Solutions and Their Behavior
Chapter 11
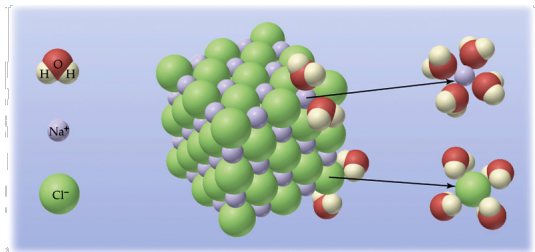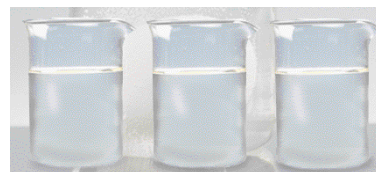

Chemistry 222
Professor Michael Russell

Last update:
4/29/24
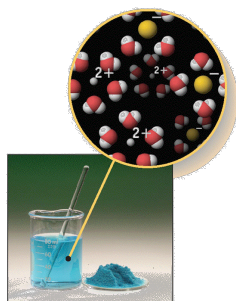
MAR

Solution Behavior

Why does a raw egg swell or shrink when placed in different solutions?

MAR

Some Definitions

A solution is a **HOMOGENEOUS** mixture of 2 or more substances in a single phase.

Solutions, **Colloids** and **Suspensions** are all examples of homogenous mixtures

**Solutions** most important to chemists

MAR

Some Definitions

A **SOLUTION** has at least two constituents

One constituent is usually regarded as the **SOLVENT** and the others as **SOLUTES**

So a **SOLUTION** = **SOLUTE** + **SOLVENT**

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
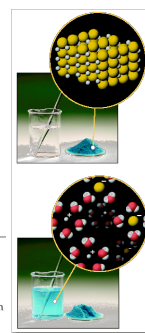
MAR

Definitions

Solutions can be classified as **unsaturated** or **saturated**.

A **saturated solution** contains the maximum quantity of solute that dissolves at that temperature.

MAR

Definitions

SUPERSATURATED SOLUTIONS contain more than is possible and are unstable.

Unstable solutions; crystallization can usually be stimulated by adding a "seed crystal" or scratching the side of the flask.
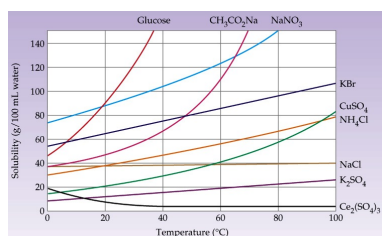

MAR

Solution Definitions

Miscible: Two (or more) liquids that are completely soluble in each other

Solubility: A measure of how much solute will dissolve in a solvent at a specific temperature

MAR

Factors Affecting Solubility

Chemists use the axiom "like dissolves like"

– The closer the intermolecular forces of two phases of matter, the more likely they will dissolve to make a solution

– Polar substances tend to dissolve in polar solvents.

– Nonpolar substances tend to dissolve in nonpolar solvents.

Alcohol	Solubility in H_2O	Solubility in C_6H_{14}
CH_3OH (methanol)	∞	0.12
CH_3CH_2OH (ethanol)	∞	∞
$CH_3CH_2CH_2OH$ (propanol)	∞	∞
$CH_3CH_2CH_2CH_2OH$ (butanol)	0.11	∞
$CH_3CH_2CH_2CH_2CH_2OH$ (pentanol)	0.030	∞
$CH_3CH_2CH_2CH_2CH_2CH_2OH$ (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.
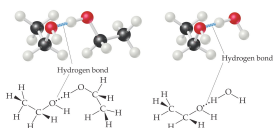
MAR

Factors Affecting Solubility

"Like dissolves like"

Example: water (polar, H-bonds) dissolves in acetone (polar)

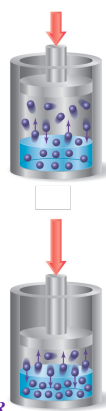*Example:* benzene (ID-ID) dissolves in toluene (ID-ID)

Example: benzene (ID-ID) does not dissolve very well in water (polar, H-bonds)

See _Solubility Handout_

We will discuss solubility more in CH 223

MAR

The solubility of liquids and solids does not change appreciably with pressure.

The solubility of a **gas** in a liquid is directly proportional to its pressure.

Henry's Law: $S_g = kP_g$

• S_g is the solubility of the gas (**M**)

• **k** is the Henry's Law constant for that gas in that solvent, and

• P_g is the partial pressure of the gas above the liquid.
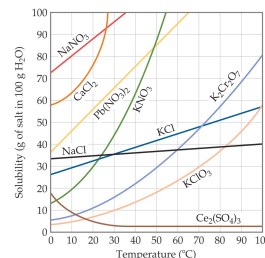
MAR

Henry's Law

Dissolving Gases & Henry's Law

Gas solubility (M) = S_g = k • P_g

k for O_2 = 1.66 x 10^{-6} M/mm Hg

When P_g drops, solubility drops.

MAR

Temperature and Solubility

Generally, the solubility of **solid** solutes in liquid solvents *increases* with increasing temperature.
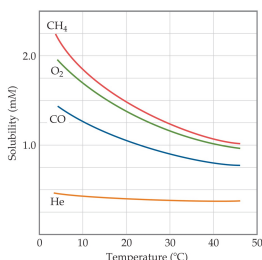
MAR

Temperature and Solubility

The opposite is true for gases.

Carbonated soft drinks are more "bubbly" if stored in the refrigerator.

Warm lakes have less O_2 dissolved in them than cool lakes.

MAR

Colligative Properties

On adding a **solute to a solvent,** the *solvent* properties are modified.

• **Vapor pressure**   decreases
• **Melting point**   decreases
• **Boiling point**   increases
• **Osmosis is possible (osmotic pressure)**

These changes are called **COLLIGATIVE PROPERTIES.**

They depend only on the **NUMBER of solute particles relative to solvent particles,** not on the **KIND** of solute particles. We need **new concentration units**! (more than molarity, M)

MAR

Concentration Units

• **MOLE FRACTION, X**

For a mixture of A, B, and C

$$X_A = \text{mol fraction A} = \frac{\text{mol A}}{\text{mol A} + \text{mol B} + \text{mol C}}$$

• **MOLALITY, m**

$$m \text{ of solute} = \frac{\text{mol solute}}{\text{kilograms solvent}}$$
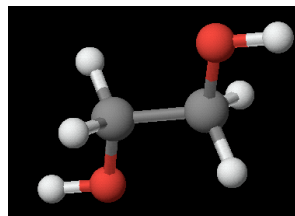
• **WEIGHT %** = grams solute per total g in solution

see Concentration Units Handout

MAR

Calculating Concentrations

Dissolve 62.1 g (1.00 mol) of ethylene glycol in 250. g of H_2O. Calculate mol fraction, molality, and weight % of glycol.

MAR

Calculating Concentrations

Dissolve 62.1 g (1.00 mol) of ethylene glycol in 250. g of H_2O. Calculate X, m, and % of glycol.

250. g H_2O = 13.9 mol

$$X_{\text{glycol}} = \frac{1.00 \text{ mol glycol}}{1.00 \text{ mol glycol} + 13.9 \text{ mol } H_2O}$$

X_{glycol} = 0.0672
X_{water} = 1 - 0.0672 = 0.9328

MAR

Calculating Concentrations

Dissolve 62.1 g (1.00 mol) of ethylene glycol in 250. g of H_2O. Calculate X, m, and % of glycol.

Calculate molality

$$\text{molality} = \frac{1.00 \text{ mol glycol}}{0.250 \text{ kg } H_2O} = 4.00 \text{ m}$$

Calculate weight %

$$\%\text{glycol} = \frac{62.1 \text{ g}}{62.1 \text{ g} + 250. \text{ g}} \times 100\% = 19.9\%$$

%water = 100% - 19.9% = 80.1%

MAR   *see Concentration Units Handout*

M *vs* m, χ and wt%

Converting between molality (m), mole fraction (χ) and weight percent (wt%) relatively straightforward

Molarity (M) = mol solute per *Liter* of *solution*

Converting from m, χ or wt% to molarity (M) requires *solution density* in units of g/mL *or* g/cm³

Recall: **solution = solute + solvent**

MAR

M *vs* m, χ and wt%

***Example:* Convert a 10.7 m aqueous NaOH solution to χ, wt% and M if the solution density = 1.33 g/cm³.**

Solution:
***Assume* 1 kg solvent and 10.7 mol solute**
1 kg water = 1000 g H_2O = 55.5 mol H_2O
10.7 mol NaOH * 40.0 g mol^{-1} = 428 g NaOH

MAR

M *vs* m, χ and wt%

***Example:* Convert a 10.7 m aqueous NaOH solution to χ, wt% and M if the solution density = 1.33 g/cm³.**

χ_{NaOH} = 10.7 / (10.7 + 55.5) = 0.162
wt%$_{NaOH}$ = 428 / (1000 + 428) * 100%
wt%$_{NaOH}$ = 30.0%

You do not need the density of the solution to calculate wt% and χ from molality!

MAR

M *vs* m, χ and wt%

***Example:* Convert a 10.7 m aqueous NaOH solution to χ, wt% and M if the solution density = 1.33 g/cm³.**
If we have 1000 g of solvent (H_2O),
then we have 428 g of solute (NaOH) or
1428 g of solution (NaOH + H_2O)

***Volume of solution* = 1428 g * (cm³ / 1.33 g)**
***Volume of solution* = 1070 mL = 1.07 L**
***Molarity* = 10.7 mol NaOH / 1.07 L solution**
**Molarity NaOH = 10.0 M**

MAR

Parts Per Million (ppm)

Expresses very dilute concentrations; used by environmental chemists, biologists, geologists, etc.

1.0 ppm = 1.0 g of a substance in a sample with a total mass of 1.0 million (10^6) g

Density of water about 1.0 g/mL, units often interconverted

Also parts per thousand (ppt), parts per billion (ppb), etc.

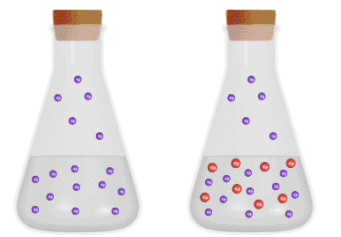Different than the lab parts per thousand, which is a measure of *precision*

Concentration, PPM or mg/L
0   1   10   100   1000   10000

MAR
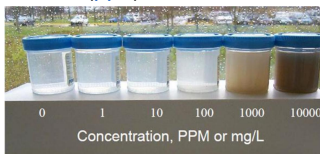
Understanding Colligative Properties

To understand colligative properties, study the LIQUID-VAPOR EQUILIBRIUM for a solution.

The right animation assumes a non-volatile solute

MAR

Understanding Colligative Properties

Vapor Pressure of H_2O over a solution depends on the number of H_2O molecules per solute molecule.

$$P_{solvent} \text{ proportional to } X_{solvent}$$

or

$$P_{solvent} = X_{solvent} \cdot P^o_{solvent}$$

Vapor Pressure of *solvent* over *solution* = (Mol frac solvent)•(VP pure solvent)

RAOULT'S LAW: The vapor pressure of solvent over a solution is always **LOWER** than the pure solvent!

MAR

Raoult's Law

Non-volatile ethylene glycol (62.1 g) is placed in 250. g of water. What is the vapor pressure of water in the solution at 30 °C? (The vapor pressure of pure H_2O is 31.8 mm Hg)

Solution

$X_{glycol} = 0.0672$ and so X_{water} = ?

Because $X_{glycol} + X_{water} = 1$

$X_{water} = 1.000 - 0.0672 = 0.9328$

$P_{water} = X_{water} \cdot P^o_{water} = (0.9328)(31.8 \text{ mm Hg})$

$P_{water} = 29.7 \text{ mm Hg}$

MAR

Raoult's Law

Previous examples assumed a non-volatile solute to calculate vapor pressure. If solute is volatile, then:

$$P_{total} = X_A \cdot P^o_A + X_B \cdot P^o_B + X_C \cdot P^o_C + ...$$

Example: At 25 ˚C, heptane (P^o = 31 torr) and octane (P^o = 11 torr) are mixed such that $X_{heptane}$ = 0.15. Calculate the total vapor pressure of the system.

Solution: This is a **two component** system.

If $X_{heptane}$ = 0.15, *then*

X_{octane} = 1 - 0.15 = **0.85**

MAR

Raoult's Law

Problem: At 25 ˚C, heptane (P^o = 31 torr) and octane (P^o = 11 torr) are mixed such that $X_{heptane}$ = 0.15 and X_{octane} = 0.85. Calculate the total vapor pressure of the system.

Solution: In a **two component** system,

$$P_{total} = X_{hept} \cdot P^o_{hept} + X_{oct} \cdot P^o_{oct}$$
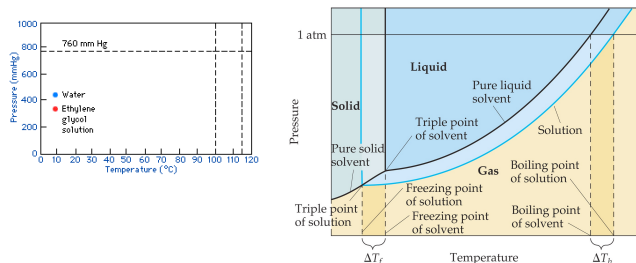
$P_{total} = 0.15 \cdot 31 \text{ torr} + 0.85 \cdot 11 \text{ torr}$

$P_{total} = 4.7 + 9.4 = 14.1 \text{ torr}$

The total vapor pressure in the mixture is 14.1 torr

MAR

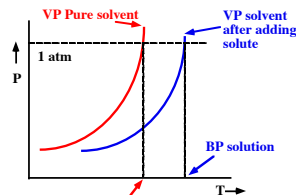## The boiling point of a solution is higher than that of the pure solvent.

MAR

Elevation of Boiling Point

Elevation in BP = ΔT_{BP} = $K_{BP} \cdot m$

(where K_{BP} is characteristic of solvent)

Solvent	Normal Boiling Point (°C)	K_b (°C/m)	Normal Freezing Point (°C)	K_f (°C/m)
Water, H_2O	100.0	0.51	0.0	1.86
Benzene, C_6H_6	80.1	2.53	5.5	5.12
Ethanol, C_2H_5OH	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

MAR

Change in Boiling Point

Dissolve 62.1 g of glycol (1.00 mol) in 250. g of water. What is the BP of the solution?

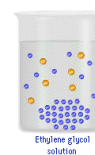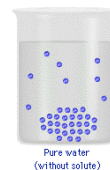K_{BP} = 0.512 ℃/molal for water (see Textbook)

Solution
1. Calculate solution molality = 4.00 m
2. ΔT_{BP} = K_{BP} • m

   ΔT_{BP} = 0.512 ℃/molal (4.00 molal)

   ΔT_{BP} = 2.05 ℃

   BP = 100.00 + 2.05 = 102.05 ℃

MAR

Change in Freezing Point

Pure water   **Ethylene glycol/water solution**

Pure water
(without solute)

Ethylene glycol
solution

The freezing point of a solution is **LOWER** than that of the pure solvent.
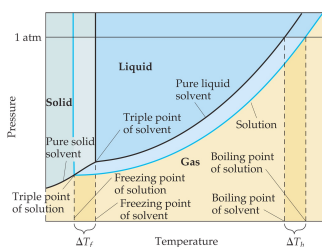
Notice how the animations incorrectly use "dense" ice!

MAR

The freezing point of a solution is lower than that of the pure solvent.

$$FP\ depression = \Delta T_{FP} = K_{FP} \bullet m$$

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_2O	100.0	0.51	0.0	1.86
Benzene, C_6H_6	80.1	2.53	5.5	5.12
Ethanol, C_2H_5OH	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

MAR

Freezing Point Depression

Calculate the FP of a 4.00 molal glycol/water solution.

K_{FP} = 1.86 ℃/molal (from *Textbook*)

Solution

ΔT_{FP} = K_{FP} • m

= (1.86 ℃/molal)(4.00 m)

ΔT_{FP} = 7.44 ℃

So the FP = 0 ˚C - 7.44 ˚C = -7.44 ˚C

**Many textbooks use *negative* K_{FP} values
If using *negative* K_{FP}, ΔT_{FP} is also negative
Concentration (molality) *must* be positive!**

MAR

Freezing Point Depression of Electrolytes

How much **NaCl** must be dissolved in 4.00 kg of water to lower FP to -10.00 ℃?

Solution

Calculate required molality

ΔT_{FP} = K_{FP} • m

(0 - -10.00 ℃) = (1.86 ℃/molal) • m

m = 5.38 molal

*Use -10 ℃ for ΔT if -1.86 ℃/m*

MAR

Freezing Point Depression of Electrolytes

How much NaCl must be dissolved in 4.00 kg of water to lower FP to -10.00 ℃?

Solution

Concentration required = 5.38 molal

This means we need 5.38 mol of dissolved particles per kg of solvent.

Recognize that *m* represents the total concentration of *all* dissolved particles.

Recall that 1 mol NaCl(aq)
--> 1 mol Na^+(aq) + 1 mol Cl^-(aq)... or: 2 mol of particles per 1 mol of ionic solute!

MAR

Freezing Point Depression of Electrolytes

How much NaCl must be dissolved in 4.00 kg of water to lower FP to -10.00 ºC?

Solution

Concentration required = 5.38 molal

We need 5.38 mol of dissolved particles per kg of solvent.

$$NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$$

2 particles per mol NaCl!
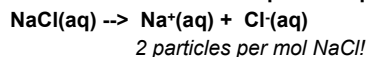
To get 5.38 mol/kg of particles we need

5.38 mol / 2 = 2.69 mol NaCl / kg

2.69 mol NaCl / kg ---> 157 g NaCl / kg

(157 g NaCl / kg)•(4.00 kg) = 629 g NaCl

MAR

Boiling Point Elevation and Freezing Point Depression

$$\Delta T = k \cdot m \cdot i$$

A generally useful equation

i = van't Hoff factor = number of particles produced per formula unit.

Compound	*Theoretical* Value of i
glycol	1
NaCl	2
CaCl$_2$	3

We will use the theoretical value of i in CH 222

MAR

Colligative Properties and Molar Mass

Can use colligative properties to find molar mass of solute

Molar mass = grams solute / moles solute

Example: **Find the molar mass of azulene if 0.640 g are dissolved in 99.0 g of benzene (k$_b$ = 2.53 ˚C/m), and the observed boiling point is 80.230 ˚C.   (normal bp = 80.100 ˚C)**

MM = (grams solute * k)/(ΔT*kg solvent)
useful for both bp and fp calculations

Solution:

$\Delta T = (80.230 - 80.100) = 0.130$ ˚C

$m = \Delta T/k_b = 0.130$ ˚C/2.53 ˚C/m = 5.14*10^{-2} mol / kg

0.0990 kg * 5.14*10^{-2} mol / kg solvent = 5.05*10^{-3} mol

Molar mass = grams solute / moles solute

Molar mass = 0.640 g / 5.05*10^{-3} moles = 127 g mol^{-1}

MAR

Osmosis

Acetic Acid   Water   Corn Syrup

Dissolving the shell in vinegar | Egg in pure water | Egg in corn syrup

MAR

Osmosis

Solvent   Solution
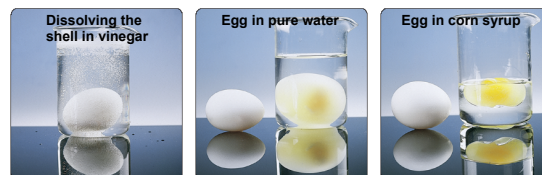
Semipermeable membrane

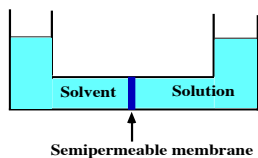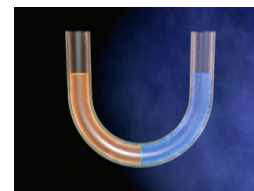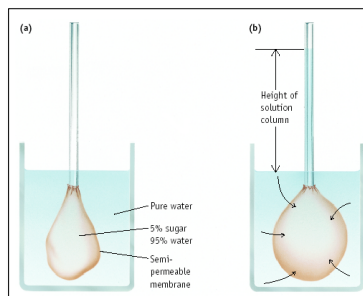**The semipermeable membrane allows only the movement of solvent molecules.**

Solvent molecules move from pure solvent to solution in an attempt to make both have the same concentration of solute.
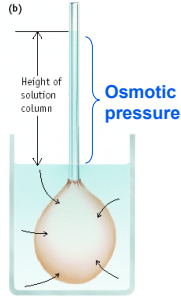
Driving force is entropy (CH 223)

MAR

Process of Osmosis

(a)   (b)

Height of solution column

Pure water

5% sugar 95% water

Semi-permeable membrane

MAR

Osmotic Pressure, ∏

Equilibrium is reached when pressure - the OSMOTIC PRESSURE, ∏ - produced by extra solution counterbalances pressure of solvent molecules moving through the membrane.
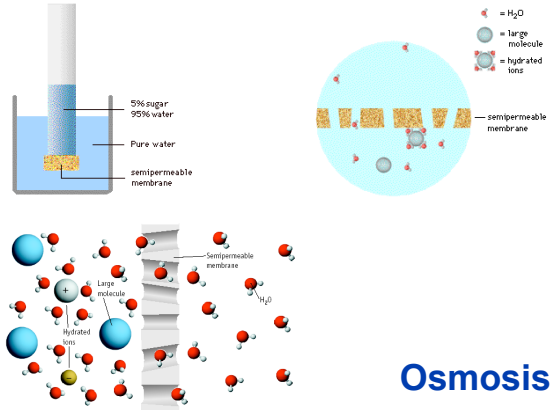
$$\Pi = icRT$$

c = conc. in mol/L
i = the van't Hoff factor
R = 0.082057 (L atm)/(mol K)
T = Kelvin Temp.

MAR

Osmosis

MAR

Osmosis
Calculating a Molar Mass

Dissolve 35.0 g of hemoglobin in enough water to make 1.00 L of solution. π measured to be 10.0 mm Hg at 25 ˚C. Calc. molar mass of hemoglobin.

Solution

(a)   Calc. π in atmospheres

π = 10.0 mm Hg • (1 atm / 760 mm Hg)

π = 0.0132 atm

MAR

Osmosis
Calculating a Molar Mass

Dissolve 35.0 g of hemoglobin in enough water to make 1.00 L of solution. π measured to be 10.0 mm Hg at 25 ˚C. Calc. molar mass of hemoglobin.

Solution

(b)   Calc. concentration from π = cRT

$$\text{Conc} = \frac{0.0132\ \text{atm}}{(0.082057\ \text{L} \bullet \text{atm/K} \bullet \text{mol})(298K)}$$

Conc = 5.40 x 10⁻⁴ mol/L (* 1 L)

(c)   Calc. molar mass
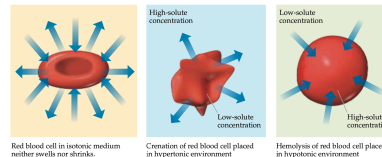Molar mass = 35.0 g / 5.40 x 10⁻⁴ mol
Molar mass = 64,800 g/mol

MAR

Osmosis

Osmosis of solvent from one solution to another can continue until the solutions are
ISOTONIC - they have the same concentration.
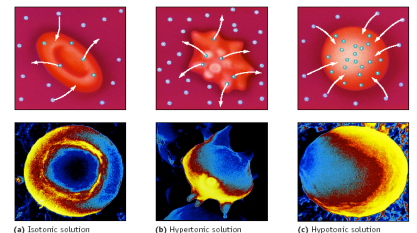
Osmotic pressure important in living systems

MAR

Osmosis & Living Cells

MAR

Reverse Osmosis Water Desalination

> 30 atm pressure

Osmotic membrane

External pressure allows for reverse osmosis

Pure water out

Seawater in

MAR

Water desalination plant
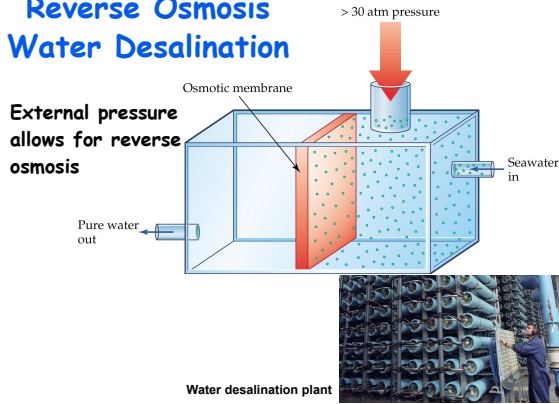
Other Homogeneous Mixtures
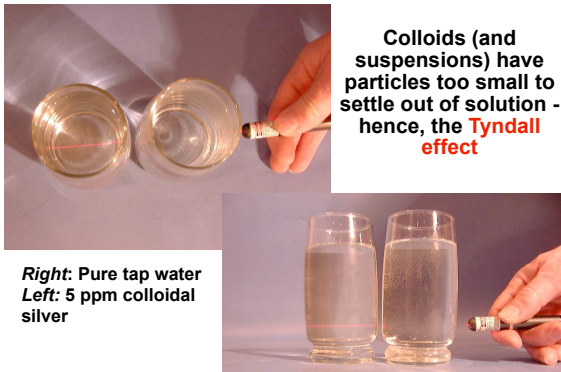
Homogeneous mixtures: more than just solutions!

• **Solutions** - most important, particles in the range 0.2 - 2 nm in diameter (salt water, acids, etc.)

• **Colloids** - a "solution" with particles in the range 2 - 1000 nm (milk, fog, etc.)

• **Suspensions** - contain particles greater than 1000 nm in diameter (blood, paint, aerosol sprays, etc.)
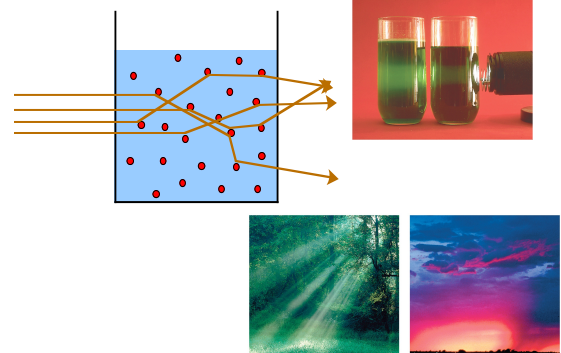
MAR

The Tyndall Effect

Colloids (and suspensions) have particles too small to settle out of solution - hence, the Tyndall effect

Right: Pure tap water
Left: 5 ppm colloidal silver

MAR

The Tyndall Effect

MAR

Colloids

Colloids have a **dispersed phase** ("solute") and a **dispersing medium** ("solvent"). Many types of colloids:

Type	D Medium	D Phase	Examples
aerosol	gas	liquid	fog, clouds
aerosol	gas	solid	smoke, viruses
foam	liquid	gas	shaving cream
emulsion	liquid	liquid	milk, mayonnaise
sol	liquid	solid	mud, paint, ink
foam	solid	gas	foam rubber, sponge
gel	solid	liquid	jelly, cheese, *yogurt*
solid sol	solid	solid	steel, bronze, pearls

MAR

Surfactant Emulsifying Agents

Surfactants (or Surfactant Emulsifying Agents) promote the formation of colloids by coating dispersed phase, preventing the formation of large particles.

Surfactants used for cleaning called **detergents**.

Polar   Polar

MAR
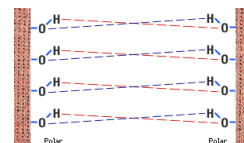
Surfactant Emulsifying Agents

Soaps and detergents: surfactants with both a hydrophobic (nonpolar) and a hydrophilic (polar) end. Can remove nonpolar oils *and* polar compounds.
Soaps often grouped in **micelles** with like-polarities grouped together.
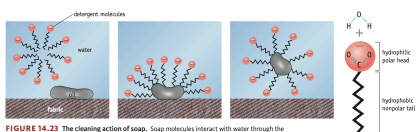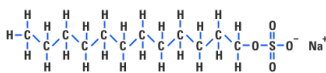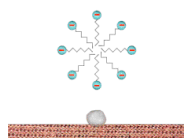

FIGURE 14.23 The cleaning action of soap. Soap molecules interact with water through the charged, hydrophilic end of the molecule. The long, hydrocarbon end of the molecule is hydrophobic, but it can bind through dispersion forces with hydrocarbons and other nonpolar substances.
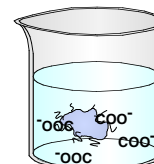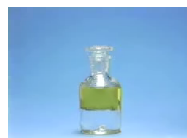
MAR

Oil and Water

Oil and **water** do not mix due to differences in polarity; water *excludes* oil due to stronger intermolecular forces**
Soap removes oil readily using nonpolar end of micelle**

MAR

when someone asks you to elevate the boiling point

See:
- *Chapter Eleven Study Guide*
- *Chapter Eleven Concept Guide*
- *Important Equations (following this slide)*
- *End of Chapter Problems (following this slide)*

MAR

End of Chapter 11

© Mark Parisi, Permission required for use.

MAR

Important Equations, Constants, and Handouts from this Chapter:

- **solution = solute + solvent**
- **see Concentration Units Handout**

Solution Concentrations:

$$Molarity\ (M) = \frac{mol\ Solute}{L\ Solution}$$

$$molality(m) = \frac{mol\ Solute}{kg\ Solvent}$$

$$weight\ \% = \frac{mass\ Solute}{Total\ mass}$$

$$mole\ fraction\ (\chi) = \frac{mol\ A}{total\ mol}$$

$$ppm = \frac{1.0\ g\ of\ substance}{1.0\ million\ g\ sample}$$

Henry's Law:

$$S_g = k \bullet P_g$$

Raoult's Law / Vapor Pressure Depression:

$$P_{solvent} = \chi_{solvent} \bullet P^o_{solvent}$$

Boiling Point Elevation / Freezing Point Depression:

$$\Delta T_{BP/FP} = K_{BP/FP} \bullet \left(\frac{mol\ Solute}{kg\ Solvent}\right) \bullet i$$

Osmosis:

$$\pi = i\left(\frac{mol\ Solute}{L\ Solvent}\right)RT$$

R = 0.082057 L atm mol⁻¹ K⁻¹
i = van't Hoff factor

MAR

End of Chapter Problems: *Test Yourself*

1. Fill in the blanks in the table. All solutions are aqueous.

Compound	Molality	Weight Percent	Mole Fraction
NaI	0.15	____	____
C_2H_5OH	____	5	____
$C_{12}H_{22}O_{11}$	____	____	0.0027

2. Hydrochloric acid is sold as a concentrated aqueous solution. If the molarity of commercial HCl is 12.0 and its density is 1.18 g/cm3, calculate the molality and the weight percent of HCl in the solution.
3. A soda can has an aqueous CO_2 concentration of 0.0506 M. What is the pressure of CO_2 gas in the can? (k_H = 4.48 x 10⁻⁵ M/mm Hg)
4. Pure nonvolatile iodine (105 g) is dissolved in 325 g of CCl_4 at 65 °C. Given that the vapor pressure of CCl_4 at this temperature is 531 mm Hg, what is the vapor pressure of the solution at 65 °C?
5. What is the boiling point of a solution composed of 15.0 g of $CHCl_3$ (which boils at 61.70 °C) and 0.515 g of the nonvolatile solute acenaphthene, $C_{12}H_{10}$?
6. An aqueous solution containing 1.00 g of bovine insulin (a protein, not ionized) per liter has an osmotic pressure of 3.1 mm Hg at 25 °C. Calculate the molar mass of bovine insulin.

MAR

End of Chapter Problems: *Answers*

1. Completed table:

Compound	Molality	Weight percent	Mole fraction
NaI	0.15	2.20	.0027
C_2H_5OH	1.1	5.00	.020
$C_{12}H_{22}O_{11}$	0.15	4.90	.0027

2. 16.2 m, 37.1%
3. 1130 mm Hg
4. 444 mm Hg
5. 62.51 °C
6. 6.0 x 10³ g/mol

MAR