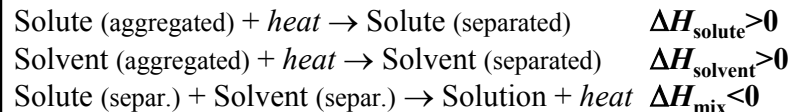
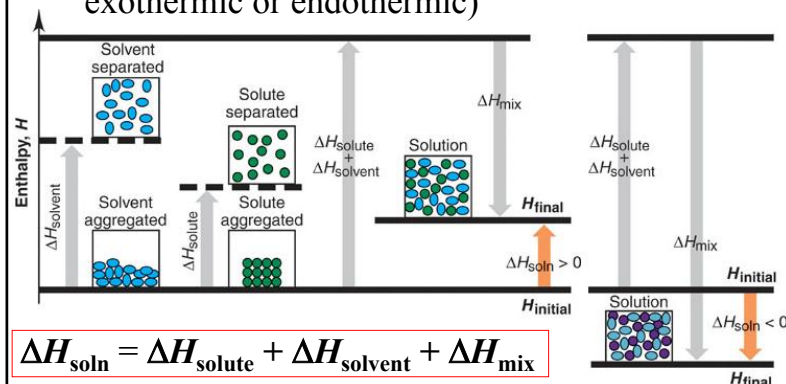


13.2 Energy Changes in the Solution Process

- **Solution cycle** – the solution process can be divided into three steps:
 - 1) **Separation of solute particles** to make room for the solvent – endothermic (energy is needed to overcome the *IFs* of attraction)
 - 2) **Separation of solvent particles** to make room for the solute particles – endothermic (energy is needed to overcome the *IFs* of attraction)
 - 3) **Mixing of solvent and solute particles** – exothermic (solute-solvent *IFs* lower the energy)



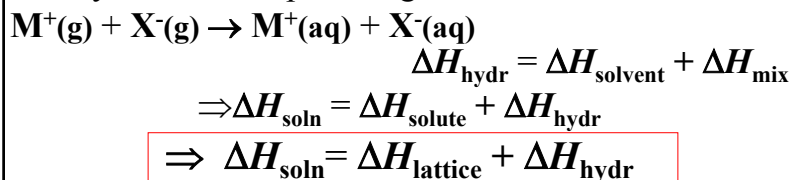
– **Heat of solution (ΔH_{soln})** – the total enthalpy change during the solution cycle (can be either exothermic or endothermic)



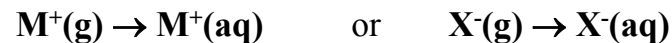
Solutions of Ionic Solids

- For dilute solutions of ionic solids, the solute separation has ΔH equal to the lattice enthalpy

$$\text{MX(s)} \rightarrow \text{M}^+(\text{g}) + \text{X}^-(\text{g}) \quad \Delta H_{\text{solute}} = \Delta H_{\text{lattice}} > 0$$
- The **hydration** of the separated solute ions is a combination of steps 2 and 3 in the solution cycle → (solvent separation + mixing)
 - **Heat (enthalpy) of hydration (ΔH_{hydr})** – ΔH for hydration of separated gaseous ions



- **Individual ionic heats of hydration** – ΔH for the hydration of 1 mol of separated gaseous cations (or anions)



- ΔH_{hydr} of ions is always exothermic ($\Delta H_{\text{hydr}} < 0$) because the ion-dipole forces that replace some of the H-bonds in water are stronger
- The overall heat of hydration is a sum of the heats for the cations and the anions

➤ **Trends in ΔH_{hydr} of ions** (same as for $\Delta H_{\text{lattice}}$)

- ΔH_{hydr} is larger (more exothermic) for ions with greater charges and smaller sizes → ions with higher **charge density**
- The charge factor is more important

Some ionic heats of hydration in kJ/mol

Li ⁺ (-558)	Be ²⁺ (-2533)		F ⁻ (-483)
Na ⁺ (-444)	Mg ²⁺ (-2003)	Al ³⁺ (-4704)	Cl ⁻ (-340)
K ⁺ (-361)	Ca ²⁺ (-1657)		Br ⁻ (-309)

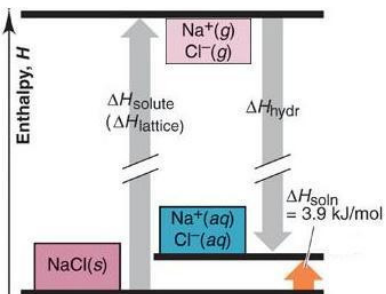
- The sign of ΔH_{soln} is hard to predict, since both $\Delta H_{\text{lattice}}$ and ΔH_{hydr} depend on the ionic charge and size and tend to cancel each other's effects

Example: NaCl

$$\Delta H_{\text{lattice}} = 787 \text{ kJ/mol}$$

$$\Delta H_{\text{hydr}} = (-444) + (-340) = -784 \text{ kJ/mol}$$

$$\Delta H_{\text{soln}} = (787) + (-784) = +4 \text{ kJ/mol}$$



The Tendency Toward Disorder

- $\Delta H_{\text{soln}} < 0$ favors the solution process since the total energy of the system is lowered; but many ionic solids have $\Delta H_{\text{soln}} > 0$ and still dissolve readily in water

⇒ There is a second factor that affects the solution process and acts in addition to the enthalpy factor

- **Disorder** – systems have a natural tendency to become more disordered

- **Entropy** – a measure of the disorder in the system

$\uparrow \text{Entropy} \leftrightarrow \uparrow \text{Disorder}$

- Mixing leads to greater disorder and \uparrow the entropy

- The solution process is governed by the combination of the enthalpy and entropy factors

- Compounds with $\Delta H_{\text{soln}} < 0$ are typically soluble since both factors are favorable
- Compounds with $\Delta H_{\text{soln}} > 0$ are soluble only if ΔH_{soln} is relatively small so the favorable entropy factor dominates
- Compounds with $\Delta H_{\text{soln}} \gg 0$ are typically insoluble since the unfavorable enthalpy factor dominates

Example: Benzene is insoluble in water because the solute-solvent *IFs* are weak so the (-) ΔH_{mix} is very small compared to the (+) ΔH_{solute} & $\Delta H_{\text{solvent}}$

$$\Rightarrow \Delta H_{\text{soln}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mix}} \gg 0$$

13.3 Solubility as an Equilibrium Process

- Typically solutes have limited solubility in a given solvent

- The solution process is countered by *recrystallization* of the dissolved solute
- **Dynamic equilibrium** – the rates of dissolution and recrystallization become equal

Solute (undissolved) \leftrightarrow Solute (dissolved)

- **Saturated solution** – no more solute can be dissolved (can be produced by equilibrating the solution with an excess of the solute; the excess solute can be filtered out after saturation)

- **Molar solubility (S)** – the concentration of the saturated solution in mol/L
- **Unsaturated solution** – more solute can be dissolved
- **Supersaturated solution** – the concentration is higher than the solubility, S (unstable, non-equilibrium state; disturbances or addition of seed crystal lead to crystallization)

Effect of Temperature on Solubility

- Most **solids** are more soluble at higher T due to their endothermic (+) ΔH_{soln}
 - (+) ΔH_{soln} means that heat is absorbed during dissolution (the heat can be viewed as a reactant)

Solute + Solvent + *heat* \leftrightarrow Saturated solution

- Increasing T provides the *heat* needed for the forward reaction to proceed ($S \uparrow$)
- Some **solids** are more soluble at higher T despite their exothermic (-) ΔH_{soln} (Why?)
 - Tabulated ΔH_{soln} values refer to the standard state (1M solution), but saturated solutions can be much more concentrated
 - At very high concentrations the hydration process is hindered so ΔH_{hydr} becomes less negative; thus ΔH_{soln} can change dramatically and even switch signs from (-) to (+)

- **Gases** are less soluble in water at higher T due to their exothermic (-) ΔH_{soln}
 - ΔH_{soln} is (-) since $\Delta H_{\text{solute}} \approx 0$ and $H_{\text{hydr}} < 0$
- Gas + Water \leftrightarrow Saturated solution + *heat*
- Increasing T provides the *heat* needed for the reverse reaction to proceed ($S \downarrow$)

Effect of Pressure on Solubility

- Pressure has little effect on the solubility of solids and liquids (low compressibility)
- The molar solubility of gases (S_{gas}) increases with increasing their partial pressures (P_{gas}) over the solution (collisions with liquid surface \uparrow)

➤ **Henry's law** - S_{gas} is directly proportional to P_{gas}

$$S_{\text{gas}} = k_{\text{H}} \times P_{\text{gas}}$$

– k_{H} – Henry's law constant (depends on the gas, solvent and T)

Example: What is the concentration of CO_2 in rain drops at 20°C and 1.0 atm in air that has 1.0% by volume CO_2 ? [$k_{\text{H}}(\text{CO}_2, 20^\circ\text{C}) = 2.3 \times 10^{-2} \text{ mol/L}\cdot\text{atm}$]

1.0% by volume $\rightarrow \chi_{\text{CO}_2} = 0.010$

$$P_{\text{CO}_2} = \chi_{\text{CO}_2} P_{\text{tot}} = 0.010 \times 1.0 \text{ atm} = 0.010 \text{ atm}$$

$$S_{\text{CO}_2} = k_{\text{H}} \times P_{\text{CO}_2} = 2.3 \times 10^{-2} \text{ mol/L}\cdot\text{atm} \times 0.010 \text{ atm} \\ = 2.3 \times 10^{-4} \text{ mol/L}$$