Chapter 13 Properties of Solutions



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.
- The ability of substances to form solutions depends on
- > natural tendency toward mixing.
- ➢ intermolecular forces.

Natural Tendency toward Mixing

- Mixing of gases is a spontaneous process.
- Each gas acts as if it is alone to fill the container.
- Mixing causes more randomness in the position of the molecules, increasing a thermodynamic quantity called *entropy*.
- The formation of solutions is favored by the increase in entropy that accompanies mixing.



In the chapter-opening photograph of dye dispersing in water, is entropy increasing or decreasing?

- a. Entropy increasing
- b. Entropy decreasing

What aspect of the kinetic theory of gas

tells us that the gases will mix?

- a. The gas molecules experience perfectly elastic collisions.
- b. The gas molecules experience no intermolecular forces.
- c. The gas molecules move constantly and randomly.
- d. The two types of molecules, Ar and O₂ are attracted to each other.



Intermolecular Forces of Attraction



Any intermolecular force of attraction (Chapter 11) can be the attraction between solute and solvent molecules.

Why does the oxygen atom in H_2O point toward Na⁺ in the ion-dipole interaction? Ion-dipole Dispersion Dipole-dipole Hydrogen bond Chloroform Acetone Ethanol Water (C_3H_6O) (CHCl₃) (C_2H_5OH) (H_2O) Heptane Pentane

a. The electron-poor O atom in O—H bond dipole in H₂O is attracted to Na⁺ ion by electrostatic attraction.

 (C_7H_{16})

 (C_5H_{12})

- b. The electron-poor H atom in O—H bond dipole in H_2O is attracted to Na⁺ ion by electrostatic attraction.
- c. The electron-rich O atom in O—H bond dipole in H₂O is attracted to Na⁺ ion by electrostatic attraction.
- d. The electron-rich H atom in O—H bond dipole in H_2O is attracted to Na⁺ ion by electrostatic attraction.

Attractions Involved When Forming a Solution



 Solute-solute interactions must be overcome to disperse these particles when making a solution.

 Solvent-solvent interactions must be overcome to make room for the solute.

 Solvent—solute interactions occur as the particles mix. Why doesn't NaCl dissolve in nonpolar solvents such as hexane, C_6H_{14} ?

- a. NaCl is a polar covalent molecule and a solvent dissolves solutes that have similar intermolecular forces as the solvent.
- b. NaCl is a neutral substance and is not attracted to nonpolar hexane.
- c. NaCl is ionic and ion-ion forces in the lattice are not broken by ion-nonpolar interactions.
- d. NaCl has large ions that are hard to separate and dissolve in any solvent.

Energetics of Solution Formation

Solvent-solute interactions between water molecules and



Hydrated Cl⁻ ion

Hydrated Na⁺ ion

How does the orientation of H_2O molecules around Na⁺ differ from that around Cl⁻?



- a. The H atom of a water molecule points toward a Na⁺ ion, and the O atom of a water molecule points toward the Cl⁻ ion.
- b. The H atom of a water molecule points toward a Cl⁻ ion, and the O atom of a water molecule points toward the Na⁺ ion.





- For a reaction to occur, ΔH_{mix} must be close to the sum of ΔH_{solute} and $\Delta H_{solvent}$.
- Remember that the randomness from entropy will affect the process, too.

How does the magnitude of ΔH_{mix} compare with the magnitude of $\Delta H_{solute} + \Delta H_{solvent}$ for exothermic solution processes?

- a. Larger
- b. Almost the same
- c. Smaller



Label the following processes as exothermic or endothermic:

(a)breaking solvent-solvent interactions to form separated particles
(b)forming solvent-solute interactions from separated particles

(a)(b)

- a. EndothermicEndothermic
- b. EndothermicExothermic
- c. ExothermicEndothermic
- d. ExothermicExothermic

Aqueous Solution vs. Chemical Reaction





Nickel metal and hydrochloric acid

Nickel reacts with hydrochloric acid, forming NiCl₂(*aq*) and H₂(*g*). The solution is of NiCl₂, not Ni metal

 $NiCl_2 \cdot 6 H_2O(s)$ remains when solvent evaporated

Just because a substance disappears when it comes in contact with a solvent, it does not mean the substance dissolved. It may have reacted, like nickel with hydrochloric acid.



What is the molar mass of nickel chloride hexahydrate, NiCl₂ · $\mathbb{ZP}_{\mathbb{P}}$ **T** • \mathbb{DZ}

a. 58.69 g/mol
b. 129.37 g/mol
c. 147.37 g/mol
d. 237.42 g/mol



Nickel metal and hydrochloric acid



Nickel reacts with hydrochloric acid, forming NiCl₂(*aq*) and H₂(*g*). The solution is of NiCl₂, not Ni metal



NiCl₂·6 H₂O(s) remains when solvent evaporated

13.2 Saturated Solutions and Solubility



Opposing Processes

 The solution-making process and crystallization are opposing processes.

Solute + solvent $\underset{\text{crystallize}}{\overset{\text{dissolve}}{\underset{\text{crystallize}}}}$ solution

- When the rate of the opposing processes is equal, additional solute will not dissolve unless some crystallizes from solution. This is a saturated solution.
- If we have not yet reached the amount that will result in crystallization, we have an unsaturated solution.



Solubility



- Solubility is the maximum amount of solute that can dissolve in a given amount of solvent at a given temperature.
- Saturated solutions have that amount of solute dissolved.
- Unsaturated solutions have any amount of solute *less* than the maximum amount dissolved in solution.
- Surprisingly, there is one more type of solution.



Supersaturated Solutions



- In supersaturated solutions, the solvent holds more solute than is normally possible at that temperature.
- These solutions are unstable; crystallization can usually be stimulated by adding a "seed crystal" or scratching the side of the flask.
- These are uncommon solutions.

What happens if a solute is added to a saturated solution?

- a. More solute dissolves.
- b. The additional solute does not dissolve and some of the original dissolved solute comes out of the solution.
- c. The additional solute does not dissolve and the solution remains saturated.
- d. The temperature of the solution changes and some of the added solute dissolves.

What is the evidence that the solution in the left photograph is supersaturated?

a. The solution is clear.

Amount of sodium acetate dissolved is greater than its

 b. There would be no crystallization after adding a seed crystal without the solution being supersaturated.



13.3 Factors Affecting Solubility



Factors That Affect Solubility

Solute—solvent Interactions

Pressure (for gaseous solutes)

Temperature



Solute–Solvent Interactions

- Simply put: "Like dissolves like."
- That does not explain everything!
- The *stronger* the solute–solvent interaction, the *greater* the solubility of a solute in that solvent.
- The gases in the table only exhibit dispersion force. The larger the gas, the more soluble it will be in water.

Table 13.1Solubilities of Gasesn Water at 20 °C, with 1 atm Ga		
Gas	Molar Mass (g/mol)	Solubility (M)
N ₂	28.0	0.69×10^{-3}
0 ₂	32.0	1.38×10^{-3}
Ar	39.9	1.50×10^{-3}
Kr	83.8	2.79×10^{-3}



Organic Molecules in Water

- Polar organic molecules dissolve in water better than nonpolar organic molecules.
- Hydrogen bonding increases solubility, since C–C and C–H bonds are not very polar.







Liquid/Liquid Solubility

- Liquids that mix in all proportions are miscible.
- Liquids that do *not* mix in one another are **immiscible**.
- Because hexane is nonpolar and water is polar, they are immiscible.



Solubility and Biological Importance

- Fat-soluble vitamins (like vitamin A) are nonpolar; they are readily stored in fatty tissue in the body.
- Water-soluble vitamins (like vitamin C) need to be included in the daily diet.



Suppose the hydrogens on the OH groups in glucose (Figure 13.10) were replaced with methyl groups, CH_3 . Would you expect the water solubility of the resulting molecule to be higher than, lower than, or about the same as glucose?

- a. Higher solubility
- b. Lower solubility
- c. About the same solubility





Sample Exercise 13.1 Predicting Solubility Patterns Predict whether each of the following substances is more likely to dissolve in the nonpolar solvent carbon tetrachloride (CCl₄) or in water: C₇H₁₆, Na₂SO₄, HCl, and I₂.



Practice Exercise 1

Which of the following solvents will best dissolve wax, which is a complex mixture of compounds that mostly are CH_3 – CH_2 –





Practice Exercise 2

r

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







Pressure Effects

- The solubility of solids and liquids are *not* appreciably affected by pressure.
- Gas solubility is affected by pressure.



Henry's Law

 The solubility of a gas is proportional to the partial pressure of the gas above the solution.

$$S_{\rm g} = kP_{\rm g}$$



Equilibrium



Pressure is increased. More CO₂ dissolves



Equilibrium restored



If the partial pressure of a gas over a solution is doubled, how has the concentration of gas in the solution changed after equilibrium is restored?

- a. Concentration of gas in the solution does not change.
- b. Concentration of gas in the solution decreases by a factor of one-half.
- c. Concentration of gas in the solution increases by a factor of two.
- d. Concentration of gas in the solution increases by a factor of four.



Equilibrium

Pressure is increased. More CO₂ dissolves

Equilibrium restored
How do the slopes of the lines vary with the molecular weight of the gas? Explain the trend.

- a. The slopes increase linearly as the molecular weights increase. Increasing molecular mass leads to greater polarizability of the gas molecules and greater intermolecular attractions between gas and water molecules.
- b. The slopes exponentially increase as the molecular weights increase. Increasing molecular mass leads to greater polarizability of the gas molecules and greater intermolecular attractions between gas and water molecules.
- c. The slopes increase linearly as the molecular weights decrease. Decreasing molecular mass leads to greater polarizability of the gas molecules and greater intermolecular attractions between gas and water molecules.
- d. The slopes exponentially decrease as the molecular weights decrease. Decreasing molecular mass leads to greater polarizability of the gas molecules and greater intermolecular attractions between gas and water molecules.





Practice Exercise 1

You double the partial pressure of a gas over a liquid at constant temperature. Which of these statements is then true?



- (a) The Henry's law constant is doubled.
- (b) The Henry's law constant is decreased by half.(c) There are half as many gas molecules in the liquid.
- (d) There are twice as many gas molecules in the liquid.
- (e) There is no change in the number of gas molecules in the liquid.





Temperature Effects



 For most solids, as temperature increases, solubility increases. However, clearly this is not always true—some increase greatly, some remain relatively constant, and others decrease.

 For *all* gases, as temperature increases, solubility decreases.
Cold rivers have higher oxygen content than warm rivers. Why do bubbles form on the inside wall of a cooking pot when water is heated on the stove, even though the water temperature is well below the boiling point of water?



- a. Some water molecules break down into gases as water is heated.
- b. Dissolved gases are less soluble in solution as temperature increases.
- c. Water molecules begin to enter the gas phase to stimulate boiling.
- d. Boiling actually begins on a small scale at temperatures below the boiling point.

How does the solubility of KCl at 80 °C compare with that of NaCl at the same temperature?

- a. NaCl is more soluble.
- b. KCl is more soluble.
- c. NaCl and KCl have about the same solubility.





- b. Just below O₂ and above CO
- c. Just below CO and above He
- d. Just below He



13.4 Expressing Solution Concentration



Solution Concentration



 We have discussed solubility and solutions qualitatively: saturated (which is quantitative), unsaturated, and supersaturated.

Now we will give specific amounts to solutions.

Units of Concentration

- 1) Mass percentage
- 2) Parts per million (ppm)
- 3) Parts per billion (ppb)
- 4) Mole fraction
- 5) Molarity
- 6) Molality



1) Mass Percentage



- Percent means "out of 100."
- Take the ratio of the mass of the solute to the total solution mass.
- Multiply by 100 to make it a percent.

Mass % of component = $\frac{\text{mass of component in soln}}{\text{total mass of soln}} \times 100$

Parts per Million (ppm) Parts per Billion (ppb)

- still relating mass of a solute to the total mass of the solution
- Since percent is out of 100, we multiplied by 100.
- ppm is per million, so we multiply by 10⁶.

ppm of component = $\frac{\text{mass of component in soln}}{\text{total mass of soln}} \times 10^6$

ppb is per billion, so we multiply by 10⁹.

Sample Exercise 13.3

(a) A solution is made by dissolving 13.5 g of glucose $(C_6H_{12}O_6)$ in 0.100 kg of water. What is the mass percentage of solute in this solution?



Practice Exercise 1

Calculate the mass percentage of NaCl in a solution containing 1.50 g of NaCl in 50.0 g of water. (a) 0.0291% **(b)** 0.0300% (c) 0.0513% (d) 2.91% **(e)** 3.00%.



Practice Exercise 2



A commercial bleaching solution contains 3.62% by mass of sodium hypochlorite, NaOCI. What is the mass of NaOCI in a bottle containing 2.50 kg of bleaching solution?

(4) Mole Fraction (χ)



- Mole fraction is the ratio of moles of a substance to the total number of moles in a solution.
- It does not matter if it is for a solute or for a solvent.

Mole fraction of component = $\frac{\text{moles of component}}{\text{total moles of all components}}$

(5) Molarity (M)(6) Molality (m)



• Be careful of your penmanship!

 Molarity was discussed in Chapter 4 as moles of solute per liter of solution.

Molarity =
$$\frac{\text{moles of solu}}{\text{liters of solu}}$$

Molality is moles of solute per kilogram of solvent.

 $Molality = \frac{moles \text{ of solute}}{kilograms \text{ of solvent}}$

Molarity vs. Molality



- When water is the solvent, dilute solutions have similar molarity and molality.
- Molality does not vary with temperature (mass does not change).
- Molarity varies with temperature (volume changes).

If an aqueous solution is very dilute, will its molality be greater than its molarity, nearly the same as its molarity, or smaller than its molarity?

- a. Molality will be greater than its molarity.
- b. Molality will be nearly the same as its molarity.
- c. Molality will be smaller than its molarity.

Converting Units



- Follow dimensional analysis techniques from Chapter 1.
- To convert between molality and molarity, the density of the *solution* must be used.

Sample Exercise 13.5 Calculation of Mole Fraction and Molality

An aqueous solution of hydrochloric acid contains 36% HCl by mass. (a) Calculate the mole fraction of HCl in the solution. (b) Calculate the molality of HCl in the solution.

Sample Exercise 13.7

A solution with a density of 0.876 g/mL contains 5.0 g of toluene (C₇H₈) and 225 g of benzene. Calculate the molarity of the solution.



Practice Exercise 1

Maple syrup has a density of 1.325 g/mL, and 100.00 g of maple syrup contains 67 mg of calcium in the form of Ca²⁺ ions. What is the molarity of calcium in maple syrup? (a) 0.017 M **(b)** 0.022 M (c) 0.89 M (d) 12.6 M (e) 45.4 M

Practice Exercise 2



A solution containing equal masses of glycerol ($C_3H_8O_3$) and water has a density of 1.10 g/mL. Calculate:

- A) The molality of glycerol
- B) The mole fraction of glycerol
- C) The molarity of glycerol in the solution

13.5 Colligative Properties



Colligative Properties



- Colligative properties depend only on the *quantity*, not on the *identity* of the solute particles.
- Among colligative properties are:
 - Vapor-pressure lowering
 - Boiling-point elevation
 - Freezing-point depression
 - Osmotic pressure

Vapor Pressure



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.



Nonvolatile solute particles

Add

solute



Equilibrium



Rate of vaporization reduced by presence of nonvolatile solute



Equilibrium reestablished with fewer molecules in gas phase

Raoult's Law



The vapor pressure of a volatile solvent over the solution is the product of the mole fraction of the solvent times the vapor pressure of the pure solvent.

$$P_{\rm solution} = X_{\rm solvent} P_{\rm solvent}^{\circ}$$

 In ideal solutions, it is assumed that each substance will follow Raoult's Law. Adding 1 mol of NaCl to 1 kg of water lowers the vapor pressure of water more than adding 1 mol of $C_6H_{12}O_6$. Explain.

- a. NaCl is highly polar whereas $C_6H_{12}O_6$ is weakly polar and this causes the difference.
- b. NaCl has a smaller molar mass than that of $C_6H_{12}O_6$ and this causes the difference.
- c. NaCl is polar whereas $C_6H_{12}O_6$ is nonpolar and this causes the difference.
- d. The total solute concentration of NaCl is twice that of C₆H₁₂O₆ because NaCl forms Na⁺ and Cl⁻ ions and this causes the difference.

Boiling-Point Elevation



Since vapor pressures are lowered for solutions, it requires a higher temperature to reach atmospheric pressure. Hence, boiling point is raised.



Freezing-Point Depression

The construction of the phase diagram for a solution demonstrates that the freezing point is lowered while the boiling point is raised.





Boiling-Point Elevation and Freezing-Point Depression



 The change in temperature is directly proportional to molality (using the van't Hoff factor).

$$\Delta T_b = T_b$$
(solution) – T_b (solvent) = iK_bm

 $\Delta T_{\rm f} = T_{\rm f}$ (solution) $- T_{\rm f}$ (solvent) $= -iK_{\rm f}m$

Table 13.3	Molal Boiling-Point-Elevation	and Freezing-Point-Depression Constants
------------	-------------------------------	---

	Normal Boiling	Normal Freezing		
Solvent	Point (°C)	$\mathbf{K}_{\mathbf{b}}(^{\circ}\mathbf{C}/m)$	Point (°C)	$\mathbf{K}_{f}(^{\circ}\mathbf{C}/\mathbf{m})$
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

The van't Hoff Factor (i)

- What is the van't Hoff factor?
- It takes into account dissociation in solution!
- Theoretically, we get 2 particles when NaCl dissociates. So, *i* = 2.
- In fact, the amount that particles remain together is dependent on the concentration of the solution.

	Concentration			
Compound	0.100 m	0.0100 m	0.00100 m	Expected Value
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

Table 13.4 Measured and Expected van't Hoff Factors for Several Substances at 25 °C



Practice Exercise 1

Which aqueous solution will have the lowest freezing point? (a) $0.050 m CaCl_2$ (b) 0.15 *m* NaCl (c) 0.10 *m* HCl (d) 0.050 *m* CH₃COOH (e) $0.20 m C_{12}H_{22}O_{11}$



Osmosis

- Some substances form semipermeable membranes, allowing some smaller particles to pass through, but blocking larger particles.
- The net movement of solvent molecules from solution of low to high concentration across a semipermeable membrane is **osmosis**. The applied pressure to stop it is **osmotic pressure**.



If the pure water in the left arm of the U-tube is replaced by a solution more concentrated than the one in the right arm, what will happen?

- a. Nothing
- b. Water flows through the semipermeable membrane from the more dilute solution to the more concentrated solution, and the liquid level in the left arm rises.
- c. Water flows through the semipermeable membrane from the more concentrated solution to the more dilute solution, and the liquid level in the right arm rises.



Types of Solutions & Osmosis



- Isotonic solutions: Same osmotic pressure; solvent passes the membrane at the same rate both ways.
- Hypotonic solution: Lower osmotic pressure; solvent will leave this solution at a higher rate than it enters with.
- Hypertonic solution: Higher osmotic pressure; solvent will enter this solution at a higher rate than it leaves with.
Of two KBr solutions, one 0.50 m and the other 0.20 m, which is hypotonic with respect to the other?

- a. The 0.20 *m* KCl solution is hypotonic with the 0.50 *m* KCl solution.
- b. The 0.50 *m* KCl solution is hypotonic with the 0.20 *m* KCl solution.
- c. Neither is hypotonic to each other.
- d. They are isotonic solutions.

Osmosis and Blood Cells



- Red blood cells have semipermeable membranes.
- If stored in a hypertonic solution, they will shrivel as water leaves the cell; this is called crenation.
- If stored in a hypertonic solution, they will grow until they burst; this is called **hemolysis**.



If the fluid surrounding a patient's red blood cells is depleted in electrolytes, is crenation or hemolysis more likely to occur?

- a. Crenation, because fluid moves from the external fluids into the blood cells.
- b. Crenation, because fluid moves from the blood cells to the external fluids.
- c. Hemolysis, because fluid moves from the external fluids into the blood cells.
- d. Hemolysis, because fluid moves from the blood cells into the external fluids.

neither swells nor shrinks.



in hypertonic environment

in hypotonic environment

Is the osmotic pressure of a 0.10 M solution of NaCl greater than, less than, or equal to that of a 0.10 M solution of KBr?



- a. The osmotic pressure of a 0.10 *M* solution of NaCl is greater than that of a 0.10 *M* solution of KBr.
- b. The osmotic pressure of a 0.10 *M* solution of NaCl is equal to that of a 0.10 *M* solution of KBr.
- c. The osmotic pressure of a 0.10 *M* solution of NaCl is less than than that of a 0.10 *M* solution of KBr.

13.6 Colloids



Colloids



Suspensions of particles larger than individual ions or molecules, but too small to be settled out by gravity, are called **colloids**.

Table 13.5	Types of Colloids			
Phase of Colloid	Dispersing (solvent-like) Substance	Dispersed (solute-like) Substance	Colloid Type	Example
Gas	Gas	Gas	—	None (all are solutions)
Gas	Gas	Liquid	Aerosol	Fog
Gas	Gas	Solid	Aerosol	Smoke
Liquid	Liquid	Gas	Foam	Whipped cream
Liquid	Liquid	Liquid	Emulsion	Milk
Liquid	Liquid	Solid	Sol	Paint
Solid	Solid	Gas	Solid foam	Marshmallow
Solid	Solid	Liquid	Solid emulsion	Butter
Solid	Solid	Solid	Solid sol	Ruby glass

Tyndall Effect





- Colloidal suspensions can scatter rays of light. (Solutions do not.)
- This phenomenon is known as the Tyndall effect.

Colloids and Biomolecules



Some molecules have a polar, **hydrophilic** (*water-loving*) end and a nonpolar, **hydrophobic** (*water-fearing*) end. Hydrophilic polar and charged groups on molecule surface help molecule remain dispersed in water and other polar solvents



Stabilizing Colloids by Adsorption



- lons can adhere to the surface of an otherwise hydrophobic colloid.
- This allows it to interact with aqueous solution.



Colloids in Biological Systems

- Colloids can aid in the emulsification of fats and oils in aqueous solutions.
- An emulsifier causes something that normally does *not* dissolve in a solvent to do so.



Which kind of intermolecular force attracts the stearate ion to the oil drop?

- a. Ion-dipole forces [hydrophilic end of stearate ion to polar oil drop]
- b. Dipole--induced dipole forces [hydrophobic end of stearate ion to nonpolar oil drop]
- c. Dipole-dipole forces [hydrophilic end of stearate ion to polar oil drop]
- d. Dispersion forces [hydrophobic end of stearate ion to nonpolar oil drop]



Brownian Motion



Motion of colloids due to numerous collisions with the much smaller solvent.

Table 13.6 Calculated Mean Free Path, after One Hour, for Uncharged Colloidal Spheres in Water at 20 °C

Radius of sphere, nm	Mean Free Path, mm		
1	1.23		
10	0.390		
100	0.123		
1000	0.039		