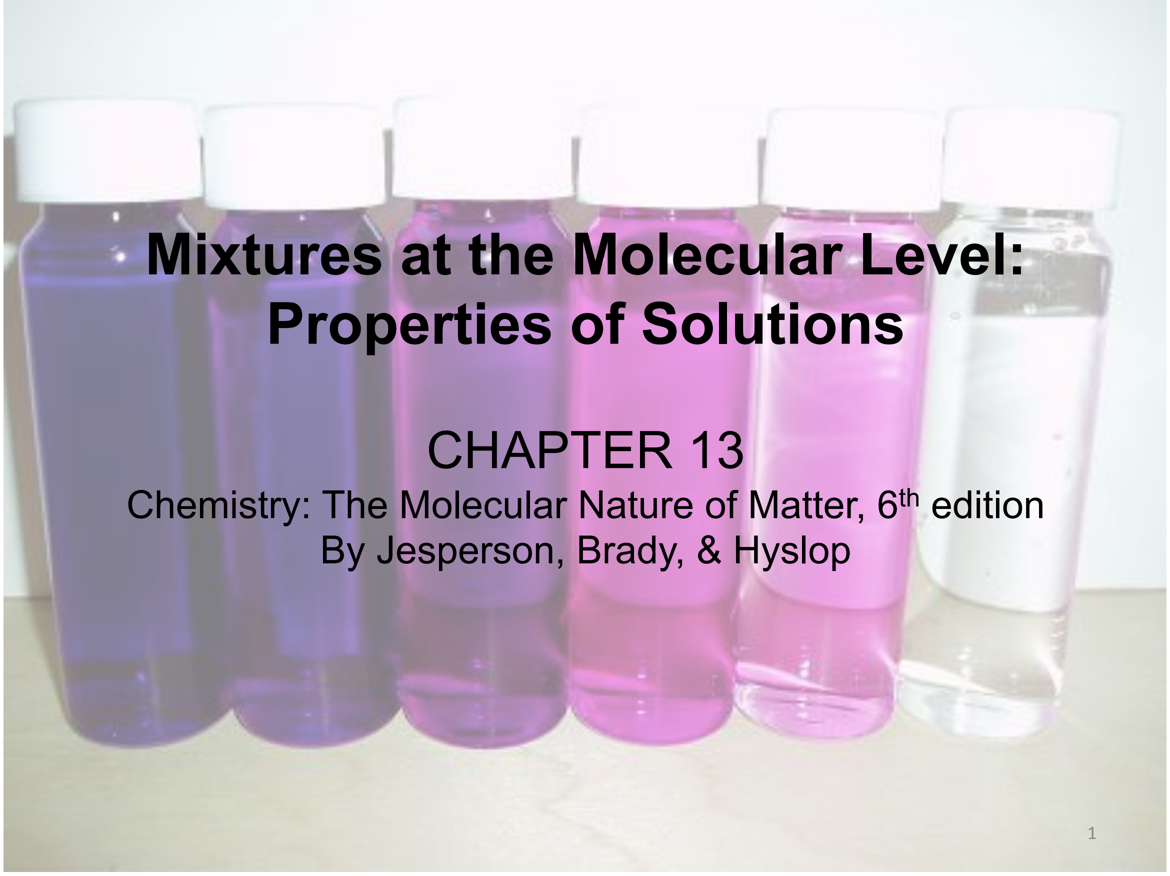


Mixtures at the Molecular Level: Properties of Solutions

CHAPTER 13

Chemistry: The Molecular Nature of Matter, 6th edition
By Jesperson, Brady, & Hyslop

CHAPTER 13 Properties of Solutions

- ☐ Describe the formation of solutions for solids, liquids, and gases
  - ☐ Intermolecular forces
  - ☐ Changes in Energy
  - ☐ Temperature Effect
- ☐ Understand and apply Henry's law
- ☐ Convert between solution concentrations with different units & between molarity and molality
- ☐ Describe colligative properties
- ☐ Describe osmosis
- ☐ Describe characteristics of suspensions and colloids

CHAPTER 13 Properties of Solutions

Lecture Road Map:

① Formation of Solutions
② Heats of Solutions
③ Solubility
④ Concentration
⑤ Colligative Properties
⑥ Osmosis

CHAPTER 13 Properties of Solutions

Formation of Solutions

Solution

- Homogeneous mixture
- Composed of solvent and solute(s)

Solvent

- More abundant component of mixture

Solute(s)

- Less abundant or other component(s) of mixture

e.g. Lactated Ringer's solution

- $NaCl$, KCl, $CaCl_2$, $NaC_3H_5O_3$ in water

Why do Solutions Form?

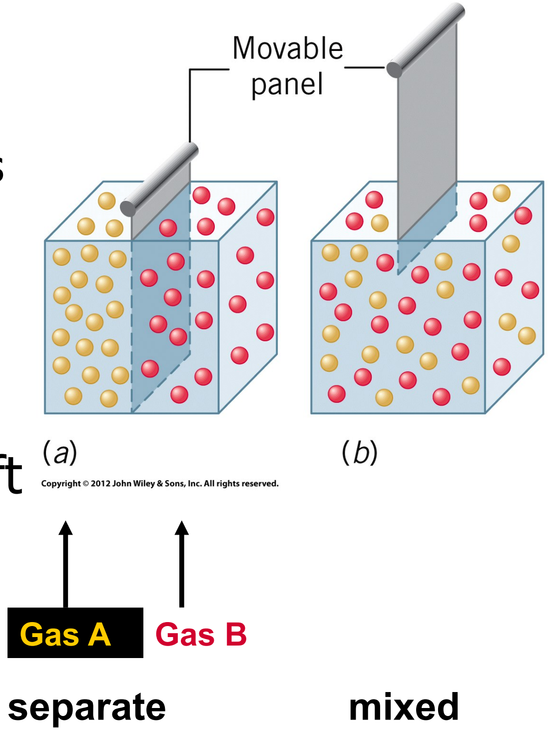
Two driving forces behind formation of solution

1. Disordering (ie, Entropy)
2. Intermolecular Forces

Whether or not a solution forms depends on both opposing forces

Spontaneous Mixing

- Two gases mix spontaneously
  - Due to random motions
  - Mix without outside work
  - Never separate spontaneously
- Tendency of system left to itself, to become increasingly disordered



Intermolecular Forces

- Attractive forces between molecules in pure substances (solvents and solutes) were considered in the last chapter
- Now we consider the attractive forces between a solvent molecule and a solute molecule
- Strength of intermolecular attractive forces in a mixture, compared to the pure substances, will indicate if a mixture can form or if the substances will remain separate

Formation of Solutions Depends on Intermolecular Forces

- When mixed, for a solution to form,
  - Solvent-to-solute attractions must be similar to attractions between solute alone and solvent alone
- Initially solute and solvent separate to make room for each other
  - Solute molecules held together by intermolecular forces: energy added
  - Solvent molecules held together by intermolecular forces: energy added

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Formation of Solutions Depends on Intermolecular Forces

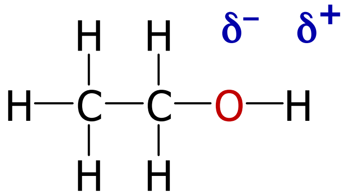
- When the separated solute and solvent are mixed to make a solution
  - Solute molecules are attracted to solvent molecules: energy released
  - Solvent molecules are attracted to solute molecules: energy released
- If there is a net release of energy, the solution will form.

Miscible Liquids

Miscible liquids

- Two liquids that dissolve in one another in all proportions
- Form solution
- Strengths of intermolecular attractions are similar in solute and solvent
- Similar polarity

e.g. Ethanol and water

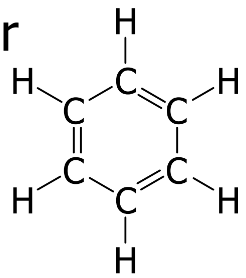


Ethanol;
polar bond

Immiscible Liquids

- Two insoluble liquids
- Do not mix
- Get two separate phases
- Strengths of intermolecular forces are different in solute and solvent
- Different polarity

e.g. Benzene and water



Benzene;
no polar bond

Rule of Thumb

- Like dissolves like
  - Use polar solvent for polar solute
  - Use nonpolar solvent for nonpolar solute
- When strengths of intermolecular attractions are similar in solute and solvent, solutions form because net energy exchange is about the same

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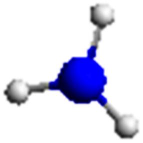
Group Problem

Which of the following are miscible in water?

water

acetic acid

carbon disulfide



ammonia

Group Problem

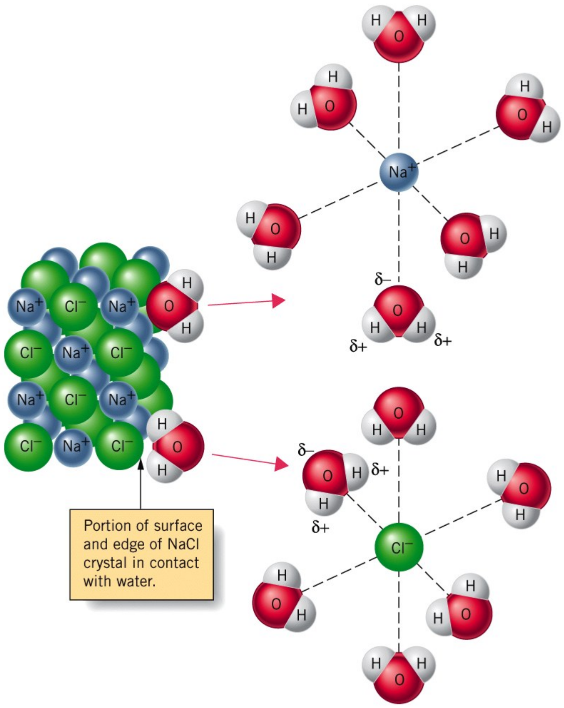
Which of the following molecules is most soluble in hexane, C_6H_{14}?

A. NH_3
B. CH_3NH_2
C. CH_3OH
D. CH_3CH_3
E. H_2O

Solutions of Solids in Liquids

- Basic principles remain the same when solutes are solids
- Sodium chloride (NaCl)
  - Ionic bonding
  - Strong intermolecular forces
  - Ions dissolve in water because ion-dipole forces of water with ions strong enough to overcome ion-ion attractions

Hydration of Solid Solute



Portion of surface and edge of NaCl crystal in contact with water.

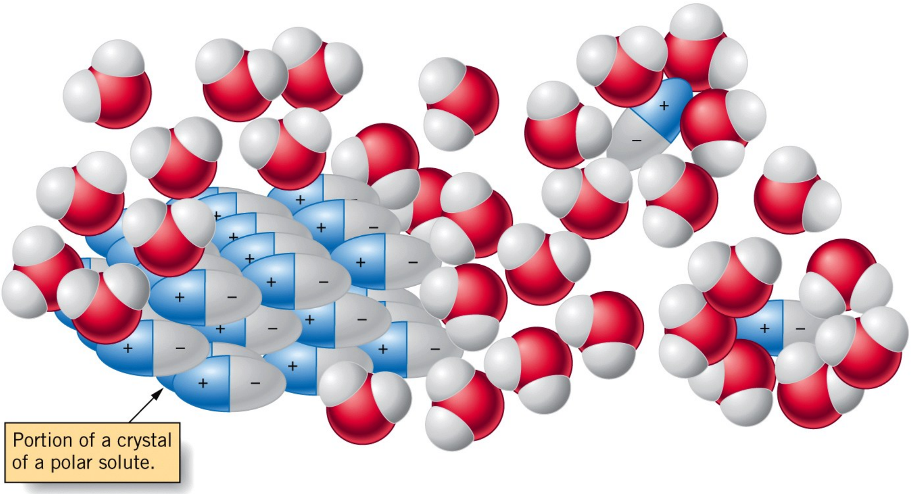
- Ions at edges, fewer ion-ion attractions
  - Multiple ion-dipole attractions formed with water
  - These overcome stronger ion-ion electrostatic attractions
- New ion at surface
  - Process continues until all ions in solution
- **Hydration of ions**
  - Completely surrounded by solvent

Hydration vs. Solvation

- **Hydration**
  - Ions surrounded by water molecules
- **Solvation**
  - General term for surrounding solute particle by solvent molecules

Polar Molecules Dissolve in Water

- H_2O reorients so
  - Positive H atoms are near negative ends of solute
  - Negative O atoms are near positive ends of solute



Solvation in Nonpolar Solvents?

- Wax is a mixture of long chain alkanes and is nonpolar
- Benzene is a nonpolar solvent
- Benzene can dissolve waxes
  - Weak London dispersion forces in both solute and solvent. Weak London forces will form between solute and solvent.
  - Wax molecules
    - Easily slip from solid
    - Slide between benzene molecules
    - Form new London forces between solvent and solute

CHAPTER 13 Properties of Solutions

Heats of Solutions

Heat of Solution

- Energy change associated with formation of solution
  - Difference in intermolecular forces between isolated solute and solvent and mixture
  - Cost of mixing
  - Energy exchanged between system and surroundings

Molar Enthalpy of Solution (ΔH_{soln})

  - Amount of enthalpy exchanged when one mole of solute dissolves in a solvent at constant pressure to make a solution

Heat of Solution

- **$\Delta H_{\text{soln}} > 0$ (positive)**
  - Costs energy to make solution
  - Endothermic
  - Increase in potential energy of system
- **$\Delta H_{\text{soln}} < 0$ (negative)**
  - Energy given off when solution is made
  - Exothermic
  - Decrease in potential energy of system
- Which occurs depends on your system

Modeling Formation of Solution

Formation of solution from solid and liquid can be modeled as two-step process

- **Step 1**: Separate solute and solvent molecules
  - Break intermolecular forces
  - Endothermic, increase in potential energy of system, "cost"
- **Step 2**: Mix solute and solvent
  - Come together
  - Form new intermolecular forces
  - Exothermic, decrease in potential energy of system, "profit"

Two-Step Process

- Application of Hess' Law
  - Way to take two things we can measure and use to calculate something we can't directly measure
    - ΔH_{soln} is path independent
  - Method works because enthalpy is state function
    - $\Delta \boldsymbol{H}_{\mathbf{soln}} = \boldsymbol{H}_{\mathbf{soln}} - \boldsymbol{H}_{\mathbf{solute}} - \boldsymbol{H}_{\mathbf{solvent}}$
- Overall, steps take us from solid solute + liquid solvent → final solution
- These steps are not the way solution would actually be made in lab

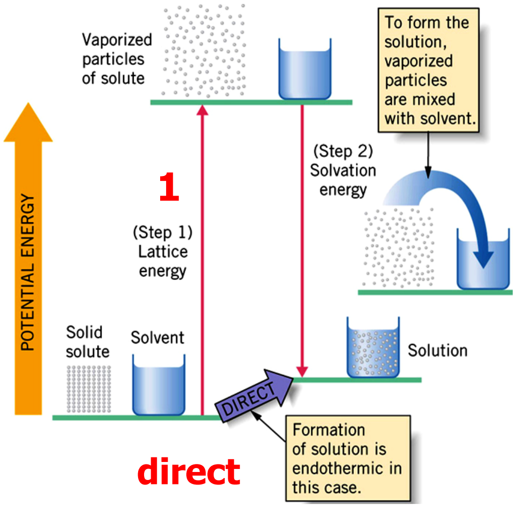
Jesperson, Brady, Hyslop. Chemistry: The Molecular Nature of Matter, 6E

Enthalpy Diagram

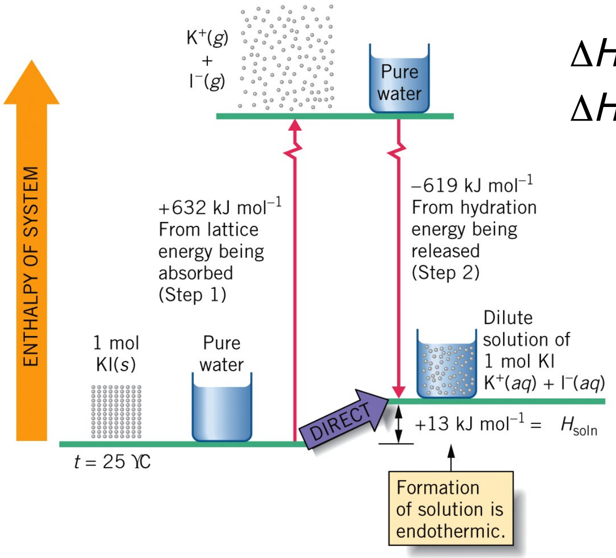
1. Break up solid lattice
   - $\Delta H_{lattice}$ = lattice enthalpy
   - Increase in potential energy
2. Dissolve gas in solvent
   - $\Delta H_{Solvation}$ = solvation enthalpy
   - Decrease in potential energy

$\Delta \boldsymbol{H}_{\mathbf{solution}} = \Delta \boldsymbol{H}_{\mathbf{lattice}} + \Delta \boldsymbol{H}_{\mathbf{Solvation}}$

- Whether $\Delta H_{solution}$ is positive or negative depends on two steps
- In lab, solution formed directly



Dissolving KI in H_2O



$\Delta H_{\text{lattice}}$ (KI) = 632 kJ mol^{-1}

$\Delta H_{\text{hydration}}$ (KI) = – 619 kJ mol^{-1}

$\boldsymbol{\Delta H_{\text{solution}} = \Delta H_{\text{latt}} + \Delta H_{\text{hydr}}}$

$\boldsymbol{\Delta H_{\text{soln}}}$ **=** 632 kJ mol^{-1}

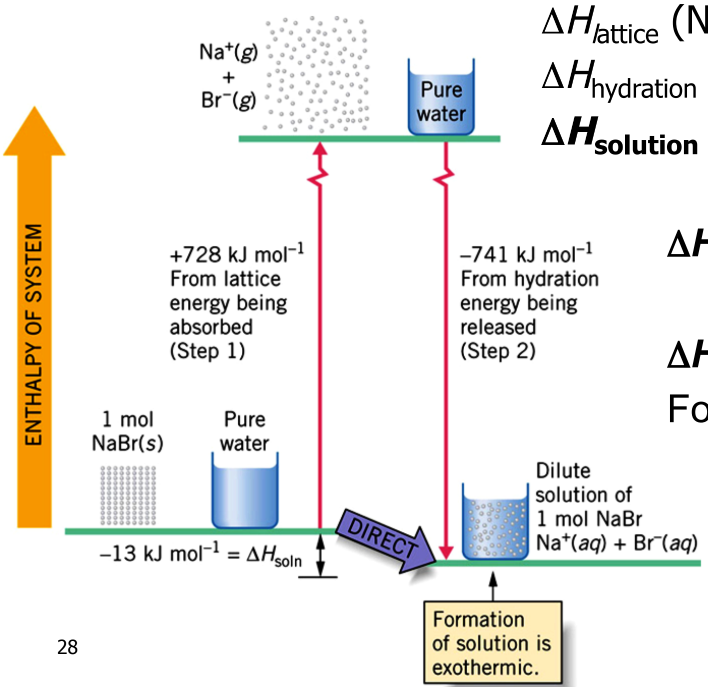
– 619 kJ mol^{-1}

$\boldsymbol{\Delta H_{\text{soln}}}$ **= +13 kJ mol^{-1}**

Formation of KI(aq) is

endothermic

Dissolving NaBr in H_2O



$\Delta H_{\text{lattice}}$ (NaBr) = 728 kJ mol^{-1}

$\Delta H_{\text{hydration}}$ (NaBr) = –741 kJ mol^{-1}

$\boldsymbol{\Delta H_{\text{solution}} = \Delta H_{\text{latt}} + \Delta H_{\text{hydr}}}$

$\boldsymbol{\Delta H_{\text{soln}}}$ **=** 728 kJ mol^{-1}

– 741 kJ mol^{-1}

$\boldsymbol{\Delta H_{\text{soln}}}$ **= – 13 kJ mol^{-1}**

Formation of NaBr(*aq*) is

exothermic

Group Problem

When 2.50 g of solid sodium hydroxide is added to 100.0 g of water in a calorimeter, the temperature of the mixture increases by 6.5 °C. Determine the molar enthalpy of solution for sodium hydroxide. Assume the specific heat of the mixture is 4.184 $J\ g^{-1}\ K^{-1}$.

A. +44.6 kJ/mol

B. +43.5 kJ/mol

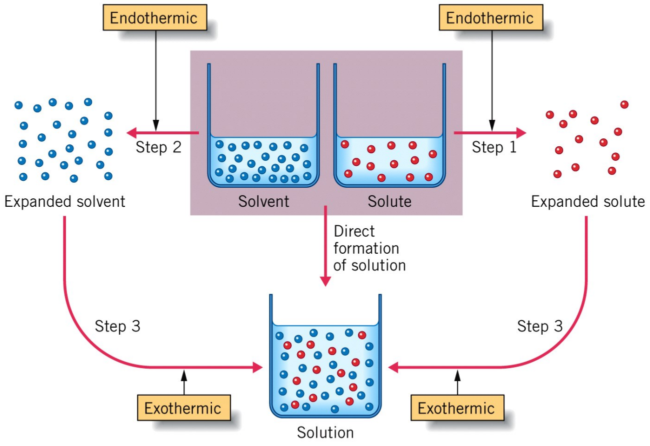
C. –44.6 kJ/mol

D. –43.5 kJ/mol

Solutions Containing Liquid Solute

Similar treatment but with three step path

1. Solute expanded to gas
   - ΔH is positive
   - Increase in potential energy
2. Solvent expanded to gas
   - ΔH is positive
   - Increase in potential energy
3. Solvation occurs
   - ΔH is negative
   - Decrease in potential energy



$$\Delta H_{soln} = \Delta H_{solute} + \Delta H_{solvent} + \Delta H_{solvation}$$

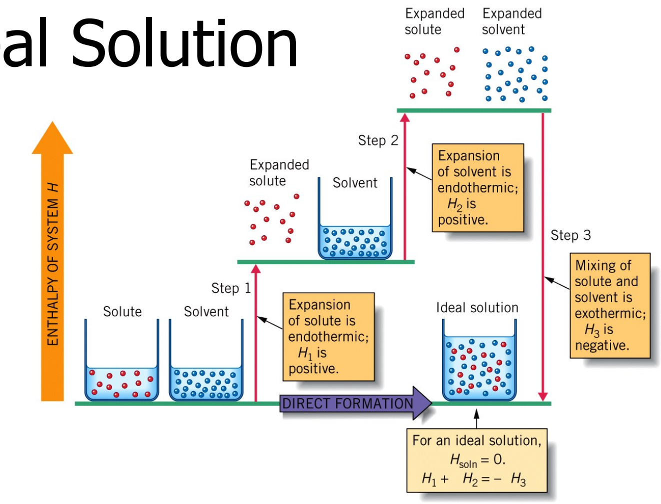
Ideal Solution

One in which intermolecular attractive forces are identical

- $\Delta H_{soln} = 0$

e.g. Benzene in CCl_4

- All London forces
- $\Delta H_{soln} \sim 0$



Step 1 + Step 2 = –Step 3

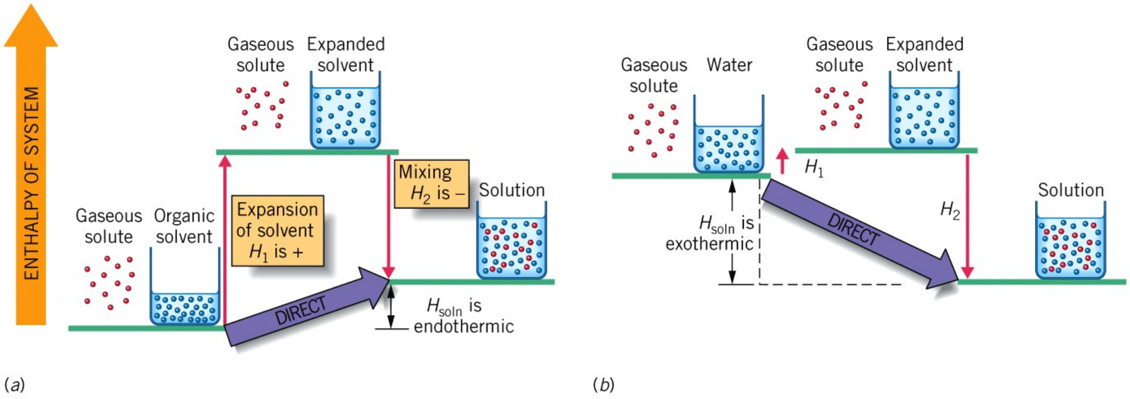
$$\Delta H_{solute} + \Delta H_{solvent} = -\Delta H_{solvation}$$

Gaseous Solutes in Liquid Solution

- Only very weak attractions exist between gas molecules
  - There are no intermolecular attractions in ideal gases
- When making solution with gas solute
  - Energy required to "expand solute" is negligible
- Heat absorbed or released when gas dissolves in liquid has two contributions:

1. Expansion of solvent $\Delta H_{solvent}$
2. Solvation of gas $\Delta H_{solvation}$

Gaseous Solutes in Liquid Solution



- Gas dissolves in organic solvent
- Generally endothermic
- $\Delta H_{solvation} > 0$

- Gas dissolves in H_2O
- Generally exothermic
- $\Delta H_{solvation} < 0$

Group Problem

The solubility of a substance increases with increased temperature if:

A. $\Delta H_{solution} > 0$
B. $\Delta H_{solution} < 0$
C. $\Delta H_{solution} = 0$

CHAPTER 13 Properties of Solutions

Solubility

Solubility

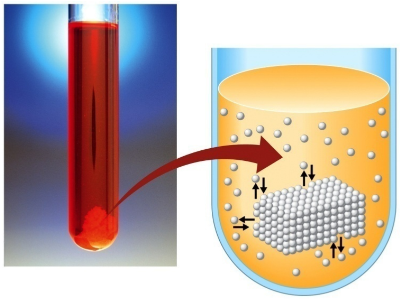
- Mass of solute that forms *saturated solution* with given mass of solvent at specified temperature

$$\text{solubility} = \frac{\text{g solute}}{\text{100 g solvent}}$$

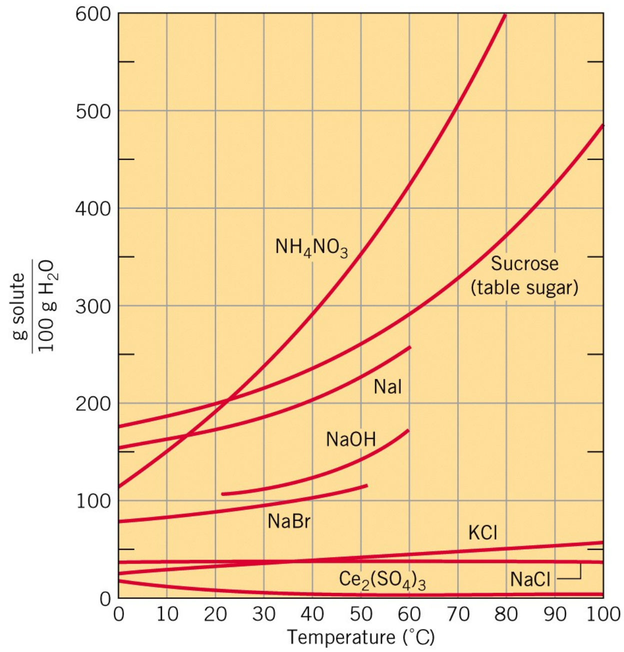
- If extra solute added to saturated solution, extra solute will remain as separate phase

$$\text{solute}_{\text{undissolved}} \rightleftharpoons \text{solute}_{\text{dissolved}}$$

- Generally substances become more soluble at elevated temperatures
  - Increased disorder in the solution is often the reason for this



Solubility of Most Substances Increases with Temperature



- Most substances become more soluble as *T* increases
- Amount solubility increases
  - – Varies considerably
  - – Depends on substance

Effect of *T* on Gas Solubility in Liquids

- Solubility of gases usually decreases as *T* increases
- Solubilities of Common Gases in Water

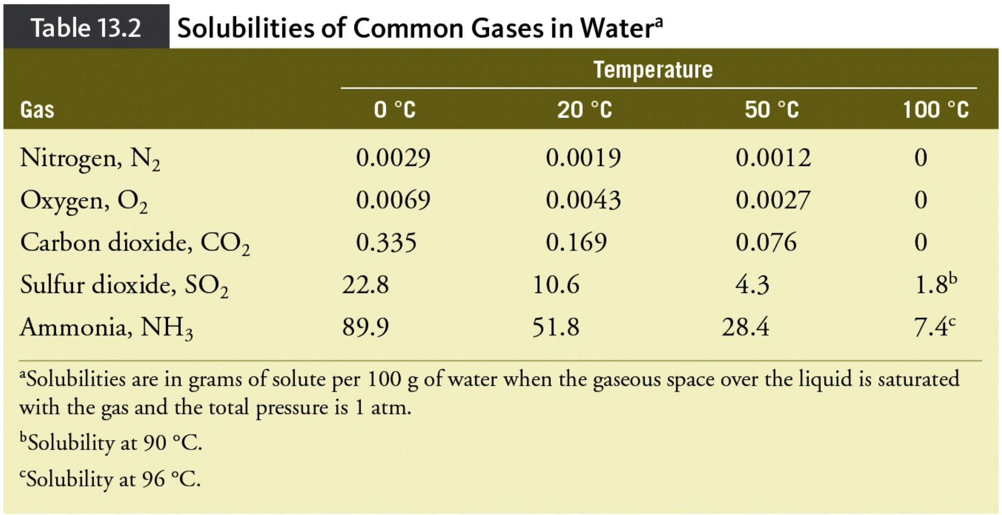


Table 13.2 Solubilities of Common Gases in Water[a]

Gas	Temperature 0 °C	20 °C	50 °C	100 °C
Nitrogen, N_2	0.0029	0.0019	0.0012	0
Oxygen, O_2	0.0069	0.0043	0.0027	0
Carbon dioxide, CO_2	0.335	0.169	0.076	0
Sulfur dioxide, SO_2	22.8	10.6	4.3	1.8[b]
Ammonia, NH_3	89.9	51.8	28.4	7.4[c]

[a] Solubilities are in grams of solute per 100 g of water when the gaseous space over the liquid is saturated with the gas and the total pressure is 1 atm.

[b] Solubility at 90 °C.

[c] Solubility at 96 °C.

Example: Dead Zones

During the industrial revolution, factories were built on rivers so that the river water could be used as a coolant for the machinery. The hot water was dumped back into the river and cool water recirculated. After some time, the rivers began to darken and many fish died. The water was not found to be contaminated by the machinery. What was the cause of the mysterious fish kills?

Increased temperature, lowered the amounts of dissolved oxygen

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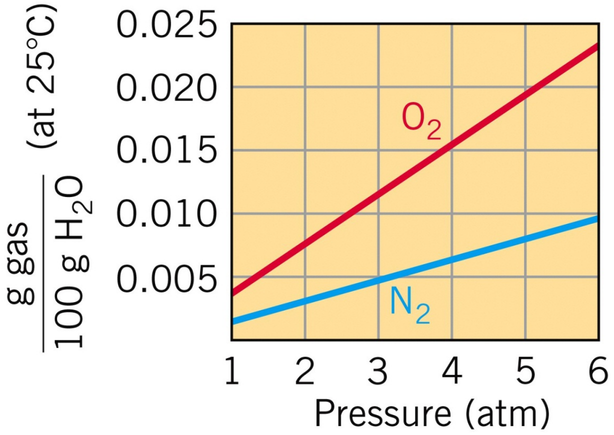
Effect of Pressure on Gas Solubility



Solubility increases as *P* increases

Effect of Pressure on Gas Solubility

A. At some *P*, equilibrium exists between vapor phase and solution

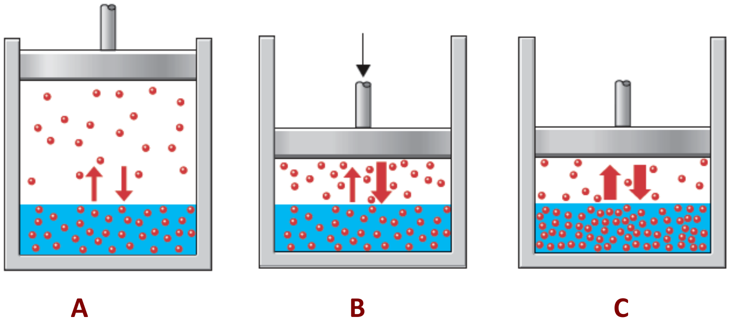
- $rate_{in} = rate_{out}$

B. Increase in *P* puts stress on equilibrium

- Increase in frequency of collisions so $rate_{in} > rate_{out}$

C. More gas dissolved

- $rate_{out}$ will increase until $rate_{out} = rate_{in}$ again



Henry's Law

- Pressure-Solubility Law
- Concentration of gas in liquid at any given temperature is directly proportional to partial pressure of gas over solution

$$C_{gas} = k_H P_{gas} \quad (T \text{ is constant})$$

C_{gas} = concentration of gas

P_{gas} = partial pressure of gas

k_H = Henry's Law constant

- » Unique to each gas
- » Tabulated

Henry’s Law

- True only at low concentrations and pressures where gases do NOT react with solvent
- Alternate form

$$\frac{C_1}{P_1} = \frac{C_2}{P_2}$$

  - – C_1 and P_1 refer to an initial set of conditions
  - – C_2 and P_2 refer to a final set of conditions

Group Problem

Using Henry’s Law

Calculate the concentration of CO_2 in a soft drink that is bottled with a partial pressure of CO_2 of 5 atm over the liquid at 25 °C. The Henry’s Law constant for CO_2 in water at this temperature is 3.12×10^{-2} mol L^{-1} atm^{-1}.

Group Problem

Using Henry's Law

Calculate the concentration of CO_2 in a soft drink after the bottle is opened and equilibrates at 25 °C under a partial pressure of CO_2 of 4.0×10^{-4} atm.

Group Problem

What is the concentration of dissolved nitrogen in a solution that is saturated in N_2 at 2.0 atm? $k_H = 8.42 \times 10^{-7}$ mol L^{-1} atm^{-1}

Group Problem

How many grams of oxygen gas at 1.0 atm will dissolve in 10.0 L of water at 25 °C if Henry's constant is 1.3×10^{-3} mol L^{-1} atm^{-1} at this temperature ?

A. 0.42 g
B. 0.013 g
C. 0.042 g
D. 0.21 g
E. 2.4 g

Solubility of Polar vs. Nonpolar Gases

- Gas molecules with polar bonds are much more soluble in water than nonpolar molecules like oxygen and nitrogen
  - CO_2, SO_2, NH_3 >> O_2, N_2, Ar
- Form H-bonds with H_2O
- Some gases have increased solubility because they **react** with H_2O to some extent

e.g.

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

$$SO_2(aq) + H_2O \rightleftharpoons H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq)$$

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Case Study

When you open a bottle of seltzer, it fizzes. How should you store it to increase the time before it goes flat?

Gases are more soluble at low temperature and high pressure.

Andy Washnik

CHAPTER 13 Properties of Solutions

Concentration

Concentration

- What units we use depends on situation
  - Stoichiometric calculations
    - Molarity $$M = \frac{\text{mol of solute}}{\text{L of solution}}$$
    - Units: mol/L

Problem: *M* varies with temperature

- Volume varies with temperature
- Solutions expand and contract when heated and cooled

- If temperature independent concentration is needed, must use other units

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Temperature Independent Concentration

1. Percent Concentrations

- Also called percent by mass or percent by weight

$$\textbf{percent by mass} = \frac{\textbf{mass of solute}}{\textbf{mass of solution}} \times \textbf{100\%}$$

- This is sometimes indicated %(*w*/*w*) where “*w*” stands for weight or mass
- The “(*w*/*w*)” is often omitted

Group Problem

Percent by Mass

What is the percent by mass of NaCl in a solution consisting of 12.5 g of NaCl and 75.0 g water?

$$\text{percent by mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

Group Problem

Seawater is typically 3.5% sea salt and has a density of 1.03 g/mL. How many grams of sea salt would be needed to prepare enough seawater solution to fill a 62.5 L aquarium?

More Temperature Independent Concentration Units

Molality (m)

- Number of moles of solute per kilogram solvent

$$\boxed{\text{molality} = m = \frac{\text{mol of solute}}{\text{kg of solvent}}}$$

- Also molal concentration
- Independent of temperature
- m vs. M
  - Similar when $d = 1.00$ g/mL
  - Different when $d >> 1.00$ g/mL or $d << 1.00$ g/mL

Group Problem

Concentration Calculation

If you prepare a solution by dissolving 25.38 g of I_2 in 500.0 g of water, what is the molality (m) of the solution?

Group Problem

Concentration Calc’ n. (cont)

What is the molarity (*M*) of this solution? The density of this solution is 1.00 g/mL.

Group Problem

M and *m* in CCl_4

What is the molality (*m*) and molarity (*M*) of a solution prepared by dissolving 25.38 g of I_2 in 500.0 g of CCl_4? The density of this solution is 1.59 g/mL

Group Problem

M and *m* in CCl_4 (cont)

What is the molarity (*M*) of this solution? The density of this solution is 1.59 g/mL.

Group Problem

Converting between Concentrations

Calculate the molarity and the molality of a 40.0% HBr solution. The density of this solution is 1.38 g/mL.

Group Problem

What is the molality of 50.0% (*w*/*w*) sodium hydroxide solution?

A. 0.500 *m*
B. 1.25 *m*
C. 0.025 *m*
D. 25 *m*
E. 50 *m*

Group Problem

What is the molarity of the 50%(w/w) solution if its density is 1.529 g/mL?

A. 19 *M*
B. 1.25 *M*
C. 1.9 *M*
D. 0.76 *M*

More Temperature-Independent Concentration Units

- **Mole Fraction**

$$X_A = \frac{\#\ \text{mol}\ A}{\text{Total moles of all components}}$$

- **Mole %**

$$\text{mol}\ \%A = X_A \times 100\%$$

CHAPTER 13 Properties of Solutions

Colligative Properties

Colligative Properties

- Physical properties of solutions
- Depend mostly on relative populations of particles in mixtures
- Don't depend on their chemical identities

Effects of solute on vapor pressure of solvents

- Solutes that can't evaporate from solution are called nonvolatile solutes

Fact: All solutions of nonvolatile solutes have lower vapor pressures than their pure solvents

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Raoult's Law

- Vapor pressure of solution, $\boldsymbol{P_{solution}}$, equals product of mole fraction of solvent, $\boldsymbol{X_{solvent}}$ and its vapor pressure when pure, $\boldsymbol{P_{solvent}}$
- Applies for dilute solutions

$$\boxed{P_{solution} = X_{solvent} P^{\circ}_{solvent}}$$

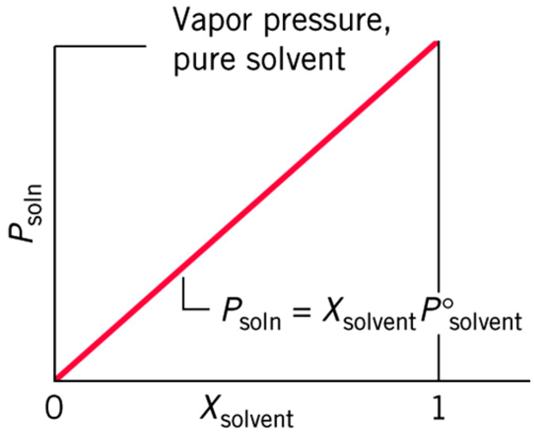
$P_{solution}$ = vapor pressure of the solution

$X_{solvent}$ = mole fraction of the solvent

$P^{\circ}_{solvent}$ = vapor pressure of pure solvent

Alternate form of Raoult's Law

- Plot of P_{soln} vs. $X_{solvent}$ should be linear
  - Slope = $X_{solvent}P^\circ_{solvent}$
  - Intercept = 0
- Change in vapor pressure can be expressed as



$$\Delta P = \text{change in } P = (P^\circ_{solvent} - P_{solution})$$

- Usually more interested in how solute's mole fraction changes the vapor pressure of solvent

$$\boxed{\Delta P = X_{solute}P^\circ_{solvent}}$$

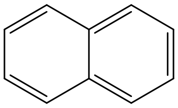
Group Problem

Glycerin (using Raoult's Law)

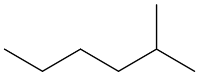
Glycerin, $C_3H_8O_3$, is a nonvolatile nonelectrolyte with a density of 1.26 g/mL at 25 °C. Calculate vapor pressure at 25 °C of a solution made by adding 50.0 mL of glycerin to 500.0 mL of water. The vapor pressure of pure water at 25 °C is 23.8 torr.

Group Problem

The vapor pressure of 2-methylhexane is 37.986 torr at 15°C. What would be the pressure of the mixture of 78.0 g 2-methylhexane and 15 g naphthalene, which is nearly non-volatile at this temperature?



naphthalene
$C_{10}H_8$
MM 128.17

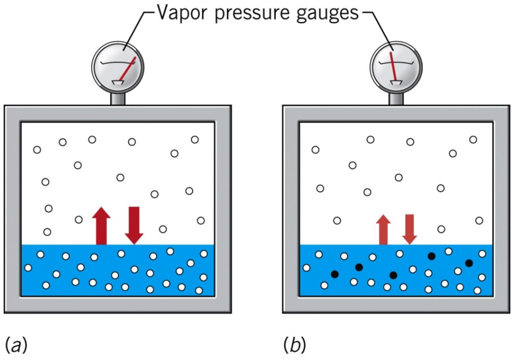


2-methylhexane
C_7H_{16}
MM 100.2

Why Nonvolatile Solute Lowers Vapor Pressure

A. Lots of solvent molecules in liquid phase
  - Rate of evaporation and condensation high and equal

B. Fewer solvent molecules in liquid
  - Rate of evaporation is lower so rate of condensation must be lower which is achieved by fewer gas particles
  - At equilibrium, fewer gas molecules give lower pressure



Solutions That Contain Two or More Volatile Components

- Vapor contains two components
  - Partial pressure of each component *A* and *B* is given by Raoult's Law

$$P_A = X_A P_A^\circ \quad \text{and} \quad P_B = X_B P_B^\circ$$

  - Total pressure of solution of components *A* and *B* given by Dalton's Law of Partial Pressures

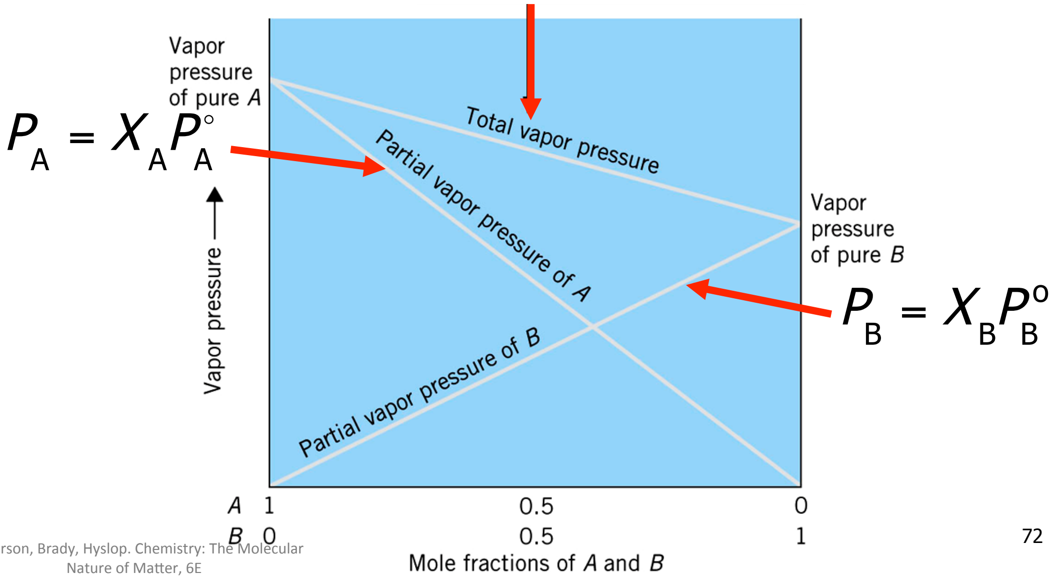
$$P_{\text{total}} = P_A + P_B = X_A P_A^\circ + X_B P_B^\circ$$

  - Since $X_A + X_B = 1$ then $1 - X_A = X_B$ and we can write

$$P_{\text{total}} = X_A P_A^\circ + (1 - X_A) P_B^\circ$$

For Ideal, Two Component Solution of Volatile Components

$$\boxed{P_{\text{total}} = P_{\text{A}} + P_{\text{B}} = X_{\text{A}} P_{\text{A}}^\circ + X_{\text{B}} P_{\text{B}}^\circ}$$



$$P_{\text{A}} = X_{\text{A}} P_{\text{A}}^\circ$$

$$P_{\text{B}} = X_{\text{B}} P_{\text{B}}^{\text{o}}$$

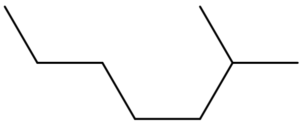
Group Problem

Benzene and Toluene

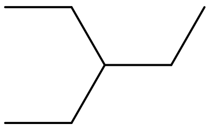
- Consider a mixture of benzene, C_6H_6, and toluene, C_7H_8, containing 1.0 mol benzene and 2.0 mol toluene. At 20 °C, the vapor pressures of the pure substances are: $P°_{\text{benzene}} = 75$ torr and $P°_{\text{toluene}} = 22$ torr
- Assuming the mixture obeys Raoult's law, what is the total pressure above this solution?

Group Problem

The vapor pressure of 2-methylheptane is 233.95 torr at 55 °C. At the same temperature, 3-ethylpentane has a vapor pressure of 207.68 torr. What would be the pressure of the mixture of 78.0 g 2-methylheptane and 15 g 3-ethylpentane?



2-methylheptane
C_8H_{18}
MM 114.23 g/mol



3-ethylpentane
C_7H_{16}
MM 100.2 g/mol

Group Problem

n-Hexane and *n*-heptane are miscible. If the vapor pressure of pure hexane is 151.28 mm Hg, and heptane is 45.67 at 25 °C, which equation can be used to determine the mole fraction of hexane in the mixture if the mixture's vapor pressure is 145.5 mm Hg?

A. X(151.28 mmHg) = 145.5 mmHg

B. X(151.28 mmHg) + (X)(45.67 mm Hg) = 145.5 mmHg

C. X(151.28 mmHg) + (1 – X)(45.67 mm Hg) = 145.5 mm Hg

A. None of these

Solutes also Affect Freezing and Boiling Points of Solutions

Facts:

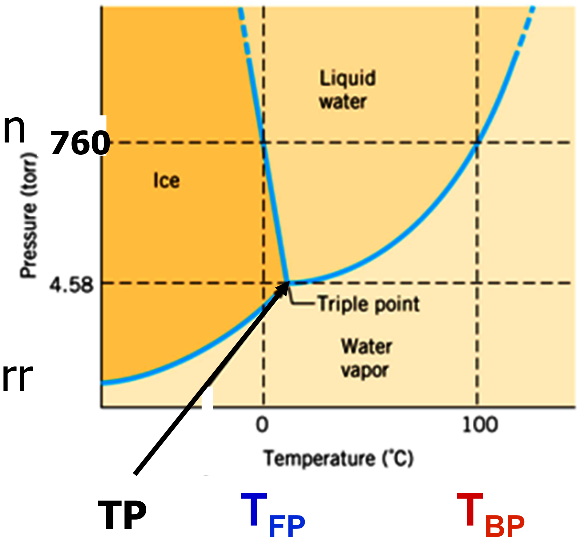
- Freezing point of solution always lower than pure solvent
- Boiling point of solution always higher than pure solvent

Why?

- Consider the phase diagram of H_2O
  - – Solid, liquid, gas phases in equilibrium
  - – Blue lines
  - – P vs. T

Pure Water

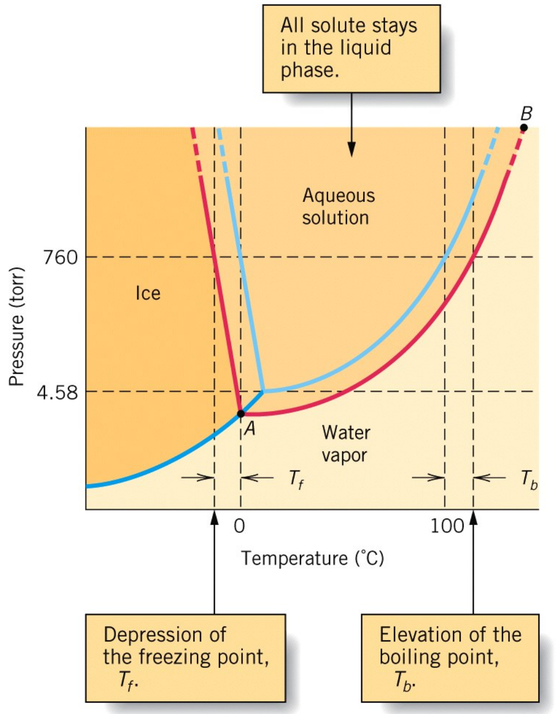
- Triple Point
  - All three phases exist in equilibrium simultaneously
- Pure H_2O
  - Dashed lines at 760 torr (1 atm) that intersect solid/liquid and liquid/gas curves
  - Give *T* for freezing point (FP) and boiling point (BP)



Jesperson, Brady, Hyslop. Chemistry: The Molecular Nature of Matter, 6E

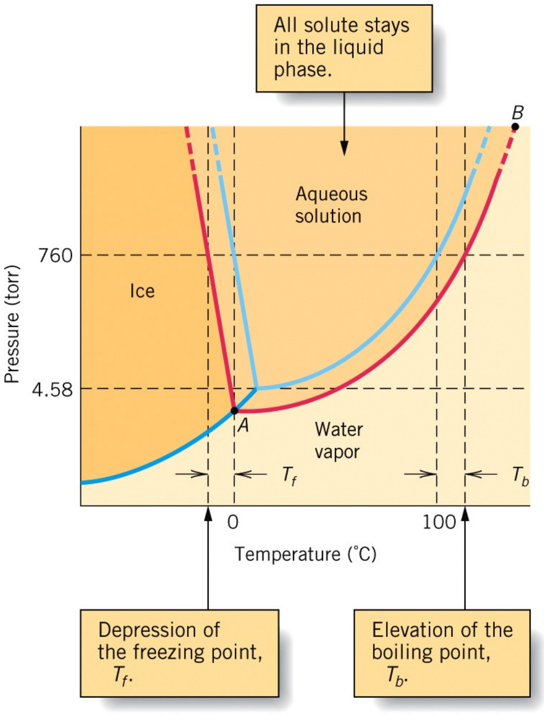
Solution—Effect of Solute

- **Solute** molecules stay in solution only
  - None in vapor
  - None in solid
    - Crystal structure prevents from entering
- Liquid/vapor
  - Decrease number solvent molecules entering vapor
  - Need higher *T* to get all liquid to gas
  - Line at higher *T* along phase border (red)



Solution—Effect of Solute

- Triple point moves lower and to the left
- Solid/liquid
  - – Solid/liquid line to left (red)
  - – Lower T all along phase boundary
  - – Solute keeps solvent in solution longer
  - – Must go to lower T to form crystal



All solute stays in the liquid phase.

Depression of the freezing point, T_f.

Elevation of the boiling point, T_b.

Freezing Point Depression and Boiling Point Elevation

Solution

- – Observe increase in boiling point and decrease in freezing point compared to pure solvent
- – Both ΔT_f and ΔT_b depend on relative amounts of solvent and solute

Colligative properties

- Boiling Point Elevation (ΔT_b)
  - – Increase in boiling point of solution vs. pure solvent
- Freezing Point Depression (ΔT_f)
  - – Decrease in freezing point of solution vs. pure solvent

Freezing Point Depression (ΔT_f)

$$\boxed{\Delta T_f = K_f\, m}$$

where

$\Delta T_f = (T_f - T_{soln})$

m = concentration in Molality

K_f = molal freezing point depression constant

Units of °C/molal

Depend on solvent, see Table 13.3

Boiling Point Elevation (ΔT_b)

$$\boxed{\Delta T_b = K_b\, m}$$

where

$\Delta T_b = (T_{soln} - T_b)$

m = concentration in Molality

K_b = molal boiling point elevation constant

Units of °C/m

Depend on solvent, see Table 13.3

Table 13.3 K_f and K_b

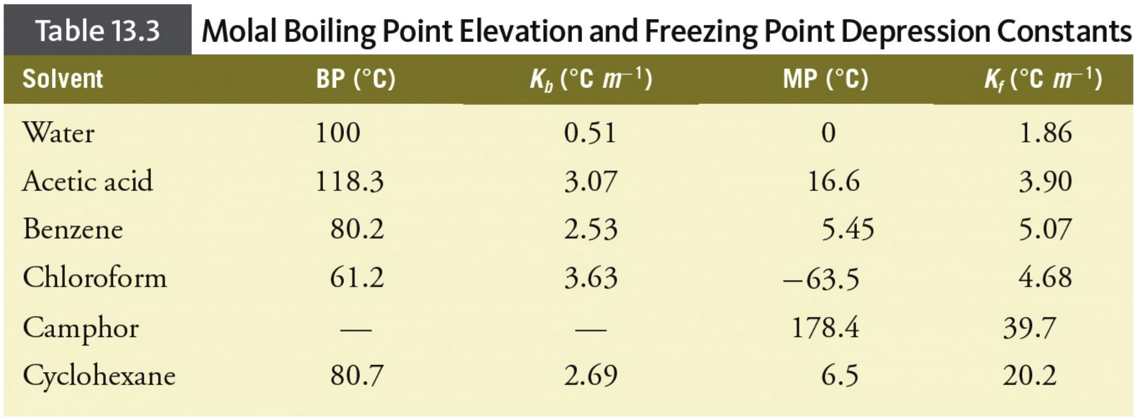


Table 13.3 Molal Boiling Point Elevation and Freezing Point Depression Constants

Solvent	BP (°C)	K_b (°C m^{-1})	MP (°C)	K_f (°C m^{-1})
Water	100	0.51	0	1.86
Acetic acid	118.3	3.07	16.6	3.90
Benzene	80.2	2.53	5.45	5.07
Chloroform	61.2	3.63	−63.5	4.68
Camphor	—	—	178.4	39.7
Cyclohexane	80.7	2.69	6.5	20.2

Group Problem

Freezing Point Depression

Estimate the freezing point of a permanent type of antifreeze solution made up of 100.0 g ethylene glycol, $C_2H_6O_2$, (MM = 62.07 g/mol) and 100.0 g H_2O (MM = 18.02 g/mol).

Group Problem

When 0.25 g of an unknown organic compound is added to 25.0 g of cyclohexane, the freezing point of cyclohexane is lowered by 1.6 °C. K_f for the solvent is 20.2 °C m^{-1}. Determine the molar mass of the unknown.

A. 505 g/mol

B. 32 g/mol

C. 315 g/mol

D. 126 g/mol

Group Problem

Boiling Point Elevation

A 2.00 g sample of a substance was dissolved in 15.0 g of CCl_4. The boiling point of this solution was determined to be 77.85 °C. Calculate the molar mass of the compound.

[For CCl_4, the K_b = 5.07 °C/m and BP = 76.50 °C]

Group Problem

According to the Sierra™ Antifreeze literature, the freezing point of a 40/60 solution of Sierra antifreeze and water is – 4 °F. What is the molality of the solution?

Group Problem

In the previous sample of a Sierra™ antifreeze mixture, 100 mL is known to contain 42 g of the antifreeze and 60. g of water. What is the molar mass of the compound found in this antifreeze if it has a freezing point of – 4 °F?

Group Problem

Beer is known to be around a 5% ethanol (C_2H_5OH) solution with a density of 1.05 g/mL. What is its expected boiling point? (K_b = 0.51 °C/m)

A. 100 °C

B. 101 °C

C. 102 °C

D. 103 °C

E. Not enough information given

CHAPTER 13 Properties of Solutions

Osmosis

Membranes and Permeability

Membranes

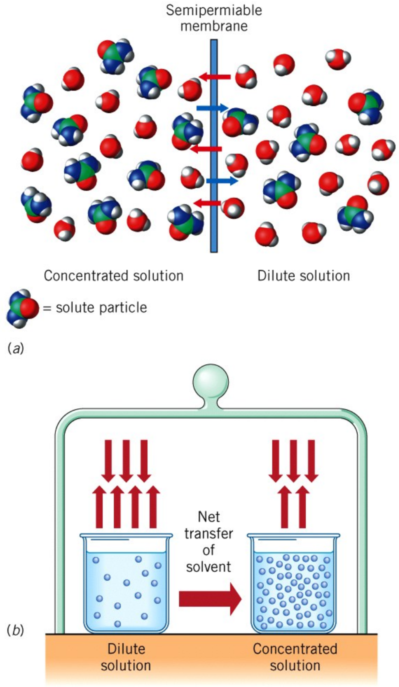
- Separators
- Example: cell walls
- Keep mixtures separated

Permeability

- Ability to pass substances through membrane

Semipermeable

- Some substances pass, others don't
- Membranes are semipermeable
  - Selective



Membranes and Permeability

- Degree of permeability depends on type of membrane
  - Some pass water only
  - Some pass water and small ions only
- Membranes separating two solutions of different concentration
  - Two similar phenomena occur
  - Depends on membrane

Dialysis

- When semipermeable membrane lets both H_2O and small solute particles through
  - Membrane called dialyzing membrane
  - Keeps out large molecules such as proteins

Osmosis

Osmotic Membrane

- Semipermeable membrane that lets only solvent molecules through

Osmosis

- Net shift of solvent molecules (usually water) through an osmotic membrane
- Direction of flow in osmosis,
  - Solvent flows from dilute to more concentrated side
  - Flow of solvent molecules across osmotic membrane
    - Increase in concentration of solute on dilute side
    - Decrease in concentration of solute on more concentrated side

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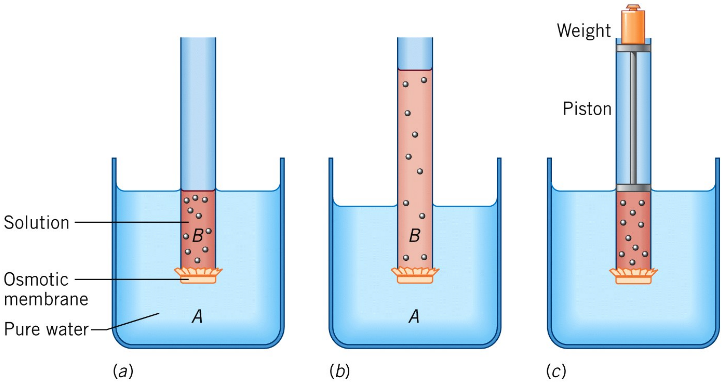
Osmosis and Osmotic Pressure



A. Initially, solution *B* separated from pure water, *A*, by osmotic membrane. No osmosis occurred yet

B. After a while, volume of fluid in tube higher. Osmosis has occurred.

C. Need back pressure to prevent osmosis = osmotic pressure.

Osmotic Pressure

- Exact back pressure needed to prevent osmotic flow when one liquid is pure solvent.

Why does osmosis eventually stop?

- Extra weight of solvent as rises in column generates this opposing pressure
- When enough solvent transfers to solution so that when osmotic pressure is reached, flow stops
- If osmotic pressure is exceeded, then reverse process occurs—solvent leaves solution
  - Reverse osmosis—used to purify sea water

Equation for Osmotic Pressure

- Similar to ideal gas law

$$\Pi V = nRT \quad \text{or} \quad \Pi = MRT$$

- Π = osmotic pressure
- V = volume
- n = moles
- M = molarity of solution (n/V)
- T = Temperature in Kelvins
- R = Ideal gas constant
  $= 0.082057\ \text{L atm mol}^{-1}\ \text{K}^{-1}$

Osmometer

- Instrument to measure osmotic pressure
- Very important in solutions used for biological samples

Isotonic solution

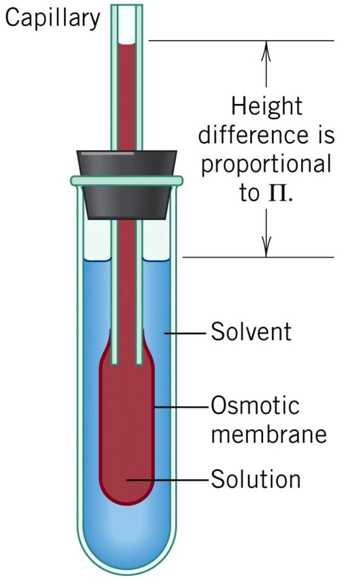
  - Same salt concentration as cells
  - Same osmotic pressure as cells

Hypertonic solution

  - Higher salt concentration than cells
  - Higher osmotic pressure than cells
  - Will cause cells to shrink and dehydrate

Hypotonic solution

  - Lower salt concentration than cells
  - Lower osmotic pressure than cells
  - Will cause cells to swell and burst



Group Problem

Osmotic Pressure

Eye drops must be at the same osmotic pressure as the human eye to prevent water from moving into or out of the eye. A commercial eye drop solution is 0.327 *M* in electrolyte particles. What is the osmotic pressure in the human eye at 25 °C?

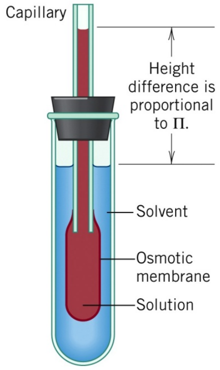
Group Problem

Using Π to determine MM

The osmotic pressure of an aqueous solution of certain protein was measured to determine its molar mass. The solution contained 3.50 mg of protein in sufficient H_2O to form 5.00 mL of solution. The measured osmotic pressure of this solution was 1.54 torr at 25 °C. Calculate the molar mass of the protein.

Group Problem

A solution of 5% dextrose ($C_6H_{12}0_6$) in water is placed into the osmometer shown at right. It has a density of 1.0 g/mL. The surroundings are filled with distilled water. What is the expected osmotic pressure at 25 °C?



Group Problem

For a typical blood plasma, the osmotic pressure at body temperature (37 °C) is 5409 mm Hg. If the dominant solute is serum protein, what is the concentration of serum protein?

Group Problem

Suppose that your tap water has 250 ppb (ppb = 1/1,000,000,000 or 1×10^{-9}) of dissolved H_2S , and that its density is about 1.0 g/mL. What is its osmotic pressure at 25 °C?

A. 0.00058 atm

B. 0.064 atm

C. 0.059 atm

D. 0.18 atm

Colligative Properties of Electrolyte Solutions Differ

- K_f (H_2O) = 1.86 °C/*m*
  - Expect 1.00 *m* solution of NaCl to freeze at −1.86 °C
  - Actual freezing point = −3.37 °C
  - About twice expected ΔT

Why?

- Colligative properties depend on concentration (number) of particles
- One NaCl dissociates to form two particles

$$\mathrm{NaCl}(s) \longrightarrow \mathrm{Na}^+(aq) + \mathrm{Cl}^-(aq)$$

Colligative Properties of Electrolyte Solutions Depend on Number of Ions

- Actual concentration of ions = 2.00 *m* (Started with 1.00 *m* NaCl)
- Now use this to calculate ΔT
- $\Delta T_f = 1.86\ °\mathrm{C}/m \times 2.00\ m = 3.72\ °\mathrm{C}$

Or

- $T_{\text{final}} = T_{\text{initial}} - \Delta T_f = 0.00 - 3.72\ °\mathrm{C}$
  $= -3.72\ °\mathrm{C}$
- Not exactly = to actual $\Delta T_f = -3.37\ °\mathrm{C}$
- This method for ions gives rough estimate if you assume that all ions dissociate 100%.

Why isn’t this Exact for Electrolytes?

- Assumes 100% dissociation of ions
  - Electrolytes don’t dissociate 100%, especially in concentrated solutions
- Some ions exist in ion pairs
  - Closely associated pairs of oppositely charged ions that behave as a single particle in solution
  - So, fewer particles than predicted
  - Result: freezing point depression and boiling point elevation not as great as expected
- As you go to more dilute solutions, electrolytes more fully dissociated and observe freezing point and boiling point closer to calculated value.
  - Model works better at dilute concentrations

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van’t Hoff Factor = i

- Scales solute molality to correct number of particles
- Measure of dissociation of electrolytes
- van’t Hoff factor is equivalent to percent ionization
- In general, it varies with concentration (see Table 13.4, page 622)

$$i = \frac{(\Delta T_f)_{\text{measured}}}{(\Delta T_f)_{\text{calcd as nonelectrolyte}}}$$

Table 13.4 van’t Hoff Factors vs. Concentration

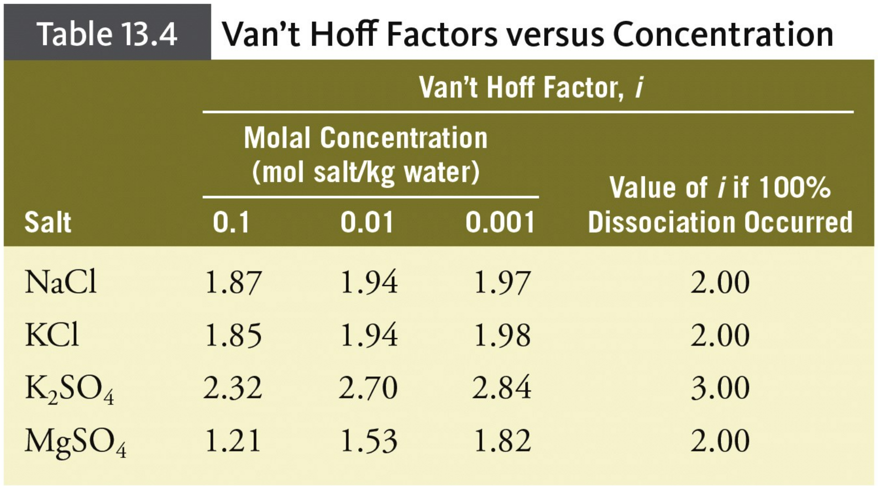


Table 13.4 Van’t Hoff Factors versus Concentration

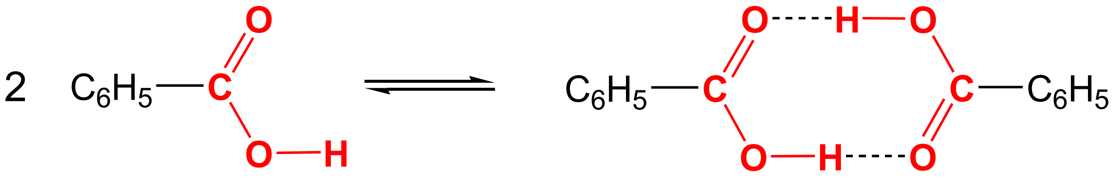
	Van’t Hoff Factor, *i*			
	Molal Concentration (mol salt/kg water)			
Salt	**0.1**	**0.01**	**0.001**	**Value of *i* if 100% Dissociation Occurred**
NaCl	1.87	1.94	1.97	2.00
KCl	1.85	1.94	1.98	2.00
K_2SO_4	2.32	2.70	2.84	3.00
$MgSO_4$	1.21	1.53	1.82	2.00

Note:

1. As concentration decreases, $i_{\text{observed}} \Rightarrow i_{\text{expected}}$
2. $MgSO_4$ much less dissociated than NaCl or KCl

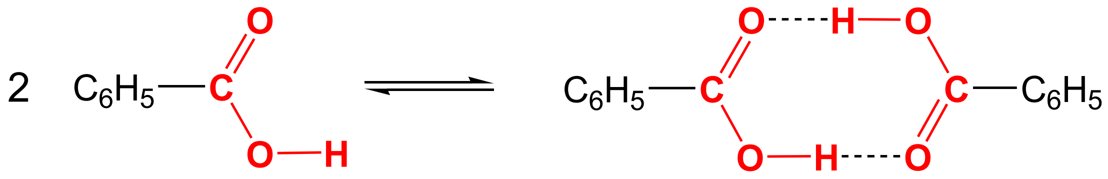
Nonelectrolytes

- Some molecular solutes produce weaker colligative effects than predicted by their molal concentrations
- Evidence of solute molecule clustering or associating



- Result: only half the number of particles expected based on molality of solution, so ΔT_f only half of what expected

Nonelectrolytes



- Result: calculated molar mass double what is expected
  - Concentration of particles is about half of what is expected and
  - ΔT_f only half of what expected
- So size of solute particles is important
- Common with organic acids and alcohols

Group Problem

In preparing pasta, 2 L of water at 25 °C are combined with about 15 g salt (NaCl, MM= 58.44 g/mol) and the solution brought to a boil. What is the change in the boiling point of the water?

Group Problem

Case Study

Suppose you run out of salt. What mass of sugar ($C_{12}H_{22}O_{11}$, MM = 342.30 g/mol) added to 2 L of water would raise the temperature of water by 0.10 °C?

Colligative Properties Summary

Colligative properties depend on number of particles

- $i = m_{\text{app}}/m_{\text{molecular}}$
- Raoult’s Law
- Freezing point depression
- Boiling point elevation
- Osmotic pressure

Must look at solute and see if molecular or ionic

- If molecular, $i = 1$
- If ionic, must include $i > 1$ in equations

Colligative Properties

- Raoult's law

  $P_{\text{solution}} = \chi_{\text{solvent}} P^{\text{o}}_{\text{solvent}}$

- Freezing point depression
  - $\Delta T_{\text{f}} = iK_{\text{f}}\, m$
- Boiling point elevation
  - $\Delta T_{\text{b}} = iK_{\text{b}}\, m$
- Osmotic pressure
  - $\Pi = iMRT$