Chapter 13

Solutions

I) Introduction

Homogeneous mixture on a molecular level

- prop. same throughout
- separable by physical means
- variable composition

Has at least 2 components:

Solvent: component present in greatest amt.
  - same phase as soln.

Solute: other component(s)

II) Types of Solutions

A) Gaseous Soln.

Miscible Fluid: fluids that mix w. or dissolve in each other in ALL proportions

Ex: Air (solvent is N_2)

B) Liquid Soln.

Solvent: liquid

Solute: gas, liquid, solid

Most common solvent: H_2O

Aqueous soln.

C) Solid Soln.

Most common solvent: metal

Alloys

A nickel (5¢): 25% Ni & 75% Cu

III) Expressing Concentration

A) Qualitatively

Dilute: relatively small amt. of solute in soln.

Concentrated: large amt. of solute

B) Quantitatively

1) Percent Conc.

$$\frac{\text{parts of solute}}{\text{100 parts of soln.}} \times 100\%$$

parts per hundred

a) Mass % (wt./wt. %)

$$\boxed{\text{mass \% of solute} = \frac{m \text{ of solute}}{m_T \text{ of soln.}} \times 100\%}$$

or

$$\boxed{\frac{w}{w}\% = \frac{\text{wt. of solute}}{\text{wt.}_T \text{ of soln.}} \times 100\%}$$

1) Ex 1: What is the w/w% of 6.4g NaCl in 100g H_2O?

2) Ex 2: You want to make 1000g of a 2.0% soln. of $AgNO_3$. What mass of H_2O is req.?

b) Weight/Volume %

$$\boxed{\frac{w}{v}\% = \frac{\text{wt. solute}}{V_T \text{ soln.}} \times 100\%}$$

wt. ⇒ grams

V ⇒ mL

- liq. soln. when solute is solid

c) Vol./Vol. %

$$\boxed{\frac{v}{v}\% = \frac{V \text{ solute}}{V_T \text{ soln.}} \times 100\%}$$

Both volumes must have same units, generally mL

2) Parts per Million

$$\boxed{\text{ppm} = \frac{\text{wt. or vol. solute}}{\text{wt. or vol. of soln.}} \times 10^6}$$

$$1\ \text{ppm} = \frac{1\ \text{g solute}}{10^6\ \text{g soln}} = \frac{1\ \text{mg solute}}{\text{kg soln.}}$$

For dilute aqueous solns,

$$\text{Density} \cong \frac{1\ \text{g soln.}}{\text{mL soln}} = \frac{1\ \text{kg soln}}{\text{L soln}}$$

$$\therefore\ 1\ \text{ppm} \cong \frac{1\ \text{mg}}{\text{L}}$$

3) Parts per Billion

$$1\ \text{ppb} = \frac{1\ \text{g solute}}{10^9\ \text{g soln.}}$$

4) Molarity (M)

$$\boxed{M = \frac{\text{moles solute}}{\text{L soln.}}}$$

5) Molality (m)

$$\boxed{m = \frac{\text{moles solute}}{\text{kg solvent}}}$$

For dilute aqueous solns,

$D \cong 1\ g/mL = 1\ kg/L$

i.e. 1 kg solvent $\cong$ 1 L soln.

$\therefore\ m \cong M$

a) Ex : what is the molality of I_2 in a soln. of 5.00g I_2 in 30.0g of CH_2Cl_2 ?

6) Mole Fraction (χ_A)

$$\boxed{\chi_A = \frac{\text{moles substance } A}{\text{Total moles soln.}}}$$

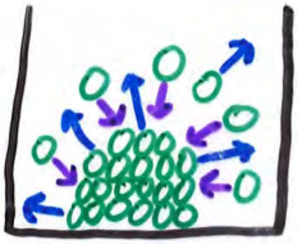
$$\text{Mole } \% = \chi_A \times 100\%$$

$$\sum_i \chi_i = 1$$

a) Ex: What are the mole fractions of I_2 & CH_2Cl_2 in the previous ex.?

IV) Solubility

50 g NaCl in 100g H_2O



14g solid remain

$$\mathrm{NaCl}(s) + H_2O \underset{\text{crystallization}}{\overset{\text{dissolution}}{\rightleftharpoons}} \mathrm{Na}^+(aq) + \mathrm{Cl}^-(aq)$$

A soln. in equilibrium w. undissolved solute is

Saturated

Solubility

conc. (amt.) of solute in a saturated soln.

g solute / 100 g solvent

N

Solubility of NaCl at 20°C,

$$\frac{36.0\,g\ NaCl}{100\,g\ H_2O} \cong \frac{36.0\,g\ NaCl}{100\ mL\ H_2O}$$

What if have 30 g NaCl in 100 g H_2O?

ALL solute dissolves & soln. contains less than equil. amt.

Un saturated

<u>Super saturated soln.</u>

Contains more solute than a saturated soln.

V) The Solution Process

Solute dissolves in solvent & is surrounded by solvent particles

Solvation

Due to IAF between solute & solvent

When

Solute ⇒ Ions

Solvent ⇒ H_2O

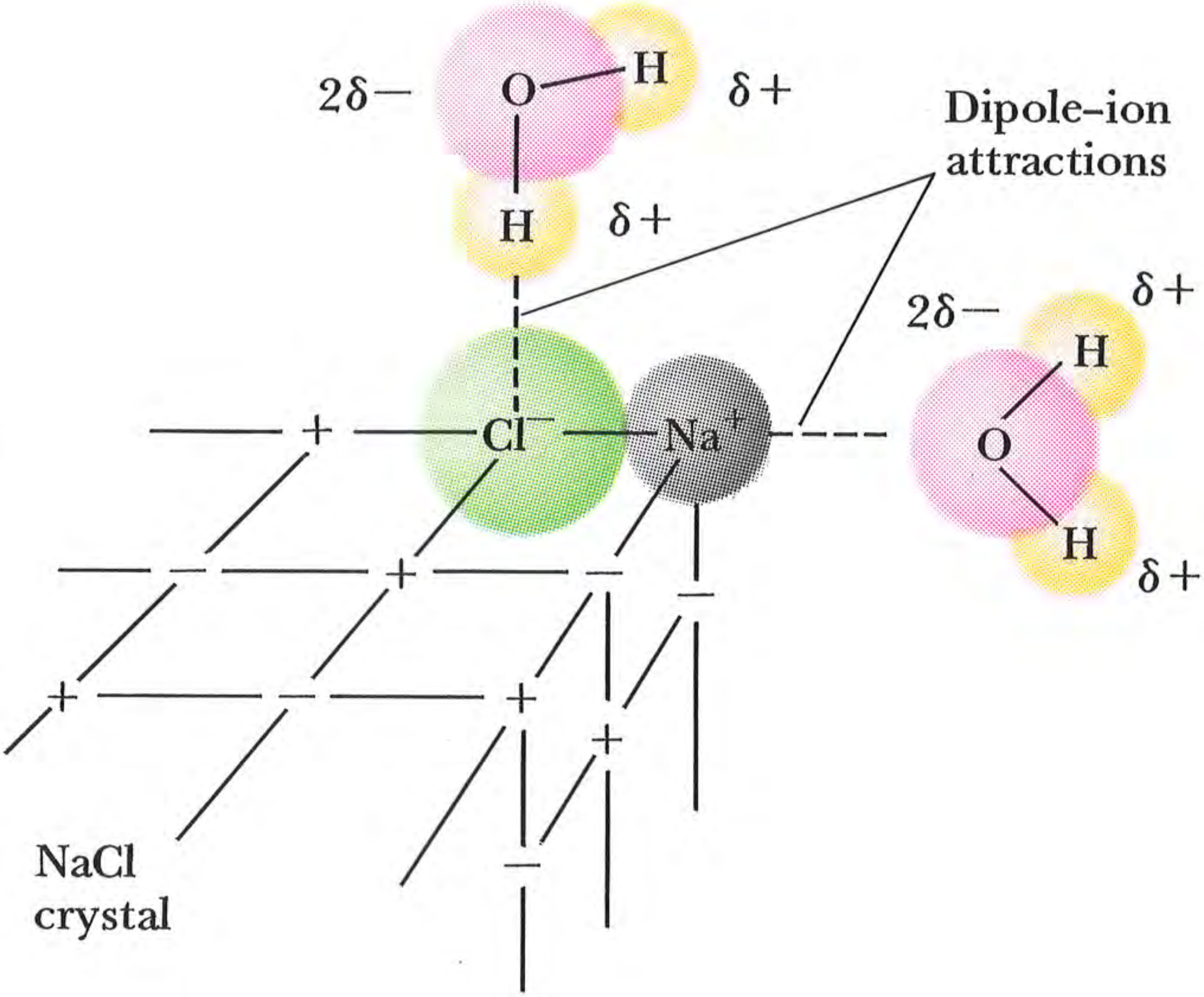
IAF ⇒ Ion-Dipole Forces

Attraction of Ions for H_2O:

Hydration

Transparency 92

Figure 13.1 Interaction between H_2O molecules and the ions of NaCl crystal



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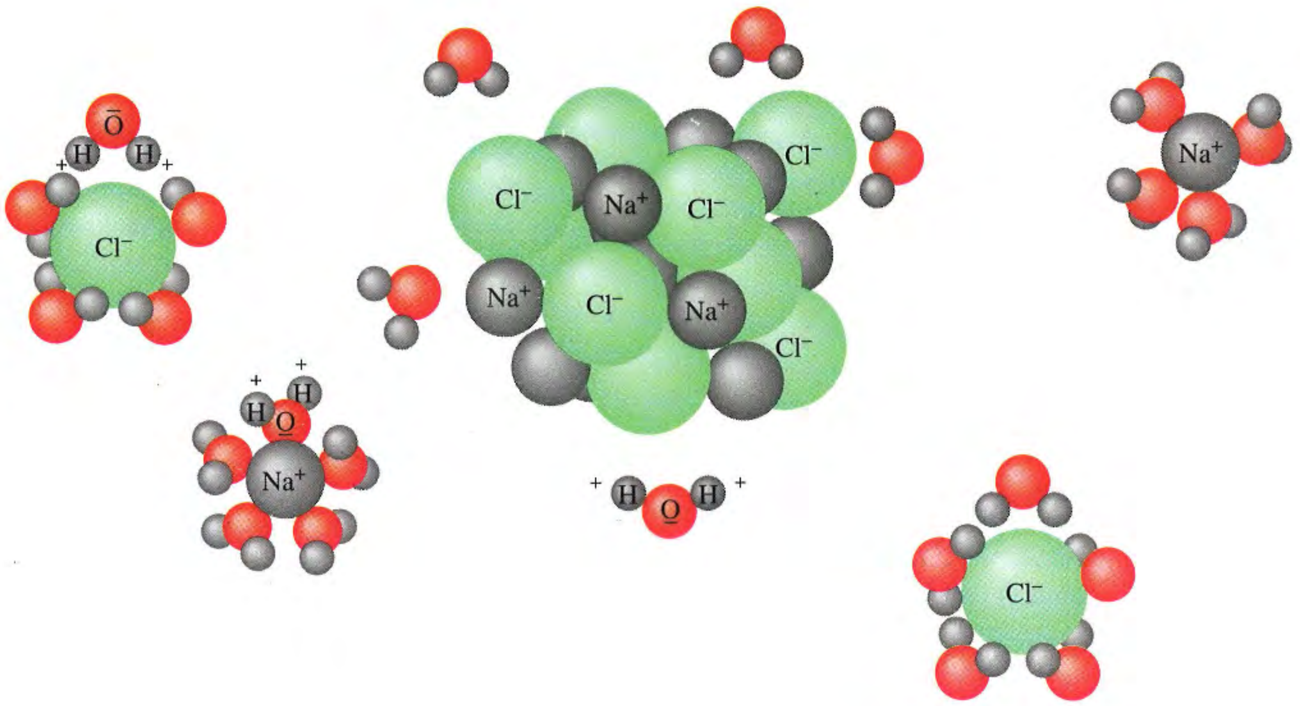

Whitten/Davis/Peck, *General Chemistry and General Chemistry with Qualitative Analysis,* 5/e

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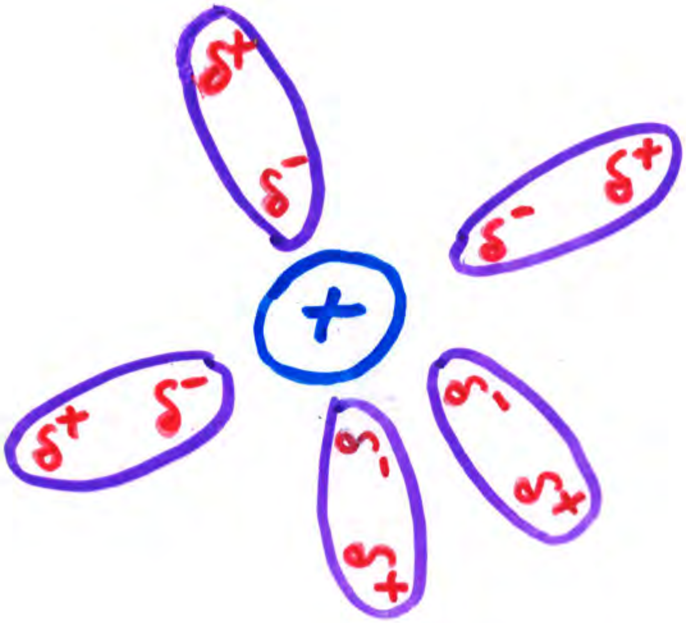
Ion-Dipole Forces

Ions & Polar molecules



Magnitude of interaction:

$$E \propto \frac{Q\mu}{d^2}$$

$Q \equiv$ charge on ion

$\mu \equiv$ dipole moment of dipole

$d \equiv$ distance from center of ion to midpoint of dipole

A) Energy Considerations

1) Solute – Solute Interactions

separate solute particles

- break IAF between like particles

$A \cdots \wr \cdots A$

Endothermic, $\Delta H_1 > 0$

2) Solvent – Solvent Interactions

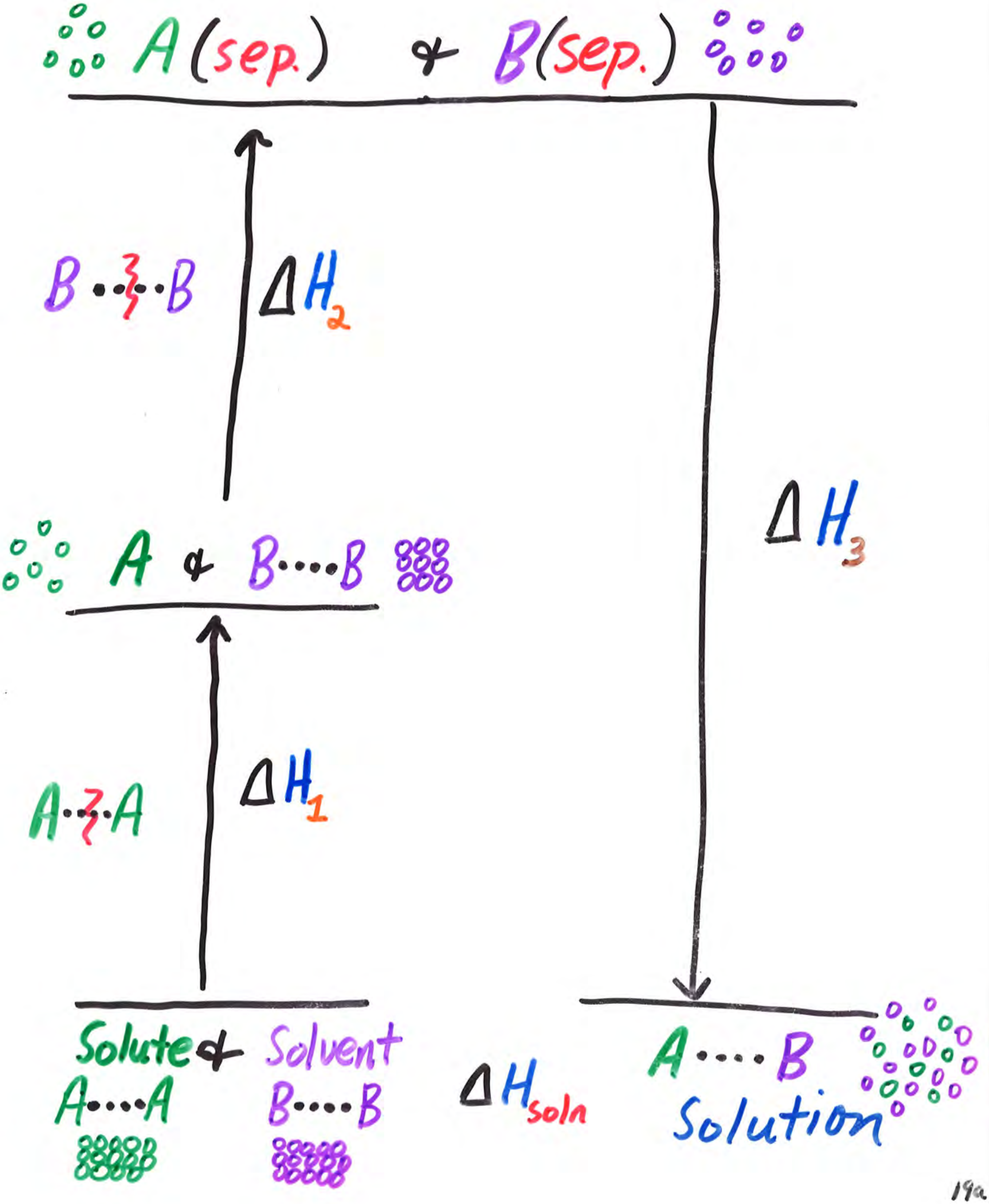
$B \cdots \wr \cdots B$, $\Delta H_2 > 0$

3) Solute – Solvent Interactions

Form IAF between solute & solvent particles

$A \cdots\cdots B$

Exothermic, $\Delta H_3 < 0$


A(sep.) & B(sep.)
B⋯⋯B
ΔH_2
A & B⋯⋯B
ΔH_3
A⋯⋯A
ΔH_1
Solute & Solvent
A⋯⋯A
B⋯⋯B
ΔH_{soln}
A⋯⋯B
Solution

4) Enthalpy of Solution

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

$$\Delta H_1 = \Delta H_{\text{separate solute}}$$

$$\Delta H_2 = \Delta H_{\text{separate solvent}}$$

$$\Delta H_3 = \Delta H_{\text{solvation}}$$

a) Ideal Soln.

$$\Delta H_{soln} = 0$$

similar IAF between all particles

Ex: $SiCl_4$ in CCl_4

b) Endothermic Case

$\Delta H_{soln} > 0$ heat absorbed

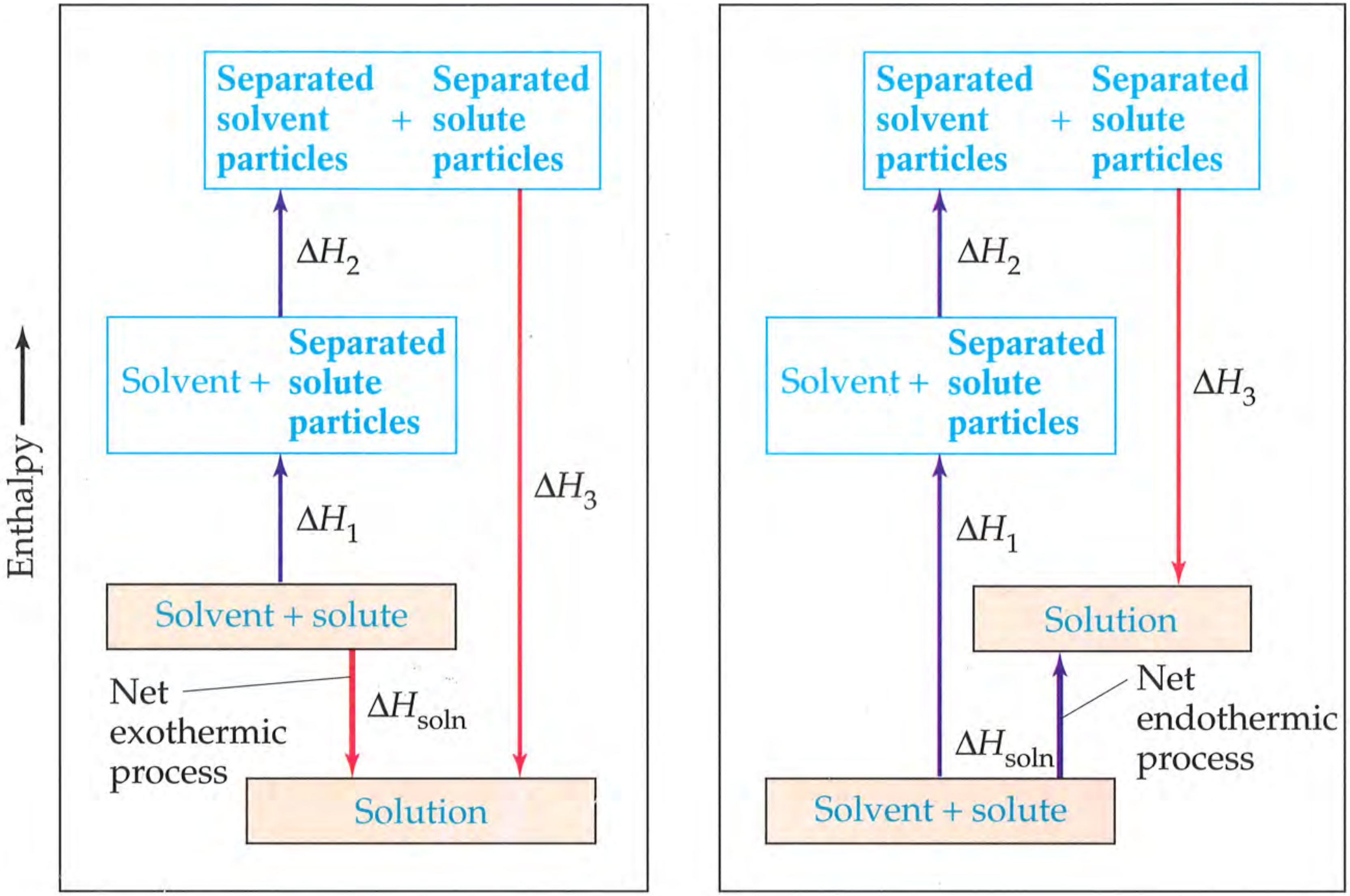
solute-solvent IAF
weaker than solute-solute
& solvent-solvent A.F.

unlike forces < like forces

$|\Delta H_{solvation}| < \Delta H_{sep.\,solute} + \Delta H_{sep.\,solvent}$

Ex: most salts in H_2O

Fig. 13.3 Analysis of Enthalpic Changes



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1) salts in H_2O

$\Delta H_{sep.\ ions} = LE$

$\Delta H_{solvation} = \Delta H_{hydration}$

$\Delta H_{sep.\ H_2O} \approx 0$

$\Delta H_{soln} = \Delta H_{hyd} + L.E.$

$\Delta H_{soln} > 0$ for most salts

Note : As charge density inc.
solubility dec.

$|L.E.| \gg \Delta H_{hyd}$

2) **Ex:** The heat of soln. for a particular substance is 65.0 kJ/mol. The lattice energy is 575.0 kJ/mol. What is the hydration energy?

c) Exothermic Case

$\Delta H_{soln} < 0$ heat evolved

solute - solvent IAF
stronger than solute - solute
& solvent - solvent A.F.

unlike forces > like forces

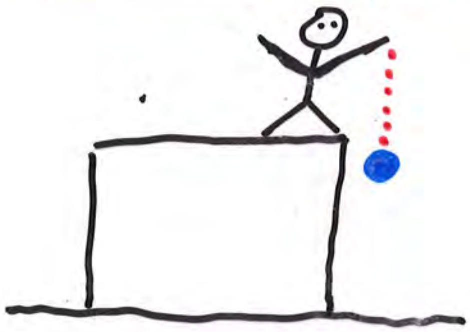
1) Ex: H_2SO_4 in H_2O

$H_2SO_4 + H_2O(l) \rightarrow 2\,H^+(aq) + SO_4^{2-}(aq)$

2) Ex: most gases in H_2O

B) Soln. Formation, Entropy, Spontaneity

1) Enthalpy Change, ΔH_{soln}



potential energy dec.

- loses energy
- spontaneous

$\Delta H < 0$

- results in a lower enthalpy state for system

Processes in which energy content of system dec. tend to occur spontaneously

2) Entropy Change, ΔS_{soln}

measure of disorder (randomness) in a system.

Process tends to occur spont. if change results in inc. in disorder

$$\Delta S > 0$$

Generally, true for soln. formation

3) Free Energy, ΔG

measure of chem. potential

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

$\Delta G < 0$, spont.

$\Delta G > 0$, nonspont.