

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

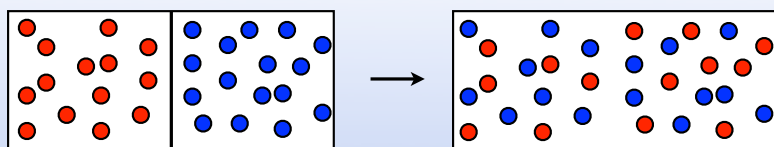
What is the sign of the change in free energy  
for me dropping an eraser?

- 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?



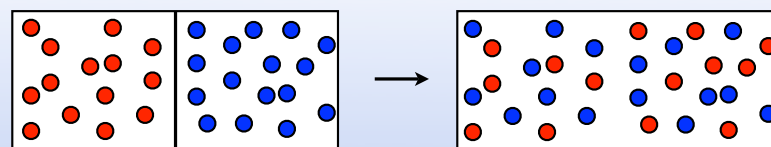
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## Mixtures

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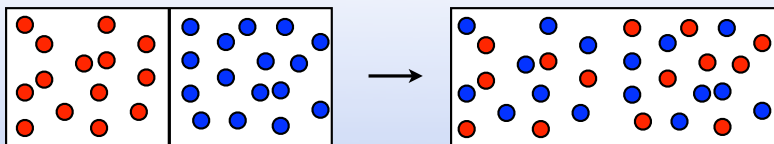
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## Mixtures

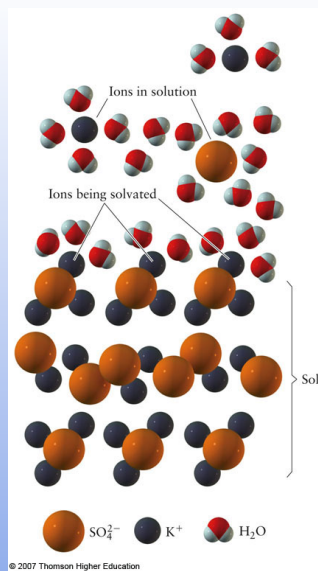
What is different than pure substances?



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

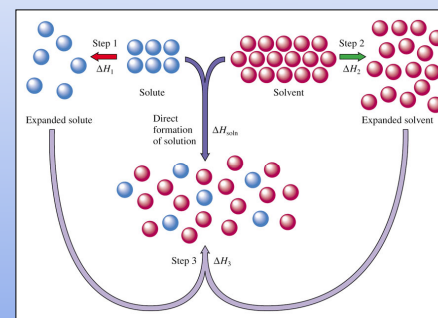


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## How we generally think of this

What is  $\Delta H_{\text{solution}}$ ?  
this is the enthalpy change for making the solution?

### Two steps

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

Next put solute into solvent  $\Delta H_{\text{solvation}}$   
(add of solute-solvent interactions) “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  $\Delta S_{\text{soln}}^{\circ}$  for Several Salts Dissolving in Water

Process	$\Delta S^{\circ}$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )
KCl(s) $\rightarrow \text{K}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq})$	75
LiF(s) $\rightarrow \text{Li}^{+}(\text{aq}) + \text{F}^{-}(\text{aq})$	-36
CaS(s) $\rightarrow \text{Ca}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq})$	-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?

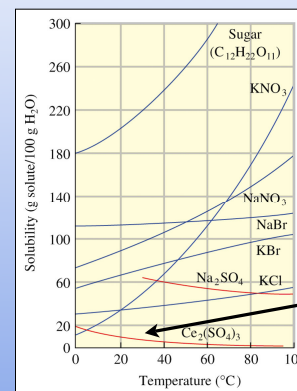
- A. methanol  $\text{CH}_3\text{OH}$  ←
- B. butanol  $\text{C}_4\text{H}_9\text{OH}$
- C. octanol  $\text{C}_8\text{H}_{17}\text{OH}$
- D. didodecanol  $\text{C}_{12}\text{H}_{25}\text{OH}$

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 at 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)
$CH_4$	$4.13 \times 10^2$
$CO_2$	$1.64 \times 10^3$
$O_2$	$4.34 \times 10^4$
$CO$	$5.71 \times 10^4$
$H_2$	$7.03 \times 10^4$
$N_2$	$8.57 \times 10^4$

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

↑  
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  $O_2$ )