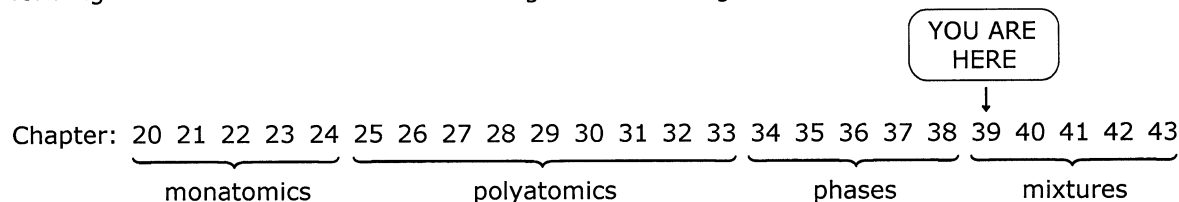


Chapter 39

MIXTURES, Part 1

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At this time, we start into the final stretch of our journey into the study of matter itself. Now we talk about mixtures. This is the tale of how different types of matter interact in a physical sense. This is not about reactions; reactions involve chemical change. This is about the physical changes associated with forming solutions and the reasons for doing so or not doing so.



39.1 Solutions

Our primary emphasis here is liquid phase solutions, especially aqueous. Our discussion will encompass all the aspects of solutions which we have been discussing since Chapter 9 such as solute, solvent, soluble and insoluble. In addition, we will add a new term: miscible. Miscible means mixable; specifically, it applies to two substances of the same phase which can dissolve into each other in any proportion. For example, the liquids methanol and water can mix in any ratio to form a homogeneous solution; we say methanol and water are miscible. Oil and water do not mix; we say oil and water are immiscible. The ability to mix in any ratio is called miscibility.

Be careful with the terms miscible and soluble. They're close in meaning but definitely not the same. Miscible goes beyond soluble. Since Chapter 10 we have described a soluble compound as one which dissolves to a significant extent, but even soluble compounds have a limit as to how much will dissolve. Miscible compounds can mix in any amount and can dissolve into each other in any amount; there is no limit. Note the distinction: both types dissolve, but soluble has a limit whereas miscible does not. Also, do not confuse immiscible with insoluble. Insoluble means the substance cannot dissolve to a significant extent; immiscible means the substance cannot dissolve to an unlimited extent. In some solvent, an immiscible compound may be soluble or it may be insoluble. For example, oil and water are immiscible and oil is insoluble in water. On the other hand, diethyl ether, $C_2H_5OC_2H_5$, is immiscible with water but it is soluble in water.

Although we will be primarily concerned with liquid phase solutions, here is a brief mention of the others. Gas solutions are not new. We covered gas mixtures in Chapter 16 and all of that still applies. All gases are fully miscible with all other gases. The air you breathe is N_2 , O_2 , Ar and whatever else is out there. It's one big gas solution which blankets the Earth, although it is constantly stirring. (I should specify filtered air because typical air does have floaters such as dust, soot, droplets, etc. Those things make the atmosphere heterogeneous.) The mixing of gases is always favored by entropy. Enthalpy does not play a significant role because the gas phase (ideally) has no IFs. This is all that we need to note here about gas solutions. Solid solutions are a different story. Some substances can homogeneously dissolve to form a solid solution although this often involves higher temperature conditions. Some alloys are solid solutions of two or more metals. (Other alloys are heterogeneous mixtures, so it's not always obvious.) Some gases can dissolve into solids; we noted this for graphite in the last Chapter.

From the discussion so far, we see that any phase can participate in forming a mixture. Nevertheless, our primary focus here will be liquid solutions. Furthermore, our primary focus will involve this planet's most important solvent, H_2O . Water's role in natural processes on Earth cannot be overstated, biologically or nonbiologically. All of life on Earth and all of surface Earth itself depend critically on the ability of water to dissolve or not to dissolve. These things are part of your world. They are an absolutely critical part of your world. And in your world, what is soluble is just as important as what is insoluble. The ions and sugars in your blood need to be soluble; your bones and cell membranes need to be insoluble.

As we proceed in our journey here, we shall continue to see the roles of enthalpy and of entropy. Together, these will determine soluble/insoluble and miscible/immiscible. We grazed the surface of this topic back in Section 10.3 with respect to ionic compounds dissolving in water.

“ It costs energy to overcome the ionic bonding in the solid compound. Something must pay that cost, or the compound will not dissolve and dissociate. The payment can come from

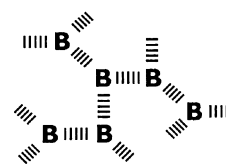
several sources, and that's where the strength of water's polarity comes into play. Another contribution can arise from entropy, but entropy can work for or against dissolving and dissociating. The entropy part is more complicated, and we're just not doing that right now. We'll come back to this point beginning in Chapter 39. For now, let's just deal with the simpler energy issues. ”

The energy (enthalpy) issues are again tied up in intermolecular forces. The entropy issues are again tied up in options. 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/immiscible), 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. We'll take a look at these parts separately. In this Chapter, we look at the enthalpy part, first from a qualitative viewpoint and then from a quantitative viewpoint. In Chapter 40, we'll bring in the entropy part and then we'll put the two parts together.

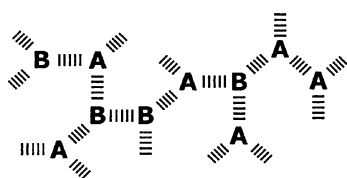
39.2 The enthalpy part



The enthalpy part of solutions is dominated by intermolecular forces. Let's begin this discussion by considering two substances, A and B. Substance A by itself (left) and substance B by itself (right) will have their own intermolecular forces operating, whichever IFs those may be. If we mix these two substances,



then the mixture of A and B will have a combination of various attractions available. Depending on the ratio of the two substances, there may still be attractions between separate molecules of A and there may still be attractions between separate molecules of B, but now we also have attractions between molecules



of A and B. I show a mix of all of these at left. The primary question to consider is how do all of these compare. The new A |||| B interactions displaced some A |||| A interactions and some B |||| B interactions. If these new A |||| B interactions are stronger than the A |||| A and B |||| B interactions which they displaced, then dissolving is exothermic. On the other hand, if the new A |||| B interactions are weaker than the displaced A |||| A and B |||| B interactions, then

dissolving is endothermic. Thus, dissolving can release energy or dissolving can cost energy. This energy of dissolving is called the enthalpy of solution, $\Delta H_{\text{soln}}^{\circ}$. An exothermic (negative) $\Delta H_{\text{soln}}^{\circ}$ favors dissolving and an endothermic (positive) $\Delta H_{\text{soln}}^{\circ}$ opposes dissolving. That's important. Let's spell it out again.

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

Know this.

The primary IFs which can operate in mixtures include our three prior IFs and also two others which we had put off from Chapter 37. We will now bring in those two additional IFs.

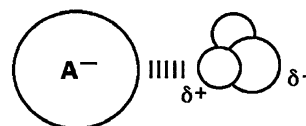
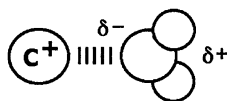
39.3 Two more IFs

The two additional intermolecular forces are ion-dipole and dipole-induced dipole interactions.

• ION-DIPOLE

The ion-dipole interaction is the attraction between an ion and a polar molecule's dipole. Actually, this is not a new consideration for us: this is the very first IF which we covered when we described it in Chapter 10 for water.

“ Opposite charges always attract each other. Those charges can be whole ion charges or they can be the fractional, partial charges of polar things. The net result is that a water molecule's partial charges will attract ions. The δ^- portion of the water molecules will attract cations. The δ^+ portion of the water molecule will attract anions. The illustration on the left shows the O side of one water molecule interacting with a generic cation (labeled C^+ for cation, not to be taken for carbon). On the right, the illustration shows the δ^+ on one H interacting with a generic anion (labeled A^-). A string of parallel lines (||||) is often used to emphasize an interaction and I've included it in the



illustrations here. (They're not always required and I won't always use them unless I want to for emphasis.) Notice how the ion charges and the partial charges are interacting, either with the polarity of the molecule overall or with the polarity of one bonded atom. These interactions are an essential feature of the hydration of ions.

The attractions between a polar molecule and an ion can be good but they're not always great. Some are better than others, but that depends on which ions are involved. For example, a water molecule is more attracted to a 3+ cation than to a 1+ cation. Even so, the attractions are often not as strong as full chemical bonds. However, they work very well for water for two reasons. First, because water's polarity is stronger than the polarity of most other liquids, each of these attractions is stronger in water than in most other solvents. Second, it's not just one water molecule which is interacting, it's a bunch. Each dissolved ion is surrounded by a bunch of water molecules, all piling around, often in layers, trying to get in on the charge attraction. There could be 10, 15, or more water molecules attracted to each and every single ion. Although one interaction is not so great, the grand sum of all interactions can be great. ”

That was only part of the discussion back then. At that time, we hadn't yet covered molecular polarity and we hadn't yet gotten into intermolecular forces, but that's what it was all about. Although we talked only about water at that time and that will remain our emphasis, the ion-dipole IF will apply for ions in any polar solvent.

In water and in other very polar solvents, the ion-dipole interaction is typically much stronger than the other IFs. There is a range of strengths for the ion-dipole interaction, and you can see in the Chapter 10 quote that the charge of the ion was one factor. Size will be another factor, but I will defer that discussion until we get into the quantitative aspects later in this Chapter.

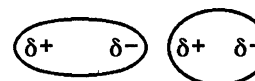
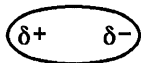
• DIPOLE-INDUCED DIPOLE

We actually did this one in Chapter 37. I used it to introduce the concept of the induced dipole.

“ Let me show you how an induced dipole can arise in a molecule. I'll pick a nonpolar molecule as our target subject here, which I'll illustrate as shown at right. Since nonpolar, it has a fully even distribution of charge throughout, on average.



If we bring a source of charge into this molecule's proximity, then that charge source will cause a distortion in the orbitals and this will form a dipole. A negative charge source repels the electrons in the orbital(s) of our target molecule; a positive charge source attracts the electrons in the orbital(s) of our molecule. I'll show this using a polar molecule, as depicted at left, as our source of nearby charge. The polar molecule has a permanent dipole and it has partial charges. When the polar molecule and our target nonpolar molecule come into proximity, the polar molecule causes (induces) a distortion in our target molecule, giving an imbalance in charge and hence a dipole. This is illustrated at right. That dipole only exists for as long as the polar molecule is close at hand. Once the polar molecule moves away, the target molecule goes back to nonpolar with an overall even distribution of charge, on average. ”



That's really the dipole-induced dipole IF, although I didn't call it such back then. Technically it can arise in single, pure compounds, but it is overshadowed by the other IFs and I simply left it out of primary coverage in Chapter 37. It's still meager even in many mixtures but this IF can become significant for mixtures of polar and nonpolar substances.

OK, this completes all IFs within our primary coverage here. We now have five primary IFs to consider for mixtures.

1. Dipole-dipole

2. Hydrogen bonding

3. Dispersion

4. Ion-dipole

5. Dipole-induced dipole

Let's take a look at some examples of some solutes in water. We'll see which of the above IFs arise in different cases. I need to point out that IFs for mixtures are much more complicated than IFs for a single compound by itself. Mixtures can be very difficult to assess, especially when water is the solvent. The principal goal here is to provide you with some illustrations so that you can see how some of these factors operate.

For typical ionic solutes in water, the ion-dipole interaction is so strong that it will typically far outweigh the other IFs. This will be the only primary IF which we consider for ionics and we won't even bother with the other IFs. On the other hand, for non-ionic solutes, we will consider the other IFs as follows.

Hydrogen bonding: If the solute can hydrogen bond with water, then this will typically be an important IF. (We will even see a variation on this below.)

Dipole-dipole: If the solute is polar, then dipole-dipole interaction can be important.

Dipole-induced dipole: Again, this IF is not usually a major contributor. It can be significant for simple, nonpolar solutes. For polar solutes, however, it will usually be outweighed by dipole-dipole and we can skip dipole-induced dipole for those cases.

Dispersion: Dispersion applies as always, and it will have a range of strengths. Expect better dispersion for larger solute molecules and/or solutes with softer atoms. Since water molecules are small, then more water molecules can be interacting all at once with a larger solute molecule.

Overall, depending on the type of molecular solute, hydrogen bonding and dispersion are typically the most important but dipole-dipole can also contribute substantially, especially for very polar solutes. Due to the additional complications with mixtures, however, we will simply list the primary IFs which operate for a particular solute in water. Here's the Operational Scheme for coming up with that list for any kind of solute.

OPERATIONAL SCHEME

Is the solute ionic or molecular?

Ionic: Ion-dipole is the only interaction which we will consider. Stop here for ionics.

Molecular (or simply atomic for Group 18): Put dispersion on the list. After that, there are two questions to consider.

Can the solute do hydrogen bonding with water?

If yes, put it on the list. If no, then don't.

Is the solute polar or nonpolar?

Polar: Add dipole-dipole to the list.

Nonpolar: Add dipole-induced dipole to the list.

This Scheme provides a general route for our purposes but, as is common, exceptions can happen.

Now, let's look at eight examples with various gas, liquid and solid solutes for illustration. We will list the primary IFs in each case between solute and water.

► He(g)

Helium is the smallest and simplest solute to consider. It is not ionic. It can do dispersion. It cannot do hydrogen bonding. It is not polar, so that leaves dipole-induced dipole. With only dispersion and dipole-induced dipole interactions with water, there's not much to work with, especially since He has the worst polarizability of any solute.

► CH₃Cl(g)

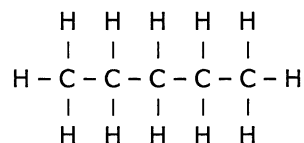
CH₃Cl is molecular. It can do dispersion. It cannot do hydrogen bonding. It is polar so it can do dipole-dipole with water.

► CH₃OH(l)

Methanol is molecular and can do dispersion with water. By itself (Section 37.6), it has hydrogen bonding going for it; it will be more than happy to do hydrogen bonding with water. Methanol is also polar, so we add dipole-dipole also to the list.

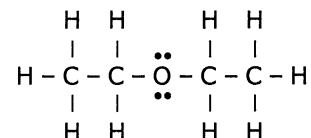
► C₅H₁₂(l)

The Lewis structure for pentane is repeated at right from Chapter 37 when we considered it by itself. Now let's consider its IFs with water. Pentane is molecular so we start with dispersion. It cannot do hydrogen bonding. It is not significantly polar, so that leaves dipole-induced dipole. The dispersion and dipole-induced dipole interactions will be greater given the bigger size of the molecule.

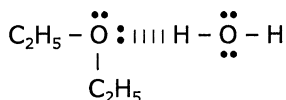


▶ $C_2H_5OC_2H_5(l)$

We also discussed diethyl ether in Chapter 37 and its Lewis structure is also repeated at right. Right away, dispersion. Diethyl ether is polar, so add dipole-dipole. What about hydrogen bonding? It certainly cannot do hydrogen bonding by itself but what about with water?



We now have a variation on hydrogen bonding to introduce at this time. All hydrogens in diethyl ether are bonded to carbons, so diethyl ether cannot donate one of its own H's into forming a hydrogen bond. On the other hand, diethyl ether does have an oxygen with lone pairs, so it can accept a hydrogen bond from water. This type of interaction is illustrated at left. This kind of hydrogen bonding opens up new possibilities for many compounds which cannot form hydrogen bonds by themselves, if the compound contains suitable lone pairs on suitable atoms.



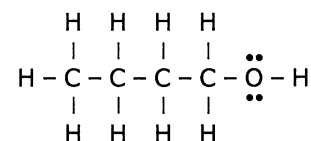
In these cases, the solute molecule acts as an acceptor of the hydrogen bond while the water molecule acts as the donor. This differs from the prior example of methanol which allowed for hydrogen bonding in both directions: both the methanol and the water could be a donor or an acceptor.

Notice that the compound must have suitable lone pairs on suitable atoms. Mostly, these will be lone pairs on O or N atoms; the O or N can be central or terminal atoms. Why lone pairs on O or N? That goes back to our discussion of hydrogen bonding back in Chapter 37: those atoms are among the best acceptors. Like all hydrogen bonding, there is a range to how strong these interactions can be.

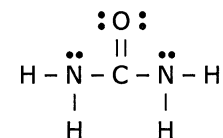
You may notice that I left fluorine compounds out of this new consideration here, although HF had been included in our hydrogen bonding in Chapter 37. Most covalent fluorine compounds lack significant acceptor strength to be included in our primary coverage. It's as if F is too electronegative to extend a lone pair to H. As such, those compounds are excluded here from our acceptor-only category. HF stands alone because it works both ways, as acceptor and as donor. That is a key feature for HF, because the acceptor and donor roles actually reinforce each other in a big way.

▶ $C_4H_9OH(l)$, 1-butanol

Let me introduce this as a new compound for consideration. The Lewis structure is at right. This compound fits in very well with our comparisons here since it is similar in size to pentane and to diethyl ether. Notably, 1-butanol and diethyl ether are isomers. 1-butanol has an OH bond, so it can do hydrogen bonding by itself and it can do hydrogen bonding with water; this hydrogen bonding is stronger than the acceptor-only hydrogen bonding for diethyl ether. 1-butanol is polar, so we can add dipole-dipole to the list. And there's always dispersion. In fact, compared to methanol earlier (which also does hydrogen bonding in both directions), the total IFs for 1-butanol in water are greater due to the larger size of the molecule.

▶ $(NH_2)_2CO(s)$, urea

This is also a new compound for consideration. Urea is an important biochemical compound since it is an important excretion product in urine. The Lewis structure is given at right. Urea is polar and it has a lot of hydrogen bonding of its own. As a solute in water, the primary IFs are hydrogen bonding, dipole-dipole and dispersion.

▶ $NaCl(s)$

I chose sodium chloride here to demonstrate a typical ionic solute. For ionic solutes, the primary IF will be ion-dipole. As noted earlier, that's the only one we'll consider.

OK, that concludes the eight examples. Again, they are meant to give some illustration of the various IFs which can apply in specific situations. We even saw a new variation on hydrogen bonding. Here, you try a few other compounds.

Example 1. Identify the primary IFs for each of the following with water. Each line is one IF.

$NH_3(g)$ _____

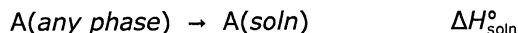
$CCl_4(l)$ _____

KBr(s)

With this, we conclude for now our qualitative discussion for enthalpy based on IFs. Now we get quantitative and we get into some thermodynamics for $\Delta H_{\text{soln}}^{\circ}$.

39.4 A quantitative look at $\Delta H_{\text{soln}}^{\circ}$

$\Delta H_{\text{soln}}^{\circ}$ is the standard enthalpy for dissolving any compound of any phase into any solvent.



For any one particular substance, we typically deal with the native phase of that substance. The native phase of a substance is its typical phase when pure and at standard (or close to standard) conditions. For example, the native phase of O_2 is (g), or the native phase of NaCl is (s), etc. For dissolving in water, we consider some generic compound A dissolving to form an aqueous solution given specifically by $A(\text{aq})$. The value of $\Delta H_{\text{soln}}^{\circ}$ primarily reflects the change in IFs upon placing A into water to form the solution. This goes back to the discussion earlier about A|B interactions versus A|A and B|B interactions, where B is now water. Depending on the native phase of A, we can break $\Delta H_{\text{soln}}^{\circ}$ into parts.

One big part of $\Delta H_{\text{soln}}^{\circ}$ involves hydration. Our description of hydration goes back to Chapters 10 and 11 in a qualitative fashion. We now quantify the strength of hydration by a new measure, the standard enthalpy of hydration, $\Delta H_{\text{hyd}}^{\circ}$. This is the standard enthalpy for the following conceptual process. Start with completely separated particles of some compound A; since fully separated, there are no IFs operating between them. Now dissolve them into water. Some energy is released as the IFs kick in between A and H_2O , forming A| H_2O interactions. On the other hand, this step also costs some energy because the solute must push away enough water molecules to make room for itself, which involves breaking up some H_2O | H_2O interactions. These costs can be significant, especially for bigger solute molecules, but the enthalpy of the overall hydration process is still dominated by the stronger A| H_2O interactions. Thus, $\Delta H_{\text{hyd}}^{\circ}$ values are always negative (exothermic).

In this scheme, the initial condition of "completely separated particles of some compound A" is depicted by the gas phase of A. Thus, we can depict the hydration process and its enthalpy $\Delta H_{\text{hyd}}^{\circ}$ by the following.



By this process, $\Delta H_{\text{hyd}}^{\circ}$ becomes an indicator of the total strength of the intermolecular forces between a solute and water. Stronger intermolecular forces between the solute and water will be reflected in a stronger enthalpy of hydration, meaning a more negative $\Delta H_{\text{hyd}}^{\circ}$. That's important; let me say it again.

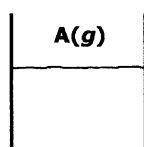
STRONGER INTERMOLECULAR FORCES BETWEEN THE SOLUTE AND WATER WILL BE REFLECTED IN A STRONGER ENTHALPY OF HYDRATION, MEANING A MORE NEGATIVE $\Delta H_{\text{hyd}}^{\circ}$.

Recall from earlier that

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

It is hydration which provides the exothermic part to the overall $\Delta H_{\text{soln}}^{\circ}$. Ultimately, stronger hydration favors dissolving. There can be more to this story and, at this stage, we will break this discussion into three Scenarios depending on the native phase of compound A.

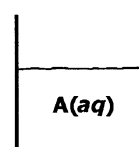
• SCENARIO 1: GAS 'A' DISSOLVING INTO WATER



For the cases where compound A is gas phase to begin with, then $\Delta H_{\text{hyd}}^{\circ}$ is the whole story and we're done. The dissolving equation is simply

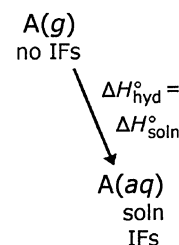


and that's the same as the hydration equation by itself.



Thus, for gas solutes, the enthalpy of solution and the enthalpy of hydration are the same. Since hydration enthalpies are always exothermic, then the enthalpy of solution for a gas phase compound is always exothermic.

At right is a pictorial summary for this process. It's very simplistic, but later summaries will be more involved. The initial system is the pure substance, $A(g)$, which has no IFs operating (assuming an ideal gas). The final system is the dissolved substance, $A(aq)$, which has one or more of the five IFs for solutions operating. Again, $\Delta H_{\text{soln}}^{\circ} = \Delta H_{\text{hyd}}^{\circ}$.



Let's look at some numbers.

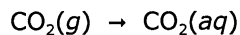
	He	O ₂	CH ₃ Cl
$\Delta H_{\text{soln}}^{\circ} = \Delta H_{\text{hyd}}^{\circ}$	-1.7 kJ	-11.7 kJ	-22.0 kJ

We had discussed He and CH₃Cl gases in our qualitative description previously. Note the piddly value for helium; it has the lowest $\Delta H_{\text{hyd}}^{\circ}$ of any substance in water because it has lousy IFs, even in solution.

By the way, all of our thermodynamic considerations from prior Chapters going back to Chapter 18 still apply here. For example, all of these values are per mole, following the convention from Chapter 19. You can say $\Delta H_{\text{hyd}}^{\circ} = -22.0$ kJ for CH₃Cl or you can say that the enthalpy of hydration for CH₃Cl is -22.0 kJ/mol. You can do stoichiometry with these kJ's for amounts other than one mol. You can also do the products-minus-reactants routine to get $\Delta H_{\text{hyd}}^{\circ}$. Here's one to do.

Example 2. Using ΔH_f° values from Appendix A, calculate $\Delta H_{\text{hyd}}^{\circ}$ for CO₂(g).

You'll need an equation.

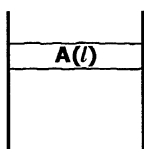


Get the ΔH_f° values and then do product-minus-reactant.

For your answer, you should get negative twenty-something.

OK, this Scenario of dissolving a gas into water is the easy one. Let's proceed to the others.

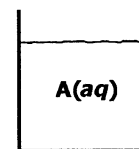
• SCENARIO 2: LIQUID 'A' DISSOLVING INTO WATER



We begin with the general equation for $A(l)$ dissolving in water; this gives the enthalpy of solution for $A(l)$.



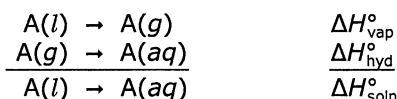
Let's bring in the definition for hydration. (Watch the phases here.)



Now we bring in the vaporization for liquid A and its corresponding enthalpy.



The reason for bringing in the enthalpy of vaporization is that these three equations are all related by the additivity of reactions or, otherwise, the conservation of mass/energy.



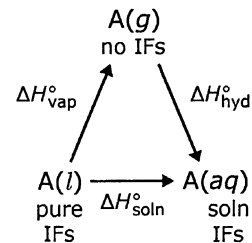
Thus, $\Delta H_{\text{soln}}^{\circ} = \Delta H_{\text{vap}}^{\circ} + \Delta H_{\text{hyd}}^{\circ}$. This combination provides us with a means to break down the solution process into separate terms, and these terms have been measured for many liquid compounds. Although the equations break down nicely, it is important to keep in mind the conceptual picture behind them.

Conceptually, we use $\Delta H_{\text{vap}}^{\circ}$ as the price which must be paid to pull apart all molecules of liquid A into individual molecules, as represented by gas phase. As we saw in Chapter 34, this price reflects the strength of the IFs between the molecules of A in its own liquid phase.

$\Delta H_{\text{hyd}}^{\circ}$ is the payback when the separated molecules of A are then dissolved into water. This payback primarily reflects the strength of the new IFs formed between molecules of A and molecules of water.

The sum is the overall dissolving or solution process. Here are two important points to note: all vaporizations are endothermic and all hydrations are exothermic. For overall dissolving, these two parts are in opposition. The grand result is that $\Delta H_{\text{soln}}^{\circ}$ can be endothermic or exothermic, depending on the relative values for $\Delta H_{\text{vap}}^{\circ}$ versus $\Delta H_{\text{hyd}}^{\circ}$.

At right is the pictorial summary for the processes involved. The dissolving equation is now the line at the bottom. The process begins with $A(l)$, which has one or more of the three IFs for pure substances holding the liquid phase together, and ends with the dissolved substance, $A(aq)$, which has one or more of the five IFs for solutions operating. We conceptually break this overall process into two steps, going through $A(g)$ which has no IFs. From the enthalpy terms for each step as shown, it can indeed be seen that the overall enthalpy, $\Delta H_{\text{soln}}^{\circ}$, is the sum of the two enthalpies, $\Delta H_{\text{vap}}^{\circ} + \Delta H_{\text{hyd}}^{\circ}$.



As you can see, this pictorial summary is more involved than the one for gas solutes previously. The summary shows all of the equations spelled out above. The summary shows the inter-relationships of all phases involved, the inter-relationships of all processes involved, and the differences in the IFs which are involved. This is the emphasis for now. On the other hand, if you only want to calculate a $\Delta H_{\text{soln}}^{\circ}$ for some substance, then you can still do this by the Chapter 19 method using ΔH_f° values and doing product-minus-reactant. All of that still applies. But for now, we keep the bigger emphasis.

Let's look at numbers for some of the liquids described earlier.

	C_5H_{12}	CH_3OH	C_4H_9OH
$\Delta H_{\text{vap}}^{\circ}$	26.8 kJ	38.00 kJ	52.4 kJ
$\Delta H_{\text{hyd}}^{\circ}$	-28.7 kJ	-45.27 kJ	-61.6 kJ
$\Delta H_{\text{soln}}^{\circ}$	-1.9 kJ	-7.27 kJ	-9.2 kJ

Notice that the enthalpies of vaporization are several dozens of kJ's as we had seen in Chapter 35. Notice that enthalpies of hydration are also several dozens of kJ's. Both of these reflect the energies of the intermolecular forces of their respective phases. Notice also how the values for $\Delta H_{\text{hyd}}^{\circ}$ of the three compounds fit our qualitative description earlier for these liquids with respect to their solution IFs.

The $\Delta H_{\text{soln}}^{\circ}$ values for all three of these compounds happen to be exothermic, so enthalpy favors dissolving for these. On the other hand, an exothermic $\Delta H_{\text{soln}}^{\circ}$ isn't always the case. For example, liquid hydrocarbons typically have values of $\Delta H_{\text{soln}}^{\circ}$ which are slightly endothermic or slightly exothermic. The $\Delta H_{\text{soln}}^{\circ}$ for pentane seen above is slightly exothermic at -1.9 kJ; we can compare this to $\Delta H_{\text{soln}}^{\circ}$ for other hydrocarbons such as hexane (C_6H_{14}) whose $\Delta H_{\text{soln}}^{\circ}$ is nearly zero, or benzene (C_6H_6) whose $\Delta H_{\text{soln}}^{\circ}$ is slightly endothermic at 2.1 kJ. Thus, in general, many liquid hydrocarbons give small +/- values for $\Delta H_{\text{soln}}^{\circ}$.

Alright, let's have you do a simple calculation.

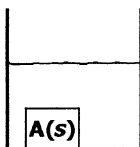
Example 3. For diethyl ether ($C_2H_5OC_2H_5$), the enthalpy of solution is -19.0 kJ. Using this, and $\Delta H_{\text{vap}}^{\circ}$ for diethyl ether in Section 35.5, calculate $\Delta H_{\text{hyd}}^{\circ}$ for this compound. Compare this result to $\Delta H_{\text{hyd}}^{\circ}$ values for C_5H_{12} and for C_4H_9OH in the list above. For these three molecules all of similar size, do the numbers fit the qualitative discussion earlier in this Chapter?

And now another Example, using ΔH_f° values.

Example 4. Using ΔH_f° values from Appendix A, calculate $\Delta H_{\text{soln}}^{\circ}$ for $CH_3OH(l)$.

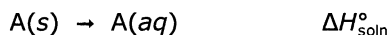
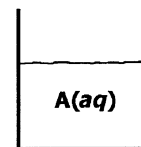
OK, this ends liquid solutes. Now solids.

• SCENARIO 3: SOLID 'A' DISSOLVING INTO WATER



For this Scenario, we will consider molecular solids and ionic solids separately. The molecular solids in our coverage will be nonelectrolytes.

The breakdown for molecular solids follows the same routine as for liquids above but we use sublimation instead of vaporization. We begin with the equation for dissolving A(s) in water.



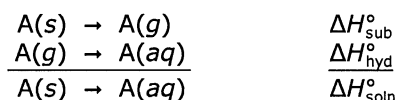
We again bring in the hydration equation.



Now we need sublimation for A(s).

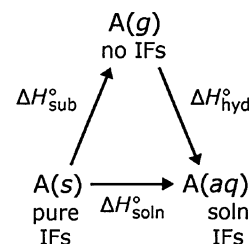


Here's the additivity part for these equations.



This leads to $\Delta H_{\text{soln}}^{\circ} = \Delta H_{\text{sub}}^{\circ} + \Delta H_{\text{hyd}}^{\circ}$. $\Delta H_{\text{sub}}^{\circ}$ is the price to pay to pull all of the molecules in the solid apart from each other. $\Delta H_{\text{hyd}}^{\circ}$ is the payback when these molecules are placed into water. The sum is $\Delta H_{\text{soln}}^{\circ}$.

At right is the pictorial summary for these processes. The initial system is the pure, molecular solid, A(s), which has one or more of the three IFs for pure substances holding the solid together. The final system is the dissolved substance, A(aq), which has one or more of the five IFs for solutions operating. We again conceptually break the overall process into two steps, going through A(g), which has no IFs. It can again be seen that the overall enthalpy, $\Delta H_{\text{soln}}^{\circ}$, is the sum of two enthalpies, now $\Delta H_{\text{sub}}^{\circ} + \Delta H_{\text{hyd}}^{\circ}$.



Here are values for urea and for naphthalene, C₁₀H₈ (mothballs, Chapter 36), for illustration purposes.

	(NH ₂) ₂ CO	C ₁₀ H ₈
$\Delta H_{\text{sub}}^{\circ}$	98.6 kJ	72.9 kJ
$\Delta H_{\text{hyd}}^{\circ}$	-84.6 kJ	-45.4 kJ
$\Delta H_{\text{soln}}^{\circ}$	14.0 kJ	27.5 kJ

Notice the positive values for $\Delta H_{\text{soln}}^{\circ}$. Unlike liquids which can be either way, solution enthalpies for molecular solids are usually endothermic because we are paying more to break up a solid.

Here, you can do *p*-dichlorobenzene, C₆H₄Cl₂.

.....
Example 5. Calculate the enthalpy of hydration for *p*-dichlorobenzene, C₆H₄Cl₂. Its enthalpy of solution is 20.5 kJ; its enthalpy of sublimation was listed in Section 36.1.

This will finish the category for molecular solids.

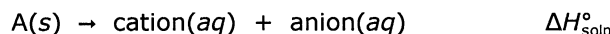
Now we consider ionic solids. These are handled a bit differently, for two important reasons. The first is that the solid is now held together by full ionic chemical bonding; this is not just IFs anymore. Thus, we must deal with the hundreds-to-thousands of kJ's per mol for ionic bonding and not just the several dozens of kJ's due to IFs. That's where ion-dipole interaction comes in; as noted earlier, this is the strongest of all IFs. The grand total in energy for all water molecules which are interacting with ions

is now in the hundreds and even thousands of kJ's per mol range; thus, the total ion-dipole interaction can now compete with chemical bond energies. Some of the strongest cases actually lead into a whole different ballgame associated with "complexes", but we're going to wait until later in Chapter 59 to get into those. For now, we'll just stick with some basics.

The second important reason is that the thermodynamic coverage typically breaks the process into fully dissociated, individual ions. Thus, the usual solution equation for dissolving



is broken into the constituent ions to give the following.

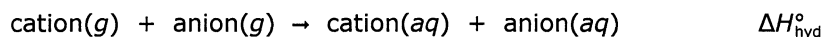


Thus, under conditions of full dissociation, $A(aq)$ becomes $\text{cation}(aq) + \text{anion}(aq)$. This is essentially a net ionic approach, as first noted near the end of Section 19.3.

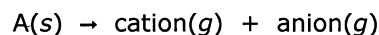
“ Here's an important point to note: if any reagent in an aqueous reaction is a strong electrolyte, then you must work in net ionic format for the balanced equation. Tables of ΔH_f° values are generally compiled for the net ionic approach. If you check Appendix A, you will find $\text{NaCl}(s)$ but you will not find $\text{NaCl}(aq)$. In net ionic format, $\text{NaCl}(aq)$ would be written as $\text{Na}^+(aq) + \text{Cl}^-(aq)$; ΔH_f° values for both of those ions are in Appendix A and you add them together to get the value for $\text{NaCl}(aq)$. This is important now and it will be important later in Chapters 39 and 44. ”

Later is now. Be careful with this.

For the hydration part, we still work with gas phase going into aqueous phase but we modify the equation to deal with the dissociated ions in both phases.



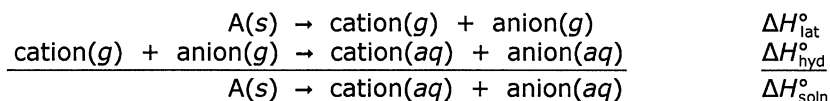
For our final part, we need to take solid A to gas phase ions.



Fortunately, this step is not a new process: this is lattice energy from Section 25.2!

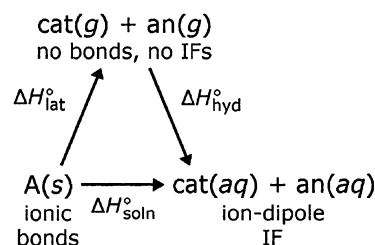


Now we can do the additivity of reactions.

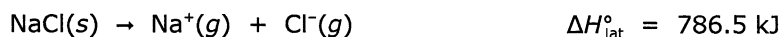


This gives us $\Delta H_{\text{soln}}^{\circ} = \Delta H_{\text{lat}}^{\circ} + \Delta H_{\text{hyd}}^{\circ}$.

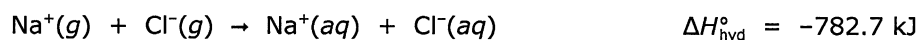
At right is the pictorial summary for these processes. The initial system is the pure ionic compound, $A(s)$, which now has full ionic bonding holding the 3D network solid together. The final system is the dissolved substance, now fully dissociated into separate cations and anions (abbreviated as $\text{cat}(aq)$ and $\text{an}(aq)$); these are held in solution by the strongest IF, ion-dipole. We again conceptually break the overall process into two steps, going through fully separated (noninteracting) cations and anions in the gas phase. It can again be seen that the overall enthalpy, $\Delta H_{\text{soln}}^{\circ}$, is the sum of two enthalpies, now $\Delta H_{\text{lat}}^{\circ} + \Delta H_{\text{hyd}}^{\circ}$.



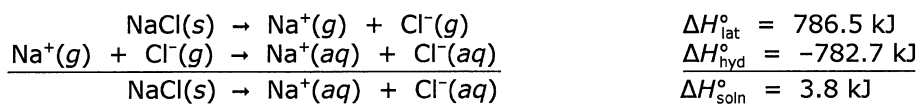
We'll do a specific example using NaCl. We dealt with the lattice energy equation for NaCl in Chapter 25.



The hydration equation for NaCl is the following.



From these, we can determine the enthalpy of solution.



Note that dissolving NaCl in water is endothermic, although the amount is modest.

It is important to point out the very large magnitudes here of $\Delta H_{\text{lat}}^{\circ}$ and $\Delta H_{\text{hyd}}^{\circ}$ compared to the enthalpies involved in our prior examples. The lattice enthalpy is in the hundreds of kJ's and not dozens of kJ's because we are dealing with full ionic bonding and not just IFs. The hydration enthalpy is likewise hundreds of kJ's due to the great strength of the grand total of all interactions between the dissociated ions and the many water molecules which interact with those ions.

Back in Chapter 25 we discussed two factors which influence lattice enthalpies: ion size and charge.

“ SMALLER IONS can form STRONGER IONIC BONDS which is reflected in HIGHER LATTICE ENTHALPIES. ”

“ HIGHER CHARGES give STRONGER IONIC BONDS as reflected in HIGHER LATTICE ENTHALPIES. ”

Now these two factors also influence the strengths of the ion-dipole IF and of the total hydration enthalpy.

SMALLER IONS and HIGHER CHARGE IONS give STRONGER ION-DIPOLE INTERACTION and STRONGER (MORE NEGATIVE) HYDRATION ENTHALPIES.

I will now introduce a new term at this time: charge density, also called charge-to-radius ratio. This term just combines the charge and size factors into one ratio.

$$\text{charge density} = \text{charge-to-radius ratio} = \frac{\text{charge of ion}}{\text{size of ion}}$$

This relationship is primarily of qualitative interest. In other words, we typically don't do actual numbers with it. We usually just use it in trends. A larger charge gives a larger charge density; a smaller ion also gives a larger charge density. An ion of higher charge and/or a smaller ion gives a more concentrated charge and that's what is strengthening these effects. We can restate the trends for lattice enthalpy and for hydration enthalpy accordingly.

A HIGHER CHARGE DENSITY gives a HIGHER LATTICE ENTHALPY and a STRONGER (MORE NEGATIVE) HYDRATION ENTHALPY.

Back in Chapter 25, we saw two lists for lattice enthalpies, one for Group 1 fluorides and one for lithium halides. Here now are two lists for standard enthalpies of hydration (kJ) for the same selection

LiF	-1,041.8	of ionic compounds. From the data at left, notice	LiF	-1,041.8
NaF	-927.0	that the hydration enthalpy weakens as the cation	LiCl	-897.4
KF	-843.9	gets larger. At right, notice the hydration enthalpy	LiBr	-866.8
RbF	-818.8	weakens as the anion gets larger. You can compare	LiI	-824.8
CsF	-794.2	these values to the values in Chapter 25 and see the		
		same trends for the lattice enthalpies back then.		

Let me illustrate a charge effect on hydration. We'll compare CaS versus NaCl. For these two, the cations are similar size and the anions are similar size, so the big difference is that CaS has a 2+/2- ion combination while NaCl has 1+/1-. $\Delta H_{\text{hyd}}^{\circ}$ for NaCl is -782.7 kJ; for CaS, $\Delta H_{\text{hyd}}^{\circ} = -3,100$ kJ which is huge. As we had seen for lattice enthalpy, charge also has a huge effect for hydration.

Notice that higher charge density makes the lattice stronger and it makes hydration stronger, but these oppose each other for dissolving. Thus, the final enthalpy of solution may be endothermic or it may be exothermic, and it will depend on the specific compound involved. We can illustrate this with several compounds from above.

.....

Example 6. Use the hydration enthalpies above and lattice enthalpies from Chapter 25 to fill in the table below; then calculate the corresponding enthalpies of solution for LiF, LiCl and KF.

.....

	LiF	LiCl	KF
$\Delta H_{\text{lat}}^{\circ}$	_____	_____	_____
$\Delta H_{\text{hyd}}^{\circ}$	_____	_____	_____
$\Delta H_{\text{soln}}^{\circ}$	_____	_____	_____

The answers for $\Delta H_{\text{soln}}^{\circ}$ are -35 kJ , -17 kJ and 5 kJ , but you figure out which is which.

Upstairs, $\Delta H_{\text{soln}}^{\circ}$ was 3.8 kJ for NaCl. Overall, if you compare these four compounds, you will find that there is no trend for the effect of ion size on $\Delta H_{\text{soln}}^{\circ}$. You just have to do the math for each case. This will be true in general: some ionic compounds will dissolve exothermically and some will dissolve endothermically. Here are just a few more examples for illustration purposes.

$\Delta H_{\text{soln}}^{\circ}$: CaCl_2 , -81.4 kJ Li_2SO_4 , -29.9 kJ NH_4Cl , 14.9 kJ KNO_3 , 37.2 kJ

Not only can $\Delta H_{\text{soln}}^{\circ}$ values be exothermic or endothermic, but they can also be small or substantial either way.

We are now seeing a large part of the explanation behind an important issue in Section 10.3 regarding the enthalpies involved for dissolving ionic compounds.

“ With respect to energies, the question of solubility and of dissociation for an ionic compound in water boils down to two opposing factors.

- ▶ 1. The strength of the ionic bonding between all the cations and all the anions in the ionic network compound.
Those ionic bonds are holding the solid together. You must break those ionic bonds, so this is the price which must be paid for solubility and for dissociation.
- ▶ 2. The strength of the attractions between water molecules and the individual cations and anions.
This is the hydration part which pays toward the total expense of solubility and dissociation.

THESE TWO STRENGTHS ARE IN OPPOSITION TO EACH OTHER. The first favors the ionic compound staying together as a solid and NOT dissolving. The second favors dissolving and dissociating. ”

We said that in Chapter 10 in a descriptive sense. Now we say it with numbers and now we know the reasons behind it. Notice that the two parts refer to $\Delta H_{\text{lat}}^{\circ}$ and $\Delta H_{\text{hyd}}^{\circ}$ respectively.

With this, we close on the ionic solids.

39.5 Not the whole story

Notice for the various examples that we have seen that some compounds have a negative $\Delta H_{\text{soln}}^{\circ}$ while other compounds have a positive $\Delta H_{\text{soln}}^{\circ}$. Don't forget the significance of this, as stated twice already in this Chapter.

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

Notice that the verbs are "favors" and "opposes". These are NOT guarantees. Some solutes with an exothermic $\Delta H_{\text{soln}}^{\circ}$ will be soluble but others will be insoluble. Some solutes with an endothermic $\Delta H_{\text{soln}}^{\circ}$ will be insoluble but others will be soluble. Why? We haven't yet covered the whole story. Keep in mind that enthalpy is only one part of dissolving. Entropy is the other part, and that's where we go next.

Problems

1. True or false.
 - a. An aqueous solution of KF has ion-dipole interaction.
 - b. Dissolving a gas into water is always exothermic.
 - c. All gases are miscible with other gases.

- d. An exothermic enthalpy of solution will favor dissolving.
 e. A zinc cation has a greater charge density than a silver cation.
2. True or false.
 a. CH_4 can do hydrogen bonding in water.
 b. All ionic compounds have a negative $\Delta H_{\text{soln}}^\circ$.
 c. Higher charge density gives stronger lattice enthalpy and stronger hydration.
 d. A sulfide ion has a higher charge density than an oxide ion.
 e. Water cannot do dispersion with any solute.
3. For each compound below in water, list the primary intermolecular forces which are operating between the compound and the water.
 a. KBr b. H_3CNH_2 c. Br_2 d. HF
4. For each compound below in water, list the primary intermolecular forces which are operating between the compound and the water.
 a. PH_3 b. SiF_4 c. C_3H_8 d. CHCl_3
5. Of the following, which one has the greatest (most negative) enthalpy of hydration?
 NaCl KBr MgO CaS BaO
6. Consider the following enthalpy terms related to phase changes and solutions.
 $\Delta H_{\text{vap}}^\circ$ $\Delta H_{\text{sub}}^\circ$ $\Delta H_{\text{lat}}^\circ$ $\Delta H_{\text{hyd}}^\circ$ $\Delta H_{\text{soln}}^\circ$
- a. Which term represents the change in enthalpy which is required to separate the molecules of a pure liquid?
 b. Which term represents the change in enthalpy upon dissolving a liquid into water?
 c. Which terms are ALWAYS negative (exothermic)?
 d. Which terms are ALWAYS positive (endothermic)?
7. a. For $\text{C}_6\text{H}_6(l)$, $\Delta H_{\text{hyd}}^\circ = -31.8 \text{ kJ}$ and $\Delta H_{\text{soln}}^\circ = 2.1 \text{ kJ}$. What is $\Delta H_{\text{vap}}^\circ$ in kJ?
 b. For $\text{I}_2(s)$, $\Delta H_{\text{sub}}^\circ = 62.42 \text{ kJ}$ and $\Delta H_{\text{soln}}^\circ = 22.6 \text{ kJ}$. What is $\Delta H_{\text{hyd}}^\circ$ in kJ?
8. Using enthalpies of formation, calculate $\Delta H_{\text{vap}}^\circ$, $\Delta H_{\text{hyd}}^\circ$ and $\Delta H_{\text{soln}}^\circ$ (in kJ) for hydrazine, N_2H_4 . (The native phase is liquid.)
9. Write the equation for $\text{ZnCl}_2(s)$ dissolving into water. Using enthalpies of formation, calculate $\Delta H_{\text{soln}}^\circ$ (in kJ). Is dissolving endothermic or exothermic?