

Have you been reading my “notes”

Two topics

Relating  $\Delta H$  and  $\Delta S$  for  
a phase transition

What is special about water

# Free Energy Change

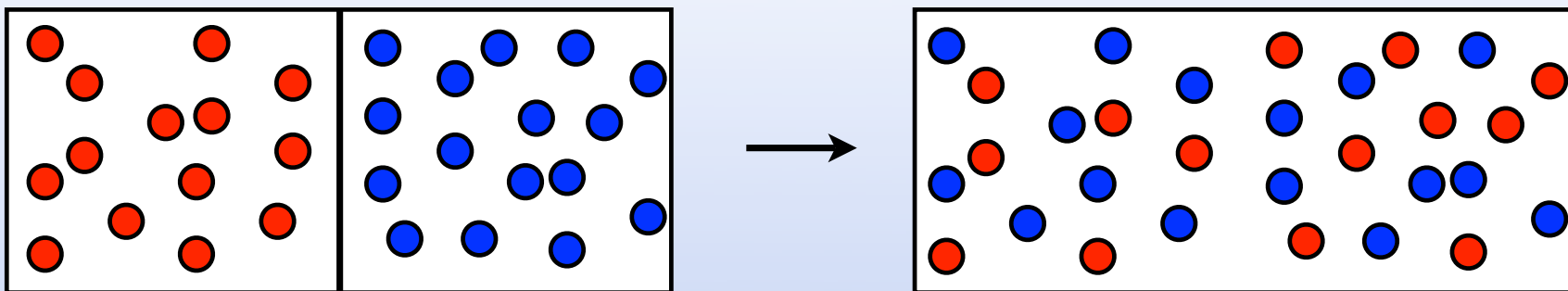
What is the sign of the change in free energy for me dropping an eraser?

- A. negative (free energy decreases)
- B. positive (free energy increases)
- C. zero (free energy is constant)
- D. it depends on the temperature

Things that happen decrease lower free energy  
(equilibrium is zero change)

## Mixtures

What is different than pure substances?



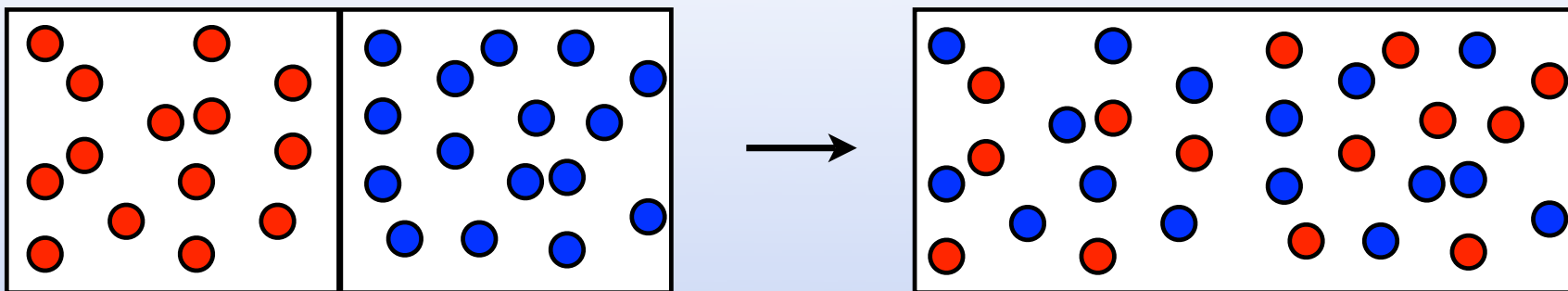
What is the free energy change for gases mixing?

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therefore free  
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## Mixtures

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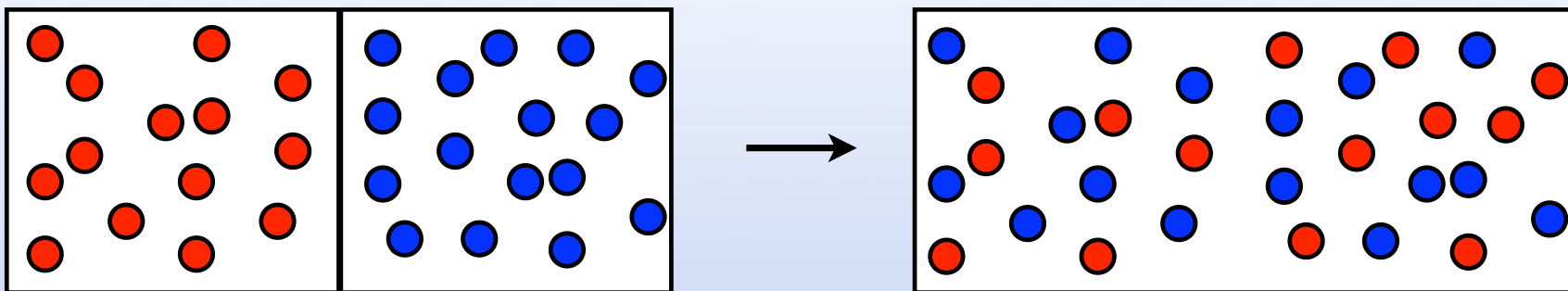
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## Mixtures

What is different than pure substances?



Why does the free energy decrease? ( $\Delta G = \Delta H - T\Delta S$ )

- A.  $\Delta H$  is positive,  $\Delta S$  is zero      Gases ~ no IMF. Therefore  $\Delta H = 0$
- B.  $\Delta H$  is zero,  $\Delta S$  is positive      The volume of each gas increases therefore  $\Delta S > 0$
- C.  $\Delta H$  is negative,  $\Delta S$  is positive
- D.  $\Delta H$  is negative,  $\Delta S$  is zero      Take home lesson generally entropy increases with mixing

When we think of mixtures we typically think about solutions

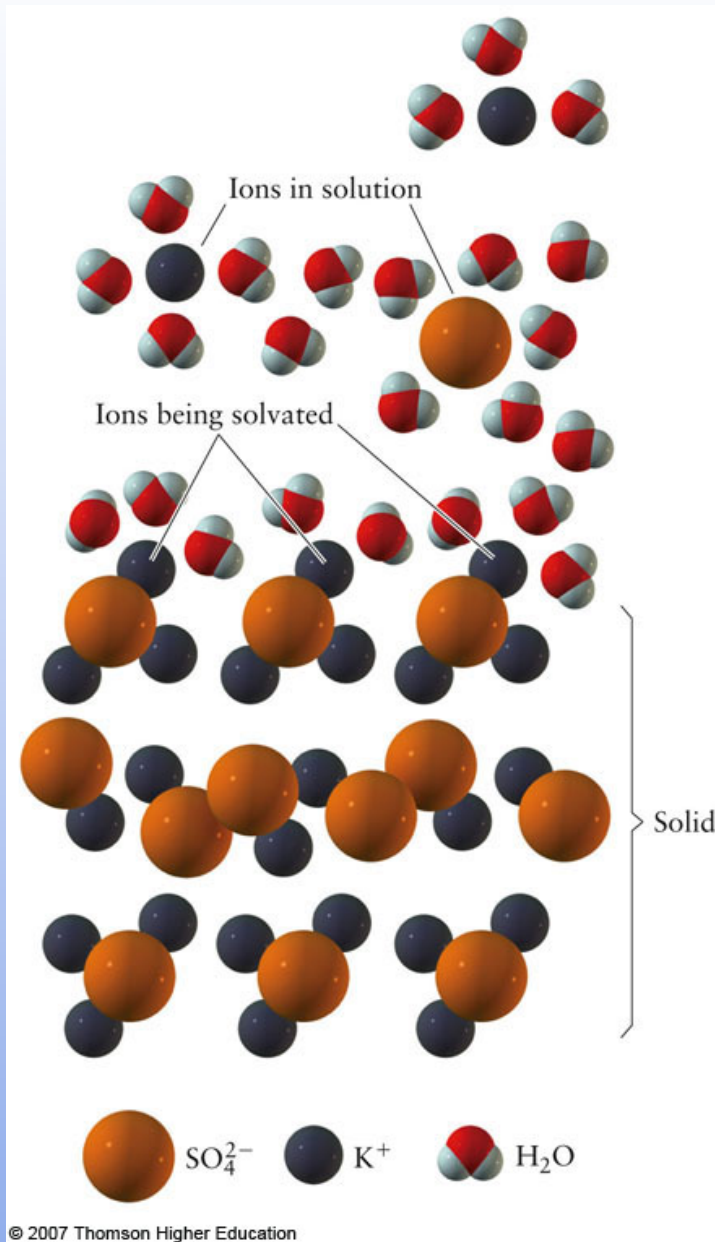
Solvent: the majority of the molecules

IMF only slightly changed  
(most solvent molecules interacting with solvent molecules)

Solute: the minority substance  
the “stuff that is dissolved”

could be a solid, liquid, or a gas

**IMF total different  
in solution, solute molecules only  
interacting with solvent molecules**



## Entropy of Solution $\Delta S_{\text{solution}}$ usually easy to predict

Solutions typically have a higher entropy  
than the unmixed compounds

Therefore

$$\Delta S_{\text{solution}} > 0$$

For most cases

Since entropy almost always favors mixing,  
the differences between different substances are  
the result of enthalpy (intermolecular forces)

# What is enthalpy change for making a solution?

Lose solute-solute interactions (IMF)

Lose solvent-solvent interactions (IMF) (this is small)

Gain solute-solvent interactions

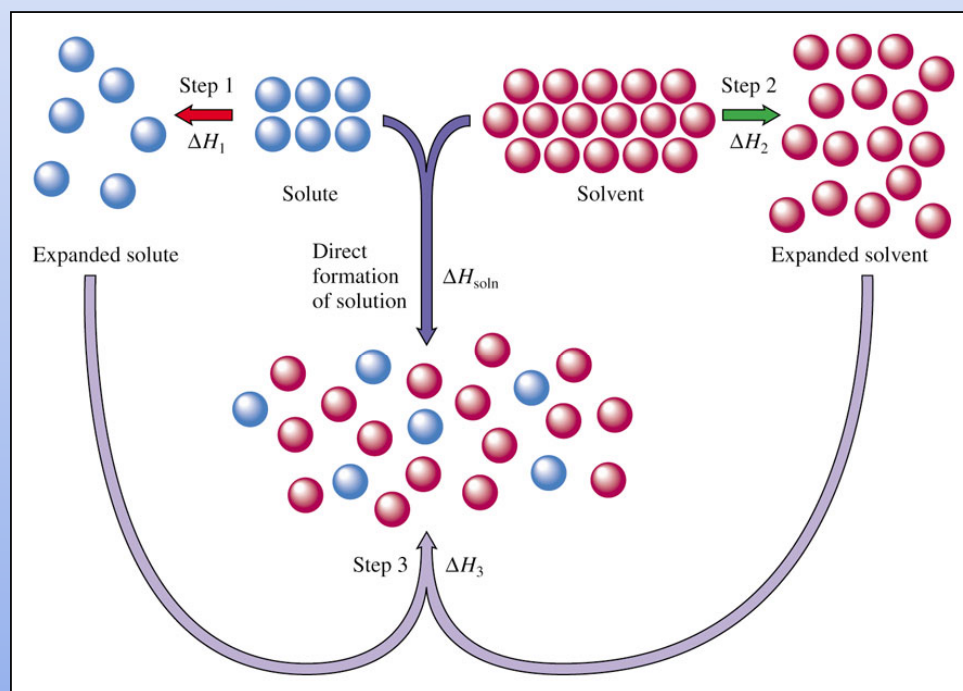


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## How we generally think of this

What is  $\Delta H_{\text{solution}}$ ?

this is the enthalpy change for making the solution?

Two steps

First break up the solute  
(loss of solute-solute interactions)  $\Delta H_{\text{Lattice Energy}}$  “costs energy” positive

Next put solute into solvent  
(add of solute-solvent interactions)  $\Delta H_{\text{solvation}}$  “releases energy” negative

$$\Delta H_{\text{solution}} = \Delta H_{\text{Lattice Energy}} + \Delta H_{\text{solvation}}$$

## Enthalpy of Solution $\Delta H_{\text{solution}}$ hard to predict

$$\Delta H_{\text{solution}} = 0$$

Ideal solution

Solute-solvent interactions are identical to  
solute-solute (and solvent-solvent)

$$\Delta H_{\text{solution}} > 0$$

Typical

Solute-solvent interactions are weaker than  
solute-solute (and solvent-solvent)

$$\Delta H_{\text{solution}} < 0$$

Unusual but possible

Solute-solvent interactions are stronger than  
solute-solute (and solvent-solvent)

Which do you think has a stronger interactions with a sodium ion?

- A. a chloride ion
- B. water
- C. they are the same

Ion-Ion interactions will be stronger than ion-dipole interactions  
(but ion dipole interactions are still strong)

What do you predict for the sign of the enthalpy of solution of NaCl in water?

- A. positive
- B. negative
- C. zero

Because the solute/solvent interactions (ion-dipole) are weaker than the solute/solute (ion-ion) it will “cost” energy to get the salt into the water

For dissolving salt in water at room temperature

$$\Delta H_{\text{solution}} > 0$$

$$\Delta S_{\text{solution}} > 0$$

which is larger?

A.  $\Delta H > T\Delta S$

B.  $\Delta H = T\Delta S$

C.  $\Delta H < T\Delta S$

This actually happens.  $\Delta G < 0$ .

This means that  $\Delta H < T\Delta S$

For dissolving water in olive oil at room temperature

$$\Delta H_{\text{solution}} > 0$$

$$\Delta S_{\text{solution}} > 0$$

which is larger?

A.  $\Delta H > T\Delta S$

B.  $\Delta H = T\Delta S$

C.  $\Delta H < T\Delta S$

This does not happen.  $\Delta G > 0$ .

This means that  $\Delta H > T\Delta S$

## When things will not dissolve

$\Delta H_{\text{solution}}$  is too large (bigger than  $T\Delta S$ )

IMF between the solvent/solute are much less favorable than solute/solute (solvent/solvent)

When will this happen?

Very different IMF

Oil (dispersion/nonpolar) and water (H-bonding, polar)

Very strong ion/ion (MgO)

## Other problems for small high charge density ions

**TABLE 17.2** Values of  $\Delta S^\circ_{\text{soln}}$  for Several Salts Dissolving in Water

Process	$\Delta S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )
KCl(s) → K <sup>+</sup> (aq) + Cl <sup>-</sup> (aq)	75
LiF(s) → Li <sup>+</sup> (aq) + F <sup>-</sup> (aq)	-36
CaS(s) → Ca <sup>2+</sup> (aq) + S <sup>2-</sup> (aq)	-138



## Gibb's Free Energy of Solvation $\Delta G_{\text{soln}}$

If  $\Delta G_{\text{soln}} < 0$  solution strongly favored

If  $\Delta G_{\text{soln}} > 0$  undissolved state is strongly favored

$$\Delta G_{\text{soln}} = \Delta H_{\text{soln}} - T \Delta S_{\text{soln}}$$

Typically  $\Delta S_{\text{soln}} > 0$ ,  $\Delta H_{\text{soln}} > 0$

need  $|T\Delta S| > |\Delta H|$

What makes an ideal solution?

Same IMF for solute-solvent and  
solute-solute and solvent-solvent

**"like dissolves like"**

Polar compounds dissolve polar compounds (ionic)

Nonpolar compound dissolve nonpolar compounds

This minimizes  $\Delta H_{\text{solution}}$

# Miscibility Demo

## Definitions:

Miscible: capable of being mixed

Immiscible: incapable of being mixed

Which is most likely to dissolve best in water?

A. methanol  $\text{CH}_3\text{OH}$  ←

B. butanol  $\text{C}_4\text{H}_9\text{OH}$

C. octanol  $\text{C}_8\text{H}_{17}\text{OH}$

D. didodecanol  $\text{C}_{12}\text{H}_{25}\text{OH}$

Which is most likely to dissolve best in hexane ( $C_6H_{14}$ )?

A. methanol  $CH_3OH$

B. butanol  $C_4H_9OH$

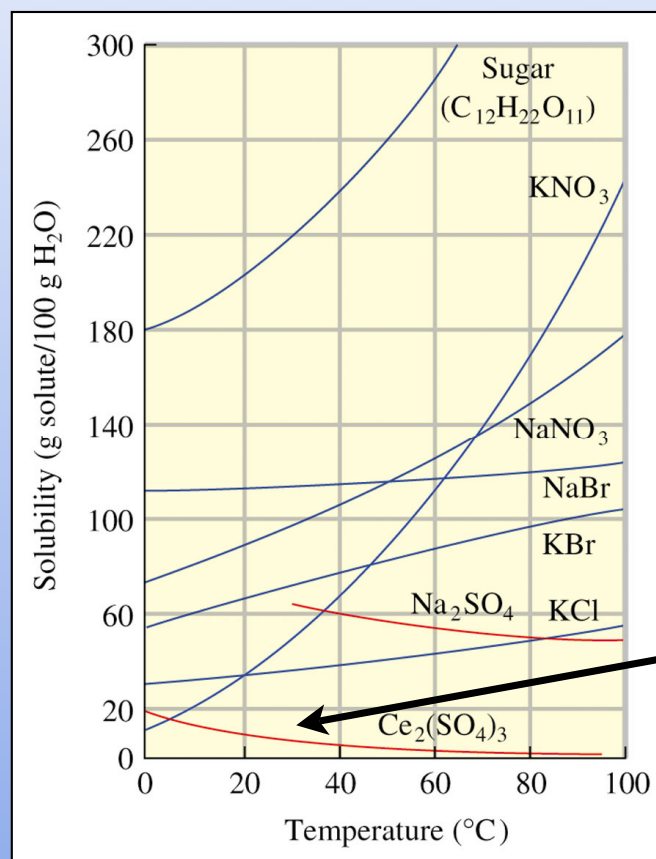
C. octanol  $C_8H_{17}OH$

D. didodecanol  $C_{12}H_{25}OH$



# Temperature Dependence

Generally as T goes up solubility increases



$\Delta H_{\text{soln}} < 0$   
(reaction with water)

# Gas Dissolved in a Liquid

## Henry's Law

**TABLE 17.3** The Values of Henry's Law Constants for Several Gases Dissolved in Water at 298 K

Gas	$k_H$ (atm)
CH <sub>4</sub>	$4.13 \times 10^2$
CO <sub>2</sub>	$1.64 \times 10^3$
O <sub>2</sub>	$4.34 \times 10^4$
CO	$5.71 \times 10^4$
H <sub>2</sub>	$7.03 \times 10^4$
N <sub>2</sub>	$8.57 \times 10^4$

$$P_{\text{solute}} = K_{\text{solvent}} X_{\text{solute}}$$



mole fraction

$$n_{\text{gas}}/n_{\text{total}}$$

## In General

Henry's Law constants increase with increasing Temperature

Less gas is dissolved at higher temperatures

$$\Delta H < 0$$

going from no attractions to being in a liquid

= bad news for fish in hot water (less dissolved O<sub>2</sub>)