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 IF's of attraction)

2) **Separation of solvent particles** to make room for the solute particles – endothermic (energy is needed to overcome the IF's of attraction)

3) **Mixing of solvent and solute particles** – exothermic (solute-solvent IF's lower the energy)

Solutions of Ionic Solids

- For dilute solutions of ionic solids, the solute separation has \( \Delta H \) equal to the lattice enthalpy: \( \text{MX(s)} \rightarrow \text{M}^+(g) + \text{X}^-(g) \quad \Delta H_{\text{solute}} = \Delta H_{\text{lattice}} > 0 \)
- 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** \( \Delta H_{\text{hydr}} \) – \( \Delta H \) for hydration of separated gaseous ions

\[
\text{M}^+(g) + \text{X}^-(g) \rightarrow \text{M}^+(aq) + \text{X}^-(aq)
\]

\[
\Delta H_{\text{hydr}} = \Delta H_{\text{solute}} + \Delta H_{\text{mix}}
\]

\[
\Rightarrow \Delta H_{\text{soln}} = \Delta H_{\text{solute}} + \Delta H_{\text{hydr}}
\]

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

\[
\text{M}^+(g) \rightarrow \text{M}^+(aq) \quad \text{or} \quad \text{X}^-(g) \rightarrow \text{X}^-(aq)
\]

- \( \Delta H_{\text{hydr}} \) 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 \( \Delta H_{\text{hydr}} \) of ions** (same as for \( \Delta H_{\text{lattice}} \))

- \( \Delta H_{\text{hydr}} \) is larger (more exothermic) for ions with greater charges and smaller sizes → ions with higher **charge density**

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

**Example: NaCl**

- $\Delta H_{\text{lattice}} = 787$ kJ/mol
- $\Delta H_{\text{hydr}} = (-444) + (-340) = -784$ kJ/mol
- $\Delta H_{\text{soln}} = (787) + (-784) = +4$ 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.

  $\Rightarrow$ 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
  
  $\uparrow$Entropy $\leftrightarrow \uparrow$Disorder

  - Mixing leads to greater disorder and $\uparrow$ the entropy.

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**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.)

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<thead>
<tr>
<th>Ion</th>
<th>$\Delta H_{\text{hydr}}$</th>
<th>$\Delta H_{\text{lattice}}$</th>
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<tbody>
<tr>
<td>Li$^+$</td>
<td>-558</td>
<td>-2533</td>
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<tr>
<td>Be$^{2+}$</td>
<td>-2533</td>
<td>787</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>-444</td>
<td>-2003</td>
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<td>Cl$^-$</td>
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<td>-483</td>
<td>-784</td>
</tr>
</tbody>
</table>
- **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 (+) \( \Delta H_{\text{soln}} \)
  
  \( (+) \Delta H_{\text{soln}} \) means that heat is absorbed during dissolution (the heat can be viewed as a reactant)

- **Gases** are less soluble in water at higher \( T \) due to their exothermic (-) \( \Delta H_{\text{soln}} \)
  
  \( \Delta H_{\text{soln}} \) is (-) since \( \Delta H_{\text{solute}} \approx 0 \) and \( H_{\text{hydr}} < 0 \)

**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 ↑)

**Solute + Solvent + heat ↔ 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 (-) \( \Delta H_{\text{soln}} \) (Why?)
  
  \( \Delta H_{\text{soln}} \) 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 \( \Delta H_{\text{hydr}} \) becomes less negative; thus \( \Delta H_{\text{soln}} \) can change dramatically and even switch signs from (-) to (+)

- **Henry’s law** - \( S_{gas} \) is directly proportional to \( P_{gas} \)

\[
S_{gas} = k_H \times P_{gas}
\]

- \( k_H \) – 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\(_2\) [\( k_H(\text{CO}_2, \ 20^\circ \text{C}) = 2.3 \times 10^{-2} \text{ mol/L.atm}\)]

- 1.0% by volume \( \rightarrow \chi_{\text{CO}_2} = 0.010 \)
- \( P_{\text{CO}_2} = \chi_{\text{CO}_2} \ P_{\text{tot}} = 0.010 \times 1.0 \text{ atm} = 0.010 \text{ atm} \)
- \( S_{\text{CO}_2} = k_H \times P_{\text{CO}_2} = 2.3 \times 10^{-2} \text{ mol/L.atm} \times 0.010 \text{ atm} \)
  
  \( = 2.3 \times 10^{-4} \text{ mol/L} \)