Why Does Something Dissolve in a Solvent?

A solute dissolves in a solvent because the attractive forces between solute and solvent molecules are similar to those between the solute particles themselves.

"Like dissolves like."

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>Solubility</th>
<th>Attractive Force</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>H₂O</td>
<td>soluble</td>
<td>ion-dipole</td>
</tr>
<tr>
<td>NaCl</td>
<td>CCl₄</td>
<td>insoluble</td>
<td>ion vs. London</td>
</tr>
<tr>
<td>H₂O</td>
<td>CH₃OH</td>
<td>soluble</td>
<td>dipole-dipole, hydrogen bonding</td>
</tr>
<tr>
<td>H₂O</td>
<td>C₇H₁₃OH</td>
<td>sl. soluble</td>
<td>dipole vs. London</td>
</tr>
<tr>
<td>I₂</td>
<td>CCl₄</td>
<td>soluble</td>
<td>London dispersion</td>
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<tr>
<td>I₂</td>
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<tr>
<td>I₂</td>
<td>CH₃OH</td>
<td>soluble</td>
<td>London dispersion</td>
</tr>
</tbody>
</table>
Dissolving a Molecular Solute in Water
Dipole-Dipole Attractions
Dissolving an Ionic Solute in Water
Ion-Dipole Attractions
Dielectric Constant and Ionic Solubility

The measure of a solvent's ability to diminish the force of attraction between the ions is the *dielectric constant*, $\varepsilon$, which modifies the expression for the force between ions in solution to become

$$F_{\text{soln}} = \frac{\varepsilon q \% q}{\varepsilon r^2}$$

The larger the value of $\varepsilon$, the better the solvent will be for dissolving ionic substances.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>H$_2$O</th>
<th>CH$_3$OH</th>
<th>CCl$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$</td>
<td>78.5</td>
<td>32.6</td>
<td>2.2</td>
</tr>
</tbody>
</table>
Dissolving Polar Covalent Compounds With Ion Formation
Ion-Dipole Attractions

HCl(g) + H₂O(l) → 6 H₃O⁺(aq) + Cl⁻(aq)
Enthalpy of Solution, $\Delta H_{\text{soln}}$

Enthalpy of solution can be endothermic or exothermic.

CaCl$_2$(s) $\rightarrow$ $\rightarrow$ Ca$^{2+}$(aq) + 2Cl$^-$ (aq) + heat $\triangleq \Delta H_{\text{soln}} < 0$ (exothermic)

heat + KNO$_3$(s) $\rightarrow$ $\rightarrow$ 6 K$^+$ (aq) + NO$_3^-$ (aq) $\triangleq \Delta H_{\text{soln}} > 0$ (endothermic)

Enthalpy of solution can be analyzed as the sum of the following processes:

1. Enthalpy to overcome attractions between solute molecules.
   \[ \sim \sim 6 \sim + \sim \] $\Delta H_1 > 0$ (endothermic)

2. Enthalpy to overcome attractions between solvent molecules.
   \[ \mid \mid 6 \mid + \mid \] $\Delta H_2 > 0$ (endothermic)

3. Enthalpy to form solvated molecules through solute-solvent attractions.
   \[ \mid + \sim 6 \mid \sim \] $\Delta H_3 < 0$ (exothermic)

$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$

If $\*\Delta H_3\* > \{\Delta H_1 + \Delta H_2\}$, then $\Delta H_{\text{soln}} < 0$ (exothermic)

If $\*\Delta H_3\* < \{\Delta H_1 + \Delta H_2\}$, then $\Delta H_{\text{soln}} > 0$ (endothermic)
Solubility and Spontaneity

When a solute is soluble in a solvent, the solution process is spontaneous.

When a solute is insoluble in a solvent, the solution process is non-spontaneous.

A spontaneous process or change proceeds in a given direction without needing to be driven by an external energy input.

Exothermic reactions or processes tend to be spontaneous.

\[
CaCl_2(s) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq) + \text{heat} \quad \Delta H_{\text{soln}} < 0 \, \text{(exothermic)}
\]

But some endothermic processes are spontaneous, too.

\[
\text{heat} + KNO_3(s) \rightarrow 6K^+(aq) + NO_3^-(aq) \quad \Delta H_{\text{soln}} > 0 \, \text{(endothermic)}
\]
Entropy and Spontaneity

L  *Entropy* is a thermodynamic measure of the *disorder* of a system.

L  At constant temperature a reaction or process that results in an increase in disorder (greater entropy) *tends* to be spontaneous.

U  When a solute dissolves in a solvent the entropy of the system increases.

U  If a solute spontaneously dissolves endothermically, the entropy factor favoring spontaneity is greater than the enthalpy factor favoring non-spontaneity.

U  The heat of solution of an insoluble solute is generally endothermic with too small an enthalpy increase to make the overall process spontaneous.
Effects of Pressure and Temperature on Solubility

Solid and Liquid Solutes

L Pressure usually has no significant effect on solubility

L Temperature increases may result in greater or lesser solubility.
  • Temperature effect is not related to $\Delta H_{\text{soln}}$.
  • Rate of dissolving is usually enhanced at higher temperature, regardless of the effect on solubility limit.

Non-reactive Gas Solutes

L Gases are more soluble at higher pressure.

L Gases are less soluble at higher temperature.
Solubility of Non-Reactive Gases with Pressure
Henry's Law
(William Henry - 1804)

L At moderate pressures (#1 atm), many non-reactive gases obey *Henry's Law*:

$$P_g = K \chi_g$$

where

- $P_g = $ partial pressure of the gas over the solution
- $K = $ a constant for the particular gas in the particular solvent at a given temperature
- $\chi_g = $ mole fraction of the gas in the solution.

L At the low concentrations typical of dissolved non-reactive gases, mole fraction is proportional to concentration in the usual units, such as mol/L or g/L, so Henry's Law can be restated as

$$C_g = k P_g$$

where

- $C_g = $ concentration of the dissolved gas
- $k = $ Henry's Law constant for the gas in concentration units per unit pressure (e.g., mol/L/atm)

L Gas solubility goes down with increasing temperature (smaller value of $k$).
Solubility of Some Gases in Water at 298 K

<table>
<thead>
<tr>
<th>Partial Pressure of Gas (atm)</th>
<th>Solubility (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.0005</td>
<td>0.0005</td>
</tr>
<tr>
<td>0.0010</td>
<td>0.0010</td>
</tr>
<tr>
<td>0.0015</td>
<td>0.0015</td>
</tr>
<tr>
<td>0.0020</td>
<td>0.0020</td>
</tr>
<tr>
<td>0.0025</td>
<td>0.0025</td>
</tr>
<tr>
<td>0.0030</td>
<td>0.0030</td>
</tr>
<tr>
<td>0.0035</td>
<td>0.0035</td>
</tr>
</tbody>
</table>

- N2
- O2
- Ar
- CO2
Solubility of Carbon Dioxide at 293 K and 298 K

The diagram shows the solubility of carbon dioxide in water as a function of partial pressure at two different temperatures: 293 K (blue line) and 298 K (red line). The solubility is measured in mol/L, and the partial pressure is given in atm. The solubility increases linearly with increasing partial pressure at both temperatures.
A Gas in Equilibrium With Its Solution

$P_g = 0.5 \text{ atm}$

$P_g = 1.0 \text{ atm}$