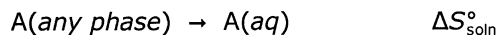


Having completed the enthalpy part, we now undertake the entropy part of the picture for solutions.

40.1 The entropy part

For any solution (dissolving) process, there will be some change in entropy which we designate as $\Delta S_{\text{soln}}^{\circ}$.



Sometimes, the system will increase entropy as a result of dissolving and then $\Delta S_{\text{soln}}^{\circ}$ is positive. On the other hand, sometimes the system will decrease entropy as a result and then $\Delta S_{\text{soln}}^{\circ}$ is negative. It depends on both the solute and the solvent. Remember that more entropy is good. Here's what you need to know.

INCREASING ENTROPY (POSITIVE $\Delta S_{\text{soln}}^{\circ}$) FAVORS DISSOLVING. DECREASING ENTROPY (NEGATIVE $\Delta S_{\text{soln}}^{\circ}$) OPPOSES DISSOLVING.

We will continue our emphasis on water as solvent, although water is complicated relative to most other solvents. The problem is that aqueous solutions are very prone to entropy effects. We'll first discuss some of these entropy effects using solutes which are liquids in their native phase, but it will also apply to solutes which are a gas or a solid. The dissolving of a liquid into water is very often opposed by entropy. Examples of this are very common, including the simple experience that oil and water do not mix.

The primary entropy problem for a solute dissolving into water relates directly to water's strong hydrogen bonding. Strong hydrogen bonding is great for enthalpy but it has a very negative effect on entropy due to the very restrictive orientation effects. This was first noted in Section 37.5 and we will now see what a big impact this can have. For any solute in water, H_2O molecules will surround the solute molecules and try to interact with those solute molecules by means of hydrogen bonds. We can envision two opposite outcomes, although there are actually ranges of these outcomes and a particular solute can fall somewhere in the middle.

For a solute which can readily engage in hydrogen bonding with water, then there is little impact on water's options for location and orientation while engaged in hydrogen bonding. This is favorable for entropy.

For a solute which cannot hydrogen bond with water, then this imposes additional restrictions on location and orientation for the water molecules which surround the solute. This decreases the entropy of the system considerably.

Interestingly, for this latter outcome, although H_2O molecules cannot hydrogen bond to the solute, they can still hydrogen bond to neighboring molecules of water, but this is the tricky part. This requires the water molecules to adopt fairly limited positions around the solute, forming a cage-like structure around the solute. These structures are not rigid; they are very dynamic, and water molecules can trade off rapidly with other water molecules in the immediate vicinity. Regardless, although this cage-like arrangement still allows the water molecules to maintain a reasonable level of hydrogen bonding, this comes at a considerable cost to entropy due to the greater restrictions on location and orientation.

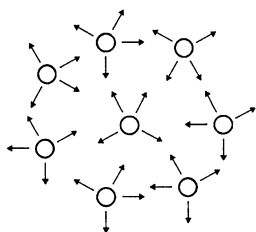
In addition to the loss of entropy for the water, other contributions to the decrease in entropy in the system can involve the solute molecule. For example, the solute molecule itself may become restricted in its own motions due to the arrangement of the surrounding water molecules. Additionally, the solute molecules may be forced to huddle together; such togetherness limits the total mixing process and restricts the options which are otherwise possible.

Let's take a look at some examples.

On a practical basis, solute molecules with N-H, O-H or F-H bonds are among the best types of solutes which can readily hydrogen bond with water, because they, too, can act as both donor (via their H) and acceptor (via their lone pairs) with water; this contributes positively to entropy and that works towards dissolving those kinds of compounds. On the other hand, on a practical basis, the most common (by far) types of compounds which cause the most entropy problems in water are hydrocarbons or, actually, any compound with CC and/or CH portions in their molecules. These kinds of compounds are everywhere in you and in your world. On the smallest of scales, they are a very significant part of the

very cells in your body; on the biggest of scales, they are a large part of the humongous energy industry of modern society. CC and CH portions are very common in massive numbers of common compounds in your world. In water, these portions cannot engage in hydrogen bonding so they have a very negative impact on entropy and that works against dissolving.

Let's put some of this to picture.



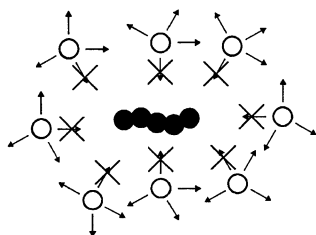
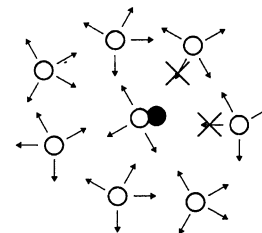
We'll start with just water by itself. One molecule of water can form up to four hydrogen bonds (two donated, two accepted) with other water molecules. This is shown at left in a very simplistic fashion with each water molecule as a circle. The arrows convey the sense of the four possible hydrogen bonds (donor or acceptor) for each water molecule. The hydrogen bonds are really three dimensional, in tetrahedral directions. At typical temperatures for liquid water, most, but not all, hydrogen bonds are engaged between neighbors at any specific moment in time. Keep in mind that the molecules of a liquid phase are in motion, and that the molecules are

bumping and pushing and turning around in different directions. For the central water molecule in the illustration, there will be a reasonably close opportunity for hydrogen bonding to a neighbor in numerous directions. This illustration is the general picture for water molecules surrounded by other water molecules. When water molecules surround molecules of another compound, then different circumstances can arise and these circumstances can have critical consequences.

(By the way, the picture above and several below show quite a bit of space between the molecules. In reality, in any liquid, the molecules are in loose contact. I spread things out in the pictures to show the arrows.)

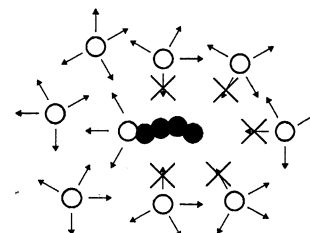
Let's now bring in different solutes to illustrate the impact of different kinds of molecules on the entropy of solution. In the last Chapter, we examined the solution enthalpies for methanol (CH_3OH), pentane (C_5H_{12}) and 1-butanol ($\text{C}_4\text{H}_9\text{OH}$). Let's now examine their solution entropies. (Go back to Chapter 39 to see their Lewis structures if you need to.)

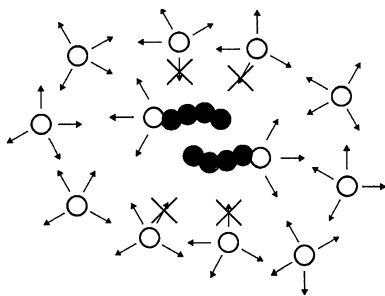
Methanol has hydrogen bonding, and this provides a very strong interaction with water molecules. At right, a CH_3OH molecule is shown surrounded by H_2O molecules. The OH part of the methanol molecule which can hydrogen bond is shown as an open circle; that OH portion can donate one hydrogen bond and can accept two hydrogen bonds. The CH_3 part which cannot hydrogen bond is shown as a dark portion. Although the CH_3 part cannot hydrogen bond, that portion is only about half the size of the molecule as a whole. There yet remains numerous options available for hydrogen bonding between the methanol molecule and the water molecules. Entropy is not a problem here. In fact, $\Delta S_{\text{soln}}^\circ$ for methanol is still slightly positive, thus favoring solubility in water.



Now let's put pentane into water. C_5H_{12} has no hydrogen bonding capability. In the illustration at left, pentane is represented by the dark chain in the center. For the water molecules which surround a pentane molecule, there are now restrictions on the directions available for hydrogen bonding. As a result, the water molecules must turn to each other in order to maintain hydrogen bonding, but that requires the water molecules to adopt the "cage-like" arrangements around the solute molecule. Ultimately, those arrangements are more restrictive; that decreases options and that decreases entropy, and that's bad news. $\Delta S_{\text{soln}}^\circ$ is negative, and this opposes solubility.

Now we turn to 1-butanol, $\text{C}_4\text{H}_9\text{OH}$, in water. As noted in the last Chapter, this molecule is much like pentane but now it has hydrogen bonding like methanol. When $\text{C}_4\text{H}_9\text{OH}$ is placed into water, we get a combination of effects with respect to entropy. As shown at right, the water molecules near the OH part will still have options for hydrogen bonding with the solute, but the water molecules along the C_4H_9 part will not. The C_4H_9 part is the majority of the size of the molecule and therefore this part will dominate the outcome. Thus, dissolving is opposed by entropy. This case is intermediate to the two cases above: $\Delta S_{\text{soln}}^\circ$ is negative but not as bad as for pentane.





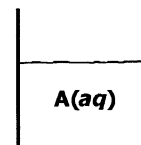
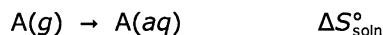
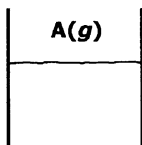
Let me show an illustration of huddling which was mentioned upstairs. At left, two molecules of 1-butanol are shown. Due to entropy, water shuns the C_4H_9 hydrocarbon parts, so those parts tend to huddle close together. Of course, things are constantly in motion so that just illustrates an average effect. Regardless, this picture is the simplest case of huddling. With more and more molecules, this huddling act can get more complicated and quite extreme: if there are too many molecules and not enough solubility, then a separate liquid layer forms. Even methanol molecules will do this huddling business to a slight extent in dilute aqueous solution, using just their CH_3 part.

These examples illustrate some of the basic considerations involved in water's interactions with other substances. As stated several times already, water's hydrogen bonding is very strong but that strength is very restrictive on orientation. If a solute cannot accommodate water's hydrogen bonding, then water throws an entropic hissy fit, shunning that molecule outright or shunning a portion of that molecule. These entropy effects have a massive impact on your world. We'll see more of this as we go.

Now, as was done for enthalpy in Chapter 39, we go ahead break this down into three Scenarios depending on the native phase of the solute.

- SCENARIO 1: GAS 'A' DISSOLVING INTO WATER

For the first Scenario, we consider gas A dissolving into water.

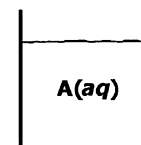
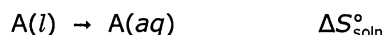
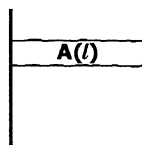


Right off the bat, this process is always opposed by entropy and the effect is quite large, regardless of the identity of the substance. The reason is straightforward: with the most options and fewest restrictions, the gas phase is by far the best for entropy. Dissolving any gas into water (or any solvent) eliminates many of those options, imposes new restrictions and decreases entropy substantially. All gases are the same for this effect: $\Delta S_{\text{soln}}^{\circ}$ is negative. Even solutes which can fully engage in hydrogen bonding with water will still have a negative $\Delta S_{\text{soln}}^{\circ}$.

This case is the easiest of our three Scenarios.

- SCENARIO 2: LIQUID 'A' DISSOLVING INTO WATER

Consider a liquid A dissolving into water.



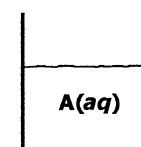
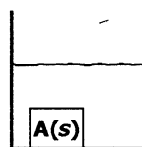
This is where the effects of hydrogen bonding by the solute can be very important, as illustrated by the liquids in the above discussion. Again, for solute molecules which can fully engage water in hydrogen bonding, $\Delta S_{\text{soln}}^{\circ}$ is likely to be positive or at least not very negative. For solute molecules which only have little capability or no capability for hydrogen bonding, then $\Delta S_{\text{soln}}^{\circ}$ is negative, and this can be considerably so.

For comparison purposes, let me throw in a general comment for typical solvents other than water. For some liquid dissolving into a nonaqueous solvent, there is usually an increase in options for the system as a whole. The solute and the solvent each have more volume so there are more options for location. There can also be more options for interactions, since solute can now interact with solvent and vice versa. Overall, more options means more entropy. Thus, there is usually an increase in entropy for the mixing of two liquids not involving water; $\Delta S_{\text{soln}}^{\circ}$ is positive and this favors the dissolving process.

Again, water is weird.

- SCENARIO 3: SOLID 'A' DISSOLVING INTO WATER

Consider a solid A dissolving into water.



It is immediately important to remember that solids have the least entropy to begin with of our three common phases. Thus, solids

have an extra advantage for dissolving because they stand to gain the most entropy by dissolving.

For this Scenario, we break the discussion into two parts as done for enthalpy in the last Chapter: one deals with molecular (nonelectrolyte) solids and the other deals with ionic solids.

For molecular solids, that extra advantage can be enough to overcome the entropy problems which are encountered with liquid solutes above. Thus, molecular solids often have a positive $\Delta S_{\text{soln}}^{\circ}$ and that favors dissolving, even for many cases without NH and OH parts. That can include some hydrocarbons, although there are also some hydrocarbons with negative $\Delta S_{\text{soln}}^{\circ}$. There are no overall trends to give you here, so just be aware that these can go either way.

Ionic solids can also go either way with entropy. Again, the extra advantage upon dissolving will contribute to an overall positive $\Delta S_{\text{soln}}^{\circ}$. Contrariwise, some ionics have a negative $\Delta S_{\text{soln}}^{\circ}$ and that opposes dissolving. Why are some negative? Again, it is due to orientation effects, but now even worse. As we saw in the last Chapter, the IFs for ions in water are dominated by the ion-dipole interaction which is even stronger than hydrogen bonding. The stronger cases of ion-dipole interactions will adopt more strongly preferred orientations which can be very restrictive, and these effects are even greater than the orientation effects for hydrogen bonding. As always, restrictions are bad for options and these cases will have a more negative impact on entropy. Thus and overall, there will be a range of effects for ionic solutes: entropy can favor some ionics to dissolve but entropy can also oppose others from dissolving. It will depend on the specific combination of cation and anion which is involved.

This completes our three Scenarios and this ends the entropy part for solubility. Now let's put things together.

40.2 Solubility and miscibility

Beginning in the last Chapter, we've now completed a number of illustrations of the enthalpy and entropy parts for a variety of compounds dissolving in water. We've also examined various Scenarios involving different native phases of solutes. We are now ready to put this information together and to address the question of whether a given compound might be soluble/insoluble and/or miscible/miscible. First, let me repeat and summarize some key points from the last Chapter.

“ In Chapters 34 - 38, the phases themselves were the outcome of the balance of enthalpy versus entropy. Now, for the determination of soluble/insoluble (and of miscible/miscible), enthalpy and entropy may still oppose each other in some cases but, in other cases, enthalpy and entropy may both favor soluble or they may both favor insoluble. ”

and

“ AN EXOTHERMIC (NEGATIVE) $\Delta H_{\text{soln}}^{\circ}$ FAVORS DISSOLVING AND AN ENDOTHERMIC (POSITIVE) $\Delta H_{\text{soln}}^{\circ}$ OPPOSES DISSOLVING. ”

For entropy from this Chapter:

INCREASING ENTROPY (POSITIVE $\Delta S_{\text{soln}}^{\circ}$) FAVORS DISSOLVING. DECREASING ENTROPY (NEGATIVE $\Delta S_{\text{soln}}^{\circ}$) OPPOSES DISSOLVING.

We can summarize these as follows.

Favor dissolving	Oppose dissolving
(-) $\Delta H_{\text{soln}}^{\circ}$	(+) $\Delta H_{\text{soln}}^{\circ}$
(+) $\Delta S_{\text{soln}}^{\circ}$	(-) $\Delta S_{\text{soln}}^{\circ}$

Know these. Watch the signs.

We now look at a number of examples and examine a few solubility properties based on our discussions to this point. We will also include miscibility for liquid phase solutes; miscibility is basically an extreme of solubility. As above and in the last Chapter, our examples cannot cover everything and we cannot get too detailed due to the complexity of all factors involved. The goal again is to illustrate how some of the various factors come into play. As we go, I'll bring in a common, quantitative unit for solubility, which is g of solute per 100 mL water. Tables of solubilities often use this unit. Note that this is a mass per volume term, unlike molarity which is a mol per volume term. Also as we go, the values cited will be for 25 °C; temperature can have a major impact on solubility, and we'll see more of this in the next Chapter.

We'll break this into our same three Scenarios.

• SCENARIO 1: GAS PHASE SOLUTES IN WATER

These are the easiest. Most gases are insoluble in water due to the great decrease in the entropy of dissolving any gas. In order for a gas to be soluble in water, then the enthalpy must be largely exothermic in order to overcome the entropy problem. Largely exothermic demands strong IFs. Let's look at several examples.

▶ He(*g*) and O₂(*g*)

The solution equation for He is: He(*g*) → He(*aq*)
and for O₂ it is: O₂(*g*) → O₂(*aq*)

You can forget helium for any kind of solubility. As seen in the last Chapter, the IFs between He and H₂O are terrible, so entropy wins hands down. Helium is one of the worst gases for solubility in water. The numerical answer is that one standard atm of He(*g*) gives a solubility for He(*aq*) of 0.00015 g per 100 mL H₂O, which is certainly not a significant extent. Notice that I specified a pressure of one atm; the solubility for gases is greatly dependent on the overhead gas pressure, as we'll see in the next Chapter.

O₂ is bigger than He and has more polarizability than He but the IFs are still weak and it's still fairly insoluble. At one standard atm of O₂(*g*), only 0.0042 g dissolves per 100 mL H₂O. For air with a typical O₂(*g*) pressure of 0.21 atm, then the solubility is only 0.00088 g per 100 mL H₂O. But that's what a fish gets to breathe. That small amount of solubility is absolutely essential to a huge host of aquatic life. (Air-breathers have it a bit easier: there's 0.027 g O₂ per 100 mL of air, at the conditions of 25 °C, one atm total *P* and 21% O₂.)

Helium and oxygen illustrate the outcome for most gases if they lack substantial IFs with water. In all of these cases, entropy rules and the gas is insoluble. The only way to get around the entropy problem is with strong IFs, especially hydrogen bonding; high polarity can also contribute.

▶ NH₃(*g*)

The solution equation is: NH₃(*g*) → NH₃(*aq*)

This one is an easy case: NH₃ in water can do dispersion, dipole-dipole and, most importantly, very strong hydrogen bonding. Despite entropy, NH₃ is soluble. In fact, it is extremely soluble: one atm of NH₃(*g*) gives a solubility of 45 g NH₃(*aq*) per 100 mL H₂O. You just won't find a lot of gases with that kind of solubility.

By the way, as we go along here, we are only considering the molecular compounds themselves and not any kind of chemical reaction which is possible in water. As we saw in Chapter 12, NH₃ is a weak base and it can form some NH₄⁺ and OH⁻ by reaction in water. We're not dealing with any of that here. Those ions are not a part of this coverage. Besides, they're a small fraction of the total anyway. Here, when we deal with a molecular compound, we only consider the neutral molecular compound in solution.

Let's try a couple other gases. Better yet, you can try them.

.....
Example 1. Consider propane, C₃H₈ (CH₃CH₂CH₃), and hydrogen fluoride, HF. Are they soluble in water or not? Why or why not?
.....

Let's go on to other solute types.

• SCENARIO 2: LIQUID PHASE SOLUTES IN WATER

Liquid solutes are highly dependent on the entropy effects associated with hydrogen bonding. You can forget about solubility for strict hydrocarbons; entropy won't allow it. At the other extreme, liquids which have dominant hydrogen bonding portions will be favored for solubility by both enthalpy and by entropy. There is a wide range between these extremes. We can illustrate this, starting with the four liquids which we have been working with since the last Chapter.

▶ $C_5H_{12}(l)$

The solution equation is: $C_5H_{12}(l) \rightarrow C_5H_{12}(aq)$

Pentane is not soluble. Despite the slightly exothermic $\Delta H_{\text{soln}}^\circ = -1.9 \text{ kJ}$ (Section 39.4), entropy says no way. The real solubility is only 0.0042 g per 100 mL H_2O , which is not a significant extent.

Pentane illustrates a very important aspect which we need to generalize. All hydrocarbons are insoluble in water, overwhelmingly as a result of entropy. The IFs with water are fairly feeble and the enthalpies are weakly exothermic or weakly endothermic (as noted in Section 39.4). Since enthalpy is feeble, it is entropy which dominates. This explains the simple observation that typical oils do not dissolve in water. Petroleum oils are hydrocarbons and are insoluble in water. Even food oils are mostly hydrocarbon with a very small polar portion; very small is not enough, and these oils do not dissolve in water because of entropy. When it comes to dissolving in water, CC and CH portions of molecules give water nothing to work with. These portions have a very negative effect on entropy and their weak IFs with water do not provide much help from enthalpy.

Let's now look at examples with polarity and hydrogen bonding. We'll look at the isomers diethyl ether and 1-butanol, both of which are similar in size and shape to pentane.

▶ $C_2H_5OC_2H_5(l)$

The solution equation is: $C_2H_5OC_2H_5(l) \rightarrow C_2H_5OC_2H_5(aq)$

We described the IFs between diethyl ether and water back in Section 39.3. Although $C_2H_5OC_2H_5$ does not have hydrogen bonding by itself, it does accept hydrogen bonding when dissolved in water. Together with the other IFs, enthalpy is good. Entropy, however, is not so good since this is still a molecule which is primarily composed of CC and CH portions. Thus, entropy will oppose solubility. Overall, compared to the pentane example above, the better IFs between diethyl ether and water will allow for solubility. $C_2H_5OC_2H_5$ is soluble, to the extent of 6.4 g per 100 mL water.

Now, 1-butanol.

▶ $C_4H_9OH(l)$

The solution equation is: $C_4H_9OH(l) \rightarrow C_4H_9OH(aq)$

1-butanol can do hydrogen bonding by itself and it can do donor and acceptor hydrogen bonding with water. With the other IFs, enthalpy is good. It's still mostly CC and CH, however, so it will be opposed by entropy for solubility in water. In the end, the solubility for 1-butanol in water is 8.0 g per 100 mL H_2O , not much more than the solubility for diethyl ether.

OK, reasonable polarity and hydrogen bonding renders diethyl ether and 1-butanol soluble. However, neither is miscible with water. We haven't gotten to miscible yet. Miscible needs more than just soluble. In order to get miscibility, we need $\Delta S_{\text{soln}}^\circ$ to be positive or, at least, not too negative; we cannot afford a lot of interference from big CC and CH portions. We also need strong IFs. Small molecules with high polarity and/or hydrogen bonding (especially multiple sites) will get us miscibility.

▶ $CH_3OH(l)$

The solution equation is: $CH_3OH(l) \rightarrow CH_3OH(aq)$

For methanol, strong hydrogen bonding will dominate the IFs and this hydrogen bonding will allow for favorable entropy as seen earlier in this Chapter. Methanol is not only soluble, it is miscible with water.

Methanol has strong hydrogen bonding like 1-butanol, but it has only a small CH portion so this does not detract much from entropy. This combination gives miscibility. We can also compare ethanol, C_2H_5OH (CH_3CH_2OH), and 1-propanol, C_3H_7OH ($CH_3CH_2CH_2OH$) to methanol: these have increasing CC and CH portions and they now have a negative $\Delta S_{\text{soln}}^\circ$. Nevertheless, they are still miscible. After that, however, you get to 1-butanol ($CH_3CH_2CH_2CH_2OH$) and you've lost miscibility although you still have solubility. If you continue this series bigger and bigger, even solubility doesn't go on forever. As more CC and CH portions are added, entropy becomes more of a problem and the smaller and smaller portion of hydrogen bonding is just not enough anymore. By the time you get to $C_8H_{17}OH$ ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$), its solubility is down to 0.06 g per 100 mL H_2O , which is not significant.

CH ₃ OH	C ₂ H ₅ OH	C ₃ H ₇ OH	C ₄ H ₉ OH	...	C ₈ H ₁₇ OH
miscible	miscible	miscible	soluble		insoluble

These compounds nicely show the interplay between enthalpy and entropy in determining whether a solute is miscible/immiscible, soluble or insoluble.

Let me do one more example here.

► C₃H₅(OH)₃(l)

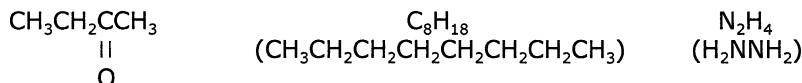
The solution equation is: C₃H₅(OH)₃(l) → C₃H₅(OH)₃(aq)

This is glycerol, the goopy syrup which was mentioned in Section 38.1. Go back and look at the Lewis structure. This molecule has multiple sites for hydrogen bonding, which gives outstanding IFs with water and a very positive value of ΔS_{soln}^o. Glycerol is miscible with water.

This concludes the examples for liquids. These things are incredibly important to you and within you. I'll come back to the "within you" part later in the Chapter. For now, let's give you a shot at some comparisons.

.....

Example 2. Rank the following liquids in terms of increasing solubility in water. (One is miscible with water.) List your reasons.



.....

Time to move on to solids.

• SCENARIO 3: SOLID 'A' DISSOLVING INTO WATER

As we've been doing, we break this into molecular and ionic solid phase solutes.

In the molecular category, values for ΔH_{soln}^o tend to be more positive (endothermic) because you have to break up the greater IFs of the solid phase. On the other hand, ΔS_{soln}^o is more favorable because there's more entropy to be gained by dissolving a solid. It's a trade-off. For best solubilities, you again want hydrogen bonding. Hydrocarbons are insoluble again, but now it can be due to enthalpy and/or entropy.

► C₁₀H₈(s), naphthalene

The solution equation is: C₁₀H₈(s) → C₁₀H₈(aq)

Naphthalene is not soluble in water. The solubility is 0.0031 g per 100 mL H₂O, which is not significant.

This is a common outcome for a solid which is entirely hydrocarbon or one which is mostly CC and CH. Waxes and fats are mostly CC and CH but they do have a very small polar portion. Those portions don't help much and those compounds are still insoluble.

► H₃BO₃(s)

The solution equation is: H₃BO₃(s) → H₃BO₃(aq)

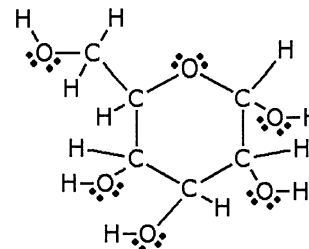
We looked at boric acid for hydrogen bonding back in Chapter 37. Hydrogen bonding is good for entropy and it's good for enthalpy although ΔH_{soln}^o is still endothermic here. Overall, boric acid is soluble. The real solubility is 5.8 g per 100 mL H₂O.

As mentioned upstairs for NH_3 , our discussion here for molecular compounds is only for the neutral compound. Although boric acid is an acid, it's extremely weak and extremely little of the dissolved compound will dissociate. Thus, we are dealing with molecular $\text{H}_3\text{BO}_3(\text{aq})$ here.

▸ $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$, glucose

The solution equation is: $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{aq})$

Glucose illustrates a typical, simple sugar. We first mentioned glucose as blood sugar way back in Chapter 3 as one isomer of $\text{C}_6\text{H}_{12}\text{O}_6$ and we also talked a bit about its use as a natural fuel for your body in Chapter 19. The Lewis structure for glucose is shown at right. As is typical for a sugar, there is polarity and there are numerous OH bonds. The OH bonds are the important parts since they provide for massive hydrogen bonding. The solubility of glucose in water is disfavored by enthalpy but readily favored by entropy. This is typical for many simple sugars and this is why they are so highly soluble in water. For glucose, the solubility is 110 g per 100 mL H_2O . That's a lot!



Glucose is a monosaccharide, a term introduced in Section 19.5. Sucrose, common table sugar, is a disaccharide with the formula $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. Its solubility is 210 g per 100 mL H_2O . Disaccharides are the smallest members of the general class of polysaccharides and, as sugars get bigger, many lose solubility. Starches are huge polysaccharides; some are soluble and some are not. Cellulose is another huge polysaccharide; it's insoluble.

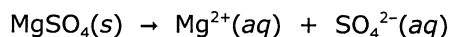
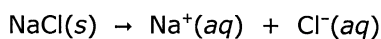
OK, that's enough examples here. Your turn.

Example 3. Consider the following two molecular solids. Which is more soluble in water? Why?



(Urea was described with its Lewis structure in Chapter 39. *p*-Dichlorobenzene received mention in Chapter 36; for its ranking here, all you need to know is that it is nonpolar.)

Now we turn to the ionic solutes. Let me show two examples of solution equations for ionic solutes.



Unfortunately, we are limited in what we can do here. As described in the last Chapter, $\Delta H_{\text{soln}}^\circ$ can be exothermic or endothermic depending on the specific values of lattice and hydration enthalpies. The hydration enthalpies primarily reflect the strength of the ion-dipole interaction. As described in this Chapter, $\Delta S_{\text{soln}}^\circ$ can be positive or negative. The negative $\Delta S_{\text{soln}}^\circ$ cases can be related to the severe orientational restrictions of the stronger ion-dipole interactions. Thus, ion-dipole IFs ultimately impact both $\Delta H_{\text{soln}}^\circ$ and $\Delta S_{\text{soln}}^\circ$ and it's all part of the balance. Ion-dipole interactions are related to charge density, especially to charge itself. In general, entropy will oppose dissolving for ionic compounds with a cation of 2+ or 3+ charge and/or an anion of 2- or 3- charge. These cases, however, will have more exothermic $\Delta H_{\text{soln}}^\circ$, so the final result is that the compound can be soluble or insoluble. For ionic compounds of 1+ cations and 1- anions, entropy generally favors solubility but many of these have an endothermic $\Delta H_{\text{soln}}^\circ$ so their solubilities, too, can go either way.

Overall, there are too many factors involved for the various ionic compounds and that precludes much of an analysis here. Nevertheless, you already have a practical guide to solubilities for ionics: they're the Solubility Trends which were given in Chapter 11. Those remain decent guides, although there can be exceptions.

It's time to close out this section.

40.3 Summary

Here is a Summary for the relationship of enthalpy and of entropy to the solubility properties for various compounds in water.

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THE INTERPLAY OF ENTROPY AND ENTHALPY ON SOLUBILITY (AND MISCIBILITY) IN WATER

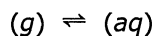
Favor dissolving

$$\begin{array}{l} (-) \Delta H_{\text{soln}}^{\circ} \\ (+) \Delta S_{\text{soln}}^{\circ} \end{array}$$

Oppose dissolving

$$\begin{array}{l} (+) \Delta H_{\text{soln}}^{\circ} \\ (-) \Delta S_{\text{soln}}^{\circ} \end{array}$$

• SCENARIO 1: GAS 'A' DISSOLVING INTO WATER

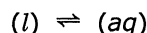


S: By themselves, gas phase compounds have the most entropy. Dissolving will lose entropy overall and substantially so (large, negative $\Delta S_{\text{soln}}^{\circ}$).

H: Gases have no IFs (ideally) so they will always gain IFs in solution, giving a negative (exothermic) $\Delta H_{\text{soln}}^{\circ}$.

Entropy is the dominant effect and this strongly opposes solubility. Gases which can hydrogen bond with water are soluble; high polarity of the solute can assist. Other gases are generally insoluble due to entropy.

• SCENARIO 2: LIQUID PHASE SOLUTES IN WATER

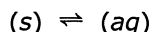


S: Portions of solutes which can hydrogen bond (as both donor and acceptor, or as acceptor-only) are best to increase or maintain entropy upon dissolving. Other types (especially hydrocarbons) will give a loss of entropy (negative $\Delta S_{\text{soln}}^{\circ}$) upon dissolving.

H: Hydrocarbon portions of solutes have a weakly positive or weakly negative impact on $\Delta H_{\text{soln}}^{\circ}$. Portions of solutes which can hydrogen bond (as both donor and acceptor, or as acceptor-only) give strong IFs with water and contribute to a more negative $\Delta H_{\text{soln}}^{\circ}$.

A combination of effects can lead to a soluble or insoluble outcome. In general, greater solubility will be obtained for solutes which can hydrogen bond (even if acceptor only) and which have no or small hydrocarbon portions. Polarity can help, but it is a smaller effect than hydrogen bonding (if present). Miscibility requires more favorable interactions for $\Delta H_{\text{soln}}^{\circ}$ and/or $\Delta S_{\text{soln}}^{\circ}$ than is present for just solubility.

• SCENARIO 3: SOLID PHASE SOLUTES IN WATER



Molecular solids

S: The solid phase has the least entropy; these solutes can therefore have the greater gain in entropy by dissolving (relative to liquid or gas solutes), but $\Delta S_{\text{soln}}^{\circ}$ can still be positive or negative.

H: Solid phase compounds have the best IFs; dissolving is often (but not always) endothermic (positive $\Delta H_{\text{soln}}^{\circ}$).

A combination of effects can lead to soluble or insoluble.

Ionic solids

Entropy and enthalpy effects can go either way, positive or negative; higher charges can enhance the effects. The combination of effects can lead to soluble or insoluble.

.....

OK, that ends the Summary. But we're not done.

We have applied the above notions to quite a range of compounds here and in the prior Chapter. But the ramifications of these interactions go further than just solubility or miscibility. You yourself are partly held together by these same interactions. We're going to expand on this and see some of the massive consequences of these interactions on various aspects of your world.

40.4 A world of consequences

That weird substance which we call water doesn't get along with everything. Oh, sure, there are other solvents with some idiosyncrasies but water stands out, due to its special combination of high polarity and strong hydrogen bonding. For ionics, some compounds are good with water and some are not so good. For molecular compounds, having hydrogen bonding is the best way to get along with water. The worst molecular compounds with water are those with no hydrogen bonding and little or no polarity, such as hydrocarbons or other molecules which are primarily composed of CC and CH portions.

Water's rejection of CC and CH compounds is more generally called hydrophobicity. The adjective is hydrophobic and the solute is the hydrophobe. We can use these terms for a molecule as a whole or for parts of the molecule. For example, we can say that pentane is a hydrophobe or that the C_4H_9 part of 1-butanol is hydrophobic. The prefix hydro- is used in the normal dictionary sense for water; the suffix -phobic is used in the normal dictionary sense for fear or aversion, which is related to phobia. Thus, the term "hydrophobic" suggests that the molecule has an aversion for water. In reality, it's the other way around: water has an entropic aversion to the hydrophobe. Water molecules can benefit by entropy when they mingle with other hydrogen bonding centers; this is not the case, however, for water molecules hanging around hydrophobic portions of molecules. As illustrated earlier for 1-butanol, this causes hydrophobic portions to huddle together when in water. By the way, CC/CH portions are not the only hydrophobes around although they are among the most common.

On the other side of the terminology, molecules or portions of molecules which have hydrogen bonding and/or polarity are said to possess hydrophilicity. The adjective is hydrophilic. The suffix -philic is used in the normal dictionary sense for tendency or desire for. A hydrophilic molecule (hydrophile) interacts well with water. For example, we can say that ammonia is a hydrophile or that the OH part of 1-butanol is hydrophilic.

Keep in mind that the above terms can be used for the molecule as a whole or for a part of a molecule. Molecules which possess both types of parts get another term: amphiphilic. The prefix amphi- is used in its normal dictionary sense for both. An amphiphilic compound (amphiphile) has both a hydrophobic portion and a hydrophilic portion. The C_4H_9 part of 1-butanol is hydrophobic and the OH part is hydrophilic; 1-butanol is amphiphilic.

Hydrophobicity and hydrophilicity influence solutes in water but they also influence how water interacts with other things. The whole phenomenon of wettability is related to these aspects. In Chapter 38 when we talked about surface tension, we mentioned that surface tension makes drops of water bead up on waxy surfaces. The beading action begins with hydrophobicity: the water does not want to make contact with the wax so it minimizes the contact surface area. Surface tension just makes the drops go round, although flattened a bit by gravity. Also at that time in Chapter 38, we discussed how surface tension is measured by water rising into a glass capillary. Glass is hydrophilic; its surface has ions and or hydrogen bonding available, so water will wet glass. Water will wet glass until you get your dirty fingerprints all over it; the oils in your fingerprints are hydrophobic and this will reduce the wettability of the glass surface.

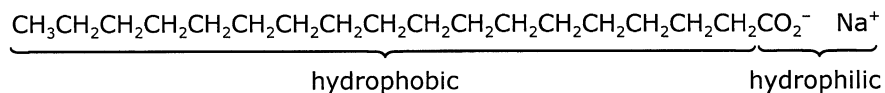
Common paper and natural cloth materials (e.g., cotton) are hydrophilic because they are made of cellulose which is a bunch of huge polysaccharides with lots of OH bonds. Water will wet these materials readily, hence their use as towel materials. Additives can change their properties; for example, wax paper is hydrophobic. Even laundering can change the properties of cloth. For example, fabric softeners are hydrophobic. Rags and towels laundered without fabric softener will absorb water better than those which are laundered with fabric softener.

You can use cloth or even paper to perform like a siphon. A siphon is a tube which is used to empty liquid from one container into a second container which is at a lower position. Instead of a tube, if you place one end of a strip of cloth in a high bucket of water and the other end in a lower bucket, then the water will move through the cloth and into the lower bucket. It's a lot slower than a tube siphon and a lot of water can evaporate in the process, but it does work. The travel of a liquid into cloth or paper or some other substance is also called wicking, as in a candle wick.

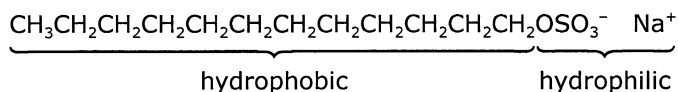
Let me talk a bit more about amphiphiles. Their behavior is vastly important to human society and also to life on Earth.

I cited 1-butanol above as an example of an amphiphile. It is soluble but its molecules do tend to huddle in aqueous solution. Now I want to talk about bigger and bigger amphiphiles containing a dozen or more carbon atoms. These can huddle into aggregates with specific kinds of structure.

We'll begin this discussion with a clean topic: soaps. Soaps are among the oldest amphiphiles which have been adopted on a large scale by human society. A typical soap contains an ionic compound whose anion is largely hydrophobic but with a small hydrophilic part. An example is sodium stearate, $\text{NaC}_{18}\text{H}_{35}\text{O}_2$.

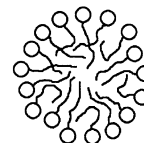


The hydrophobic part is composed of sp^3 carbon atoms in tetrahedral shape; these give a long, flexible chain. The final $-\text{CO}_2^-$ part carries the anion charge; this and the Na^+ provide for strong ion-dipole interaction with water. Soaps are one form of detergent; they are typically associated with a biological origin and they have historically been made by heating fats with a strong base. Soaps serve many purposes well but they do not work well in all applications. Hence, over the years, other detergents have been designed from nonbiological sources. A common one which has been around a while is called SDS, which stands for sodium dodecyl ("doe-deckel") sulfate, $\text{NaC}_{12}\text{H}_{25}\text{SO}_4$.



This also goes by the name sodium lauryl sulfate and that name is commonly found on commercial labels for shampoos, hand soaps, dish soaps, etc. Read the label.

Regardless of origin or of their exact chemical identity, detergents typically contain a large hydrophobic portion for favorable interaction with grease, and a hydrophilic portion (usually ionic) for favorable interaction with water. A schematic for these types of compounds is shown at left. The wiggly line is the long, flexible hydrophobic tail and the circle represents the hydrophilic end portion. In water, when extremely dilute, the long hydrophobic tail of one amphiphilic ion will huddle with the long hydrophobic tail of one or several others. As the concentration of the amphiphile increases but still fairly dilute (e.g., 10^{-4} through 10^{-2} M range), these can aggregate into specific structures called micelles. Micelles are extremely small, encased structures; some are spherical as shown at right. (OK, the picture is only two dimensions. These things are really three dimensional. The picture represents a slice of a micelle.) The ionic, hydrophilic parts make up the outside surface of the sphere; the hydrophobic tails are inside the sphere. One micelle may contain less than one hundred of the separate amphiphile ions. These micelles form as a result of entropy. Due to entropy, water wants nothing to do with the long tail portions; micelles provide a means to avoid water-hydrophobe contacts. The water molecules interact with the ionic groups on the outside of the micelle. Inside the micelle, it's like a tiny oil bath and the tails can behave as if they were a simple oily liquid.



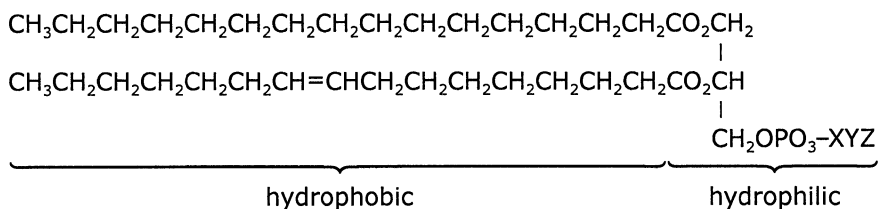
So how do these work as detergents?

Detergents are used to cut oils, greases, etc. Oils, greases, etc. are hydrophobic and therefore they are shunned by water. Detergents bridge these two extremes. The hydrophobic portion of the detergent interacts with the hydrophobic oil (or grease, etc.) while the hydrophilic portion allows interaction with water. Depending on the chemical identity of the detergent and its concentration, and depending on the oil and its amount, the detergent can huddle or even encapsulate tiny amounts of oil, thus allowing the oil to be lifted. The oil, formerly sticking to your hand or clothing, is now binding with the detergent and can be washed away.

Let's change the subject a bit and consider hydrophobicity's natural impact on you.

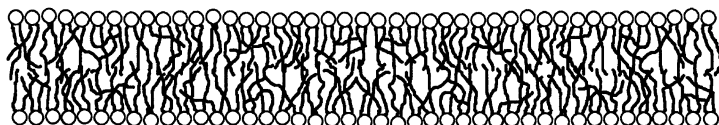
Every cell in your body is held together by the principles which have been spelled out here, simply taken to an extreme. The amphiphiles are different and the aggregation is different, but it's still driven for the most part by entropy.

Your cells are encased by membranes composed of amphiphiles. A typical membrane amphiphile has two long hydrophobic chains instead of one; it also has a hydrophilic portion which is ionic but some of these also contain OH portions for hydrogen bonding. There are a lot of different kinds of these depending on the cell and conditions. Here's a representative example shown with $\text{C}_{15}\text{H}_{31}$ and $\text{C}_{15}\text{H}_{29}$ hydrophobic portions.



The hydrophilic portions involve an OPO_3 part which carries a 1^- charge; furthermore, there are still quite a few more atoms shown generically by 'XYZ' which can contain more ionic parts or hydrogen bonding parts. Thus, the hydrophilic part is VERY hydrophilic.

With two, long hydrophobic tails, these things get too crowded to form simple micelles. Instead, they line up one after another into a big two-dimensional layer. Let's start with one of these for illustration purposes, as shown at left; again, the open circle is the hydrophilic part, and now there are two tails. At right, I show a bunch of these lined up to form one layer. It can't just stop there, however, because that would leave all the hydrophobic tails still open to contact with H_2O molecules. So, two of these layers come together, tail-to-tail, to form a "bilayer", as shown below. That picture represents a piece of a cell membrane, shown as a thin slice.



media inside and outside your cell. Within the bilayer, you have a miniature layer of oil. There are also many other things peppered around the membrane to allow things to pass in and out and to allow for other functions, but this bilayer structure is the basic part of the membrane of the cells in your body. This is what organizes your cells.

The importance of these things to your life cannot be overstated. For further example, consider proteins. Proteins in your cells or floating around in your blood are huge, chain-like molecules, many with masses over 10,000 g/mol and many over 100,000 g/mol. Some portions of the chain are hydrophilic and some portions are hydrophobic. Proteins are extremely diverse in composition, and humans have 10,000 - 20,000 different proteins. Proteins are also extremely versatile in function. Each protein chain can adopt a highly folded structure, and the specific folding can determine whether that protein is functioning properly or not. Much (although not all) of the specific folding is dependent on the same hydrophobic and hydrophilic interactions outlined here. If not folded correctly, that "misfolded" protein might be harmless or it might be deadly. There are numerous protein misfolding diseases, including Alzheimer's disease, Parkinson's disease, prion diseases, and a host of others. Thus, hydrophilic and hydrophobic interactions can be a matter of life and death.



This really is about you. It's about your cells. It's about your proteins and still many more molecules which make up your life. Hydrophobicity is primarily due to entropy. It is entropy which brings order to your cells and to many other aspects of your existence.

40.5 Balance in perspective

In this and the last Chapter, we have applied principles for enthalpy and for entropy in our analysis of mixtures. In the five Chapters previous to the present two, we applied enthalpy and entropy to the simple phases. I have spent a lot of time on enthalpy and entropy because they are ultimately so important to so many things. It's not just about phases and about mixtures. It's about every process and every reaction. It's about everything that is possible and everything that will ever happen, biological or not. It's about your world, your universe.

I used enthalpy and entropy to explain phases but, all along, there has been another motive: I have used phases and mixtures to introduce you to the effects and the balance of enthalpy and entropy. From the existence of a simple phase to the construction of every membrane holding your cells together, enthalpy and entropy rule. Ironically, in the end, it is only entropy that rules on a grander scale, but enthalpy plays a role. We shall see this beginning in Chapter 44. It's important. It's very important.

Remember the balance. You are being prepared for a relationship of universal proportions. But we're not there yet; that will come later. We're not yet done with mixtures.

Problems

- True or false.
 - Entropy opposes food oils from dissolving into water.
 - Entropy always favors ionic compounds dissolving in water.
 - The mixing of $C_6H_{14}(l)$ and $H_2O(l)$ is favored by entropy.
 - $\Delta S_{\text{soln}}^\circ$ for dissolving $NH_3(g)$ into water is negative.
 - Soaps are amphiphilic.
- Consider each of the following types of compounds dissolving in water. For each case, indicate whether dissolving is favored or disfavored by entropy.
 - polar gas
 - nonpolar liquid without hydrogen bonding
 - ionic solid
- Consider the following compounds for dissolving into water.
 $CH_4(g)$ $CH_3F(g)$ $CH_3CH_2CH_2CH_3(g)$ $CH_3OH(l)$ $C_4H_9OH(l)$
 - Which compound is most favored by entropy for dissolving into water?
 - Which compound is most opposed by entropy for dissolving into water?
- Consider the following compounds, all of which are liquids in their native phase.
 C_8H_{18} H_2O_2 CH_2Cl_2 $H_2NCH_2CH_2NH_2$
 - Two are miscible in water. Which are they?
 - One is soluble but immiscible. Which is it?
 - One is insoluble and immiscible. Which is it?
- Of the following, which one is the most soluble in water (on a molar basis)?
 $N_2(g)$ $I_2(s)$ $PH_3(g)$ $CH_3CO_2H(l)$ $C_6H_6(l)$
- For each compound, indicate whether it is hydrophobic, hydrophilic or amphiphilic.
 - C_3H_8
 - $C_6H_{13}OH$
 - N_2H_4