Lecture 7

Spring 2022

General Chemistry II

Chem 102

Solutions

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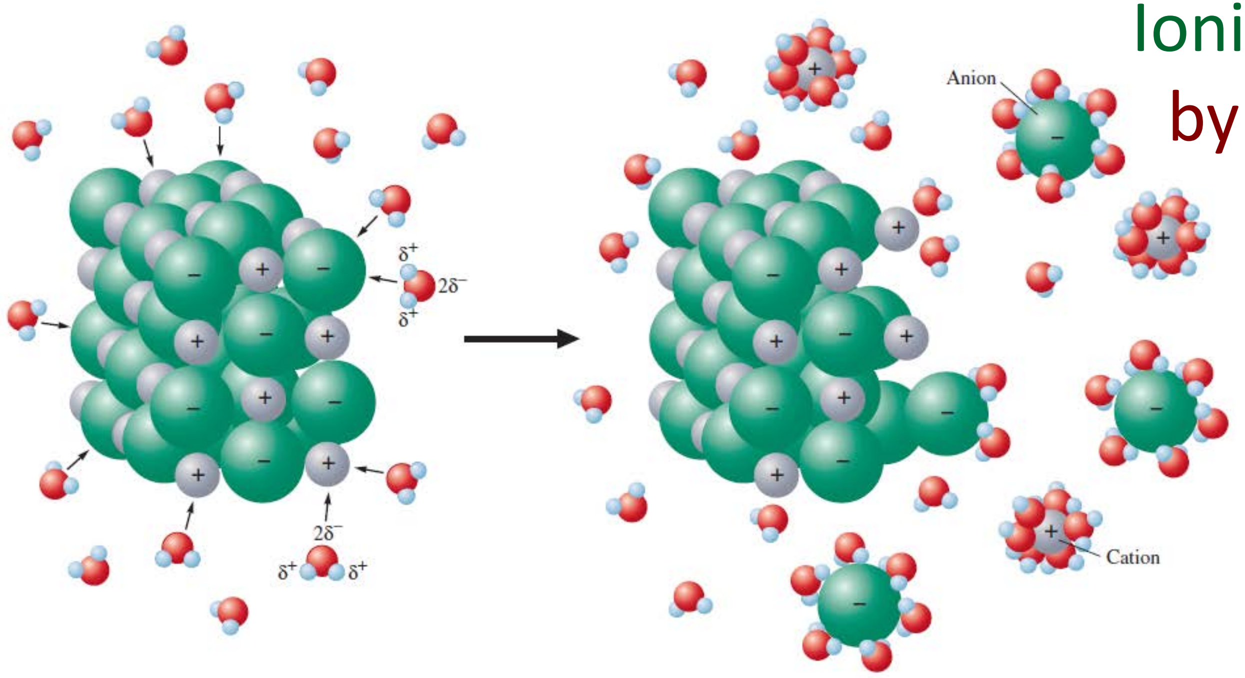
Solution

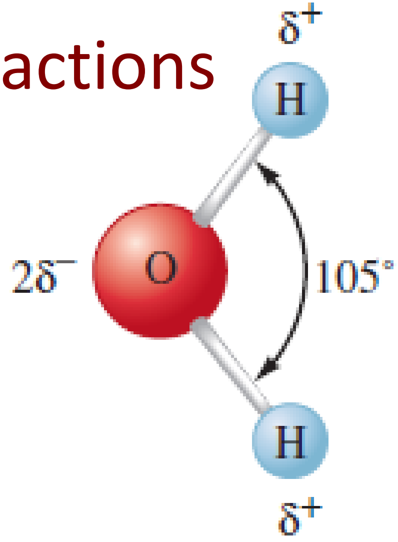
- is a homogeneous mixture of two or more components.
- The component whose phase retains ($1£7) is called "Solvent" and the other component whose phase disappears is called "Solute".
- If all components are in the same phase, the one in greatest amount will be the "Solvent" and other components are "Solutes".
- Solutions, in which water is the solvent are called aqueous solutions.
- The polarity in **H_2O** is responsible of its great ability to dissolve several compounds.

Hydration in Aqueous Solutions

- When water dissolves an ionic solid, the "positive ends" of 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".



Ionic forces are replaced by stronger water–ion interactions



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 (not ionic but polar) dissolves in H_2O
- **Non polar solvents** dissolve non polar substances

Heat of Solution ΔH_{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

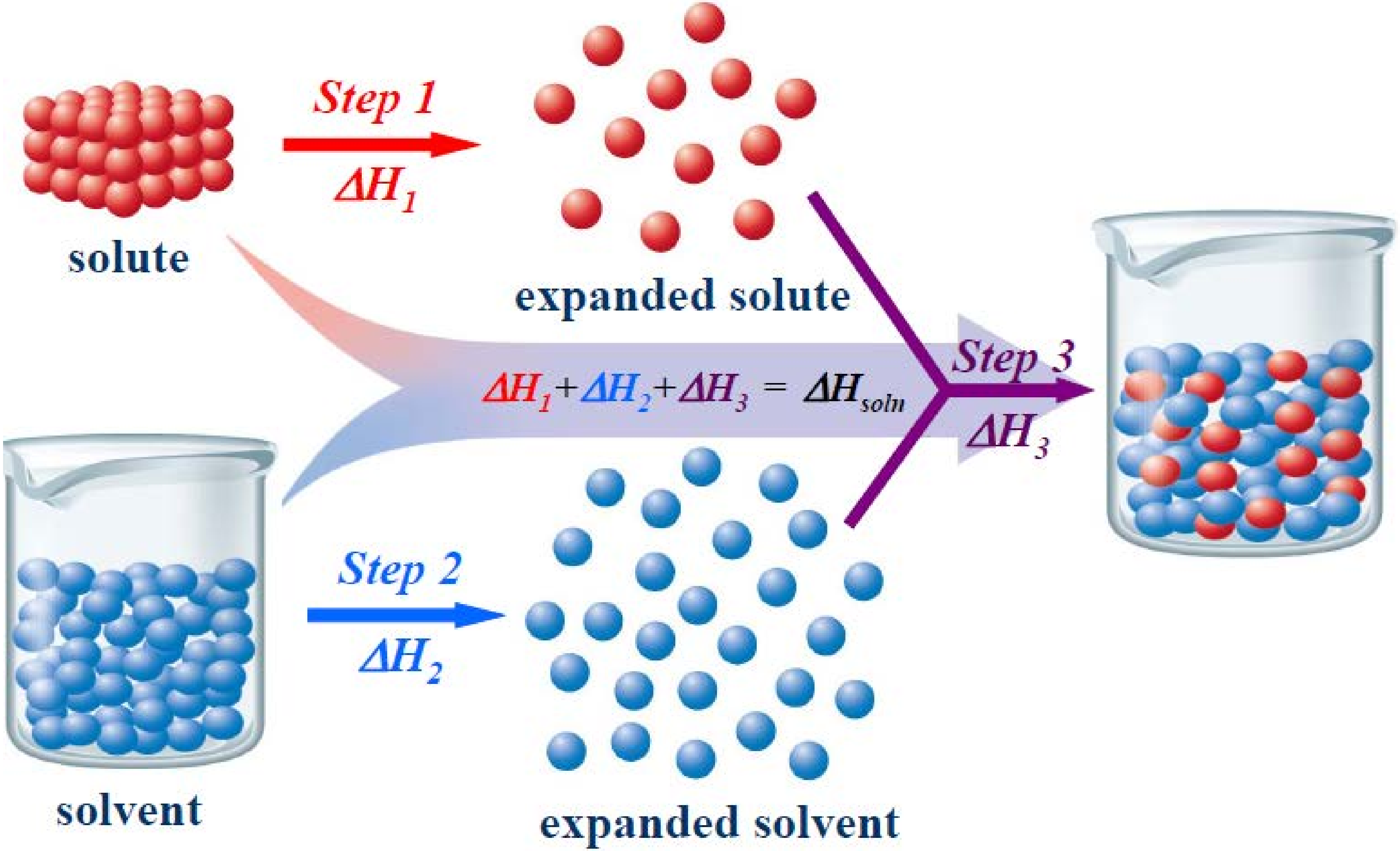
- Separation of solute (**ΔH_1**) and solvent (**ΔH_2**) particles
  - This needs energy **(+ve ΔH)**, i.e., **Endothermic**
- Attraction of solute and solvents particles
  - This releases energy (**–ve ΔH_3**), i.e., **Exothermic**

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

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

- If $\Delta H_1 + \Delta H_2 \neq \Delta H_3$, $\Delta H_{sol} \neq 0$ → Non ideal solution

Energy (heat) of solution



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

When do solutions form?

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

large

+Ve or –Ve

Solutions does not form

Small

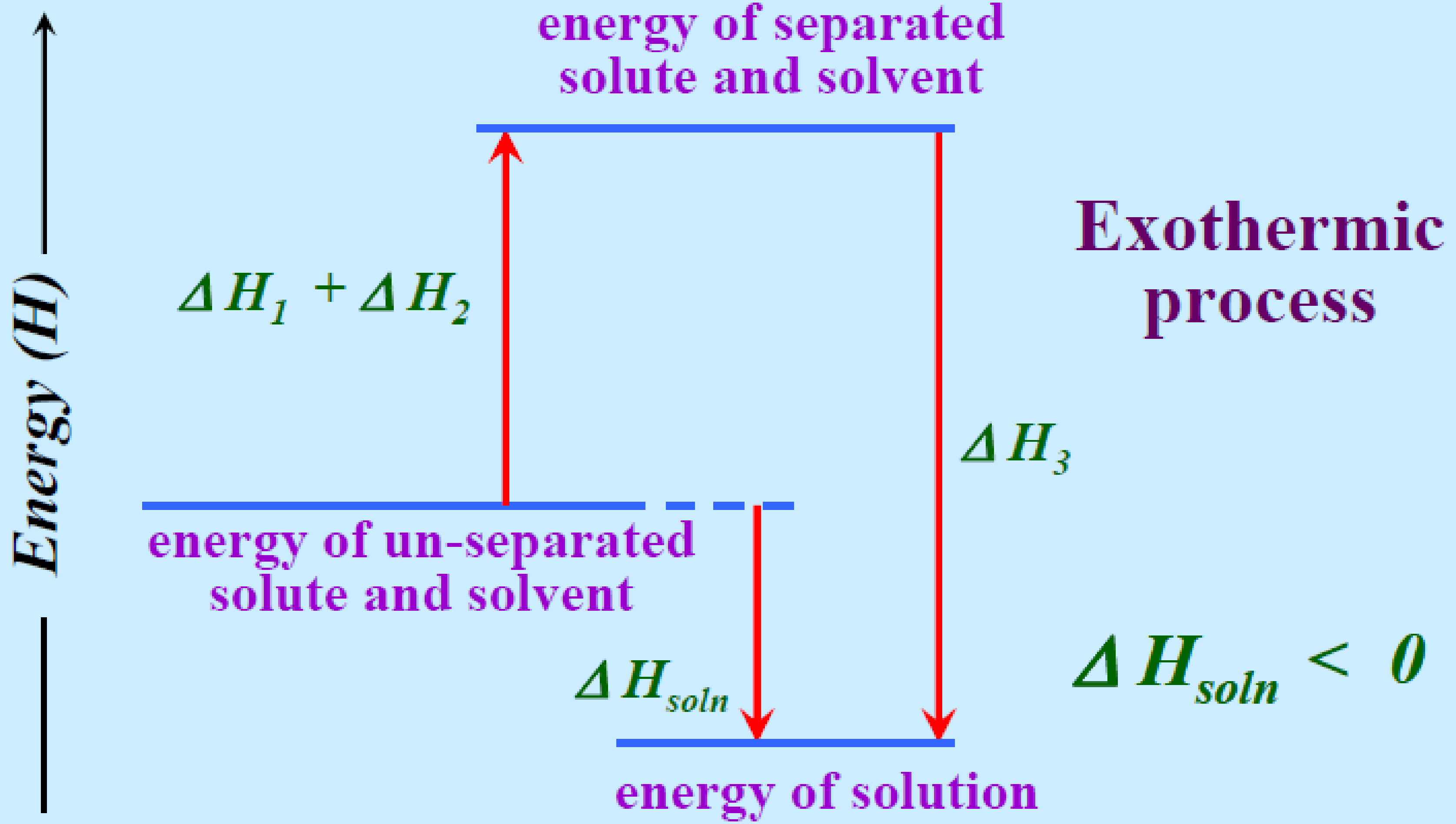
+Ve or –Ve

Solutions form

Dissolution of a solute in a solvent to form a solution does not involve a chemical transformation.

Exothermic Process

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



Energy (H)

energy of separated solute and solvent

$\Delta H_1 + \Delta H_2$

ΔH_3

Exothermic process

energy of un-separated solute and solvent

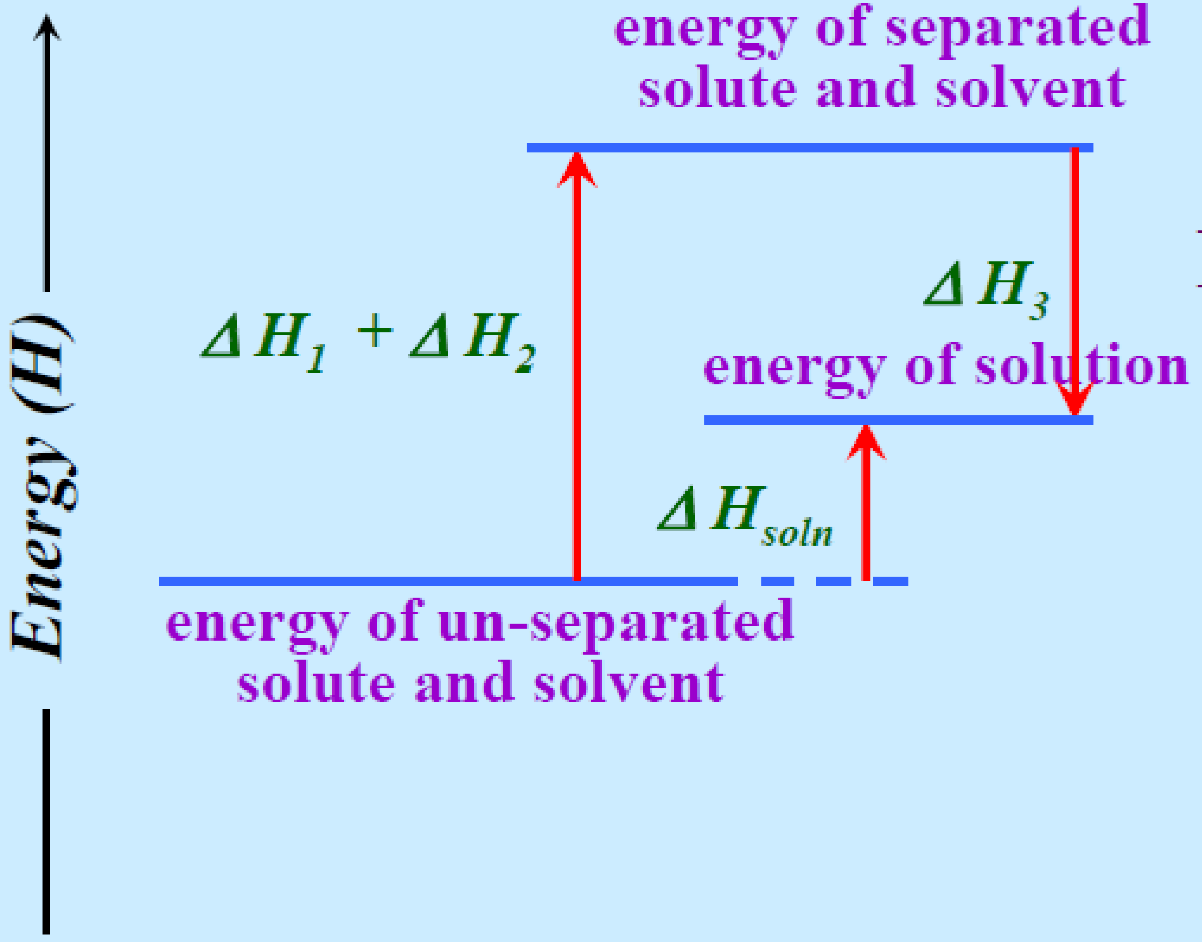
ΔH_{soln}

$\Delta H_{soln} < 0$

energy of solution

Endothermic Process

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



Energy (H)

energy of separated solute and solvent

$\Delta H_1 + \Delta H_2$

ΔH_3

energy of solution

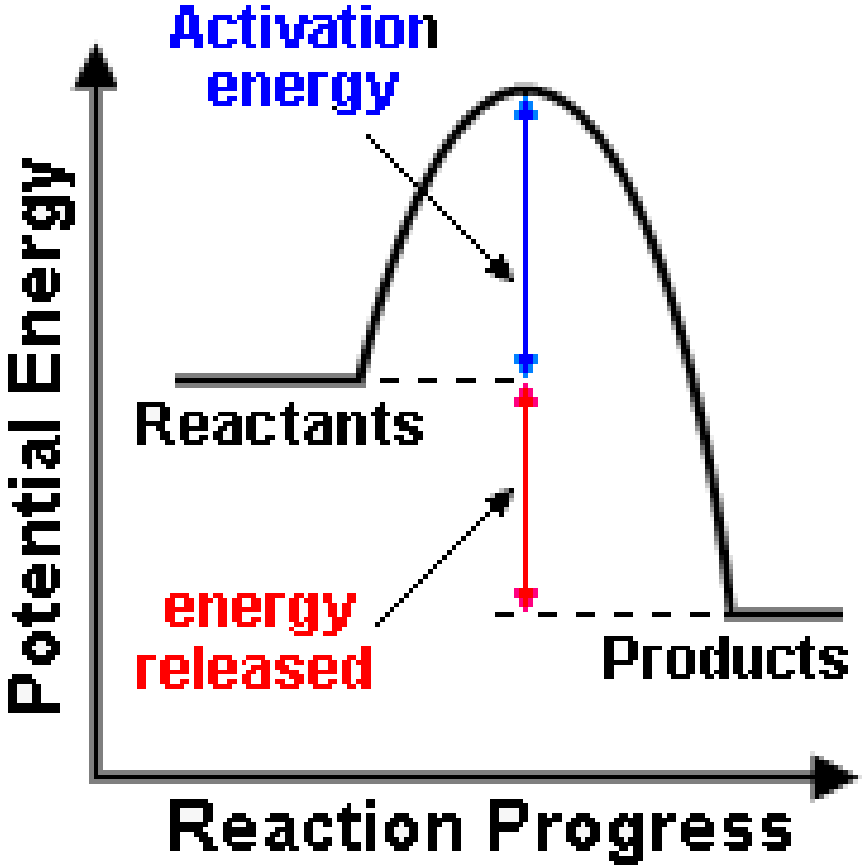
ΔH_{soln}

energy of un-separated solute and solvent

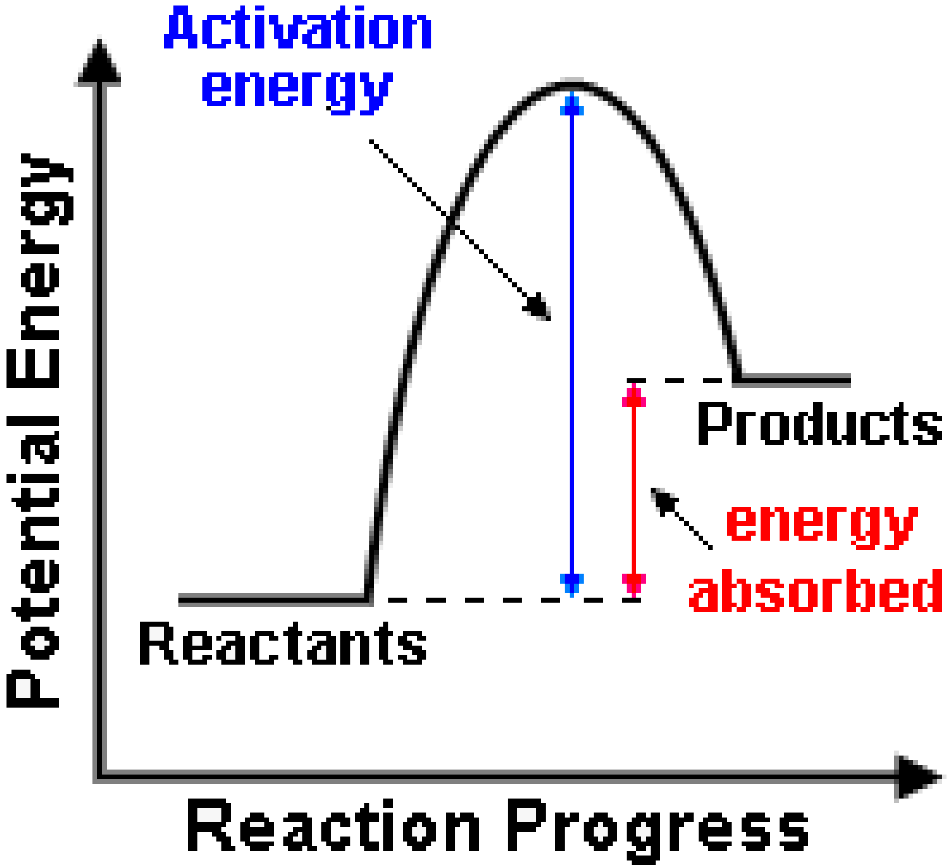
Endothermic process

$\Delta H_{soln} > 0$

Potential Energy Diagrams



Exothermic reaction



Endothermic reaction

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

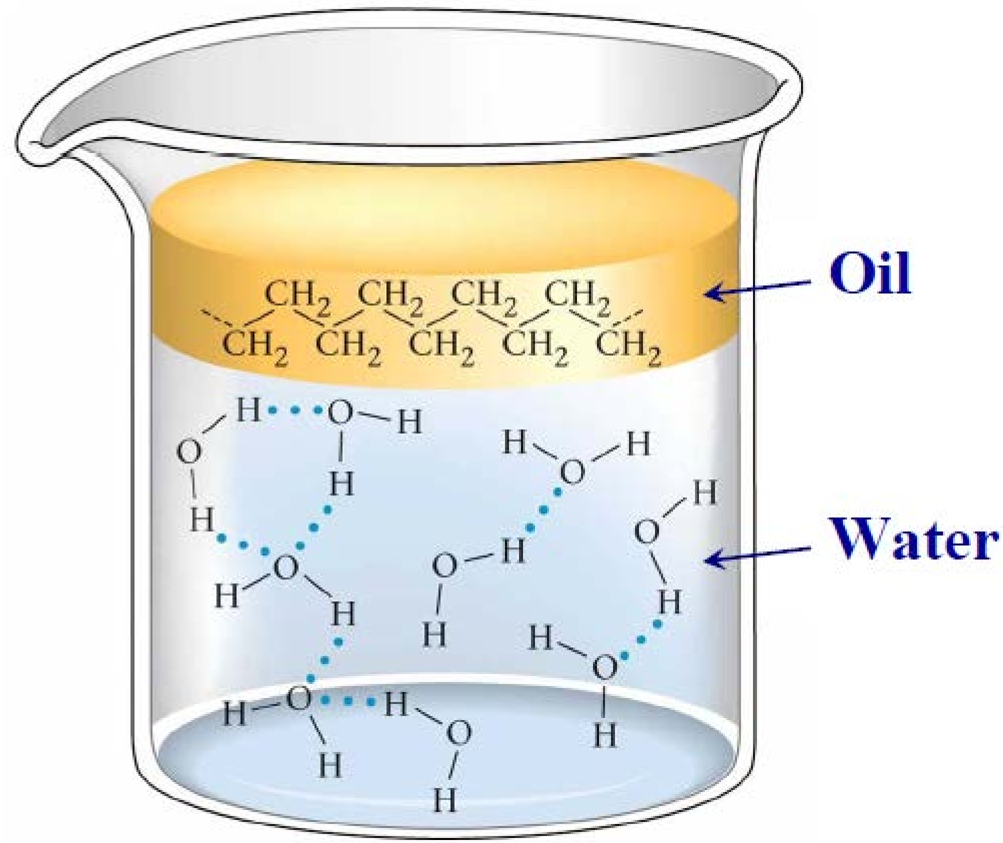
Why NaCl is soluble in water?

- 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

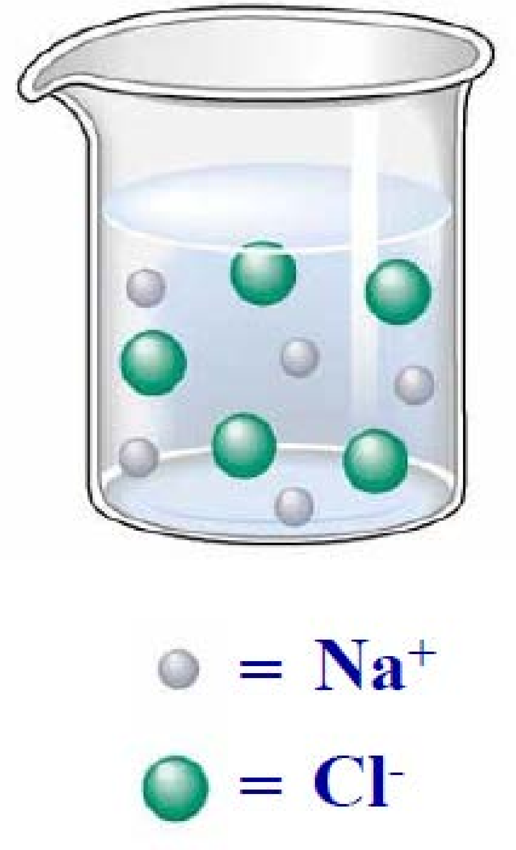
$$\boldsymbol{\Delta H_{sol} = \Delta H_1 + \Delta H_2 + \Delta H_3} = \text{small +Ve} = +3.9\ \text{kJ mol}^{-1}$$

A solution forms

Nature of solutes and Solvents

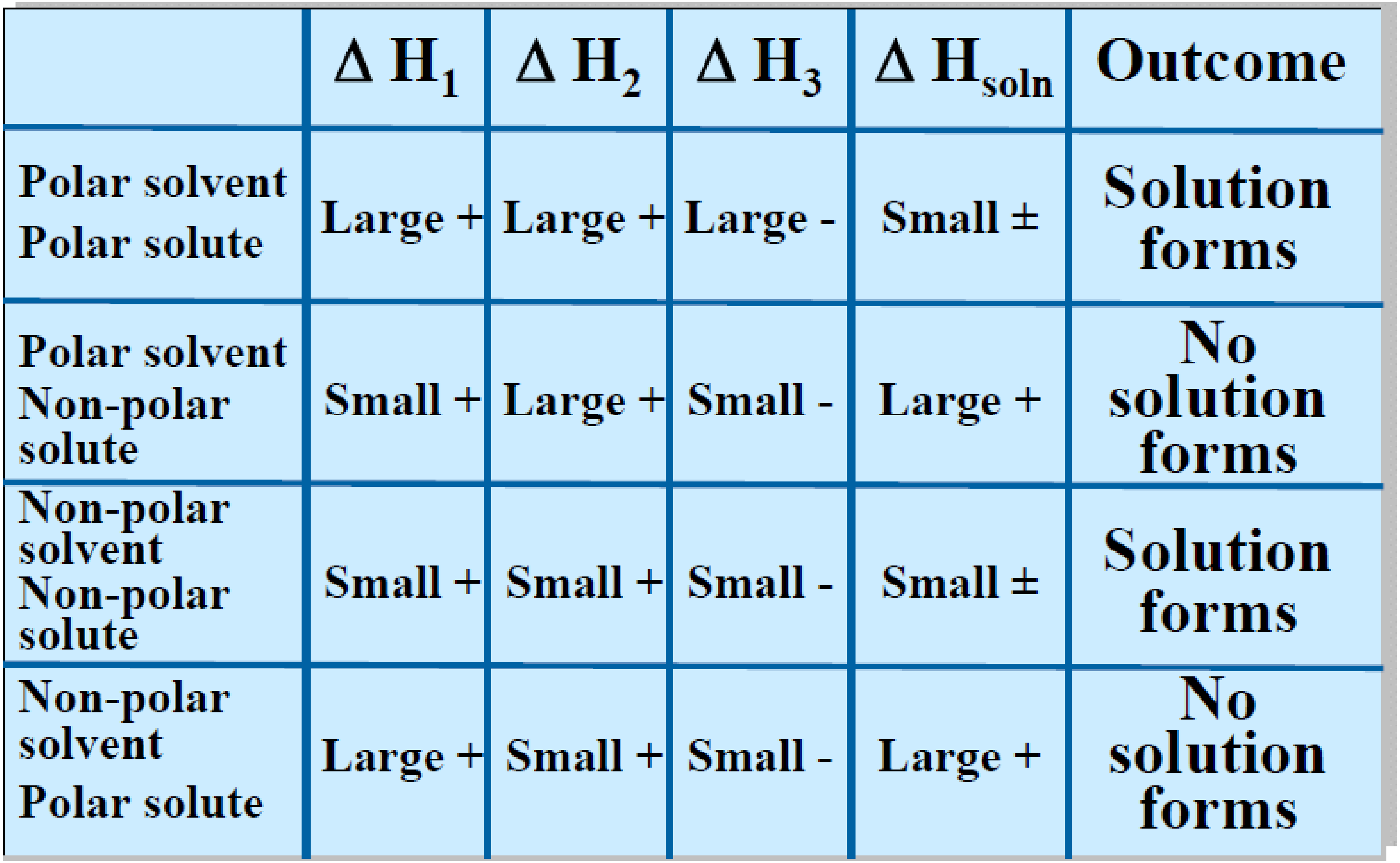


Polar solvents don't dissolve non-polar solutes



Polar solvents dissolve polar solutes

Nature of solutes and Solvents



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

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 solution

- is a solution containing **more solutes** than the equilibrium amount.
- It is unstable and tends to move toward saturation under proper conditions

Unsaturated solution

Saturated solution

Supersaturated solution

Solubility (S) and equilibrium

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

$$\mathbf{Solute}_{\mathbf{undissolved}} + \mathbf{Solvent} \leftrightarrow \mathbf{Solute}_{\mathbf{dissolved}}$$

- **Factors affecting solubility**
  - Temperature
  - Pressure
  - Concentration
  - Nature of solutes and solvents

Effect of Temp. on S 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 S of solids and liquids in liquids

$$\mathbf{Solute}_{\mathbf{undissolved}} + \mathbf{Solvent} \leftrightarrow \mathbf{Solute}_{\mathbf{dissolved}}$$

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

For endothermic reactions

$$\mathbf{Solute}_{\mathbf{undissolved}} + \mathbf{Solvent} + \mathbf{heat} \leftrightarrow \mathbf{Solute}_{\mathbf{dissolved}}$$

- Increasing T shifts the reaction to right increasing S

For exothermic reactions

$$\mathbf{Solute}_{\mathbf{undissolved}} + \mathbf{Solvent} \leftrightarrow \mathbf{Solute}_{\mathbf{dissolved}} + \mathbf{heat}$$

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

Effect of Pressure on S 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 much lower than that used in the bottling process.

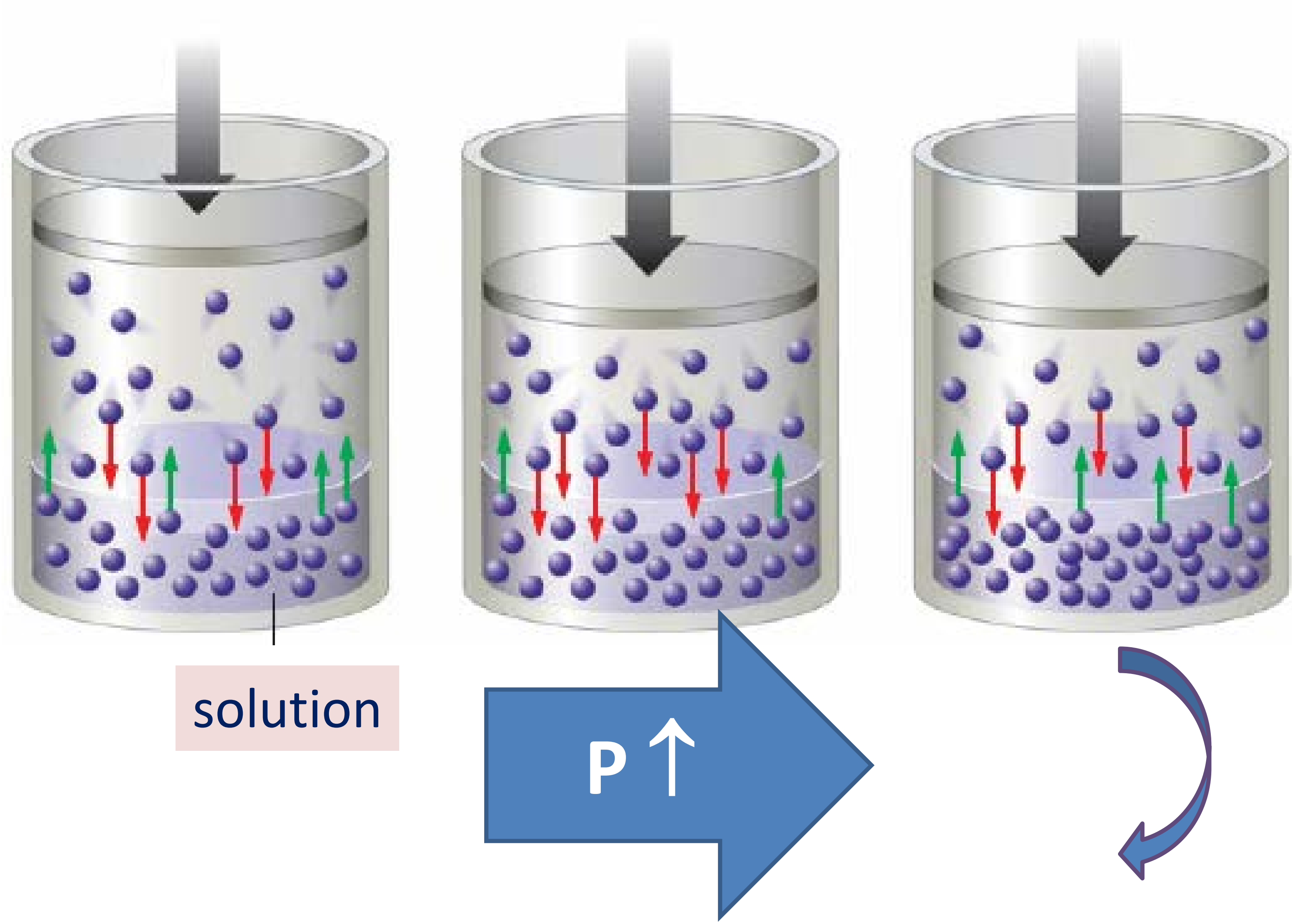
- Consider a closed container that is partially filled with a solution (gas in liquid)

$$\boxed{\textbf{Gas} + \textbf{Solvent} \leftrightarrow \textbf{Solution}}$$

- 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.



solution

P ↑

- new equilibrium with a 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.

$$\boxed{C = kP}$$

- C: concentration of the dissolved gas (S),
- 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

$$\mathbf{HCl} \xrightarrow{\mathbf{H_2O}} \mathbf{H^+(aq) + Cl^-(aq)}$$

Exercise

A certain soft drink is bottled so that a bottle at 25°C contains CO_2 gas at a pressure of 5.0 atm over the liquid. Assuming that the partial pressure of CO_2 in the atmosphere is 4.0×10^{-4} atm, calculate the equilibrium concentrations of CO_2 in the soda both before and after the bottle is opened. The Henry's law constant for CO_2 in aqueous solution is 3.1×10^{-2} mol/L atm . atm at 25°C.

Solution

Before opening

$$\mathbf{C} = \mathbf{kP} = \left(\frac{3.1 \times 10^{-2}\mathrm{mol}}{\mathrm{L.\,atm}}\right) \times (5.0\ \mathrm{atm})$$

$$= 0.16\ \mathrm{mol/L}$$

After opening

$$\mathbf{C} = \mathbf{kP} = \left(\frac{3.1 \times 10^{-2}\mathrm{mol}}{\mathrm{L.\,atm}}\right) \times (4.0 \times 10^{-4}\ \mathrm{atm})$$

$$= 1.2 \times 10^{-5}\ \mathrm{mol/L}$$

- Note the **large change** from $\mathbf{0.16}$ to $\mathbf{1.2 \times 10^{-5}}\ \mathrm{mol/L}$ in concentration of CO_2.

- This is why soda **disappears** after being open for a while.

Effect of structure on S

- **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.

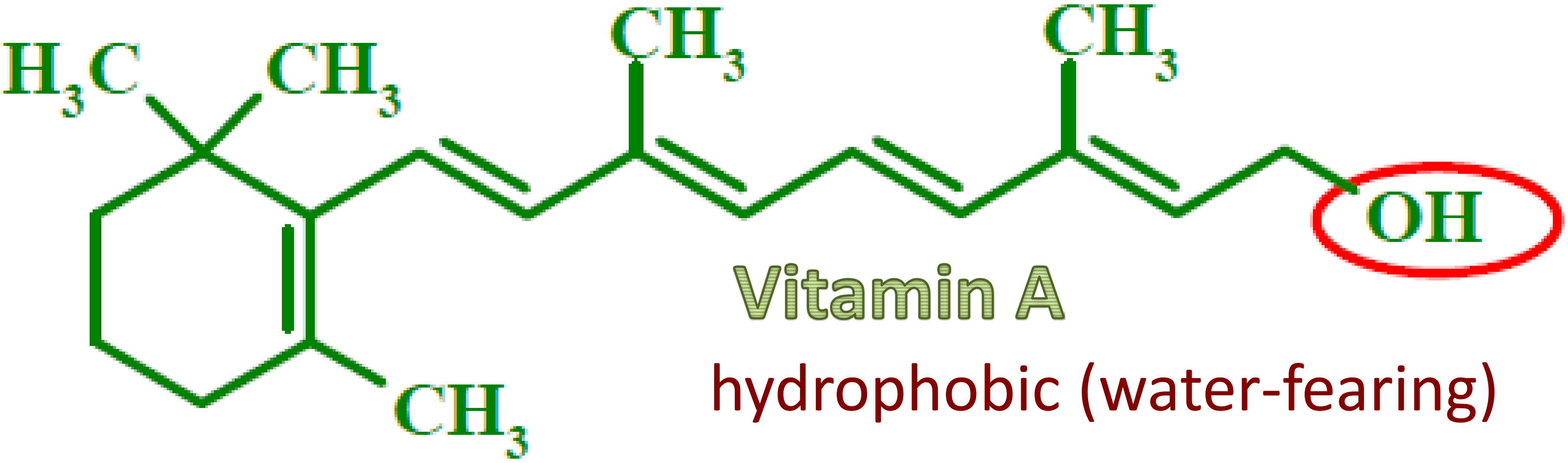
Vitamins can be divided into two classes:

Fat-soluble

Vitamins A, D, E and K

Water-soluble

Vitamins B and C



Vitamin A

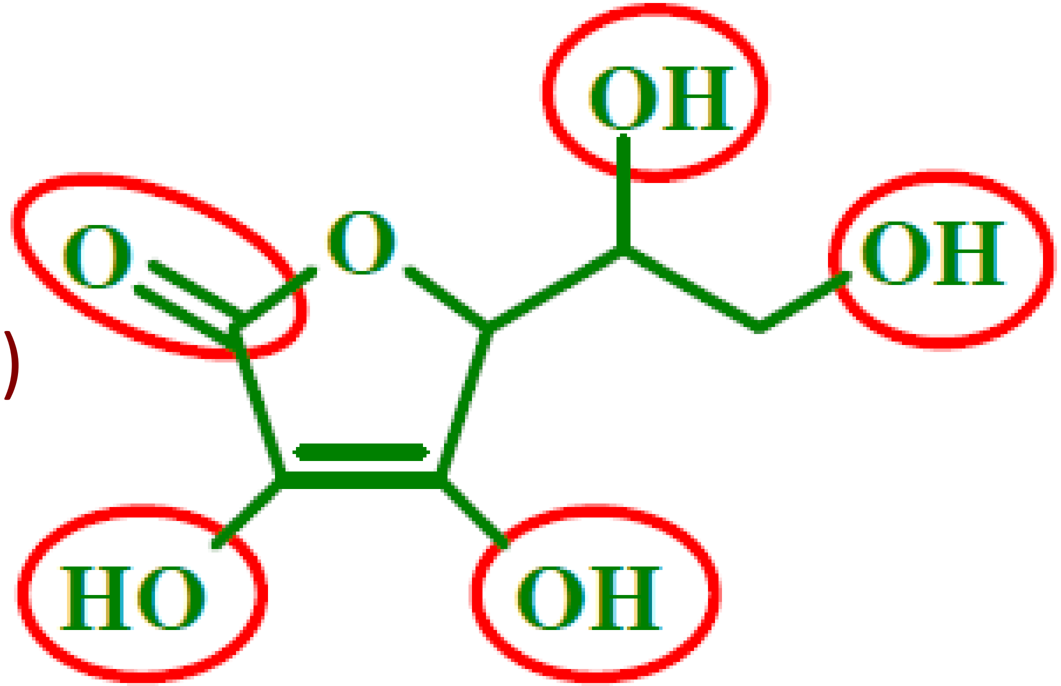
hydrophobic (water-fearing)

soluble in **nonpolar** materials such as body fat

Vitamin C

water-soluble

hydrophilic (water-loving)



Concentrations

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, X

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

$$X_A = \frac{n_A}{n_A + n_B + n_C + \ldots\ldots + n_Z}$$

Unitless

$$\sum \mathbf{X_i} = \mathbf{1}$$

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

$$(mass\ fraction)_A = \frac{m_A}{m_A + m_B + m_C + \ldots.. + m_Z}$$

Unitless

$$\sum (mass\ fraction)_i = 1$$

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 H_2O or 100 g of solution

Molality (Molal concentration)

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

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

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

n_{solute} : 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

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

n_{solute} : no. of moles of solute

Mwt_{solute} : molar mass of solute

W_{solute} : mass of solute

V : Volume of solution in liter

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

Normality

- The number of equivalents of solute per liter of solution

$$\mathbf{No.\,Equivalent} = \frac{\text{mass}_{\text{solute}}(\text{g})}{\text{Equivalent mass}_{\text{solute}}\ (\text{g/equivalent})}$$

$$= \frac{\text{w}_{\text{solute}}}{\text{Eq. wt}_{\text{solute}}}$$

The definition of the "equivalent mass" and "equivalent" depends on the reaction taking place in the solution.

Equivalent mass

Acid-Base Rxs

$$\textbf{Eq.wt} = \frac{\text{molar mass}}{\text{No of replacable H}^{+}\text{or OH}^{-}}$$

An "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_2SO_4	98	98/2 = 49	1M = 2N
NaOH	40	40	1M = 1N
$Ca(OH)_2$	74	74/2 = 37	1M = 2N

Equivalent mass

Oxidation-Reduction Rxs

The “equivalent” is defined as the quantity of oxidizing or reducing agent that can accept or furnish 1 mole of electrons.

$$\boxed{\mathbf{MnO_4{}^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O}}$$

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

$$= \frac{158\ \text{g}}{5} = 31.6\ \text{g}$$

Equivalent mass

Salt-formation Rxs

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

NaCl: Eq. wt = MWt/1

Na_3PO_4: Eq.Wt = Mwt / 3

Normality

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

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

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

Exercise

A solution is prepared by mixing 1.00 g ethanol (C_2H_5OH) 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

$$M = \frac{w_{solute}}{Mwt_{solute} \times V\ (L)}$$

$$= \frac{1.0\ g}{46.07\ g\ mol^{-1} \times 101\ mL} \times \frac{1000\ mL}{1\ L}$$

$$= 0.215\ mol/L$$

$$= 0.215\ M$$

mass percent of ethanol

$$= \frac{m_{ethanol}}{m_{ethanol}+m_{water}} \times 100$$

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

$$X_{ethanol} = \frac{n_{ethanol}}{n_{ethanol} + n_{water}} = \frac{1.0\ \text{g} \big/ 46.07\ \text{g mol}^{-1}}{1.0\ \text{g} \big/ 46.07\ \text{g mol}^{-1} + 100.0\ \text{g} \big/ 18.0\ \text{g mol}^{-1}}$$

$$= 0.00389$$

$$\mathrm{m} = \frac{\mathrm{w_{ethanol}}}{\mathrm{Mwt_{e\ tan\ ol}}} \times \frac{1000}{\mathrm{w_{water}\ (g)}}$$

$$= \frac{1.0\ \mathrm{g}}{46.07\ \mathrm{g\ mol^{-1}}} \times \frac{1000}{100.0\ \mathrm{(g)}}$$

$$= 0.217\ \mathrm{mol\ kg^{-1}} = 0.217\ \mathrm{m}$$

Exercise

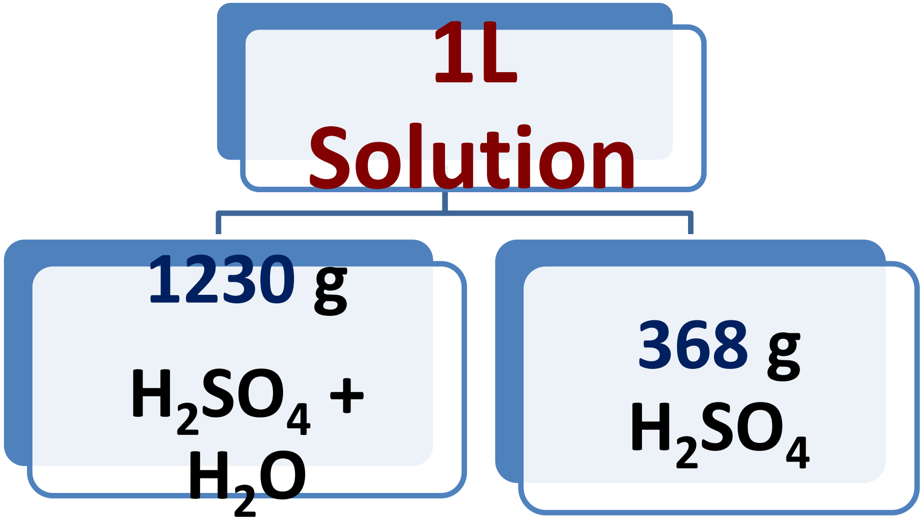
molar mass of sulfuric acid= 98 g/mol

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 g/mL = 1230 g/L → 1230 g solution (H_2SO_4 + H_2O) in every liter of solution (H_2SO_4 + H_2O)

- Molarity of H_2SO_4 = 3.75 M → means we have 3.75 mole (368 g) of H_2SO_4 in every liter of solution (H_2SO_4 + H_2O)



1L Solution

1230 g H_2SO_4 + H_2O

368 g H_2SO_4

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

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

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

$$\mathrm{m} = \frac{\mathrm{w}_{\text{sufuric acid}}}{\mathrm{Mwt}_{\text{sufuric acid}}} \times \frac{1000}{\mathrm{w}_{\text{water}}\ (\mathrm{g})}$$

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

$$\mathrm{N} = \mathrm{M} \times 2 = 3.75 \times 2$$

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