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Solutions and Their Physical Properties

Types of Solutions: Some Terminology

Solvent

The solvent is the component that is present in the greatest quantity or that determines the state of matter in which a solution exists.

Solute

Other solution components, called solutes, are said to be dissolved in the solvent.

Concentrated Solution

A concentrated solution has a relatively large quantity of dissolved solute(s).

Dilute Solution

A dilute solution has a relatively small quantity of dissolved solute(s).

Other Type of Solutions

Although liquid solutions are most common, solutions can exist in gaseous and solid states as well. For instance, the U.S. five-cent coin, the nickel, is a solid solution of 75% Cu and 25% Ni. Solid solutions with a metal as the solvent are also called alloys.

Solution Concentration

Concentration is a measure of the quantity of solute in a given quantity of solvent (or solution). In this section, we describe several methods of expressing concentration, each of which serves a different purpose.

Mass Percent, Volume Percent, and Mass/Volume Percent

If we dissolve 5.00 g NaCl in 95.0 g we get 100.0 g of a solution that is 5.00% NaCl, by *mass*. Mass percent is widely used in industrial chemistry. Thus, we might read that the action of 78% $\text{H}_2\text{SO}_4(\text{aq})$ on phosphate rock $[\text{3 Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2]$ produces 46% H_3PO_4 .

Because liquid volumes are so easily measured, some solutions are prepared on a *volume* percent basis. For example, a handbook lists a freezing point of -15.6°C for a methyl alcohol water antifreeze solution that is 25.0% CH_3OH by volume. Such a solution could be prepared by dissolving 25.0 mL $\text{CH}_3\text{OH}(\text{l})$ with water until the total solution volume is 100.0 mL.

Another possibility is to express the mass of solute and volume of solution. An aqueous solution with 0.9 g NaCl in 100.0 mL of solution is said to be 0.9% NaCl (*mass/volume*). Mass/volume percent is extensively used in the medical and pharmaceutical fields.

Parts per Million, Parts per Billion, and Parts per Trillion

In solutions where the mass or volume percent of a component is very low, we often switch to other units to describe solution concentration. We can describe the solute concentration more succinctly as:

1 ppm	1 mg/L	1 part per <i>million</i>
1 ppb	1 $\mu\text{g/L}$	1 part per <i>billion</i>
1 ppt	1 ng/L	1 part per <i>trillion</i>

For example, a consumer in İstanbul might read in an annual water quality report from the municipal water department that the maximum contaminant level allowed for nitrate ion is 45 ppm and for carbon tetrachloride, 0.5 ppb.

Mole Fraction and Mole Percent

To relate certain physical properties (such as vapor pressure) to solution concentration, we need a unit in which all solution components are expressed on a mole basis. We can do this with the mole fraction.

The mole fraction of component i , designated x_i , is the fraction of all the molecules in a solution that are of type i . The mole fraction of component j is x_j , and so on. The mole fraction of a solution component is defined as:

$$x_i = \frac{\text{amount of component } i \text{ (in moles)}}{\text{total amount of all solution components (in moles)}}$$

The sum of the mole fractions of all the solution components is 1.

$$x_i + x_j + x_k + \cdots = 1$$

The *mole percent* of a solution component is the percent of all the molecules in solution that are of a given type. Mole percents are mole fractions multiplied by 100%.

Molarity

Molarity is a conversion factor relating the amount of solute and the volume of solution.

$$\text{molarity (M)} = \frac{\text{amount of solute (in moles)}}{\text{volume of solution (in liters)}}$$

Molality

A concentration unit that is independent of temperature, and also proportional to mole fraction in dilute solutions, is molality (*m*) – the number of moles of solute per kilogram of solvent (not of solution).

$$\text{molality (m)} = \frac{\text{amount of solute (in moles)}}{\text{amount of solvent (in kilograms)}}$$

A solution in which 1.00 mol of urea, CO(NH₂)₂, is dissolved in 1.00 kg of water is described as a 1.00 molal solution and designated as 1.00 *m* urea.

Example:

An ethanol water solution is prepared by dissolving 10.00 mL of ethanol, CH₃CH₂OH (*d* = 0.789 g/mL), in a sufficient volume of water to produce 100.0 mL of a solution with a density of 0.982 g/mL. What is the concentration of ethanol in this solution expressed as (a) volume percent; (b) mass percent; (c) mass/volume percent; (d) mole fraction; (e) mole percent; (f) molarity; (g) molality?

Answer:

a) Volume percent ethanol

$$\text{volume percent ethanol} = \frac{10.00 \text{ mL ethanol}}{100.0 \text{ mL solution}} \times 100\% = 10.00\%$$

b) Mass percent ethanol

$$\text{mass ethanol} = 10.00 \text{ mL ethanol} \times \frac{0.789 \text{ g ethanol}}{100.0 \text{ mL solution}} = 7.89 \text{ g ethanol}$$

$$\text{mass soln} = 100 \text{ mL soln} \times \frac{0.982 \text{ g soln}}{1.0 \text{ mL solution}} = 98.2 \text{ g soln}$$

$$\text{mass percent ethanol} = \frac{7.89 \text{ g ethanol}}{98.2 \text{ g solution}} \times 100\% = 8.03\%$$

c) Mass/volume percent ethanol

$$\frac{\text{Mass}}{\text{volume}} \text{ percent ethanol} = \frac{7.89 \text{ g ethanol}}{100.0 \text{ mL solution}} \times 100\% = 7.89\%$$

d) Mole fraction of ethanol

Convert the mass of ethanol from part (b) to an amount in moles.

$$? \text{ mol } \text{CH}_3\text{CH}_2\text{OH} = 7.89 \text{ g } \text{CH}_3\text{CH}_2\text{OH} \times \frac{1 \text{ mol } \text{CH}_3\text{CH}_2\text{OH}}{46.07 \text{ g } \text{CH}_3\text{CH}_2\text{OH}} = 0.171 \text{ mol } \text{CH}_3\text{CH}_2\text{OH}$$

Determine the mass of water present in 100.0 mL of solution.

$$98.2 \text{ g soln} - 7.89 \text{ g ethanol} = 90.3 \text{ g water}$$

Convert the mass of water to the number of moles present.

$$? \text{ mol } \text{H}_2\text{O} = 90.3 \text{ g } \text{H}_2\text{O} \times \frac{1 \text{ mol } \text{H}_2\text{O}}{18.02 \text{ g } \text{H}_2\text{O}} = 5.01 \text{ mol } \text{H}_2\text{O}$$

$$x_{\text{CH}_3\text{CH}_2\text{OH}} = \frac{0.171 \text{ mol } \text{CH}_3\text{CH}_2\text{OH}}{0.171 \text{ mol } \text{CH}_3\text{CH}_2\text{OH} + 5.01 \text{ mol } \text{H}_2\text{O}} = \frac{0.171}{5.18} = 0.0330$$

e) Mole percent ethanol

$$\text{mole percent } \text{CH}_3\text{CH}_2\text{OH} = x_{\text{CH}_3\text{CH}_2\text{OH}} \times 100\% = 0.0330 \times 100\% = 3.30\%$$

f) Molarity of ethanol

Divide the number of moles of ethanol from part (d) by the solution volume,

$$100.00 \text{ mL} = 0.1000 \text{ L}$$

$$\text{molarity} = \frac{0.171 \text{ mol } \text{CH}_3\text{CH}_2\text{OH}}{0.1000 \text{ L soln}} = 1.71 \text{ M } \text{CH}_3\text{CH}_2\text{OH}$$

g) Molality of ethanol

First, convert the mass of water present in 100.0 mL of solution [from part (d)] to the unit kg.

$$? \text{ kg } H_2O = 90.3 \text{ g } H_2O \times \frac{1 \text{ kg } H_2O}{1000 \text{ g } H_2O} = 0.0903 \text{ kg } H_2O$$

Use this result and the number of CH_3CH_2OH moles of from part (d) to establish the molality.

$$\text{molality} = \frac{0.171 \text{ mol } CH_3CH_2OH}{0.0903 \text{ kg } H_2O} = 1.89 \text{ m } CH_3CH_2OH$$

Intermolecular Forces and the Solution Process

If there is even a little water in the fuel tank of an automobile, the engine will misfire. This problem would not occur if water were soluble in gasoline. Why does water not form solutions with gasoline? We can often understand a process if we analyze its energy requirements; this approach can help us to explain why some substances mix to form solutions and others do not.

Enthalpy of Solution

In the formation of some solutions, heat is given off to the surroundings; in other cases, heat is absorbed (ΔH_{soln}).

Let's think in terms of a three-step approach to (ΔH_{soln}):

1. Solvent molecules must be separated from one another to make room for the solute molecules. Some energy is required to overcome the forces of attraction between solvent molecules. As a result, this step should be an endothermic one: $\Delta H_a > 0$.
2. The solute molecules must be separated from one another. This step, too, will take energy and should be endothermic: $\Delta H_b > 0$.
3. Finally, we can imagine that we allow the separated solvent and solute molecules to be attracted to one another. These attractions will bring the molecules closer together and energy should be released. This is an exothermic step: $\Delta H_c < 0$.

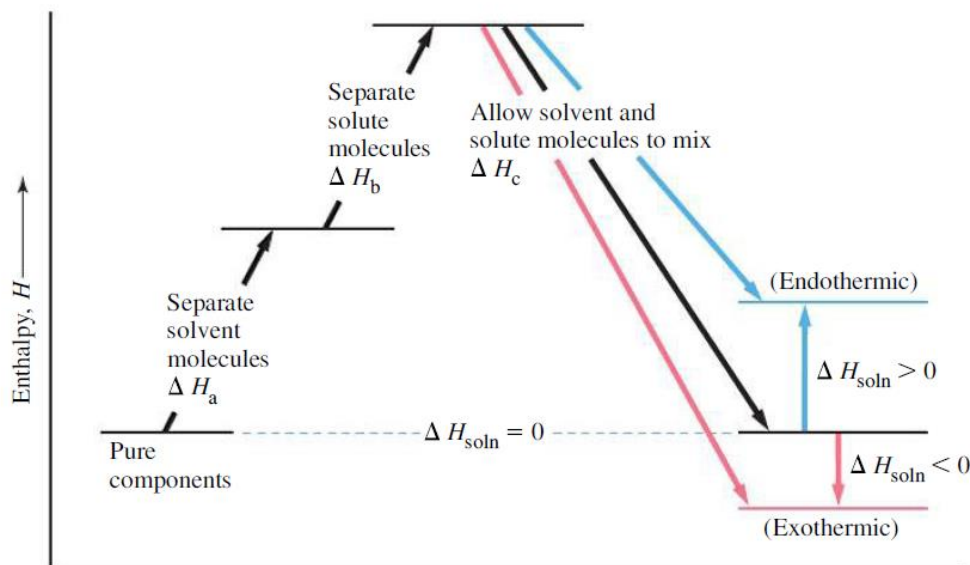
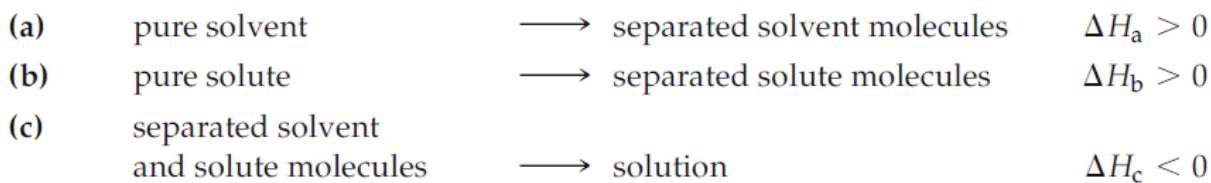


Figure 1. Enthalpy diagram for solution formation. The solution process can be endothermic (blue arrow), exothermic (red arrow), or has $\Delta H_{\text{soln}} = 0$ (black arrow), depending on the magnitude of the enthalpy change in the mixing step.

The enthalpy of solution is the sum of the three enthalpy changes just described, and depending on their relative values: ΔH_{soln} . ΔH_{soln} is either positive (endothermic) or negative (exothermic). This three-step process is (see Figure 1):

Equation 1



Overall: pure solvent + pure solute → solution

$$\Delta H_{\text{soln}} = \Delta H_a + \Delta H_b + \Delta H_c$$

Intermolecular Forces in Mixtures

We see from equation (Equation 1) that the magnitude and sign of ΔH_{soln} depends on the values of the three terms ΔH_a , ΔH_b and ΔH_c . These, in turn, depend on the strengths of the three kinds of intermolecular forces of attraction represented in Figure 1. Four possibilities for the relative strengths of these intermolecular forces are described in the discussion that follows.

1. If the intermolecular forces of attraction shown in Figure 1 are of the same type and of equal strength, the solute and solvent molecules mix randomly. A homogeneous mixture or solution results. Because properties of solutions of this type can generally be predicted from the properties of the pure components, they are called **ideal solutions**. There is no overall enthalpy change in the formation of an ideal solution from its components, and $\Delta H_{soln} = 0$. This means:

$$\Delta H_c = -(\Delta H_a + \Delta H_b)$$

Many mixtures of liquid hydrocarbons (e.g. toluene-benzene mixture) fit this description, or very nearly so (Figure 2).



Figure 2. Two components of a nearly ideal solution

2. If forces of attraction between unlike molecules exceed those between like molecules, a solution also forms. The properties of such solutions generally cannot be predicted, however, and they are called **nonideal solutions**. Interactions between solute and solvent molecules (ΔH_c) release more heat than the heat absorbed to separate the solvent and solute molecules ($\Delta H_a + \Delta H_b$). The solution process is exothermic ($\Delta H_{soln} < 0$) meaning that:

$$|\Delta H_c| > \Delta H_a + \Delta H_b$$

Solutions of acetone and chloroform fit this type. As suggested by Figure 3, weak hydrogen bonding occurs between the two kinds of molecules, but the conditions for hydrogen bonding are not met in either of the pure liquids alone.

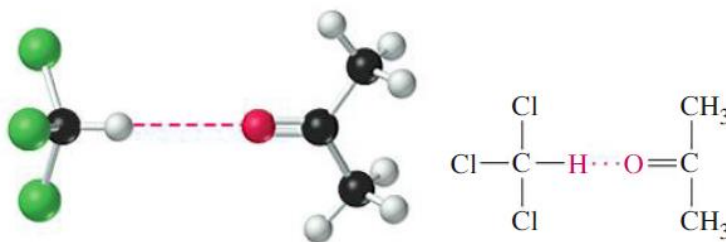


Figure 3. Intermolecular force between unlike molecules leading to a nonideal solution.

3. If forces of attraction between solute and solvent molecules are somewhat weaker than between molecules of the same kind, complete mixing may still occur, but the solution formed is **nonideal**. The solution has a higher enthalpy than the pure components, and the solution process is endothermic ($\Delta H_{soln} > 0$). This means:

$$|\Delta H_c| < \Delta H_a + \Delta H_b$$

This type of behavior is observed in mixtures of carbon disulfide (CS_2), a nonpolar liquid, and acetone, a polar liquid. In these mixtures, the acetone molecules are attracted to other acetone molecules by dipole dipole interactions and hence show a preference for other acetone molecules as neighbors.

4. Finally, if forces of attraction between unlike molecules are much weaker than those between like molecules, the components remain segregated in a heterogeneous mixture. Dissolution does not occur to any significant extent.

$$|\Delta H_c| \ll \Delta H_a + \Delta H_b$$

In a mixture of water and octane (a constituent of gasoline), strong hydrogen bonds hold water molecules together in clusters. The nonpolar octane molecules cannot exert a strong attractive force on the water molecules, and the two liquids do not mix.

Example:

Predict whether or not a solution will form in each of the following mixtures and whether the solution is likely to be ideal:

- a) Ethyl alcohol, and water.
- b) The hydrocarbons hexane, and octane.
- c) Octanol and water.

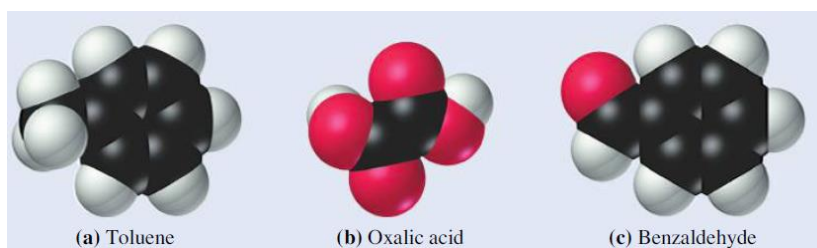
Answer:

Keep in mind that ideal or nearly ideal solutions are not too common. They require the solvent and solute(s) to be quite similar in structure.

- If we think of water $\text{H}-\text{OH}$, as ethyl alcohol ($\text{CH}_3\text{CH}_2-\text{OH}$) is similar to water. Both molecules meet the requirements of hydrogen bonding as an important intermolecular force. The strengths of the hydrogen bonds between like molecules and between unlike molecules are likely to differ, however. We expect ethyl alcohol and water to form nonideal solutions.
- In hexane, the carbon chain is six atoms long, and in octane it is eight. Both substances are virtually nonpolar, and intermolecular attractive forces (of the dispersion type) should be quite similar both in the pure liquids and in the solution. We expect a solution to form, and it should be nearly ideal.
- At first sight, this case may seem similar to (a), with the substitution of a hydrocarbon group for a H atom in $\text{H}-\text{OH}$. Here, however, the carbon chain is eight members long. This long carbon chain is much more important than the terminal $-\text{OH}$ group in establishing the physical properties of octanol. Viewed from this perspective, octanol and water are quite dissimilar. Therefore, we do not expect a solution to form.

Example:

Which of the following organic compounds do you think is most readily soluble in water?



Answer:

- Toluene is a nonpolar molecule. Therefore $|\Delta H_c| \ll \Delta H_a + \Delta H_b$. This will result in an immiscible mixture.
- Oxalic acid ($\text{HOOC}-\text{COOH}$) can establish hydrogen bonding with water molecules. $|\Delta H_c| > \Delta H_a + \Delta H_b$. Oxalic acid will mix with water to give a nonideal solution.
- The aldehyde group, $-\text{CHO}$, of benzaldehyde is a polar group. But the remainder of the molecules is consisting of phenyl ring which is nonpolar. Phenyl ring is also relatively large

compared to the aldehyde group. Any polarity conferred by the aldehyde group therefore becomes insignificant, and the molecule as a whole is insoluble in polar solvents such as water.

Example:

In which solvent is solid iodine likely to be more soluble, water or carbon tetrachloride?

Answer:

Solid iodine (I_2) is a nonpolar molecule. On the other hand, water is a polar molecule while carbon tetrachloride is nonpolar. Therefore, iodine will be more soluble in carbon tetrachloride.

Formation of Ionic Solutions

The interaction between an ion and a dipole is an intermolecular force known as an ion–dipole force. If these ion–dipole forces of attraction are strong enough to overcome the interionic forces of attraction in the crystal, dissolving will occur. Moreover, these ion–dipole forces also persist in the solution. An ion surrounded by a cluster of water molecules is said to be **hydrated**. Energy is released when ions become hydrated (Figure 4). The greater the hydration energy compared with the energy needed to separate ions from the ionic crystal, the more likely that the ionic solid will dissolve in water.

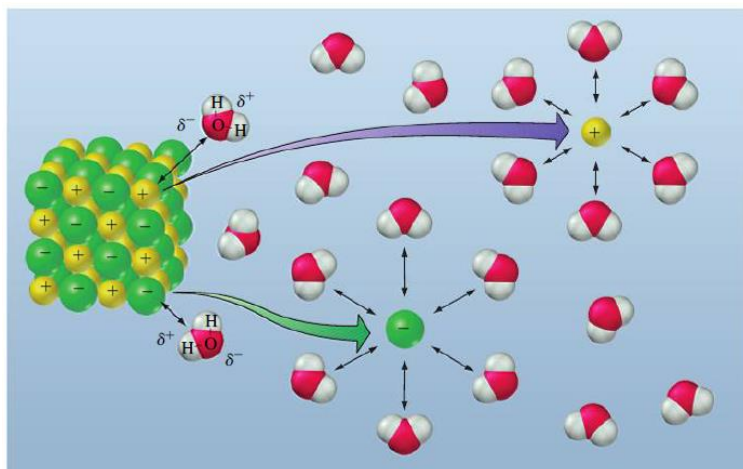
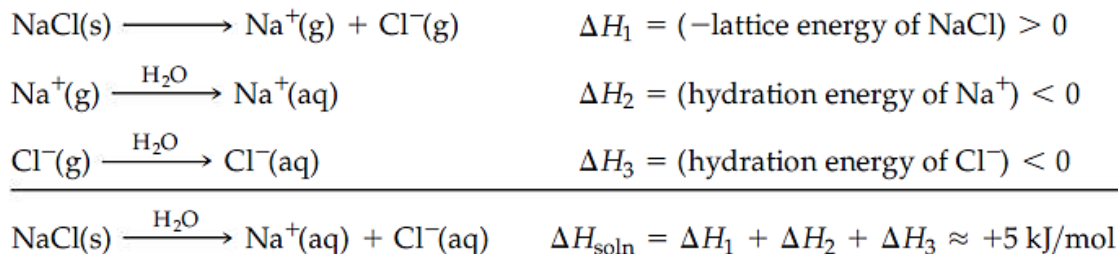


Figure 4. An ionic crystal dissolving in water

be **hydrated**. Energy is released when ions become hydrated (Figure 4). The greater the hydration energy compared with the energy needed to separate ions from the ionic crystal, the more likely that the ionic solid will dissolve in water.

We can again use a hypothetical three-step process to describe the dissolution of an ionic solid. The energy requirement to dissociate a mole of an ionic solid into separated gaseous ions, an endothermic process, is the negative of the lattice energy. Energy is released in the next two steps—hydration of the gaseous cations and anions. The enthalpy of solution is the sum of these ΔH three values, described below for NaCl.



The dissolution of sodium chloride in water is endothermic, and this is also the case for the vast majority (about 95%) of soluble ionic compounds. Why does NaCl dissolve in water if the process is endothermic?

In fact, two factors must be considered in determining whether a process will occur spontaneously. Enthalpy change is only one of them. The other factor, called **entropy**, concerns the natural tendency for microscopic particles—atoms, ions, or molecules to spread themselves out in the space available to them. The dispersed condition of the microscopic particles in NaCl(aq) compared with pure NaCl(s) and offsets the +5 kJ/mol increase in enthalpy in the solution process.

In summary, if the hypothetical three-step process for solution formation is *exothermic*, we expect dissolution to occur; but we also expect a solution to form for an endothermic solution process, as long as ΔH_{soln} is not too large.

Solution Formation and Equilibrium

When dissolution and crystallization occur at the same rate, the solution is in a state of dynamic equilibrium.

The quantity of dissolved solute remains constant with time, and the solution is said to be a **saturated solution**. The concentration of the saturated solution is called the **solubility** of the solute in the given solvent. Solubility varies with temperature, and a solubility temperature graph is called a *solubility curve*. Some typical solubility curves are shown in Figure 5.

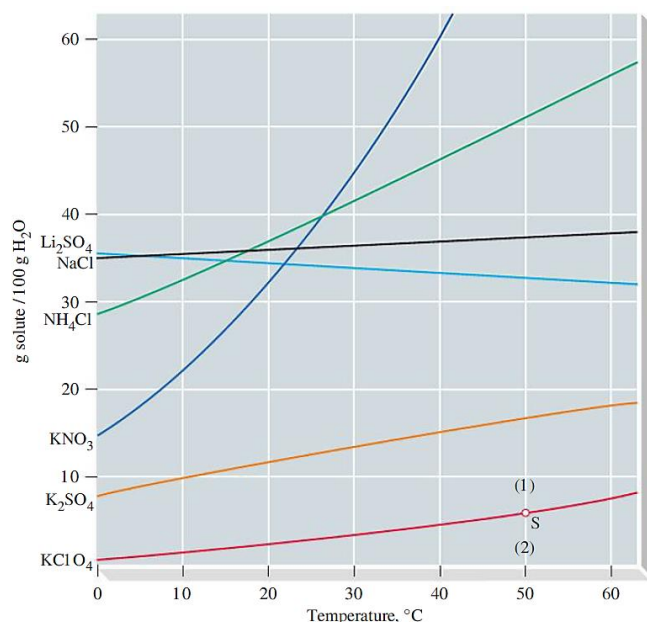


Figure 5. Aqueous solubility of several salts as a function of temperature (points on the curve (S) represent saturated solutions. Regions above the curve (1) correspond to supersaturated solutions and below the curve (2), to unsaturated solutions).

If, in preparing a solution, we start with less solute than would be present in the saturated solution, the solute completely dissolves, and the solution is an **unsaturated solution**.

Usually, the excess solute crystallizes from solution, but occasionally all the solute may remain in solution. In these cases, because the quantity of solute is greater than in a saturated solution, the solution is said to be a **supersaturated solution**. A supersaturated solution is unstable, and if a few crystals of solute are added to serve as particles on which crystallization can occur, the excess solute crystallizes.

Solubility as a Function of Temperature

As a general observation, the solubilities of ionic substances (about 95% of them) increase with increasing temperature. Exceptions to this generalization tend to be found among compounds containing the anions SO_3^{2-} , SO_4^{2-} , AsO_4^{3-} , and PO_4^{3-} .

When $\Delta H_{\text{soln}} > 0$, raising the temperature stimulates dissolving and **increases** the solubility of the solute. Conversely, if $\Delta H_{\text{soln}} < 0$ (exothermic), the solubility **decreases** with increasing temperature. In this case, crystallization being endothermic is favored over dissolving.

Fractional Crystallization

Compounds synthesized in chemical reactions are generally impure, but the fact that the solubilities of most solids increase with increased temperature provides the basis for one simple method of purification. Usually, the impure solid consists of a high proportion of the desired compound and lesser proportions of the impurities. Suppose that both the compound and its impurities are soluble in a particular solvent and that we prepare a concentrated solution at a high temperature. Then we let the concentrated solution cool. At lower temperatures, the solution becomes saturated in the desired compound. The excess compound crystallizes from solution. The impurities remain in solution because the temperature is still too high for these to crystallize. This method of purifying a solid, called **fractional crystallization**, or **recrystallization**.

Example:

A solution is prepared by dissolving 95 g NH_4Cl in 200.0 g H_2O at 60 °C. What mass of NH_4Cl will recrystallize when the solution is cooled to 20 °C?

Answer:

We need to know the solubility of NH_4Cl at 20 °C and at 60 °C. We obtain the required data from Figure 5, which shows the solubility of several salts as a function of temperature.

Using Figure 5, we estimate that the solubility of NH_4Cl at 20 °C is 37 g NH_4Cl / 100 g H_2O . The quantity of NH_4Cl in the saturated solution at 20 is:

$$200.00 \text{ g } \text{H}_2\text{O} \times \frac{37 \text{ g } \text{NH}_4\text{Cl}}{100 \text{ g } \text{H}_2\text{O}} = 74 \text{ g } \text{NH}_4\text{Cl}$$

The mass of NH_4Cl recrystallized is:

$$95 - 74 = 21 \text{ g } \text{NH}_4\text{Cl}$$

Example:

Use Figure 5 to examine the solubility curves for the three potassium salts: KClO_4 , K_2SO_4 , and KNO_3 . If saturated solutions of these salts at 40 °C are cooled to 20 °C, rank the salts in order of highest percent yield for the recrystallization.

Answer:

Saturated solutions at 40 °C contains:

Salt	g salt / 100 g H ₂ O
KClO ₄	4
K ₂ SO ₄	16
KNO ₃	60

When the solutions cooled down to 20 °C the amounts of salts to be recrystallized:

Salt	Solubility at 20 °C (g)	Recrystallized salt (g)
KClO ₄	2	4 – 2 = 02
K ₂ SO ₄	12	16 – 12 = 04
KNO ₃	33	60 – 33 = 27

If we analyze the results, the order of highest percent yield will be:



Solubilities of Gases

The effect of temperature on the solubility of gases is generally different from that on solid solutes. Additionally, the pressure of a gas strongly affects its solubility.

Effect of Temperature

We cannot make an all-inclusive generalization about the effect of temperature on the solubilities of gases (*C*) in solvents. It is certainly true, though, that the solubilities of most gases in water **decrease** with an increase in temperature.

$$T \uparrow \quad C \downarrow$$

For solutions of gases in organic solvents, the situation is often the reverse of that just described; that is, gases may become more soluble at higher temperatures.

$$T \uparrow \quad C \uparrow$$

Effect of Pressure

Pressure affects the solubility of a gas in a liquid much more than does temperature. The English chemist William Henry (1775-1836) found that the solubility of a gas increases with increasing pressure. A mathematical statement of Henry's law is

$$C = k \times P_{gas}$$

In this equation, C represents the solubility of a gas in a particular solvent at a fixed temperature, P_{gas} is the partial pressure of the gas above the solution, and k is a proportionality constant.

Example:

At 0 °C and an O_2 pressure of 1.00 atm, the aqueous solubility of $O_2(g)$ is 48.9 mL O_2 per liter. What is the molarity of O_2 in a saturated water solution when the O_2 is under its normal partial pressure in air, 0.2095 atm?

Answer:

Determine the molarity of O_2 at 0 °C when $P_{O_2} = 1 \text{ atm}$.

$$\text{molarity} = \frac{0.0489 \text{ L } O_2 \times \frac{1 \text{ mol } O_2}{22.4 \text{ L } O_2(\text{STP})}}{1 \text{ L soln}} = 2.18 \times 10^{-3} M O_2$$

Evaluate the Henry's law to find constant.

$$k = \frac{C}{P_{gas}} = \frac{2.18 \times 10^{-3} M O_2}{1.00 \text{ atm}}$$

Apply Henry's law.

$$C = k \times P_{gas} = \frac{2.18 \times 10^{-3} M O_2}{1.00 \text{ atm}} \times 0.2095 \text{ atm} = 4.57 \times 10^{-4} M O_2$$

Example:

A handbook lists the solubility of carbon monoxide in water at 0 °C and 1 atm pressure as 0.0354 mL CO per milliliter of H_2O . What pressure of $CO(g)$ must be maintained above the solution to obtain 0.0100 M CO?

Answer:

Find the concentration of CO at 0 °C when $P_{CO} = 1 \text{ atm}$.

$$M_{CO} = \frac{0.0354 \text{ mL CO} \times \frac{10^{-3} \text{ L}}{1 \text{ mL}} \times \frac{1 \text{ mol CO}}{22.4 \text{ L CO (STP)}}}{1 \text{ mL CO} \times \frac{10^{-3} \text{ L}}{1 \text{ mL}}} = 1.58 \times 10^{-3} M$$

Then find the proportionality constant.

$$k = \frac{C}{P_{CO}} = \frac{1.58 \times 10^{-3} \frac{\text{mol}}{\text{L}}}{1 \text{ atm CO}} = 1.58 \times 10^{-3} \frac{\text{mol}}{\text{L atm}}$$

Finally, find the pressure.

$$P_{CO} = \frac{C}{k} = \frac{0.0100 \frac{\text{mol}}{\text{L}} \text{ CO}}{1.58 \times 10^{-3} \frac{\text{mol}}{\text{L atm}}} = 6.33 \text{ atm}$$

Vapor Pressures of Solutions

Separating compounds from one another is a task that chemists commonly face. If the compounds are volatile liquids, this separation often can be achieved by **distillation**. To understand how distillation works, we need to know something about the **vapor pressures** of solutions.

In the 1880s, the French chemist F. M. Raoult found that a dissolved solute **lowers** the vapor pressure of the solvent. Raoult's law states that the partial pressure exerted by solvent vapor above an ideal solution, P_A , is the product of the mole fraction of solvent in the solution, x_A , and the vapor pressure of the pure solvent at the given temperature, P_A^0 .

$$P_A = x_A \times P_A^0$$

This equation relates to Raoult's observation that a dissolved solute lowers the vapor pressure of the solvent because if $x_A + x_B = 1.00$, x_A must be less than 1.00, and P_A must be smaller than P_A^0 .

Example:

The vapor pressures of pure benzene and pure toluene at 25 °C are 95.1 and 28.4 mmHg, respectively. A solution is prepared in which the mole fractions of benzene and toluene are both 0.500. What are the partial pressures of the benzene and toluene above this solution? What is the total vapor pressure?

Answer:

$$P_{\text{benz}} = x_{\text{benz}} \times P_{\text{benz}}^0 = 0.500 \times 95.1 \text{ mmHg} = 47.6 \text{ mmHg}$$

$$P_{\text{tol}} = x_{\text{tol}} \times P_{\text{tol}}^0 = 0.500 \times 28.4 \text{ mmHg} = 14.2 \text{ mmHg}$$

$$P_{total} = P_{benz} + P_{tol} = 47.6 \text{ mmHg} + 14.2 \text{ mmHg} = 61.8 \text{ mmHg}$$

Example:

Calculate the vapor pressures of benzene, C_6H_6 , and toluene, C_7H_8 , and the total pressure at 25 °C above a solution with equal masses of the two liquids. Use the vapor pressure data given in the example above.

Answer:

Molar masses:

Benzene	78 g/mol
Toluene	92 g/mol

Let's consider the amounts of benzene and toluene are m .

$$n_{benz} = \frac{m}{78} \text{ moles}, n_{tol} = \frac{m}{92} \text{ moles}$$

$$n_{total} = \frac{m}{78} + \frac{m}{92} = 0.0237m$$

$$P_{total} = P_{ben} + P_{tol} = x_{benz} \times P_{ben}^{\circ} + x_{tol} \times P_{tol}^{\circ}$$

$$P_{total} = \frac{n_{benz}}{n_{total}} \times P_{ben}^{\circ} + \frac{n_{tol}}{n_{total}} \times P_{tol}^{\circ} = \frac{\frac{m}{78}}{0.0237m} \times 95.1 \text{ mmHg} + \frac{\frac{m}{92}}{0.0237m} \times 28.4 \text{ mmHg}$$

$$P_{total} = 0.54 \times 95.1 \text{ mmHg} + 0.46 \times 28.4 \text{ mmHg} = 64.42 \text{ mmHg}$$

Osmotic Pressure

In the previous section our primary emphasis was on solutions containing a volatile solvent and volatile solute. Another common type of solution is one with a volatile solvent, such as water, but one or more nonvolatile solutes, such as glucose, sucrose, or urea. Raoult's law still applies to the solvent in such solutions the vapor pressure of the solvent is lowered.

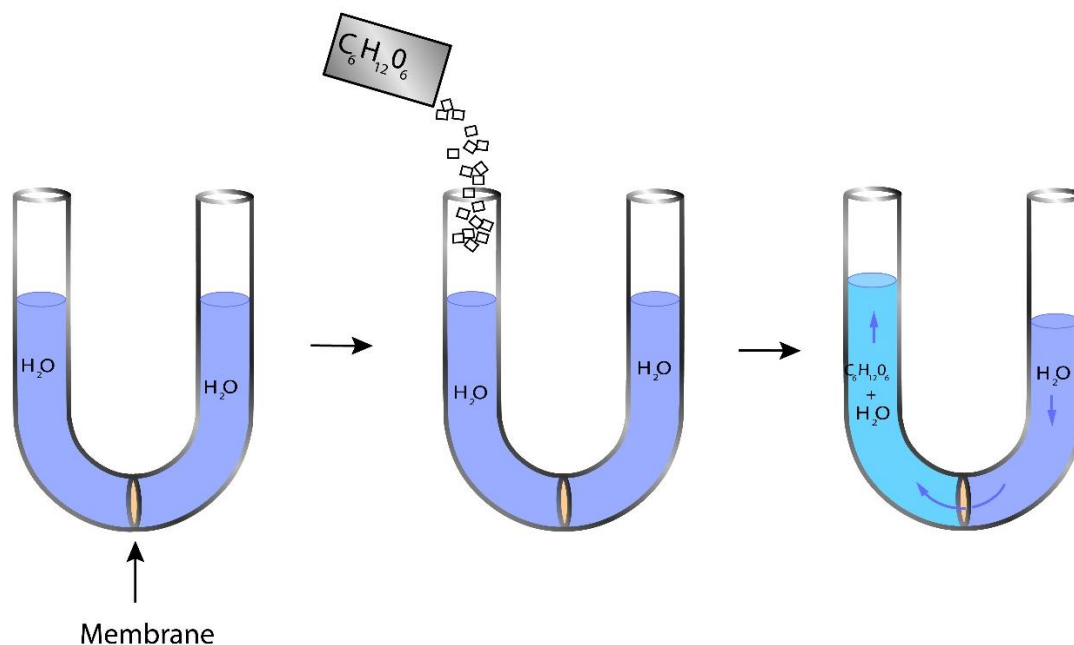


Figure 6. Osmosis in a U-shaped tube.

Osmosis

As show in Figure 6, an aqueous sucrose (sugar) solution in a long glass tube is separated from pure water by a semipermeable membrane (permeable to water only). Water molecules can pass through the membrane in either direction, and they do. But because the concentration of water molecules is greater in the pure water than in the solution, there is a net flow from the pure water into the solution. This net flow, called **osmosis**, causes the solution to rise in the tube. The more concentrated the sucrose solution, the higher the solution level rises.

Osmotic Pressure

Applying pressure to the sucrose solution slows down the net flow of water across the membrane into the solution. With a sufficiently high pressure, the net influx of water can be stopped altogether. The necessary pressure to stop osmotic flow is called the **osmotic pressure** of the solution. For a 20% sucrose solution, this pressure is about 15 atm.

Colligative Properties

The magnitude of osmotic pressure depends only on the number of solute particles per unit volume of solution. It does not depend on the identity of the solute. Properties of this sort, whose values depend only on the concentration of solute particles in solution and not on what the solute is, are called **colligative properties**.

Osmotic pressure can be calculated by using following equation:

$$\pi V = nRT$$
$$\pi = \frac{n}{V}RT = M \times RT$$

where,

π = osmotic pressure (atm)

V = volume (L)

n = amount of solute (moles)

R = gas constant (0.08206 L atm mol⁻¹ K⁻¹)

T = temperature (K)

M = molarity

Example:

What is the osmotic pressure at 25 °C of an aqueous solution that is 0.0010 M C₁₂H₂₂O₁₁ (sucrose)?

Answer:

$$\pi = \frac{0.0010 \text{ mol} \times 0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{1 \text{ L}} = 0.024 \text{ atm (18 mmHg)}$$

Example:

What mass of urea [CO(NH₂)₂] would you dissolve in 225 mL of solution to obtain an osmotic pressure of 0.015 atm at 25 °C?

Answer:

Molar mass of urea is 60 g/mol. On the other hand,

$$\pi V = nRT \Rightarrow \pi V = \frac{m}{M_w} RT \Rightarrow m = \frac{\pi V M_w}{RT}$$

$$m = \frac{0.015 \text{ atm} \times 0.225 \text{ L} \times 60 \frac{\text{g}}{\text{mol}}}{0.08206 \text{ L atm mol}^{-1} \text{K}^{-1} \times 298 \text{ K}} = 0.0083 \text{ g urea}$$

Example:

A 50.00 mL sample of an aqueous solution contains 1.08 g of human serum albumin, a blood-plasma protein. The solution has an osmotic pressure of 5.85 mmHg at 298 K. What is the molar mass of the albumin?

Answer:

$$\pi = 5.85 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 7.70 \times 10^{-3} \text{ atm}$$

Using the same equation above

$$\pi V = \frac{m}{M_w} RT \Rightarrow M_w = \frac{mRT}{\pi V}$$

$$M_w = \frac{1.08 \text{ g} \times 0.08206 \text{ atm L mol}^{-1} \text{K}^{-1} \times 298 \text{ K}}{7.70 \times 10^{-3} \text{ atm} \times 0.0500 \text{ L}} = 6.86 \times 10^4 \text{ g/mol}$$

Freezing-Point Depression and Boiling-Point Elevation of Nonelectrolyte Solutions

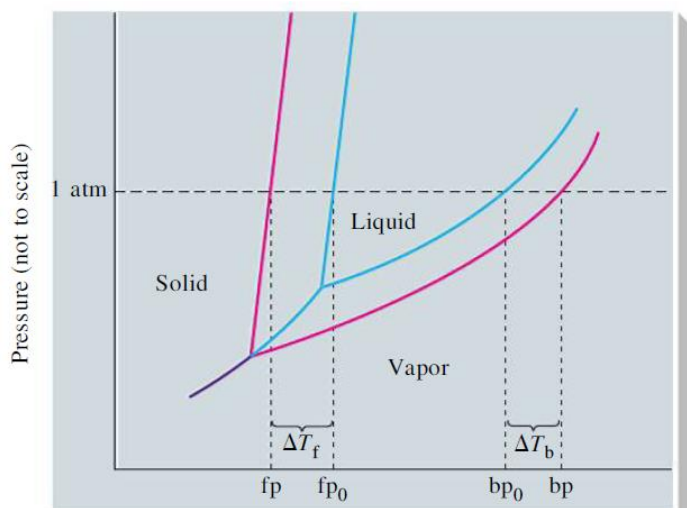


Figure 7. Vapor-pressure lowering by a nonvolatile solute.

In Figure 7 the blue curves represent the vapor pressure, fusion, and sublimation curves in the phase diagram for a pure solvent.

The vapor pressure curve of the solution (red) intersects the sublimation curve at a lower temperature than is the case for the pure solvent. The solid liquid fusion curve, because it originates at the intersection of the sublimation and vapor pressure curves, is also displaced

to lower temperatures. Four points of intersection are highlighted in Figure 7 the freezing points and the boiling points of the pure solvent and of the solvent in a solution. The freezing point of the solvent in solution is depressed, and the boiling point is elevated.

In dilute solutions, the solute mole fraction is proportional to its molality, and so we can write:

$$\Delta T_f = -K_f \times m$$

$$\Delta T_b = K_b \times m$$

where,

ΔT_f = freezing-point depression ($^{\circ}\text{C}$)

ΔT_b = boiling-point elevation ($^{\circ}\text{C}$)

K_f and K_b = proportionality constants ($^{\circ}\text{C}/m$)

m = solute molality (mol/kg)

Historically, chemists have used the group of colligative properties (vapor-pressure lowering, freezing-point depression, boiling-point elevation, and osmotic pressure) for molecular mass determinations.

Example:

Nicotine, extracted from tobacco leaves, is a liquid completely miscible with water at temperatures below 60°C .

- (a) What is the *molality* of nicotine in an aqueous solution that starts to freeze at -0.450°C ?
- (b) If this solution is obtained by dissolving 1.921 g of nicotine in 48.92 g H_2O , what must be the molar mass of nicotine?
- (c) Combustion analysis shows nicotine to consist of 74.03% C, 8.70% H, and 17.27% N, by mass. What is the molecular formula of nicotine?

Answer:

(a)

$$\Delta T_f = -0.450^{\circ}\text{C} - 0^{\circ}\text{C} = -0.450^{\circ}\text{C}$$

$$\text{molality} = \frac{\Delta T_f}{-K_f} = \frac{-0.450\text{ }^{\circ}\text{C}}{-1.86\text{ }^{\circ}\text{C m}^{-1}} = 0.242\text{ m}$$

(b)

$$m = \frac{\text{mol}}{\text{kg}} = \frac{n_{\text{nicotine}}}{\text{kg water}} = \frac{\frac{\text{g nicotine}}{M_w \text{ nicotine}}}{\text{kg water}}$$

from here

$$M_w = \frac{\text{g nicotine}}{m \times \text{kg water}} = \frac{1.921\text{ g nicotine}}{0.242 \frac{\text{mol}}{\text{kg}} \times 0.04892\text{ kg water}} = 162\text{ gr/mol}$$

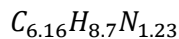
(c)

$$n_C = \frac{74.03\text{ g C}}{12 \frac{\text{g}}{\text{mol}}} = 6.169\text{ mol}$$

$$n_H = \frac{8.70\text{ g H}}{1 \frac{\text{g}}{\text{mol}}} = 8.70\text{ mol}$$

$$n_N = \frac{17.27\text{ g N}}{14 \frac{\text{g}}{\text{mol}}} = 1.23\text{ mol}$$

using these moles the empirical formula of nicotine is:



when the floating numbers are converted to whole numbers the empirical formula is:



The molar mass of empirical formula is 81 g/mol and the molar mass of nicotine (from b) is 162 g/mol.

$$\frac{162}{81} = 2$$

If multiply the subscripts of empirical formula with 2, we obtain the molecular formula of nicotine which is:



Question:

Vitamin B₂, riboflavin, is soluble in water. If 0.833 g of riboflavin is dissolved in 18.1 g H₂O, the resulting solution has a freezing point of $-0.227\text{ }^{\circ}\text{C}$. (a) What is the molality of the solution? (b)

What is the molar mass of riboflavin? (c) What is the molecular formula of riboflavin if combustion analysis shows it to consist of 54.25% C, 5.36% H, 25.51% O, and 14.89% N?

Solutions of Electrolytes

Although Arrhenius developed his theory of electrolytic dissociation to explain the electrical conductivities of solutions, he was able to apply it more widely. One of his first successes came in explaining certain anomalous values of colligative properties described by the Dutch chemist Jacobus van't Hoff (1852-1911).

Anomalous Colligative Properties

Certain solutes produce a greater effect on colligative properties than expected. For example, consider a 0.0100 *m* aqueous solution. The predicted freezing-point depression of this solution is

$$\Delta T_f = -K_f \times m = -1.86^\circ\text{C } m^{-1} \times 0.0100\text{ } m = -0.0186^\circ\text{C}$$

We expect the solution to have a freezing point of -0.0186°C . If the 0.0100 *m* solution is 0.0100 *m* **urea**, the measured freezing point is just about -0.0186°C . If the solution is 0.0100 *m* **NaCl**, however, the measured freezing point is about -0.0361°C .

Van't Hoff defined the factor *i* as the ratio of the measured value of a colligative property to the expected value if the solute is an electrolyte. For 0.0100 *m* NaCl,

$$i = \frac{\text{measured } \Delta T_f}{\text{expected } \Delta T_f} = \frac{-0.0361^\circ\text{C}}{-1.86^\circ\text{C} \times 0.0100\text{ } m} = 1.94$$

Arrhenius's theory of electrolytic dissociation allows us to explain different values of the van't Hoff factor *i* for different solutes.

- For such solutes as urea, glycerol, and sucrose (all nonelectrolytes), $i = 1$.
- For a strong electrolyte such as NaCl, which produces *two* moles of ions in solution per mole of solute dissolved, we would expect the effect on freezing-point depression to be twice as great as for a nonelectrolyte. We would expect that $i = 2$.
- Similarly, for MgCl_2 our expectation would be that $i = 3$.

This discussion suggests that osmotic pressure, boiling point elevation and freezing point depression equations should all be rewritten in the form

$$\pi = i \times M \times RT$$

$$\Delta T_f = -i \times K_f \times m$$

$$\Delta T_b = i \times K_b \times m$$

If these equations are used for nonelectrolytes, simply substitute $i = 1$. For strong electrolytes, predict a value of i as suggested above.

Example:

Predict the freezing point of aqueous 0.00145 m MgCl_2 .

Answer:



Because **three** moles of ions are obtained per mole of formula units dissolved, we expect the value $i = 3$.

$$\begin{aligned}\Delta T_f &= -i \times K_f \times m \\ &= -3 \times 1.86\text{ }^{\circ}\text{C} \times 0.00145\text{ }m \\ &= -0.00181\text{ }^{\circ}\text{C}\end{aligned}$$

The predicted freezing point is $-0.00181\text{ }^{\circ}\text{C}$.

Colloidal Mixtures

In a mixture of sand and water, the sand (silica, SiO_2) quickly settles to the bottom of the container. Yet mixtures can be prepared containing up to 40% by mass of SiO_2 , and the silica may remain dispersed in the aqueous medium for many years. In these mixtures, the silica is not present as ions or molecules. Rather, much larger particles of silica are present, though they are still submicroscopic in size. The mixture is said to be a **colloid**.

To be classified **colloidal**, a material must have one or more of its dimensions (length, width, or thickness) in the approximate range of 1–1000 nm. If all the dimensions are smaller than 1 nm, the particles are of molecular size. If all the dimensions exceed 1000 nm, the particles are of ordinary, or macroscopic, size (even if they are visible only under a microscope).



Fe_2O_3 nanoparticles

Au nanoparticles

Figure 8. The Tyndall effect. The flashlight beam is not visible as it passes through a true solution (left), but it is readily seen as it passes through the colloidal dispersion of Fe_2O_3 or Au (right).

One method of determining whether a mixture is a true solution or a colloid is illustrated in Figure 8. When light passes through a true solution, an observer viewing from a direction perpendicular to the light beam sees no light. In a colloidal dispersion, light is scattered in many directions and is readily seen. This effect, first studied by John Tyndall in 1869, is known as the **Tyndall effect**. A common example is the scattering of light by dust particles in a flashlight beam.