

## Chapter 40

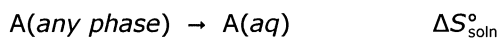
## MIXTURES, Part 2

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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  $\Delta S_{\text{soln}}^{\circ}$ .



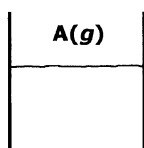
Sometimes, the system will increase entropy as a result of dissolving and then  $\Delta S_{\text{soln}}^{\circ}$  is positive. On the other hand, sometimes the system will decrease entropy as a result and then  $\Delta S_{\text{soln}}^{\circ}$  is negative. It depends on both the solute and the solvent. 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.

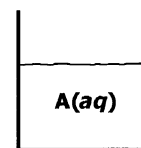
We will continue our emphasis on water as solvent, although water is complicated relative to most other solvents. The problem is that aqueous solutions are very sensitive to entropy effects. We'll see this as we go.

Just as was done for the enthalpy part in the last Chapter, we will break this down into three scenarios depending on the original phase of the solute.

## • GAS 'A' DISSOLVING INTO WATER



For our first scenario, we consider a gas A dissolving into water.

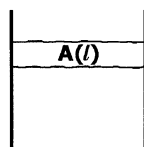


This process is always opposed by entropy and the effect is quite large. The reason is straightforward: with the most options and fewest restrictions, the gas phase is by far the best for entropy.

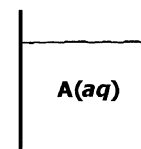
Dissolving any gas into water (or any solvent) eliminates many of those options, imposes new restrictions and decreases entropy substantially. All gas solutes are the same for this effect.  $\Delta S_{\text{soln}}^{\circ}$  is negative for all of these cases.

This case is the easiest of our three scenarios.

## • LIQUID 'A' DISSOLVING INTO WATER



Consider a liquid A dissolving into water.



This is where we first hit a number of complications for water as the solvent. Let me back up a moment and make a general comment first for 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;  $\Delta S_{\text{soln}}^{\circ}$  is positive and this favors the dissolving process.

OK, that much is fine, but water has to be weird. For water, it's usually the other way around: the dissolving of most liquids into water is usually opposed by entropy. This is an incredibly important outcome for many common occurrences, even as simple as why oil and water do not mix. Although incredibly important and although known for many decades, this entropy effect is proving difficult to understand. Interestingly, new experimental techniques in recent years are questioning some of the prominent, long term beliefs. There is ongoing research on how this entropy effect operates for the many different kinds of solutes in water. Thus, the full answer is not yet known but we can touch on a few points here for illustration.

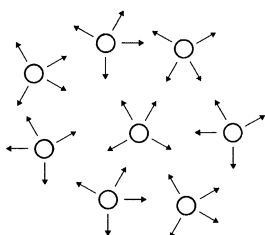
The entropy problem for water relates directly to its strong hydrogen bonding. Strong hydrogen bonding is great for enthalpy but it can have a very negative effect on entropy due to the very restrictive

orientation effects. This was first noted in Section 37.5 and we will now see what a big impact that has. For any solute in water,  $\text{H}_2\text{O}$  molecules will surround the solute molecules and try to interact with those solute molecules by means of hydrogen bonds. For a solute which can engage in hydrogen bonding with water, then this is favorable for entropy. For a solute which lacks the ability to hydrogen bond with water, then this decreases entropy for the water molecules which surround the solute molecule, although the details aren't fully understood. It has been generally believed that  $\text{H}_2\text{O}$  molecules adopt specific arrangements around a solute molecule so that the water molecules can still hydrogen bond to neighboring water molecules. Although these arrangements are dynamic and neighbors do trade off with other neighbors, these arrangements do impose some restrictions on location and orientation and those restrictions decrease system entropy. Other contributions to the loss of entropy in the system 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. Furthermore, the solute molecules may be forced to huddle together; such togetherness limits the total mixing process and restricts the options which are otherwise possible. Like I said, many details are just not fully understood right now and much is still under study.

Although the explanation is not fully understood, we can still deal with entropy on a somewhat practical basis.

On a practical basis, NH and OH bonds in solute molecules can fully hydrogen bond 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 negative impact on entropy and that works against dissolving.

Let's put some of this to picture.



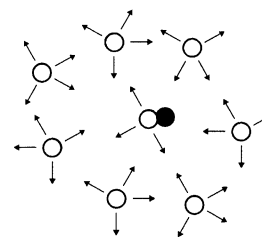
We'll start with just water by itself. One molecule of water can form up to four hydrogen bonds (two donated, two accepted) with other water molecules. This is shown at left in a simplistic fashion with each water molecule as a circle. The arrows convey the sense of the four possible hydrogen bonds for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

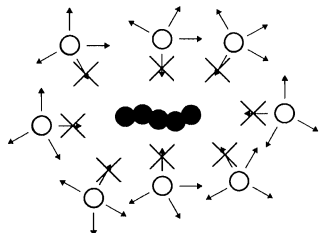
(By the way, the picture above and several below show quite a bit of space between the molecules. In reality, in any liquid, the molecules are in loose contact. I spread things out in the pictures to show the arrows.)

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 ( $\text{CH}_3\text{OH}$ ), pentane ( $\text{C}_5\text{H}_{12}$ ) and 1-butanol ( $\text{C}_4\text{H}_9\text{OH}$ ). Let's now examine their solution entropies.

Methanol has hydrogen bonding, and this provides a very strong interaction with water molecules. At right, a  $\text{CH}_3\text{OH}$  molecule is shown surrounded by  $\text{H}_2\text{O}$  molecules. The OH part of the methanol molecule which can hydrogen bond is shown as an open circle; the  $\text{CH}_3$  part which cannot hydrogen bond is shown as a dark portion. Although the  $\text{CH}_3$  part cannot hydrogen bond, that portion is only about half the size of the molecule as a whole. There yet remains a reasonable number of options available for hydrogen bonding for the methanol molecule and the water molecules.

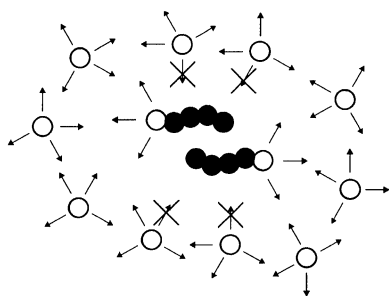
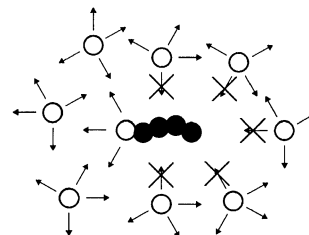


Entropy is not a problem here. In fact,  $\Delta S_{\text{soln}}^{\circ}$  for methanol is still slightly positive, thus favoring solubility in water.



Now let's put pentane into water.  $\text{C}_5\text{H}_{12}$  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 turn to each other in order to maintain hydrogen bonding but that requires the water molecules to adopt certain arrangements around the uncooperative 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 but the water molecules along the  $\text{C}_4\text{H}_9$  part will not. The  $\text{C}_4\text{H}_9$  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.

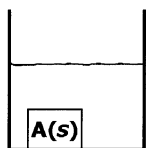


Let me show an illustration of huddling which was mentioned upstairs. At left, two molecules of 1-butanol are shown. Due to entropy, water shuns the  $\text{C}_4\text{H}_9$  hydrocarbon parts so those parts tend to huddle close together. Of course, things are constantly in motion so that just illustrates an average effect. 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  $\text{CH}_3$  part.

Again, many details of these entropy effects are not completely understood and some are beyond what we can cover here. I want to show you some of the basics. These examples illustrate some of the most important considerations for liquid solutes in water. 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 later.

This now ends the scenario for liquid solutes.

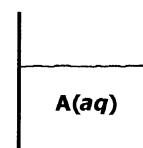
#### • SOLID 'A' DISSOLVING INTO WATER



Consider a solid A dissolving into water.



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.



Right off the bat, keep in mind that solids have the least entropy to begin with of our three standard phases. Thus, solids have an extra advantage for dissolving because they stand to gain the most entropy by dissolving.

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. There will still be some hydrocarbons



You can forget helium for solubility. As seen in the last Chapter, the IFs between He and H<sub>2</sub>O are terrible, so entropy wins. Helium is one of the worst gases for solubility in water. The numerical answer is that one standard atm of He gives a solubility for He(aq) of 0.00014 g per 100 mL H<sub>2</sub>O, which is certainly not a significant extent. Notice that I specified a pressure of one atm; the solubility for gases is directly proportional to pressure, as we'll see in the next Chapter.

O<sub>2</sub> is bigger than He and has more polarizability than He but the IFs are still weak and it's still insoluble. At one standard atm of O<sub>2</sub>(g), only 0.0042 g dissolves per 100 mL H<sub>2</sub>O, which is not a significant extent. For typical air with a typical O<sub>2</sub>(g) pressure of 0.21 atm, then the solubility is only 0.00087 g per 100 mL H<sub>2</sub>O. Fortunately, insoluble and "not a significant extent" don't mean much to a fish; fish will breathe that little bit of dissolved O<sub>2</sub>(aq) right out of the water. That tiny amount of solubility is absolutely essential to much aquatic life.

Helium and oxygen illustrate the way most gases will fall 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.

► NH<sub>3</sub>(g)

The solution equation is:  $\text{NH}_3(g) \rightarrow \text{NH}_3(aq)$

This one is an easy case: NH<sub>3</sub> in water can do dispersion, dipole-dipole and, most importantly, very strong hydrogen bonding. Despite entropy, NH<sub>3</sub> is soluble. In fact, it is extremely soluble: one atm of NH<sub>3</sub>(g) gives a solubility of 45 g NH<sub>3</sub>(aq) per 100 mL H<sub>2</sub>O. 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, NH<sub>3</sub> is a weak base and it can form some NH<sub>4</sub><sup>+</sup> and OH<sup>-</sup> 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, C<sub>3</sub>H<sub>8</sub> (CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>), and hydrogen fluoride, HF. Are they soluble in water or not? Why or why not?  
 .....

Let's go on to other solute types.

#### • LIQUID PHASE SOLUTES IN WATER

Liquids are more complicated than gases. The enthalpy of solution is now derived from two parts,  $\Delta H_{\text{soln}}^{\circ} = \Delta H_{\text{vap}}^{\circ} + \Delta H_{\text{hydr}}^{\circ}$ . Entropy is also more involved. 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 entropy. In between these extremes, solubility will be opposed by entropy but hydrogen bonding and/or polarity can win out if these are a big enough part of the compound.

Let's do some examples.

► C<sub>5</sub>H<sub>12</sub>(l)

The solution equation is:  $\text{C}_5\text{H}_{12}(l) \rightarrow \text{C}_5\text{H}_{12}(aq)$

Pentane is not soluble. Despite the slightly exothermic  $\Delta H_{\text{soln}}^{\circ} = -1.9$  kJ (Section 39.4), entropy says no way. The real solubility is only 0.0042 g per 100 mL H<sub>2</sub>O, 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.

▸  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5(l)$

The solution equation is:  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5(l) \rightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_5(aq)$

We described the IFs between diethyl ether and water back in Section 39.3. Although  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$  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.  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$  is soluble, to the extent of 6.4 g per 100 mL water.

Now, 1-butanol.

▸  $\text{C}_4\text{H}_9\text{OH}(l)$

The solution equation is:  $\text{C}_4\text{H}_9\text{OH}(l) \rightarrow \text{C}_4\text{H}_9\text{OH}(aq)$

1-butanol can do hydrogen bonding by itself and it can do full 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  $\text{H}_2\text{O}$ , not much more than the solubility for diethyl ether.

OK, reasonable polarity and/or hydrogen bonding renders diethyl ether and 1-butanol soluble. However, neither is miscible. 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.

▸  $\text{CH}_3\text{OH}(l)$

The solution equation is:  $\text{CH}_3\text{OH}(l) \rightarrow \text{CH}_3\text{OH}(aq)$

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,  $\text{C}_2\text{H}_5\text{OH}$  ( $\text{CH}_3\text{CH}_2\text{OH}$ ), and 1-propanol,  $\text{C}_3\text{H}_7\text{OH}$  ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ ) to methanol: these have increasing CC and CH portions and they now have a negative  $\Delta S_{\text{soln}}^\circ$  but they are still miscible. After that, however, you get to 1-butanol ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ) 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  $\text{C}_8\text{H}_{17}\text{OH}$  ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ), its solubility is down to 0.06 g per 100 mL  $\text{H}_2\text{O}$ , which is not significant.

$\text{CH}_3\text{OH}$	$\text{C}_2\text{H}_5\text{OH}$	$\text{C}_3\text{H}_7\text{OH}$	$\text{C}_4\text{H}_9\text{OH}$	...	$\text{C}_8\text{H}_{17}\text{OH}$
miscible	miscible	miscible	soluble		insoluble

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

Let me do one more example here.

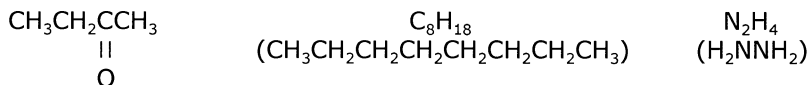
▸  $\text{C}_3\text{H}_5(\text{OH})_3(l)$

The solution equation is:  $\text{C}_3\text{H}_5(\text{OH})_3(l) \rightarrow \text{C}_3\text{H}_5(\text{OH})_3(aq)$

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  $\Delta S_{\text{soln}}^{\circ}$ . 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. List your reasons.



Time to move on. We'll do solids, breaking these up into molecular and ionic cases again.

• MOLECULAR, SOLID PHASE SOLUTES IN WATER

This category runs similar to the case of liquids above. Values for  $\Delta H_{\text{soln}}^{\circ}$  are typically positive (endothermic) because you have to break up the greater IFs of the solid phase. On the other hand,  $\Delta S_{\text{soln}}^{\circ}$  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 entropy and/or enthalpy.

▸  $\text{C}_{10}\text{H}_8(\text{s})$ , naphthalene



Naphthalene is not soluble in water. The solubility is 0.0031 g per 100 mL  $\text{H}_2\text{O}$ , 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.

▸  $\text{H}_3\text{BO}_3(\text{s})$



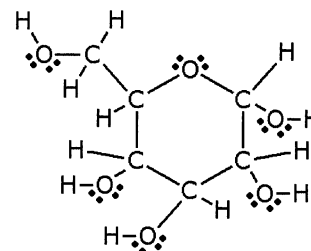
We looked at boric acid for hydrogen bonding back in Chapter 37. Hydrogen bonding is good for entropy and it's good for enthalpy although  $\Delta H_{\text{soln}}^{\circ}$  is still endothermic here. Overall, boric acid is soluble. The real solubility is 5.8 g per 100 mL  $\text{H}_2\text{O}$ .

As mentioned upstairs for  $\text{NH}_3$ , 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



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<sub>2</sub>O. 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 C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>. Its solubility is 210 g per 100 mL H<sub>2</sub>O. As sugars get even bigger and more complicated, however, 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?

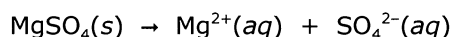
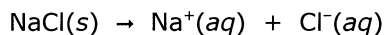


(Urea was described with its Lewis structure in Chapter 39. *p*-Dichlorobenzene received mention in Chapter 36. For this ranking, all you need to know for the latter is that it is nonpolar.)

Let's go to our final category.

#### • IONIC, SOLID PHASE SOLUTES IN WATER

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.

We're going to leave this at that, and close out this section.

We have covered quite a range of compounds here. We have seen the impact of enthalpy and of entropy on the interaction of various solutes with water and how this results in soluble/insoluble and miscible/immiscible. But the ramifications of these interactions go further than just simple 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.

### 40.3 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 CC and CH compounds or molecules which have portions thereof.



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<sub>4</sub>H<sub>9</sub> 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, a hydrophobic molecule has an aversion for water. Ironically, it's really 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 strong tendency or desire for. A hydrophilic molecule (hydrophile) interacts well with water. For example, we can say that ammonia is hydrophilic 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. (The word amphibian is one of the most common uses of this prefix.) An amphiphilic compound (amphiphile) has both a hydrophobic portion and a hydrophilic portion. The C<sub>4</sub>H<sub>9</sub> 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.

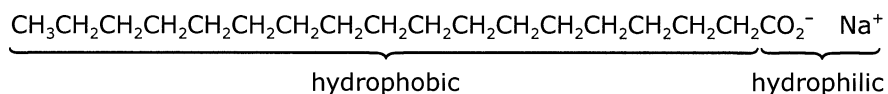
Common paper and natural cloth materials (e.g., cotton) are hydrophilic because they are made of cellulose which is a bunch of huge polysaccharides with lots of OH bonds. Water will wet these materials readily, hence their use as towel materials. Additives can change their properties; for example, wax 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 by 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.

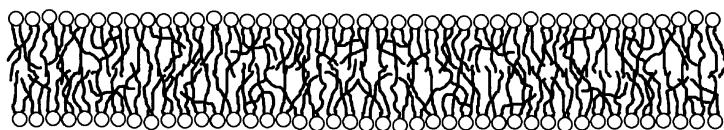
I cited 1-butanol above as an example of an amphiphile. It is soluble but its molecules do tend to huddle in aqueous solution. Now I want to talk about bigger and bigger amphiphiles containing a dozen or more carbon atoms. These can huddle into aggregates of specific kinds of structure.

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, NaC<sub>18</sub>H<sub>35</sub>O<sub>2</sub>.





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<sub>2</sub>O 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.



These bilayers wrap around the cell, totally encasing the cell; a portion is shown below right (not to correct scale). On both sides of the bilayer, you have the hydrophilic (ionic) portions in contact with the aqueous

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, the proteins in your cells or floating around in your blood are composed of hydrophilic and hydrophobic parts. Proteins can be huge molecules, many with masses over 10,000 g/mol and many over 100,000 g/mol. They can adopt a highly folded structure and the specific folding can determine whether you are healthy or ill, alive or dead. Much (although not all) of the specific folding is dependent on the same hydrophobic and hydrophilic interactions outlined here.



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.

#### 40.4 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

1. True or false.
  - a. Entropy opposes food oils from dissolving into water.
  - b. Entropy always favors ionic compounds dissolving in water.
  - c. The mixing of C<sub>6</sub>H<sub>14</sub>(l) and H<sub>2</sub>O(l) is favored by entropy.
  - d. Dissolving a gas in a solvent is favored by entropy.
  - e. Soaps are amphiphilic.

2. Consider each of the following types of compounds dissolving in water. For each case, indicate whether dissolving is favored or disfavored by entropy.
- a. polar gas            b. nonpolar liquid without hydrogen bonding            c. ionic solid
3. Consider the following compounds for dissolving into water.
- $\text{CH}_4(g)$              $\text{CH}_3\text{F}(g)$              $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3(g)$              $\text{CH}_3\text{OH}(l)$              $\text{C}_4\text{H}_9\text{OH}(l)$
- a. Which compound is most favored by entropy for dissolving into water?  
b. Which compound is most opposed by entropy for dissolving into water?
4. Consider the following compounds, all of which are liquids by themselves.
- $\text{C}_8\text{H}_{18}$              $\text{H}_2\text{O}_2$              $\text{CH}_2\text{Cl}_2$              $\text{HNO}_3 ((\text{HO})\text{NO}_2)$
- a. Two are miscible in water. Which are they?  
b. One is soluble but not miscible. Which is it?  
c. One is insoluble and immiscible. Which is it?
5. Of the following, which one is the most soluble in water (on a molar basis)?
- $\text{N}_2(g)$              $\text{I}_2(s)$              $\text{PH}_3(g)$              $\text{CH}_3\text{CO}_2\text{H}(l)$              $\text{C}_6\text{H}_6(l)$
6. For each compound, indicate whether it is hydrophobic, hydrophilic or amphiphilic.
- a.  $\text{C}_3\text{H}_8$             b.  $\text{C}_6\text{H}_{13}\text{OH}$             c.  $\text{N}_2\text{H}_4$