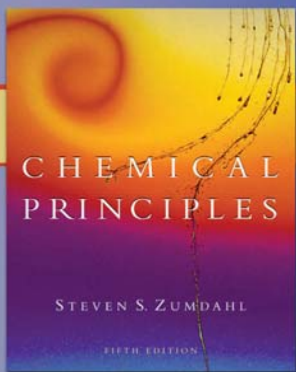



# CHAPTER SEVENTEEN(a)

## Properties of Solutions

**TABLE 17.1** Various Types of Solutions

| Example | State of Solution | State of Solute | State of Solvent |
|---|---|---|---|
| Air, natural gas | Gas | Gas | Gas |
| Vodka in water, antifreeze | Liquid | Liquid | Liquid |
| Brass, steel | Solid | Solid | Solid |
| Carbonated water (soda) | Liquid | Gas | Liquid |
| Seawater, sugar solution | Liquid | Solid | Liquid |
| Hydrogen in platinum | Solid | Gas | Solid |

## Figure 17.1: The formation of a liquid solution can be divided into three steps

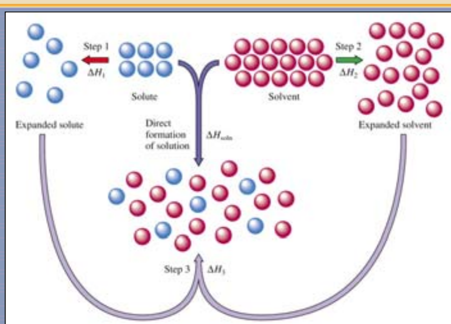
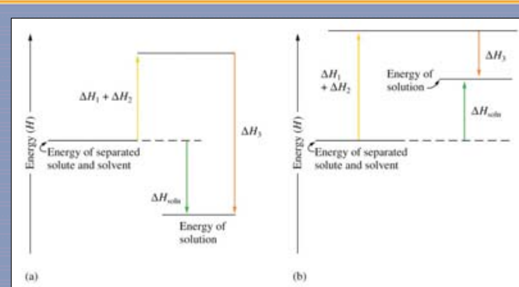


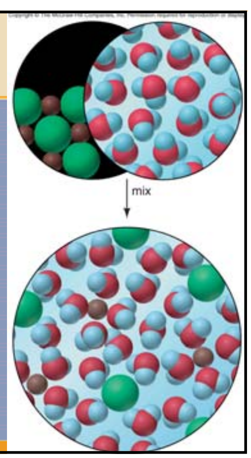

 

Figure 17.2: (a) Enthalpy of solution $\Delta H_{soln}$ has a negative sign (the process is exothermic) if Step 3 releases more energy than is required by Steps 1 and 2. (b) $\Delta H_{soln}$ has a positive sign (the process is endothermic) if Stpes 1 and 2 require more energy than is released in Step 3.



Entropy Usually Favors Making Solutions Because There Are More Possible Arrangements of the Atoms or Molecules






Concentration

Molarity =
Moles of solute/Liters of Solution (M)

Molality =
Moles of solute/Kg of Solvent (m)

Mole Fraction=
Moles solute/total number of moles

Mass %=
Mass solute/total mass x 100

Concentration

Molarity =
Moles of solute/Liters of Solution (M)

Molality =
Moles of solute/Kg of Solvent (m)

Mole Fraction=
Moles solute/total number of moles

Mass %=
Mass solute/total mass x 100

 17a–7

Concentration

Molarity =
Moles of solute/Liters of Solution (M)

Molality =
Moles of solute/Kg of Solvent (m)

Mole Fraction=
Moles solute/total number of moles

Mass %=
Mass solute/total mass x 100

 17a–8

A sample of $NaNO_3$ weighing 8.5 grams is placed in a 500 ml volumetric flask and distilled water was added to the mark on the neck of the flask. Calculate the Molarity of the resulting solution.

Convert the given grams of solute to moles of solute :

$$8.5 \text{ g } NaNO_3 \frac{1 \text{ mole } NaNO_3}{85 \text{ g } NaNO_3} = 0.1 \text{ mole } NaNO_3$$

Convert given ml of solution to liters

$$500 \text{ ml} \frac{1 \text{ liter}}{1000 \text{ ml}} = 0.5 \text{ liter}$$

Apply the definition for Molarity: Molarity = moles $NaNO_3$ / volume of the solution in liters

M = 0.1 mole / .500 liters = <u>0.200 Molar $NaNO_3$</u>

 17a–9

Molarity =
Moles of solute/Liters of Solution (M)

Molality =
Moles of solute/Kg of Solvent (m)

Mole Fraction=
Moles solute/total number of moles

Mass %=
Mass solute/total mass x 100

 17a–10

Molarity =
Moles of solute/Liters of Solution (M)

Molality =
Moles of solute/Kg of Solvent (m)

Mole Fraction=
Moles solute/total number of moles

Mass %=
Mass solute/total mass x 100

 17a–11

**Determine the mole fraction of KCl in 3000 grams of aqueous solution containing 37.3 grams of Potassium Chloride KCl.**

1. **Convert grams KCl to moles KCl using the molecular weight of KCl**

$$37.3 \text{ g KCl} \frac{1 \text{ mole KCl}}{74.6 \text{ g KCl}} = 0.5 \text{ mole KCl}$$

2. **Determine the grams of pure solvent water from the given grams of solution and solute**

**Total grams = 3000 grams = Mass of solute + Mass of water**
**Mass of pure solvent = (3000 - 37.3) gram**
**= 2962.7** gram

 17a–12

**Determine the mole fraction of KCl in 3000 grams of aqueous solution containing 37.3 grams of Potassium Chloride KCl.**

**3. Convert grams of solvent $H_2O$ to mols**

$$(2962.7 \text{ grams water}) \frac{1 \text{ mol}}{18.0 \text{ grams}} = 164.6 \text{ mols } H_2O$$

**4. Apply the definition for mole fraction mole fraction = moles of KCl / Total mols of KCl and water =**
**0.5 / (0.5 + 164.6) = 0.5 / 165.1 = <u>0.00303</u>**




**Assuming the density of water to be 1 g/mL we approximate the density of a dilute aqueous solution to be 1 g/mL**

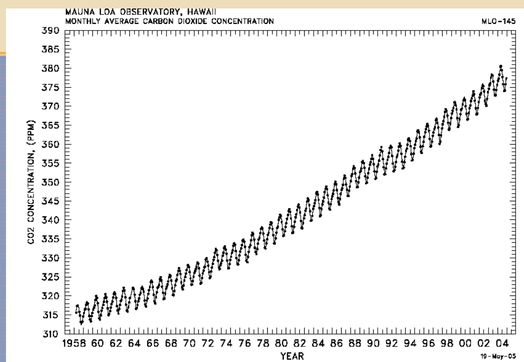
$$1 \text{ ppm} = \frac{1 \mu g}{1 \text{ g}}$$

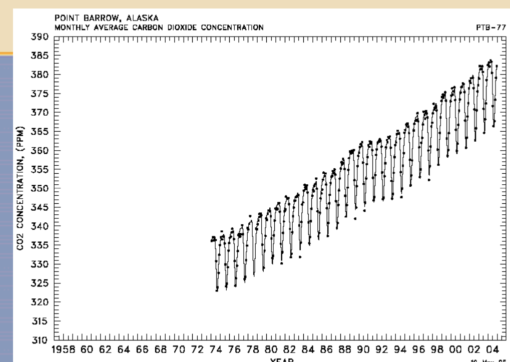
$$= \frac{1 \mu g}{1 \text{ g}} \frac{1 \text{ g}}{1 \text{ ml}} = \frac{1 \mu g}{1 \text{ ml}}$$

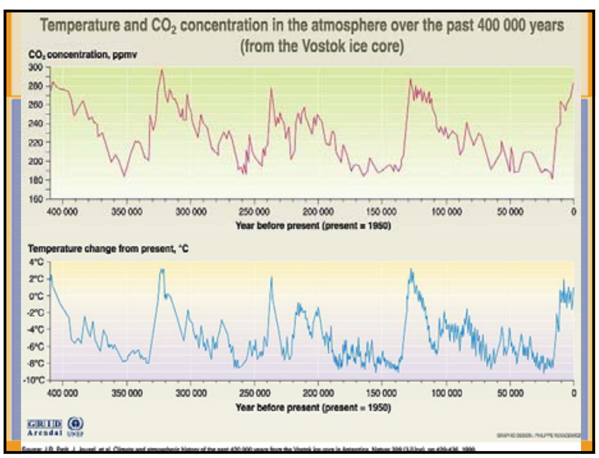
**→ 1 ppm = 1 μg/mL = 1 mg/L**

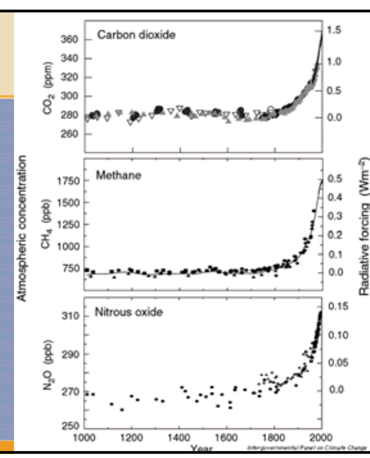
**→ 1 ppb = 1 ng/mL = 1 μg/L**



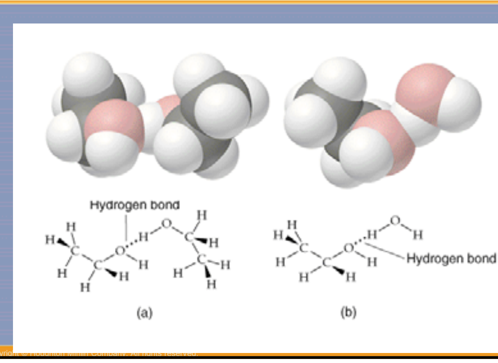



## *Factors Affecting Solubility*
**Solute-Solvent** Interactions

- Polar liquids tend to dissolve in polar solvents.
- Miscible liquids: mix in any proportions.
- Immiscible liquids: do not mix.
- Intermolecular forces are important: water and ethanol are miscible because the broken hydrogen bonds in both pure liquids are re-established in the mixture.
- The number of carbon atoms in a chain affect solubility: the more C atoms the less soluble in water.



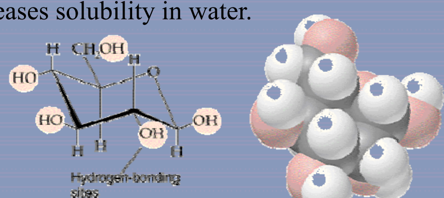
## *Factors Affecting Solubility*
**Solute-Solvent** Interactions






## *Factors Affecting Solubility*
**Solute-Solvent** Interactions

- The number of -OH groups within a molecule increases solubility in water.



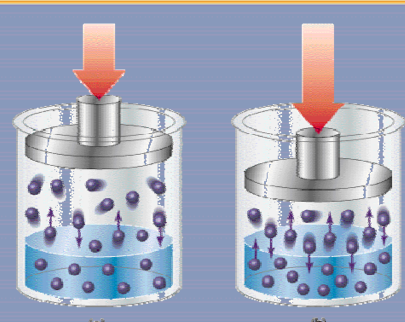



## *Factors Affecting Solubility*
**Solute-Solvent** Interactions

- Generalization: "like dissolves like".
- The more polar bonds in the molecule, the better it dissolves in a polar solvent.
- The less polar the molecule the less it dissolves in a polar solvent and the better is dissolves in a non-polar solvent.
- Network solids do not dissolve because the strong intermolecular forces in the solid are not re-established in any solution.



## *Factors Affecting Solubility*
**Gas – solvent:** Pressure Effects





## *Factors Affecting Solubility*
**Gas – solvent:** Pressure Effects

- Solubility of a gas in a liquid is a function of the pressure of the gas.
- The higher the pressure, the more molecules of gas are close to the solvent and the greater the chance of a gas molecule striking the surface and entering the solution.
  - Therefore, the higher the pressure, the greater the solubility.
  - The lower the pressure, the fewer molecules of gas are close to the solvent and the lower the solubility.

## *Factors Affecting Solubility*
### Gas – solvent: Pressure Effects

**Henry's Law:** $C_g = kP_g$

$C_g$ *is* the solubility of gas, $P_g$ the partial pressure, $k$ = Henry's law constant.

Carbonated beverages are bottled under > 1 atm. As the bottle is opened, $P_g$ decreases and the solubility of $CO_2$ decreases. Therefore, bubbles of $CO_2$ escape from solution.




### Gas – solvent: Pressure Effects

$CO_2(g) + H_2O \rightleftharpoons H_2CO_3(aq)$

$K_H = \frac{[H_2CO_3]}{[CO_2][H_2O]} = \frac{[H_2CO_3]}{P_{CO_2}}$

[NB: → $[H_2CO_3] = K_H \cdot P_{CO_2}$ solubility]

$K_H = 3.4 \times 10^{-2} \frac{mol}{1.\ atm}$

→ at 350 ppb: $[H_2CO_3] = (3.4 \times 10^{-2}) \times (0.00035) = 1.2 \times 10^{-5} \frac{mol}{liter}$




### Gas – solvent: Pressure Effects

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.5 \times 10^{-7}$

$= \frac{x^2}{1.2 \times 10^{-5}}$

→ $x = [H^+] = 2.3 \times 10^{-6}$ mol/liter

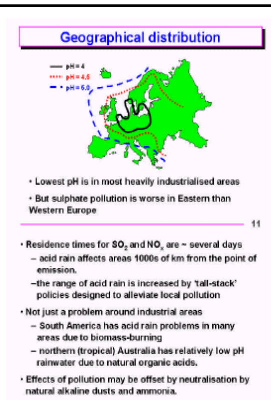
→ $pH = -\log[H^+] = 5.6$




### dissolution of $SO_2$ and $NO_x$ → ACID RAIN

$CaCO_3(s) + H^+ \rightarrow CO_2(g) + H_2O + Ca^{2+}$







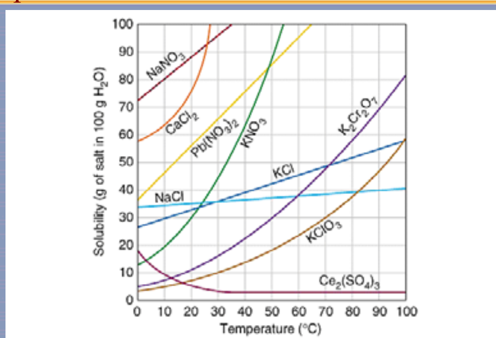
## *Factors Affecting Solubility*
### Temperature Effects

Experience tells us that sugar dissolves better in warm water than cold, but Coca Cola goes flat when warm.

- As temperature increases, solubility of **solids** generally *increases*.
- As temperature increases, solubility of **gasses** generally *decreases*.

## *Factors Affecting Solubility*

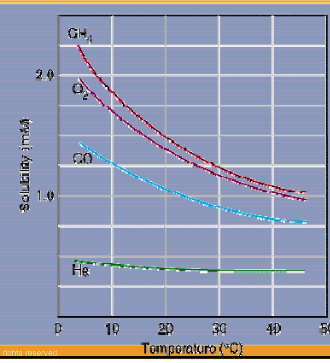
Temperature Effects: solids




 17a-31

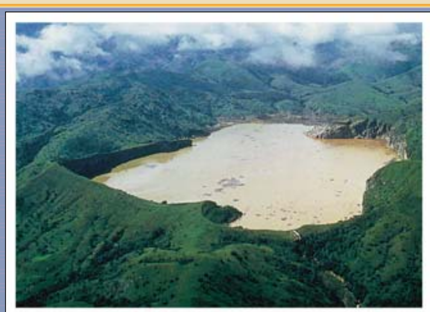
## *Factors Affecting Solubility*

Temperature Effects: gasses




 17a-32

## Lake Nyos in Cameroon



***Source:*** Corbis

 17a-33

## Thermodynamics of Solubility

**ΔG = ΔH - TΔS**

Solubility increases if ΔG becomes more negative .

When ΔS is positive, ΔG becomes more negative when T increases.
Solubility will increase when T increases.

When ΔS is negative, ΔG becomes more positive when T increases.
Solubility will decrease when T increases.

**Compare**

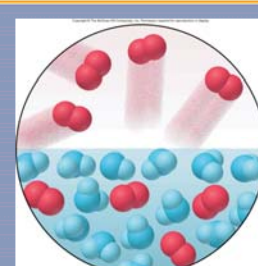
| | |
|---|---|
| KCl(s) → $K^+$ (aq) + $Cl^-$ (aq) | ΔS positive - ΔG ↓ |
| gas → liquid | ΔS negative - ΔG ↑ |

## Thermodynamics of Solubility

 17a-35

## Temperature Dependence of Gas Solubility

- ΔG = ΔH - TΔS
- gas→solution
- ΔS is negative
- ΔH is negative
- -TΔS is positive
- ΔG becomes more positive when T increases
- Therefore, solubility decreases



$C_g = kP_g$

Henry's Law Constant Depends on T

 17a-36

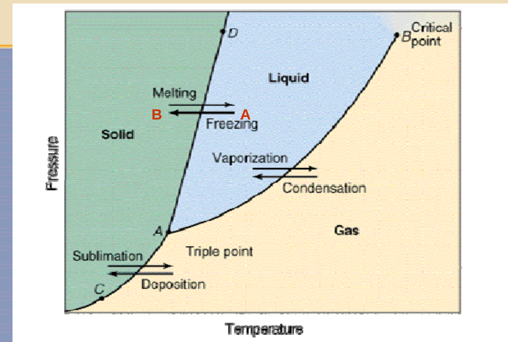
## *Factors Affecting Solubility*

Temperature Effects

- Gases are less soluble at higher temperatures.
- Thermal pollution: if lakes get too warm, $CO_2$ and $O_2$ become less soluble and are not available for plants or animals.
- In global warming modeling, $CO_2$ may be released from the oceans

 17a–37

### Thermodynamics of Phase Changes



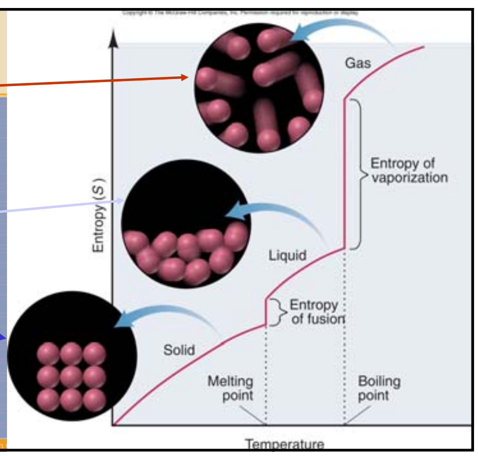

Why does a liquid at A form a solid when the temperature is lowered to B

 17a–38

Gases: Large Entropy

Liquid: Smaller Entropy

Solids: Smallest Entropy




### Thermodynamics for Phase Change

$\Delta G = \Delta H - T\Delta S$

$\Delta G$: Negative for spontaneous process; $\Delta H$: Negative for liquid to solid; $-T\Delta S$: Positive for liquid to solid

- liquid→solid
- $\Delta H$ is negative (stronger intramolecular forces)
- $\Delta S$ is negative (more order)
- $-T\Delta S$ is positive
- As T decreases, $-T\Delta S$ becomes smaller
- $\Delta G$ goes to zero when $\Delta H = T\Delta S$ (at $T = T_{fusion}$)
- For T less than $T_{fusion}$, $\Delta G$ is negative, solid is stable.

## *Colligative Properties*

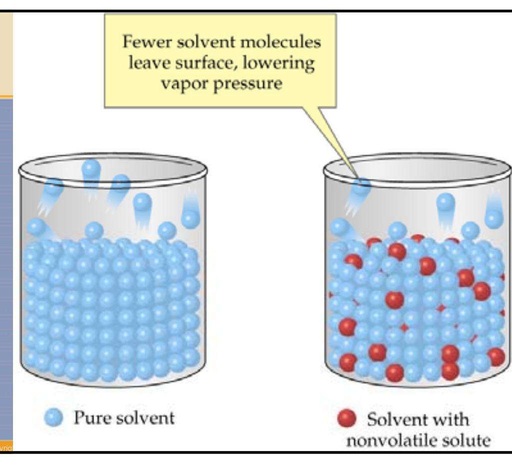
- **Colligative properties depend on quantity of solute molecules.**

*(E.g. freezing point depression and boiling point elevation.)*

.

*NB: quantity is what? Mass? Volume? Number?*

 17a–41



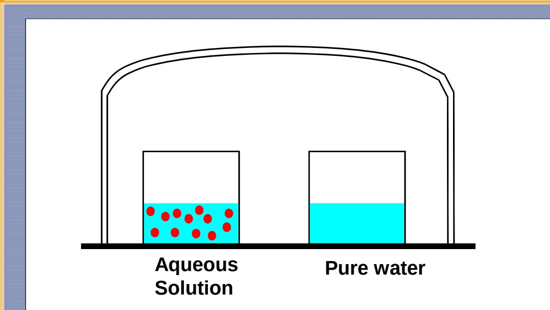
## *Colligative Properties*
Lowering the Vapor Pressure

- Non-volatile solvents reduce the ability of the surface solvent molecules to escape the liquid.
- Therefore, vapor pressure is lowered.
- The amount of vapor pressure lowering depends on the amount of solute.

*(mass, number, volume, what?)*

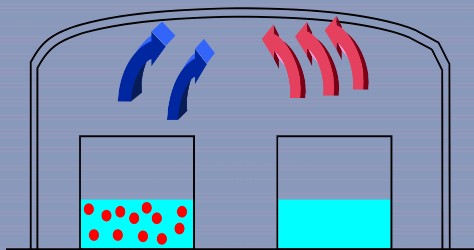
 17a–43

## Question of the Day
What happens?



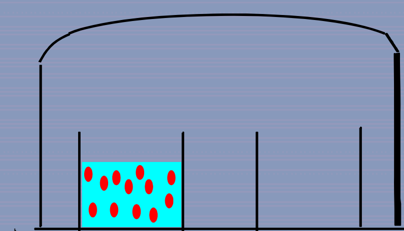

 17a–44

The vapor pressure of pure water is greater than the vapor pressure of the solution



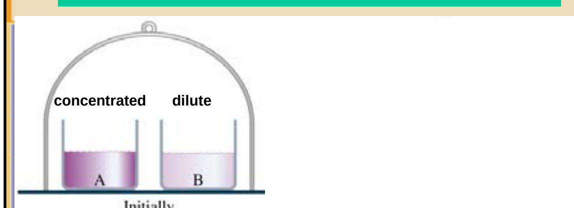

 17a–45

Water condenses in the solution because the vapor pressure in the chamber is greater than the equilibrium vapor pressure of the solution




 17a–46

## An Interesting Phenomenon



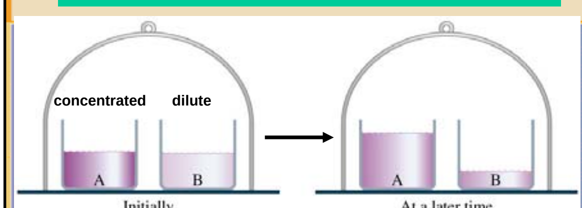

Vapor pressures for A and B are unequal

Vapor pressure is a colligative property: It depends on the amount of solute

Which has the lower vapor pressure?

 17a–47

## An Interesting Phenomenon




After a time, the levels are unequal.

•What conditions exist when the equilibrium point is reached and no further change in the volumes occurs?

 17a–48

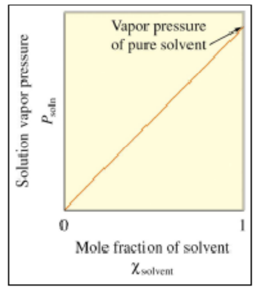
## Raoult's Law

- Raoult's Law:
  $P_A$ is the vapor pressure of A with solute
  $P_A°$ is the vapor pressure of A alone
  $X_A$ is the mole fraction of A

$$P_A = X_A P_A^o$$




**For a solution that obeys Raoult's law, a plot of $P_{soln}$ versus $x_{solvent}$ yields a straight line.**




$y = mx + b;\ b = 0$

$y = P_{soln}$
$x = x_{solvent}$
$m = P°_{solvent}$

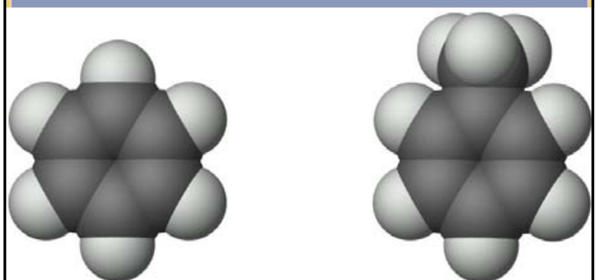


## Raoult's Law for two liquids

$$P_{Total} = X_A P_A^o + X_B P_B^o$$



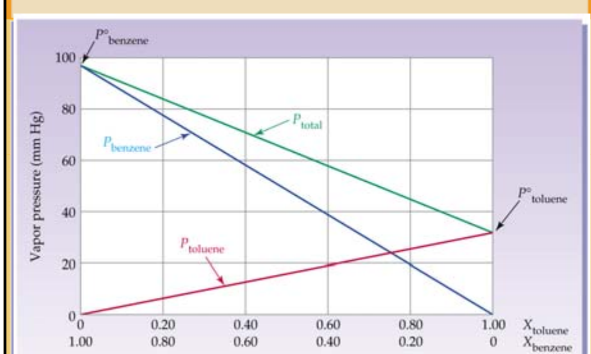

## Example of a Near-Ideal Solution



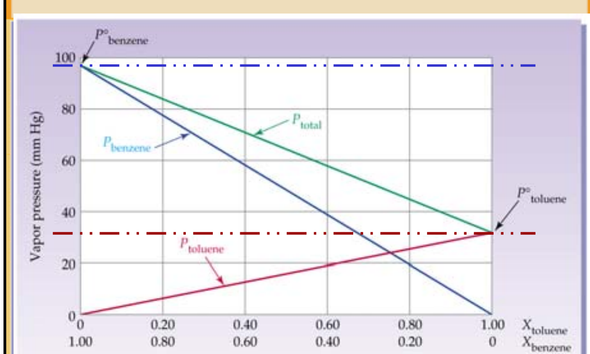
Benzene, $C_6H_6$    Toluene, $C_6H_5CH_3$



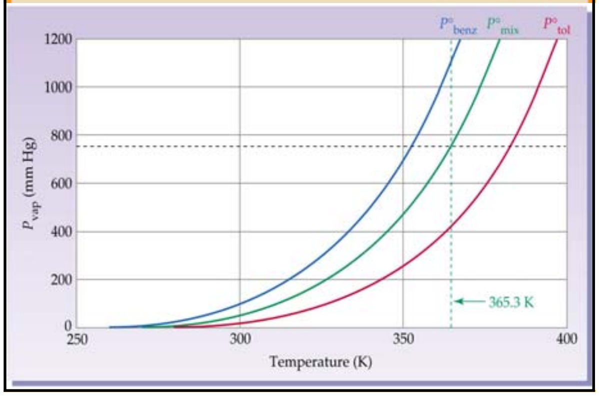

## Benzene and Toluene




## Benzene and Toluene



## Vapor Pressure of Benzene-Toluene




## Calculation of Vapor Composition

(50/50 mix of boiling benzene and toluene)

- $P^o$ toluene = 38 Torr; $P^o$ benzene = 92 Torr
- Take $X_b = X_t = 0.50$
- $P_A = X_A P_A^o$ Raoult's Law
- $P_b$ = (92 Torr)(0.5)=46 Torr;
- $P_t$ =(38 Torr)(0.5)=19 Torr
- $P_{total}$ = 46 + 19 = 65 Torr

---

- What is the composition above the solution?

## Calculation of Vapor Composition

(50/50 mix of boiling benzene and toluene)

- $P^o$ toluene = 38 Torr; $P^o$ benzene = 92 Torr
- Take $X_b = X_t = 0.50$
- $P_A = X_A P_A^o$ Raoult's Law
- $P_b$ = (92 Torr)(0.5)=46 Torr;
- $P_t$ =(38 Torr)(0.5)=19 Torr
- $P_{total}$ = 46 + 19 = 65 Torr

---

- $X_A^{vap} = P_A / P_{tot}$
- $X_b^{vap}$ = 46 Torr/65 Torr = 0.71
- $X_t^{vap}$ = 1.00 – 0.71 = 0.29

## Liquid and Vapor Composition Differ

$X_b^{vap} = 0.71$ $X_t^{vap} = 0.29$

Vapor above Boiling Liquid

$X_b = 0.50$ $X_t = 0.50$

$P_b^o = 92$ Torr $P_t^o = 38$ Torr

Liquid at Boiling Point

 17a–58

## Raoult's Law

- Ideal solution: one that obeys Raoult's law.
- Raoult's law breaks down when the solvent-solvent and solute-solute intermolecular forces differ from solute-solvent intermolecular forces.

 17a–59

## Example of a non-ideal solution


50 ml ethanol

\+

50 ml water

95 ml solution

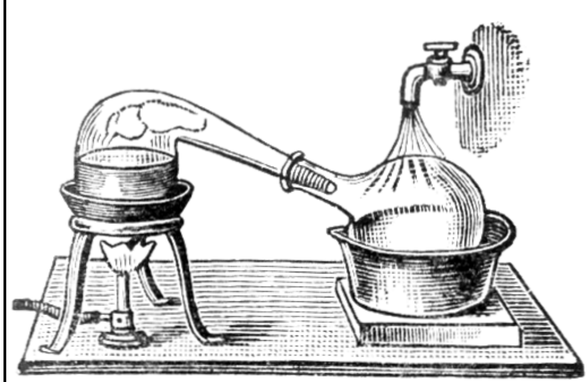
Volumes are not additive

17a–60

## A Distillation Apparatus


2 volatile components

Apply Raoult's Law



**Abu Musa Jabir ibn Hayyan**

(جابر بن حيا)

## A Problem

- 20 g of an unknown solid is dissolved in 125 g of water at 25°C. What is the molecular weight of the solid if the observed vapor pressure was 21.72 torr and pure water usually has a vapor pressure of 23.76 torr at this temperature?

## The Solution

- $P_{tot} = \chi_{H_2O} P_{H_2O}$
- $\chi_{H_2O} = P_{soln} / P_{H_2O} = 21.72/23.76 = 0.9141$

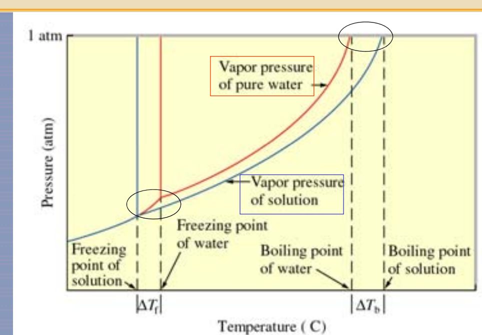
$\chi_{H_2O}$ = mol $H_2O$/(mol $H_2O$ + mol unknown)

$$0.9141 = \frac{125\text{ g}/(18\text{ g/mol }H_2O)}{125\text{ g}/(18\text{ g/mol }H_2O) + 20\text{ g}/(X\text{ g/mol})}$$

**X = 30.87 g/mol**

## *Colligative Properties*

Boiling-Point Elevation and Freezing-Point Depression



## *Colligative Properties*
Boiling-Point Elevation

Molal boiling-point-elevation constant, $K_b$, expresses how much $\Delta T_b$ changes with **molality**, *m*:

$$\Delta T_b = K_b m$$

 17a–67

## *Colligative Properties*
Freezing-Point Depression

- Decrease in freezing point ($\Delta T_f$) is directly proportional to **molality** ($K_f$ is the molal freezing-point-depression constant):

$$\Delta T_f = K_f m$$

 17a–68

## Problem:

- A 0.0182-g sample of an unknown substance is dissolved in 2.135 g of benzene.
- The solution freezes at 5.14 °C instead of at 5.50 °C for pure benzene.
- $K_f$ (benzene) = 5.12 °C kg/mol
- What is the molecular weight of the unknown substance?

 17a–69

## Solution:
Freezing point depression → molality

$\Delta T_f = (5.50\text{-}5.14) = 0.36$ °C

- $\Delta T_f = K_f\, m$
- M = 0.36 °C / (5.12 °C kg/mol) = 0.070 m

 17a–70

## Solution:

- Find the moles of unknown solute from the definition of molality:
- $Mol_{solute}$ = m x kg solvent

$$= \frac{0.070\text{ mol}}{1\text{ kg solvent}} \times 0.002135\text{ kg solvent}$$

$$= 1.5 \times 10^{-4}\text{ mol}$$

 17a–71

## Solution:

$$\text{Molar mass} = \frac{0.0182\text{ g}}{1.5 \times 10^{-4}\text{ mol}} = 1.2 \times 10^{2}\text{ g/mol}$$

(molecular weight = $1.2 \times 10^2$ g/mol)

 17a–72

## FPD And BPE Constants

**TABLE 12.2 Molal Freezing Point Depression and Molal Boiling Point Elevation Constants**

| Solvent | Normal Freezing Point, °C | $K_f$, °C $m^{-1}$ | Normal Boiling Point, °C | $K_b$, °C $m^{-1}$ |
|---|---|---|---|---|
| Acetic acid | 16.63 | 3.90 | 117.90 | 3.07 |
| Benzene | 5.53 | 5.12 | 80.10 | 2.53 |
| Cyclohexane | 6.55 | 20.0 | 80.74 | 2.79 |
| Nitrobenzene | 5.8 | 8.1 | 210.8 | 5.24 |
| Water | 0.00 | 1.86 | 100.00 | 0.512 |

*NB: PROPERTY OF THE SOLVENT (NOT OF THE SOLUTE)*



## Colligative Properties of Ionic Solutions

- For solutes that are electrolytes, we must rewrite the formulas for boiling-point elevation and freezing-point depression.

[redacted]

- Here *i* is the number of ions resulting from each formula unit of the solute.



## Discrepancy between real and ideal Van't Hoff (i)

Consider:

$AlCl_3 \rightarrow Al^{+3} + 3\,Cl^-$

ideal i = 4 since four particle but in actuality

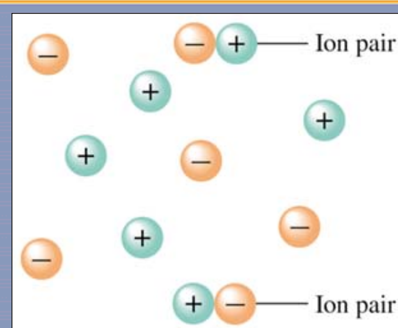
real i = 3.2

The reason measured value (3.2) is lower than ideal: Strong electrostatic attraction between oppositely charged ions causes some of the ions to be held together through ion-pair.

Van't Hoff factor follows ideal value best when the concentration is very small. Large deviation from Van't Hoff factor with very large concentration.



## Figure 17.21: In a aqueous solution a few ions aggregate, forming ion pairs that behave as a unit.






## Van't Hoff factor (i)

Factor which accounts for deviation of colligative property due to electrolytic nature of solute

Van't Hoff Factor (i)

Can be measured by

$$i = \frac{\text{measured colligative property (from Expt)}}{\text{Expected value if solute were nonelectrolyte}}$$

a) Typical non-electrolyte i.e., urea, sucrose, glucose :van't Hoff, i = 1.

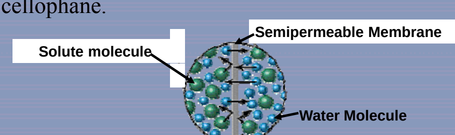
b) For electrolytic solute:

| Electrolyte | ideal (i) | measured (i) |
|---|---|---|
| NaCl | 2 | 1.9 |
| $HIO_3$ | 2 | 1.7 |
| $MgCl_2$ | 3 | 2.7 |
| $AlCl_3$ | 4 | 3.2 |



## Osmosis

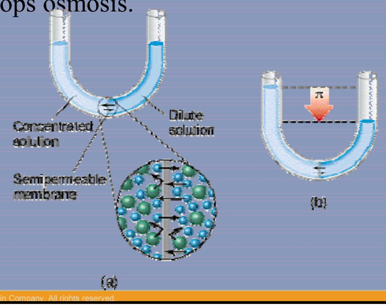
- Semipermeable membrane: permits passage of some components of a solution. Example: cell membranes and cellophane.




- Osmosis: the movement of a solvent from low solute concentration to high solute concentration.
- There is movement in both directions across a semipermeable membrane.
- As solvent moves across the membrane, the fluid levels in the arms becomes uneven – their concentrations even.

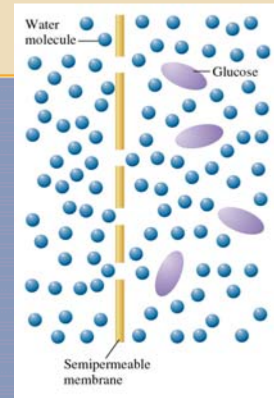
## *Colligative Properties*
### Osmosis

- Eventually the pressure difference between the arms stops osmosis.



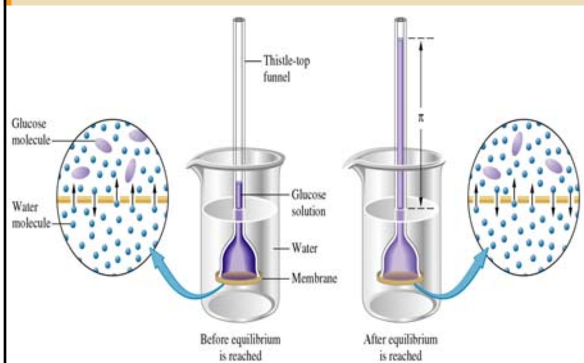

 17a–79

A semipermeable membrane separating water and an aqueous solution of glucose.



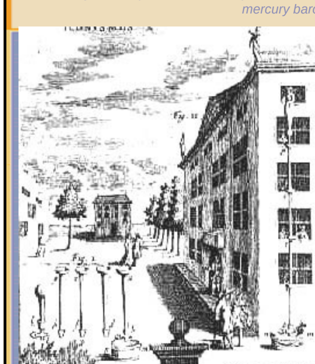

 17a–80

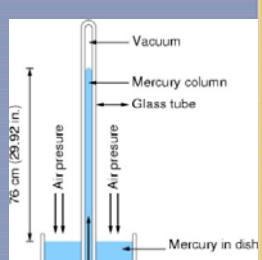
## An experiment in osmosis.




 17a–81


*Water in Torricelli's water barometer, located to the right of the building corner, rose to a height of over thirty- four feet and was topped by a dummy that moved up and down with changes in air pressure. Mercury is raised to a height of only about thirty inches in a mercury barometer.*






 17a–83

## Osmosis

- Osmotic pressure, π, is the pressure required to stop osmosis:

$$\pi = MRT$$

Π = osmotic pressure   M = Molarity (mol/L)

R = Ideal Gas Constant   T = Temperature (K)

 17a–84

## Osmotic Pressure is a VERY sensitive measure of Molarity

Seawater contains 3.4 g NaCl per liter

M = 3.4 g/58.5 g/L = 0.0582 M

$\Pi$ =(0.0582 mol/L)(0.0821L atm/mol K )(298K)

$\Pi$ = 1.42 atm

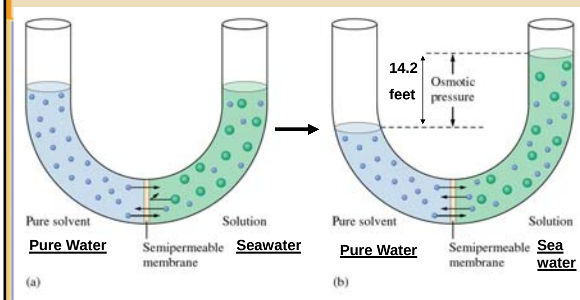
1 atm supports column of water 10.34 m length

(0.42 atm)(10.34 m/atm) = 4.34 m

(4.34 m)(3.28 ft/m) ~ 14.2 feet

 17a–85

## Pure solvent/solution

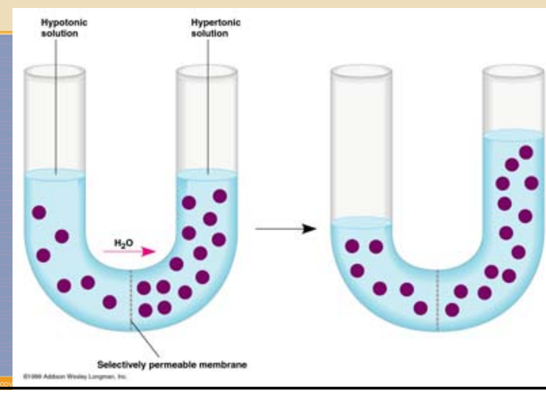



 17a–86

## Tonicity is a relative term

- **Hypotonic Solution - One solution has a lower concentration of solute than another.**
- **Hypertonic Solution - one solution has a higher concentration of solute than another.**
- **Isotonic Solution - both solutions have same concentrations of solute.**

 17a–87




## Osmosis

- Crenation:
  - red blood cells placed in <u>hypertonic</u> solution (relative to intracellular solution);
  - there is a <u>higher</u> solute concentration in the surrounding tissue than in the cell ;
  - osmosis occurs and water passes through the membrane <u>out of</u> the cell.
  - The cell shrivels up.

 17a–89

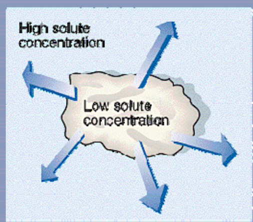
## Osmosis

- Hemolysis:
  - red blood cells placed in a <u>hypotonic</u> solution;
  - there is a <u>lower</u> solute concentration outside the cell;
  - osmosis occurs and water moves <u>into</u> the cell.
  - The cell bursts.
- To prevent crenation or hemolysis, IV (intravenous) solutions must be isotonic.

 17a–90

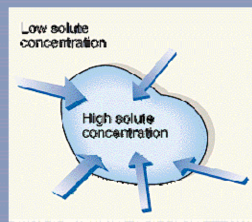
## Osmosis

Crenation Hemolysis:




Hypertonic solution

Larger Π

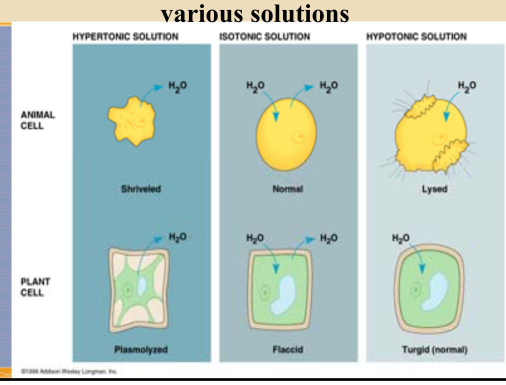



Hypotonic Solution

Smaller Π

 17a–91

## Plant and Animal Cells put into various solutions




17a–92

## Crenation of Red Blood Cells, Electron Micrograph

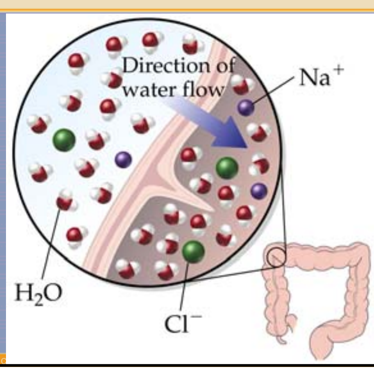
17a–93

## Osmosis

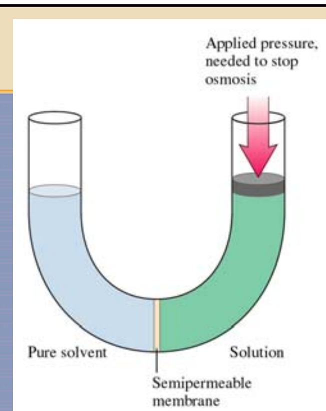
- Examples of osmosis:
  - Cucumber placed in NaCl solution loses water to shrivel up and become a pickle.
  - Limp carrot placed in water becomes firm because water enters via osmosis.
  - Salty food causes retention of water and swelling of tissues (edema).
  - Water moves into plants through osmosis.
  - Salt added to meat or sugar to fruit prevents bacterial infection (a bacterium placed on the salt will lose water through osmosis and die).

 17a–94

## Drinking Seawater will Cause Dehydration of Body Tissues

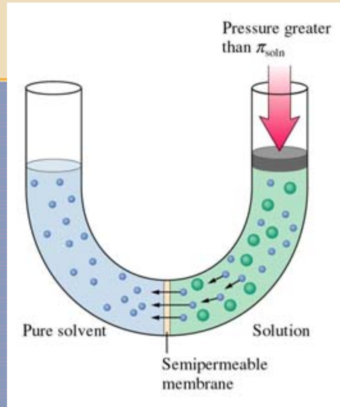



17a–95



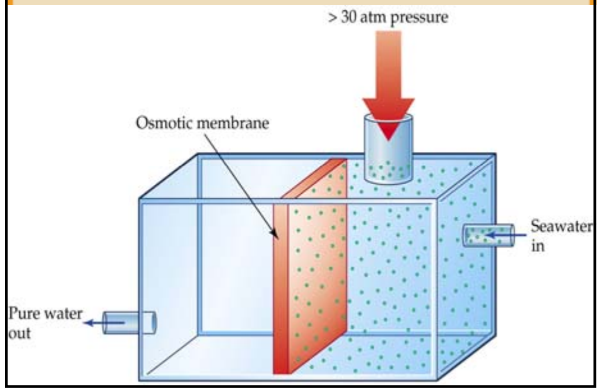

 17a–96

## Reverse osmosis

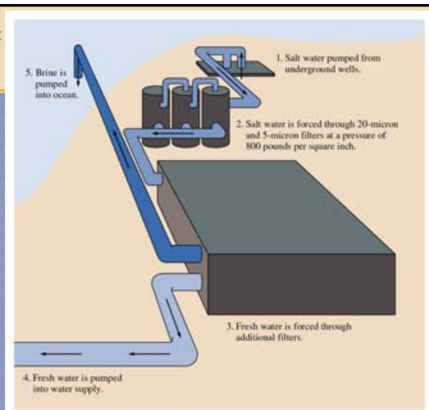



 17a–97

## Reverse Osmosis Water Purification




## Desalination plant

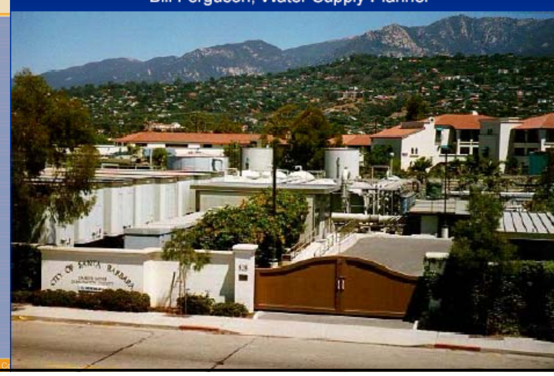



 17a–99

City of Santa Barbara

## Charles Meyer Desalination Facility

Bill Ferguson, Water Supply Planner



## Colligative properties

- Vapor pressure – Mole fraction
- Freezing point depression – molality
- Boiling point elevation – molality
- Osmosis - Molarity

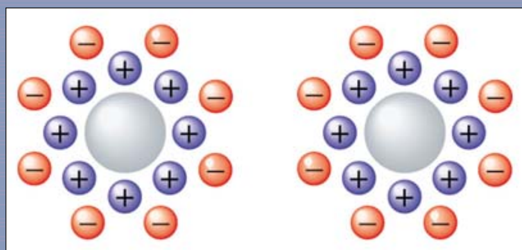
 17a–101

## Figure 17.22: The Tyndall effect

***Source:*** Stock Boston

 17a–102

## Figure 17.23: Representation of two colloidal particles



 17a–103