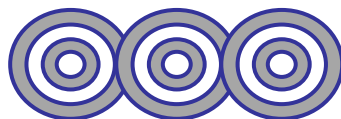




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Chapter 13

Properties of Solutions

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13.1

The Solution Process

Solutions

- **Solutions** are homogeneous mixtures of two or more pure substances.
- In a solution, the **solute** is dispersed uniformly throughout the **solvent**.
- Solutions may be solids, liquids or gases.

State of Solution	State of Solvent	State of Solute	Example
Gas	Gas	Gas	Air
Liquid	Liquid	Gas	Oxygen in water
Liquid	Liquid	Liquid	Alcohol in water
Liquid	Liquid	Solid	Salt in water
Solid	Solid	Gas	Hydrogen in palladium
Solid	Solid	Liquid	Mercury in silver
Solid	Solid	Solid	Silver in gold

The ability of substances to form solutions depends on two general factors:

- (1) The types of intermolecular interactions involved in the solution process,
- (2) The natural tendency of substances to spread into larger volumes when not restrained in some way.

The Effect of Intermolecular Forces

Any of the various kinds of intermolecular forces can operate between solute and solvent particles in a solution.

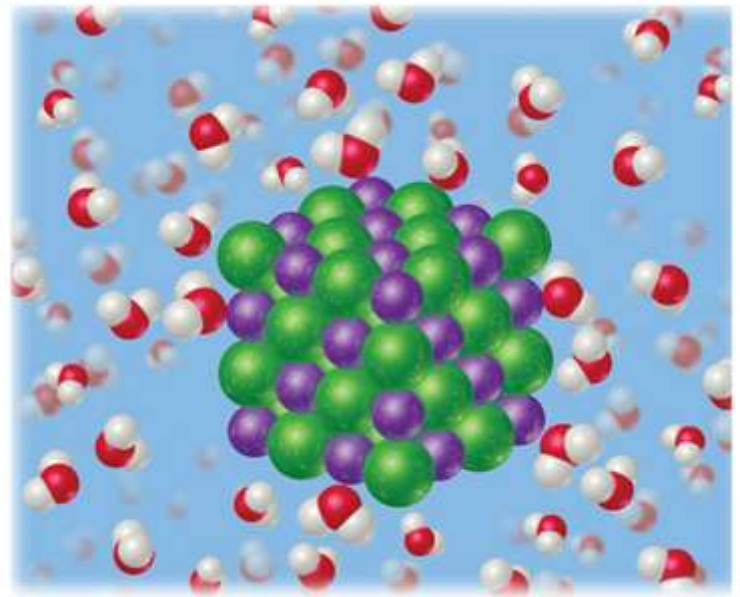
The extent to which one substance is able to dissolve in another depends on the relative magnitudes of the solute-solvent, solute-solute, and solvent-solvent interactions involved in the solution process.

C_6H_{14} dissolves in another nonpolar one like CCl_4 . Indeed, a major factor determining whether a solution forms is the relative strengths of intermolecular forces between and among the solute and solvent particles.

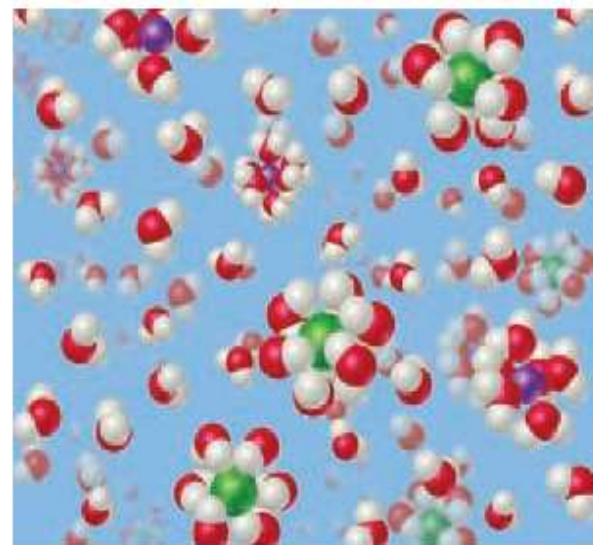
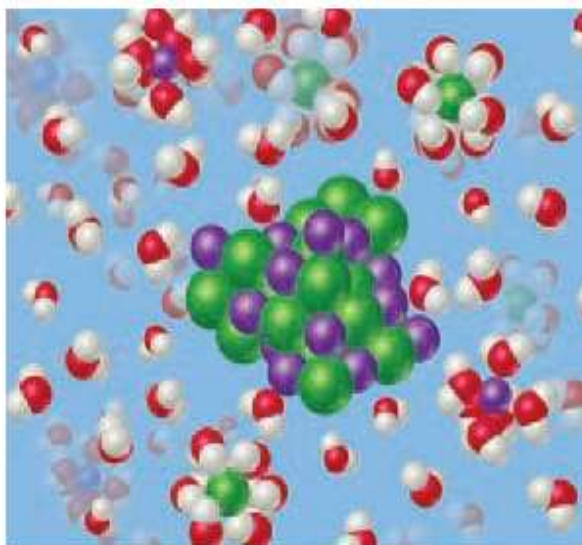
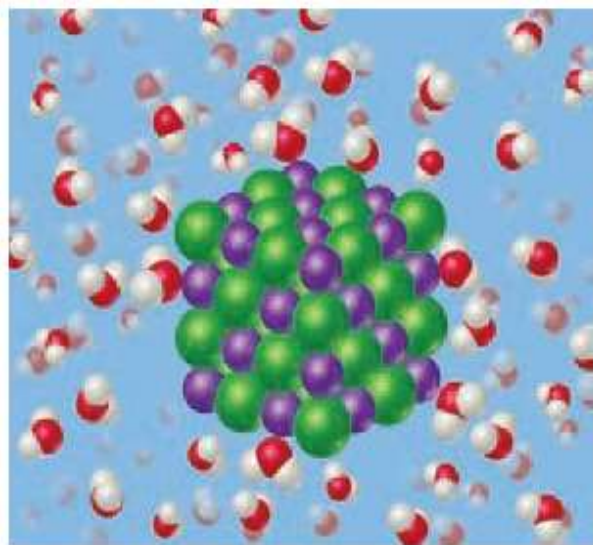


In a solution, the **solute** is dispersed uniformly throughout the **solvent**.

The intermolecular forces between solute and solvent particles must be strong enough to compete with those between solute particles and those between solvent particles.

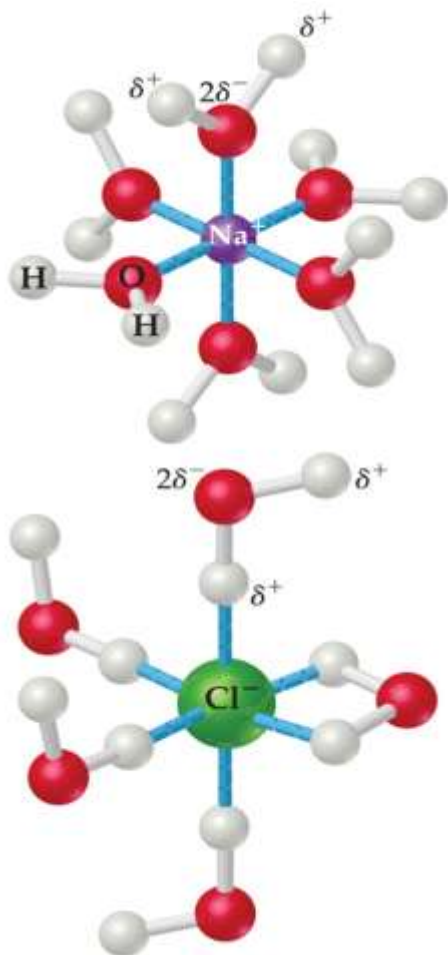


Solutions form when the magnitudes of the attractive forces between solute and solvent particles are comparable to or greater than those that exist between the solute particles themselves or between the solvent particles themselves.



For example, the ionic substance **NaCl** dissolves readily in water because the attractive interactions between the ions and the polar **H₂O** molecules (solute-solvent interactions) overcome the attraction between the ions in the solid **NaCl** (solute-solute interactions) and between **H₂O** molecules in the solvent (solvent-solvent interactions).

How Does a Solution Form?



When **NaCl** is added to **H₂O**, **H₂O** molecules orient themselves on the surface of the **NaCl** crystals. The +ve end of **H₂O** dipole is oriented toward the **Cl⁻** ions, and the -ve end of the **H₂O** dipole is oriented toward the **Na⁺** ions.

The ion-dipole attractions between the ions and **H₂O** molecules are strong enough to pull the ions from their positions in the crystal.

Once separated from the crystal, the **Na⁺** and **Cl⁻** ion are surrounded by **H₂O** molecules.

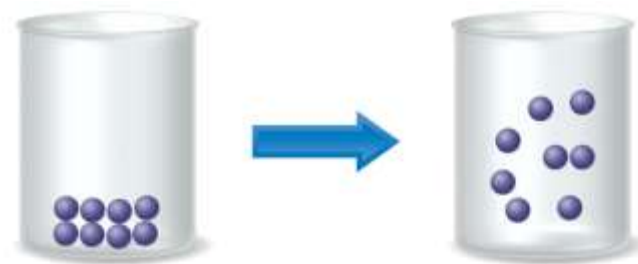
This type of interaction between solute and solvent molecules are known as **solvation**. When the solvent is water, the interaction are called **hydration**.

Hydrated **Na⁺** and **Cl⁻** ions, the -ve ends of water dipoles point toward the +ve ion, and the +ve ends point toward the -ve ion.

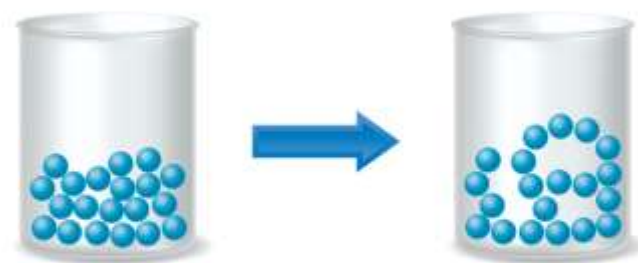
Energy Changes in Solution

Three processes affect the energetics of solution:

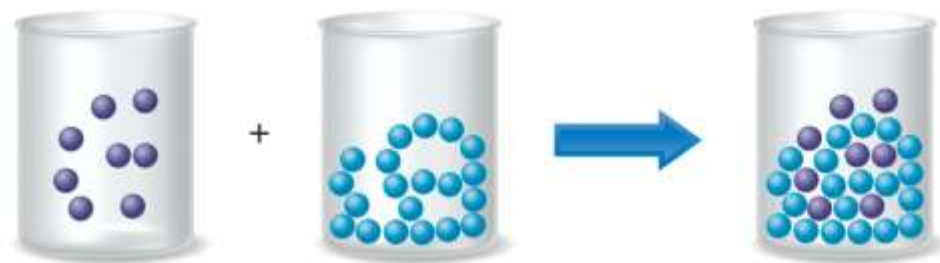
- separation of solute particles (breaking solute-solute interactions),
- separation of solvent particles (breaking solvent-solvent interactions),
- new interactions between solute and solvent (forming the solute-solvent interactions).



ΔH_1 : Separation of solute molecules



ΔH_2 : Separation of solvent molecules



ΔH_3 : Formation of solute-solvent interactions

The overall enthalpy change in forming a solution, ΔH_{soln} , is the sum of the three associated processes.:

$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Regardless of the particular solute being considered, separation of the solute particles from one another requires an input of energy to overcome their attractive interactions. The process is therefore endothermic ($\Delta H_1 > 0$). Separation of solvent molecules to accommodate the solute also always requires energy ($\Delta H_2 > 0$). The third component, which arises from the attractive interactions between solute and solvent, is always exothermic ($\Delta H_3 < 0$).

Depending on the relative magnitudes of the terms, the sum of the three components are either –ve or +ve value. Thus, the formation of a solution can be either **exothermic** or **endothermic**.

Processes that are exothermic tend to proceed spontaneously. A solution will not form if ΔH_{soln} is too endothermic.

The solvent-solute interaction must be strong enough to make ΔH_3 comparable in magnitude to $\Delta H_1 + \Delta H_2$.

This fact explain why ionic solutes such as **NaCl** do not dissolve in nonpolar liquids such as gasoline. The nonpolar hydrocarbon molecules of the gasoline would experience only weak attractive interactions with the ions, and these interactions would not compensate for the energies required to separate the ions from one another.

By similar reasoning, a polar liquid such as water does not form solutions with a nonpolar liquid such as octane (**C₈H₁₈**). The water molecules experience strong hydrogen-bonding interactions with one another. These attractive forces must be overcome to disperse the water molecules throughout the nonpolar liquid. The energy required to separate the water molecules is not recovered in the form of attractive interactions between **H₂O** and **C₈H₁₈** molecules.

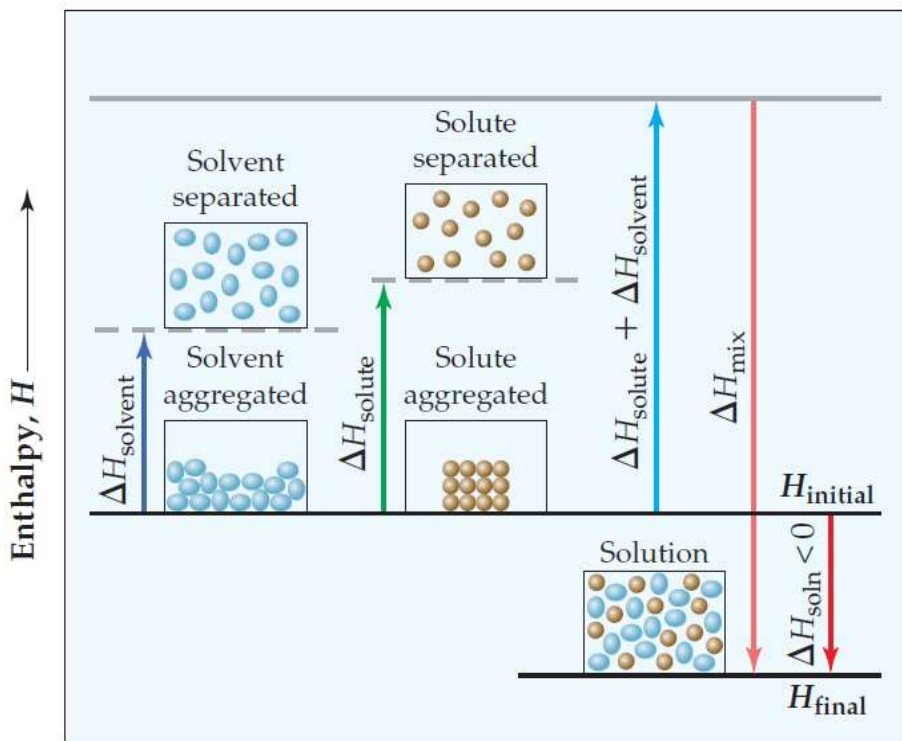
For example, when magnesium sulfate, **MgSO₄**, is added to water, the resultant solution gets quite warm: $\Delta H_{soln} = -91.2 \text{ kJ/mol}$.

In contrast, the dissolution of ammonium nitrate (**NH₄NO₃**) is endothermic $\Delta H_{soln} = 26.4 \text{ kJ/mol}$. These particular substances have been used to make the instant heat packs and ice packs that are used to treat athletic injuries.

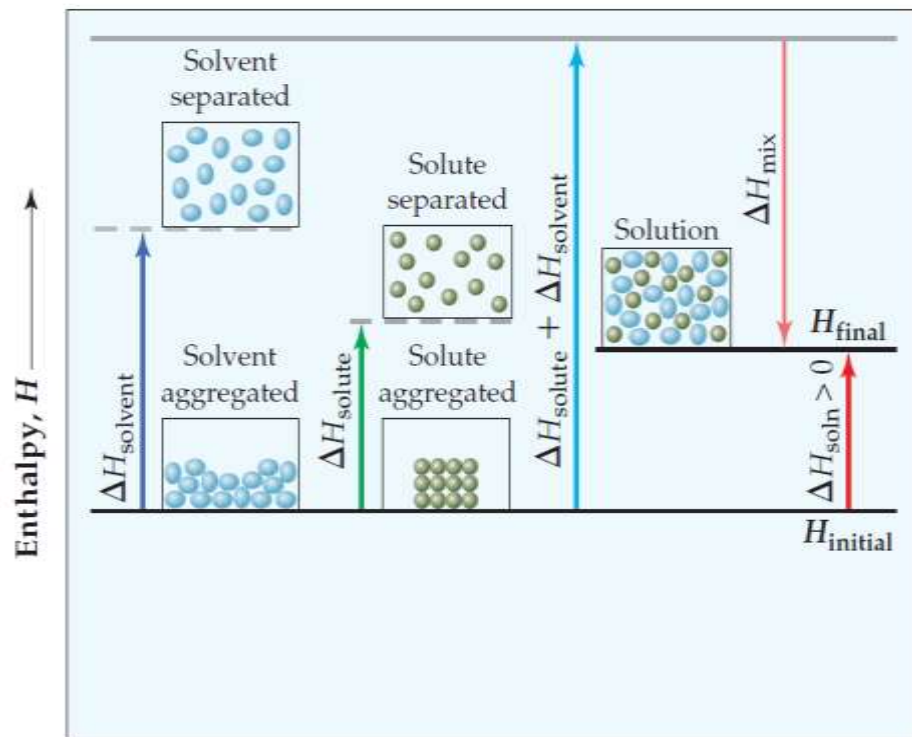
The packs consist of a pouch of water and a dry chemical, **MgSO₄** for hot packs and **NH₄NO₃** for cold packs. When the pack is squeezed, the seal separating the solid from water is broken and a solution forms, either increasing or decreasing the temperature.



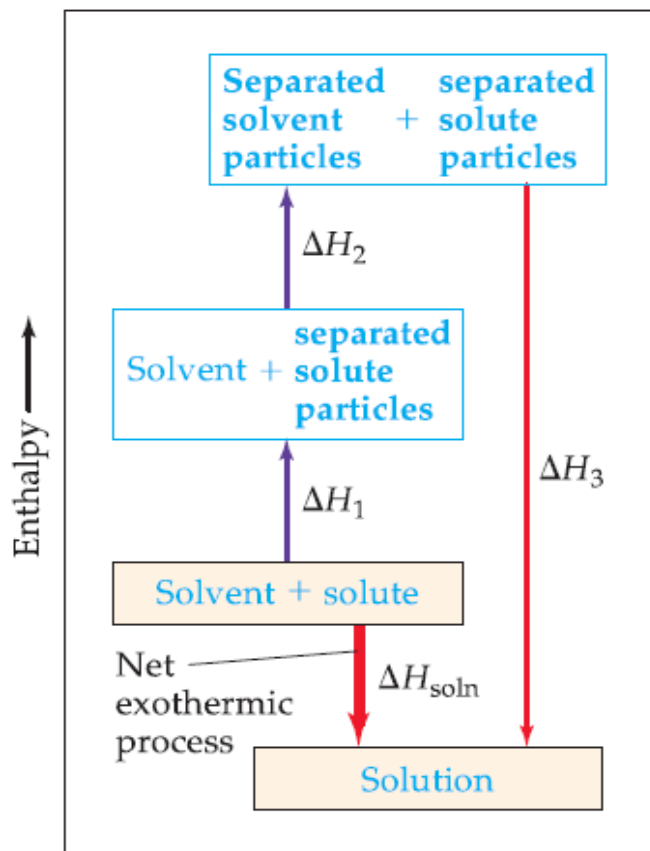
Enthalpy Changes in Solution



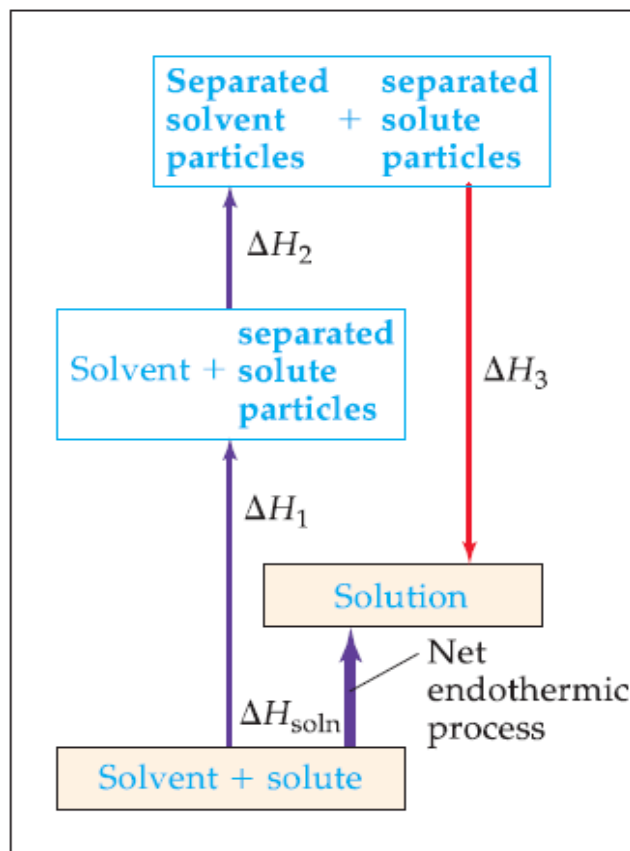
Exothermic solution process



Endothermic solution process



(a) Exothermic



(b) Endothermic

The three processes illustrated in the figure.

The diagram on the left illustrates a net exothermic process ($\Delta H_{soln} < 0$).

That on the right shows a net endothermic process ($\Delta H_{soln} > 0$).

The enthalpy change of the overall process depends on ΔH for each of these steps.

Depending on the relative magnitudes of the terms, the sum of the three components are either -ve or +ve value (exothermic or endothermic solution).

Solution Formation, Spontaneity and Entropy

Enthalpy is only part of the picture

Processes that occur spontaneously involve two distinct factors. The most obvious factor is energy, which we have used to analyze the dissolving of **NaCl** in water.

The other factor is the distribution of each component into a larger volume – the tendency in nature for substances to mix and spread out into larger volumes.

Processes in which the energy content of the system decreases tend to occur spontaneously.

Most spontaneous processes tend to be exothermic.



(a)



(b)

Some spontaneous processes, however, do not result in lower energy for a system, and even some endothermic processes occur spontaneously. These processes are characterized by a more dispersed state of one or more components, resulting in an overall increase in randomness of the system.

Formation of a homogeneous solution has increased the degree of dispersal, or randomness, because the molecules of each substance are now mixed and distributed in a volume twice as large as that which they occupied individually before mixing.

The degree of randomness in the system, sometimes referred to as disorder, is given by a thermodynamic quantity called **entropy**.

Thus, processes occurring at a constant temperature in which the randomness or dispersal in space (entropy) of the system increases tend to occur spontaneously.

Increasing the disorder or randomness (**entropy**) of a system tends to lower the energy of the system.

So even though enthalpy may increase, the overall energy of the system can still decrease if the system becomes more disordered.

For the moment, we need to be aware that the solution process involves two factors: **A change in enthalpy and a change in entropy.**

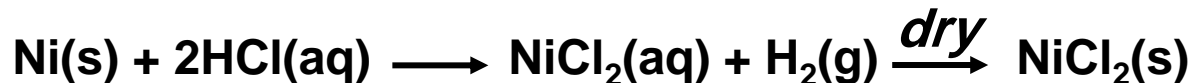
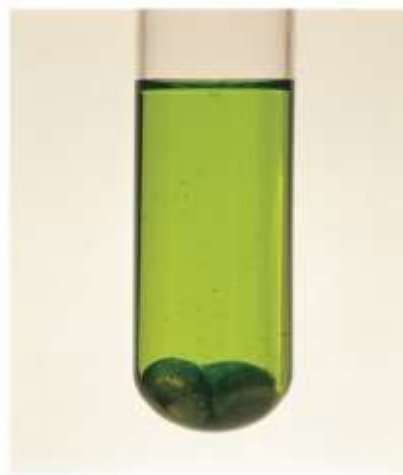
In most cases, the formation of solutions is forward by the increase in entropy that accompanies. Consequently, a solution will form unless solute-solute or solvent-solvent interactions are too strong relative to the solute-solvent interactions.

Solution Formation and Chemical Reactions

In all our discussions of solutions, we must be careful to distinguish the physical process of solution formation from chemical reactions that lead to a solution.

e.g., nickel metal is dissolved on contact with **HCl** solution because the following reaction occurs:

**Dissolution
vs.
Reaction**



In this instance the chemical form of the substance being dissolved is changed from **Ni** to **NiCl₂**. If the solution is evaporated to dryness, **NiCl₂(s)** not **Ni(s)**, is recovered. When **NaCl(s)** is dissolved in water, on the other hand, no chemical reaction occurs. If the solution is evaporated to dryness, **NaCl** is recovered.

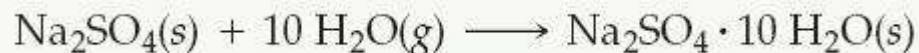
Just because a substance disappears when it comes in contact with a solvent, it doesn't mean the substance dissolved.

Dissolution is a physical change - you can get back the original solute by evaporating the solvent.

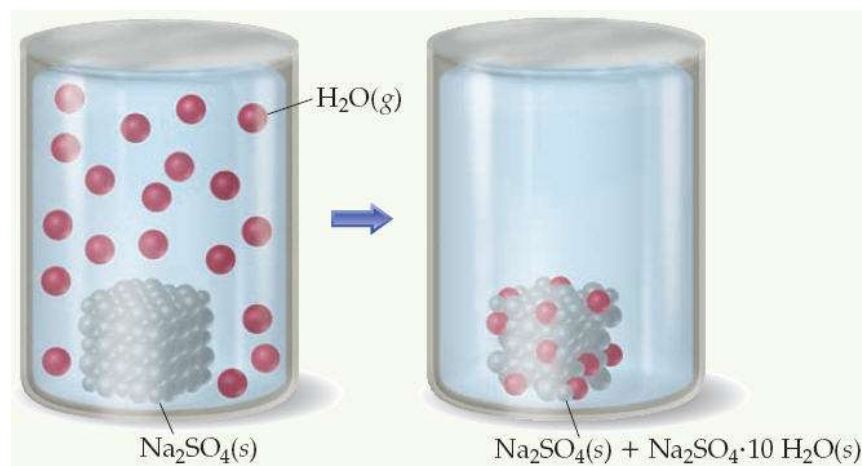
If you can't, the substance didn't dissolve, it reacted.

Sample Exercise Assessing Entropy Change

In the process illustrated below, water vapor reacts with excess solid sodium sulfate to form the hydrated form of the salt. The chemical reaction is



Essentially all of the water vapor in the closed container is consumed in this reaction. If we consider our system to consist initially of $\text{Na}_2\text{SO}_4(\text{s})$ and $10 \text{H}_2\text{O}(\text{g})$, **(a)** does the system become more or less ordered in this process, and **(b)** does the entropy of the system increase or decrease?



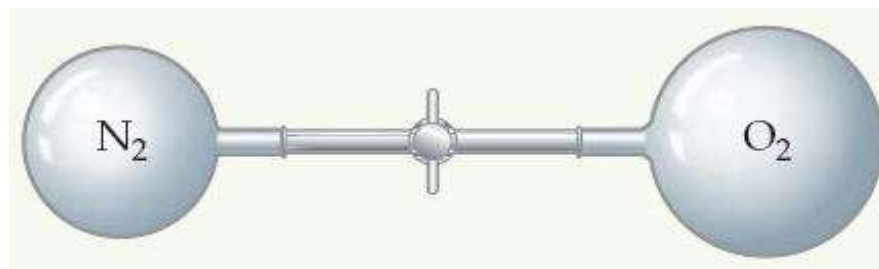
Solution

(a) In the course of forming the hydrate of $\text{Na}_2\text{SO}_4(\text{s})$, the water vapor moves from the vapor state, in which it is dispersed throughout the entire volume of the container, to the solid state, where it is confined to the lattice. This means that the water vapor becomes less dispersed (more ordered, or less random).

(b) When a system becomes less dispersed, or more ordered, its entropy is decreased.

Practice Exercise

Does the entropy of the system increase or decrease when the stopcock is opened to allow mixing of the two gases in this apparatus?



Answer: The entropy increases because each gas eventually becomes dispersed in twice the volume it originally occupied.

13.3

Factors Affecting Solubility

Factors Affecting Solubility

The extent to which one substance dissolves in another depends on:

- **Solute – Solvent Interactions**
nature of both solute and solvent.
- **Pressure Effects**
at least for gases.
- **Temperature Effects.**

Solute – Solvent Interactions

Chemists use the axiom “**like dissolves like**”.

Polar substances tend to dissolve in polar solvents.

Nonpolar substances tend to dissolve in nonpolar solvents.

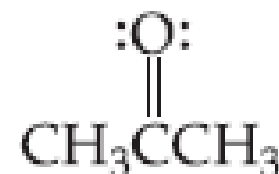
The more similar the intermolecular attractions, the more likely one substance is to be soluble in another.

The stronger the intermolecular attractions between solute and solvent, the more likely the solute will dissolve.

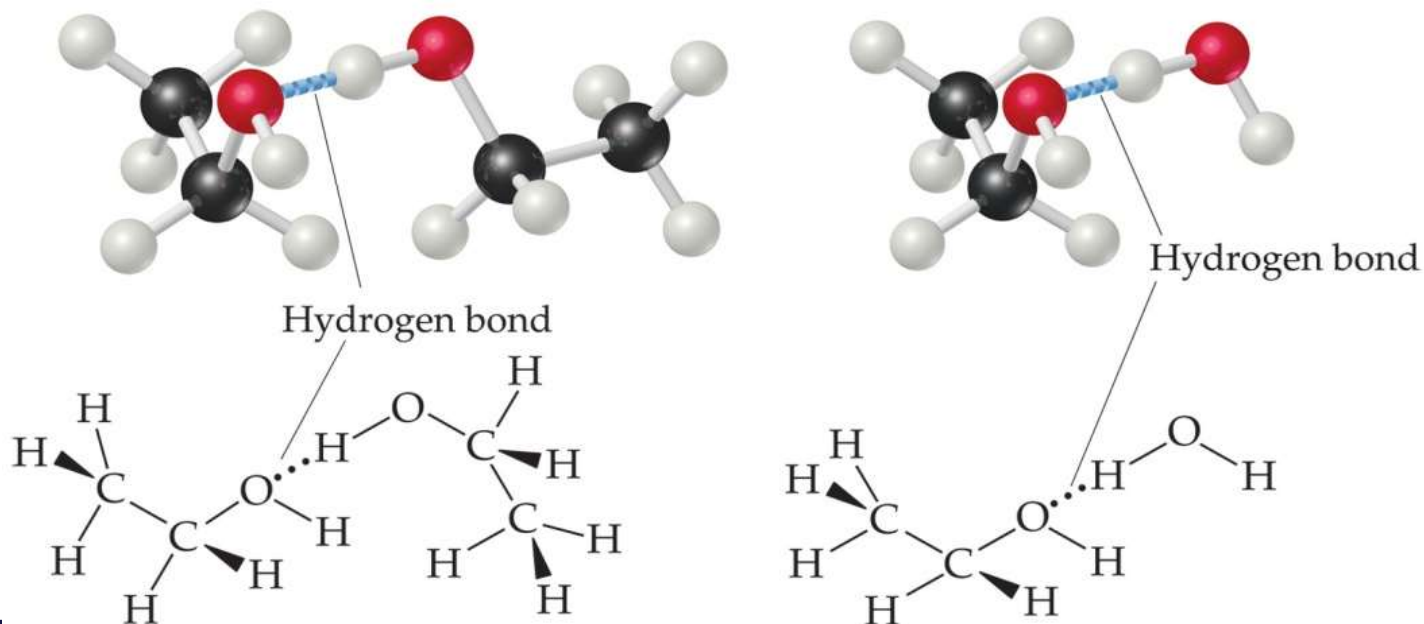
Polar liquids tend to dissolve readily in polar solvents because of favorable dipole-dipole attractions between solvent molecules and solute molecules.

Water (H_2O) is both polar and able to form hydrogen bonds. Thus, polar molecules, especially those that can form hydrogen bonds with water molecules, tend to be soluble in water.

For example, acetone has a strongly polar $\text{C}=\text{O}$ bond and pairs of nonbonding electrons on the O atom that can form hydrogen bonds with water.



Example
ethanol in water



Nonpolar liquids tend to be insoluble in polar liquids

Gasoline, which is a mixture of hydrocarbons, is immiscible with water.

Hydrocarbons are nonpolar substances because of several factors: the **C-C** bonds are nonpolar, the **C-H** bonds are nearly nonpolar, and the shapes of the molecules are symmetrical enough to cancel much of the weak **C-H** bond dipoles.

The attraction between the polar water molecules and the nonpolar hydrocarbon molecules is not sufficiently strong to allow the formation of a solution.



Hexane is insoluble in water (hexane is in the top layer because it is less dense than water).

Pairs of liquids that mix in all proportions are **miscible**, whereas those that do not dissolve in one another are **immiscible**.

TABLE 13.3 ■ Solubilities of Some Alcohols in Water and in Hexane*

Alcohol	Solubility in H ₂ O	Solubility in C ₆ H ₁₄
CH ₃ OH (methanol)	∞	0.12
CH ₃ CH ₂ OH (ethanol)	∞	∞
CH ₃ CH ₂ CH ₂ OH (propanol)	∞	∞
CH ₃ CH ₂ CH ₂ CH ₂ OH (butanol)	0.11	∞
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ OH (pentanol)	0.030	∞
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ OH (hexanol)	0.0058	∞

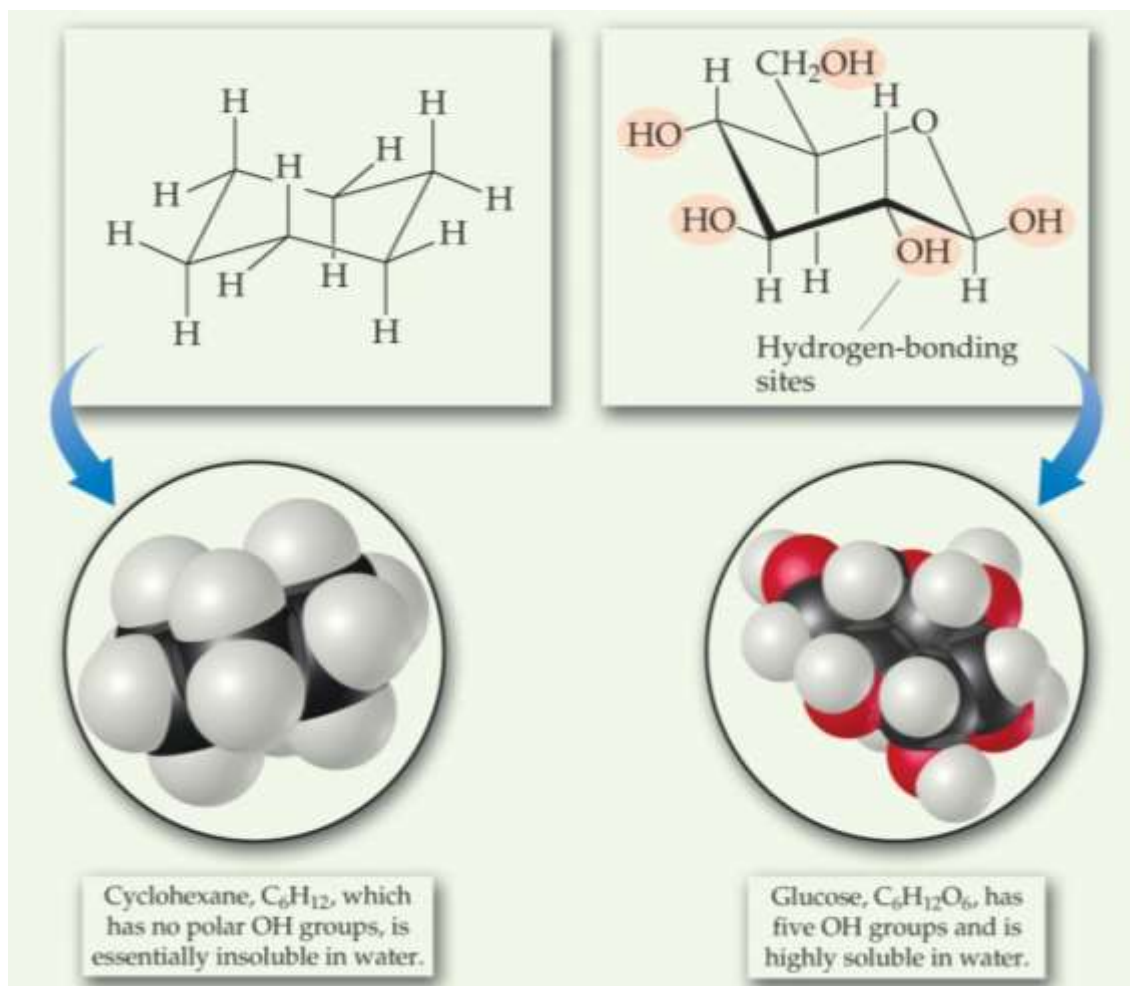
*Expressed in mol alcohol/100 g solvent at 20 °C. The infinity symbol (∞) indicates that the alcohol is completely miscible with the solvent.

The number of carbon atoms in an alcohol affects its solubility in water. As the length of the carbon chain increases, the polar **OH** group becomes an ever smaller part of the molecule, and the molecule behaves more like a hydrocarbon. The solubility of the alcohol in water decreases correspondingly. On the other hand, the solubility of the alcohols in a nonpolar solvent like hexane (**C₆H₁₄**) increases as the nonpolar hydrocarbon chain increases in length.

One way to enhance the solubility of a substance in water is to increase the number of polar groups it contains.

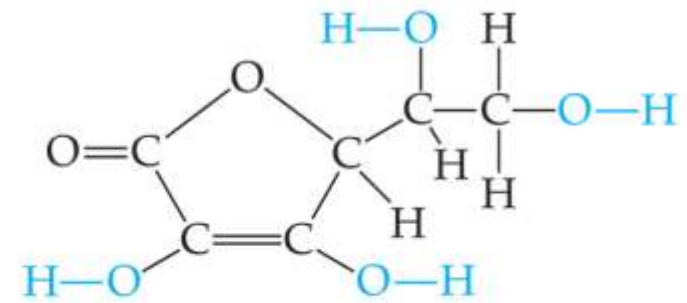
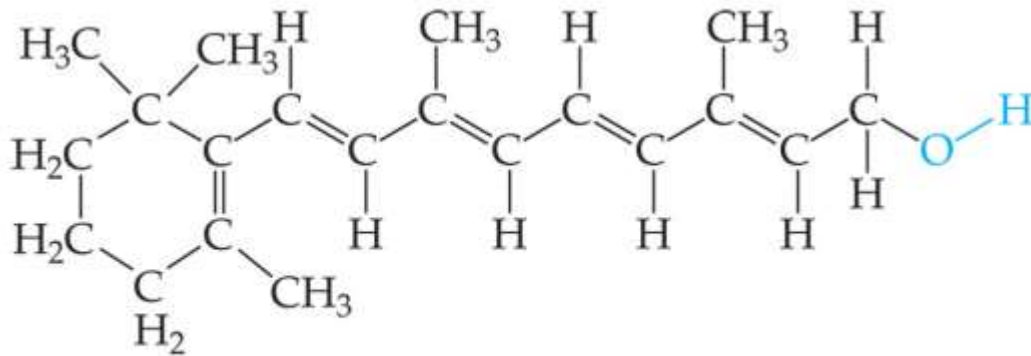
For example, increasing the number of **OH** groups along a carbon chain of a solute increases the extent of hydrogen bonding between that solute and water, thereby increasing solubility.

Glucose (which has hydrogen bonding) is very soluble in water, while **cyclohexane** (which only has dispersion forces) is not.



Vitamin A is soluble in nonpolar compounds (fat soluble vitamin).

Vitamin C is soluble in water (water soluble vitamin).



Vitamin A



Vitamin C

Sample Exercise Predicting Solubility Patterns

Predict whether each of the following substances is more likely to dissolve in the nonpolar solvent carbon tetrachloride (CCl_4) or in water: C_7H_{16} , Na_2SO_4 , HCl , and I_2 .

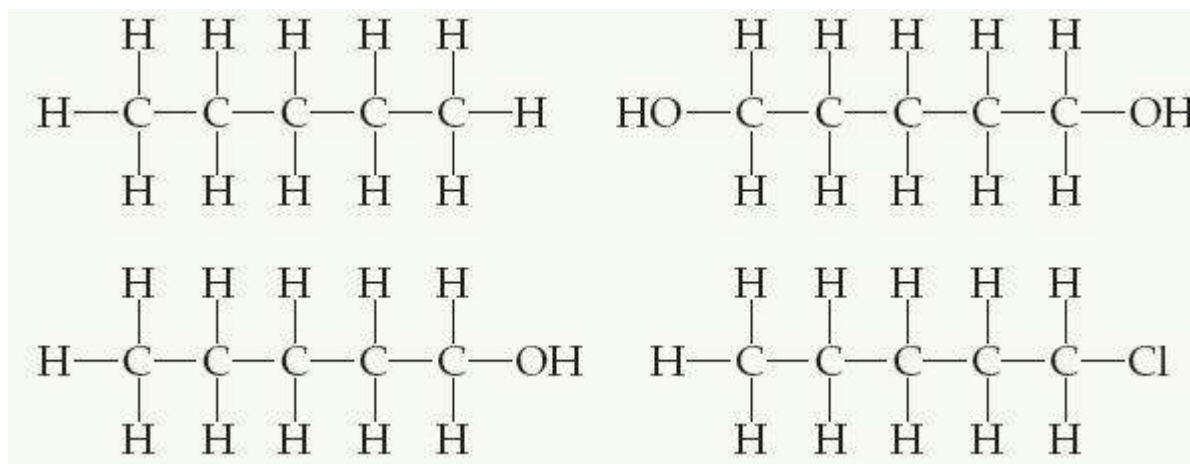
Solution

C_7H_{16} is a hydrocarbon, so it is molecular and nonpolar. Na_2SO_4 , a compound containing a metal and nonmetals, is ionic. HCl , a diatomic molecule containing two nonmetals that differ in electronegativity, is polar. I_2 , a diatomic molecule with atoms of equal electronegativity, is nonpolar.

We would therefore predict that C_7H_{16} and I_2 (the nonpolar solutes) would be more soluble in the nonpolar CCl_4 than in polar H_2O , whereas water would be the better solvent for Na_2SO_4 and HCl (the ionic and polar covalent solutes).

Practice Exercise

Arrange the following substances in order of increasing solubility in water:



Answer: $C_5H_{12} < C_5H_{11}Cl < C_5H_{11}OH < C_5H_{10}(OH)_2$ (in order of increasing polarity and hydrogen-bonding ability)

Pressure Effects

The solubility of solids and liquids are not appreciably affected by pressure.

The solubility of a gas in any solvent is increased as the pressure over the solvent increases.

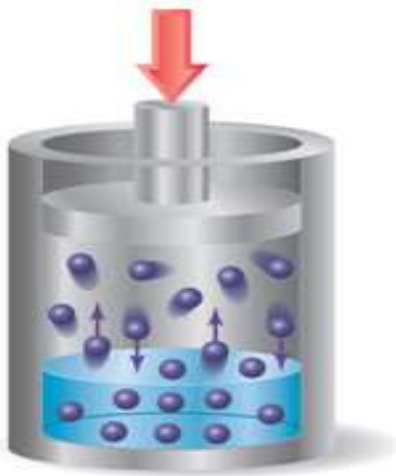
TABLE 13.2 ■ Solubilities of Gases in Water at 20 °C, with 1 atm Gas Pressure

Gas	Solubility (M)
N ₂	0.69×10^{-3}
CO	1.04×10^{-3}
O ₂	1.38×10^{-3}
Ar	1.50×10^{-3}
Kr	2.79×10^{-3}

The attractive forces between the gas and solvent molecules are mainly of the **London dispersion** type, which increase with increasing size and mass of the gas molecules.

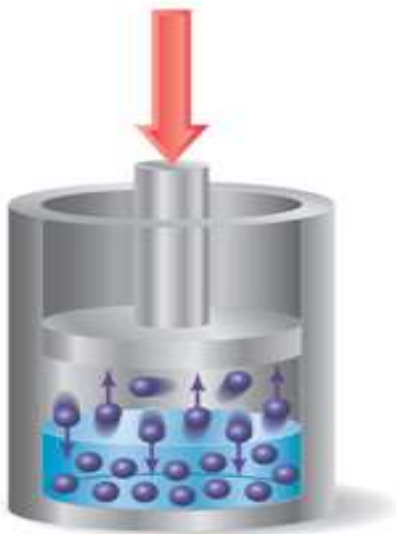
The solubility of gases in water increase as the attraction between the solute (gas) and solvent (water) increases.

In general, when other factors are comparable, the stronger the attractions are between solute and solvent molecules, the greater the solubility.



The solubility of a gas in a liquid is directly proportional to its pressure (increasing pressure above solution forces more gas to dissolve).

As a result, the solubility of the gas in the solution would increase until equilibrium is again established, that is, solubility increases until the rate at which gas molecules enter the solution equals the rate at which solute molecules escape from the solution.



Thus, the solubility of the gas increases in direct proportion to its partial pressure above the solution.

When the pressure is increased, the rate at which gas molecules enter the solution increases. The concentration of solute molecules at equilibrium increases in proportion to the pressure.

Henry's Law

The relationship between pressure and the solubility of a gas is expressed by a simple equation known as **Henry's law**:

$$S_g = kP_g$$

Where:

S_g is the solubility of the gas (usually expressed as molarity).

k is a proportionality constant known as the Henry's Law constant for that gas in that solvent, its different for each solute-solvent pair. It also varies with temperature.

P_g is the partial pressure of the gas over the solution.

As an example, the solubility of N_2 gas in water at 25 °C and 0.78 atm pressure is 5.3×10^{-4} M. The Henry's law constant for N_2 in water at 25 °C is thus given by

$$5.3 \times 10^{-4} \text{ mol/L} / 0.78 \text{ atm} = 6.8 \times 10^{-4} \text{ mol/L-atm}.$$

If the partial pressure of N_2 is doubled, Henry's law predicts that the solubility in water at 25 °C will also double, to 1.36×10^{-3} M.

Bottles use the effect of pressure on solubility in producing carbonated beverages such as soft drinks.

These are bottled under a carbon dioxide pressure greater than 1 atm.

When the bottles are opened to the air, the partial pressure of **CO₂** above the solution decreases.

Hence, the solubility of **CO₂** decreases, and **CO₂(g)** escapes from the solution as bubbles.



Solubility decreases as pressure decreases. CO₂ bubbles out of solution when a carbonated beverage is opened, because the CO₂ partial pressure above the solution is reduced.

Sample Exercise A Henry's Law Calculation

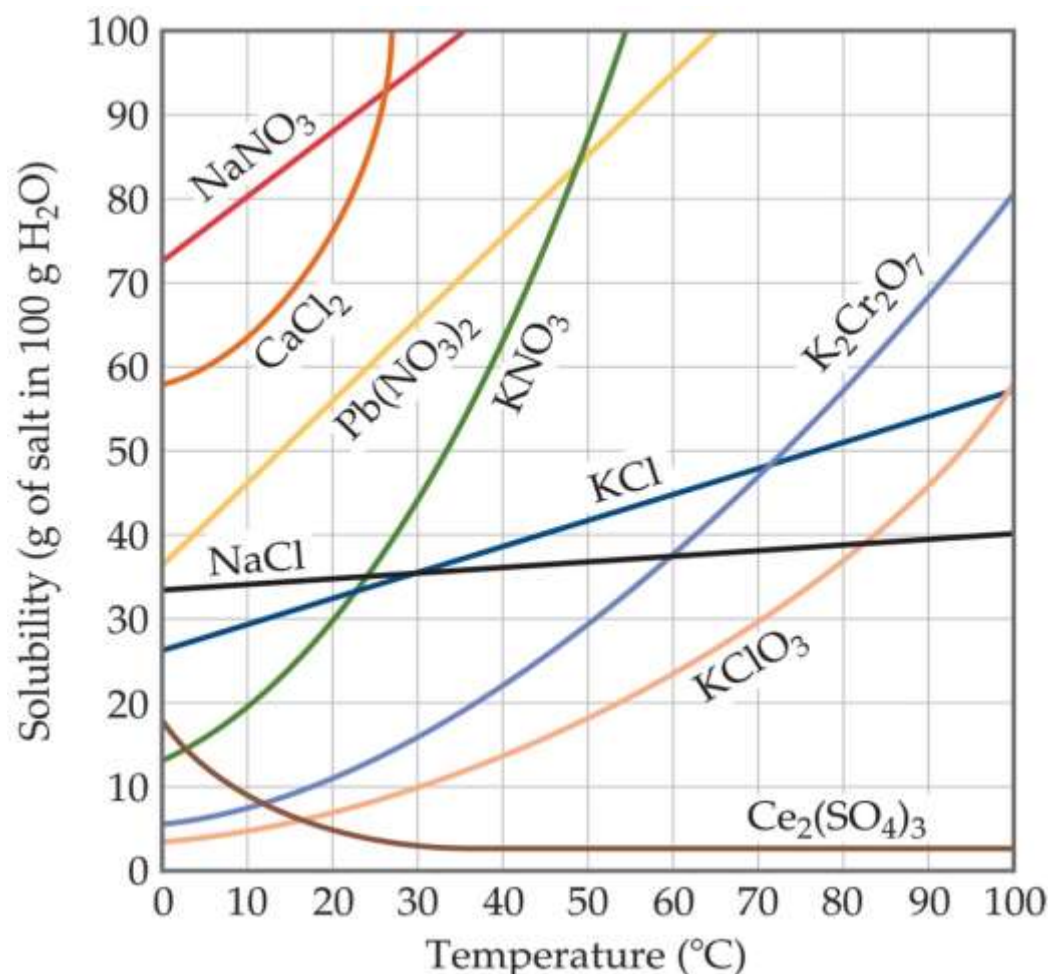
Calculate the concentration of CO₂ in a soft drink that is bottled with a partial pressure of CO₂ of 4.0 atm over the liquid at 25 °C. The Henry's law constant for CO₂ in water at this temperature is 3.1×10^{-2} mol/L-atm.

Solution

Solve: $S_{\text{CO}_2} = kP_{\text{CO}_2} = (3.1 \times 10^{-2} \text{ mol/L-atm})(4.0 \text{ atm})$
 $= 0.12 \text{ mol/L} = 0.12 \text{ } M$

Temperature Effects

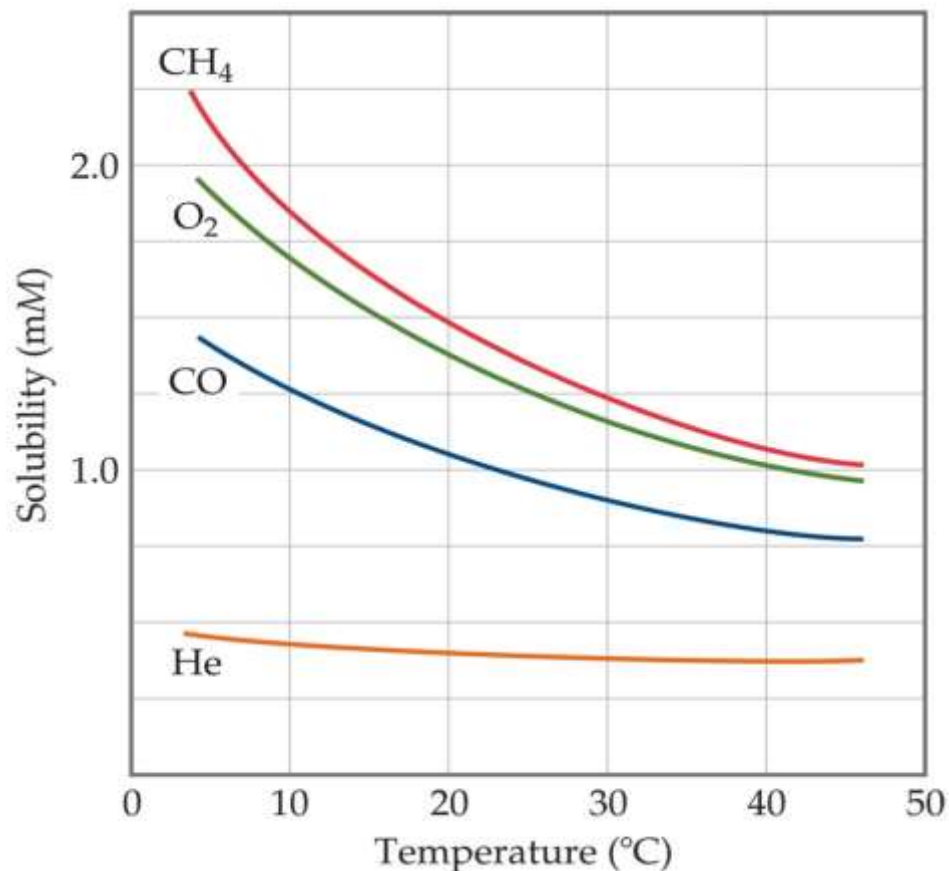
Generally, the solubility of most solid solutes in water increases as the temperature of the solution increases.



The opposite is true of gases.

The solubility of gases in water decreases with increasing temperature.

- As the temperature of the solution increases, the solubility of CO_2 decreases, and $\text{CO}_2(\text{g})$ escapes from the solution.
- Carbonated soft drinks are more “bubbly” if stored in the refrigerator.
- When a glass of cold tap water is warmed, you can see bubbles of air on the inside of the glass.
- Warm lakes and streams have less O_2 dissolved in them than cool lakes (thermal pollution). The effect is particularly serious in deep lakes because warm water is less dense than cold water, it therefore tends to remain on top of cold water, at the surface (fish may suffocate and die under these conditions).



13.5

Colligative Properties

Colligative Properties

Some physical properties of solutions differ in important ways from those of pure solvent. For example, pure water freezes at 0 °C, but aqueous solutions freeze at lower temperatures.

Ethylene glycol is added to the water in radiators of cars as an antifreeze to lower the freezing point of the solution. It also raises the boiling point of the solution above that of pure water.

Colligative properties depend only on the number or concentration of solute particles present, not on the identity or kind of the solute particles.

Among colligative properties are:

- Vapor pressure lowering.
- Boiling point elevation.
- Melting point depression.
- Osmotic pressure.

Lowering the Vapor Pressure

A liquid in a closed container will establish equilibrium with its vapor. When that equilibrium is reached, the pressure exerted by the vapor is called the **vapor pressure**. A substance that has no measurable vapor pressure is **nonvolatile**, whereas one that exhibits a vapor pressure is **volatile**.

As solute molecules are added to a solution, the solvent becomes less volatile (decreased vapor pressure).

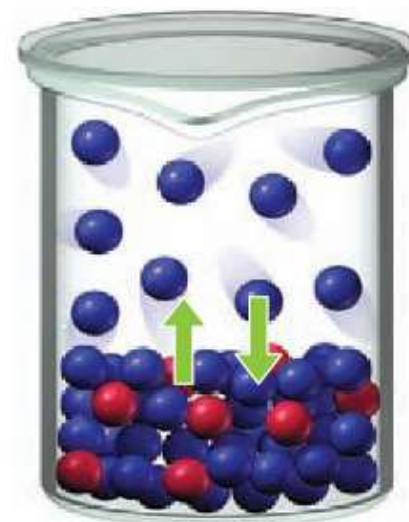
Solute-solvent interactions contribute to this effect, because of solute-solvent intermolecular attraction, higher concentrations of nonvolatile solutes make it harder for solvent to escape to the vapor phase.

Therefore, the vapor pressure of a solution is lower than that of the pure solvent.



Solvent alone

(a)



Solvent + solute

(b)

Raoult's Law

The extent to which a nonvolatile solute lowers the vapor pressure is proportional to its concentration. This relationship is expressed by Raoult's law.

Raoult's law states that the partial pressure exerted by solvent vapor above a solution, P_A , equals the product of the mole fraction of the solvent in the solution, X_A , times the vapor pressure of the pure solvent, P°_A .

$$P_A = X_A P^\circ_A$$

where:

X_A is the mole fraction of solvent A in solution.

P°_A is the normal vapor pressure of pure solvent A at that temperature.

NOTE: This is one of those times when you want to make sure you have the vapor pressure of the ***solvent***.

For example, the vapor pressure of water is 17.5 torr at 20 °C. Imagine holding the temperature constant while adding glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) to the water so that the resulting solution has $X_{\text{H}_2\text{O}} = 0.8$ and $X_{\text{C}_6\text{H}_{12}\text{O}_6} = 0.2$.

The vapor pressure of water over the solution will be 80% of that of pure water:

$$P_{\text{H}_2\text{O}} = (0.8) \times (17.5 \text{ torr}) = 14.0 \text{ torr}$$

In other words, the presence of the nonvolatile solute lowers the vapor pressure of the volatile solvent by $17.5 \text{ torr} - 14.0 \text{ torr} = 3.5 \text{ torr}$.

An **ideal gas** obeys the **ideal gas equation**, and an **ideal solution** obeys **Raoult's law**. Real solutions best approximate ideal behavior when the solute concentration is low and when the solute and solvent have similar molecular sizes and similar types of intermolecular attractions.

Sample Exercise Calculation of Vapor-Pressure Lowering

Glycerin ($\text{C}_3\text{H}_8\text{O}_3$) is a nonvolatile nonelectrolyte with a density of 1.26 g/mL at 25 °C. Calculate the vapor pressure at 25 °C of a solution made by adding 50.0 mL of glycerin to 500.0 mL of water. The vapor pressure of pure water at 25 °C is 23.8 torr (Appendix B), and its density is 1.00 g/mL.

Solution

To calculate the mole fraction of water in the solution, we must determine the number of moles of $\text{C}_3\text{H}_8\text{O}_3$ and H_2O :

$$\text{Moles } \text{C}_3\text{H}_8\text{O}_3 = (50.0 \text{ mL } \text{C}_3\text{H}_8\text{O}_3) \left(\frac{1.26 \text{ g } \text{C}_3\text{H}_8\text{O}_3}{1 \text{ mL } \text{C}_3\text{H}_8\text{O}_3} \right) \left(\frac{1 \text{ mol } \text{C}_3\text{H}_8\text{O}_3}{92.1 \text{ g } \text{C}_3\text{H}_8\text{O}_3} \right) = 0.684 \text{ mol}$$

$$\text{Moles } \text{H}_2\text{O} = (500.0 \text{ mL } \text{H}_2\text{O}) \left(\frac{1.00 \text{ g } \text{H}_2\text{O}}{1 \text{ mL } \text{H}_2\text{O}} \right) \left(\frac{1 \text{ mol } \text{H}_2\text{O}}{18.0 \text{ g } \text{H}_2\text{O}} \right) = 27.8 \text{ mol}$$

$$X_{\text{H}_2\text{O}} = \frac{\text{mol } \text{H}_2\text{O}}{\text{mol } \text{H}_2\text{O} + \text{mol } \text{C}_3\text{H}_8\text{O}_3} = \frac{27.8}{27.8 + 0.684} = 0.976$$

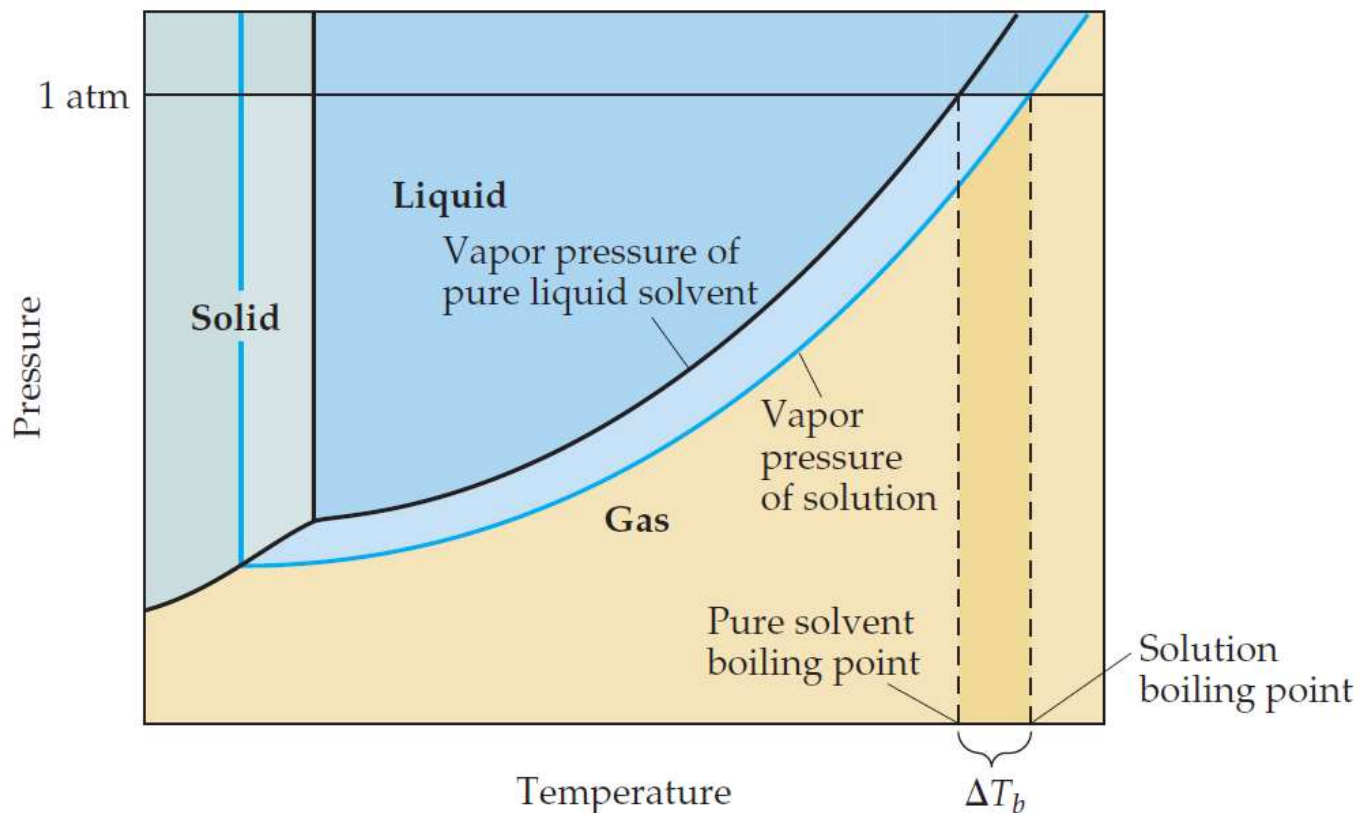
$$P_{\text{H}_2\text{O}} = X_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^{\circ} = (0.976)(23.8 \text{ torr}) = 23.2 \text{ torr}$$

The vapor pressure of the solution has been lowered by 0.6 torr relative to that of pure water

Boiling Point Elevation

Nonvolatile solute-solvent interactions also cause solutions to have higher boiling points than the pure solvent.

The vapor pressure curve of the solution shifted downward relative to the vapor pressure of the pure liquid at any given temperature.



Phase diagram for a pure solvent and for a solution of a nonvolatile solute.

At the normal boiling point of the pure liquid, the vapor pressure of the solution will be less than 1 atm. Therefore, a higher temperature is required to attain a vapor pressure of 1 atm. Thus, the boiling point of the solution is higher than that of the pure liquid.

The change in boiling point is proportional to the **molality** (m) of the solution:

$$\Delta T_b = K_b m$$

where:

K_b is the molal boiling point elevation constant, a property of the solvent.

ΔT_b is *added to* the normal boiling point of the solvent.

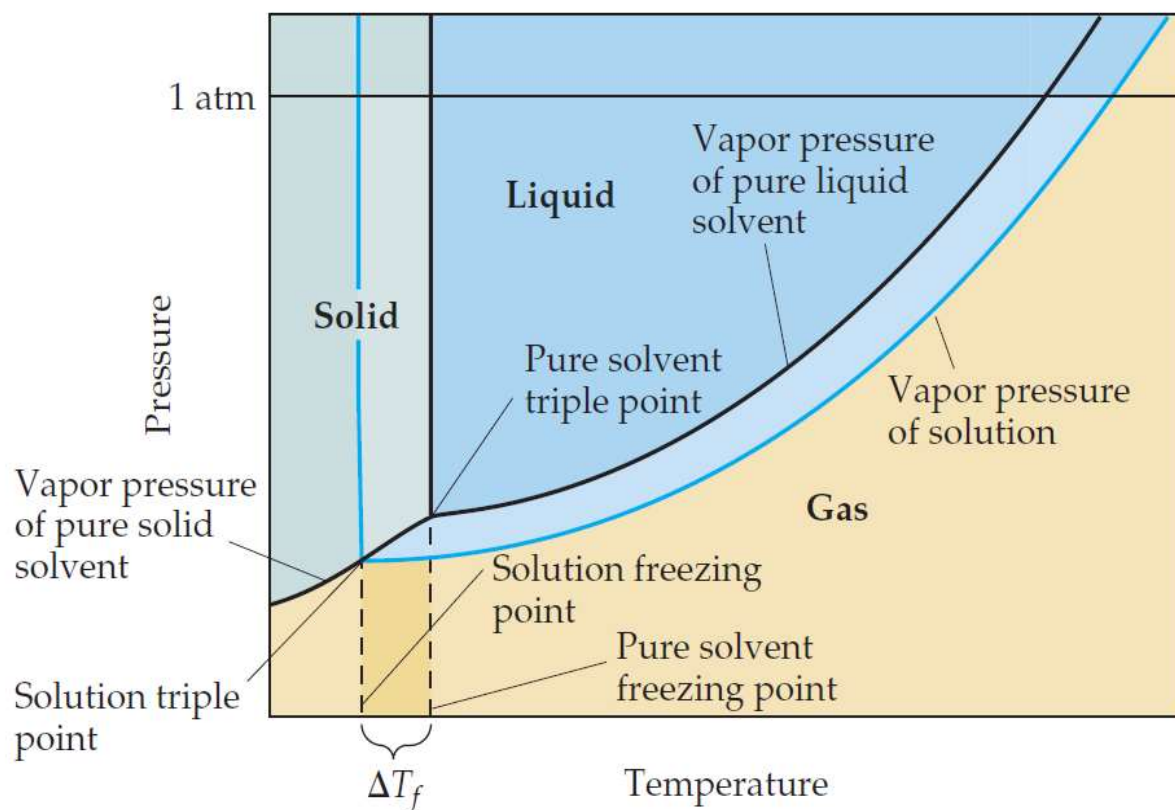
The increase in boiling point relative to that of the pure solvent, ΔT_b is a +ve quantity obtained by subtracting the boiling point of the pure solvent from the boiling point of the solution.

$$\Delta T_b = T_{soln} - T_{pure\ solvent}$$

Freezing Point Depression

Nonvolatile solute-solvent interactions also cause solutions to have lower freezing points than the pure solvent.

e.g., Antifreeze being added to an automobile radiator. Antifreeze consists of an aqueous solution of ethylene glycol, $\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$.



Phase diagram for a pure solvent and for a solution of a nonvolatile solute.

The change in freezing point can be found similarly:

$$\Delta T_f = K_f m$$

where:

K_f is the molal freezing point depression constant of the solvent.

ΔT_f is *subtracted from* the normal freezing point of the solvent.

The decrease in freezing point, ΔT_f is a +ve quantity obtained by subtracting the freezing point of the solution from the freezing point of the pure solvent.

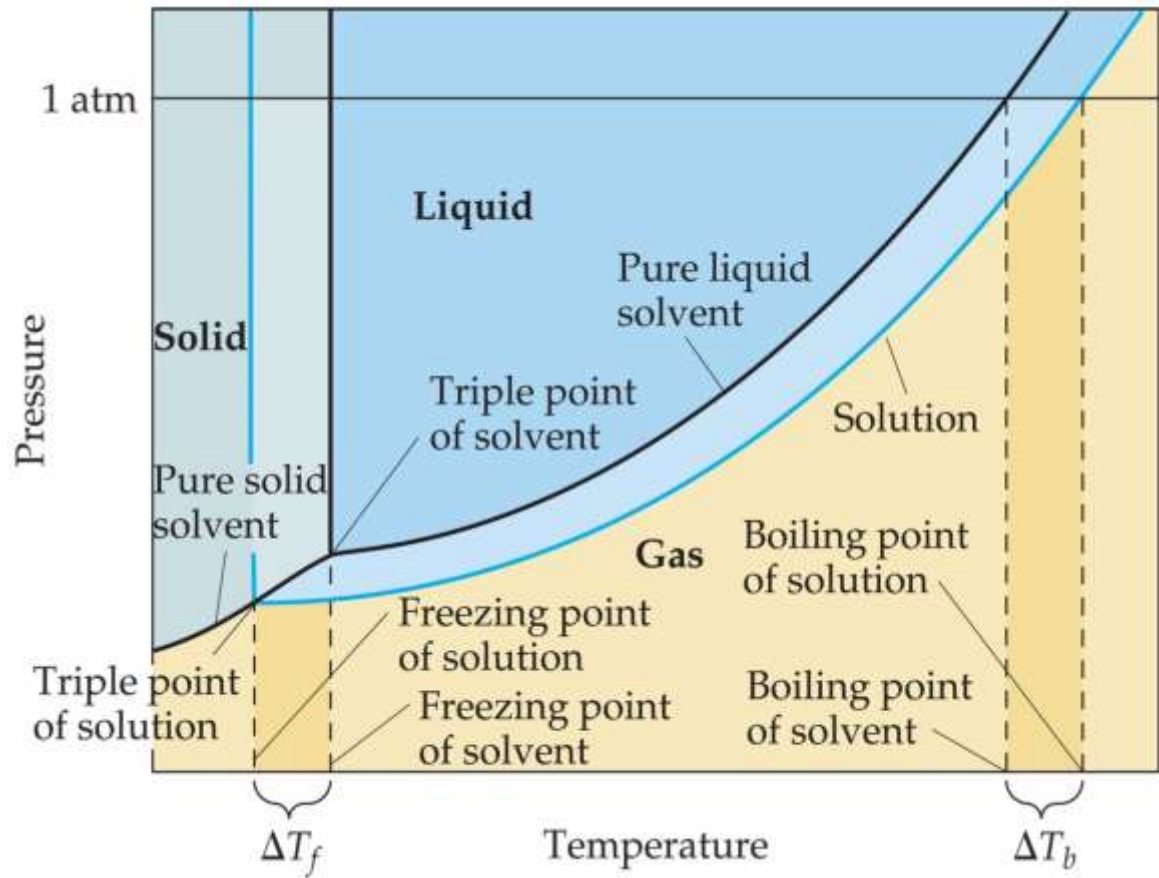
$$\Delta T_f = T_{\text{pure solvent}} - T_{\text{soln}}$$

Boiling Point Elevation and Freezing Point Depression

$$\Delta T_b = K_b \cdot m$$

$$\Delta T_f = K_f \cdot m$$

Note that in both equations, ΔT does not depend on what the solute is, but only on how many particles are dissolved.



Phase diagram for a pure solvent and for a solution of a nonvolatile solute. The vapor pressure of the solid solvent is unaffected by the presence of solute if the solid freezes out without containing a significant concentration of solute as is usually the case.

TABLE 13.4 ■ Molal Boiling-Point-Elevation and Freezing-Point-Depression Constants

Solvent	Normal Boiling Point (°C)	K_b (°C/ m)	Normal Freezing Point (°C)	K_f (°C/ m)
Water, H ₂ O	100.0	0.51	0.0	1.86
Benzene, C ₆ H ₆	80.1	2.53	5.5	5.12
Ethanol, C ₂ H ₅ OH	78.4	1.22	−114.6	1.99
Carbon tetrachloride, CCl ₄	76.8	5.02	−22.3	29.8
Chloroform, CHCl ₃	61.2	3.63	−63.5	4.68

For water, K_b is 0.51 °C/ m ; therefore, a 1 m aqueous solution of sucrose or any other aqueous solution that is 1 m in nonvolatile solute particles will boil 0.51 °C higher than pure water. The boiling-point elevation is proportional to the concentration of solute particles, regardless of whether the particles are molecules or ions.

When **NaCl** dissolves in water, 2 mol of solute particles (1 mol of **Na⁺** and 1 mol of **Cl[−]**) are formed for each mole of **NaCl** that dissolves. Therefore, a 1 m aqueous solution of **NaCl** is 1 m in **Na⁺** and 1 m in **Cl[−]**, making it 2 m in total solute particles. As a result, the boiling-point elevation of a 1 m aqueous solution of **NaCl** is approximately (2 m) (0.51 °C/ m) = 1 °C, twice as large as a 1 m solution of a nonelectrolyte such as sucrose. Thus, to properly predict the effect of a particular solute on the boiling point (or any other colligative property), it is important to know whether the solute is an electrolyte or a nonelectrolyte.

TABLE 13.4 ■ Molal Boiling-Point-Elevation and Freezing-Point-Depression Constants

Solvent	Normal Boiling Point (°C)	K_b (°C/ m)	Normal Freezing Point (°C)	K_f (°C/ m)
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Ethanol, C ₂ H ₅ OH	78.4	1.22	−114.6	1.99
Carbon tetrachloride, CCl ₄	76.8	5.02	−22.3	29.8
Chloroform, CHCl ₃	61.2	3.63	−63.5	4.68

For water, K_f is 1.86 °C/ m ; therefore, a 1 m aqueous solution of sucrose or any other aqueous solution that is 1 m in nonvolatile solute particles (such as 0.5 m **NaCl**) will freeze 1.86 °C lower than pure water.

The freezing-point lowering caused by solutes explains the use of antifreeze in cars and the use of calcium chloride (**CaCl₂**) to melt ice on roads during winter.

Sample Exercise Calculation of Boiling-Point Elevation and Freezing-Point Lowering

Automotive antifreeze consists of ethylene glycol, $\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$, a nonvolatile nonelectrolyte. Calculate the boiling point and freezing point of a 25.0 mass % solution of ethylene glycol in water.

Solution

The molality of the solution is calculated as follows:

$$\begin{aligned}\text{Molality} &= \frac{\text{moles C}_2\text{H}_6\text{O}_2}{\text{kilograms H}_2\text{O}} = \left(\frac{250 \text{ g C}_2\text{H}_6\text{O}_2}{750 \text{ g H}_2\text{O}}\right)\left(\frac{1 \text{ mol C}_2\text{H}_6\text{O}_2}{62.1 \text{ g C}_2\text{H}_6\text{O}_2}\right)\left(\frac{1000 \text{ g H}_2\text{O}}{1 \text{ kg H}_2\text{O}}\right) \\ &= 5.37 \text{ } m\end{aligned}$$

We can now use Equations 13.11 and 13.12 to calculate the changes in the boiling and freezing points:

$$\begin{aligned}\Delta T_b &= K_b m = (0.51 \text{ } ^\circ\text{C}/m)(5.37 \text{ } m) = 2.7 \text{ } ^\circ\text{C} \\ \Delta T_f &= K_f m = (1.86 \text{ } ^\circ\text{C}/m)(5.37 \text{ } m) = 10.0 \text{ } ^\circ\text{C}\end{aligned}$$

Hence, the boiling and freezing points of the solution are

$$\begin{aligned}\text{Boiling point} &= (\text{normal bp of solvent}) + \Delta T_b \\ &= 100.0 \text{ } ^\circ\text{C} + 2.7 \text{ } ^\circ\text{C} = 102.7 \text{ } ^\circ\text{C} \\ \text{Freezing point} &= (\text{normal fp of solvent}) - \Delta T_f \\ &= 0.0 \text{ } ^\circ\text{C} - 10.0 \text{ } ^\circ\text{C} = -10.0 \text{ } ^\circ\text{C}\end{aligned}$$

Comment: Notice that the solution is a liquid over a larger temperature range than the pure solvent.

Sample Exercise Freezing-Point Depression in Aqueous Solutions

List the following aqueous solutions in order of their expected freezing point: $0.050\text{ }m\text{ CaCl}_2$, $0.15\text{ }m\text{ NaCl}$, $0.10\text{ }m\text{ HCl}$, $0.050\text{ }m\text{ CH}_3\text{COOH}$, $0.10\text{ }m\text{ C}_{12}\text{H}_{22}\text{O}_{11}$.

Solution

CaCl_2 , NaCl , and HCl are strong electrolytes, CH_3COOH (acetic acid) is a weak electrolyte, and $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ is a nonelectrolyte. The molality of each solution in total particles is as follows:

$0.050\text{ }m\text{ CaCl}_2 \Rightarrow 0.050\text{ }m\text{ in Ca}^{2+}\text{ and }0.10\text{ }m\text{ in Cl}^- \Rightarrow 0.15\text{ }m\text{ in particles}$

$0.15\text{ }m\text{ NaCl} \Rightarrow 0.15\text{ }m\text{ Na}^+\text{ and }0.15\text{ }m\text{ in Cl}^- \Rightarrow 0.30\text{ }m\text{ in particles}$

$0.10\text{ }m\text{ HCl} \Rightarrow 0.10\text{ }m\text{ H}^+\text{ and }0.10\text{ }m\text{ in Cl}^- \Rightarrow 0.20\text{ }m\text{ in particles}$

$0.050\text{ }m\text{ CH}_3\text{COOH} \Rightarrow \text{weak electrolyte} \Rightarrow \text{between }0.050\text{ }m\text{ and }0.10\text{ }m\text{ in particles}$

$0.10\text{ }m\text{ C}_{12}\text{H}_{22}\text{O}_{11} \Rightarrow \text{nonelectrolyte} \Rightarrow 0.10\text{ }m\text{ in particles}$

Because the freezing points depend on the total molality of particles in solution, the expected ordering is $0.15\text{ }m\text{ NaCl}$ (lowest freezing point), $0.10\text{ }m\text{ HCl}$, $0.050\text{ }m\text{ CaCl}_2$, $0.10\text{ }m\text{ C}_{12}\text{H}_{22}\text{O}_{11}$, and $0.050\text{ }m\text{ CH}_3\text{COOH}$ (highest freezing point).

Osmosis

Consider a situation in which only solvent molecules are able to pass through a membrane (**semipermeable membranes**, allowing some smaller particles to pass through, but blocking other larger particles). If such a membrane is placed between two solutions of different concentration, solvent molecules move in both directions through the membrane.

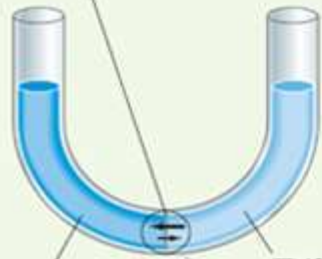
The concentration of solvent is higher in the solution containing less solute (lower solute concentration) to the more concentrated solution (higher solute concentration) is greater than the rate in the opposite direction.

Thus, there is a net movement of solvent molecules **from the less concentrated solution into the more concentrated one**. In this process, called **osmosis**, the net movement of solvent is always toward the solution with the higher solute concentration.

In biological systems, most semipermeable membranes allow water to pass through, but solutes are not free to do so.

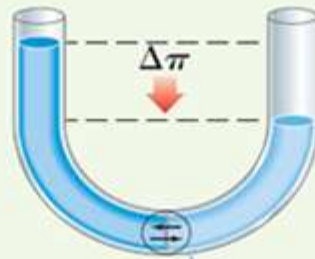


Semipermeable membrane



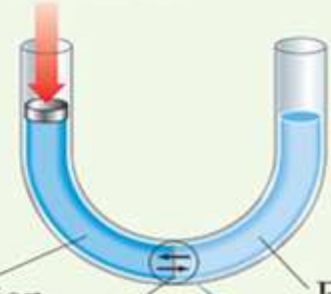
Dilute solution

Concentrated solution



$\Delta\pi$

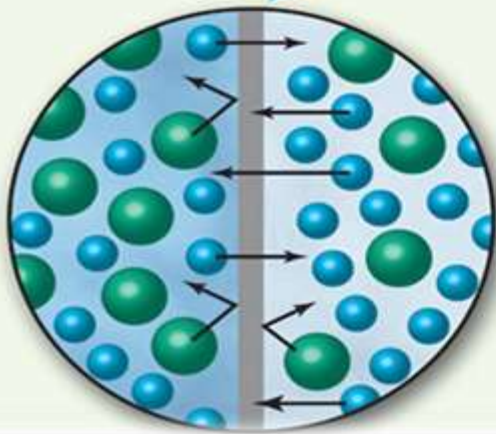
Applied pressure, π , stops net movement of solvent.



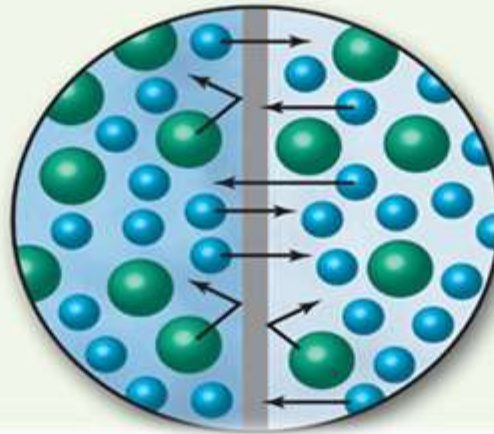
Solution

Pure solvent

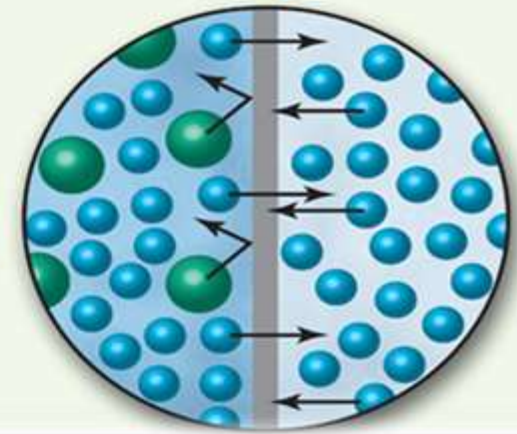
Semipermeable membrane



Net movement of solvent from the pure solvent or a solution with low solute concentration to a solution with high solute concentration.



Osmosis stops when the column of a soln on the left becomes high enough to exert sufficient pressure at the membrane to counter the net movement of solvent. At this point the soln on the left has become more dilute, but there still exists a difference in concentrations between the two solns.



Applied pressure on the left arm of the apparatus stops net movement of solvent from the right side of the semipermeable membrane. This applied pressure is the osmotic pressure of the soln.

The pressure required to stop or to prevent osmosis by pure solvent, known as **osmotic pressure**, π , of the solution.

The osmotic pressure obeys a law similar in form to the ideal gas law:

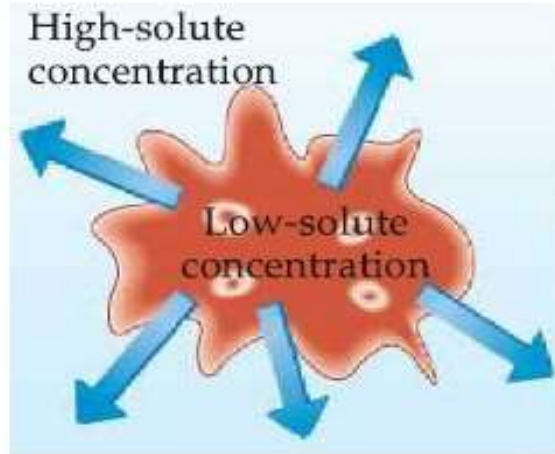
$$\Pi = \left(\frac{n}{V} \right) RT = MRT$$

Where: ***M*** is the molarity of the solution, ***V*** is the volume of the solution, ***n*** is the number of moles of solute, ***R*** is the ideal gas constant, and ***T*** is the temperature on the Kelvin scale

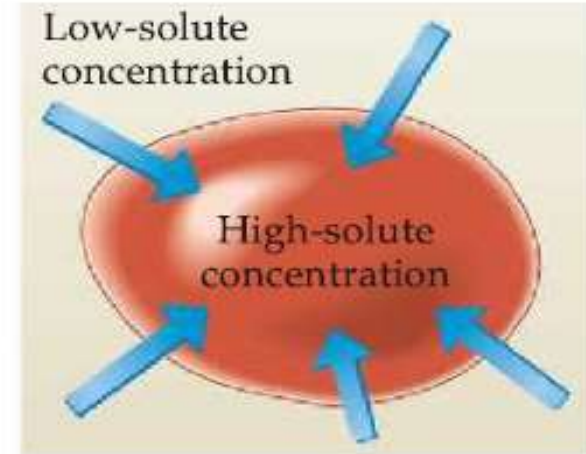
If two solutions of identical osmotic pressure are separated by a semipermeable membrane, no osmosis will occur. The two solutions are **isotonic**. If one solution is of lower osmotic pressure, it is **hypotonic** with respect to the more concentrated solution. The more concentrated solution is **hypertonic** with respect to the dilute solution.

Osmosis plays a very important role in living systems.

The membranes of red blood cells, for example, are semipermeable.



(a) Crenation



(b) Hemolysis

The blue arrows represent the net movement of water molecules.

Water will flow out of the cell, and **crenation** results (causes the cell to **shrivel**).

Water will flow into the cell, and **hemolysis** results (causes the cell to **rupture**).

Sample Exercise Calculations Involving Osmotic Pressure

The average osmotic pressure of blood is 7.7 atm at 25 ° C. What molarity of glucose (C₆H₁₂O₆) will be isotonic with blood?

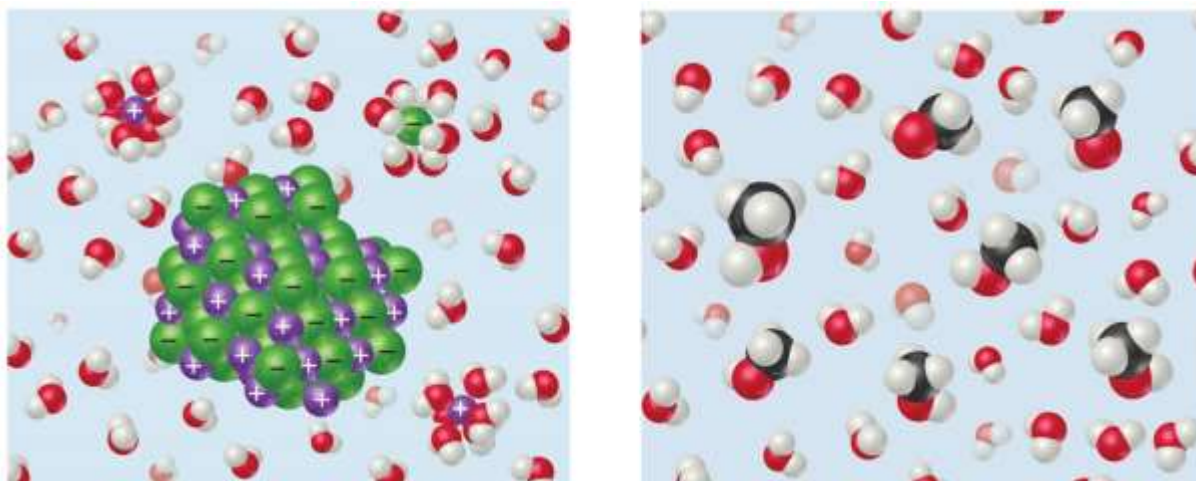
Solution

$$\begin{aligned} \Pi &= MRT \\ M &= \frac{\Pi}{RT} = \frac{7.7 \text{ atm}}{\left(0.0821 \frac{\text{L-atm}}{\text{mol-K}}\right)(298 \text{ K})} = 0.31 M \end{aligned}$$

Comment: In clinical situations the concentrations of solutions are generally expressed as mass percentages. The mass percentage of a 0.31 *M* solution of glucose is 5.3%. The concentration of NaCl that is isotonic with blood is 0.16 *M*, because NaCl ionizes to form two particles, Na⁺ and Cl⁻ (a 0.155 *M* solution of NaCl is 0.310 *M* in particles). A 0.16 *M* solution of NaCl is 0.9 mass % in NaCl. This kind of solution is known as a physiological saline solution.

Colligative Properties of Electrolytes

Since these properties depend on the number of particles dissolved, solutions of electrolytes (which dissociate in solution) should show greater changes than those of nonelectrolytes. The ideal value of i can be determined for a salt from the number of ions per formula unit.

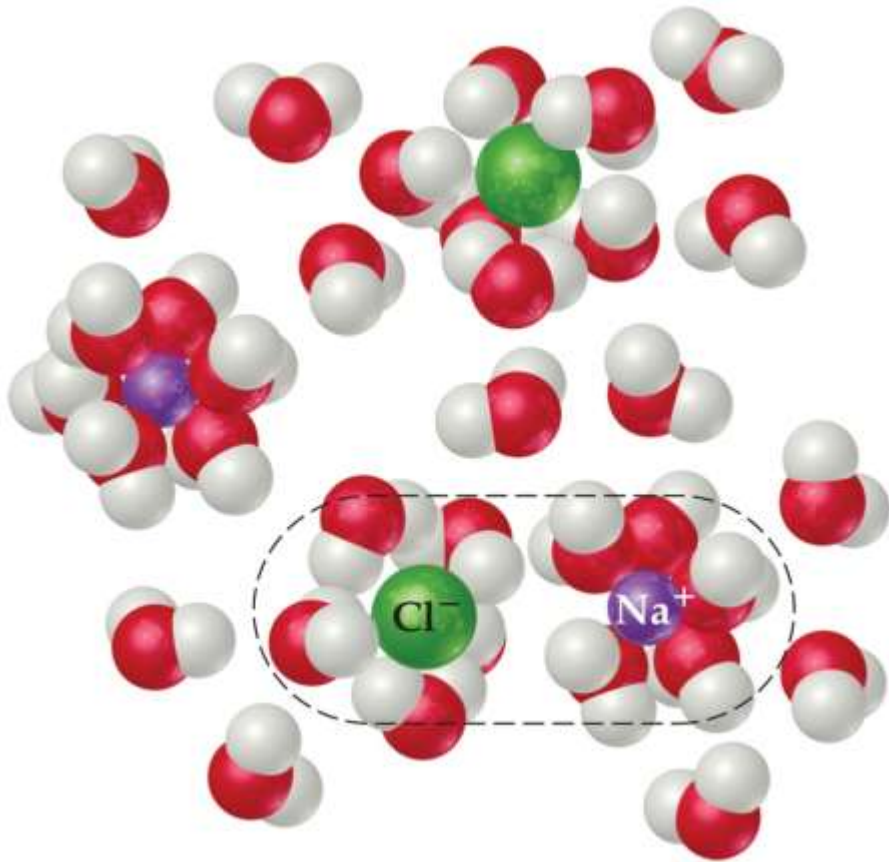


e.g. **NaCl** dissociates to form 2 ion particles; consists of one Na^+ and one Cl^- per formula unit, its limiting van't Hoff factor is 2.

For **K_2SO_4** it is 3 because it consists of two K^+ and one SO_4^{2-} .

van't Hoff Factor

One mole of NaCl in water does not really give rise to two moles of ions.



Some **Na⁺** and **Cl⁻** reassociate for a short time, so the true concentration of particles is somewhat less than two times the concentration of **NaCl**.

The difference between the expected and observed colligative properties for strong electrolytes is due to electrostatic attractions between ions.

The ions move, opposite charges collide, stick together for a brief moments. While they are together, they behave as a single particle called an **ion pair**. The number of independent particles is thereby reduced, causing a reduction in the colligative properties.

One measure of the extent to which electrolytes dissociate is the **van't Hoff factor, i** .

This factor is the ratio of the actual value of a colligative property to the value calculated when the substance is assumed to be a nonelectrolyte.

Using the freezing point depression, for example, we have

$$i = \frac{\Delta T_f(\text{measured})}{\Delta T_f(\text{calculated for nonelectrolyte})}$$

Reassociation is more likely at higher concentration.

Therefore, the number of particles present is concentration-dependent.

TABLE 13.5 ■ van't Hoff Factors for Several Substances at 25 °C

Compound	Concentration			Limiting Value
	0.100 <i>m</i>	0.0100 <i>m</i>	0.00100 <i>m</i>	
Sucrose	1.00	1.00	1.00	1.00
NaCl	1.87	1.94	1.97	2.00
K ₂ SO ₄	2.32	2.70	2.84	3.00
MgSO ₄	1.21	1.53	1.82	2.00

We modify the previous equations by multiplying by the van't Hoff factor, *i*.

i = 1 for non-electrolytes

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

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

Determination of Molar Mass from Colligative Properties

Sample Exercise Molar Mass for Freezing-Point Depression

A solution of an unknown nonvolatile nonelectrolyte was prepared by dissolving 0.250 g of the substance in 40.0 g of CCl_4 . The boiling point of the resultant solution was 0.357°C higher than that of the pure solvent. Calculate the molar mass of the solute.

Solution

From Equation 13.11 we have

Thus, the solution contains 0.0711 mol of solute per kilogram of solvent. The solution was prepared using 40.0 g = 0.0400 kg of solvent (CCl_4). The number of moles of solute in the solution is therefore

The molar mass of the solute is the number of grams per mole of the substance:

$$\text{Molality} = \frac{\Delta T_b}{K_b} = \frac{0.357^\circ\text{C}}{5.02^\circ\text{C}/m} = 0.0711\ m$$

$$(0.0400\ \text{kg CCl}_4) \left(0.0711 \frac{\text{mol solute}}{\text{kg CCl}_4} \right) = 2.84 \times 10^{-3}\ \text{mol solute}$$

$$\text{Molar mass} = \frac{0.250\ \text{g}}{2.84 \times 10^{-3}\ \text{mol}} = 88.0\ \text{g/mol}$$

Sample Exercise

The osmotic pressure of an aqueous solution of a certain protein was measured to determine the protein's molar mass. The solution contained 3.50 mg of protein dissolved in sufficient water to form 5.00 mL of solution. The osmotic pressure of the solution at 25 °C was found to be 1.54 torr. Treating the protein as a nonelectrolyte, calculate its molar mass.

Solution

Solving Equation 13.13 for molarity gives

$$\text{Molarity} = \frac{\Pi}{RT} = \frac{(1.54 \text{ torr})\left(\frac{1 \text{ atm}}{760 \text{ torr}}\right)}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(298 \text{ K})} = 8.28 \times 10^{-5} \frac{\text{mol}}{\text{L}}$$

Because the volume of the solution is 5.00 ml = 5.00×10^{-3} L, the number of moles of protein must be

$$\text{Moles} = (8.28 \times 10^{-5} \text{ mol/L})(5.00 \times 10^{-3} \text{ L}) = 4.14 \times 10^{-7} \text{ mol}$$

The molar mass is the number of grams per mole of the substance. The sample has a mass of 3.50 mg = 3.50×10^{-3} g. The molar mass is the number of grams divided by the number of moles:

$$\text{Molar mass} = \frac{\text{grams}}{\text{moles}} = \frac{3.50 \times 10^{-3} \text{ g}}{4.14 \times 10^{-7} \text{ mol}} = 8.45 \times 10^3 \text{ g/mol}$$



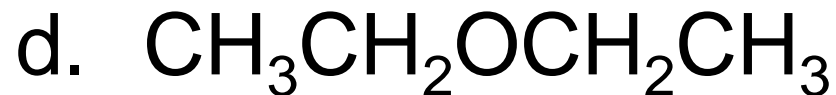
Q & A



The “like dissolves like” rule states that substances with similar _____ will dissolve in each other.

- a. molecular weights
- b. molecular shapes
- c. intermolecular attractive forces
- d. densities

Which substance below is miscible with water?



_____ Law states that the solubility of a gas in a liquid increases as the pressure of the gas above the liquid increases.

- a. Boyle's
- b. Charles'
- c. Henry's
- d. Raoult's

_____ Law states that the vapor pressure of a solution is directly proportional to the mole fraction of solvent present.

- a. Boyle's
- b. Charles'
- c. Henry's
- d. Raoult's

Which aqueous solution should have the lowest freezing point?

- a. 0.100 *m* NaCl
- b. 0.100 *m* CaCl₂
- c. 0.100 *m* KI
- d. 0.100 *m* LiNO₃

Isotonic solutions have the same:

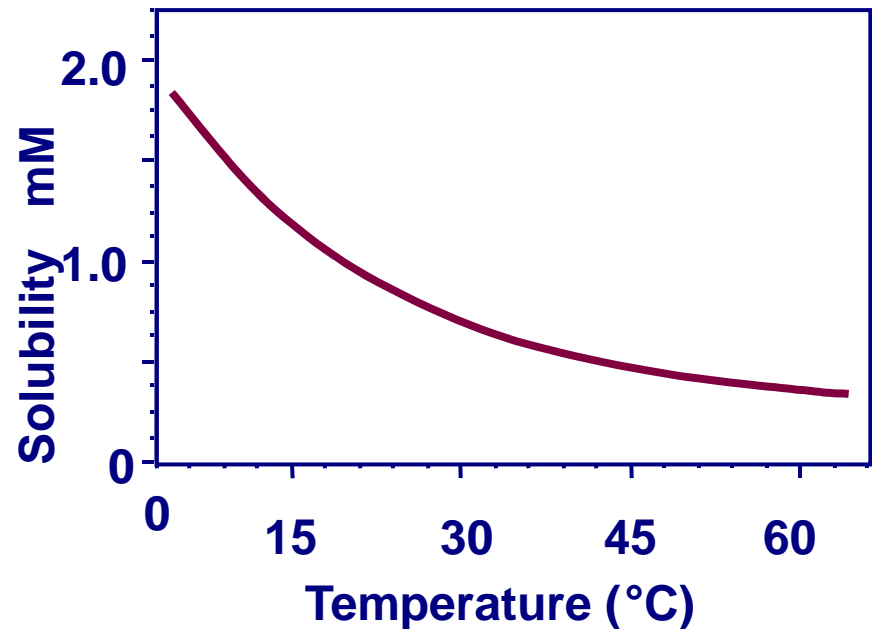
- a. density.
- b. volume.
- c. vapor pressure.
- d. osmotic pressure.

A solution contains 0.02755 g of a protein in 25.0 mL of solution. The osmotic pressure is 3.22 torr at 298 K. What is the molecular weight of the protein?

- a. 254 g/mole
- b. 6360 g/mole**
- c. 159,000 g/mole
- d. 2,340,000 g/mole

The curve describes the solubility properties of

- a liquid.
- an ionic solid.
- a covalent solid.
- a gas.
- a gas or liquid.



Considering the substances given below, predict which will be soluble in water.

- 1



1

- 2

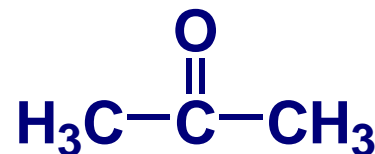
- 3

- 2, 3

- 1, 2, 3



2



3

Predict which aqueous solution will have the lowest freezing point.

- 0.25 *m* C₂H₅OH
- 0.15 *m* CaCl₂
- 0.20 *m* NaCl
- 0.15 *m* NH₄NO₃
- 0.15 *m* Na₃PO₄

Arrange the aqueous solutions according to increasing boiling point.

- $\text{AlCl}_3 < \text{KNO}_3 < \text{Na}_2\text{SO}_4$
- $\text{Na}_2\text{SO}_4 < \text{AlCl}_3 < \text{KNO}_3$
- $\text{Na}_2\text{SO}_4 < \text{KNO}_3 < \text{AlCl}_3$
- $\text{KNO}_3 < \text{AlCl}_3 < \text{Na}_2\text{SO}_4$
- $\text{KNO}_3 < \text{Na}_2\text{SO}_4 < \text{AlCl}_3$

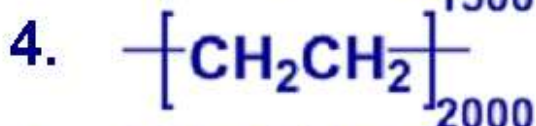
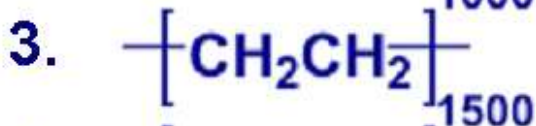
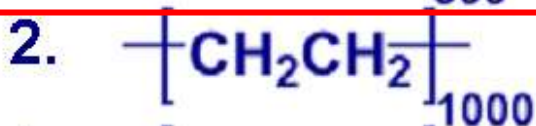
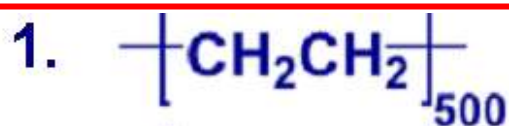
0.10 *m* Na_2SO_4

0.15 *m* AlCl_3

0.20 *m* KNO_3

Which polyethylene solution will produce the largest osmotic pressure?

Assume that all solutions use the same solvent and have the same concentration.



5. All will have the same osmotic pressure.

Calculate the concentration of CO_2 in a soft drink after the bottle is opened and equilibrates at 25°C under a CO_2 partial pressure of $3.0 \times 10^{-4} \text{ atm}$.

Answer: $9.3 \times 10^{-6} \text{ M}$

The vapor pressure of pure water at 110 °C is 1070 torr. A solution of ethylene glycol and water has a vapor pressure of 1.00 atm at 110 °C. Assuming that Raoult's law is obeyed, what is the mole fraction of ethylene glycol in the solution?

Answer: 0.290

Calculate the freezing point of a solution containing 0.600 kg of CHCl_3 and 42.0 g of eucalyptol ($\text{C}_{10}\text{H}_{18}\text{O}$), a fragrant substance found in the leaves of eucalyptus trees. (See Table 13.4.)

Answer: $-65.6\text{ }^{\circ}\text{C}$

Which of the following solutes will produce the largest increase in boiling point upon addition to 1 kg of water: 1 mol of $\text{Co}(\text{NO}_3)_2$, 2 mol of KCl , 3 mol of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$)?

Answer: 2 mol of KCl because it contains the highest concentration of particles, 2 m K^+ and 2 m Cl^- , giving 4 m in all

What is the osmotic pressure at 20 °C of a 0.0020 *M* sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) solution?

Answer: 0.048 atm, or 37 torr

Camphor ($\text{C}_{10}\text{H}_{16}\text{O}$) melts at $179.8\text{ }^{\circ}\text{C}$, and it has a particularly large freezing-point-depression constant, $K_f = 40.0\text{ }^{\circ}\text{C}/\text{m}$. When 0.186 g of an organic substance of unknown molar mass is dissolved in 22.01 g of liquid camphor, the freezing point of the mixture is found to be $176.7\text{ }^{\circ}\text{C}$. What is the molar mass of the solute?

Answer: 110 g/mol

A sample of 2.05 g of polystyrene of uniform polymer chain length was dissolved in enough toluene to form 0.100 L of solution. The osmotic pressure of this solution was found to be 1.21 kPa at 25 °C. Calculate the molar mass of the polystyrene.

Answer: $4.20 \times 10^4 \text{ g/mol}$.

