

11.2 The Energies of Solution Formation

What factors affect solubility? “Like dissolves like”

“Like dissolves like”, referring to the polarity. Polar dissolves polar.

Formation of a liquid solution involves:

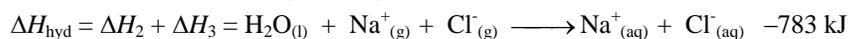
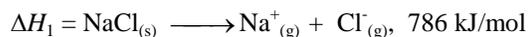
- 1.) ΔH_1 , Breaking up of solute (endothermic)
Would be large for ionic substances or large non-polar molecules
 - 2.) ΔH_2 , Overcoming intermolecular attractions of the solvent (endothermic)
Large for water, overcoming H-bonds
 - 3.) ΔH_3 , Allowing the solute and solvent to interact to form solution (usually exothermic)
- $\Sigma = \Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$ = Enthalpy of solution

*For Ionic substances:

Enthalpy of hydration combines ΔH_2 (expanding polar water solvent and H-bonds) and ΔH_3 (solute/solvent interactions). Enthalpy of hydration represents the enthalpy change associated with the dispersal of a gaseous solute in water. Therefore the heat of *solution* for dissolving an ionic substance:

$$\Delta H_{\text{solution}} = \Delta H_{\text{Lattice Energy}} + \Delta H_{\text{hydration}}$$

Ex. NaCl:



$$\Delta H_{\text{solution}} = 786 - 783 = 3 \text{ kJ/mol, favored by an increase in disorder.}$$

Process with a large amounts of energy tend not to occur. See table below:

	ΔH_1	ΔH_2	ΔH_3	ΔH_{soln}	Outcome
Polar Solvent, Polar Solute	Large	Large	Large, negative	Small	Solution forms
Polar Solvent, Non-polar Solute	Small	Large	Small	Large, positive	No solution forms
Nonpolar Solvent, nonpolar solute	Small	Small	Small	Small	Solution forms
Nonpolar solvent, Polar Solute	Large	Small	Small	Large, positive	No solution forms

11.3 Factors affecting Solubility

a.) Structure Effects

Hydrophobic: “water fearing” portion of molecule. Ex. $(\text{CH}_2)_n$, alkane hydrocarbon chains.

Hydrophilic: “water loving” -OH groups

b.) Pressure Effects (read; Hydrogen Beer)

Henry’s Law: The amount of gas dissolved in a solution is directly proportional to the pressure above the gas above the solution.

$$C = kP$$

P= partial pressure of the solute gas above the solution.

C= concentration of the dissolved gas

k= constant for a particular solution ([see constants](#))

Obeded best with dilute gases that do not dissociate or react with solvent.

Ex. O_2 gas is good but HCl ($\text{HCl} \longrightarrow \text{H}^+ + \text{Cl}^-$) is poor

Practice: 11.4, At 25°C partial pressure of CO₂ over liquid is 5.0 atm. Partial pressure of CO₂ in the atmosphere is 4.0x10⁻⁴ atm. What is the concentration of CO₂ in a closed and open bottle? At 25°C the Henry's Law constant for CO₂, k is 3.1x10⁻² mol/L atm. Find the concentration of CO₂ in the bottle when opened and closed.

Ans: **Closed:** 5.0atm / 32 L atm/mol = 0.16 M CO₂
Open: 4.0x10⁻⁴ atm/32 L atm/mol = 1.3x10⁻⁵ M CO₂

The solubility of solids and liquids is not affected by pressure.

c.) Temperature Effects (for Aqueous Solutions)

The dissolving of a solid occurs more rapidly at higher temperatures, but the amount of solid that can be dissolved increases or decreases with temperature. (*Interesting exception with ionic salts; sodium sulfate and cerium(III) sulfate decrease with an increase in temperature*)

For gases in an aqueous solution, higher temperatures decrease solubility.

Colligative Properties:

11.4 The Vapor Pressures of Solutions

A non-volatile solute will lower the vapor pressure of a solution.

Raoult's Law: $P_{\text{soln}} = \chi_{\text{solvent}} P^0_{\text{solvent}}$

fits the linear form of $y=mx + b$,

$y = P_{\text{soln}}$

$x = \chi_{\text{solvent}}$, mole fraction of solvent

$m = P^0_{\text{solvent}}$, vapor pressure of a pure solvent

$b = 0$, origin

Also gives a convenient way to "count" molecules and determine the molecular mass.

Ex. Predict the vapor pressure of a solution made by dissolving 35.0 grams of *Na₂SO₄ in 175 g of H₂O.

*Ionic solutes that dissociate 100%. Ex., Na₂SO₄ → 2Na⁺ SO₄²⁻

Molarity of Na₂SO₄ is $\frac{35\text{g}}{142\text{g/mol}} = 0.246 \times 3 = 0.738\text{ mol}$, $\chi_{\text{H}_2\text{O}} = \frac{9.72\text{mol}}{(9.72\text{mol} + 0.738\text{mol})} = 0.929$

$P_{\text{soln}} = 23.76\text{ torr} (0.929) = 22.1\text{ torr}$

For a mixture of volatile substances: $P_{\text{total}} = P_A + P_B = \chi_A P^0_A + \chi_B P^0_B$

If a mixture obeys Raoult's Law then it is an *Ideal Solution*

Deviations from Ideal Behavior:

- Solute and solvent are very much alike, simply dilute each other: Ideal solution
- Interactions of A-B are strong, ΔH_{soln} is large and negative, ΔT solution formation is positive, fewer molecules escape as vapor: Negative Deviation
- If two liquids mix endothermically, ΔH_{soln} is positive and ΔT for solution formation is negative, because of weak interactions of A-B, molecules have a higher tendency to escape, Positive Deviation

Ex.

5.81g of acetone (C₃H₆O, molar mass = 58.1 g/mol, VP @35°C 345 torr) and 11.9 g of chloroform (CHCl₃, molar mass = 119.4 g/mol, VP @35°C 293 torr) At 35°C the solution has a vapor pressure of 260. torr. Is this an ideal solution? What is the composition of the vapor?

$\chi_{\text{C}_3\text{H}_6\text{O}} = 0.5$, $\text{VP}_{\text{acetone}} = 0.5 \times 345\text{ torr} = 172.5\text{ torr}$

$\chi_{\text{CHCl}_3} = 0.5$, $\text{VP}_{\text{chloroform}} = 0.5 \times 293\text{ torr} = 146.5\text{ torr}$

Expected $\text{VP}_{\text{soln}} = 319\text{ torr}$, 260 torr is observed, this exhibits a non-ideal negative deviation

Practice Problems (Set 2): P.519 #14, 16, 17, 20, 34, 37, 38, 39, 40, 41, 43, 46, 47, 48, 49, 52, 53, 54, 77, 102