

# ***GENERAL CHEMISTRY***

## ***Chapter 7***

# **Properties of Solutions**

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# The Solution

- A solution is a homogeneous mixture of a solute dissolved in a solvent
- The solvent is generally in excess
  - Solution may be gas, liquid, or solids (state of a solution is determined by the state of the solvent)
  - Each substance present is a component of the solution.
  - Solvent is the substances used to dissolve the solute.
- $\text{Solution} = \text{solvent} + \text{solute}$
- Solvent: large amount
- Solute: small amount
- Dissolution process: solvent dissolve solute

# Types of Solutions

**TABLE 13.1** Examples of Solutions

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

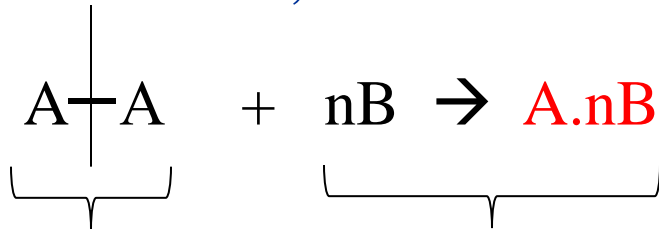
We focus only on liquid solution (the solvent is liquid)

# Process of making solutions

In the process of making solutions with condensed phases, intermolecular forces become rearranged.

- Intermolecular forces hold the solute particle and the solvent that surrounds it together.
- Solutions form when the attractive forces between solute and solvent can overcome the attractive forces within the solute or solvent particles.

- A is solute, B is solvent



Similar to  
phase change

Solvation

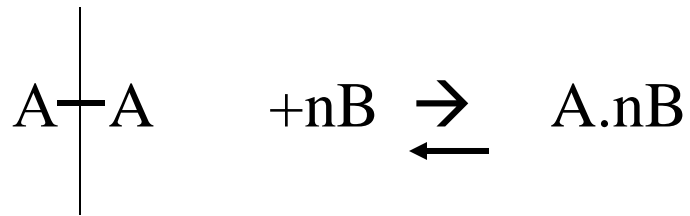
B is water (aqueous solution)

Hydration process

B will attack the structure of A,  
break the interaction within A,  
Form new interaction: A.nB  
Driving force: enthalpy of new  
interaction and entropy

# Saturated solution

- A is solute, B is solvent: dissolution process/process of making solution



It is possible that A in solution collide with other A to form back A-A (A in original solute form)

(Reverse direction)

After some time, system reaches equilibrium → saturated solution

Max amount of solute presented in the solution

$\Delta G^0$  and  $K_{\text{eq}}$

# saturated sugar solution

- Imagine there is a saturated sugar solution. (Saturated means that the maximum amount is dissolved in the solution, under normal conditions.) There are undissolved sugar crystals at the bottom of the solution. This can be shown by the equation,



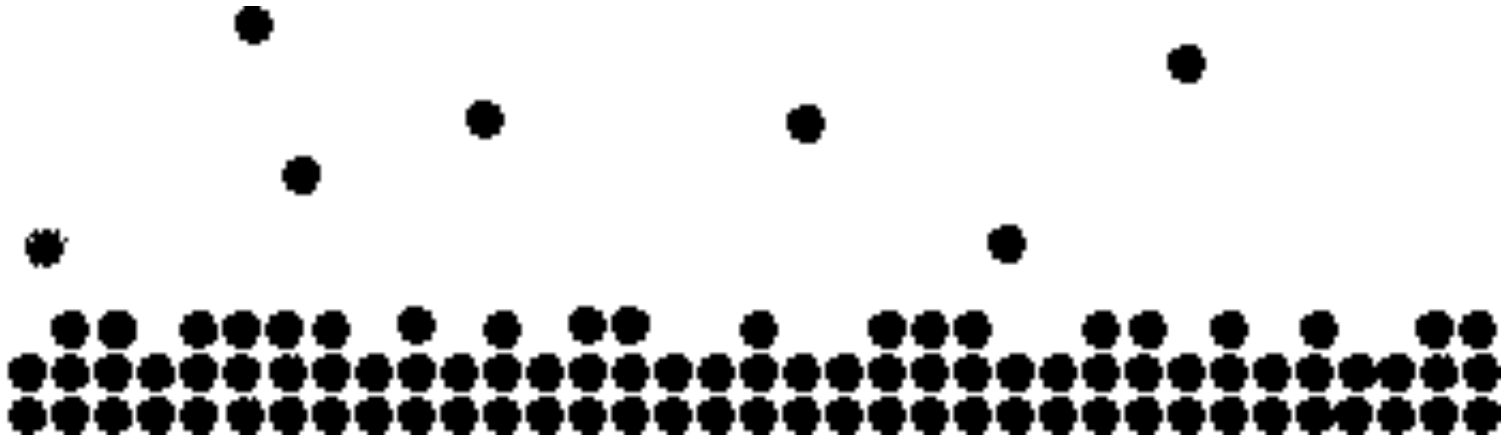
The equation describes that sugar crystals (sugar(s)) will dissolve in water (H<sub>2</sub>O) and produce sugar molecules in solution (sugar(aq)).

# **saturated sugar solution**

- **Since the amount of sugar at the bottom does not change once equilibrium is attained, it would seem that the process stops. In other words, it seems that sugar does not go into solution or come out of solution anymore.**
- **However, this is not true. The amounts of undissolved sugar crystals and sugar in solution do not change because the rate at which sugar molecules go into solution is the same rate as sugar molecules coming out of solution (forming crystals).**

# **saturated sugar solution**

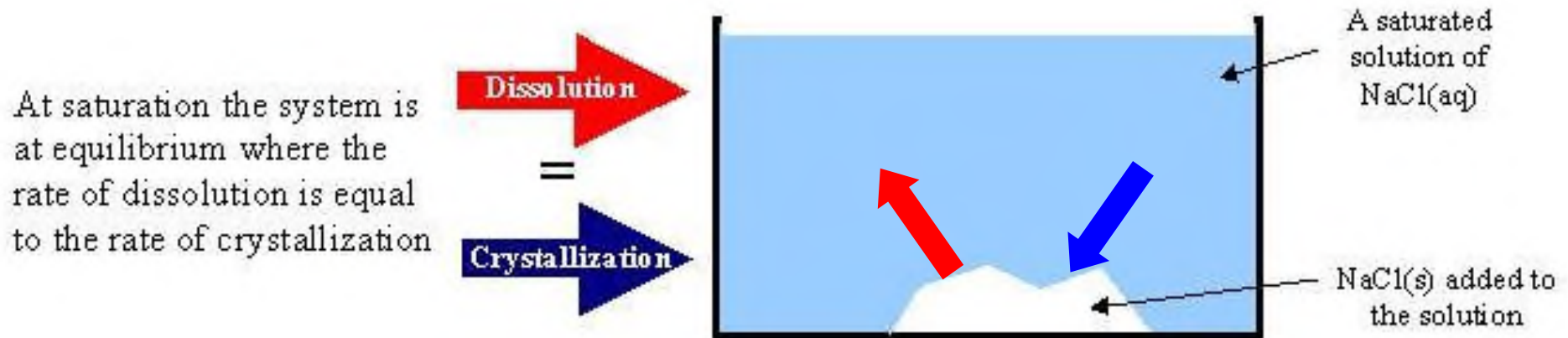
- **The animation represents this process:**



- **the blue "molecules" escape into solution from the ordered crystal. At the same time, molecules are coming out of solution and depositing on the solid. Since this is a continual process and the concentrations do not change, it is called dynamic equilibrium.**



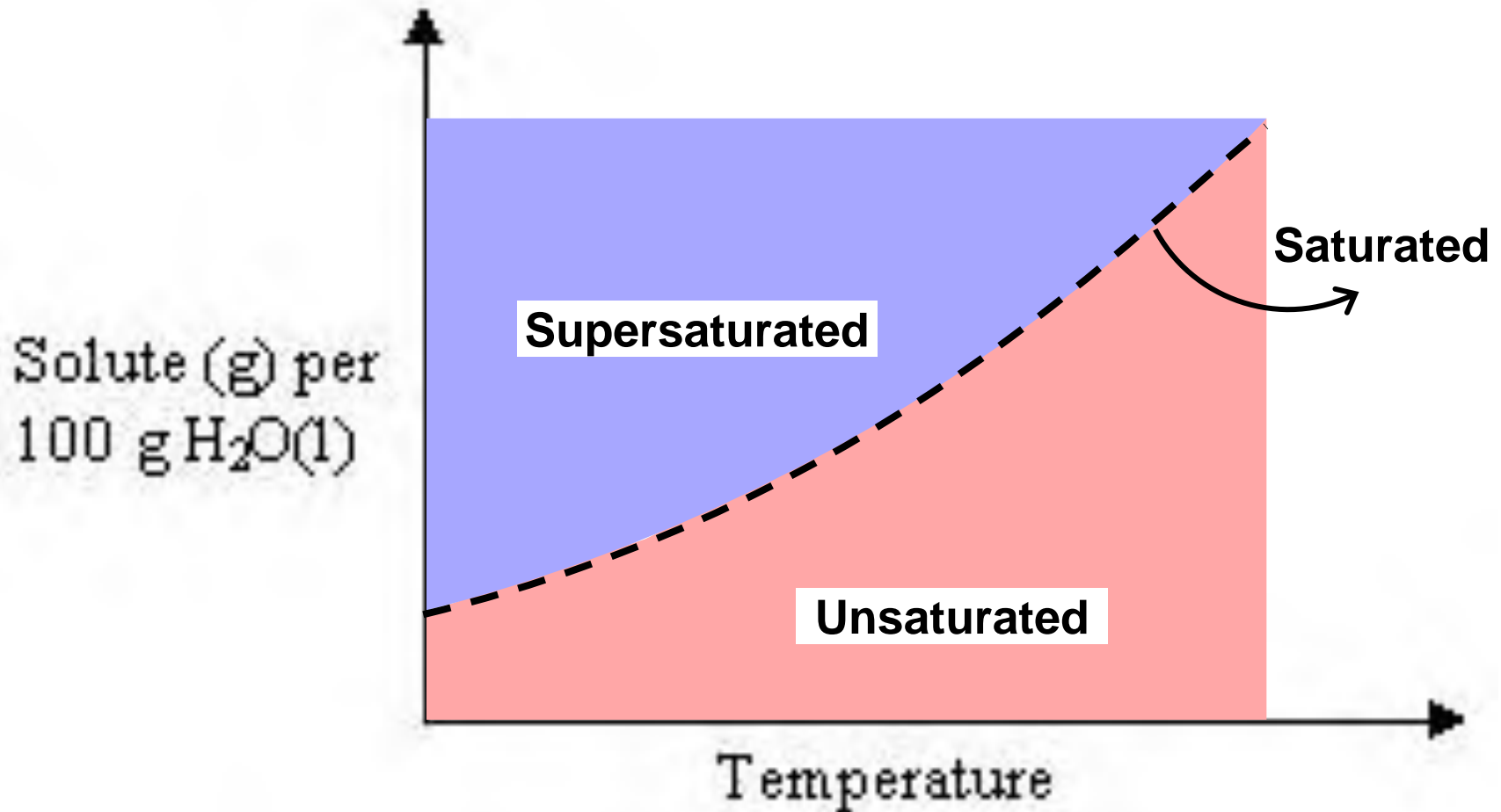
# Saturated solution



Rate of dissolution

= rate of crystallization / deposition / precipitation

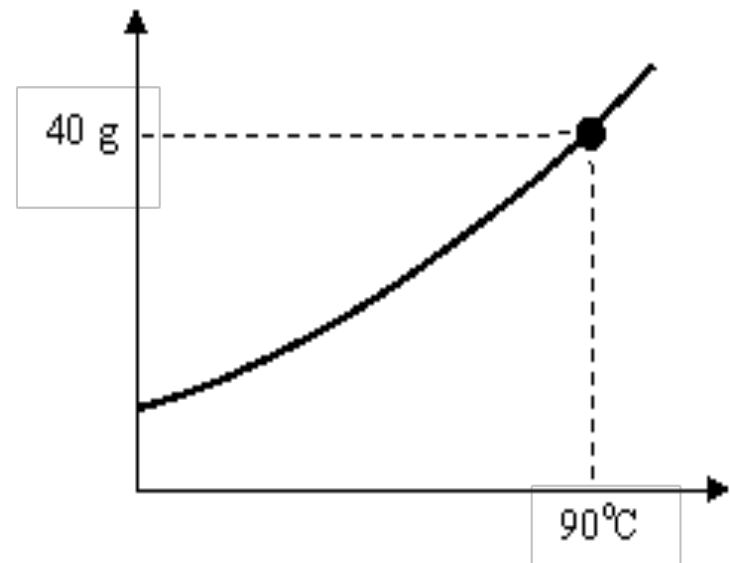
# Solubility curve



Solubility: concentration of saturated solution or equilibrium  
Usually: expressed in g of solute in 100g of solvent (of sat. solution)

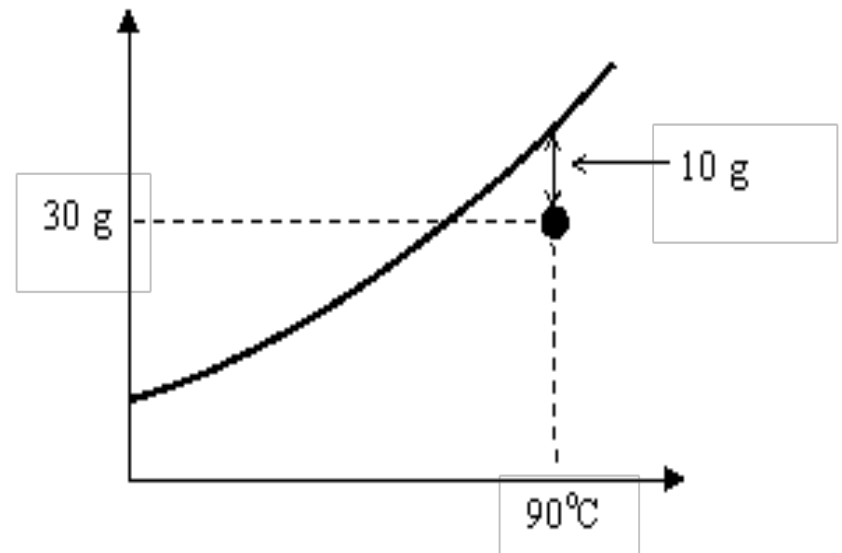
# Solubility curve

- **Any point on a line represents a saturated solution.**
- In a saturated solution, the solvent contains the maximum amount of solute.
- **Example**
- At  $90^{\circ}\text{C}$ , 40 g of  $\text{NaCl(s)}$  in 100g  $\text{H}_2\text{O(l)}$  represent a saturated solution.



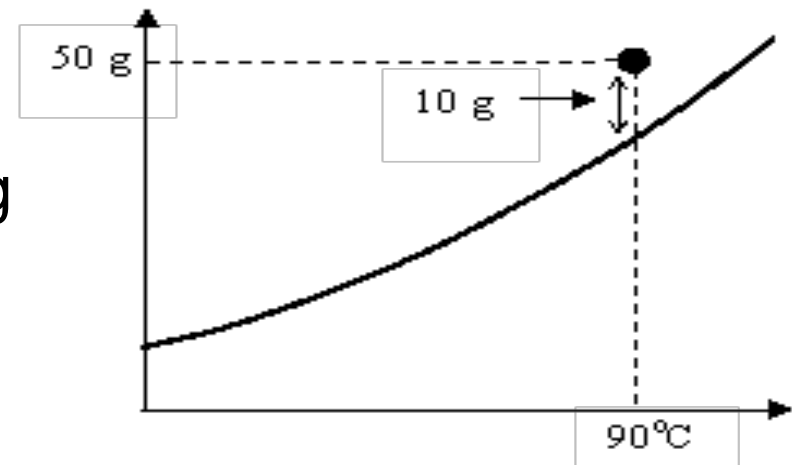
# Solubility curve

- Any point below a line represents an unsaturated solution.
- In an unsaturated solution, the solvent contains less than the maximum amount of solute.
- **Example**
- At  $90^{\circ}\text{C}$ , 30 g of  $\text{NaCl(s)}$  in 100g  $\text{H}_2\text{O(l)}$  represent an unsaturated solution. 10 g of  $\text{NaCl(s)}$  have to be added to make the solution saturated.



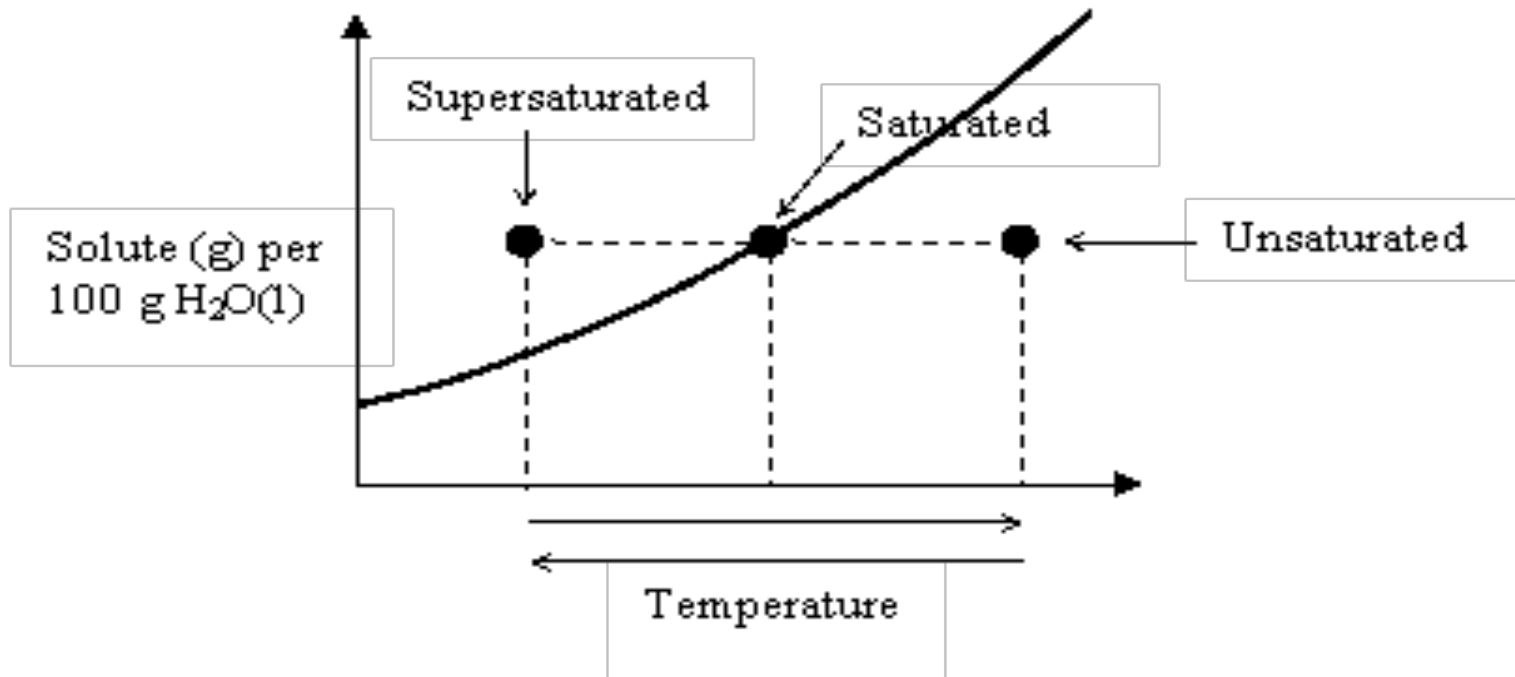
# Solubility curve

- **Any point above a line represents a supersaturated solution.**
- In a supersaturated solution, the solvent contains more than the maximum amount of solute. A supersaturated solution is very unstable and the amount in excess can precipitate or crystallize.
- **Example**
- At  $90^{\circ}\text{C}$ , 50 g of  $\text{NaCl(s)}$  in 100g  $\text{H}_2\text{O(l)}$  represent a supersaturated solution. Eventually, 10 g of  $\text{NaCl(s)}$  will precipitate.



# Solubility curve

Any solution can be made saturated, unsaturated, or supersaturated by changing the temperature.



# **SOLUBILITY**

**The solubility of a solute in a given amount of solvent is dependent on the**

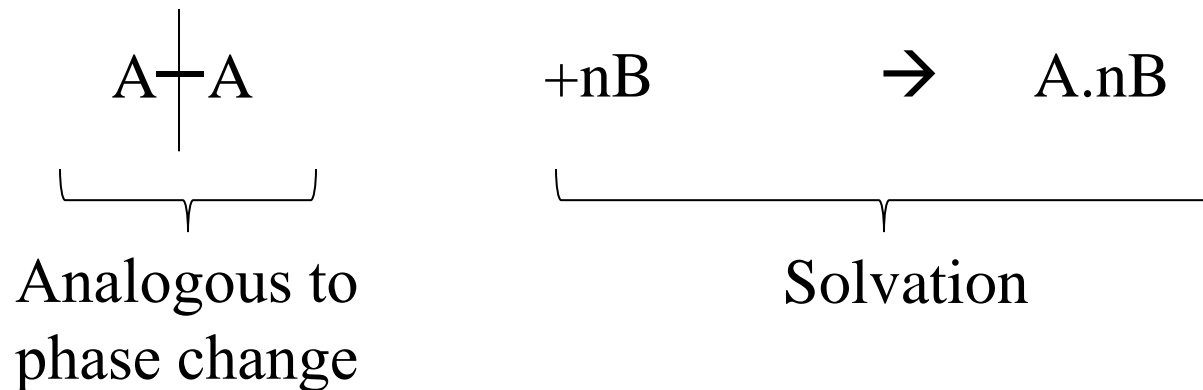
**temperature,**

**the pressure,**

**and the chemical natures of the solute and solvent.**

# Formation of a Solution

- Consider A (solute) dissolving in B (solvent):
  - The interaction within B have to be interrupted,
  - The interaction within A have to be interrupted,
  - Forming the new interaction between A and B.
  - Such interaction between solute and solvent are called solvation.
    - If water is the solvent, we say hydration.





# Energy Changes in Solution Formation

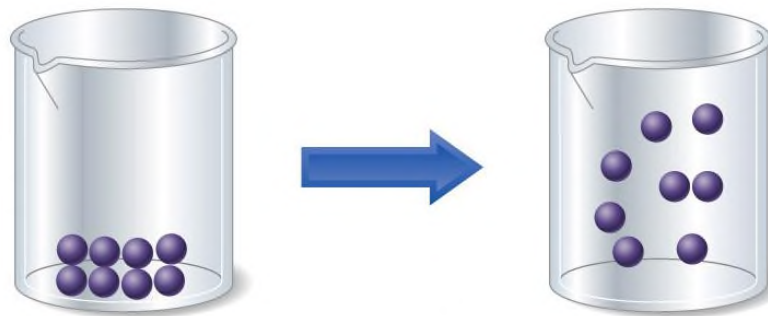
- There are three energy steps in forming a solution:
  - Separation of solute molecules ( $\Delta H_1$ ),
  - Separation of solvent molecules (not mentioned), and formation of solute-solvent interactions ( $\Delta H_2$ ).
- We define the enthalpy change in the solution process as

$$\Delta H_{\text{dissolution}} = \Delta H_1 + \Delta H_2.$$

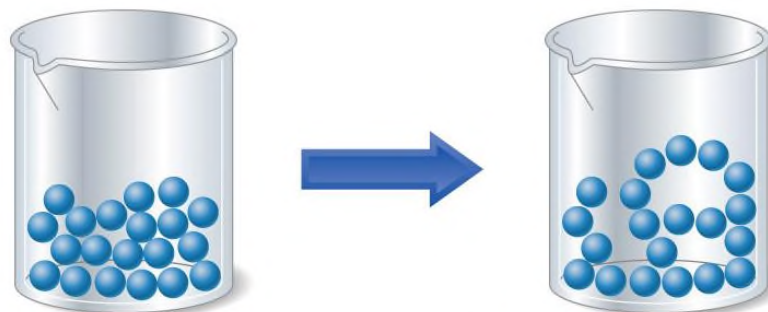
- $\Delta H_{\text{dissolution}}$  can either be positive or negative depending on the intermolecular forces.

# Enthalpic Contributions

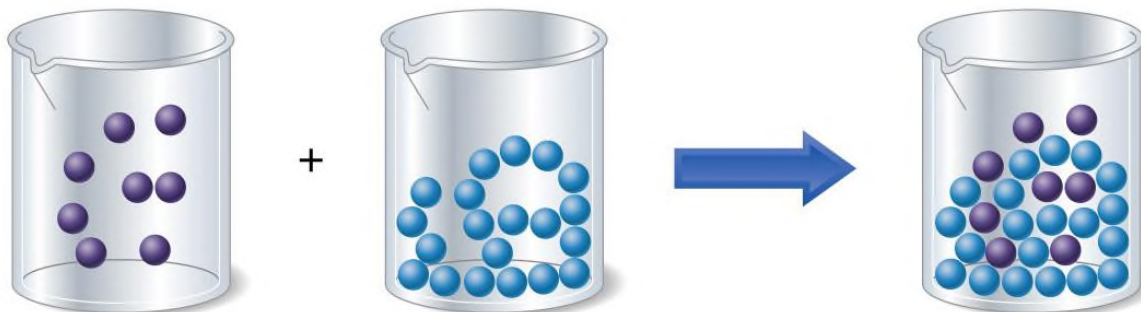
- Breaking attractive intermolecular forces is always endothermic.
- Forming attractive intermolecular forces is always exothermic.



$\Delta H_1$ : Separation of solute molecules



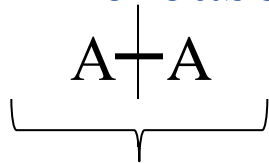
$\Delta H_2$ : Separation of solvent molecules



$\Delta H_3$ : Formation of solute-solvent interactions

# Effect of temperature on solubility of solid

- Solute is **solid** (neglecting the separation of solvent)  
 $\Delta H_1 > 0$  and large (break interaction in solid)  
 $\Delta H_2 < 0$  and usually small (usually forming a weak interaction)
- Overall:  $\Delta H_{\text{dissolution}} = \Delta H_1 + \Delta H_2 > 0$  (generally or most cases)
- Dissolution of **solid** in liquid is usually an endothermic process
- T increases  $\rightarrow$  Solubility of solid in liquid increases



Analogous to  
phase change



Solvation

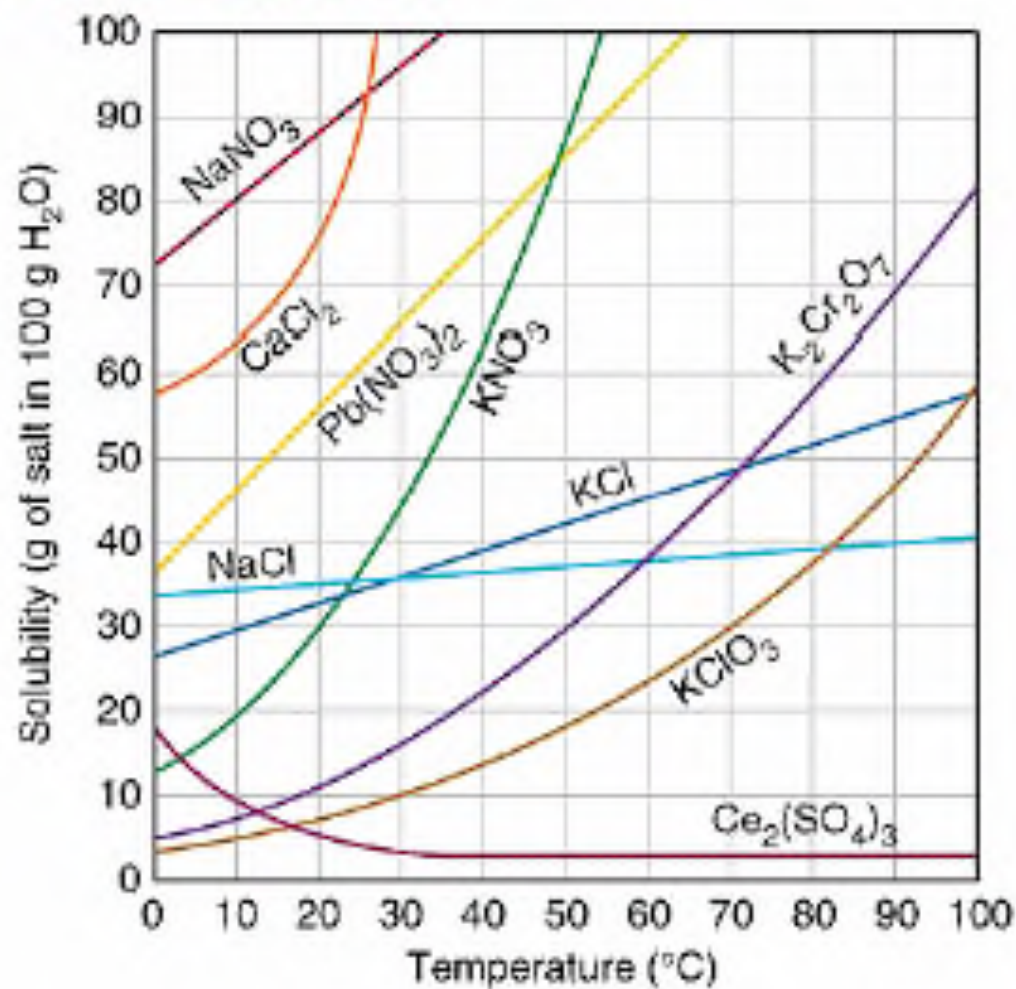
# *Factors Affecting Solubility*

## Temperature Effects

Exception

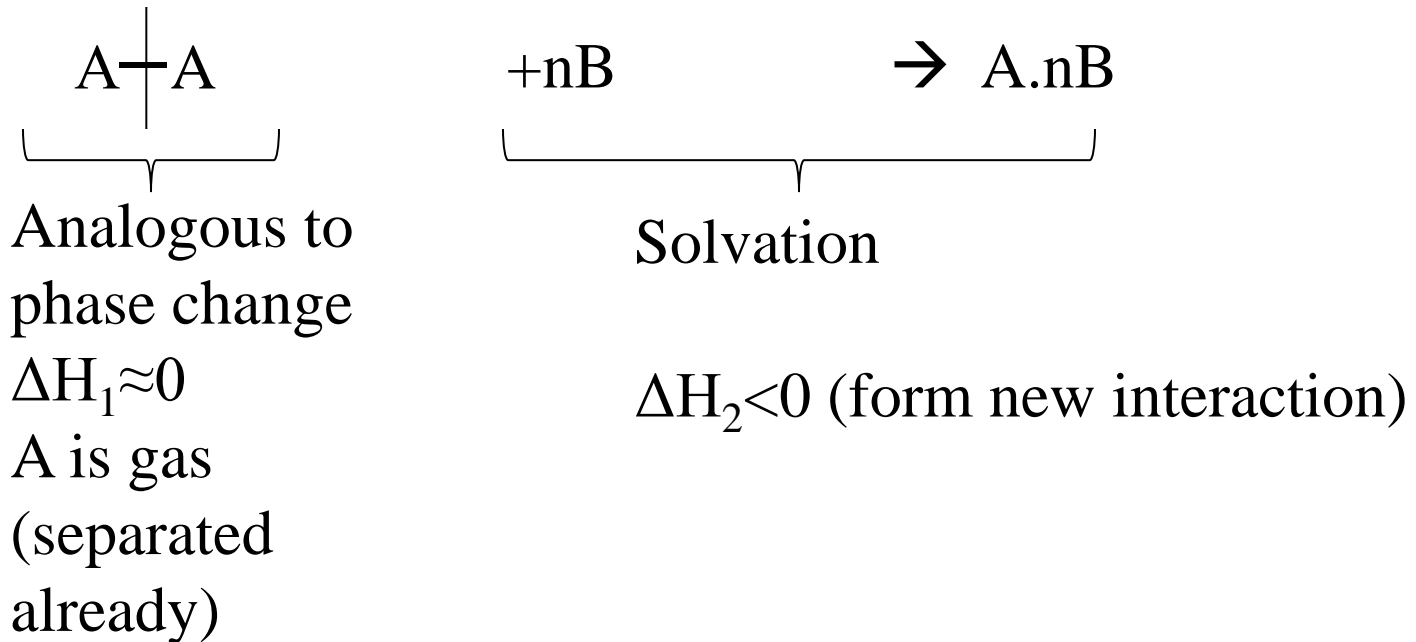
Some compounds, the dissolution process is exothermic (strong interaction with water)

Sulphate salts



# Effect of temperature on solubility of gas

- A is solute (gas), B is solvent



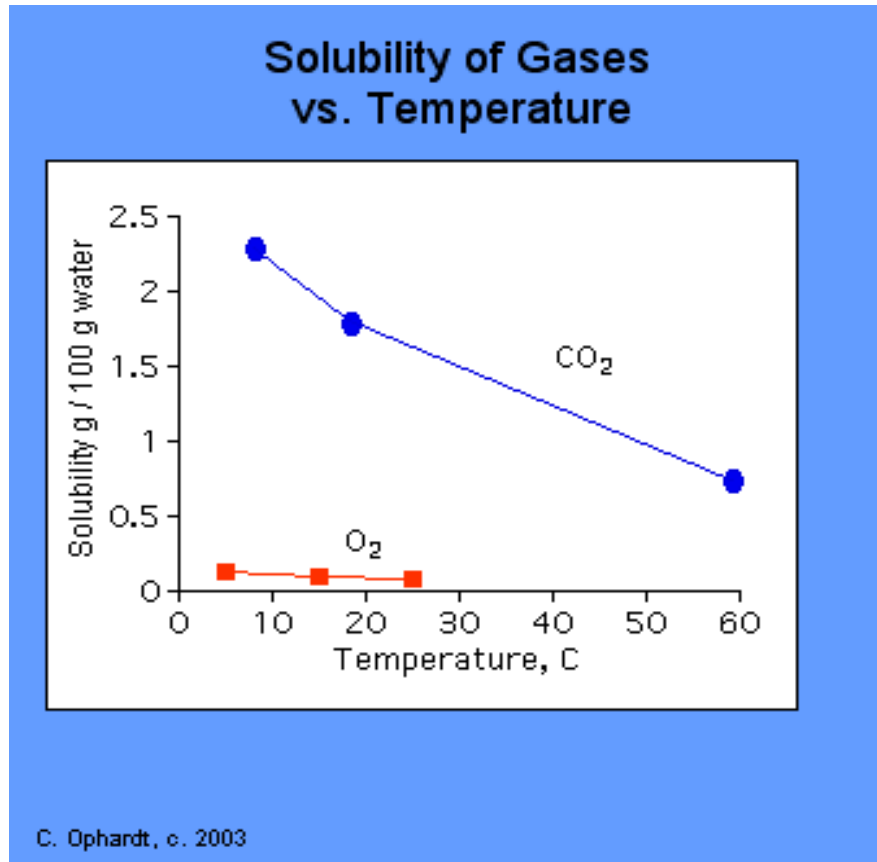
Overall:  $\Delta H_{\text{dissolution}} = \Delta H_1 + \Delta H_2 < 0$

Dissolution of gas in liquid is an exothermic process

T increases  $\rightarrow$  solubility of gas in liquid decreases

# Solubility of Gases vs. Temperature

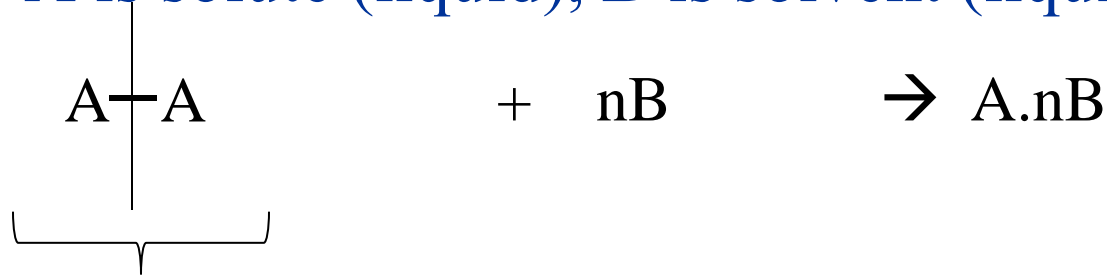
- The variation of solubility for a gas with temperature can be determined by examining the graph below:



- As the temperature increases, the solubility of a gas decrease as shown by the downward trend in the graph .

# Effect of temperature on solubility of liquid

- A is solute (liquid), B is solvent (liquid)



Phase change  
 $\Delta H_1 > 0$   
 (liquid-liquid)

Solvation  
 $\Delta H_2 < 0$  (form new interaction)  
 (liquid-liquid)

Overall:

$\Delta H_{\text{dissolution}} = \Delta H_1 + \Delta H_2$  difficult to compare  $\Delta H_1$  and  $\Delta H_2$

**Ignore** this type (effect of T on solubility of **liquid** in liquid)

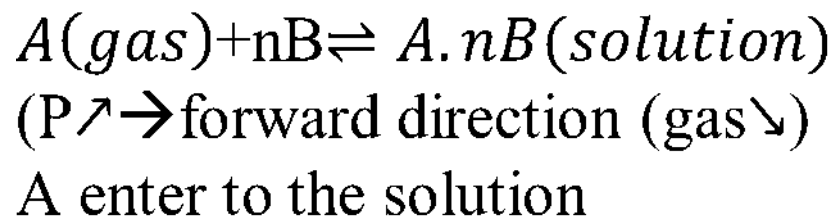
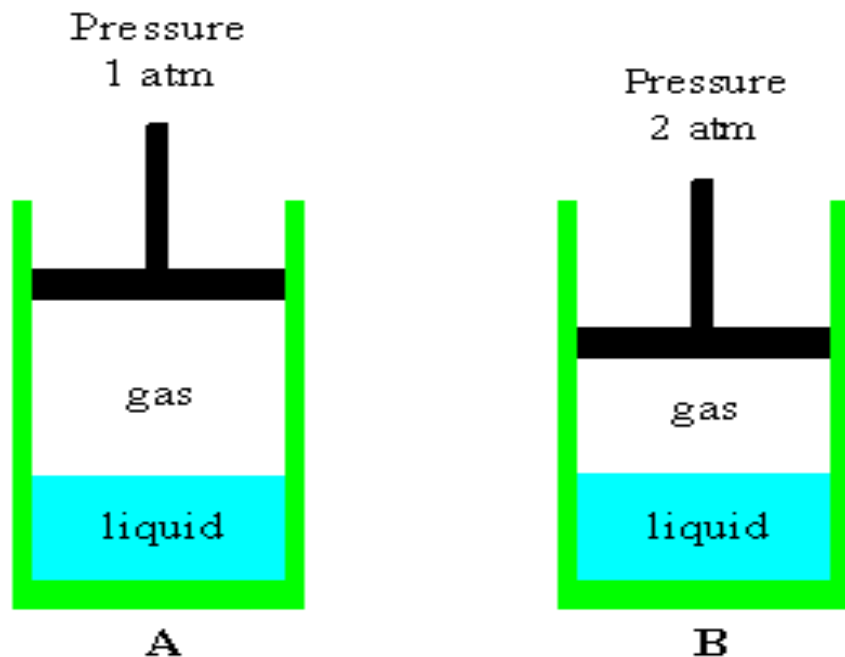
# Summary of temperature effect on solubility

- **solid in liquid:**
- solubility of an **endothermic dissolving** solid in a liquid increases with increasing temperature, (generally)
- but for an **exothermic dissolving** one solubility decreases with increasing temperature. (not usually)
- **liquid in liquid:** (skip)
- for **partially dissolving liquids** like dimethyl ether( $\text{CH}_3\text{-O-CH}_3$ ) in water ( $\text{H}_2\text{O}$ ), solubility increases with increasing temperature,
- but for a **completely dissolving liquids** like ethyl alcohol( $\text{C}_2\text{H}_5\text{OH}$ ) in water( $\text{H}_2\text{O}$ ), solubility decreases with increasing temperature.
- **gas in liquid:**
- solubility of a gas in a liquid almost always decreases with increasing temperature



# Pressure

**The solubility of a gas increases as the pressure increases.**



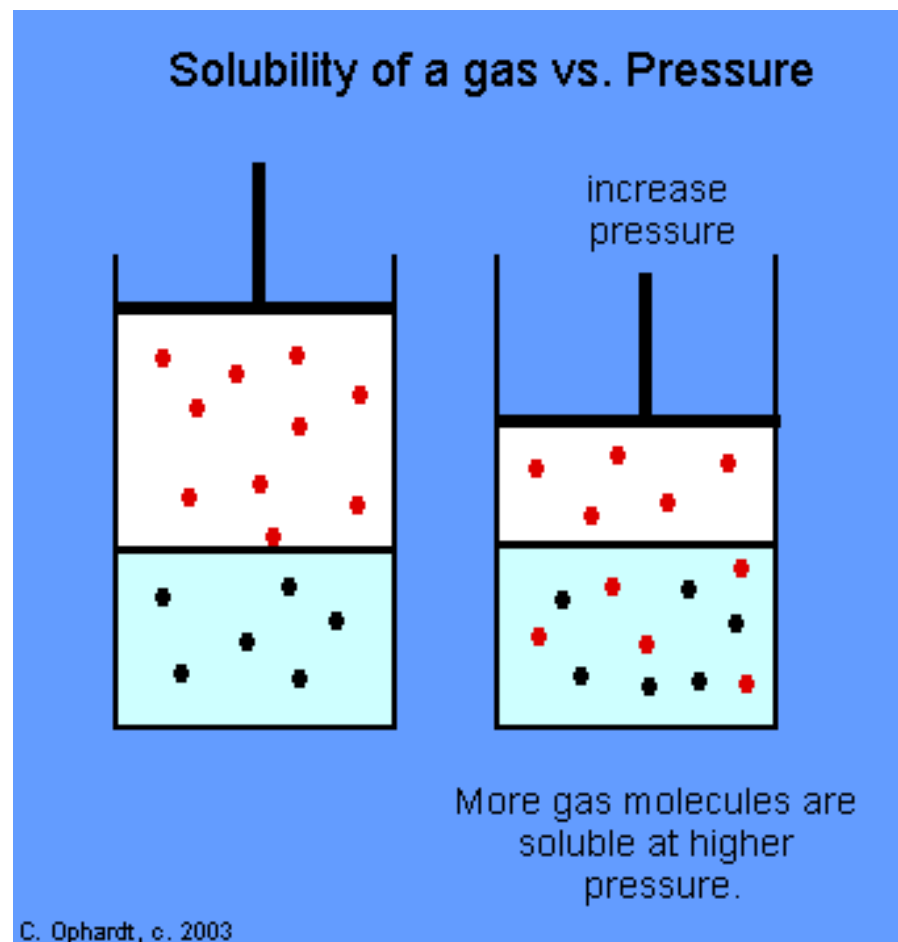
Liquid B has more gas particles dissolved in it.

## Example

Carbon dioxide,  $\text{CO}_2(\text{g})$  in carbonated drinks is dissolved in the solvent by increasing the pressure and also decreasing the temperature.

# Gas Pressure and Solubility

- Liquids and solids exhibit practically no change of solubility with changes in pressure. Gases as might be expected, increase in solubility with an increase in pressure.
- **Henry's Law states that: The solubility of a gas in a liquid is directly proportional to the pressure of that gas above the surface of the solution.**
- If the pressure is increased, the gas molecules are "forced" into the solution since this will best relieve the pressure that has been applied. The number of gas molecules is decreased. The number of gas molecules dissolved in solution has increased as shown in the graphic on the right.



$$S_{gas} = kP_{gas}$$

k: Henry's constant

# Gas Pressure and Solubility

- Carbonated beverages provide the best example of this phenomena. All carbonated beverages are bottled under pressure to increase the carbon dioxide dissolved in solution.
- When the bottle is opened, the pressure above the solution decreases. As a result, the solution effervesces and some of the carbon dioxide bubbles off.
- Quiz: Champagne continues to ferment in the bottle. The fermentation produces  $\text{CO}_2$ . Why is the cork wired on a bottle of champagne?
- Answer: As more  $\text{CO}_2$  is formed , the pressure of the gas increase. The wire is to prevent the cork from blowing off.

# **Gas Pressure and Solubility**

- **Deep sea divers may experience a condition called the "bends" if they do not readjust slowly to the lower pressure at the surface.**
- **As a result of breathing compressed air and being subjected to high pressures caused by water depth, the amount of nitrogen dissolved in blood and other tissues increases.**
- **If the diver returns to the surface too rapidly, the nitrogen forms bubbles in the blood as it becomes less soluble due to a decrease in pressure. The nitrogen bubbles can cause great pain and possibly death.**
- **To alleviate this problem somewhat, artificial breathing mixtures of oxygen and helium are used. Helium is only one-fifth as soluble in blood as nitrogen. As a result, there is less dissolved gas to form bubbles.**

# **Gas Pressure and Solubility**

- **Quiz: If a diver had the "bends", describe how this can be treated.**
- **Answer: Decompression chambers are used to keep a high pressure and gradually lower the pressure.**
- **Another application of Henry's Law is in the administration of anesthetic gases. If the partial pressure of the anesthetic gas is increased, the anesthetic solubility increases in the blood.**

# **Gas Pressure and Solubility**

- Quiz: The amount of dissolved oxygen in a mountain lake at 10,000 ft and 50°F is \_\_\_?\_ than the amount of dissolved oxygen in a lake near sea level at 50°F.**
- Answer: Less at higher altitude because less pressure.**
- A Coke at room temperature will have \_\_\_?\_ carbon dioxide in the gas space above the liquid than an ice cold bottle.**
- Answer: More gas, because the warm coke can hold less of the gas in solution.**

# **Gas Pressure and Solubility**

- **Hyperbaric therapy, which involves exposure to oxygen at higher than atmospheric pressure may be used to treat hypoxia (low oxygen supply in the tissues). Explain how the treatment works.**
- **Answer: The increase in pressure in the chamber will cause more gases to enter into lungs.**

# Natures of the solute and solvent

- “Rule”: polar solvents dissolve polar solutes. Non-polar solvents dissolve non-polar solutes.
- “Likes dissolve likes”
- **Example**
  - Alcohol (polar substance) dissolves in water (polar substance)
  - Water (polar substance) does not dissolve in oil (nonpolar substance)



# Nature of the solute and solvent

**“Likes dissolve likes”**

- **When two similar compounds are mixed:**  $\Delta H_1 \approx \Delta H_2$  (enthalpy of the separation and enthalpy of the formation). Therefore,  $\Delta H_{\text{dissolution}} \approx 0$ .  
This disordering process (diffusion) that largely drives solution formation. (Entropy increases)
- **When two dissimilar compounds (a polar substance and a nonpolar substance) are mixed:** the new interaction (polar-nonpolar) is not strong enough to compensate for the separation of old interaction (polar-polar).
- **Polar – polar > nonpolar – polar interaction**
- **Polar-polar interaction will not change (oil in water)**



# Ways of Expressing Concentration

## Mass Percentage, ppm, and ppb

- All methods involve quantifying amount of solute per amount of solvent (or solution): concentration → intensive properties
- Generally amounts or measures are masses (g), moles or volume (liters).
- Qualitatively solutions are dilute or concentrated.
- Concentration: intensive properties (amount/amount)
- Definitions:

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

# Ways of Expressing Concentration

## Mass Percentage, ppm, and ppb

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

- Parts per million (ppm) can be expressed as 1 mg of solute per kilogram of solution.
  - If the density of the solution is 1 g/mL, then 1 ppm = 1 mg solute per liter of solution = 1 mg/L.

Mineral water bottle:  $\text{Ca}^{2+}$  2 ppm = 2 mg/L

# Ways of Expressing Concentration

## Mass Percentage, ppm, and ppb

$$\text{ppb of component} = \frac{\text{mass of component in solution}}{\text{total mass of solution}} \times 10^9$$

ppb:  $\mu\text{g}$  of solute per kg of solution

# Ways of Expressing Concentration

## Mole Fraction, Molarity, and Molality

- Recall mass can be converted to moles using the molar mass.

$$\text{Mole fraction of component } i = X_i = \frac{\text{moles of component in solution}}{\text{total moles of solution}}$$

$$\text{Molarity}(C_M \text{ or } M) = \frac{\text{moles solute}}{\text{volume of solution (L)}} \quad (\text{mol} / \text{L or } M)$$

$$\text{Molality, } C_m \text{ or } m = \frac{\text{moles solute}}{\text{mass of solvent (kg)}} \quad (m \text{ or mol} / \text{kg solvent})$$

- Converting between molarity ( $M$ ) and molality ( $m$ ) requires density of solution.

# Class Guided Practice Problems

1) A solution containing equal masses of glycerol ( $\text{C}_3\text{H}_8\text{O}_3$ ) and water has a density of  $1.10 \text{ g/mL}$ . Calculate the: (a) Molarity, (b) Mole Fraction of glycerol, (c) Molality of the solution. (glycerol is the solute)

2) Calculate the percent by mass of  $\text{CaCl}_2$  in a solution containing  $5.2\text{g CaCl}_2$  in  $450\text{g}$  of water.

3) Calculate the ppm, by mass, of  $\text{CaCl}_2$  in a solution containing  $0.149$  moles of  $\text{CaCl}_2$  in  $443\text{g}$  of water.

# **Class Guided Practice Problems**

1) Calculate the molarity when 0.020 moles of glycerol,  $\text{C}_3\text{H}_8\text{O}_3$ , is dissolved in 50 g of water at room temperature. Water has a density of 1.00g/mL.

# Class Practice Problem

- 1) A 0.500 L hydrochloric acid (HCl) solution, which has a density of 1.10 g/mL, contains 36% HCl by mass. Calculate the mole fraction of HCl.
- 2) A solution containing equal masses of NaCl and water has a density of 1.10g/mL. Calculate the molality of the solution.
- 3) Calculate the ppm, by mass, of  $\text{CaCl}_2$  in a solution containing 0.149 moles of  $\text{CaCl}_2$  in 443g of water.



# Colligative Properties

- Colligative properties depend on **quantity** of solute molecules (not on nature of solute). (E.g. freezing point depression and boiling point elevation.)

## Lowering Vapor Pressure

- **Solution**= solvent + solute
- **Non-volatile solutes** reduce the ability of the surface solvent molecules to escape the liquid/ interaction with solvent. → solvent: more difficult to escape to vapor phase
  - Therefore, vapor pressure is lowered.
- The amount of vapor pressure lowering depends on the amount of solute present.
- Non-volatile: does not vaporize

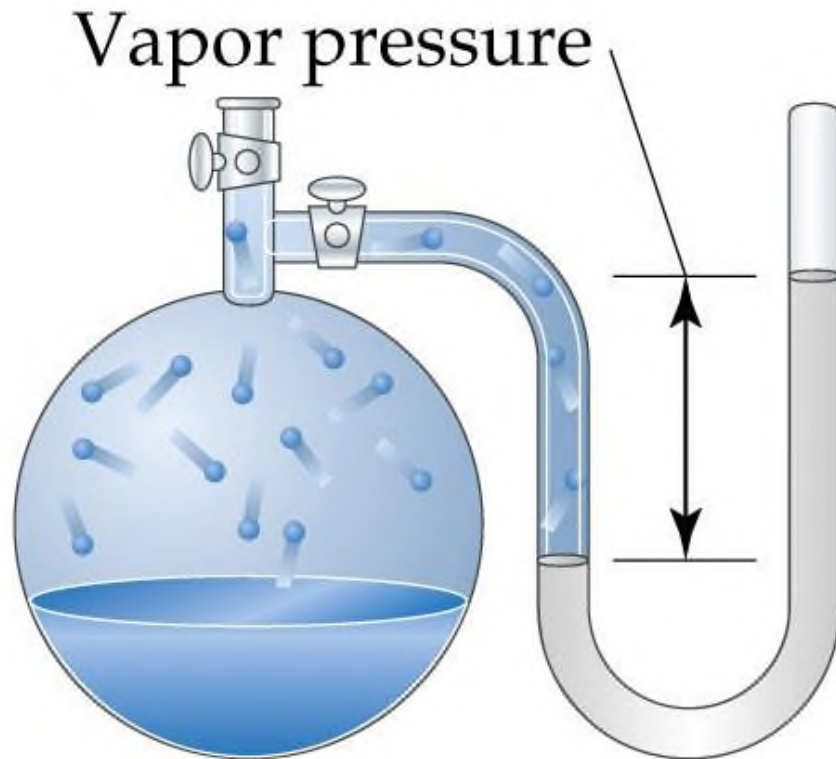
# Lowering Vapor Pressure

Non-volatile: not vaporize

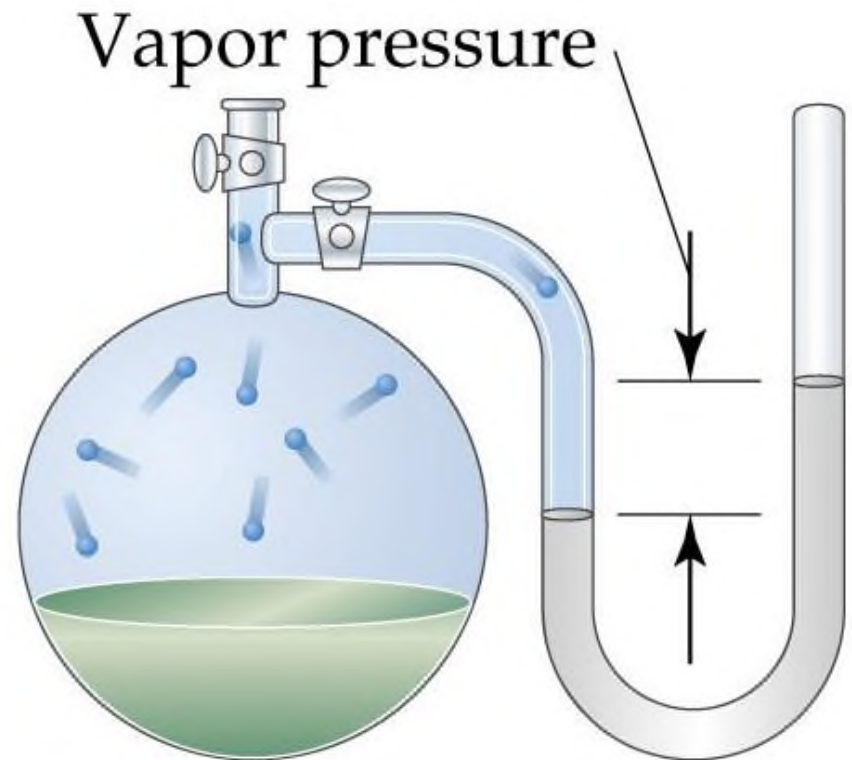
- **Non-volatile** solutes, only solvent vaporize
- Solutes reduce the ability of the surface solvent molecules to escape the liquid, solute interact with the solvent → make the solvent more difficult to escape to gas phase
  - Therefore, vapor pressure is lowered.
- The amount of vapor pressure lowering depends on the amount of solute present.

# Colligative Properties

## Lowering Vapor Pressure



Solvent alone



Solvent + solute

# Raoul's Law

- Raoul's Law: A is the solvent,  $P_A$  is the vapor pressure with solute,  $P_A^\circ$  is the vapor pressure without solute (solvent alone), and  $X_A$  is the mole fraction of A, then

$$P_{\text{solution}} = P_A = X_A P_A^\circ$$

- Another formulae: in term of the mole fraction of solute:

$$X_{\text{solute}} + X_{\text{solvent}} = 1$$

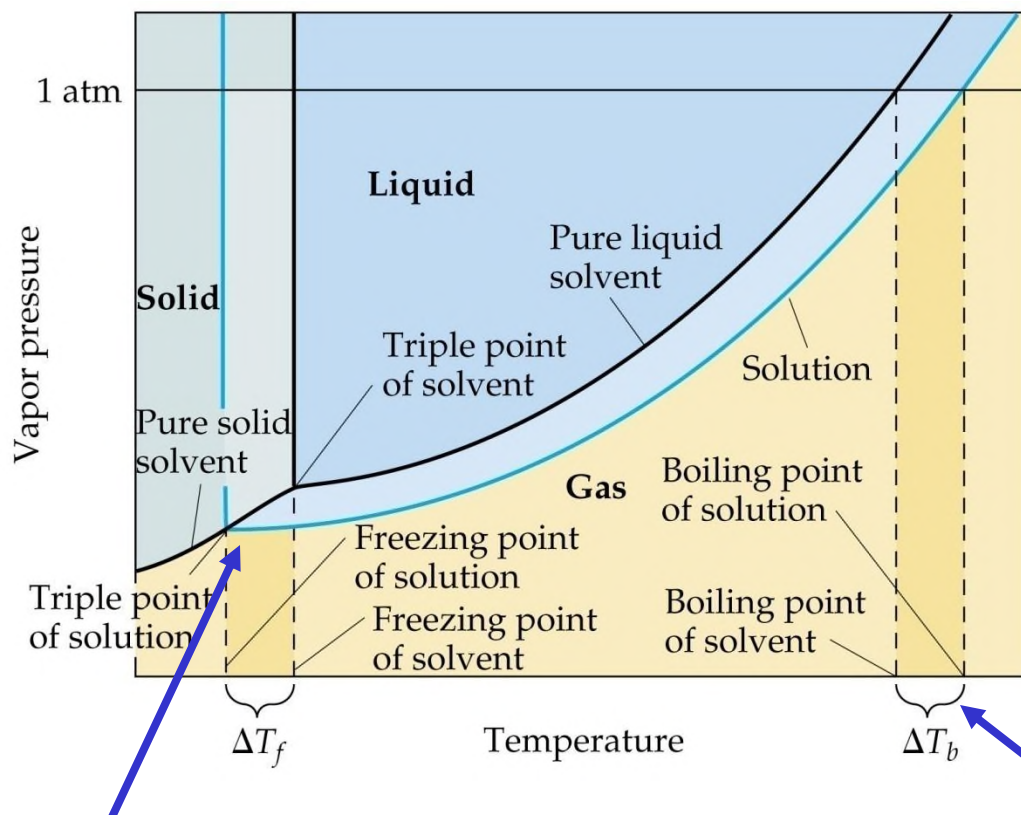
$$P_A = P_A^\circ (1 - X_{\text{solute}})$$

Lowering vapor pressure:  $\Delta P = P_A^\circ - P_A = P_A^\circ X_{\text{solute}}$

Relative: 
$$\frac{\Delta P}{P_A^\circ} = X_{\text{solute}}$$

# Phase Diagram

## Pure Solvent and Nonvolatile Solute Solution

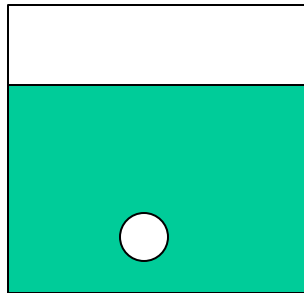


- The triple point - critical point curve is lowered.

- $\Delta T_b$  is directly related to the number of solute molecules present.

# Boiling-Point

- Water is boiling: bubbles appeared inside
- Water completely transform to vapor (happen inside the liquid, not only at the surface)
- Why the bubbles appear? Water vapor (not air)
- $P$  of water vapor  $>$  applied  $P$  (external pressure, surrounding pressure)  $\rightarrow$  bubbles can form
- If not, bubbles can not be formed
- Boiling point:  $P$  of solvent vapor  $= P$  of the surrounding



# Boiling-Point Elevation

- At the normal boiling point of pure solvent, the vapor pressure the solution still  $< 1\text{ atm}$  (**non-volatile solute**).
- At boiling point of pure solvent, the solution not yet boil
- Therefore, a higher temperature is required to attain a vapor pressure of 1 atm for the solution ( $\Delta T_b$ ).: boiling point elevation  $= T_b - T_b^0$
- **Boiling-point-elevation constant**,  $K_b$ , expresses how much  $\Delta T_b$  changes with molality,  $m$ :

$$\Delta T_b = T_b - T_b^0 = K_b C_m$$

- $K_b$  is dependent only on the solvent used in the making of the solution (independent on solute)

# Freezing Point Depression

- The freezing point is the temperature at which the first crystal forms (**solvent** freezes, solute: not freezes).
- When a solution freezes, almost pure solvent is formed first. (solvent → solid)
- Role of solutes: similar to vaporization process, solutes just make the freezing process become difficult (solute interact with the solvent) → solvent more difficult to escape from the liquid to solid (liquid-solid surface)
- Lower temperature is required to make the solvent freeze → freezing point depression



# Freezing Point Depression Cont.

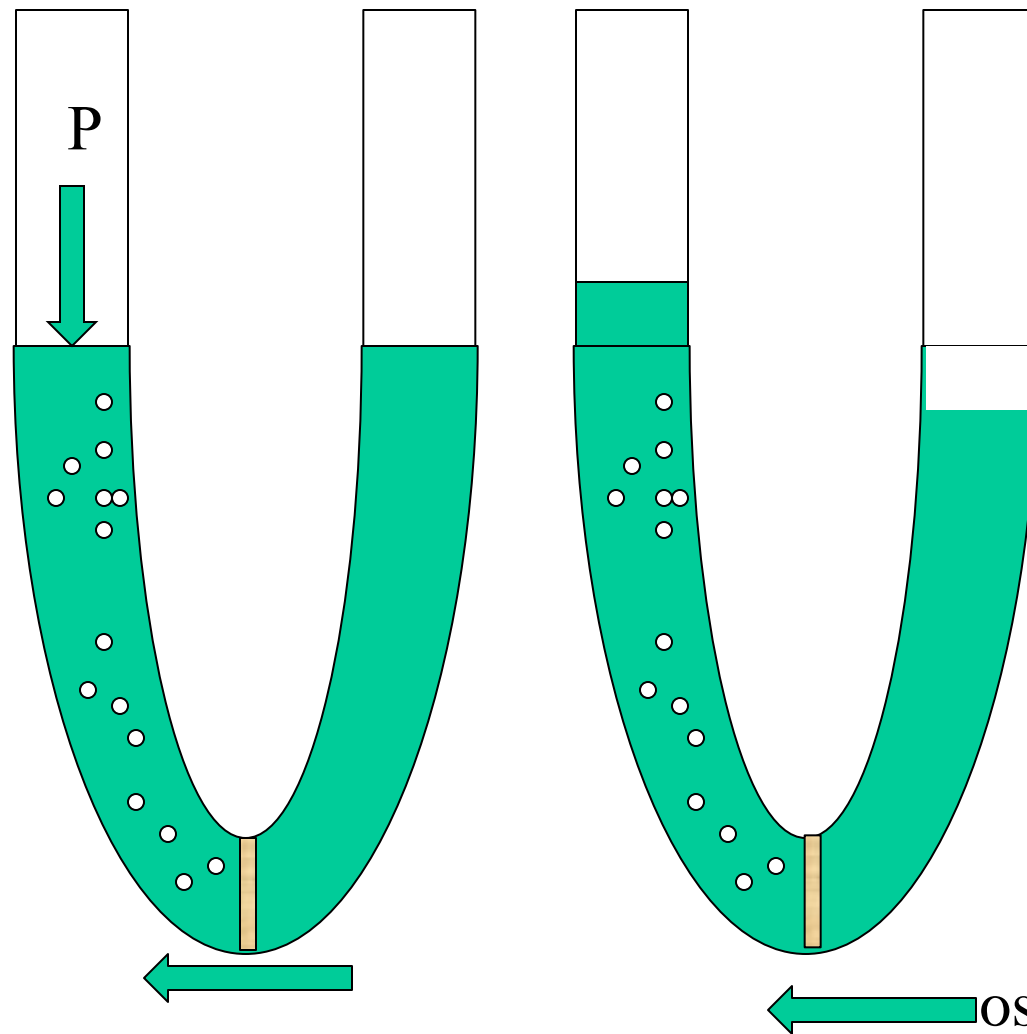
- The change in freezing point can be defined by

$$\Delta T_f = T_f - T_f^0 = K_f C_m$$

- Decrease in freezing point ( $\Delta T_f$ ) is directly proportional to molality ( $K_f$  is the freezing-point-depression constant, depend on solvent, not depend on solute):
- For water:  $K_b=0.52$   $K_f=-1.86$
- Lowering of freezing points by added solute explains the use of antifreeze in cars and the use of calcium chloride to melt ice on the road.

# Osmosis

- Osmosis: the movement of a solvent from low solute concentration to high solute concentration.
- Movement of solute: diffusion
- Semipermeable membrane: permits passage of **some** components of a solution. Example: cell membranes
- There is movement in both directions across a semipermeable membrane. (semi is not one-way)
- As solvent moves across the membrane, the fluid levels becomes uneven.



Uneven liquid level  
Difference in pressure

First, only water flow  
from R to L  
When the liquid level  
rises, water flow from L to  
R and increase with  
increasing in liquid level  
Reach equilibrium: flow  
from R to L = flow from L  
to R  
“Stop” “no flow”  
(macroscopic viewpoint)  
At beginning, apply an  
pressure → prevent the  
osmosis

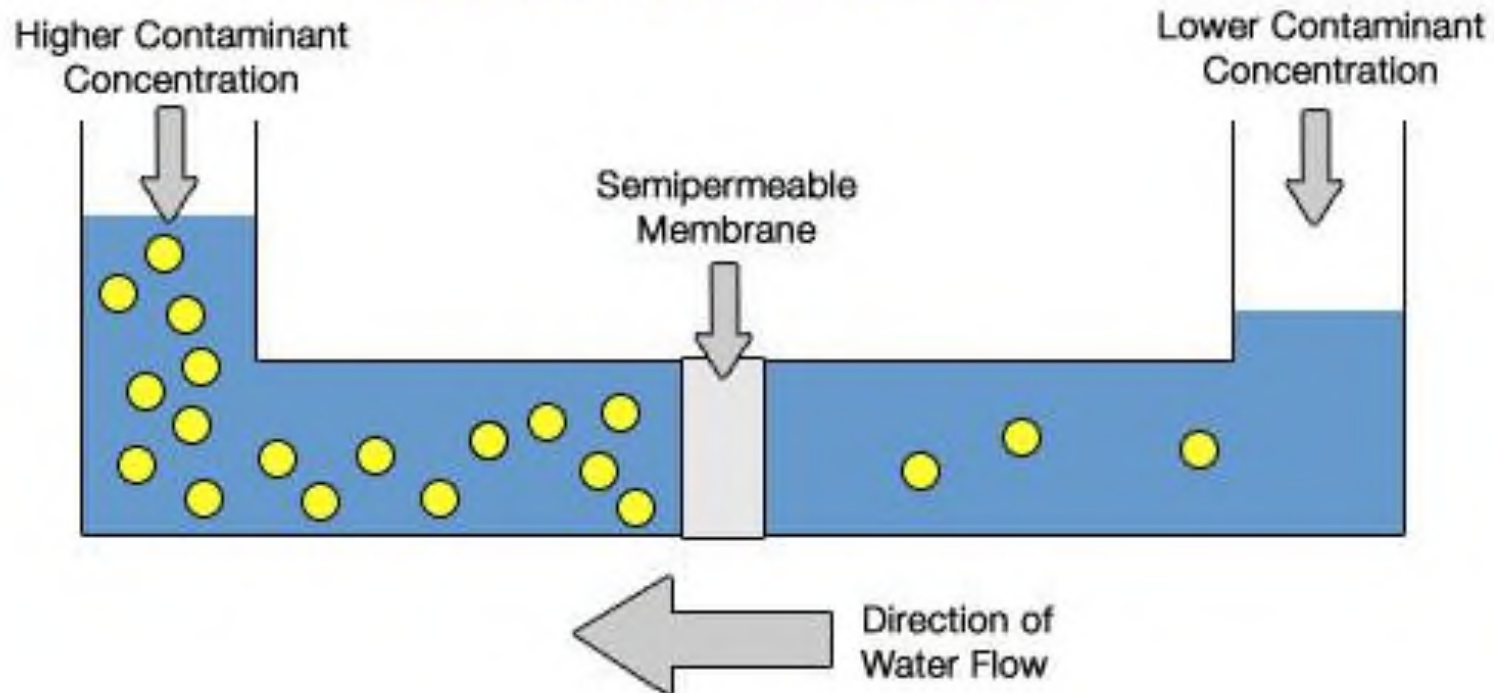
# Osmotic Pressure

- Osmotic pressure,  $\pi$ , is the pressure required to stop osmosis:

$$\begin{aligned}\pi V &= nRT \\ \pi &= \left( \frac{n}{V} \right) RT \\ &= C_M RT\end{aligned}$$

- $R=0.082 \text{ atm.L}/(\text{mol.K})$  ,  $\pi$  is atm
- Isotonic solutions: two solutions with the same  $\pi$  separated by a semipermeable membrane.
- Hypotonic solutions: a solution of lower  $\pi$  with respects to the more concentrated solution.
- The osmotic process is spontaneous.

## Normal Osmosis



- Exercise:
- Solution of glucose in water with mass percentage is 15% with  $d = 1.12$ , at  $25^{\circ}\text{C}$ . Calculate:
  - a/ Mole fraction , molality, molarity, and ppm of glucose in solution.
  - b/ Calculate vapor pressure of solution, knew  $P^0$  of water is 26 mmHg.
  - c/ Calculate boiling temperature and freezing temp., knew  $K_b = 0.52$  and  $K_f = -1.86$ .
  - d/ Calculate the osmotic pressure of this solution at  $25^{\circ}\text{C}$ .