the osmotic pressure is effectively a measure of the concentration of the solution.

The osmotic pressure Π in a solution of volume V liters containing n moles of solvent is given by the *van't Hoff* equation¹:

$$\Pi V = nRT \quad (6)$$

Recalling that Π (π is the Greek equivalent of P), does this look familiar? Much effort was expended around the turn of the century to explain the similarity between this relation and the ideal gas law, but it is now generally agreed that this similarity has little significance. In fact, the van't Hoff equation turns out to be only a very rough approximation of the real osmotic pressure law, which was derived later. As such, this equation gives valid results only for extremely dilute solutions.

¹The Dutch scientist Jacobus van't Hoff (1852-1911) was one of the giants of physical chemistry. He discovered this equation after a chance encounter with a botanist friend during a walk in a park in Amsterdam; the botanist had learned that the osmotic pressure increases by about 1/273 for each degree of temperature increase. van't Hoff immediately grasped the analogy to the ideal gas law.

6.4 Physiological aspects of osmosis

Because many plant and animal cell membranes and tissues tend to be permeable to water and other small molecules, osmotic flow plays an essential role in many physiological processes.

- The interiors of cells contain salts and other solutes that dilute the intracellular water. If the cell membrane is permeable to water, placing the cell in contact with pure water will draw water into the cell, tending to rupture it. This is easily and dramatically seen if red blood cells are placed in a drop of water and observed through a microscope as they burst. This is the reason that “isotonic” saline solution, rather than pure water, is administered in order to maintain blood volume or to infuse therapeutic agents during medical procedures. For the same reason, it is less irritating to irrigate the eyes, throat or bowel with saline solution than with pure water.
- The gill tissue in the respiratory organ of a fish allows O_2 and CO_2 to pass freely between the blood and the surrounding water, but this tissue also tends to be permeable to H_2O molecules, especially in freshwater fish. In these fish, water enters the bloodstream by osmosis and is removed by the kidneys, resulting in a continuous flow of water through the fish. The blood of a fish contains about 1% salt, while seawater is about 3% salt, so marine fish are in danger of dehydration and would die of thirst in the absence of countermeasures. One of these is the presence, in the blood, of higher concentrations of other solutes that bring the osmotic pressure up closer to that of seawater.
- The use of sugar to preserve jams and jellies, and the use of salt to preserve certain meats, is also based on osmosis. The salt or sugar reduces the water concentration to a level below that in living organisms. Any bacterial cell that wanders into such a medium will have water osmotically drawn out of it, and will die of dehydration. A similar effect is noticed by anyone who holds a hard sugar candy against the inner wall of the mouth for an extended time; the affected surface becomes dehydrated and noticeably rough when touched by the tongue.
- The presence of excessive solutes in the bowel draws water from the intestinal walls, giving rise to diarrhea. This can occur when a food is eaten that cannot be properly digested (as, for example, milk in lactose-intolerant people,). The undigested material contributes to the solute concentration, raising its osmotic pressure. The situation is made even worse if the material undergoes bacterial fermentation which results in the formation of methane and carbon dioxide which produce a frothy discharge.
- The osmotic pressure of intracellular fluids (“sap”) in plants brings about the intake of water through the root system and contributes to the rise of sap in trees (however this is not the sole mechanism; capillary rise is also important.) If the soil becomes dry or saline, the osmotic pressure outside the root becomes greater than that inside the plant, and the plant suffers from “water tension”, i.e., wilting.

6.5 Molecular weight determination

Since all of the colligative properties of solutions depend on the concentration of the solvent, their measurement can serve as a convenient experimental tool for determining the concentration, and thus the molecular weight, of a solute.

Osmotic pressure is especially useful in this regard, because a small amount of solute will produce a much larger change in this quantity than in the boiling point, freezing point, or vapor pressure. According to Eq. 6, an ideal solution containing 1 mole of dissolved particles per

kilogram of solvent at 0 °C will have an osmotic pressure of 22.4 atm; even a 10⁻⁶ molal (mol/kg) solution would have a measurable osmotic pressure. Molecular weight determinations are very frequently made on proteins or other high molecular weight polymers. These substances, owing to their large molecular size, tend to be only sparingly soluble in most solvents, so measurement of osmotic pressure is often the only practical way of determining their molecular weights.

The experiment is quite simple: pure solvent is introduced into one side of a cell that is separated into two parts by a semipermeable membrane. The polymer solution is placed in the other side, which is enclosed and connected to a manometer or some other kind of pressure gauge. As solvent molecules diffuse into the solution cell the pressure builds up; eventually this pressure matches the osmotic pressure of the solution and the system is in osmotic equilibrium. The osmotic pressure is read from the measuring device and substituted into the van't Hoff equation to find the number of moles of solute.

Problem Example 14

The average molecular weight of a synthetic polymer varies greatly with the conditions under which it is made. A 0.20 g sample of polyisobutylene dissolved in 100 mL of benzene had a density of 0.88 g cm⁻³ and supported a column of liquid 2.4 mm high when placed in an osmotic cell containing pure benzene in the other compartment. Calculate (a) the osmotic pressure of the solution and (b) the molecular weight of the polyisobutylene.

Solution: To find the osmotic pressure, we convert “mm of solution” into mm of mercury and thence into atmospheres. Because the density of mercury (13.6 g cm⁻³) is greater than that of the solution, the osmotic pressure in torr (mm of Hg) will be proportionatly smaller.

$$\text{osmotic pressure in mm of Hg} = 2.4 \text{ mm} \times \frac{0.88 \text{ g cm}^{-3}}{13.6 \text{ g cm}^{-3}} = 0.155 \text{ mm}$$

which corresponds to a pressure of $0.155 \div 760 = 2.0 \times 10^{-4}$ atm.

The solution molarity (n/V) is found by substituting directly into the van't Hoff equation:

$$\frac{n}{V} = \frac{\Pi}{RT} = \frac{2.0 \times 10^{-4} \text{ atm}}{0.0821 \text{ L atm mol}^{-1} \text{ K}^1 \times 298 \text{ K}} = 8.2 \times 10^{-6} \text{ mol L}^{-1}$$

The molecular weight of the solute is thus $(2.0 \text{ g L}^{-1}) \div (8.2 \times 10^{-6} \text{ mol L}^{-1}) = \underline{2.4 \times 10^5 \text{ g mol}^{-1}}$.

7 Ions in aqueous solution

A very large part of everyday chemistry is concerned with aqueous solutions containing ionic substances: after all, most of the Earth's surface and most of the mass of our bodies consist of such solutions. It is therefore worth taking some time to consider some of the properties of water that make it such a good solvent for ionic substances, and look briefly at some of the special properties of aqueous ionic solutions.

7.1 Water: a familiar but extraordinary liquid

Why are aqueous solutions so important in Chemistry? The answer lies not so much in the ubiquity of water as in certain special properties that set it apart from nearly all other liquids. The most important of these properties are its dipole moment and dielectric constant; these, in turn, derive from the composition and shape of the water molecule.

Dipole moment of water

Oxygen is the second most electronegative of the elements, whereas hydrogen is intermediate in electronegativity. As a consequence, the shared electron pair that comprises the bond between these two elements is skewed toward the oxygen atom; the O–H bond is a highly *polar* one.

If the H–O–H molecule were linear, the electric dipoles associated with the two O–H bonds would cancel out, since they would be oriented in opposite directions. It turns out, however, that the water molecule is bent at an angle of 104.5°. This allows the polarities of the two O–H bonds to reinforce each other, giving rise to a permanent dipole moment associated with the molecule as a whole.²

The table below shows the dipole moment of water in comparison with the dipole moments of some other molecules. Clearly, the dipole moment of water is not exceptionally large, so this parameter alone cannot account for the unique properties of water.

molecule	NH ₃	CH ₃ CH ₂ OH	CH ₃ COOH	H ₂ O	HF	HCN	HCl
μ , debyes	1.3	1.69	1.74	1.84	1.91	2.95	1.08

The special thing about water is the small size of the molecule in relation to the magnitude of its dipole moment. This property is also shared by HF and HCN, and it means that an ion can come very close to any of these molecules and thus interact very strongly with the molecular dipole moment. This means, in turn, that ions tend to bind to water molecules through ion-dipole attraction, which is one of the strongest of the “weak” intermolecular forces.

In order for a solute to dissolve in a solvent, the solvent molecules must be shoved aside to make room for the solute. If the solvent is water, this means breaking up the local hydrogen-bonded structural arrangements that are the result of dipole-dipole attractions between adjacent water molecules. This requires an input of energy, which can only be recovered if a stronger attractive interaction can be established between the water molecules and the solute. This will happen if the solute itself is sufficiently polar to replace the broken water-water interactions with water-solute interactions of comparable strength. If the solute is an ion, this condition is guaranteed, because ion-dipole attractions are always stronger than dipole-dipole attractions.

Dielectric constant of water

According to Coulomb’s law, the force between two charged particles is directly proportional to the product of the two charges, and inversely proportional to the square of the distance d between them:

$$\text{force} = \frac{q_1q_2}{Dd^2} \quad (7)$$

The proportionality constant D is the *dielectric constant*. Its value in empty space is unity, but in a other media it will be larger. Since D appears in the denominator, this means that the force

²If one electronic charge were displaced by 1 Å (10^{−8} cm), the dipole moment would be 4.80 debyes. Most chemical bond lengths are several angstroms, but the charge displacement is much less than one full electronic charge, so bond dipoles tend to be small. However, in a molecule that contains a number of polar bonds oriented in such a way that they can reinforce each other, the overall molecular dipole moments can be quite large; the dipole moment of the amino acid glycine, H₂N–CH₂–COOH is 15 d.

<i>substance</i>	<i>formula</i>	<i>D</i>
benzene	C ₆ H ₆	2.28
diethyl ether	CH ₃ CH ₂ OCH ₂ CH ₃	4.23
acetone	CH ₃ CH ₂ CO	20.7
ethyl alcohol	CH ₃ CH ₂ OH	24.3
methyl alcohol	CH ₃ OH	32.6
water	H ₂ O	78.5
sulfuric acid	H ₂ SO ₄	101
hydrogen cyanide	HCN	107

Table 4: Dielectric constants of several liquids.

between two charged particles within a gas or liquid will be less than if the particles were in a vacuum.

Water has one of the highest dielectric constants of any known liquid; the exact value varies with the temperature, but 80 is a good round number to remember. When two oppositely-charged ions are immersed in water, the force acting between them is only $\frac{1}{80}$ as great as it would be between the two gaseous ions at the same distance.

Why is this important? You may recall that one of the energetic factors that determines the ease of forming a solution is the energy required to disperse the solute— to pull the solute particles away from each other in the pure solid or liquid. Ionic solids are held together by Coulombic attractions that are quite strong; it takes a lot of work to pull the oppositely-charged ions apart. If, however, this pulling-apart takes place in aqueous solution, the work required would be only 1/80 of what it would otherwise be. For many (but not all) ionic solids, this will be enough to make the difference between solubility and insolubility.

The effect of substituting other liquids for water can be found by taking the inverse ratios of their dielectric constants. For example, the work required to disperse an ionic solid into ethyl alcohol would be greater than that in water by a factor of $\frac{80}{24}$, or more than three times greater.

In summary:

- The high dielectric constant of liquid water reduces the energy required to break up the oppositely-charged particles in an ionic solid. It also reduces the attraction between the dissolved ions, thus discouraging their recombination.
- The dipole moment of water causes water molecules to attach themselves to ions by ion-dipole interaction. This further stabilizes the dissolved ions. Because they are now quite large, oppositely-charged hydrated ions cannot get very close to each other, and the tendency for them to recombine is reduced.

The dielectric constant, by the way, is a *bulk property* of matter, rather than being a property of the molecule itself, as is the dipole moment. It is a cooperative effect of all the molecules in the liquid, and is a measure of the extent to which an applied electric field will cause the molecules to line up with the negative ends of their dipoles pointing toward the positive direction of the electric field. The high dielectric constant of water is a direct consequence of hydrogen

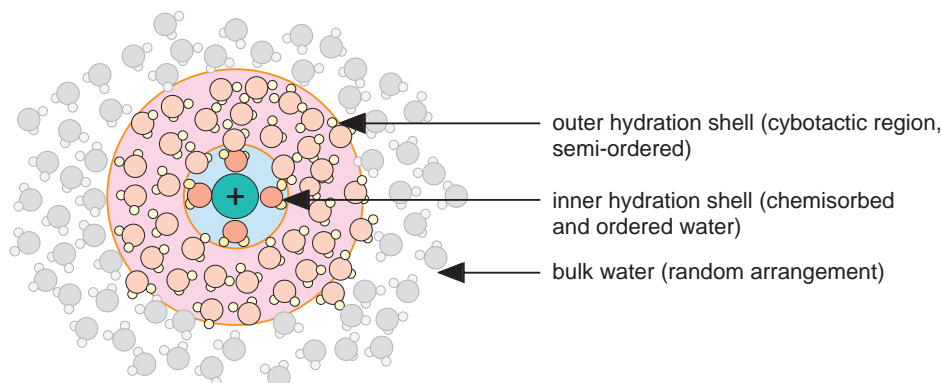


Figure 9: An ion in aqueous solution with its hydration shells.

bonding, and thus of the dipole moment. When one molecule is reoriented by the action of an external electric field, local hydrogen bonding tends to pull neighboring molecules into the same alignment, thus producing an additive effect that would be absent if the molecules were all acting independently.

7.2 Ionic species in aqueous solutions

Hydration

All ions dissolved in water are hydrated. The water molecules closest to the ion are the most tightly bound, and comprise the *primary hydration shell*. Thermal motion is still able to disrupt this binding, however, so the number of water molecules attached to a given ion will be continually changing. Various experimental methods allow one to determine the average number of water molecules bound to an ion; this is known as the *hydration number* of the ion.

The smaller and more highly charged the ion (i.e., the greater its *charge density*), the more highly hydrated it will be. Since anions tend to have larger radii than cations, the latter tend to be more strongly hydrated. Thus the average number of water molecules associated with the Li^+ ion, whose radius (in the crystal) is 0.68 \AA , is about 4, while that of K^+ (1.33 \AA) is only 2. A higher charge makes a large difference; the hydration number of Mg^{2+} is 10. The small fluoride ion has a hydration number of between 2 and 4; the larger halide ions have hydration numbers of about unity.

Many ions bind water molecules so strongly that they remain hydrated even in their crystalline forms. Thus each Cu^{2+} ion in solid $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ is surrounded by four H_2O molecules; each Al^{3+} ion in the double hydrate $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is surrounded by six. Some of the water molecules in these crystals are bound to specific ions, while others belong to the crystal structure as a whole.

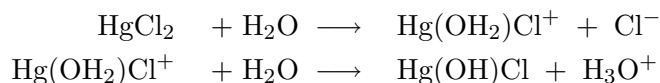
7.3 Weak electrolytes

Incomplete dissociation and ion-pair formation

Measurements of the electrical conductivity and colligative properties of their aqueous solutions show that many acids, bases and salts do behave as if they are 100-% dissociated into ions.

This happens with weak acids and bases which are neutral species in their pure forms and only dissociate to a small degree when dissolved in water. Even stronger acids such as H_2SO_4 tend to be less dissociated in more concentrated solutions.

There are also many salts, such as HgCl_2 and AsCl_3 , whose solids possess only a small amount of ionic character. These consist mainly of molecules which react with water in several steps:



The details of this reaction are not important, and need not be memorized. The important point to understand is that not all salts are ionic in character, and that most salts yield aqueous solutions that contain a smaller concentration of ions (although often in considerably more *variety!*) than one would predict from the stoichiometry of the salt.

Finally, many ions tend to pair up in solution, forming species of reduced or zero charge; examples are CaCl^+ and CaCO_3^0 . Ion pairing reduces the number of solute particles, and can thus be detected by measuring the colligative properties of the solution. Since the electric charges of the particles are reduced or even completely canceled out, the conductivity of the solution is greatly reduced.

Ion-pair formation is especially favored at high solute concentrations; for this reason, the conductivity per mole of solute will diminish as the solution becomes more concentrated.

7.4 Electrolytic solutions

One of the major discoveries of the mid-nineteenth century was Michael Faraday's demonstration that aqueous solutions of salts and some acids would conduct an electric current. If a sample of matter is to conduct electricity, two requirements must be met:

1. The matter must contain electrically charged particles.
2. These particles must be *mobile*; that is, they must be free to move under the influence of an external applied electric field.

The charge carriers in solutions are the ions that form which substances such as acids, bases and salts dissolve and dissociate. Faraday's discovery of electrolytic conductivity led him to propose the existence of mobile electrically charged particles which he called "ions". This was one of the greatest discoveries of Chemical science, because it led eventually to the realization that electrical forces play a role in all forms of chemical combination, and thus to our present theories of chemical bonding.

A solid such as NaCl is composed entirely of ions, and thus meets the first requirement set out above, but the ions are held so tightly in the crystal lattice that they are unable to move about, so the second requirement is not met and solid salt is in fact an insulator. If the salt is melted or dissolved in water, the ions can move freely and the liquid becomes a conductor.

In pure water, only one out of about 10 million water molecules is ionized, so pure water is practically non-conductive. Really pure water, however, is very hard to come by; on exposure to the air, carbon dioxide quickly dissolves in water, producing a solution of H^+ and HCO_3^- which has a conductivity 100 times as great as pure water. This is still very small compared to the conductivity of .05 M HCl, which is half a million times that of pure water.

Colligative properties of electrolytic solutions

The presence of a solute will reduce the concentration of the solvent, thus depressing its vapor pressure and freezing point, raising its boiling point, and promoting osmotic flow of additional solvent into the solution through a semipermeable membrane.

A salt such as CaCl_2 that dissociates into three moles of ions per mole of salt will dilute the water 1.5 times more than will the same nominal concentration of NaCl, and will thus have its boiling point elevation and other colligative properties enhanced by the same factor.

How ions carry electricity through a solution

Conduction of electricity through an ionic solution is very different from metallic conduction. The mobile electrons which conduct charge through a metal act as an essentially massless fluid which can flow very freely through the metallic lattice and change its motion instantaneously in response to the applied potential difference, even up to very high alternating frequencies. Metallic conduction falls off with temperature as the more vigorous thermal vibrations of the atoms in the metal begin to interfere with the free flow of the electron fluid through the metal.

In electrolytic solutions, by contrast, the ions with their hydration shells are relatively massive objects which, like ships in the sea, must push the molecules of the medium aside as they move through it. Electrolytic conductance is therefore highly dependent on the viscosity of the medium, and thus is more efficient at higher temperatures.³ As the ions move, they are continually being buffeted by the thermal motions of nearby water molecules, so the path of an ion between two electrodes is far from a direct one; it has been estimated that the imposition of an electric field of about 1 volt per cm causes only about one out of 10^5 jumps an ions makes to be in a non-random direction influenced by the field. Finally, the inertia of the ion and of the hydration shell it must drag along with it prevents it from responding to rapid changes in potential.

Molar conductivity of solutions

The conductivity of a solution depends primarily on the concentration of ionic charges in the solution, and it increases with the charge concentration. For example, we would expect a solution

³This is the main reason why it is more difficult to start your car on a very cold day; the electrolyte in the battery becomes sufficiently viscous to seriously impede the flow of ions between the electrodes, thus limiting the amount of current the battery can deliver.

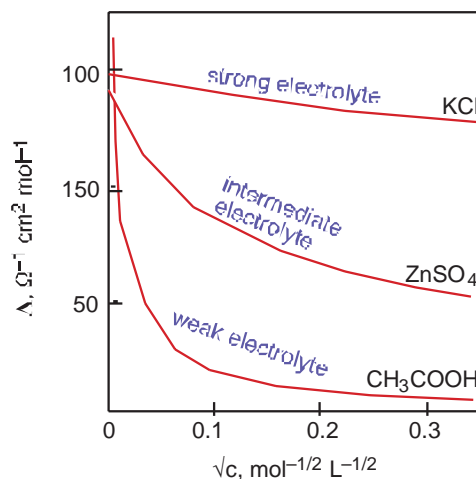


Figure 10: Strong, intermediate, and weak electrolytes.

of CaCl_2 (with four charges per dissociated formula unit) to twice as conductive as an equimolar solution of NaCl which dissociated into only two moles of charges per mole of solid. In order to fairly compare the conductivities of solutions of different electrolytes, a quantity known as the *molar conductivity* has been defined that takes these charge concentrations into account. Thus if all electrolytes dissociate completely into ions, and if each ion moves at the same speed and independently of the other ions, then all electrolytes would have the same molar conductivity.

As is apparent from Fig. 10, this does not happen, and in fact both of the above assumptions are incorrect. The most important trend to note is that the molar conductivities increase as the electrolyte concentration approaches zero. (Of course, the overall conductivity decreases with concentration; remember that we are talking about the conductivity per mole of charge here.) On the basis of these plots (in which the X-axis is the square root of the concentration), most electrolytes can be classified into one of the following categories:

Strong electrolytes Highly ionic salts such as NaCl which are essentially totally dissociated in solution give nearly-linear plots.

Intermediate electrolytes These are salts of more polarizable ions whose molar conductivity at higher concentrations is suppressed by the formation of electrically neutral ion pairs such as ZnSO_4^0 .

Weak electrolytes Weak acids and bases are only very slightly dissociated in concentrated solutions, but the degree of dissociation increases as the solution becomes more dilute, so the conductivity per mole of charged particles increases without apparent limit as the electrolyte concentration decreases.⁴

Notice in Fig. 10 that the molar conductivities of strong and intermediate electrolytes have definite values at the limit of zero concentration. Since the actual conductivity of such a solution

⁴The experimental observation of this rapid rise in the molar conductivities in weak acids and bases is what led Svante Arrhenius to propose in 1877 that the characteristic properties of these substances derive from their dissociation into hydrogen and hydroxide ions.

will be essentially zero, you may wonder what what physical meaning these quantities have. The answer is that they measure the ability of the ions formed by dissociation of a particular salt to conduct electricity in an environment in which they are surrounded only by water molecules and do not interact with other ions. Measurements of molar conductances of salts "at infinite dilution" (to use the more common but somewhat misleading terminology) allows us to determine the *electrochemical mobility* of an ionic species.