Section 14.2 and 14.3
Control of Solubility

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Control of Solubility

In these sections…

Molecular structure control:

a. Entropy and thermodynamic control
b. Gas mixtures
c. Mixtures of neutral molecules in liquids
d. Mixtures of ionic compounds in water

External (conditions) control:

a. pressure
b. temperature

Enthalpy and Entropy

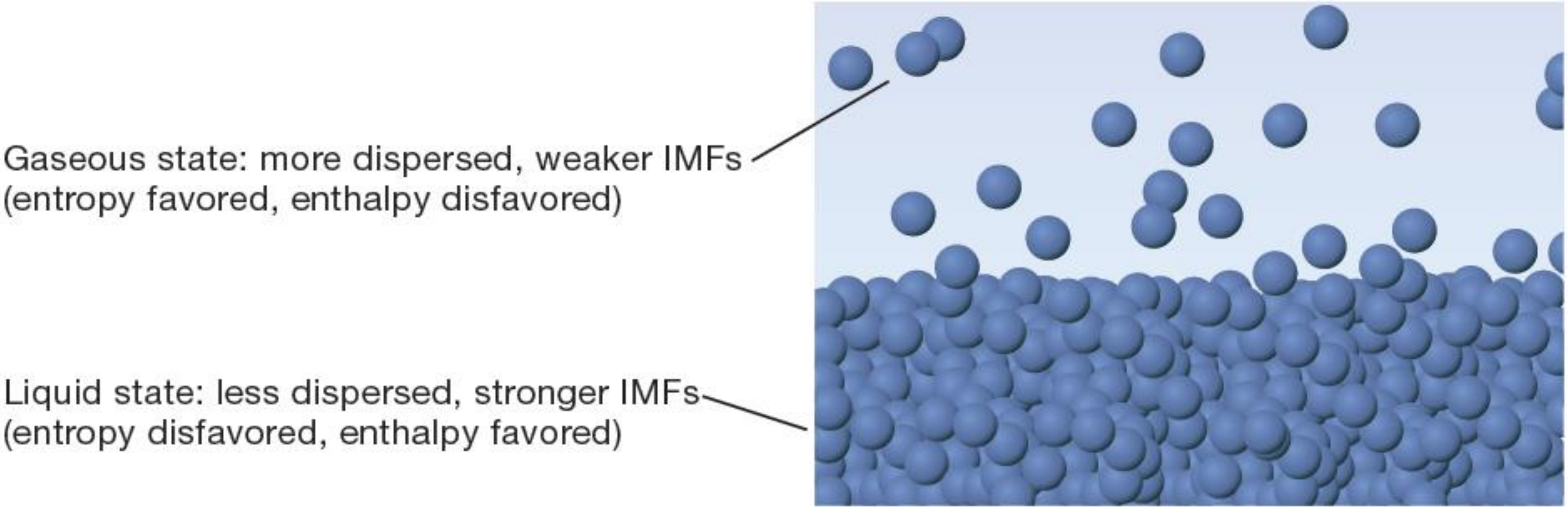
Enthalpy: Bond strength- stronger bonds = lower enthalpy = more stable

Entropy: Free motion of atoms- freer mobility = higher entropy = more stable

Table 13.2.1 Entropy, Enthalpy, and Dissolution

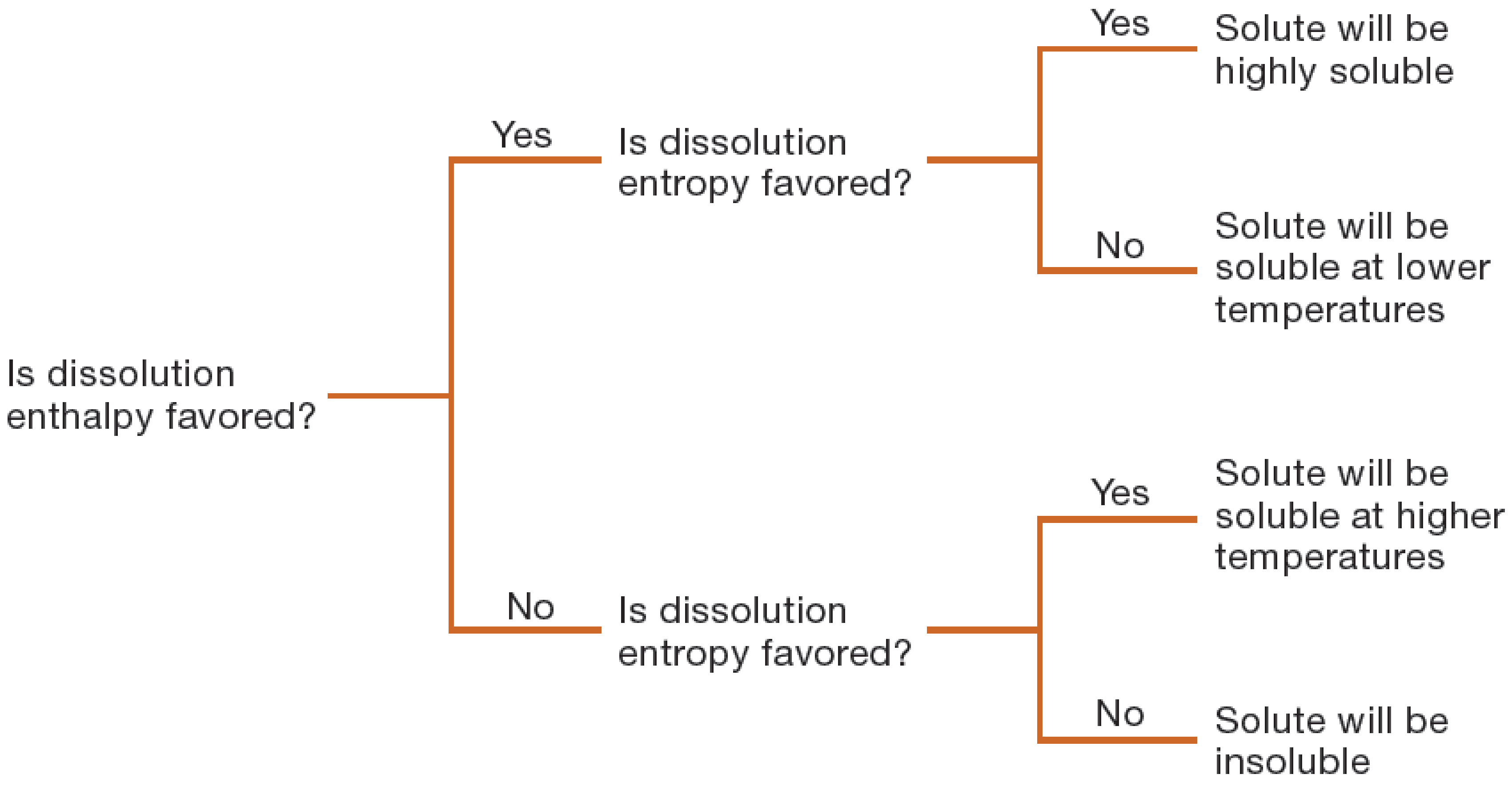
	Positive Enthalpy Change (Reduction in Strength of IMFs)	Negative Enthalpy Change (Increase in Strength of IMFs)
Positive Entropy Change (Increase in Mobility of Particles)	Favored at higher temperatures	Favored at all temperatures
Negative Entropy Change (Reduction in Mobility of Particles)	Disfavored at all temperatures	Favored at lower temperatures

Example: Enthalpy and Entropy of Evaporation

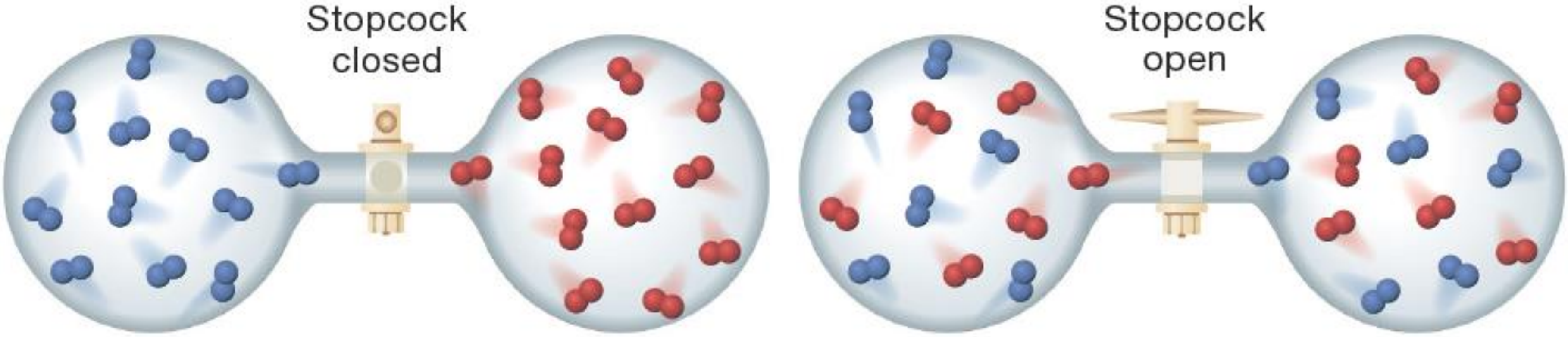


A molecular-scale view of evaporation

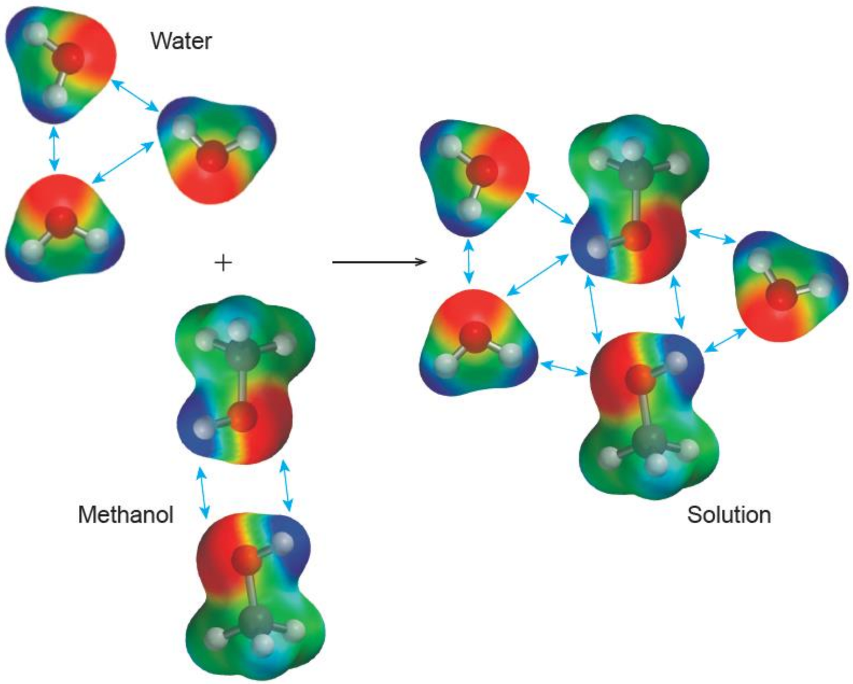
Enthalpy and Entropy Control of Dissolution



Gas Mixtures



Liquid-Liquid Mixtures



Predicting Miscibility of Two Liquids

For now, we are examining molecular compounds- not ionic compounds.

General rules:

1. polar solutes dissolve in polar solvents
2. nonpolar solutes dissolve in nonpolar solvents

“Like dissolves Like”

Oil and water don’t mix: is oil polar or nonpolar?

Hydrophilic groups:

–OH and –NH groups

Examples: CH_3OH, NH3, H-O-O-H

Hydrophobic groups:

Long hydrocarbon groups:

$CH_3CH_2CH_2CH_2CH_2CH_2$

Examples: $CH_3CH_2CH_2CH_2CH_3$

$CH_3CH_2CH_2CH_2Cl$

Which of these will not dissolve in water?

1. NH_3
2. CH_3CH_3
3. CH_3OH

Which of these is least soluble in water?

1. CH_3OH
2. $CH_3CH_2CH_2OH$
3. $CH_3CH_2CH_2CH_2OH$

Why don't oil and water mix?

What controls Solubility:

Enthalpy (enthalpy of solution)

Negative if new forces are stronger than original forces

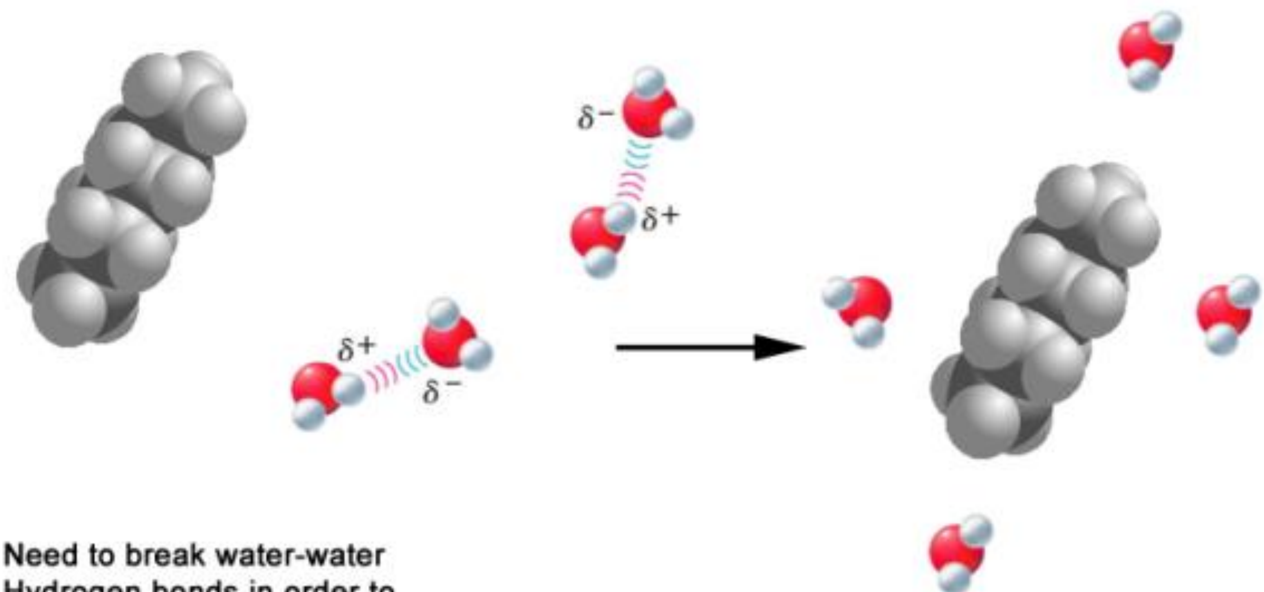
Entropy

Depends on the entropy change of both the water and the solute.

Assume they mix fully

Why Don't Oil and Water Mix?

Explanation #1



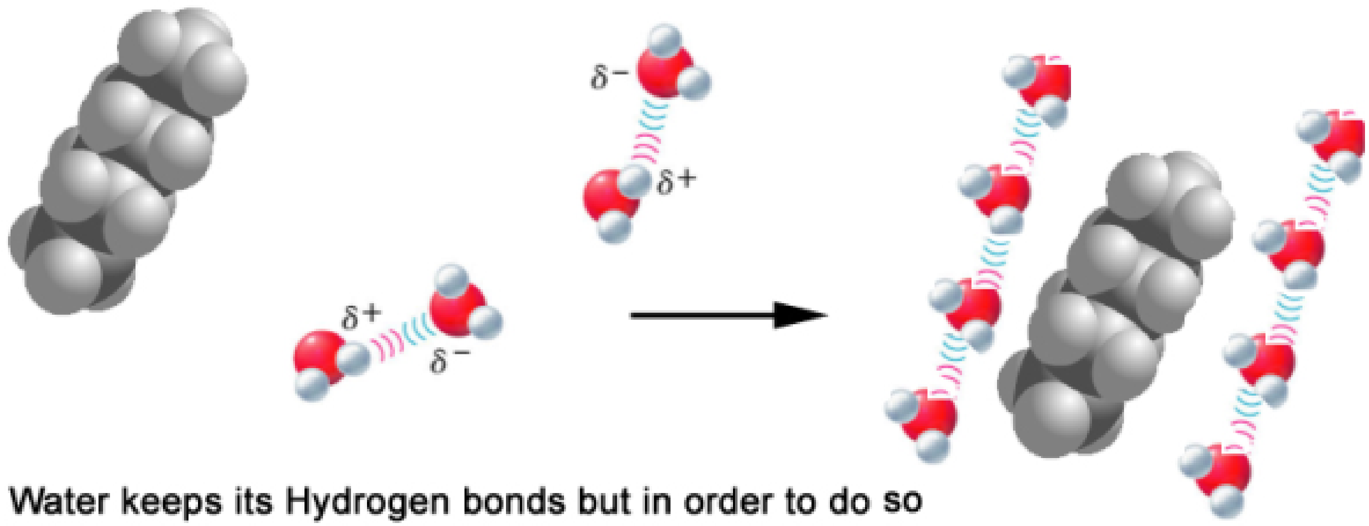
Need to break water-water Hydrogen bonds in order to insert nonpolar hydrocarbon between them,

delta H would be: _____

delta S would be: _____

Assume water retains its hydrogen bonds

Explanation #2



Water keeps its Hydrogen bonds but in order to do so with the hydrocarbon there, the water molecules need to stay in a very specific orientation around the nonpolar molecule.

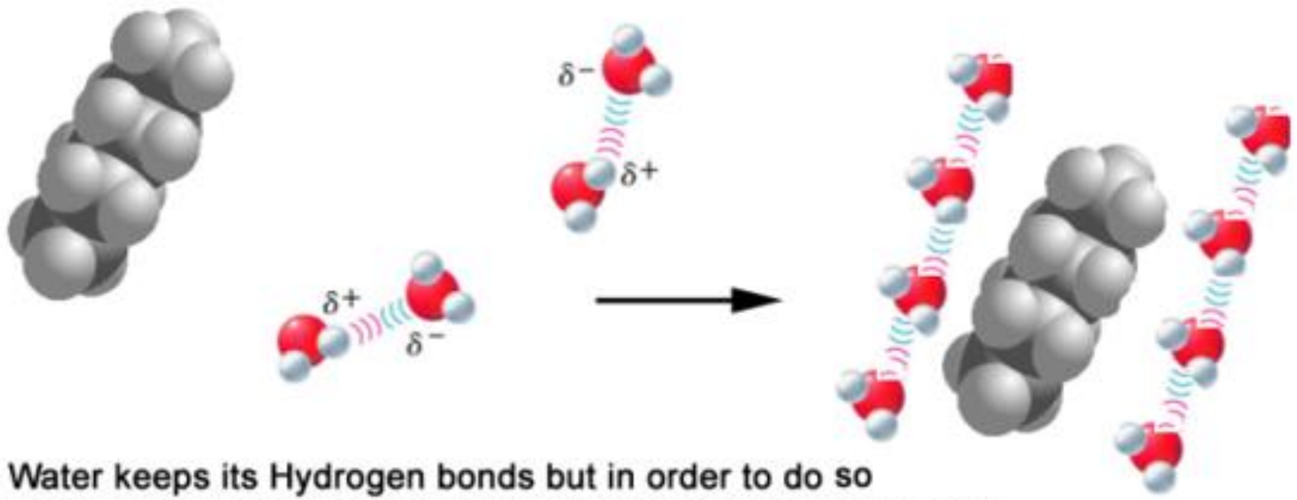
delta H would be: _____ delta S would be: _____

Which is it?

Experiments show mixing water and oil has:

ΔH close to zero

ΔS highly negative



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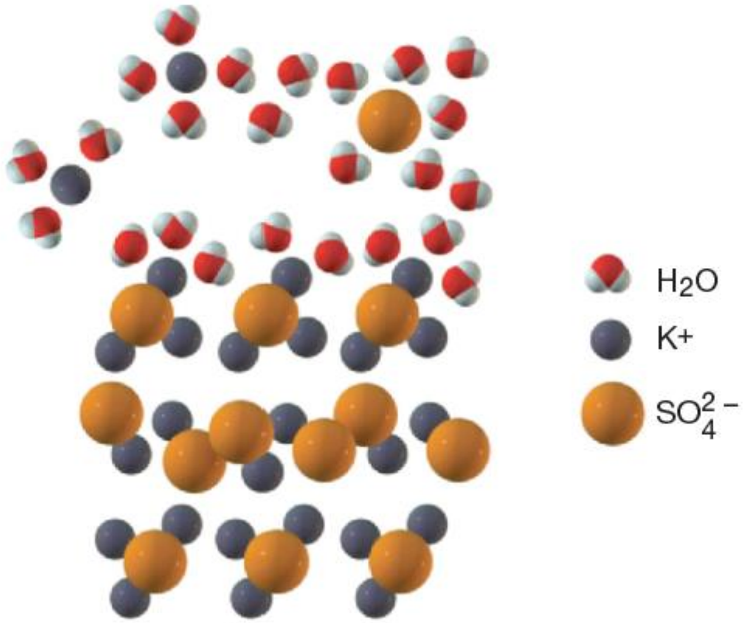
Control of Solubility of Ionic Compounds

Solubility Rules for Ionic Compounds in Water

Soluble Ionic Compounds*	Notable Exceptions
All sodium (Na^+), potassium (K^+), and ammonium (NH_4^+) salts	
All nitrate (NO_3^-), acetate ($CH_3CO_2^-$), chlorate (ClO_3^-), and perchlorate (ClO_4^-) salts	
All chloride (Cl^-), bromide (Br^-), and iodide (I^-) salts	Compounds also containing lead, silver, or mercury(I) (Pb^{2+}, Ag^+, Hg_2^{2+}) are insoluble.
All fluoride (F^-) salts	Compounds also containing calcium, strontium, barium, or lead (Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}) are insoluble.
All sulfate (SO_4^{2-}) salts	Compounds also containing calcium, mercury(I), strontium, barium, or lead (Ca^{2+}, Hg_2^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}) are insoluble.
Insoluble Ionic Compounds	**Exceptions**
Hydroxide (OH^-) and oxide (O^{2-}) compounds	Compounds also containing sodium, potassium, or barium (Na^+, K^+, Ba^{2+}) are soluble.
Sulfide (S^{2-}) salts	Compounds also containing sodium, potassium, ammonium, or barium (Na^+, K^+, NH_4^+, Ba^{2+}) are soluble.
Carbonate (CO_3^{2-}) and phosphate (PO_4^{3-}) salts	Compounds also containing sodium, potassium, or ammonium (Na^+, K^+, NH_4^+) are soluble.

Control of Solubility of Ionic Compounds



Molecular-scale view of the dissolution of K_2SO_4 in water

Enthalpy Control

Table 13.2.2 Enthalpies of Hydration of Selected Metal Cations (kJ/mol)

+1 Ions			+2 Ions			+3 Ions		
Ion	Radius (pm)	ΔH_{hyd}	Ion	Radius (pm)	ΔH_{hyd}	Ion	Radius (pm)	ΔH_{hyd}
Cs	181	−263	Ra		−1259	La	117	−3283
Rb	166	−296	Ba	149	−1304	Lu	100	−3758
K	152	−321	Sr	132	−1445	Y	104	−3620
Na	116	−405	Ca	114	−1592	Sc	88	−3960
Li	90	−515						
H		−1091						

Entropy Control

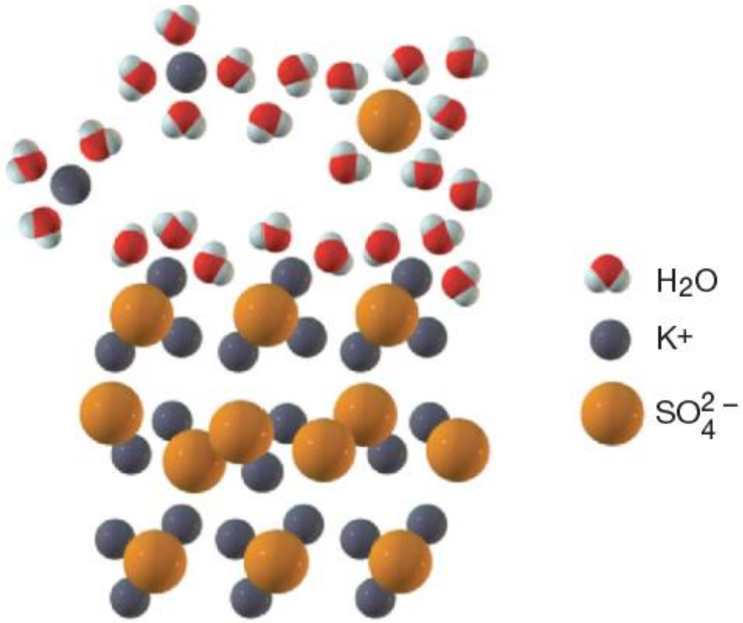
Hydration Numbers of Some Hydrated Ions

Ion	Hydration number	Ion	Hydration number
Li^+	22	Mg^{2+}	36
Na^+	13	Ca^{2+}	29
K^+	7	Sr^{2+}	29
Cs^+	6	Ba^{2+}	28
		Cd^{2+}	39
		Zn^{2+}	44

Control of Solubility of Ionic Compounds

Enthalpy: lattice energies and hydration energies follow same trends and mostly offset

Entropy: smaller ions and ions of high charge have larger hydration spheres and are entropy disfavored from dissolving



Molecular-scale view of the dissolution of K_2SO_4 in water

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Carbonate (CO_3^{2-}) and phosphate (PO_4^{3-}) salts	Compounds also containing sodium, potassium, or ammonium (Na^+, K^+, NH_4^+) are soluble.

External Control of Solubility

Pressure Effects: Solubility of Gases in Liquids

As P of a gas increases, its solubility increases.

Henry's Law:

$$S = k_{\mathrm{H}} \times P$$

Table 13.3.1 Some Henry's Law Constants for the Solubility of Gases in Water (25 °C)

Gas	k_H (mol/L · atm) at 25 °C
N_2	6.47×10^{-4}
O_2	1.28×10^{-3}
CO_2	3.36×10^{-2}
He	3.26×10^{-4}

What is the solubility of O_2 under a pressure of 0.66 atm?

External Control of Solubility

Temperature Effects

In general,

- if $\Delta H_{dissolution}$ is exothermic, solubility decreases as temperature increases
- if $\Delta H_{dissolution}$ is exothermic, solubility decreases as temperature increases

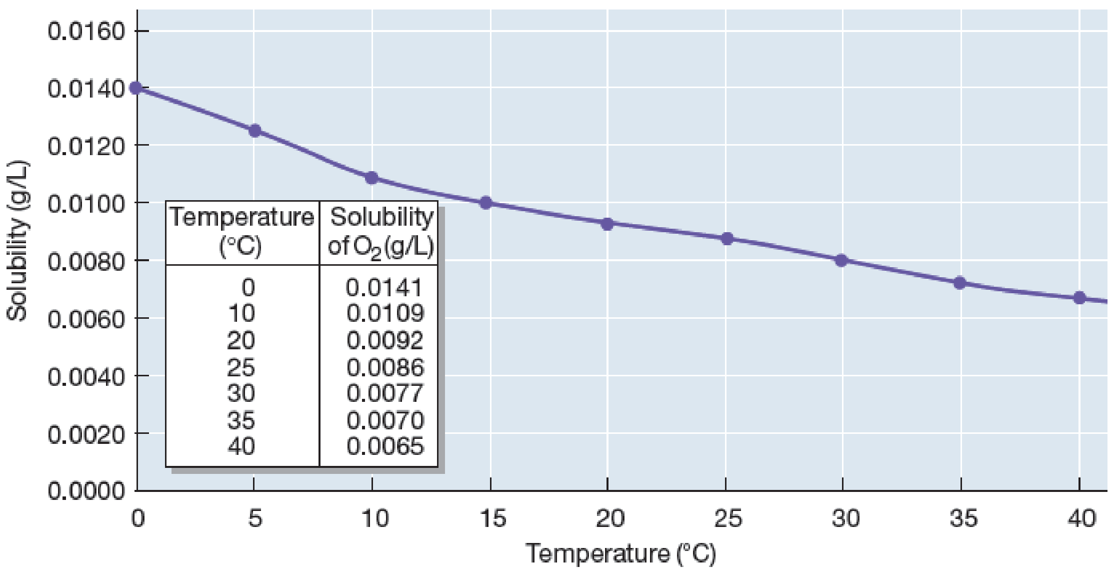


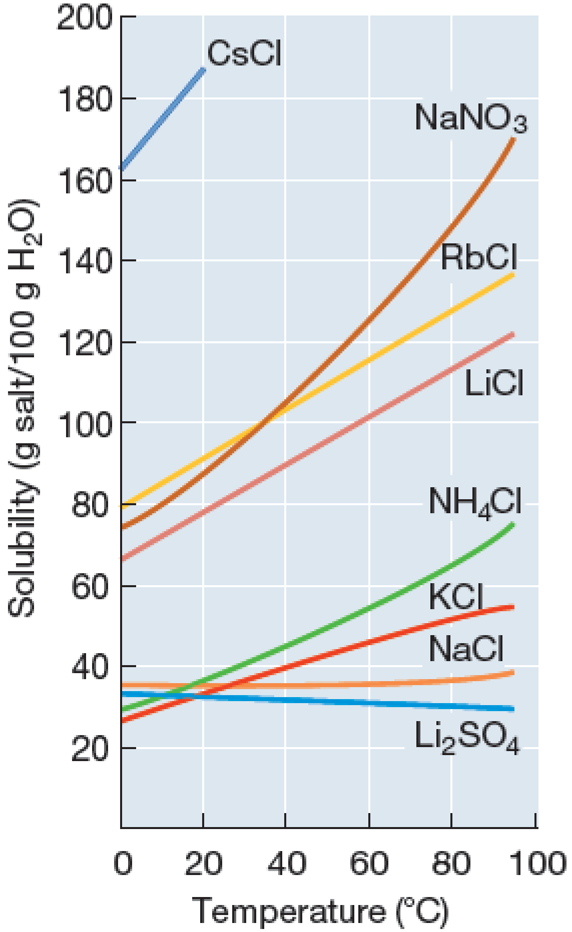
Figure 13.3.4 Solubility of oxygen in water at various temperatures

In general, but not always:

- if $\Delta H_{dissolution}$ is exothermic, solubility decreases as temperature increases
- if $\Delta H_{dissolution}$ is endothermic, solubility increases as temperature increases

$$Li_2SO_4(s) \rightarrow Li_2SO_4(aq) \qquad \Delta H^\circ = -29.8 \text{ kJ/mol}$$

$$LiCl(s) \rightarrow LiCl(aq) \qquad \Delta H^\circ = -37.0 \text{ kJ/mol}$$



What do we expect for ammonium nitrate?

$$NH_4NO_3(s) \rightarrow NH_4NO_3(aq) \qquad \Delta H^\circ = +25.7 \text{ kJ/mol}$$