CHAPTER 14 – SOLUTIONS

1 Spontaneity of the Dissolution Process (*The Dissolution Process*)

- solute + solvent → solution
  - 25 mL H_2O + 15 mL CH_3CH_2OH + 125 mL CH_3COCH_3 → solution
  - solute solute solvent
  - **note that the solvent will always be in much higher concentration than the solute will be in*
- the 7 homogeneous possibilities:

solute	solvent	example
solid	liquid	salt water
liquid	liquid	mixed drinks
gas	liquid	carbonated drinks
liquid	solid	dental amalgams
solid	solid	alloys
gas	solid	metal pipes
gas	gas	air (O, H, and N)

- the 2 heterogeneous possibilities:

solute	solvent	example
solid	gas	dust in the air
liquid	gas	clouds and fog

- two major factors affect the dissolution of solutes:
  - #1 -- enthalpy -- a measure of heat, $\Delta H_{solution}$
    - where $+\Delta H$ is exothermic (dissolution is favored) and $-\Delta H$ is endothermic (dissolution is NOT favored)
  - #2 -- entropy -- a measure of randomness/disorder, ΔS_{mixing}
    - where $+\Delta S$ is an increase in disorder (dissolution is favored) and $-\Delta S$ is a decrease in disorder (dissolution is NOT favored)
      - $NaCl_{(s)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$ $+\Delta S$, increasing entropy (>0, favorable)
      - $Na^+_{(aq)} + Cl^-_{(aq)} \rightarrow NaCl_{(s)}$ $-\Delta S$, decreasing entropy (<0, not fav.)
    - disorder almost always increases when mixing a solution ($+\Delta S$), so ΔS is almost always > 0
  - the ideal situation is:
    - $-\Delta H$ (exothermic), $\Delta H < 0$
    - $+\Delta S$ (more disordered), $\Delta S > 0$
- solutes nearly always become more disordered upon dissolution
- the main factors that determine the heat of solution, $\Delta H_{solution}$, are:
  - solute-solute attractions -- things like ion-ion attraction, dipole-dipole attraction, etc.; overcoming solute-solute attractions requires the absorption of energy
    ($+\Delta H$, endothermic)
    - $Na^+|Cl^- + H_2O$ ... ← breaking the bond between Na^+ and Cl^- in NaCl
  - solvent-solvent attractions -- one example is hydrogen bonding in water; overcoming solvent-solvent attractions requires the absorption of energy
    ($+\Delta H$, endothermic)

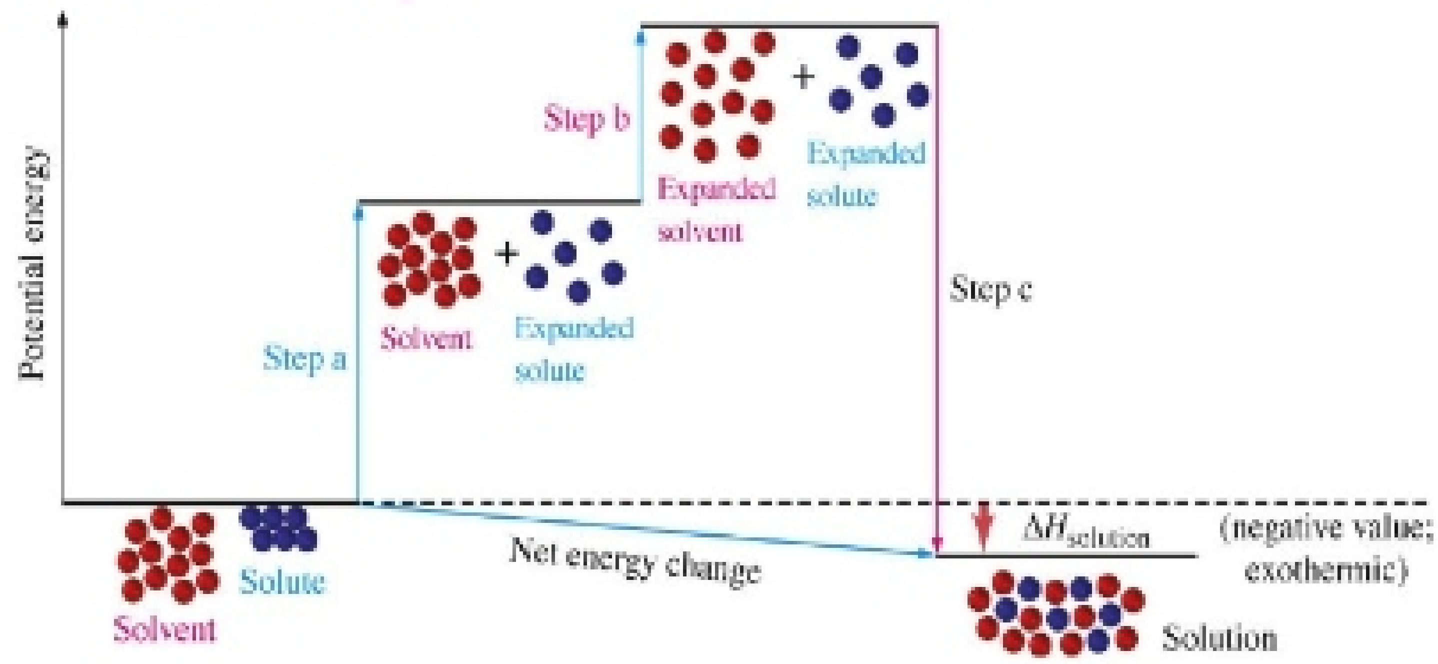
H_2O - - | - - H_2O ← overcoming the attractive forces between the O's and
the H's
NaCl + H_2O → +ΔH

solvent-solute attractions -- known as solvation; this releases energy
(-ΔH, exothermic)

if the solvation energy is *greater than* the sum of the solute-solute and solvent-solvent attractions, then the dissolution is exothermic, -ΔH or $\Delta H_{solution} < 0$

if the solvation energy is *less than* the sum of the solute-solute and solvent-solvent attractions, then the dissolution is endothermic, +ΔH or $\Delta H_{solution} > 0$

so, $\Delta H_{solution}$ is a sum of the three processes described above, and dissolution is favored when the first two factors are small and the third factor is large!



2 Dissolution of Solids in Liquids (*The Dissolution Process*)

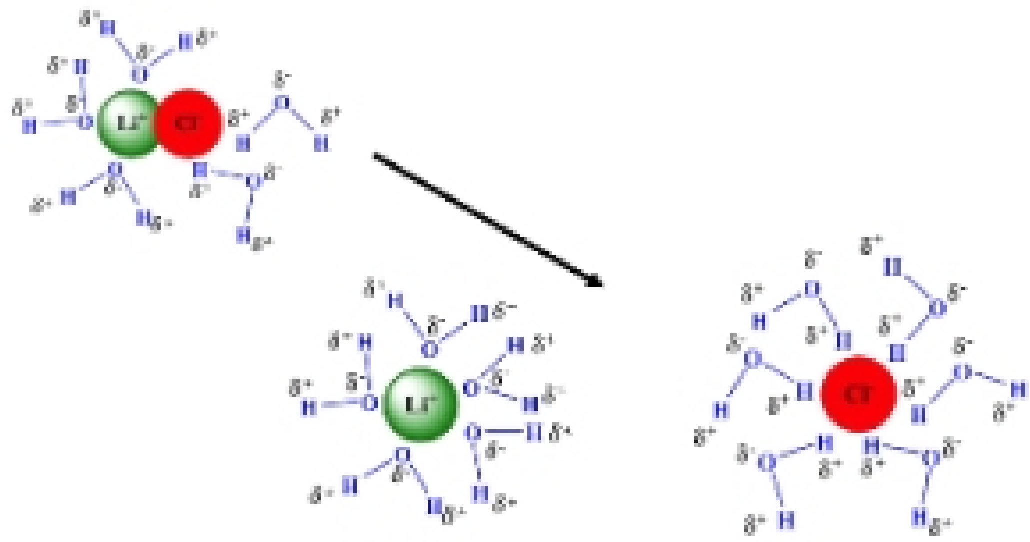
- many solids that are very soluble in water are ionic
- crystal lattice energy -- the energy released (-ΔH, exothermic) when 1.00 mol of formula units of a solid is formed from its constituent ions (molecules or atoms for non-ionic solids) in the gas phase; a measure of the attractive forces in a solid

  $M^+_{(g)} + X^-_{(g)} \rightarrow M^+X^-_{(s)}$ + crystal lattice energy

  crystal lattice energy + $M^+X^-_{(s)} \rightarrow M^+_{(g)} + X^-_{(g)}$

  **note that if the first equation is an endothermic process, then the second equation is an exothermic process; also, if the first equation is an exothermic process, then the second equation is an endothermic process*

  crystal lattice energy increases as charge density increases (↑↑)!
- in the picture below, the Li^+ ion and the Cl^- ion in the bottom right are hydrated ions



- energy of solvation or hydration energy (if the solvent is water) -- the energy released when solute particles are dissolved (when a solvent dissolves a solute) in an exothermic dissolution
- molar energy of hydration -- the amount of energy absorbed when 1.00 mol of formula units, in the form of gaseous ions, becomes hydrated

  $M^{n+}{}_{(g)} + xH_2O \rightarrow [M(OH_2)_x]^{n+}$ + hydration energy for M^{n+}

  $X^{y-}{}_{(g)} + nH_2O \rightarrow [X(H_2O)_n]^{y-}$ + hydration energy for X^{y-}
- hydration energy increases with increasing charge density (↑↑)!

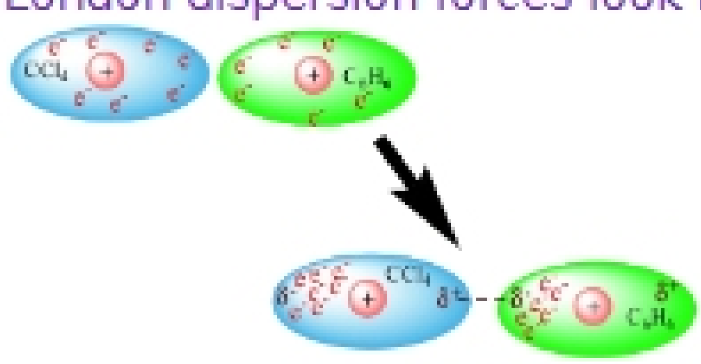
ion	radius (Å)	charge/radius ratio	heat of hydration
K^+	1.33	0.75	-351 kJ/mol
Ca^{2+}	0.99	2.02	-1650 kJ/mol
Cu^{2+}	0.72	2.78	-2160 kJ/mol
Al^{3+}	0.50	6.00	-4750 kJ/mol

notice that the hydration energy increases as the charge density increases

remember the trend for ionic radii:

K^+ ● Ca^{2+} • Al^{3+} · N^{3-} ● O^{2-} • F^- ·

- the "like dissolves like" rule says that polar molecules are soluble in polar solvents and that non-polar molecules are soluble in non-polar solvents
- London dispersion forces look like this:



3 Dissolution of Liquids in Liquids (Miscibility) (*The Dissolution Process*)

- non-polar molecules essentially *slide* in between each other, fitting very close to one another; this close fit enhances London dispersion forces, which increases miscibility

  for example, CCl_4 is very miscible in C_6H_6 (benzene)