

Chapter 41

SOLUTION EQUILIBRIA

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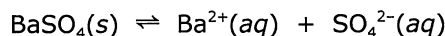
We continue with mixtures, specifically with solutions, but with a different emphasis. Our focus in this Chapter is on the equilibrium process of solubility and the factors which can influence that equilibrium.

41.1 Solubility and equilibrium

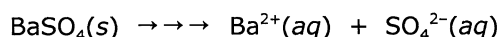
Solubility and insolubility are important equilibrium processes. These actually provided our very first introduction to equilibrium back in Chapter 12 as applied to ionic solutes.

“ Chemical equilibrium will occur whenever opposing forces are operating within a chemical system. There will be a competition.

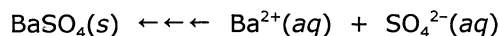
Let's apply this to our solubility discussion from Chapter 10. When you have an ionic solid in contact with water and part of that ionic solid is dissolved, even a tiny part, then you have an equilibrium. The opposing forces are the ionic bonds and water's hydration: the ionic bonds are trying to hold the solid together while the water is trying to pull the ions apart. We commonly designate an equilibrium process by a chemical equation which uses double-half-arrows instead of the usual single-full-arrow. I'll give an example, using barium sulfate again since we had talked about it so much previously.



Here's the important meaning of the double-half-arrows: BOTH directions of the reaction are possible. One direction is the forward, left-to-right direction



which tells us that some BaSO_4 can dissolve (although it's a tiny amount). The other direction is the backwards or the reverse



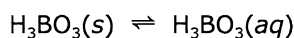
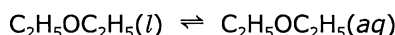
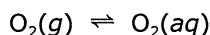
and it tells us that barium ions and sulfate ions can form solid barium sulfate (which is precipitation). I want to emphasize here that the double-half-arrows mean both directions are possible. They don't mean both directions are equally important. As a matter of fact, most equilibria are not equally important in both directions. For barium sulfate, we know dissolving is minuscule. ”

Back in those Chapters, the important contributions to solubility were the energies of the ionic bonds (now reflected in $\Delta H_{\text{lat}}^\circ$) and the energies of hydration (now $\Delta H_{\text{hyd}}^\circ$). We couldn't do much with entropy back then, although its importance had been forecast in Chapter 10.

“ 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. ”

Now here in Chapter 41, thirty-one chapters after the introduction of barium sulfate as our first example of an insoluble compound, I will tell you that both enthalpy and entropy oppose dissolving BaSO_4 . Its $\Delta H_{\text{soln}}^\circ$ is endothermic, 26.3 kJ/mol, and it has a negative $\Delta S_{\text{soln}}^\circ$.

Equilibrium is true for all soluble and insoluble solutes, not just ionic solids. Thus, the solubility equations described in the last Chapter can be written in their equilibrium format, such as shown in the following examples.



Equilibrium is about balance and the ability to go in either direction to achieve balance. Equilibria are dynamic. Let me illustrate these points for each example shown.

For $O_2(g)$ in contact with water, some $O_2(g)$ molecules can dissolve into the water and some $O_2(aq)$ molecules can escape back to gas phase.

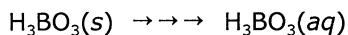
For a liquid layer of diethyl ether floating on top of water, some molecules of $C_2H_5OC_2H_5(l)$ can dissolve into water and some $C_2H_5OC_2H_5(aq)$ molecules can return to its own liquid phase.

For solid boric acid in contact with water, some $H_3BO_3(s)$ molecules can dissolve and some $H_3BO_3(aq)$ molecules can return to the solid phase.

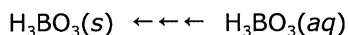
Thus, both directions of each equilibrium can occur. At the point of equilibrium, the two directions will continue to operate but they operate at the same speed. At the point of equilibrium, enthalpy and entropy are in balance. At the point of balance, there will be some steady concentration of the solute in the solution.

Let me bring in a bit of terminology here.

For cases which deal with solids as solutes, the process of going from dissolved solute to solid phase can go by several terms. Two of the terms are related: they are crystallization or recrystallization. Citing the boric acid example above, we can say that the forward direction



represents the dissolving or solution process while the reverse direction



represents the crystallization or recrystallization process. These terms can apply for molecular solids and also for ionic solids. On the other hand, for gas and liquid solutes, there are no commonly used terms which are analogous to the terms crystallizing or recrystallizing.

The other terminology which I want to bring in here goes back to the paragraph which you starred in Chapter 35 for vaporization/condensation.

“ "Saturated" means the system contains the equilibrium amount of water vapor. Since the system is at equilibrium, condensation and vaporization occur at the same speed. "Unsaturated" means the actual vapor pressure is less than EVP; under this condition, more vaporization is possible before reaching EVP. "Supersaturated" means the actual vapor pressure is greater than EVP; under this condition, more condensation is possible before reaching EVP. ”

At that time, we applied those terms to water in the gas phase. Now we apply the same terms to a solute in water (or in any solvent, for that matter).

A saturated solution contains the equilibrium amount of substance dissolved in solution. If excess of that substance is also present as its own (s), (l) or (g) phase, then the system is at equilibrium.

An unsaturated solution has less substance dissolved than the equilibrium amount.

A supersaturated solution has more substance dissolved than the equilibrium amount.

Notice that unsaturated and supersaturated solutions are not at equilibrium.

As a specific example, I'll refer again to boric acid. In the last Chapter, its solubility was given as 5.8 g per 100 mL H_2O .

At equilibrium, with some $H_3BO_3(s)$ also present, the solution is saturated and it contains 5.8 g $H_3BO_3(aq)$ per 100 mL H_2O .

A solution which contains 5.0 g $H_3BO_3(aq)$ per 100 mL H_2O is unsaturated.

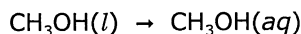
A solution which contains 7.0 g $H_3BO_3(aq)$ per 100 mL H_2O is supersaturated.

An unsaturated solution can still dissolve more. A supersaturated solution has too much dissolved relative to the point of equilibrium. A saturated solution at equilibrium has a steady concentration of the dissolved solute. In all of these cases, the system is still dynamic, and both the forward and the reverse directions can be happening, but these directions are in balance and in equilibrium only in the case of saturation.

Supersaturated solutions are not as common as unsaturated or saturated. You can't just throw a pure compound into a bucket of water and have the solution become supersaturated. It won't work that way. Supersaturated conditions are usually achieved by changing the temperature, by changing the pressure, or by chemical reactions. They can be a bit tricky to achieve.

That ends the terminology for now. Before closing out this section, I need to make an important distinction for miscibility. As just described, soluble and insoluble solutes involve equilibrium. On the

other hand, miscible solutes do not involve equilibrium. They can mix in any amount and they cannot saturate. Let's illustrate with methanol.

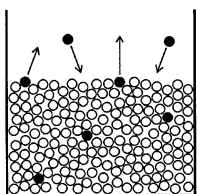
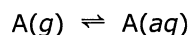


Left to itself, any amount of methanol dissolved in water will stay dissolved and will not reform the liquid phase. Thus, there is no opposing process here and this is not an equilibrium system. That's all there is to know for miscibles.

For now, we are going to work a bit more with equilibrium aspects for solubility. Most of these aspects deal with gas phase solutes and we will cover these first. For liquid and solid phase solutes, there will only be a little to add at this time. Later in Chapters 59 and 60, however, we will go further into the quantitative aspects of the equilibria of solubility, especially for ionic solutes.

41.2 Solution equilibria for gas-phase solutes

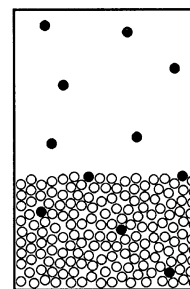
Consider a gas phase in contact with liquid water. Upstairs we looked at the equilibrium equation for O_2 but let's now go generic with some gas compound A. The equilibrium process is



which we can break down as follows. Molecules of $\text{A}(g)$ are whizzing around above the water's surface. Through their normal travels, they will sometimes strike the surface of the water; upon striking the water surface, they usually bounce off and stay in the gas phase but sometimes they are trapped into the solution. The latter is the dissolving process. Molecules of $\text{A}(aq)$ are now in the solution, mixed in with the H_2O molecules. Through the normal, albeit more restricted, motions of the liquid phase, molecules of $\text{A}(aq)$ can eventually arrive back at the surface and can then escape back to gas phase.

(By the way, the water itself is also doing its usual vaporization and condensation, so there are also $\text{H}_2\text{O}(g)$ molecules in the gas space. That part is totally separate from the process involving solute A. We already covered vaporization and condensation in Chapter 35 so that's not part of this present discussion, although there are some parallels.)

In a closed container with some fixed, total amount of compound A, there will come a time when the speed of $\text{A}(g)$ dissolving into solution equals the speed of $\text{A}(aq)$ escaping to gas phase. That's the point of balance, the point of equilibrium. At this point, there will be a steady concentration of $\text{A}(aq)$ in solution and a steady concentration of $\text{A}(g)$ in the gas space. The steady concentration of $\text{A}(aq)$ at equilibrium represents the solubility of A. For the gas phase part, as always, we can relate the concentration of $\text{A}(g)$ to its pressure.



$$P = \text{concentration} \times R \times T$$

$$P = \frac{n}{V} \times R \times T$$

This connection allows us to treat $\text{A}(g)$ in terms of concentration or pressure (at a fixed temperature). We'll use pressure.

If we increase the total amount of A in the system, then there will be more $\text{A}(g)$ in the gas space and more $\text{A}(aq)$ dissolved in solution at equilibrium. Both amounts will be higher, but it turns out that their ratio is fixed: the ratio of the concentration of $\text{A}(aq)$ to the pressure of $\text{A}(g)$ is a constant at equilibrium. We can write this as follows.

$$\frac{\text{concentration of } \text{A}(aq)}{\text{pressure of } \text{A}(g)} = \text{a constant}$$

Rearrangement gives us a common version of the relationship.

$$\text{concentration of } \text{A}(aq) = \text{constant} \times \text{pressure of } \text{A}(g)$$

This equation says that the equilibrium concentration of dissolved $\text{A}(aq)$ is proportional to the pressure of $\text{A}(g)$ in the overhead gas space. In other words, the solubility of solute A is proportional to its gas's pressure. That's what I said in the last Chapter with our first example of $\text{He}(g)$ dissolving in $\text{H}_2\text{O}(l)$.

“ Notice that I specified a pressure of one atm; the solubility for gases is greatly dependent on the overhead gas pressure, as we'll see in the next Chapter. ”

If you double the pressure overhead, then the solubility doubles; if you halve the pressure overhead, then the solubility is halved. It's all directly proportional.

The constant in the above equations goes by the moniker of "Henry constant". (The proportionality relationship for gas solubility was historically known as Henry's law.) Various symbols have been used over the years for the constant such as k_H , K_H , H , etc.; we'll use k_H . The solubility of A in solution can be expressed in various concentration units; here, we'll use molarity. For the pressure of A in the gas phase, we'll use atm. With these units, we can write the proportionality as

$$[A(aq)] = k_H \times P_A$$

and k_H will have the units of M/atm. Again, this equation applies for equilibrium; $[A(aq)]$ is the solubility of A in a saturated solution. This is also for ideal conditions, which means it may be somewhat off for real systems. Deviations will be more likely at higher concentrations of $A(aq)$, which means a higher value of k_H and/or a higher pressure of $A(g)$.

Here are values of k_H (in M/atm) for various gases discussed in the last Chapter.

He, 0.00038

O₂, 0.0013

C₃H₈, 0.0015

NH₃, 60.

A larger value for k_H means a greater solubility of the gas. Here are some values for other gases, for illustration purposes.

N₂, 0.00065

CO, 0.00098

CO₂, 0.034

H₂S, 0.10

CH₃SCH₃, 0.54

SO₂, 1.4

As you can see, the values can range from very small up through several dozen for the most soluble gases such as NH₃. The very small values represent "insoluble" gases. All values given here are for 25 °C.

Let's do a simple calculation. What is the solubility of O₂ in water if the O₂(g) pressure is 1.00 atm?

The first thing you need is your gas solubility equation.

$$[O_2(aq)] = k_H \times P$$

Enter the k_H from the list above and enter the given pressure.

$$[O_2(aq)] = 0.0013 \frac{\text{M}}{\text{atm}} \times 1.00 \text{ atm} = 0.0013 \text{ M}$$

Thus, the solubility of O₂ is 0.0013 M and that's all there is to this.

Now, repeat the problem for a bucket of water which is open to air in which O₂ has a pressure of 0.21 atm.

$$[O_2(aq)] = 0.0013 \frac{\text{M}}{\text{atm}} \times 0.21 \text{ atm} = 0.00027 \text{ M}$$

Now, the solubility of O₂ is 0.00027 M. Notice the solubility decreased at the lower pressure.

These are fairly straightforward so far, although they can get a bit more complicated. Once you have a molarity, you can derive other amounts also. For example, let's say the water volume in the above bucket is 3.26 L. Now, how many grams of O₂ are dissolved at equilibrium? Well, this is really nothing new. You have the molarity from the above calculation; molarity and volume get you moles; moles and molar mass get you grams.

$$3.26 \text{ L soln} \times \frac{0.00027 \text{ mol O}_2}{\text{L soln}} \times \frac{32.00 \text{ g O}_2}{\text{mol O}_2} = 0.028 \text{ g O}_2$$

That tells you that 0.028 g of O₂ is dissolved in the water in the bucket. For a container of water exposed to air, then all of the components of air are dissolved in that water. Thus, an open bucket of water contains N₂(aq), O₂(aq), Ar(aq), etc. Here, you do a calculation.

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Example. For the 3.26 L H₂O in the above bucket, how many grams of N₂ are dissolved in the water at equilibrium? Use P of N₂(g) = 0.78 atm.

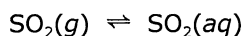
Start with the gas solubility equation to get a molarity. Then convert molarity to mol for the given volume, and then to g using molar mass.

$$\text{Gas solubility: } [N_2(aq)] = \frac{\text{M}}{\text{atm}} \times \text{atm}$$

$$\text{Then: } 3.26 \text{ L soln} \times \frac{\text{mol } N_2}{\text{L soln}} \times \frac{\text{g } N_2}{\text{mol } N_2} = \text{g } N_2$$

To avoid a round-off error, don't round off the molarity before plugging it into the second equation.

You can go the other way around with these calculations, also. Let's say you have a solution of SO_2 dissolved in water. You pour this into a fresh container, evacuate the air, and then close off the container while leaving a gas space inside. Some $SO_2(aq)$ will escape to the gas phase, eventually giving a dynamic equilibrium.



If $[SO_2(aq)] = 0.064 \text{ M}$ at equilibrium, what is the pressure of $SO_2(g)$ in the gas space of the container?

To do this, start with your solubility equation.

$$[SO_2(aq)] = k_H \times P$$

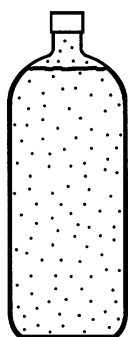
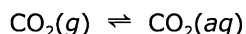
Enter the given concentration and the k_H .

$$0.064 \text{ M} = 1.4 \frac{\text{M}}{\text{atm}} \times P$$

Rearrange and solve for P : you get 0.046 atm for the pressure of $SO_2(g)$ in the gas space.

These calculations have a lot of importance in many areas. An extremely important application involves environmental chemistry. Any air-borne substance will also be water-borne. In other words, any gas component in the atmosphere, friend or foe, can dissolve in a body of water, even if it's a minuscule amount. Also, if compounds are produced or dumped into water, then they can escape to the atmosphere. An important natural example is dimethyl sulfide, CH_3SCH_3 , whose k_H is included in the list above. This compound is produced in huge amounts by microorganisms in the oceans of the Earth. It then escapes to the atmosphere and it's actually part of the smell of the ocean. In the atmosphere, it ultimately reacts and contributes to acid rain. In such an application, k_H values provide important connections for calculating the equilibrium distribution of a compound in air versus its concentration in an ocean or lake or whatever. (k_H values are even known for solutes in sea water.)

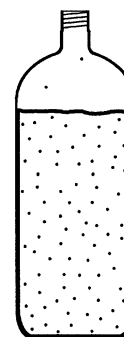
Let me mention another application of the gas solubility relationship but from a strictly qualitative viewpoint. It's a bubbly topic: carbonated beverages. Carbonated beverages have $CO_2(g)$ in the gas space at the top of the bottle in equilibrium with dissolved $CO_2(aq)$.

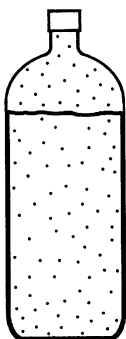


It's in equilibrium until you open the bottle or can, and then you screw up the equilibrium balance. Let's take a look at what is going on.

Let's say you have a 2 L bottle of a carbonated drink. Brand new, it has a lot of CO_2 in it, with a high P (commonly 3 - 4 atm) of CO_2 in the gas space and a considerable $[CO_2(aq)]$ in the solution at equilibrium. I illustrate this at left (not to scale, of course), with the black dots representing some of the multitudinous CO_2 molecules. In addition to the CO_2 in the gas space, there can also be some air. (There will also be some $H_2O(g)$, but that will be small and is left out of this illustration.)

When you open the bottle, you get the swoosh sound as gas zooms out of the bottle until the gas pressure remaining inside the bottle equals the surrounding air pressure. You've just lost $CO_2(g)$ which throws off the equilibrium. Now, pour out some of the beverage and you also lose some of the solution with $CO_2(aq)$, as depicted at right. As you recap the bottle, the system has lost quite a bit of CO_2 and the system is no longer at equilibrium. The solution is now supersaturated with dissolved CO_2 . The gas space mostly contains air which came in as solution was poured out.

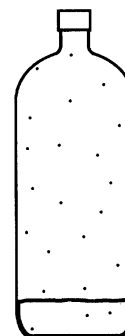




As the bottle sits closed up, the system moves toward a new point of equilibrium. There is a net transfer of $\text{CO}_2(aq)$ to $\text{CO}_2(g)$; $[\text{CO}_2(aq)]$ decreases while P of $\text{CO}_2(g)$ increases. The gain in $\text{CO}_2(g)$ increases the total gas pressure in the bottle and the total pressure ($\text{CO}_2 + \text{air}$) is again greater than one atm at equilibrium. The system reaches balance, at left, with a new value for $[\text{CO}_2(aq)]$ and a new value for P of $\text{CO}_2(g)$; both values are less than those in the bottle originally because the system has less total CO_2 than originally present.

Then you open up the bottle again.

Another swoosh occurs due to the pressure that has built up inside. More $\text{CO}_2(g)$ is lost. As you pour out beverage, you lose $\text{CO}_2(aq)$. Again, you recap the bottle. Again, it has lost quite a bit of CO_2 . Again, it is not at equilibrium. Again, as the bottle sits closed up, the system returns to equilibrium but with less total CO_2 . $[\text{CO}_2(aq)]$ decreases and P of $\text{CO}_2(g)$ increases. Eventually, it reaches a balance with a still smaller value for $[\text{CO}_2(aq)]$ and a smaller value for P of $\text{CO}_2(g)$ than in the prior step. Although both values are smaller, their ratio is the same (k_H) at equilibrium.



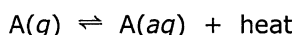
This process repeats itself every time you open the bottle. Each time, the system loses total CO_2 . Each time, the system ends at a smaller $[\text{CO}_2(aq)]$ and a smaller P of $\text{CO}_2(g)$. Eventually (at right), most of the carbonation is lost and the drink goes flat.

If you leave a bottle or a can or a cup of carbonated beverage standing around open, even in the fridge, it also goes flat. The $\text{CO}_2(g)$ diffuses away into the air; more $\text{CO}_2(aq)$ escapes to the gas phase; more $\text{CO}_2(g)$ diffuses away; etc. etc. etc.

The same principles as shown for CO_2 in water apply to other gases in water. Here's a laboratory example: aqueous ammonia, which is a very common reagent. It's simply $\text{NH}_3(g)$ dissolved in water to give $\text{NH}_3(aq)$. In the lab hood, if the bottle is left open or if it's repeatedly opened and closed, then the bottle loses $\text{NH}_3(g)$ to the atmosphere and the concentration of $\text{NH}_3(aq)$ decreases. As another example, a bottle of $\text{HCl}(aq)$ will likewise lose $\text{HCl}(g)$ under similar circumstances.

Let's now turn to another aspect of gas solubility. In our discussion of k_H values as done so far, they are constants but that only applies for a constant temperature. Our values so far are for 25 °C. Let's take a look at temperature effects, since this is another important factor for the solubility of a gas in solution.

Recall from Chapter 39 that $\Delta H_{\text{hyd}}^\circ$ is always exothermic and that $\Delta H_{\text{hyd}}^\circ = \Delta H_{\text{soln}}^\circ$ for dissolving a gas. Since exothermic, we can depict heat as a product of the reaction.



This is a good example of where you need to be able to see every equilibrium as a two-way street. We can say that dissolving releases heat; this is the forward direction for the equilibrium as written.



We can also say that escaping back to the gas phase requires heat; this is the reverse direction for the equilibrium as written above.



Keep in mind what this enthalpy represents. In the forward direction, heat is released upon dissolving because the solution IFs are kicking in. In the reverse direction, heat is required because that energy pays to overcome those solution IFs.

At higher temperature, the system possesses more heat energy. The higher heat energy can pay for more escape from the solution, so the point of equilibrium balance will have more $A(g)$ and less $A(aq)$ than at a lower temperature. Less $A(aq)$ at equilibrium means lower solubility. The grand result is that a gas is less soluble at higher temperature; in other words, solubility decreases in hotter water. Likewise, values for k_H will decrease as temperature increases. Here are some values for O_2 .

0 °C: 0.0021 M/atm

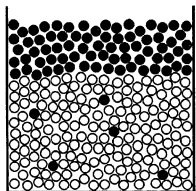
25 °C: 0.0013 M/atm

50 °C: 0.0009 M/atm

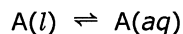
Notice the significant drop. This temperature effect makes a big deal to fish and other aquatic life: warm water can kill simply by decreasing the O_2 concentration.

With this, we wrap up the discussion for gas phase solutes. Remember: higher pressure overhead and/or lower temperature gives greater solubility for any gas. Now, we move on to other solute phases.

41.3 Solution equilibria for liquid-phase and solid-phase solutes

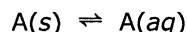
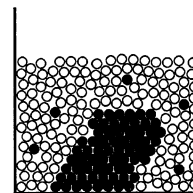


The pictures for these processes are described as follows. At left, I illustrate one liquid, $A(l)$, atop a volume of water, both liquids being in contact with each other. (Most liquids float on water because they are less dense than water. There are some, however, that are denser and these do sink in water.) Some molecules of A will leave its liquid phase and dissolve into the water to give dissolved $A(aq)$. Over time, some molecules of solute A can return to the interface between the two liquids and return to $A(l)$. At the point of balance, the speeds of these two processes are equal.



(In addition, some water molecules dissolve into $A(l)$, but that is a separate equilibrium process. Our emphasis here remains the aqueous solution and so that will be our only focus.)

At right, I illustrate a solid phase, $A(s)$, in contact with water. Particles of the solid can dissolve into the water to give solute $A(aq)$. Eventually, these can migrate back to the solid and recrystallize onto the solid. At the point of balance, the speeds of these processes are equal.



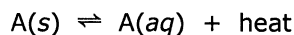
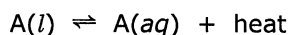
Recrystallization can occur at various locations on the solid and need not occur at the points vacated by particles which had dissolved. This can change the physical appearance of the solid. Recrystallization can even occur along the container bottom or walls and a new piece of solid can grow. It's all part of the dynamic nature of equilibrium. This parallels a similar effect which had been noted in Chapter 36 for sublimation/deposition.

Beyond the pictures shown here, these systems get more complicated than for gas-phase solutes. Thus, I will add only a few aspects for now.

Unlike the case for gas-phase solutes, pressure is not a significant factor for solubility of liquid- and solid-phase solutes. As noted in Chapter 36, pressure usually only matters when a gas phase is involved in something and that is not the case here. So we don't need to worry about P .

Temperature, however, is a big factor for solubility. The discussion for temperature depends on whether the solute is molecular or ionic. We'll start with molecular solutes.

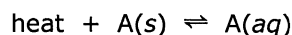
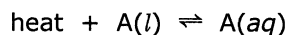
For molecular solutes, the sign of $\Delta H_{\text{soln}}^{\circ}$ can tell us the effect of temperature on solubility. For exothermic cases, the explanation is the same as for $A(g)$ above. Let's look at this.



As temperature increases, there is more heat energy to escape the IFs of the solution and to return to its own liquid or solid phase. The reverse directions of the above equilibria are therefore more favored at higher T so, at equilibrium balance, there is less $A(aq)$ present. Overall, for exothermic cases, solubility decreases at higher temperature.

(I'm using the sign of $\Delta H_{\text{soln}}^{\circ}$ here as our indicator but that's not quite right. To be really technical about it, we would use the sign of ΔH_{soln} at saturation conditions, not at standard conditions. For molecular solutes, the signs typically stay the same, so it's not an issue in our coverage here.)

The opposite applies for endothermic cases. Here's how we write those out.



For these cases, heat energy is required in order to escape from the liquid or solid and dissolve into the water. As T increases, the greater heat energy allows more escape. Thus, the forward direction of the equilibrium system is more favored at higher T and, at equilibrium balance, there is more $A(aq)$ present. Overall, for endothermic cases, solubility increases at higher temperature.

As seen in Chapter 39, liquid phase solutes can have exothermic or endothermic values for $\Delta H_{\text{soln}}^{\circ}$. As a result, these solutes can accordingly decrease or increase their solubility as temperature increases. Citing two examples from Chapter 39, the solubility of 1-butanol, $\text{C}_4\text{H}_9\text{OH}$, ($\Delta H_{\text{soln}}^{\circ} = -9.2 \text{ kJ}$) decreases in hotter water but the solubility of benzene, C_6H_6 , ($\Delta H_{\text{soln}}^{\circ} = 2.1 \text{ kJ}$) increases.

Also as seen in Chapter 39, most molecular solids have an endothermic $\Delta H_{\text{soln}}^{\circ}$. Thus, their solubility will usually increase in hotter water. For example, sugars dissolve endothermically and they have greater solubility in hotter water.

These aspects so far apply to molecular solutes. For ionic solutes, in general, the solubilities in water as a function of temperature are subject to more complications. Much of these complications arise from a process called hydrate formation, and the solubility is then of the hydrate and not of the original compound. Hydrate formation itself can also depend on temperature, so these aspects can get very messy. I am simply going to pass on this aspect. We'll leave the ionics out of our trends here for temperature effects on solubility.

Problems

1. True or false.
 - a. An unsaturated solution is not at equilibrium.
 - b. As k_{H} increases, the solubility of the gas decreases.
 - c. The solubility of a gas increases at higher temperature.
 - d. If dissolving a molecular solute is exothermic, then more solute will dissolve at higher temperature.
 - e. All salts increase in solubility as temperature increases.
2. Your 2 L bottle of carbonated water has gone flat. If the solution in the bottle at equilibrium at 25 °C contains $[\text{CO}_2(\text{aq})] = 0.00064 \text{ M}$, then what is the pressure (in atm) of the $\text{CO}_2(\text{g})$ in the gas space?
3. How many grams of propane, C_3H_8 , can dissolve in 5.00 gallons (18.9 L) of water at 25 °C if the pressure of $\text{C}_3\text{H}_8(\text{g})$ is 553 Torr at equilibrium?