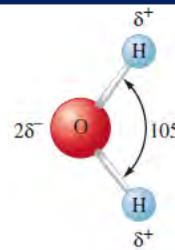


Part 5

Solutions

Solutions

- ✚ A solution is a homogeneous mixture of two or more **components**.
- ✚ The component whose phase is retained when the solution forms is called "**Solvent**".
- ✚ If all components are in the same phase, the one in greatest amount will be the "**Solvent**" and other components are called "**Solutes**".
- ✚ Solutions, in which **water** is the dissolving medium (**solvent**) are called **aqueous solutions**.
- ✚ The polarity in H_2O is responsible of its great ability to dissolve several compounds.

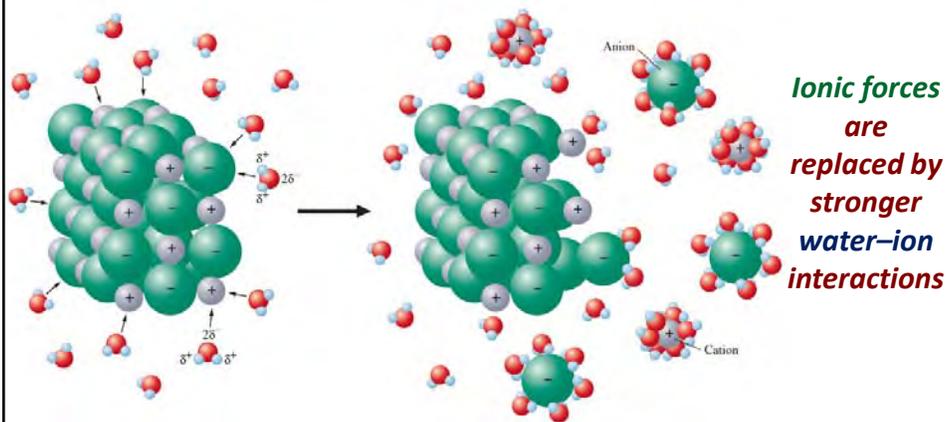


Examples of solutions

Solute	Solvent	Solution	Example
Gas	Gas	Gas	Air , natural gas
Gas	Liquid	Liquid	O ₂ in H ₂ O, Soda
Gas	Solid	Solid	H ₂ in Pt
Liquid	Gas	Gas	Moisture in air
Liquid	Liquid	Liquid	Alcohol in H ₂ O
Liquid	Solid	Solid	Hg in Ag, Drops o f H ₂ O in sugar
Solid	Gas	Gas	Dust in air
Solid	Liquid	Liquid	NaCl in H ₂ O, sea water
Solid	Solid	Solid	Alloys (Brass, steel)

Aqueous Solutions

✚ When water dissolves an ionic solid, the “positive ends” of the water molecules are attracted to the negatively charged anions and the “negative ends” are attracted to the positively charged cations. This process is called “**hydration**”.



Why do solutions form?

Tendency to Randomness or Disordering

✚ This the only reason operating for gaseous solutions

Solute/Solvent Attractions *Like Dissolves Like*

- ✚ *Polar solvents* dissolve polar substances.
 - ✚ *Ethanol*, which is not ionic but polar, dissolves in H_2O
- ✚ *Non polar solvents* dissolve non polar substances

Heat of Solution

$$\Delta H_{sol}$$

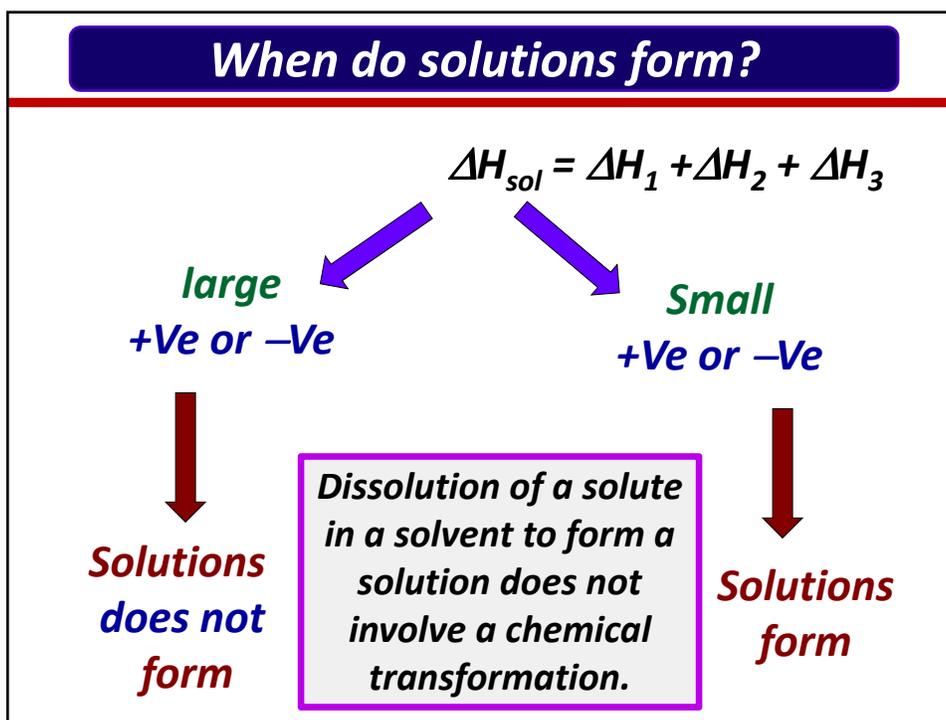
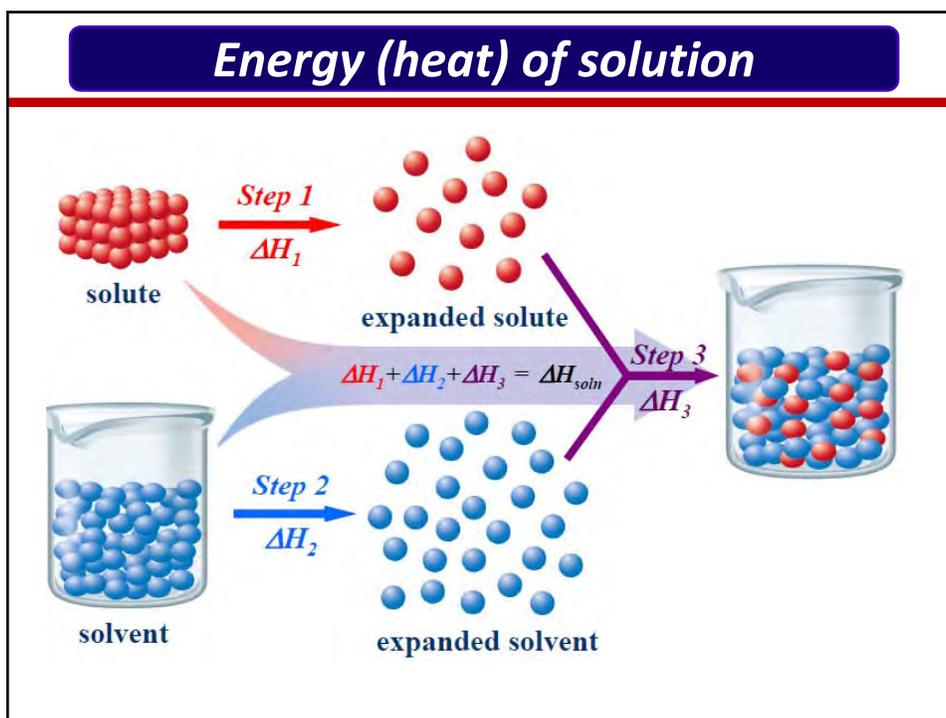
The amount of heat evolved or absorbed when one mole of a solute dissolves in a solvent at constant pressure to make a dilute solution

Steps involved in forming a solution

- ✚ Separation of solute (ΔH_1) and solvent (ΔH_2) particles
 - ✚ This needs energy (+ve ΔH), i.e., Endothermic
- ✚ Attraction of solute and solvents particles
 - ✚ This releases energy (ΔH_3 is -ve), i.e., Exothermic

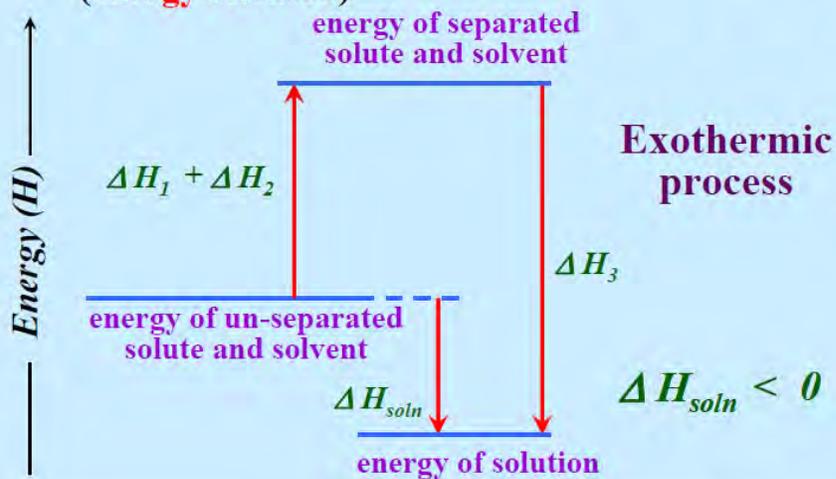
$$\Delta H_{sol} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

- ✚ If $\Delta H_1 + \Delta H_2 = \Delta H_3$ (in value but opposite signs), $\Delta H_{sol} = 0 \rightarrow$ *ideal solution*
 - ✚ almost equal attraction forces between solute/solute, solvent/solvent, and solute/solvent)
- ✚ If $\Delta H_1 + \Delta H_2 \neq \Delta H_3$, $\Delta H_{sol} \neq 0 \rightarrow$ *Non ideal solution*



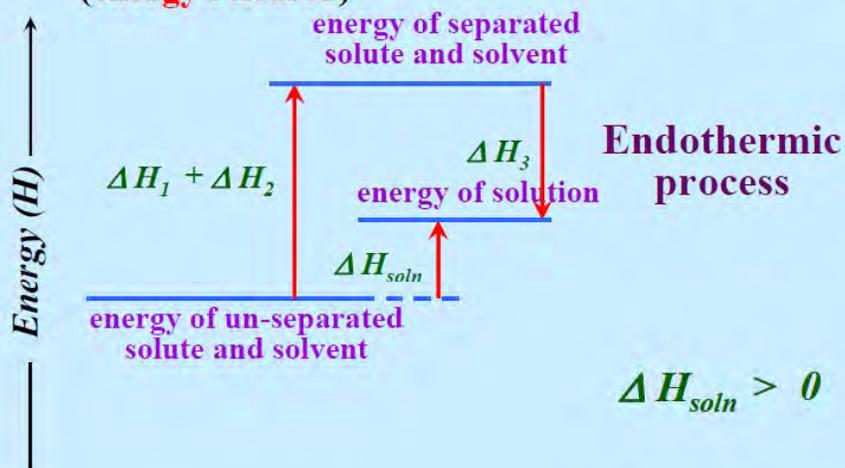
Exothermic Process

ΔH_{soln} could be positive (energy absorbed) or negative (energy released)



Endothermic Process

ΔH_{soln} could be positive (energy absorbed) or negative (energy released)



Nature of solutes and Solvents

Why oil is insoluble in water?

Oil: a mixture of non polar molecules having only the weak London dispersion forces, i.e., ΔH_1 is small +Ve

Water: is a polar solvent having the relatively strong H-bonding, i.e., ΔH_2 is large +Ve

Oil–Water interaction: is almost negligible, i.e., ΔH_3 is small –Ve

$\Delta H_{sol} = \Delta H_1 + \Delta H_2 + \Delta H_3 = \text{large +Ve}$ **Solution does not form**

Nature of solutes and Solvents

Why NaCl is soluble in water?

NaCl: is an ionic solid having the strong ionic bond, i.e., ΔH_1 is large +Ve

Water: is a polar solvent having the relatively strong H-bonding, i.e., ΔH_2 is large +Ve

NaCl–Water interaction: is strong, i.e., ΔH_3 is large –Ve

$\Delta H_{sol} = \Delta H_1 + \Delta H_2 + \Delta H_3 = \text{small +Ve}$ **A Solution forms**
 $+3.9 \text{ kJ mol}^{-1}$

Nature of solutes and Solvents

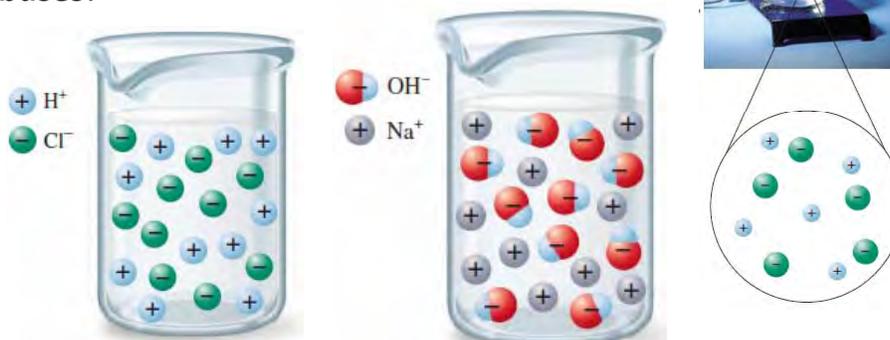
	ΔH_1	ΔH_2	ΔH_3	ΔH_{soln}	Outcome
Polar solvent Polar solute	Large +	Large +	Large -	Small \pm	Solution forms
Polar solvent Non-polar solute	Small +	Large +	Small -	Large +	No solution forms
Non-polar solvent Non-polar solute	Small +	Small +	Small -	Small \pm	Solution forms
Non-polar solvent Polar solute	Large +	Small +	Small -	Large +	No solution forms

Nature of solutes and Solvents



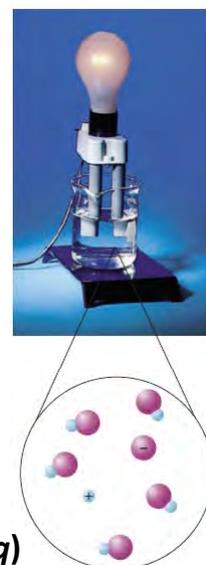
Strong Electrolytes

Substances that are completely ionized (i.e., **conduct electricity efficiently**) when they are dissolved in water. Examples include soluble salts, strong acids, and strong bases.



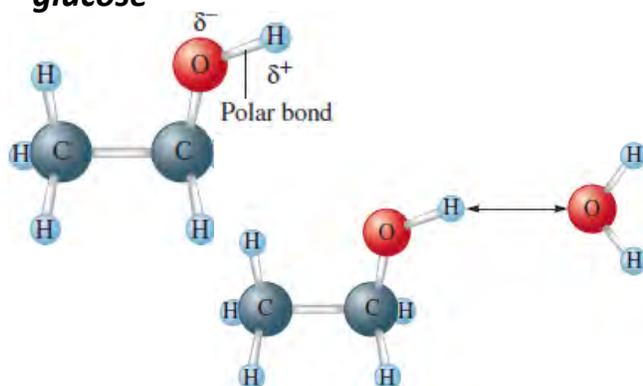
Weak Electrolytes

- ✚ Substances that exhibit a small degree of ionization in water (i.e., **conduct only a small current**).
- ✚ They produce relatively few ions when dissolved in water.
- ✚ Examples include **weak acids (acetic acid)** and **weak bases (ammonia)**.



Nonelectrolytes

- ✚ *Substances that dissolve in water but do not produce any ions (i.e., non conductors for electricity).*
- ✚ *Examples include ethanol and glucose*



Composition of Solutions

Mass of a solute per mass of solvent or solution

- ▶ Mole fraction and Mole percent,
- ▶ Mass fraction and Mass percent,
- ▶ Molality

Mass of a solute per Volume of solution

- ▶ Molarity
- ▶ Normality

Mole fraction

- **The ratio of the no. of moles of a given component in a solution to the total no. of moles of all components**

$$X_A = \frac{n_A}{n_A + n_B + n_C + \dots + n_Z} \quad \text{Unitless}$$

$$\sum X_i = 1$$

Mole Percent

is the mole fraction multiplied by 100

Mass fraction

- **The ratio of the mass of a given component in a solution to the total mass of all components**

$$(\text{mass fraction})_A = \frac{m_A}{m_A + m_B + m_C + \dots + m_Z} \quad \text{Unitless}$$

$$\sum (\text{mass fraction})_i = 1$$

Mass Percent *is the mass fraction multiplied by 100*

A solution labeled "0.9 % NaCl" means 0.9 g NaCl is dissolved in 99.1 g H₂O or 100 g of solution

Molality (Molal concentration)

■ The no. of moles of solute dissolved in 1 kg of solvent

$$m = \frac{n_{\text{solute}}}{\text{mass of solvent (kg)}}$$

$$m = \frac{W_{\text{solute}}}{Mwt_{\text{solute}}} \times \frac{1000}{w_{\text{solvent}} \text{ (g)}}$$

n_{solute} : no. of moles of solute

Mwt_{solute} : molar mass of solute

W_{solute} : mass of solute

W_{solvent} : mass of solvent

Molarity (Molar concentration)

■ The no. of moles of solute dissolved in 1 liter of solution

$$M = \frac{n_{\text{solute}}}{\text{Volume of solution (L)}} = \frac{W_{\text{solute}}}{Mwt_{\text{solute}} \times V \text{ (L)}}$$

n_{solute} : no. of moles of solute

Mwt_{solute} : molar mass of solute

W_{solute} : mass of solute

V : Volume of solution in liter

$$w_{\text{solute}} \text{ (g)} = M \text{ (mol / L)} \times Mwt_{\text{solute}} \text{ (g / mol)} \times V \text{ (L)}$$

Normality

 **The number of equivalents of solute per liter of solution**

The definition of an equivalent depends on the reaction taking place in the solution.

For an acid–base reaction, the equivalent is the mass of acid or base that can furnish or accept exactly 1 mole of protons (H⁺ ions).

Acid/Base	Mwt, g/mol	Equivalent mass	M/N relationship
HCl	36.5	36.5	1M = 1N
H ₂ SO ₄	98	98/2 = 49	1M = 2N
NaOH	40	40	1M = 1N
Ca(OH) ₂	74	74/2 = 37	1M = 2N

Normality

For oxidation–reduction reactions, the equivalent is defined as the quantity of oxidizing or reducing agent that can accept or furnish 1 mole of electrons.



For example, MnO₄⁻ reacts in acidic solution absorbing five electrons to produce Mn²⁺:

$$\text{Equivalent mass of KMnO}_4 = \frac{\text{molar mass}}{5} = \frac{158 \text{ g}}{5} = 31.6 \text{ g}$$

For salts,

$$\text{Equivalent mass of a salt} = \frac{\text{molar mass}}{\text{no. of ions} \times \text{its valency}}$$

NaCl: Eq. wt = Mwt/1

Na₃PO₄: Eq.Wt = Mwt / 3

Normality

$$N = \frac{\text{no. equivalents}_{\text{solute}}}{\text{Volume of solution (L)}} = \frac{W_{\text{solute}}}{\text{Eq.wt}_{\text{solute}} \times V \text{ (L)}}$$

n_{solute} : no. of moles of solute

$\text{Eq.wt}_{\text{solute}}$: Equivalent mass of solute

W_{solute} : mass of solute

V : Volume of solution in liter

$$w_{\text{solute}} \text{ (g)} = N \text{ (equivalents/L)} \times \text{Eq.wt}_{\text{solute}} \text{ (g/equivalents)} \times V \text{ (L)}$$

Exercise

A solution is prepared by mixing 1.00 g ethanol ($\text{C}_2\text{H}_5\text{OH}$) with 100.0 g water to give a final volume of 101 mL. Calculate the molarity, mass percent, mole fraction, and molality of ethanol in this solution.

Solution

molar mass of ethanol = 46.07 g/mol

$$\begin{aligned} M &= \frac{W_{\text{solute}}}{\text{Mwt}_{\text{solute}} \times V \text{ (L)}} \\ &= \frac{1.0 \text{ g}}{46.07 \text{ g mol}^{-1} \times 101 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.215 \text{ mol/L} \\ &= 0.215 \text{ M} \end{aligned}$$

$$\text{mass percent of ethanol} = \frac{m_{\text{ethanol}}}{m_{\text{ethanol}} + m_{\text{water}}} \times 100$$

$$= \frac{1.0}{1.0 + 100.0} \times 100 = 0.990 \%$$

$$X_{\text{ethanol}} = \frac{n_{\text{ethanol}}}{n_{\text{ethanol}} + n_{\text{water}}} =$$

$$\frac{1.0 \text{ g} / 46.07 \text{ g mol}^{-1}}{1.0 \text{ g} / 46.07 \text{ g mol}^{-1} + 100.0 \text{ g} / 18.0 \text{ g mol}^{-1}}$$

$$= 0.00389$$

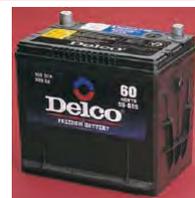
$$m = \frac{w_{\text{ethanol}}}{Mwt_{\text{ethanol}}} \times \frac{1000}{w_{\text{water}} (g)}$$

$$= \frac{1.0 \text{ g}}{46.07 \text{ g mol}^{-1}} \times \frac{1000}{100.0 (g)} = 0.217 \text{ mol kg}^{-1} = 0.217 \text{ m}$$

Exercise

molar mass of sulfuric acid = 98 g/mol

The electrolyte in automobile lead storage batteries is a 3.75 M sulfuric acid solution that has a density of 1.230 g/mL. Calculate the mass percent, molality, and normality of the sulfuric acid.

**Solution**

- + $d = 1.230 \text{ g/mL} = 1230 \text{ g/L} \rightarrow$ means we have 1230 g solution ($\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$) in every liter of solution ($\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$)
- + Molarity of $\text{H}_2\text{SO}_4 = 3.75 \text{ M} \rightarrow$ means we have 3.75 mole (368 g) of H_2SO_4 in every liter of solution ($\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$)

**1L
Solution**

1230 g

 $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$

368 g

 H_2SO_4

mass of water in 1L solution = $1230 - 368 = 862 \text{ g}$

mass percent of ethanol =

$$\frac{m_{\text{sulfuric acid}}}{m_{\text{sulfuric acid}} + m_{\text{water}}} \times 100$$

$$= \frac{368}{368 + 862} \times 100 = 29.9 \%$$

$$m = \frac{w_{\text{sulfuric acid}}}{Mwt_{\text{sulfuric acid}}} \times \frac{1000}{w_{\text{water}} (g)}$$

$$= \frac{368 \text{ g}}{98 \text{ g mol}^{-1}} \times \frac{1000}{862 (g)} = 4.35 \text{ m}$$

$$N = M \times 2 = 3.75 \times 2$$

$$= 7.5 \text{ equivalents per liter (N)}$$

Solubility

✿ The mass of solute necessary to form a saturated solution with a given mass of solvent at a specific temperature.

Its unit is usually expressed in **g solute/100 g solvent** or in **mole solute/g solvent**.

✿ **A saturated solution:** is a solution containing the maximum amount of solute soluble in a definite amount of solvent at a given temperature (equilibrium concentration)

Supersaturated solutions

- ❖ **A supersaturated solution:** is a solution containing more solutes than the equilibrium amount.
- ❖ It is unstable and tends to move towards saturation under proper conditions



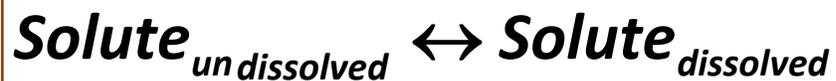
**Unsaturated
solution**

**Saturated
solution**

**Supersaturated
solution**

Solubility and equilibrium

- ❖ **In saturated solutions,** a dynamic equilibrium exists between the undissolved solute and the soluble solute in solution



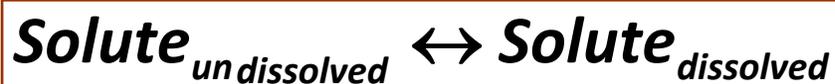
- ❖ **Factors affecting solubility**

- + Temperature
- + Pressure
- + Concentration
- + Nature of solutes and solvents

Effect of Temp. on the Solubility of a gas in a liquid

- At constant pressure, the solubility of gases in liquids always decreases with T.
- The reasons are complicated where a very close competition exists between the two parameters responsible for solution formation (randomness and attractions)

Effect of Temp. on the Solubility of a solids and liquids in liquids



- If equilibrium is distorted by any factor, the equilibrium will shift toward the direction restoring equilibrium (Le Chatelier Principle)

For endothermic reactions



- Increasing temperature shifts the reaction to right increasing the solubility of the solute

Effect of Temp. on the Solubility of a solids and liquids in liquids

For exothermic reactions



- Increasing temperature shifts the reaction to left lowering the solubility of the solute

Effect of Pressure on the Solubility of gases

- Pressure has a significant effect in case of gaseous solutes since liquids and solids are incompressible
- Carbonated beverages, for example, are always bottled at high pressures of carbon dioxide to ensure a high concentration of carbon dioxide in the liquid.
- The **fizzing** that occurs when you open a **can of soda** results from the escape of gaseous carbon dioxide, **because** under these conditions the pressure of CO_2 above the solution is now much lower than that used in the bottling process.

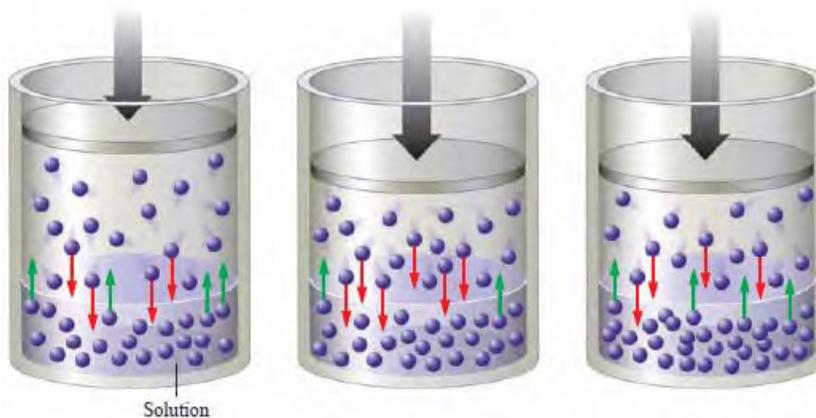
Effect of Pressure on the Solubility of gases

- Consider a closed container that is partially filled with a solution (gas in liquid)



- The gas molecules are entering and leaving the solution at the same rate.
- If P is suddenly increased, the number of gas molecules per unit volume increases, and the gas enters the solution at a higher rate than it leaves.
- As the concentration of dissolved gas increases, the rate of the escape of the gas also increases until a new equilibrium is reached, where the solution contains more dissolved gas than before.

Effect of Pressure on the Solubility of gases



- Pressure increase** → new equilibrium with higher solubility

Henry's law

- The amount of a gas dissolved in a solution is directly proportional to the pressure of the gas above the solution.

$$C = kP$$

- C : concentration of the dissolved gas,
- K : a constant characteristic of a particular solution,
- P : the partial pressure of the gaseous solute above the solution.

Henry's law

- Henry's law is obeyed most accurately for dilute solutions of gases that do not dissociate in or react with the solvent.
- For example, Henry's law is obeyed by oxygen gas in water, but it does not correctly represent the behavior of gaseous hydrogen chloride in water because of the dissociation reaction



Exercise

✚ A certain soft drink is bottled so that a bottle at 25°C contains CO₂ gas at a pressure of 5.0 atm over the liquid. Assuming that the partial pressure of CO₂ in the atmosphere is 4.0 × 10⁻⁴ atm, calculate the equilibrium concentrations of CO₂ in the soda both before and after the bottle is opened. The Henry's law constant for CO₂ in aqueous solution is 3.1 × 10⁻² mol/L . atm at 25°C.

Solution✚ **Before Opening**

$$C = kP = (3.1 \times 10^{-2} \text{ mol / L.atm}) \times (5.0 \text{ atm}) = 0.16 \text{ mol / L}$$

✚ **After Opening**

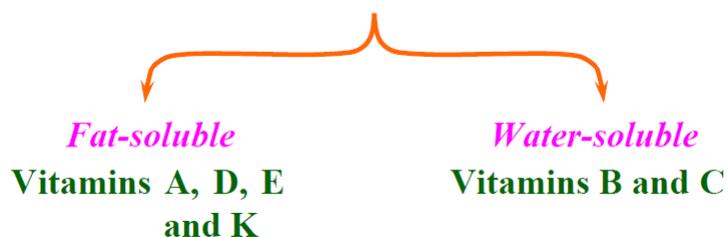
$$C = kP = (3.1 \times 10^{-2} \text{ mol / L.atm}) \times (4.0 \times 10^{-4} \text{ atm}) = 1.2 \times 10^{-5} \text{ mol / L}$$

Note the large change in concentration of CO₂. This is why soda goes "flat" after being open for a while.

Effect of structure on the Solubility

✚ **Solubility is favored if the solute and solvent have similar polarities. Since it is the molecular structure that determines polarity, there should be a definite connection between structure and solubility.**

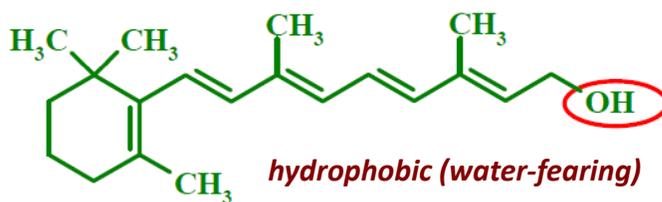
Vitamins can be divided into two classes:



Effect of structure on the Solubility

Vitamin A

*soluble in
nonpolar
materials such
as body fat*



Vitamin C

water-soluble

hydrophilic (water-loving)

