

Sections 8.8 – 8.13 Solubility of Gases, Liquids, and Solids in Liquids

Up to this point we have dealt primarily with pure compounds. The next two sets of lectures deal with what happens when mixtures are created. The lectures are in two parts:

- The thermodynamics of what happens when you mix a liquid with a solid, a liquid with a liquid and a liquid with a gas
- The interesting properties that are a consequence of mixing—specifically, colligative properties which are properties that depend only on the relative concentrations of the components. These colligative properties include freezing point depression and boiling point elevation, vapor pressure lowering and osmotic pressure.

A bit of nomenclature associated with mixing:

A **solution** is the consequence of mixing two or more compounds

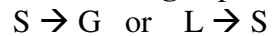
A **solute** is the smaller quantity in the solution

A **solvent** is the larger quantity in the solution

For example, sea water is a **solution** consisting of the **solute**, NaCl, mixed with the **solvent**, water.

Note difference between sections 8.1 – 8.7

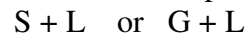
where we **changed** phases



and look at $\Delta G = \Delta H - T\Delta S$

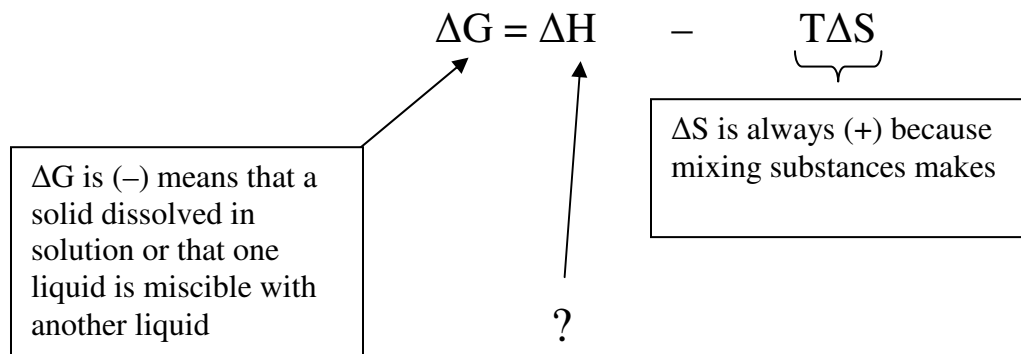
and sections 8.8– 8.13

where we **mix** phases



and look at $\Delta G = \Delta H - T\Delta S$

There are some consistent ideas associated with the process of mixing:



The complicating issue is the heat of mixing-- ΔH can be either endo or exothermic and is quite varied

ΔH_{soln} is (+) for NaCl in H_2O
 ΔH_{soln} is (-) for Na_2SO_4 in H_2O
 ΔH_{soln} is (-) for O_2 in H_2O

Consider the case that ΔH_{mix} is negative: since ΔS_{mix} is positive then ΔG_{soln} will have to be negative and the reaction happens.

Now consider the case that ΔH_{mix} is positive: in this case the spontaneity of the reaction is temperature dependence and follows the arguments outlined in Chapter 7 for temperature dependent reaction spontaneity. For example, if a process is endothermic it can be made spontaneous by increasing T.

Now let's look at the three cases of dissolving solids, liquids and gases in a liquid:

Case 1: Dissolving salts in water:

What happens when a salt in H_2O . Is it soluble?

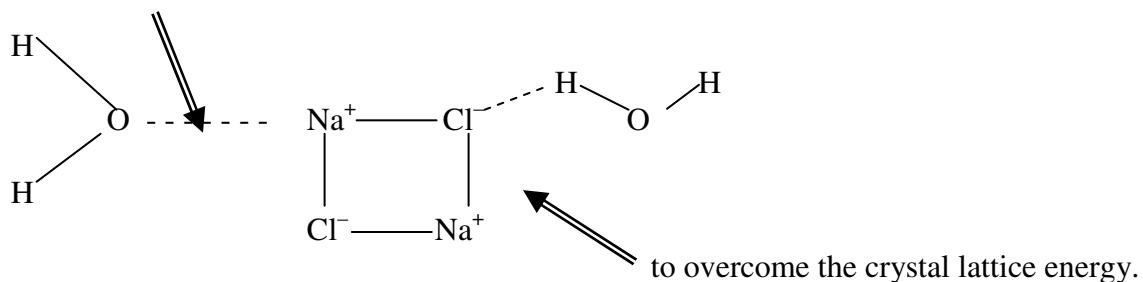
The answer is that it depends on the magnitude of $\Delta H_{\text{solution}}$ which in turn depends on the following:

$$\Delta H_{\text{solution}} = \Delta H_{\text{solvation or hydration}} - \Delta H_{\text{C.L.energy}}$$

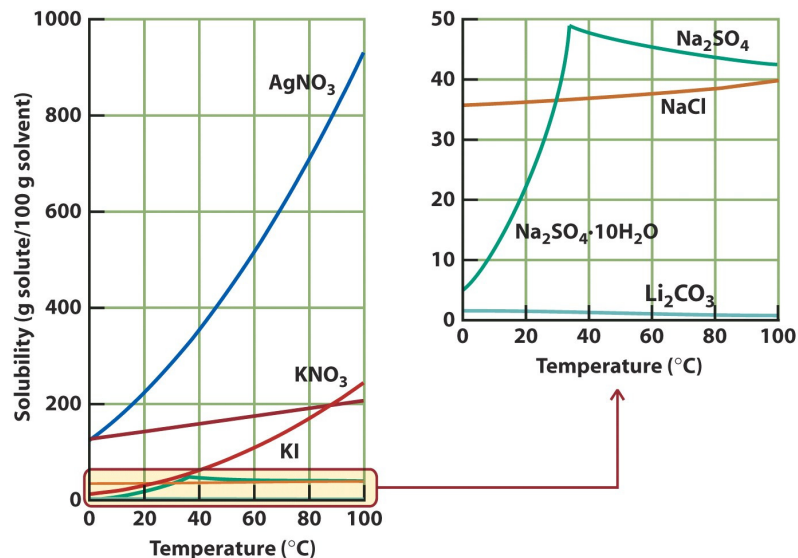
Value that goes in $\Delta G = \Delta H - T\Delta S$ Energy of forming a salt crystal

Energy of solvating an ion

These compete and we want solvation effects



Of course, even if the $\Delta H_{\text{solution}}$ ends up slightly endothermic (like NaCl) the positive ΔS_{mix} can make up for it and salt dissolve in water (at high T.)



Some examples of temperature dependence and solubility are shown. Note that most of the salts exhibit an increasing solubility with temperature, including NaCl which was described above. Two exceptions, sodium sulfate and lithium carbonate have a solubility that decreases with temperature. This occurs for compounds that have an exothermic heat of mixing and will be explained in the Chapter 9 with LeChatelier's principle.

Charge Density and $\Delta H_{\text{Hydration}}$: Let's look at things quantitatively and see the relationship between charge density and $\Delta H_{\text{Hydration}}$

Remember from last semester that we predicted:

Na – Cl with singly charged ions dissolves easier than Ca – O with doubly charged ions

Question: What is rank of $\Delta H_{\text{Hydration}}$ for K^+ , Na^+ , Ca^{++} , Al^{+3}

Ion	Charge	Å Size	Charge Density	$\Delta H_{\text{Hydration}}$
K^+	+ 1	1.5	0.6	350 kJ
Na^+	+ 1	1.2	0.9	440 kJ
Ca^{++}	+ 2	1.1	1.8	1900 kJ
Al^{+++}	+ 3	0.7	4.4	4800 kJ

← The smaller charge density means weaker IMF means *easier* to melt and dissolve

← The larger charge density means larger IMF means *harder* to melt and dissolve

Which is why K_2O dissolves easily in H_2O and Al_2O_3 (glass) does not.

Another table shows more explicitly the inverse relationship between size and hydration energy for ions of like charge.

TABLE 8.7 Enthalpies of Hydration, ΔH_{hyd} , at 25°C, of Some Halides, in Kilojoules per Mole*

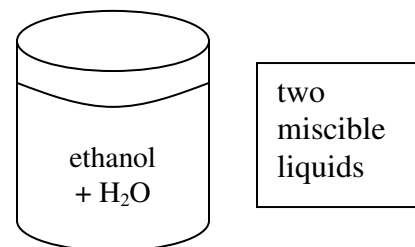
Cation	Anion			
	F ⁻	Cl ⁻	Br ⁻	I ⁻
H ⁺	-1613	-1470	-1439	-1426
Li ⁺	-1041	-898	-867	-854
Na ⁺	-927	-784	-753	-740
K ⁺	-844	-701	-670	-657
Ag ⁺	-993	-850	-819	-806
Ca ²⁺	—	-2337	—	—

*The entry where the row labeled Na⁺ intersects the column labeled Cl⁻, for instance, is the enthalpy change, -784 kJ·mol⁻¹, for the process Na⁺(g) + Cl⁻(g) → Na⁺(aq) + Cl⁻(aq); the values here apply only when the resulting solution is very dilute.

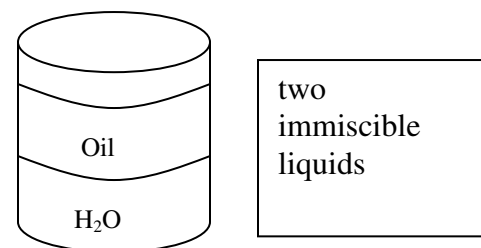
Case 2: Dissolving liquids in liquids

First an additional piece of terminology: to

Miscible means two liquids that are mixed together form a single phase: $\Delta G(-)$



Immiscible means two liquids do not mix together and so two phases exist: $\Delta G(+)$



So how do you know if two compounds will be miscible?

The rule you always hear about miscibility is “like dissolves like” which is an easy way of saying that if the intermolecular forces (IMF) are alike, then compounds are miscible and if the IMFs are not alike, they are not miscible (immiscible). The explanation is that if you are replacing one form of intermolecular interaction with another, the more alike the intermolecular forces for the compound that is being added to solution, the less energy that is required for the solution to form.

Examples:

$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow$ Both are H-bond \rightarrow Miscible

$\text{H}_2\text{O} + \text{C}_2\text{H}_6 \rightarrow$ 1 H-bond, 1 dispersive \rightarrow Immiscible

$\text{C}_2\text{H}_6 + \text{C}_3\text{H}_8 \rightarrow$ Both are dispersive \rightarrow Miscible

Sample Question: Which of the following is most miscible with H_2O ?

CH_3OH or $\text{CH}_3\text{CH}_2\text{OH}$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

Answer: CH_3OH is most alike. All have H-bonding but the dispersive part (CH_3CH_2 ---) gets bigger and bigger

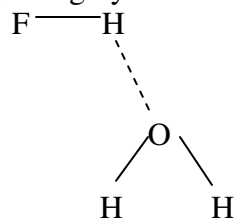
Note, by the way, how many important biomolecules (from nucleotides to fatty acids to amino acids) have both a hydrophilic component (with OH-like bonding) and a hydrophobic component (with hydrocarbon-like bonding.) Micelles and surfactants (soaps) also have these dual features that work in tandem to solubilize dirty (greasy) materials.

Dirt \rightarrow $:\text{CH}_3-(\text{CH}_2 \text{ CH}_2 \text{ CH}_2 \text{ CH}_2 \text{ CH}_2 \text{ CH}_2 \text{ CH}_2 - \text{COONa}:$ \leftarrow **water**
(fatty end) (water soluble end)

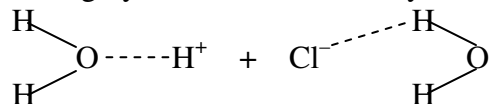
Case 3: Gases Mixing with Liquids

Consider specifically gases in H_2O . We know gases dissolve because we hear the fizz from CO_2 and we know that fish can breathe O_2 . But H_2O is polar, with hydrogen bonding and according to “like dissolves like” it should prefer certain gases over others. Here are some examples:

- CO_2 is very soluble in H_2O . Why? Because it reacts to make H_2CO_3 . So it is the chemical reactivity that drives the solubility. This is a pretty special case.
- HF is very soluble in H_2O . Why? Highly soluble because of hydrogen bonding

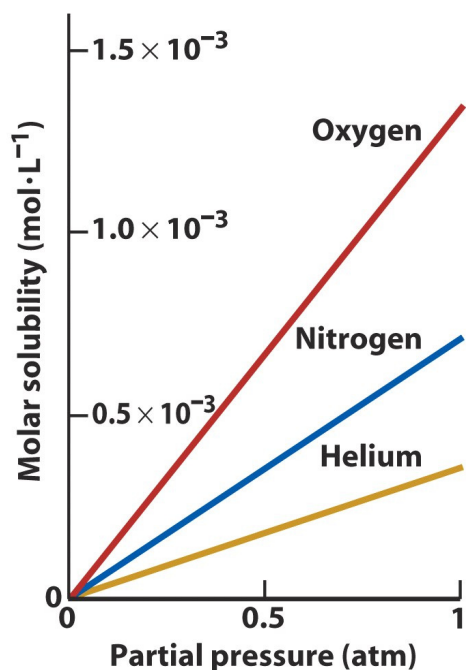


HCl and HI are highly soluble in H_2O . Why? Because HCl and HI dissociate completely to make



- But what about *non-polar* gases? Why does a non-polar molecule like O_2 dissolve in water?

Example: O_2 at 25°C dissolves .0041g/l in H_2O which is enough for fish to breathe.



The plot demonstrates something called Henry's Law. The rather obvious idea that as the pressure of a gas above a liquid increases, the solubility of the gas in the solvent increases proportionally. It also indicates that the concept of "like dissolves like" doesn't apply so readily to dissolving non-polar gases in polar solvents like water. The reason? Small gas molecules benefit from the ΔS_{mix} and occupy space in the spaces of the hydrogen bonding water complex without significantly upsetting the hydrogen bonding.

Temperature and Solubility—A Prelude to LeChatelier's Principle

We will learn in the chapter on chemical equilibria, LeChatelier's Principle tells us that the extent of a chemical reaction can be controlled by the temperature. We will learn that:

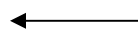
- If a reaction is endothermic, applying heat to the system shifts the reaction to the right and cooling the system shifts the reaction to the left
- If a reaction is exothermic, applying heat to the system shifts the reaction to the left and cooling the system shifts the reaction to the right

We will wait for an explanation in Chapter 9 and for now simply use these rules to make the following observations:

- To dissolve NaCl you heat it up. This is because $\Delta H_{\text{solution}}$ for NaCl is endothermic

- But if you heat up O_2 in H_2O , the oxygen leaves the water. This is because $\Delta H_{\text{solution}}$ for O_2 is exothermic. Some data for a couple of temperature is shown below:

	25°C	50°C
O_2 in H_2O	.0041 g/L	.0026 g/L



Note that at higher temperatures, O_2 concentration goes down

So why is this of practical significance? It explains why you don't want the temperature of water in your fish tank (or the oceans) to increase. It drives O_2 out of the water and kills the fish.