# Chapter Thirteen

## Physical Properties Of Solutions

# Review: Solution Terms & Types

**Solvent:** Larger portion of a solution

**Solute:** Smaller portion of a solution

**Solution:** A homogeneous mixture of two or more elements or compounds

**Solubility:** Measure of max amount of solute in solution

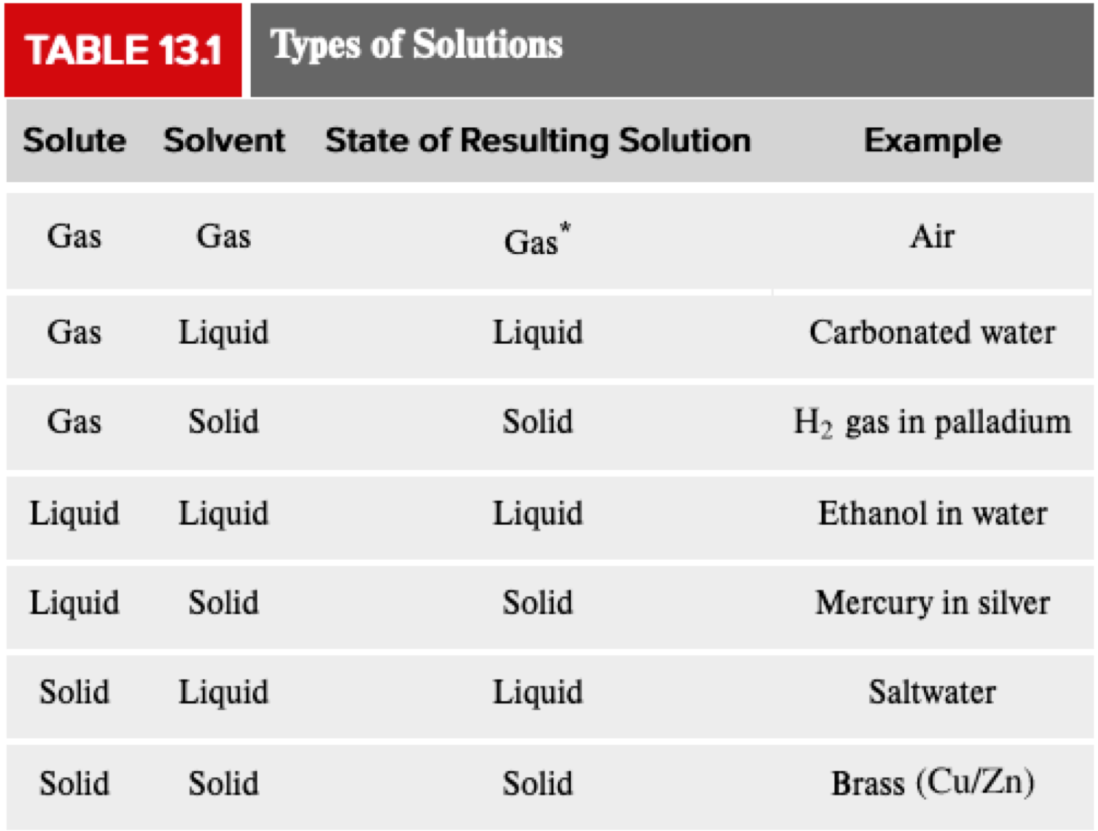


**TABLE 13.1** Types of Solutions

| Solute | Solvent | State of Resulting Solution | Example |
|---|---|---|---|
| Gas | Gas | Gas* | Air |
| Gas | Liquid | Liquid | Carbonated water |
| Gas | Solid | Solid | $H_2$ gas in palladium |
| Liquid | Liquid | Liquid | Ethanol in water |
| Liquid | Solid | Solid | Mercury in silver |
| Solid | Liquid | Liquid | Saltwater |
| Solid | Solid | Solid | Brass (Cu/Zn) |

# More Solubility Terms

## Saturated solution:

Maximum amount of solute that stays in solution

- Any additional solute will precipitate

## Unsaturated solution:

Contains less solute than in saturated solution

## Supersaturated solution:

Contains more solute than in saturated solution

- Extremely unstable (easy to make extra precipitate)

## Crystallization:

Extra solute in supersaturated solution precipitates & forms crystals

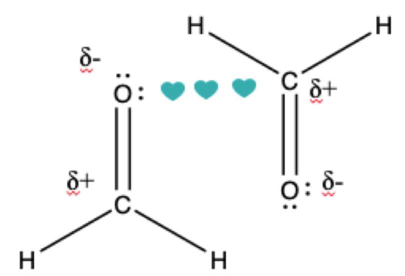
## Precipitation:

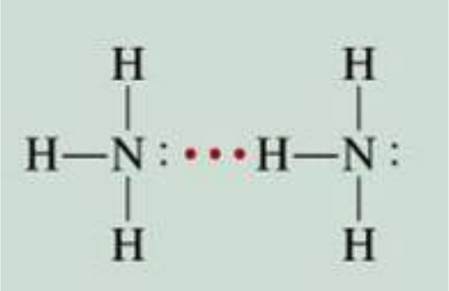
Solid comes out of solution, not always a crystal

# Intermolecular Attractive Forces Review

## Polar molecules interact using:

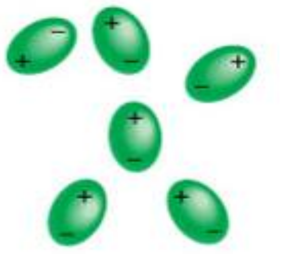
- Dipole-dipole interactions – attraction between permanent partial charges
- Hydrogen bonding – dipole-dipole attraction involving H bonded to O, N, or F





## Nonpolar molecules interact using:

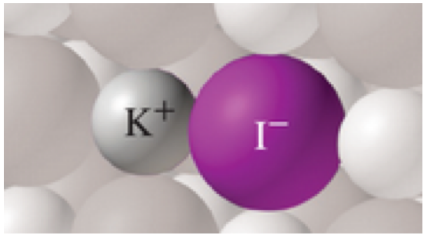
- Dispersion forces



Charges are **temporary**

## Ions interact using:

- The attraction between their positive and negative charges



# Intermolecular Attractive Forces Review

## In solutions, other important intermolecular forces include:

- Ion–dipole attractions: between an ion and the permanent dipole on a molecule

- Dipole–induced dipole attractions: a permanent dipole causes a temporary dipole in a nonpolar molecule or atom

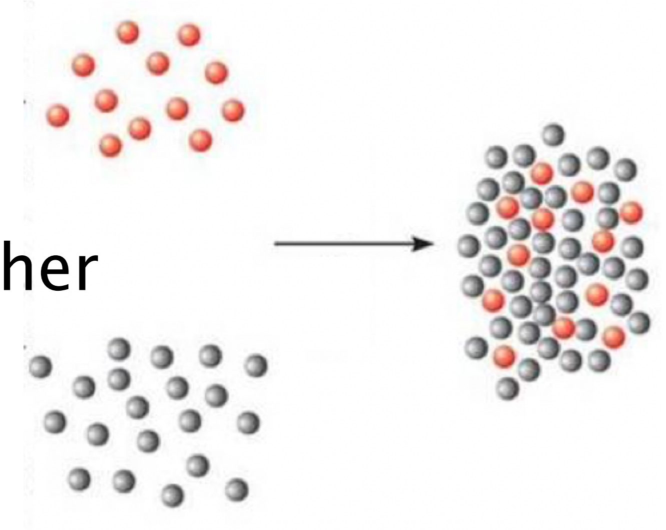
- Ion–induced dipole attractions: the charge on an ion causes a temporary dipole in a nonpolar molecule or atom

# Solvent/Solute Intermolecular Forces & Solubility

## Rule of thumb is that "like dissolves like."

Intermolecular forces are strongest for similar compounds

- Polar solvent/polar solute
- Nonpolar solvent/nonpolar solute
- Similar attractive forces lead to solvent and solute that are "miscible"
- **miscible** = fully dissolve in one another
  - – resulting solution is stable



Examples:

- water/ethanol solutions
- Dissolution of ionic salts in $H_2O$
- $CCl_4$ in benzene ($C_6H_6$)

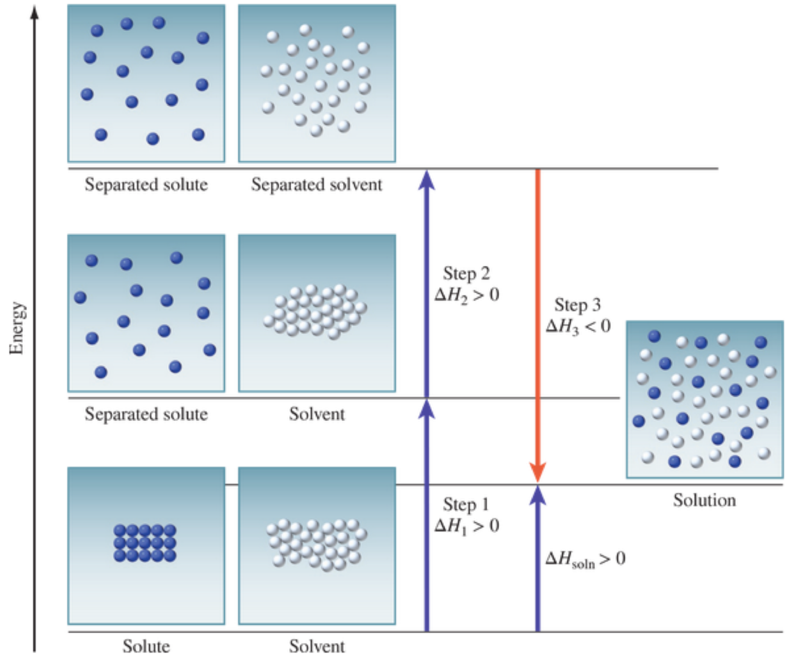
# Energy & Entropy in Solution Formation

In order for something to dissolve:

- Solvent particles must separate ($\Delta H_1$, endothermic)
- Solute particles must separate ($\Delta H_2$, endothermic)
- Solute & solvent particles must mix ($\Delta H_3$, generally exothermic)
- Overall process is $\Delta H_{solvation} = \Delta H_1 + \Delta H_2 + \Delta H_3$
  - Hess's Law!

Energy required to separate < Energy released by mixing = Exothermic Process

Energy required to separate > Energy released by mixing = Endothermic Process



# Energy & Entropy in Solution Formation

If overall process of dissolving is exothermic, resulting system (solution) has lower energy

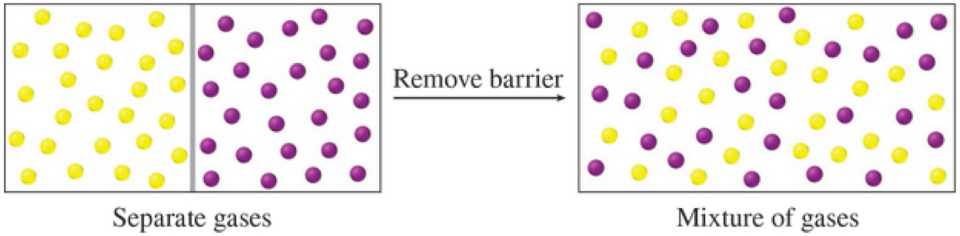
- The process is favored by enthalpy

If overall process of dissolving is endothermic, resulting system (solution) has higher energy

- The process is NOT favored by enthalpy
- The material is able to dissolve because the process is favored by ENTROPY

The **ENTROPY** of a system is a measure of how dispersed or spread out its energy is

- A measure of the DISORDER of a system
- Greater disorder = greater entropy
- Explains why gases mix spontaneously



The natural tendency is for entropy to increase

# Concentration Units Review

$$\text{Molarity (M)} = \frac{\text{Moles Solute}}{\text{Liters of solution}} = \frac{\text{mol}}{\text{L}}$$

$$\text{Molality (m)} = \frac{\text{Moles Solute}}{\text{kg of solvent}} = \frac{\text{mol}}{\text{kg}}$$

Molarity is temperature dependent,
Molality is NOT temperature dependent

$$\text{Percent by mass} = \frac{\text{Mass solute (g)}}{\text{Mass of solution (g)}} \times 100$$

Grams cancel so no units, just % sign

ppm = part per million ($1\text{g}/1\text{x}10^6\text{g}$)

# How many grams of sodium hydroxide are present in 0.500 kg of water if the solution concentration is 0.500 m?

**A: 10.0 g**

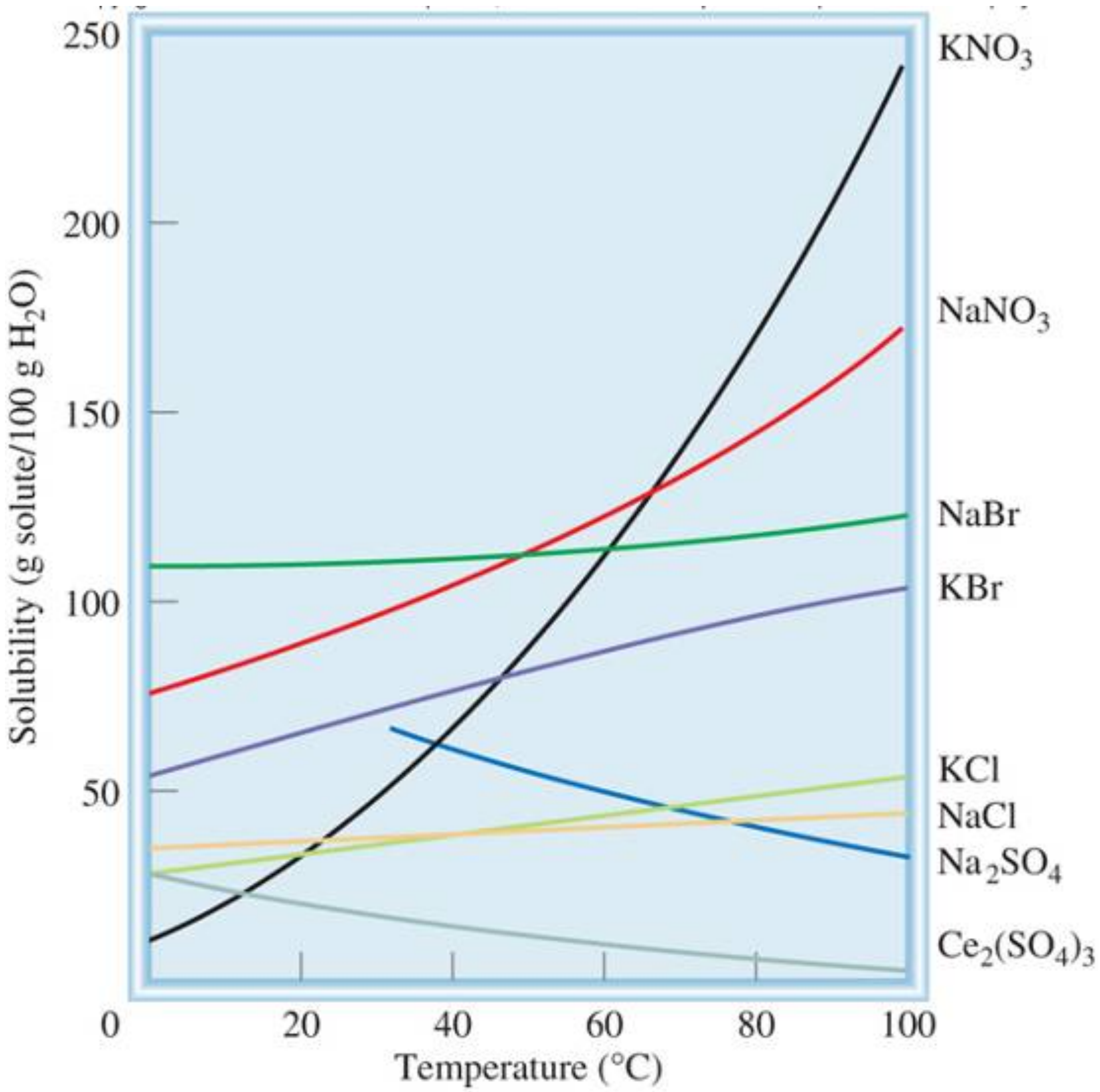
# What mass of sodium hydroxide would be needed to make 4.00 L of a 0.300 m solution at 20°C? (density of water is 0.998 g/mL at 20°C)

**A: 47.9 g**

# A 14.0% by mass acetic acid ($CH_3COOH$) solution has a density of 1.02 g/mL. What is its molality? What is its molarity?

**Molality = 2.71 m**
**Molarity = 2.38 M**

# Solubility of **Solids** As A Function Of Temperature



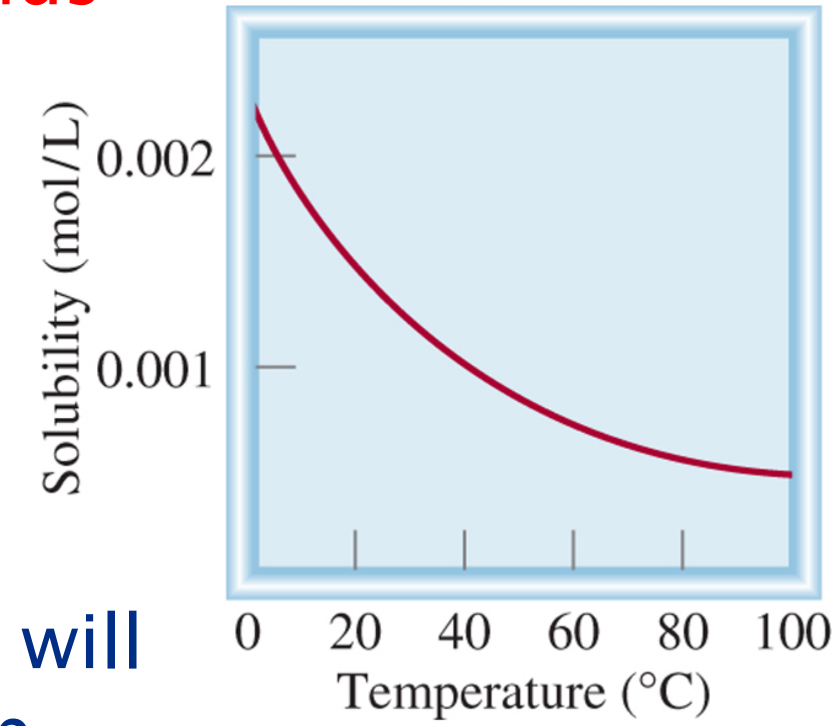
For most solids, as temp increases, solubility increases.

# The Solubilities Of Gases: Effect of Temperature

Gases are *less* soluble in liquids as temperature increases

- Molecules move faster
- Disrupt intermolecular forces
- Gases escape the liquid
- Fewer gas molecules/atoms in liquid = Lower solubility

Solubility of $O_2$ in water



In sealed container, pressure will increase with increasing temp.

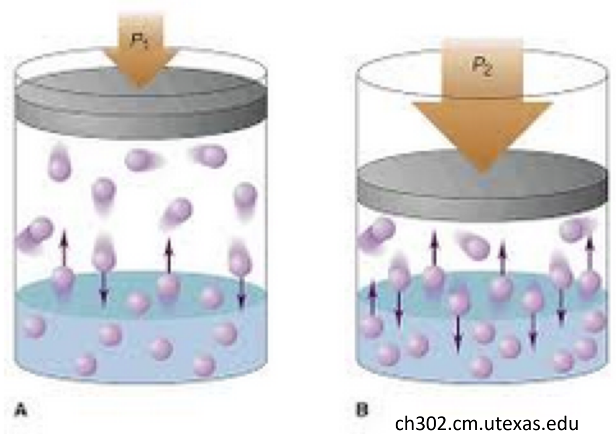
- More gas out of solution, moving faster, colliding more with container

Gas laws (Chapter 5!) govern gas phase and thus solubility

# The Solubilities Of Gases: Effect of Pressure

**Gas solubility in liquids increases as pressure increases**

- Molecules pushed too close together so they are forced back into liquid



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If pressure is decreased.....

**Henry's Law** c=kP

c= solubility or concentration
P= pressure
k= proportionality constant

Common units for k: c= moles/L and P= atm

If you know the concentration at one pressure, k allows you to determine concentrations at different pressures

# Solutions Of Electrolytes

## Colligative properties:

- Physical properties of solutions that depend on the number of solute particles but ***NOT* on the identity** of the solute.
- Ex: Boiling Point, Freezing Point, Osmotic Pressure

## van’t Hoff factor, *i*

- Used in solution equations for colligative properties (ex. Boiling point elevation: $\Delta T_b = iK_bm$)
- Nonelectrolytic solutions: $i = 1$.
- Electrolyte solutions: $i$ = the number of ions the solute will dissociate into
- Ex*: Hexane, $i = 1$
  NaCl, $i = 2$
  $Pb(NO_3)_2$, $i = 3$

*Note that these are the theoretical values. The experimental values are somewhat different due to formation of ion pairs.

# Vapor-Pressure Lowering

## Raoult's Law:

$$P_a = X_a P°_a$$

$P_a$: Vapor pressure of solvent "$a$" above a solution

$P^o{}_a$: Vapor pressure of pure solvent "$a$"

$x_a$: Mole fraction of "$a$" in the solution

$$x_i = \frac{moles_i}{Moles_{total\ solution}} = \frac{n_i}{n_{total\ moles}}$$

Non-volatile solutes: Vapor pressure of the solution = vapor pressure of the solvent

- Vapor pressure will be lowered by presence of solute

Volatile solutes: Vapor pressure of the solution is sum of the partial pressures of the solute and the solvent

Works perfectly for ideal solutions; OK for dilute solutions

# What is the vapor pressure of water in a 100.0g solution that contains 10.0g sucrose, $C_{12}H_{22}0_{11}$ at 40°C? The vapor pressure of pure water is 55.5 torr at 40°C.

MM: sucrose = 342.30 g/mol; water = 18.015 g/mol)

Step 1:Determine mole fraction of water

Step 2:Determine vapor pressure given P°= 55.5 torr at 40°C

**A: 55.2 torr**

What mass (g) of ethanol (46.069 g/mol) must be added to 550.0 g water (18.015 g/mol) to give a solution with a vapor pressure of water 1.5 mmHg less than that of pure water at 30°C?

Vapor pressure of water at 30°C is 31.8 mmHg.

**A: 69.6 g**

# Boiling Point Elevation

## Vapor pressure above a solution is always less than vapor pressure above pure solvent.

1. Higher temperature needed for vapor pressure to hit 1 atm.
2. Boiling point of solution higher than boiling point of pure solvent
3. Boiling Point Elevation depends on:
    - Type of solvent
    - # of solute particles

$$\Delta T_b = iK_bm$$

$$T_b = T°_b + \Delta T_b$$

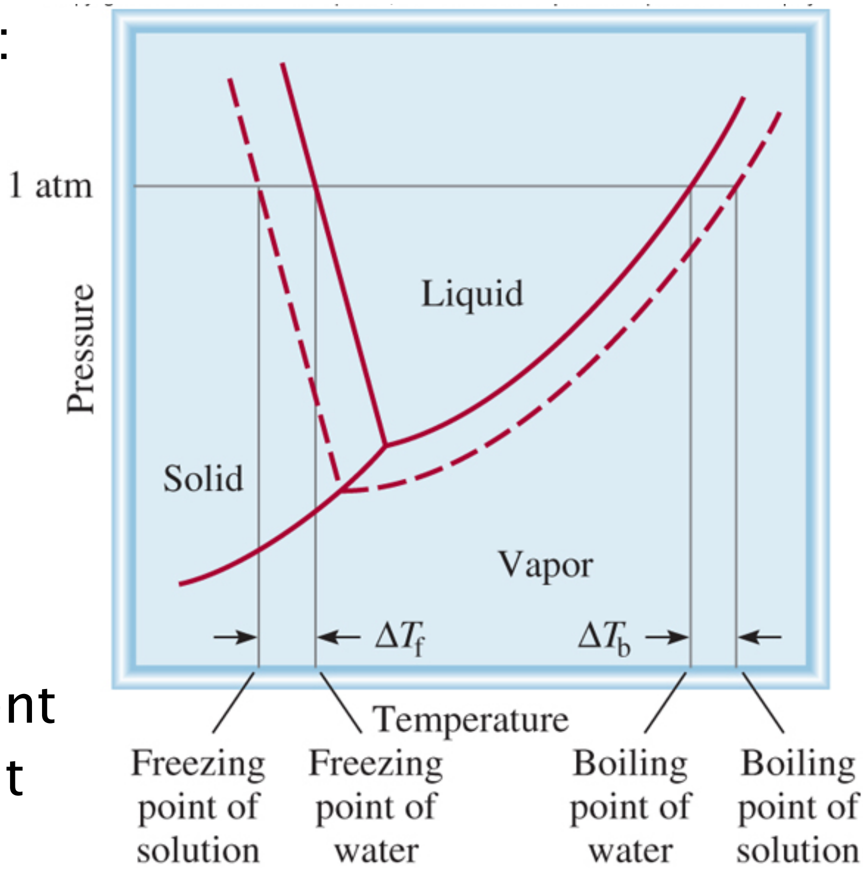
m = solute molality

$T_b$ = boiling point of solution

$T°_b$ = boiling point of pure solvent

$K_b$ = constant – based on solvent

i = van't Hoff factor



# Freezing Point Depression

Solution freezes at lower temperature than pure solvent

Freezing Point Depression depends on

- Type of solvent
- # of solute particles

$$\Delta T_f = iK_f m$$

$$T_f = T°_f - \Delta T_f$$

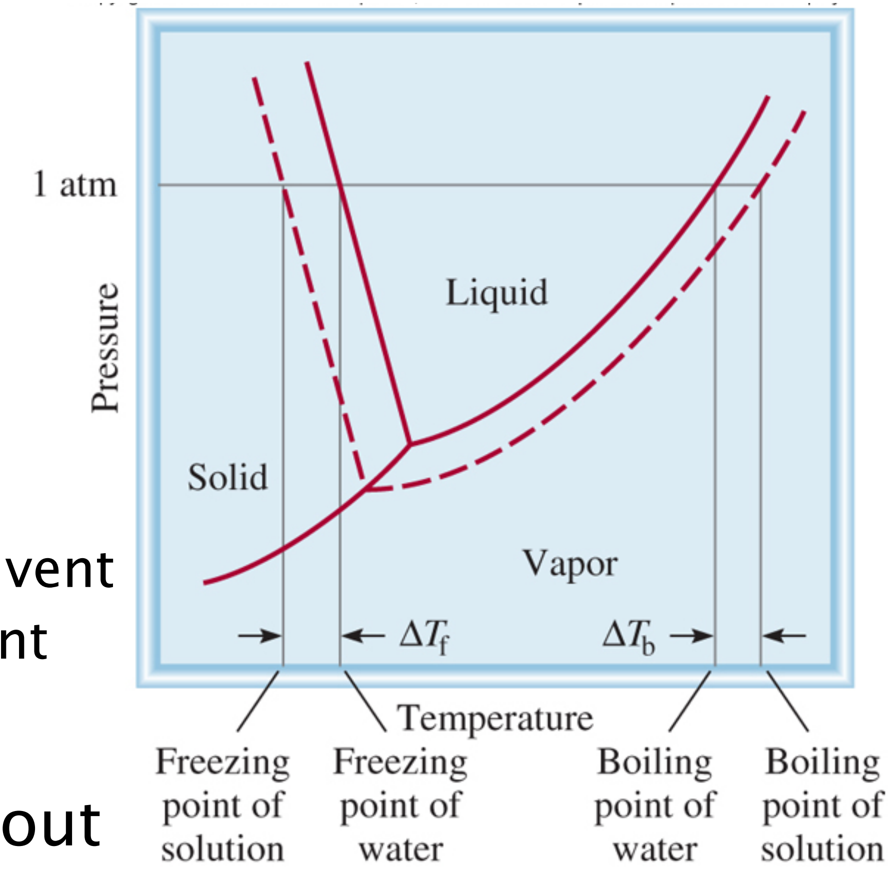
m = solute molality

$T_f$ = freezing point of solution

$T°_f$ = freezing point of pure solvent

$K_f$ = constant – based on solvent

i = van’t Hoff factor



- Only the pure solvent freezes out
- Pure substances:"sharp" melting point
- Impure materials: broad melting point range

What is the boiling point of a 0.886 m solution of pentane in benzene? For benzene: bpt = 80.1°C, $K_b$ = 2.53°C/m

A: 82.3°C

What is the melting point of a 1.00 m solution of $CaCl_2$ in water? For water: mpt = 0.0°C, $K_f$ = 1.86°C/m

A: - 5.6°C

# A solution of 2.366 g solute in 82.10 g cyclohexane freezes at 2.65°C. Determine the molar mass of the solute. For cyclohexane, $K_f$= 20.0°C/m and $T^\circ_f = 6.55$°C.

Have freezing point of solution & pure solvent – can use $\Delta T_f = iK_f m$ to determine the molality of the solution

Use mass of solvent & molality to calculate moles solute

Given mass solute, so can calculate molar mass of solute

A: 148 g/mol

# Constants

## Will be provided on exams if needed

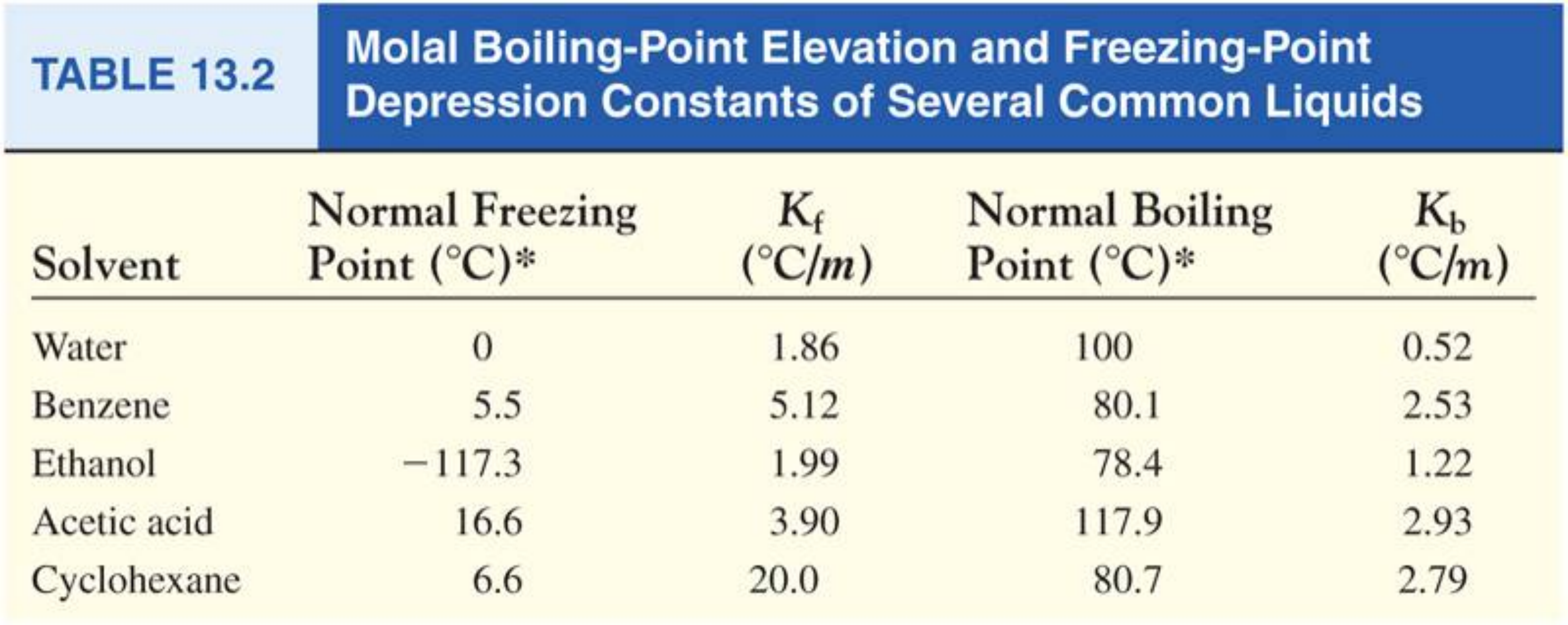


**TABLE 13.2** Molal Boiling-Point Elevation and Freezing-Point Depression Constants of Several Common Liquids

| Solvent | Normal Freezing Point (°C)* | $K_f$ (°C/*m*) | Normal Boiling Point (°C)* | $K_b$ (°C/*m*) |
|---|---|---|---|---|
| Water | 0 | 1.86 | 100 | 0.52 |
| Benzene | 5.5 | 5.12 | 80.1 | 2.53 |
| Ethanol | −117.3 | 1.99 | 78.4 | 1.22 |
| Acetic acid | 16.6 | 3.90 | 117.9 | 2.93 |
| Cyclohexane | 6.6 | 20.0 | 80.7 | 2.79 |

# Osmotic Pressure

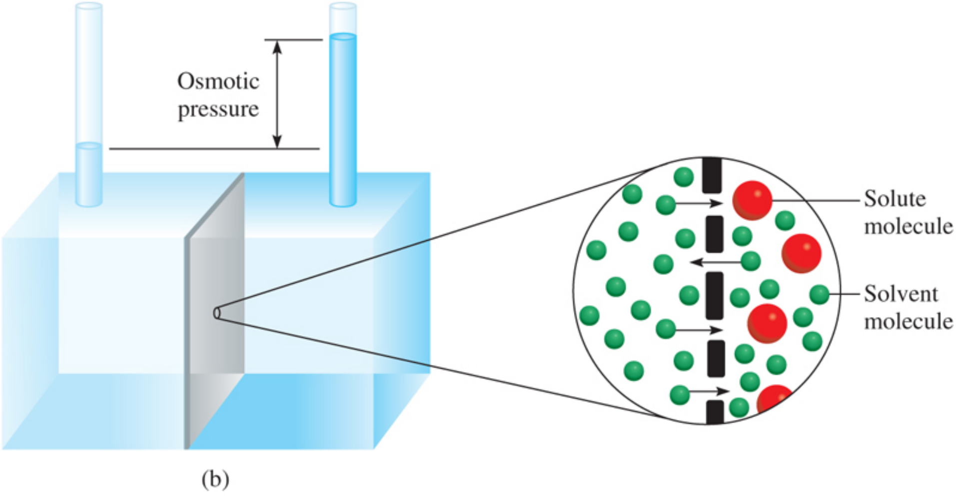
**Semi-permeable membranes:** Materials with tiny pores that only allow solvent molecules to pass

- solute cannot get through the membrane

**Osmosis:** Net flow of solvent molecules through a semi-permeable membrane from dilute to concentrated solution.

**Osmotic Pressure ($\pi$ ):** Pressure needed to stop osmotic flow

- $\pi$ depends on:
  - concentration
  - temperature



$$\pi = iMRT$$

M= molarity

R= gas constant $\left(0.0821 \frac{\text{L atm}}{\text{mol K}}\right)$

T= temperature

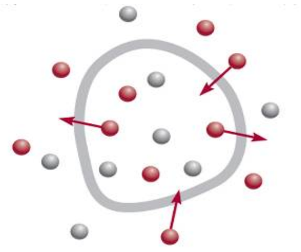
What is the osmotic pressure of a 0.238 M aqueous sugar solution at 25°C?

A: 5.83 atm

What is the molar mass of a solute if 397.2 g of the compound dissolved in water produces 592.4 mL of a solution that has an osmotic pressure of 1.98 atm at 35°C?

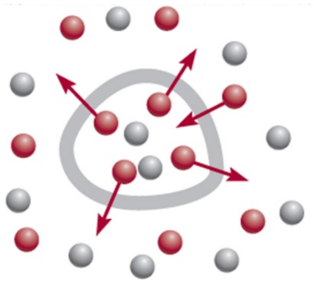
A: 8570 g/mol

# Practical Applications Of Osmosis



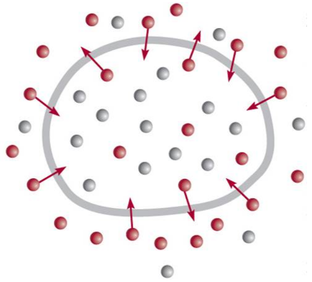
## Isotonic Solution: Organ Transplants

- Same concentration on both sides of membrane
- Organs would burst if stored in water



## Hypertonic Solution: Food Preservation

- Higher concentration outside the membrane
- Salt pulls water from microbes and kills them



## Hypotonic Solution: Tree Growth

- Lower concentration outside the membrane
- Water pulled through sap to top of trees

## Reverse osmosis: Water Purification

- Reversing the net flow of solvent through a membrane by applying pressure greater than osmotic pressure.
- Obtain water with low solute concentration