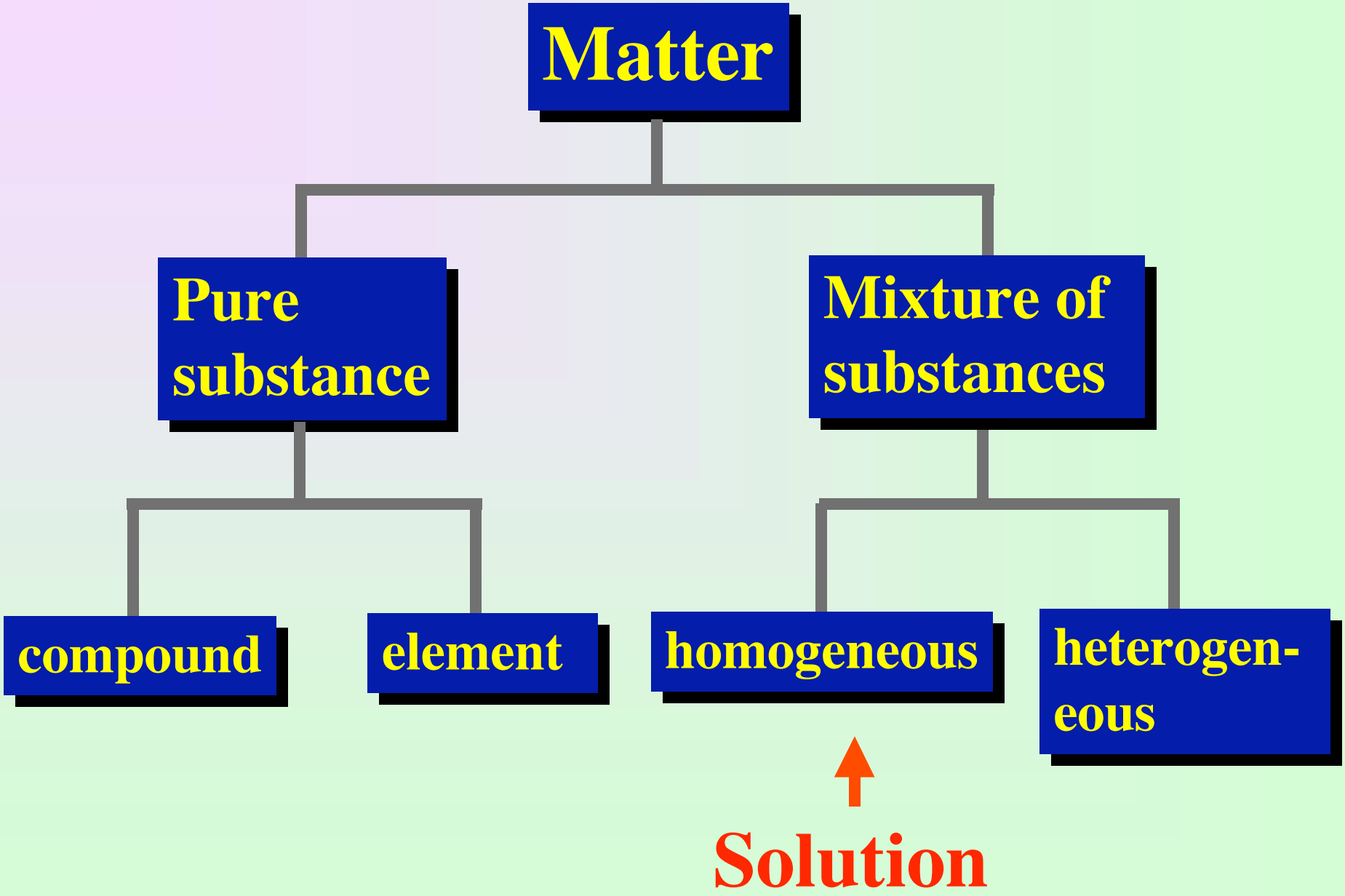
Properties of Solutions

Review


Matter
Pure substance
Mixture of substances
compound
element
homogeneous
heterogen-eous
Solution

Definitions

A solution is a homogeneous mixture of two or more substances.

The substance present in smaller amount is called the solute.

The substance present in larger amount is called the solvent.

Types of Solutions

saturated

Contains the maximum amount of a solute in a given solvent (at a specific temperture)

unsaturated

Contains less solute than it has the capacity to dissolve

supersaturated

Contains more solute than is present in saturated solution

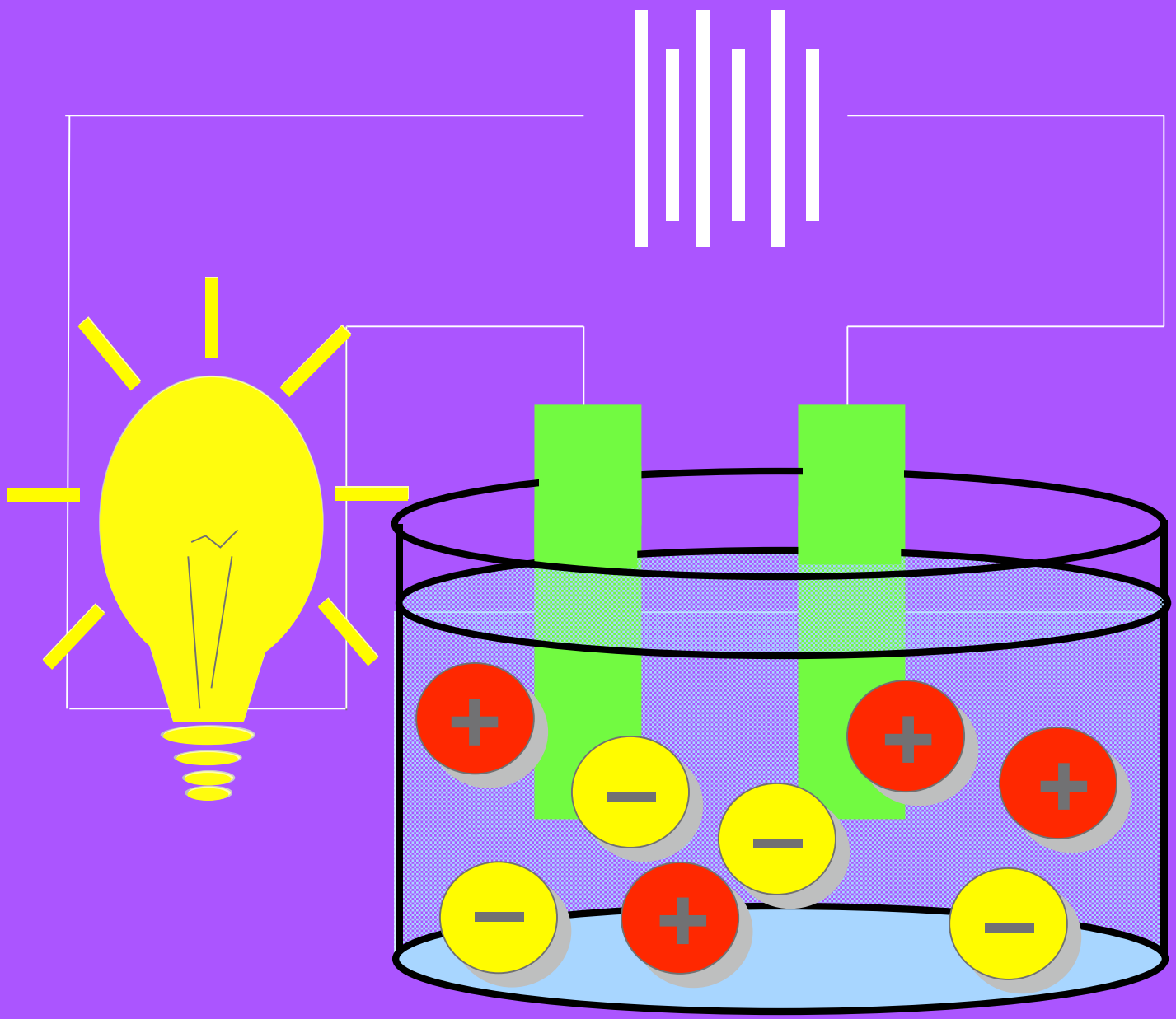
Solubility

The amount of solute that can be dissolved in a given amount of a saturated solution at a fixed temperature is the solubility of the solute in the solvent.

Electrolytes vs Nonelectrolytes

An **electrolyte** is a substance that, when dissolved in water, gives a solution that can conduct electricity

A **nonelectrolyte** does not conduct electricity when dissolved in water.



Electrolytes vs Nonelectrolytes

Nonelectrolyte

not ionized in water

Weak electrolyte

incompletely ionized in water

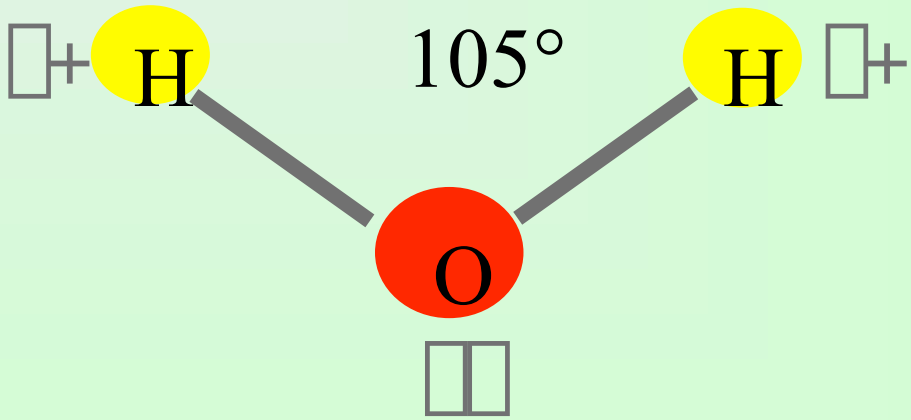
Strong electrolyte

completely ionized in water

The most import property of water when dealing with aqueous solution is its polarity

Structure of water

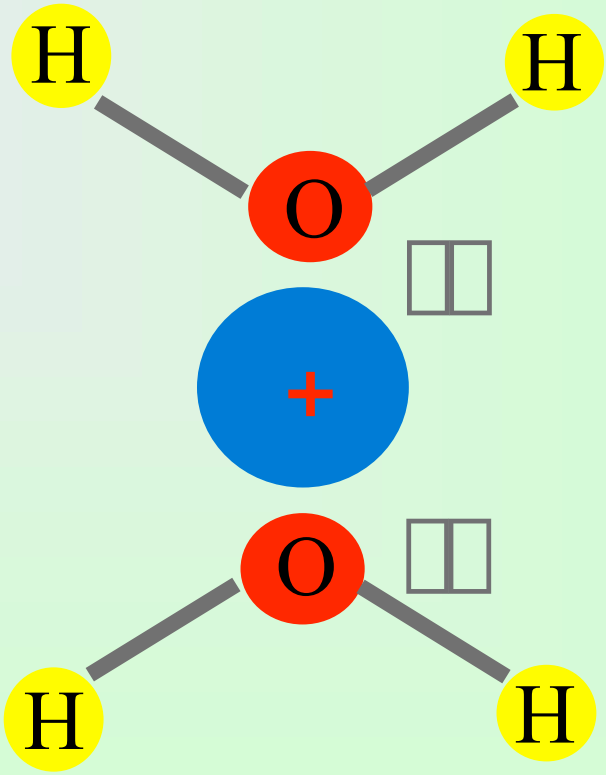
O—H bonds are covalent but “polar”



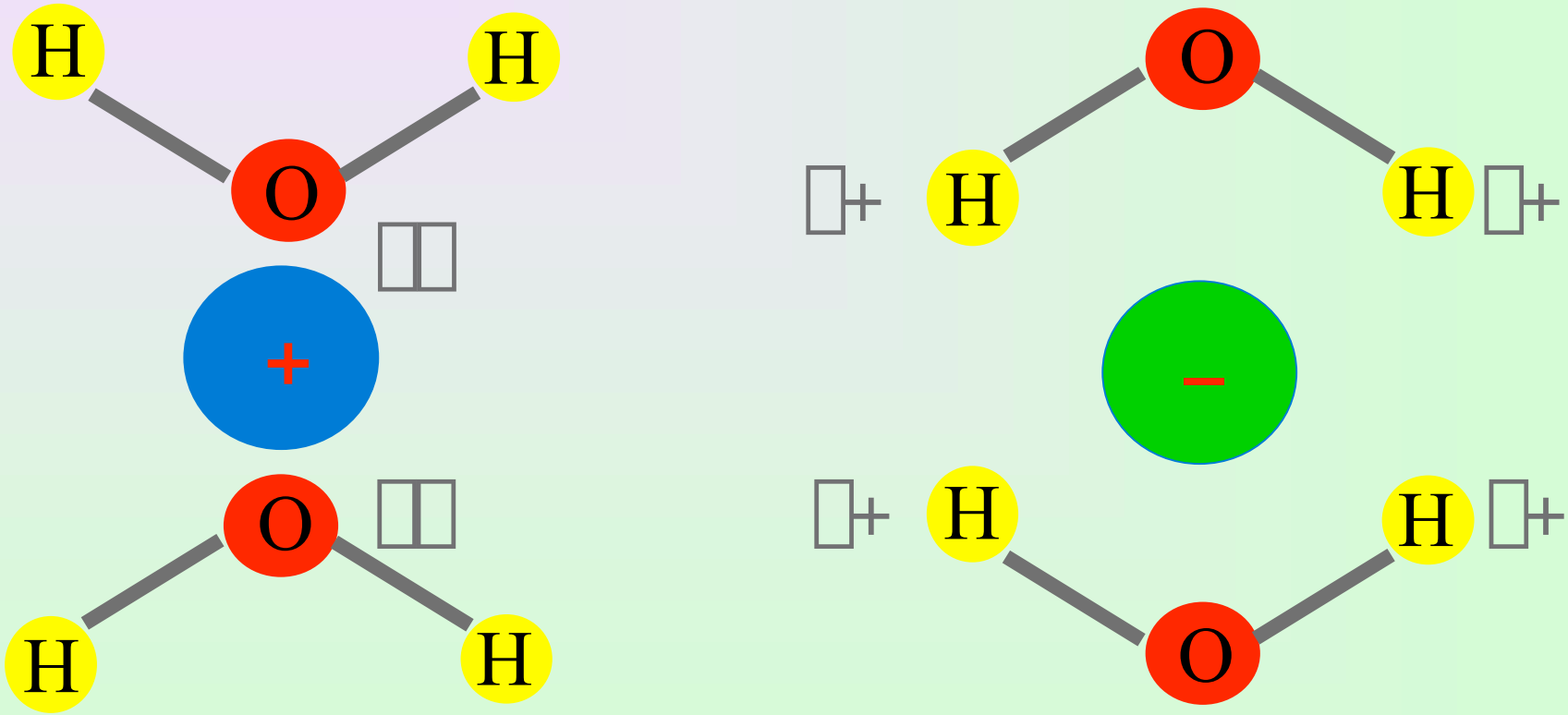
Solvation

Clustering of molecules of solvent around solute:

hydration is specific term for solvation when water is solvent

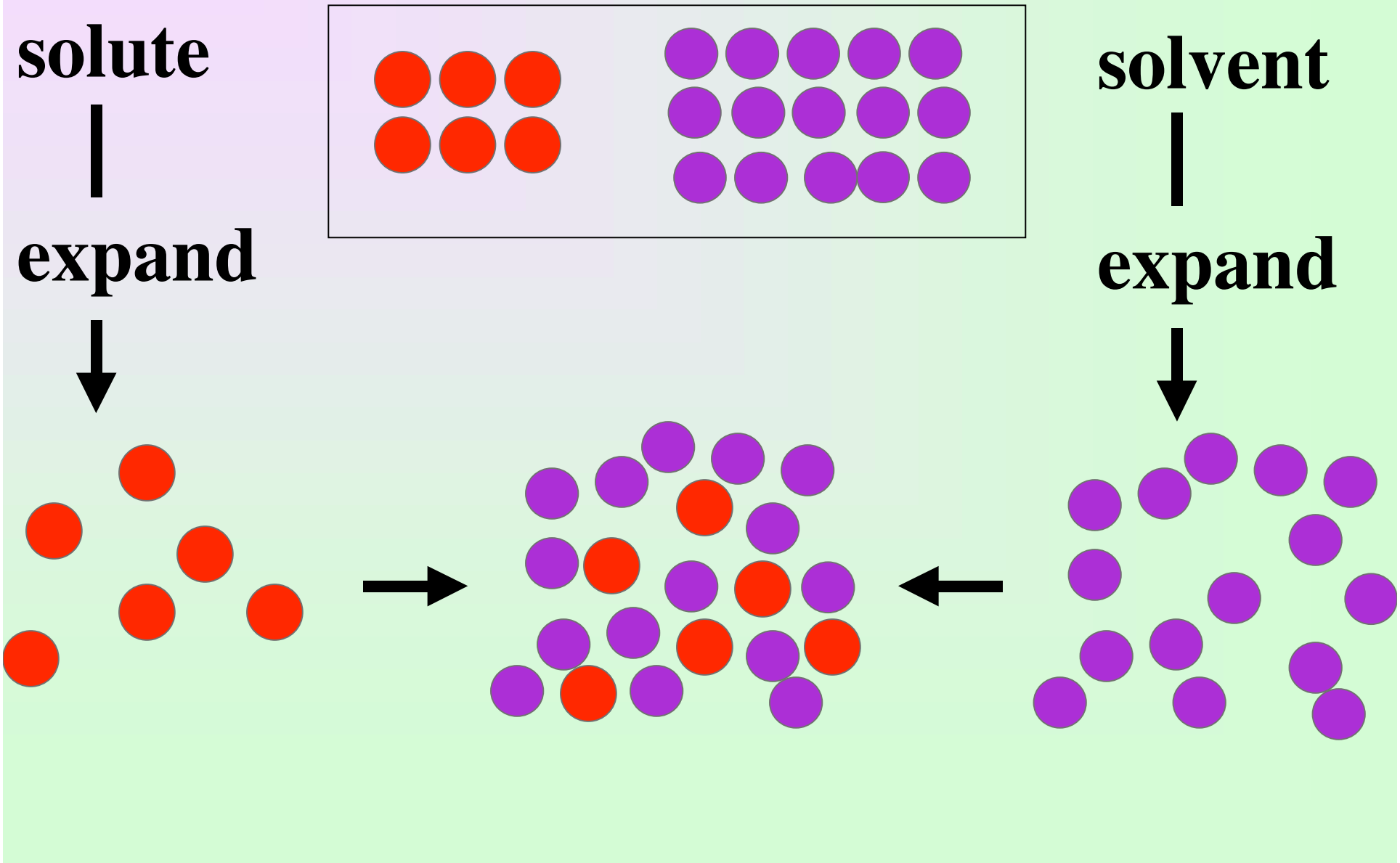


Water can solvate both cations and anions



A molecular View of the Solution Process

Model of the solution process



The total heat energy change of a solution (ΔH°_{soln}) is a combination of:

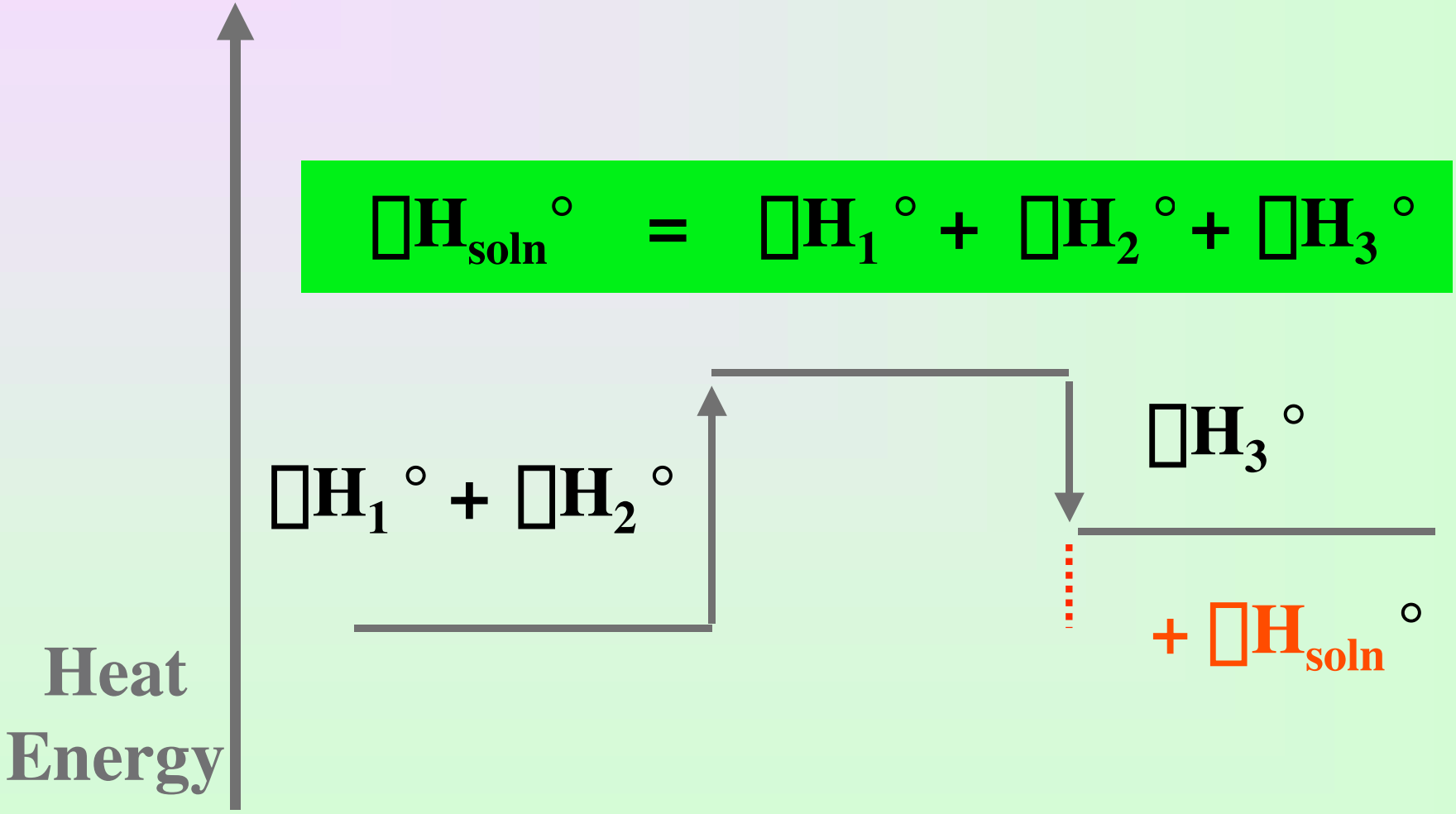
(ΔH_1°) for breaking intermolecular attractive forces in solute **sign is +**

(ΔH_2°) for breaking intermolecular attractive forces in solvent **sign is +**

(ΔH_3°) for attractive forces between solute and solvent **sign is -**

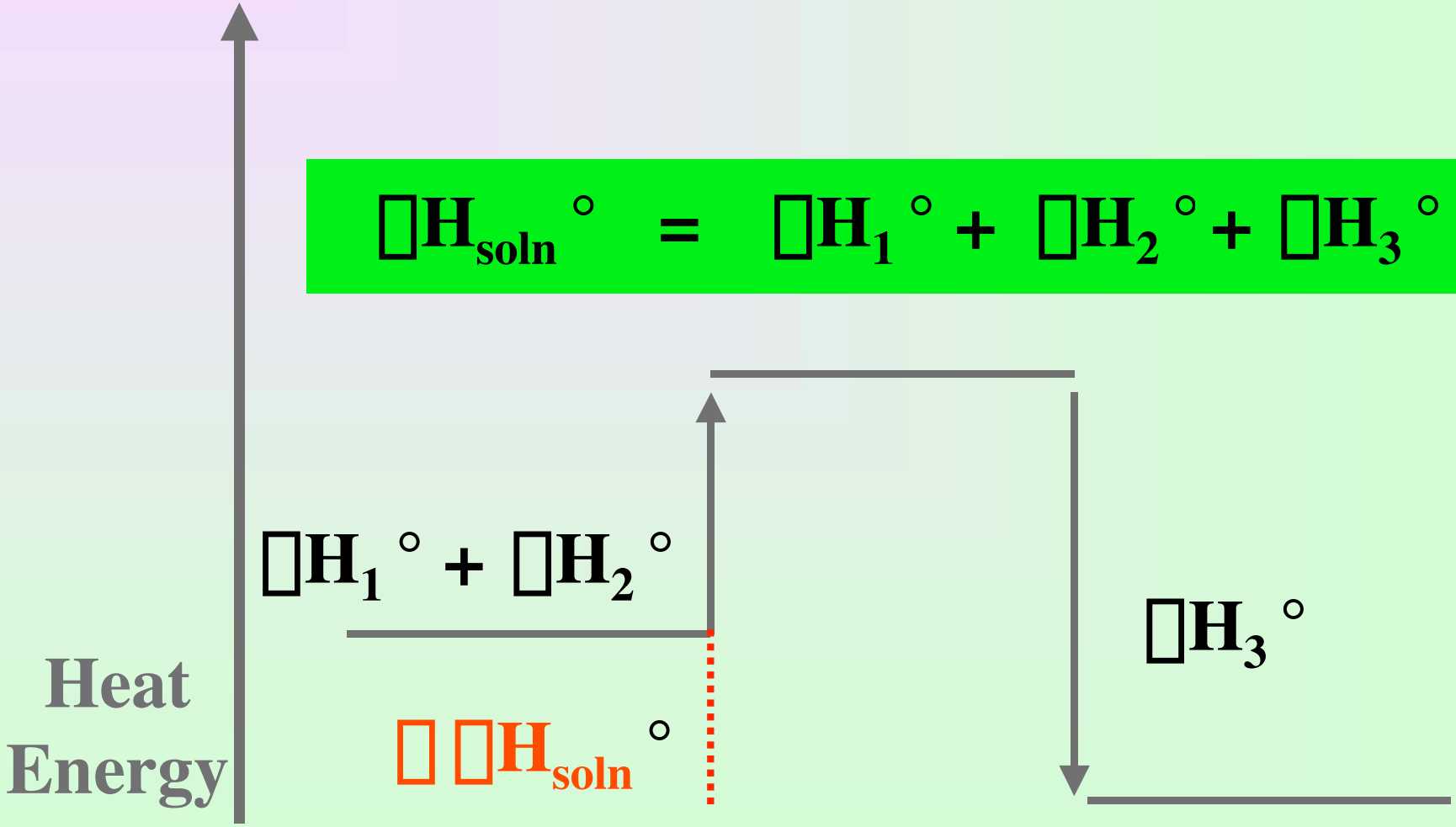
Endothermic Heat of Solution

$$\Delta H_{soln}^{\circ} = \Delta H_1^{\circ} + \Delta H_2^{\circ} + \Delta H_3^{\circ}$$



Exothermic Heat of Solution

$$\Delta H_{soln}^{\circ} = \Delta H_1^{\circ} + \Delta H_2^{\circ} + \Delta H_3^{\circ}$$



We can easily calculate enthalpies of solution from tables of thermodynamic data

$KOH_{(S)}$ ΔH°(formation) = -426 kJ/mol

$K^+_{(aq)}$ ΔH°(formation) = -251 kJ/mol

$OH^-_{(aq)}$ ΔH°(formation) = -230 kJ/mol

$$KOH_{(S)} \longrightarrow KOH_{(aq)}$$

ΔH = -481 kJ - (- 426 kJ) = -56 kJ

exothermic

What do the thermodynamic values reveal about ammonium nitrate when it dissolves in water ?

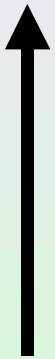
$NH_4NO_{3(S)}$ ΔH°(formation) = -366 kJ/mol

$NH_4NO_{3(aq)}$ ΔH°(formation) = -340 kJ/mol

What is ΔH° for the process ?

$NH_4NO_{3(aq)}$

$\Delta H^\circ_f = -340$ kJ/mol



$\Delta H^\circ_{sol} = +26$ kJ/mol

$NH_4NO_{3(S)}$

endothermic

$\Delta H^\circ_f = -366$ kJ/mol

So...

Dissolution of some substances in water is endothermic

Why does it dissolve at all ?

Entropy (S)

Entropy is a measure of the disorder of a system

ΔS

Positive sign (+) disorder increases

negative sign (-) disorder decreases

Processes tend to be spontaneous when

Potential energy decreases and disorder increases

- **ΔH° is negative**
- **ΔS° is positive**

Axiom

like dissolves like

Polar solutes dissolve in polar solvents

nonpolar solutes dissolve in nonpolar solvents

A solute can be:

Hydrophilic **"water loving"**

water soluble

or

Hydrophobic **"water hating"**

fat soluble

Polar solute

polar solvent

Attractive forces between solute and solvent are sufficient to over come solute-solute attractive forces and solvent-solvent attractive forces

nonpolar solvent

Attractive forces between solute and solvent are not sufficient to over come solute-solute attractive forces

nonpolar solute

polar solvent

Attractive forces between solute and solvent are not sufficient to over come solvent-solvent attractive forces

nonpolar solvent

all Attractive forces are weak ; ΔH° is small and the entropy term dominates

Heat of Hydration

$$NaCl_{(S)} \rightarrow Na^+_{(g)} + Cl^-_{(g)} \qquad \Delta H_1^\circ = +786 \text{ kJ/mol}$$

$$H_2O_{(l)} + Na^+_{(g)} + Cl^-_{(g)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

$$\Delta H_2^\circ + \Delta H_3^\circ = -783 \text{ kJ/mol}$$

the second step here combines ΔH_2° (expanding the solvent) and ΔH_3° (solvent solute interactions)

Heat of Hydration $\qquad \Delta H_{hyd}^\circ = -783 \text{ kJ/mol}$

$$NaCl_{(S)} \rightarrow NaCl_{(aq)} \qquad \Delta H_{soln}^\circ = +3 \text{ kJ/mol}$$

Solutions of liquids in liquids

Miscible

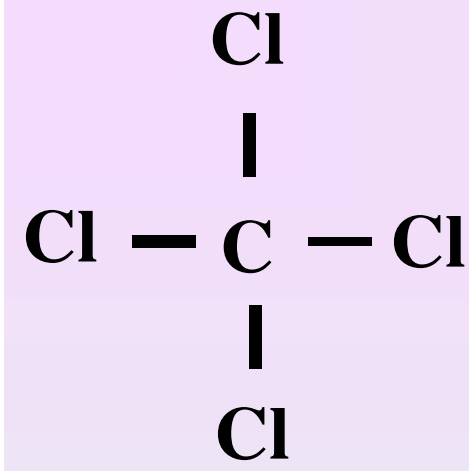
Two liquids are said to be miscible if they are completely soluble in each other in all portions

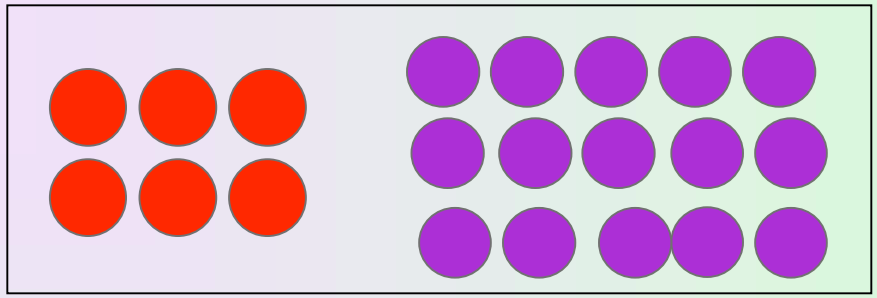
Two nonpolar liquids

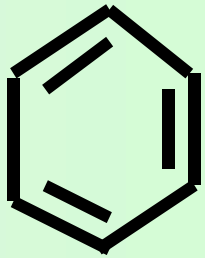
Carbon tetrachloride and benzene are completely soluble in each other in all proportions (miscible)

Intermolecular attractions in CCl_4 are weak

Intermolecular attractions in C_6H_6 are weak







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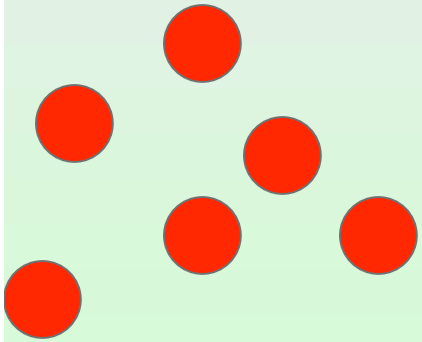

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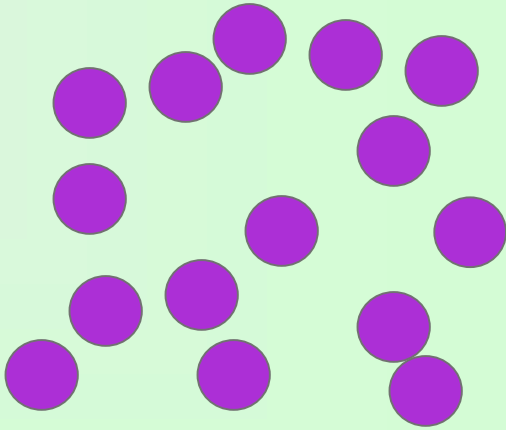


Two nonpolar liquids

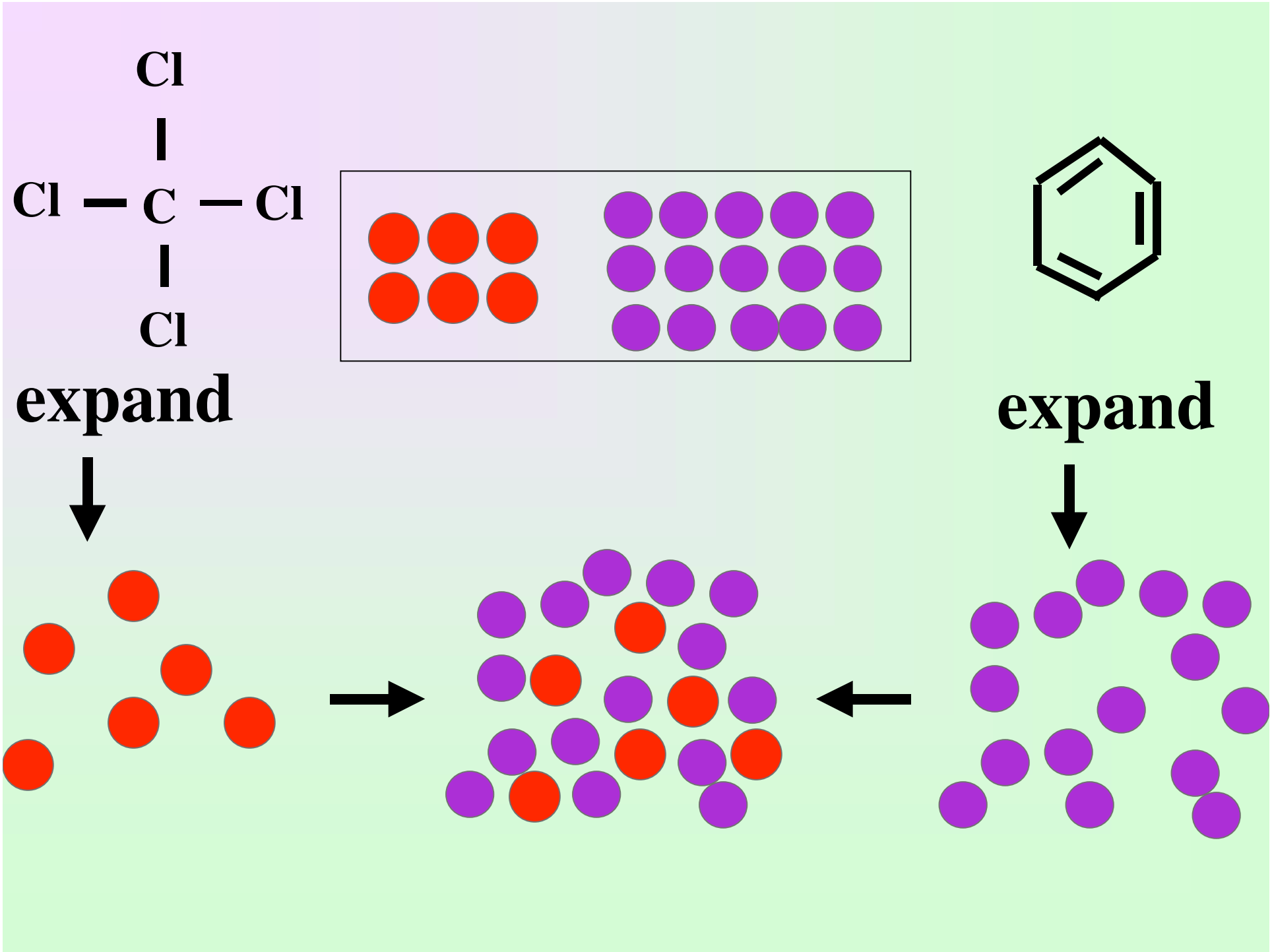
Carbon tetrachloride and benzene are completely soluble in each other in all proportions (miscible)

Intermolecular attractions in CCl_4 are weak

Intermolecular attractions in C_6H_6 are weak

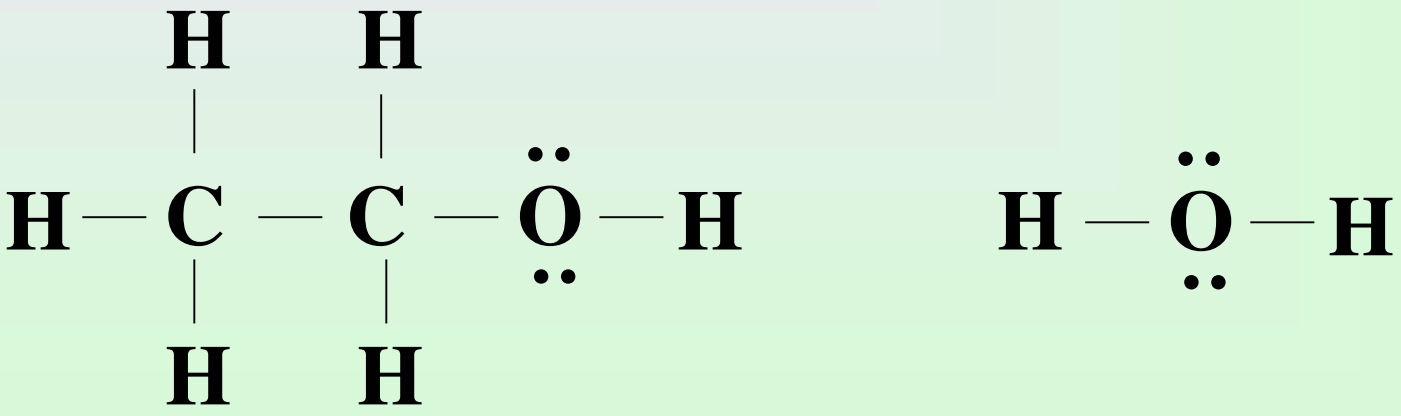
Intermolecular attractions between C_6H_6 and CCl_4 are weak

Overall ΔH is close to zero; solubility is driven by an increase entropy


Cl
Cl C Cl
Cl
expand
expand

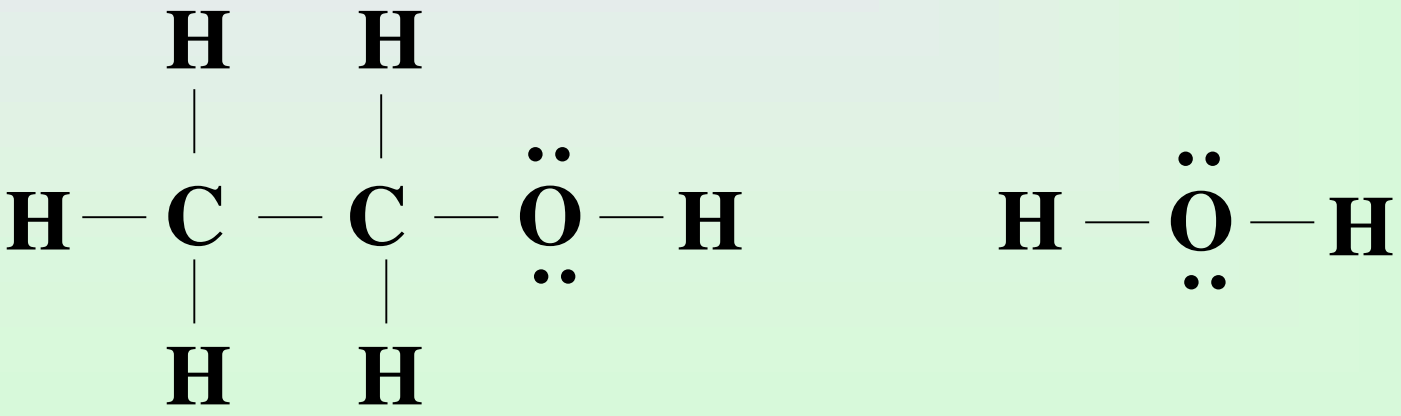
Two polar liquids

ethanol and water are completely soluble in each other in all proportions (miscible)

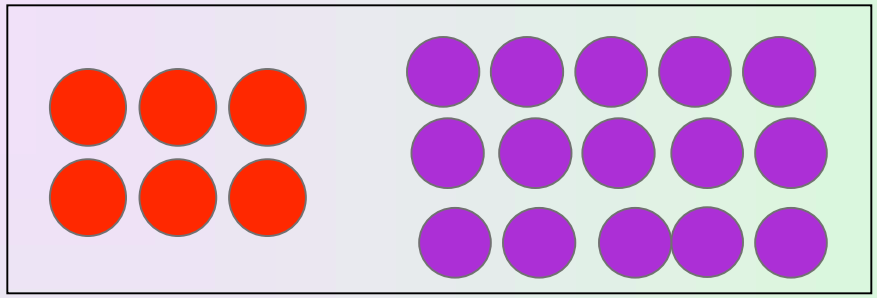


Two polar liquids

hydrogen bonding is present in ethanol
hydrogen bonding is present in water

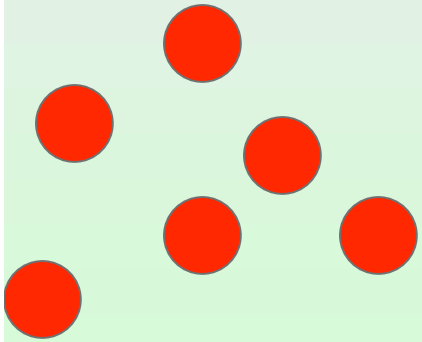


ethanol



water

expand



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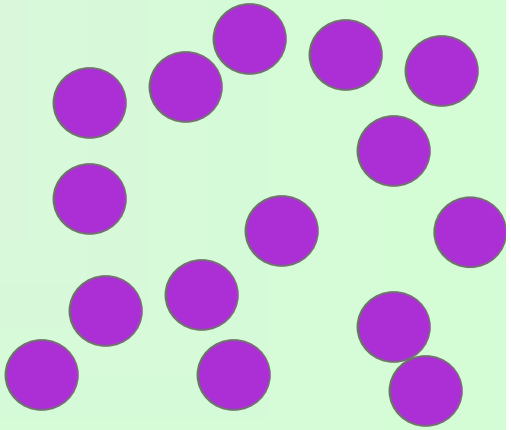


Two polar liquids

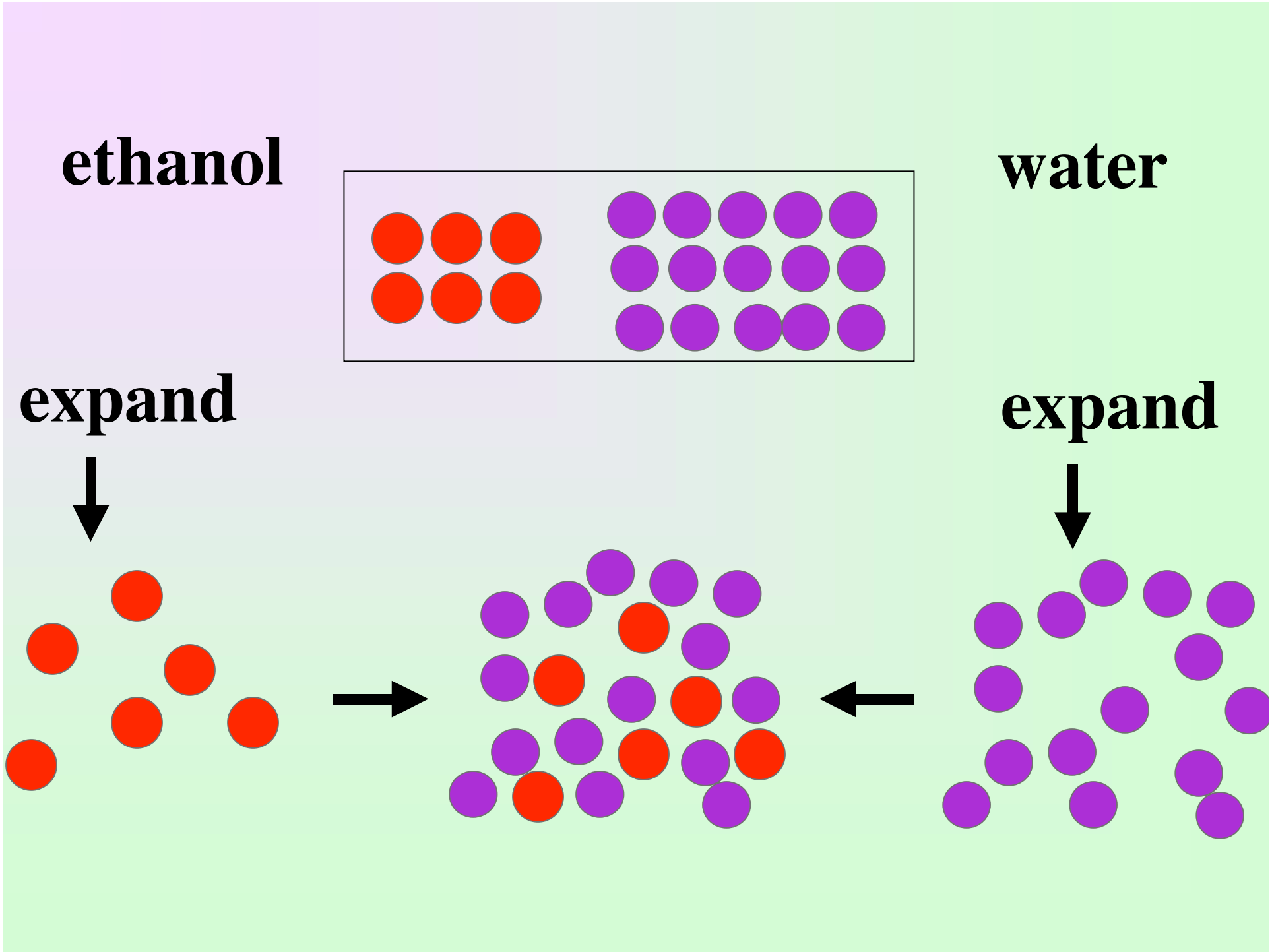
ethanol and water are completely soluble in each other in all proportions (miscible)

hydrogen bonding in ethanol

hydrogen bonding in water

hydrogen bonding in a solution of ethanol and water

Overall ΔH is close to zero; solubility is driven by an increase entropy


ethanol
water
expand
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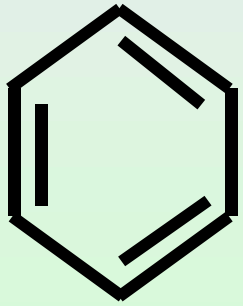
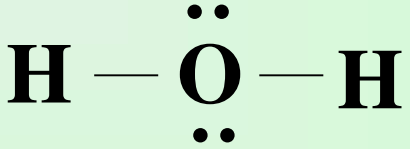
Polar and nonpolar liquids

Benzene and water do not dissolve in one another

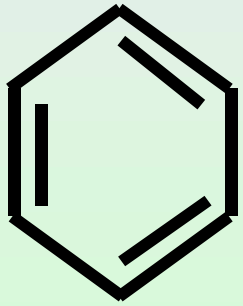


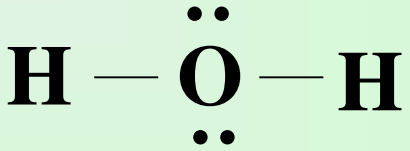


Polar and nonpolar liquids

Intermolecular forces in benzene are weak

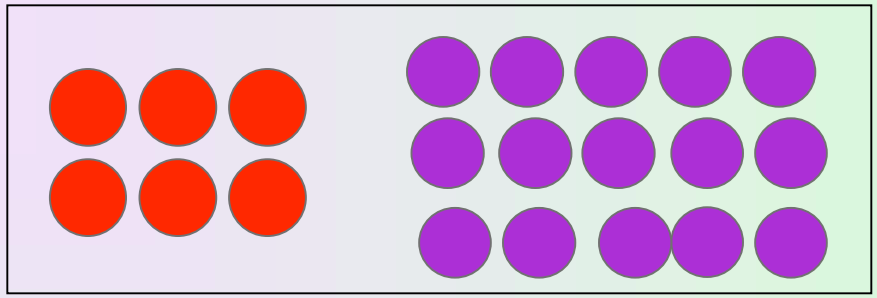
Intermolecular forces in water are strong





benzene

water



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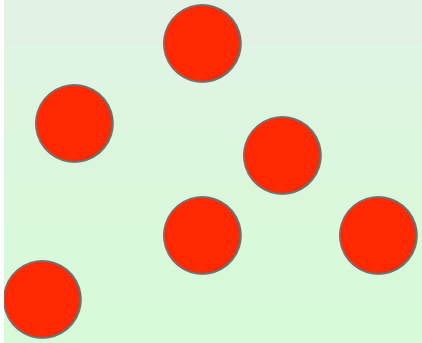

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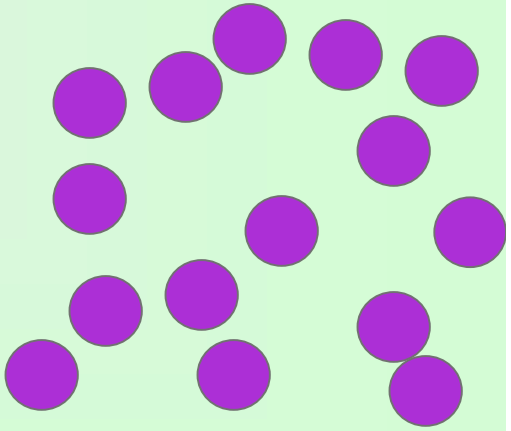


Polar and nonpolar liquids

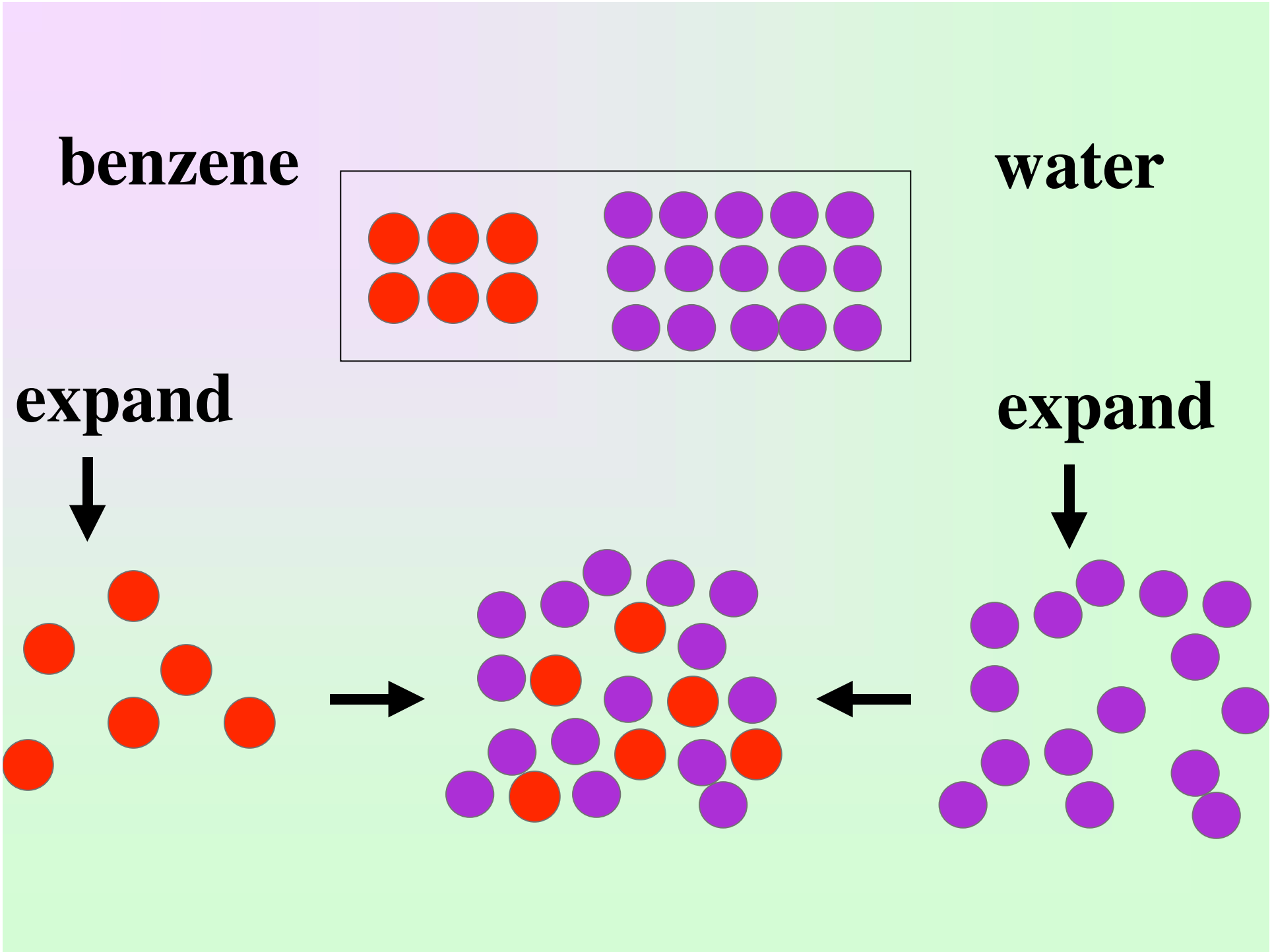
Benzene and water do not dissolve in one another

Induced dipole-induced dipole forces in benzene

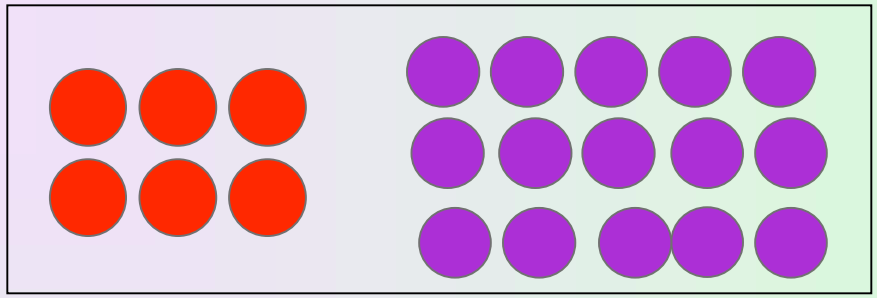
hydrogen bonding in water

Intermolecular between benzene and water are weak

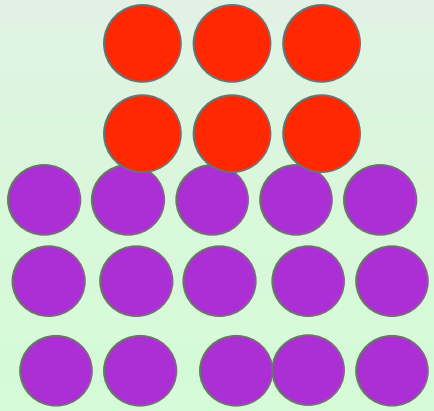
Overall ΔH is +; increase entropy is insufficient to over come endothermicity


benzene
water
expand
expand

benzene



water

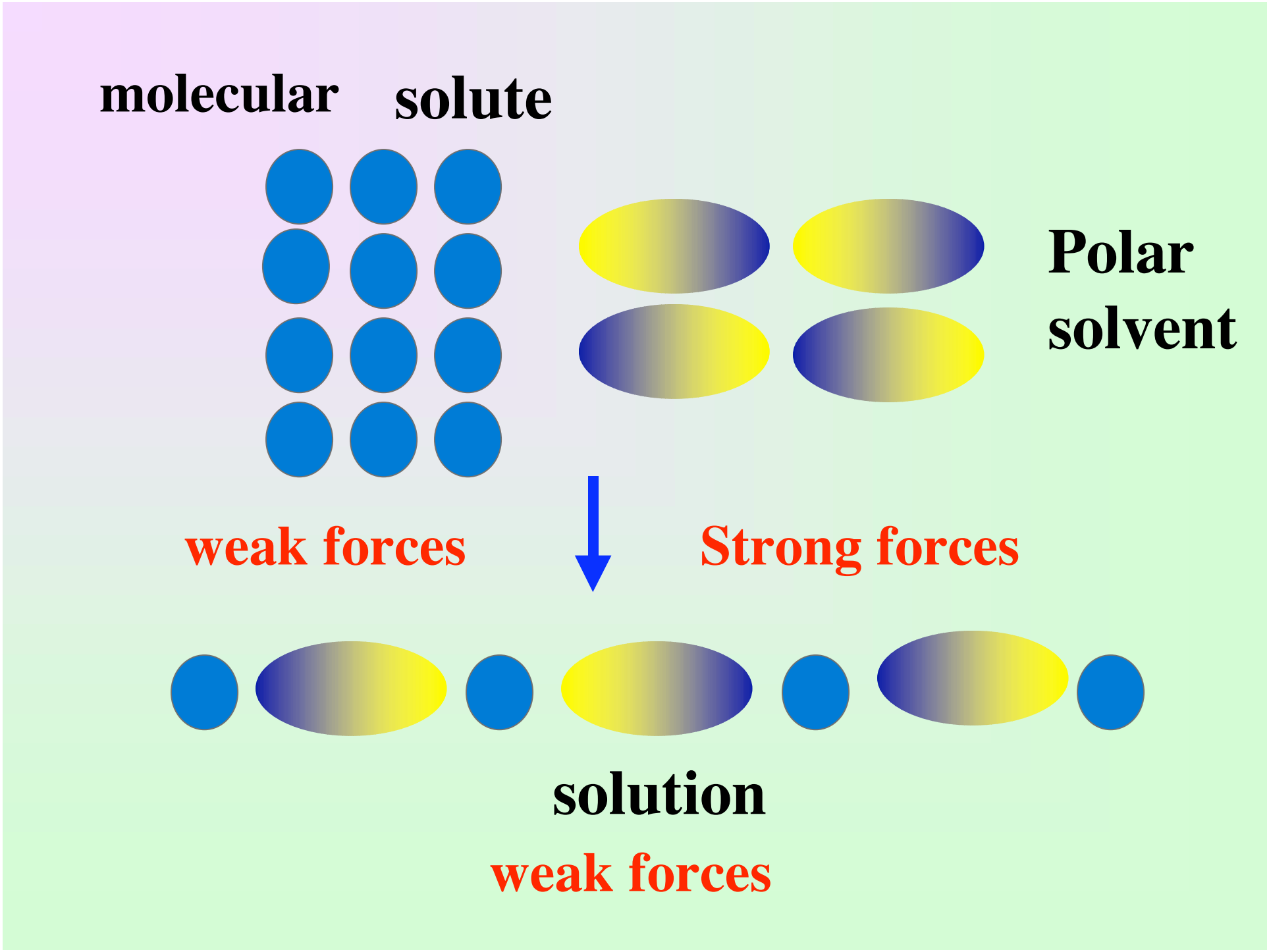


Solutions of Solids and Liquids

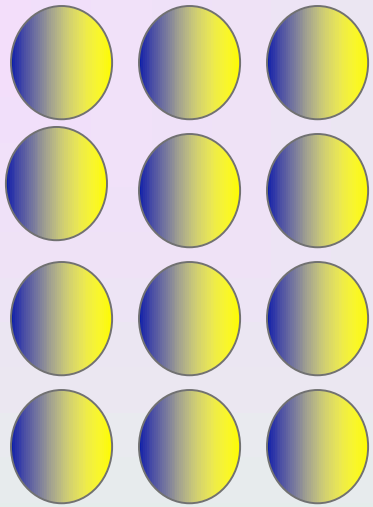
“As a rule, network covalent solids, such as graphite and quartz, do not dissolve in any solvent.”

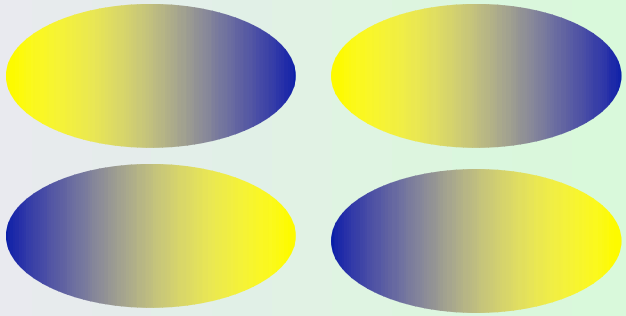
“Nor do metals…..”

“Ionic and molecular compounds will dissolve in certain solvents ”


molecular solute
Polar solvent
weak forces
Strong forces
solution
weak forces

Ionic solute

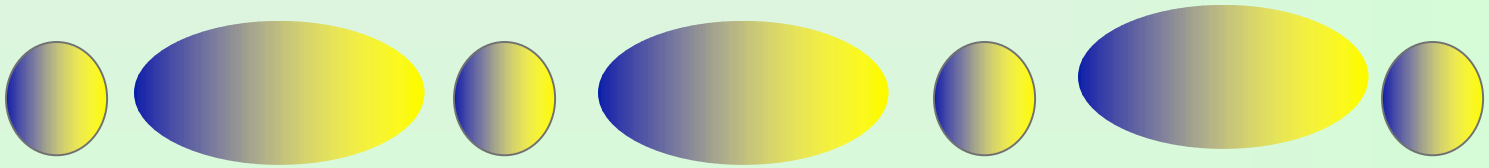




Polar solvent

strong forces

Strong forces



solution

strong forces

Metals

not soluble in any liquid without chemical change taking place

$$2Na(s) + H_2O(liq) \longrightarrow 2NaOH(aq) + H_2(g)$$

$$Na(s) \longrightarrow Na^+ + e^-$$

metals can form solutions with other metals (alloys)

Example

Predict the relative solubilities in the following cases:

(a) Br_2 in benzene (C_6H_6) (μ = 0 D) and in water (μ = 1.87 D)

(b) KCl in carbon tetrachloride (μ = 0 D) and in liquid ammonia (μ = 1.46 D)