Why Does Something Dissolve in a Solvent?

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

<div style="text-align:center">

"Like dissolves like."

</div>

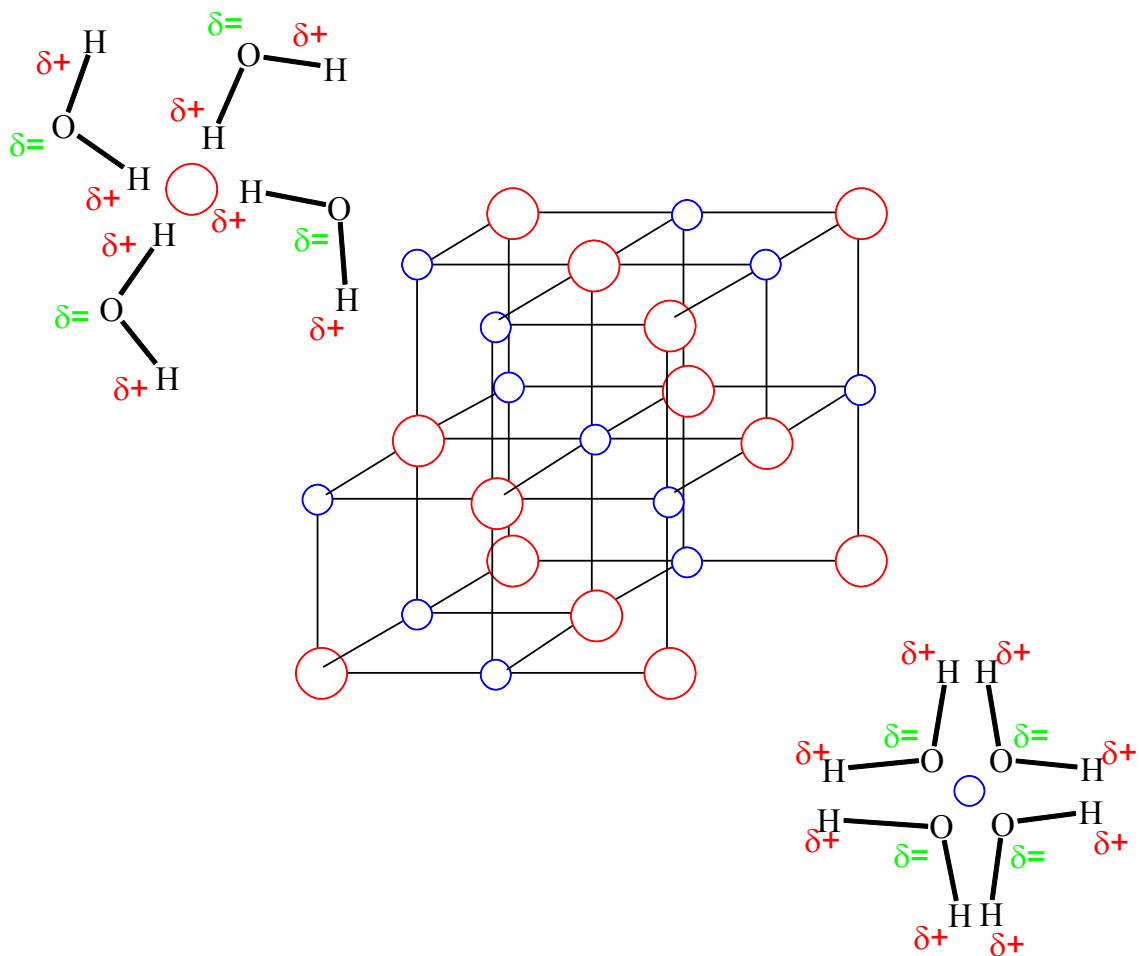| A	B	Solubility	Attractive Force
NaCl	H_2O	soluble	ion-dipole
NaCl	CCl_4	insoluble	ion vs. London
H_2O	CH_3OH	soluble	dipole-dipole, hydrogen bonding
H_2O	$C_7H_{13}OH$	sl. soluble	dipole vs. London
I_2	CCl_4	soluble	London dispersion
I_2	H_2O	sl. soluble	London dispersion
I_2	CH_3OH	soluble	London dispersion

Dissolving a Molecular Solute in Water
Dipole-Dipole Attractions
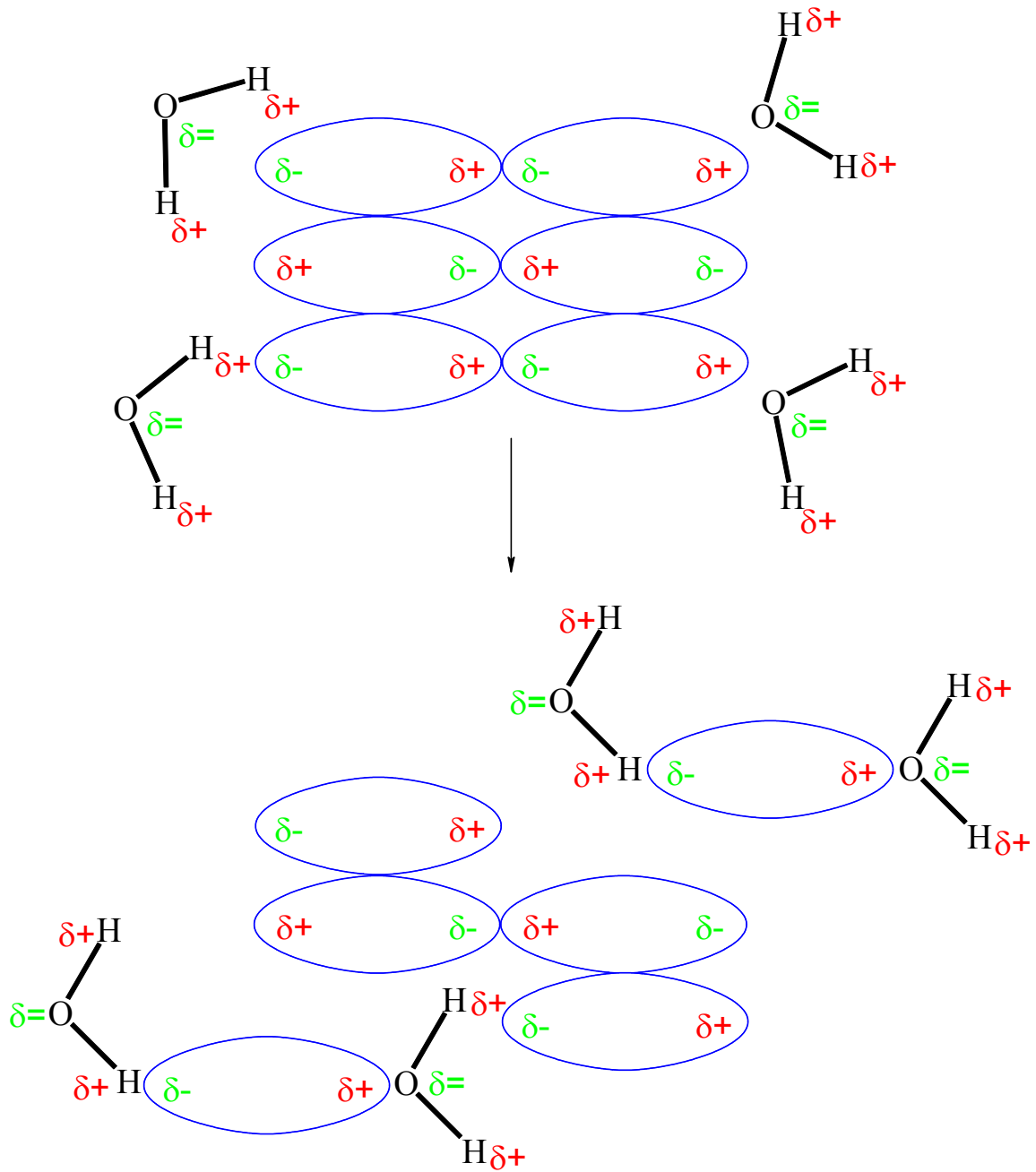
Dissolving an Ionic Solute in Water
Ion-Dipole Attractions

Dielectric Constant and Ionic Solubility

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

$$F_{soln} \propto \frac{q^+ q^-}{\varepsilon r^2}$$

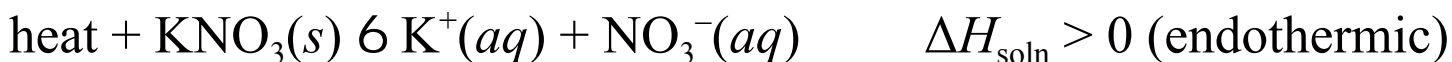L   The larger the value of ε, the better the solvent will be for dissolving ionic substances.

Solvent	H_2O	CH_3OH	CCl_4
ε	78.5	32.6	2.2

Dissolving Polar Covalent Compounds With Ion Formation
Ion-Dipole Attractions

$$HCl(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$
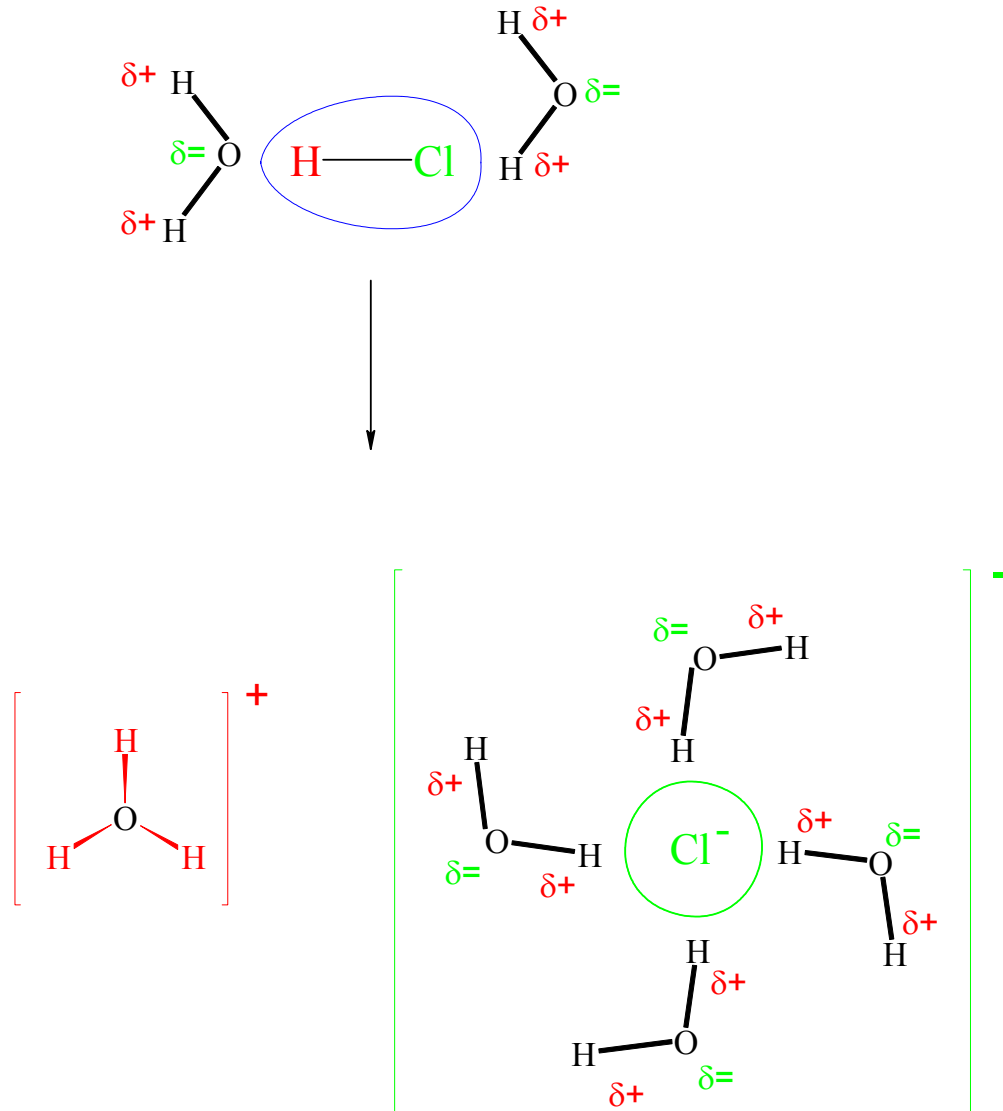
Enthalpy of Solution, ΔH_{soln}

L   Enthalpy of solution can be endothermic or exothermic.

$CaCl_2(s) \ 6 \ Ca^{2+}(aq) + 2Cl^-(aq) + heat$ $\Delta H_{soln} < 0$ (exothermic)

$heat + KNO_3(s) \ 6 \ K^+(aq) + NO_3^-(aq)$ $\Delta H_{soln} > 0$ (endothermic)
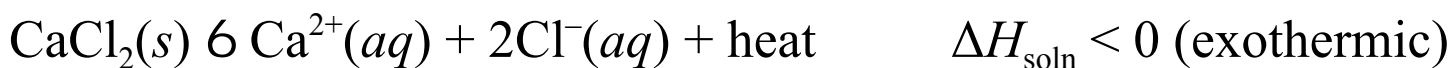
L   Enthalpy of solution can be analyzed as the sum of the
     following processes:

1.   Enthalpy to overcome attractions between solute molecules.

        ~~ 6 ~ + ~ $\Delta H_1 > 0$ (endothermic)

2.   Enthalpy to overcome attractions between solvent
     molecules.

        …..6 …+ … $\Delta H_2 > 0$ (endothermic)

3.   Enthalpy to form solvated molecules through solute-solvent
     attractions.
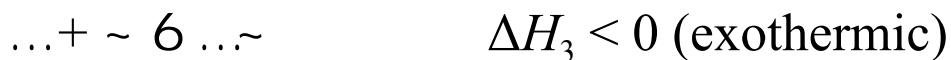
        …+ ~ 6 …~ $\Delta H_3 < 0$ (exothermic)

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

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

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

Solubility and Spontaneity

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

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

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

U   Exothermic reactions or processes *tend* to be spontaneous.

$CaCl_2(s) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq) + heat$ $\Delta H_{soln} < 0$ (exothermic)
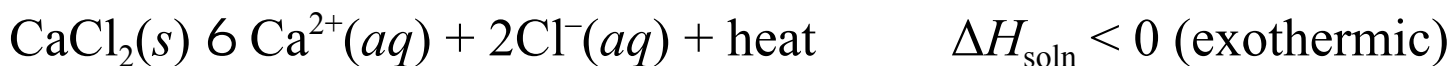
❓   But some endothermic processes are spontaneous, too.

$heat + KNO_3(s) \rightarrow K^+(aq) + NO_3^-(aq)$ $\Delta H_{soln} > 0$ (endothermic)
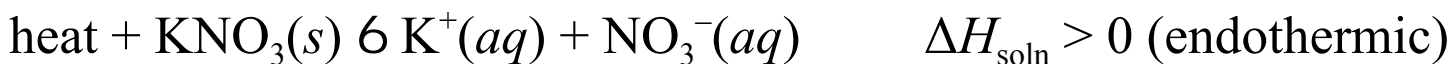
Entropy and Spontaneity

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 ΔH_{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
  χ_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
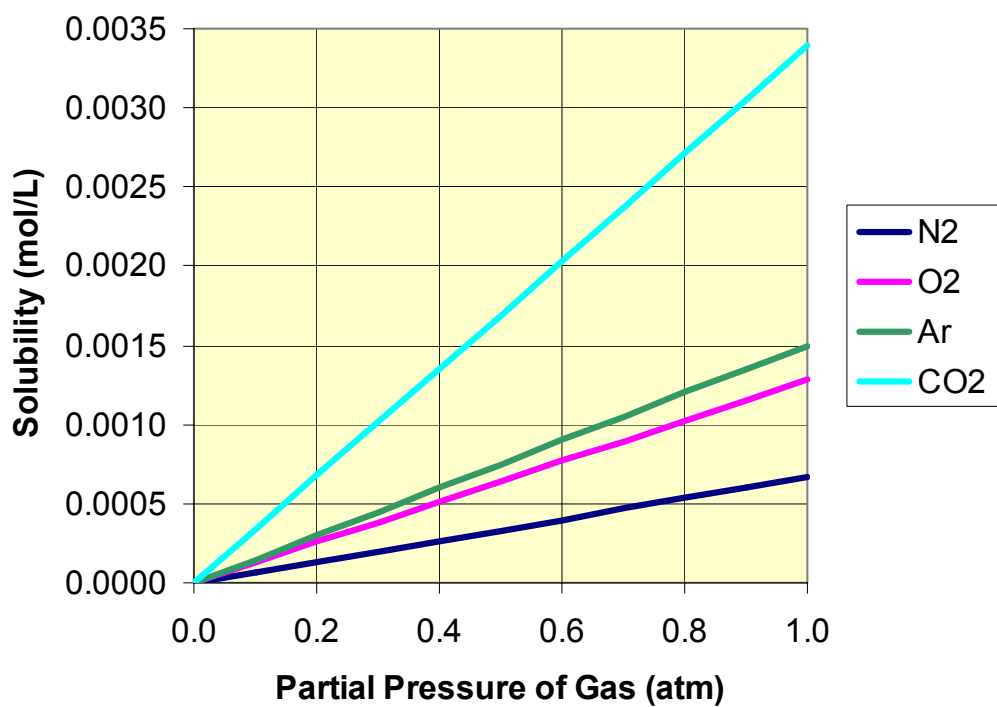
$$C_g = k\, P_g$$

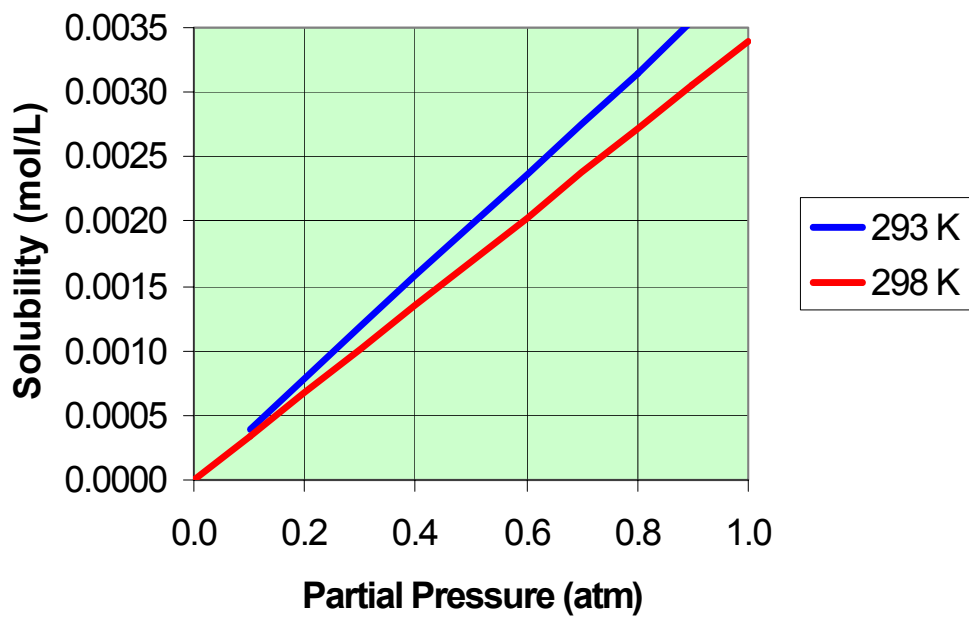where

  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

Partial Pressure of Gas (atm)

Solubility (mol/L)

N2
O2
Ar
CO2

Solubility of Carbon Dioxide at 293 K and 298 K

A Gas in Equilibrium With Its Solution

$P_g = 0.5$ atm

$P_g = 1.0$ atm

Gas

Solution