## **Chapter 11**

# **AQUEOUS REACTIONS, Part 1**

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We've set up our background for water and part of what makes water so special. We can now proceed to specific types of reactions which are common in water. Before doing that, however, we need to discuss some aspects about dealing with the individual ions in solution.

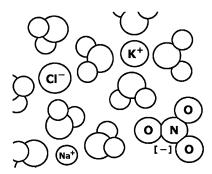
#### 11.1 Independent ions

Cations and anions which are dissociated in solution are independent from each other. Furthermore, when more than one compound is dissolved, all the separated ions are all mixed up. If you dissolve sodium chloride (NaCl) in a bucket of water, you get separate Na $^+$  cations and separate Cl $^-$  anions. If you add potassium nitrate (KNO $_3$ ) to the bucket, it dissolves and gives separate K $^+$  cations and separate NO $_3^-$  anions. You now have a bucket which contains separate Na $^+$ , K $^+$ , Cl $^-$  and NO $_3^-$  ions. This is the same outcome as dissolving sodium nitrate (NaNO $_3$ ) and potassium chloride (KCl) together in a different bucket. In both buckets, you get the same combination of Na $^+$ , K $^+$ , Cl $^-$  and NO $_3^-$  ions.

$$NaCl(aq) + KNO_3(aq)$$
  
gives the same solution as  
 $NaNO_3(aq) + KCl(aq)$ 

This is the picture which I show on the right.

(By the way, these pictures can get busy and complicated, so I will often leave out the solvent water molecules. Besides, as previously mentioned, there are lots more  $H_2O$  molecules than solute and things are in fairly close contact. I'm trying to keep things simple. From now on, just remember that everything is hydrated, whether I show the water molecules or not.)



Since dissociation gives separated ions, these ions can act as independent chemical units. A reaction can occur involving one but not the other: the cations might do a reaction and the anions might do nothing, or, the anions might do a reaction and the cations might do nothing. This is very common.

Let's consider a simple reaction in which only some of the ions are involved. Let's do baking soda (sodium bicarbonate) and acid. You may know this one. When you mix baking soda with vinegar, you get lots of bubbles. The bubbles are carbon dioxide. The primary acid in vinegar is acetic acid, but many acids will do likewise. I'll use hydrochloric acid for now since that is the acid we talked about in the last Chapter.

The overall reaction between the complete compounds is the following.

I'll throw in some phases to illustrate how they're handled.

$$NaHCO_3(aq) + HCI(aq) \rightarrow NaCI(aq) + H_2O(l) + CO_2(g)$$

Remember that (aq) means dissolved in water, not just floating around in pieces. Also, notice that  $H_2O$  is designated (l); a common error for students is to write  $H_2O(aq)$ , but this doesn't really work since it means "aqueous water" or water dissolved in water. That's not a correct designation. You need to remember that the phase for  $H_2O$  is always given as (l) for aqueous reactions. Finally, since I mentioned that  $CO_2$  bubbles out, it's a gas and it gets (g).

We can envision this process as follows. The starting solution of sodium bicarbonate is actually composed of dissociated  $Na^+(aq)$  and  $HCO_3^-(aq)$  ions. The starting solution of hydrochloric acid is composed of dissociated  $H^+(aq)$  and  $Cl^-(aq)$  ions. Thus, we have the following present at the start of the process.

$$Na^{+}(aq) + HCO_{3}^{-}(aq) + H^{+}(aq) + Cl^{-}(aq)$$

The separate solutions are then mixed and the reaction occurs.

$$Na^{+}(aq) + HCO_{3}^{-}(aq) + H^{+}(aq) + Cl^{-}(aq) \rightarrow CO_{2}(g) + H_{2}O(l) + Na^{+}(aq) + Cl^{-}(aq)$$

Carbon dioxide gas bubbles out of the solution. Molecules of water are formed, but they just mix in with the water molecules of the solvent and they are not distinguishable from them. The  $Na^+(aq)$  and  $Cl^-(aq)$ 

ions do not change: they are the same on both sides of the equation, so they don't do anything. Since the sodium ions and the chloride ions are just sitting around and do not get involved, they're called "spectator ions". In other words, spectator ions are those ions which do not undergo a change in chemical identity. Because spectator ions are not involved in chemical change, we can write a chemical equation without them.

$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2O(l) + CO_2(g)$$

This form of chemical equation is called a "net ionic equation". It only shows the actual reactants and actual products involved in chemical change. It does <u>not</u> show spectator ions. This is a very handy form of chemical equation and we will be doing a lot with this type. Don't forget the undissociated format, which is how we started this example and which is still often used.

$$NaHCO_3(aq) + HCI(aq) \rightarrow NaCI(aq) + H_2O(l) + CO_2(g)$$

This format still works since there is a change in chemical identity for the compounds as a whole. Thus, we have two ways to write a balanced equation for a solution reaction: the net ionic equation and the undissociated equation.

Net ionic equations introduce us to a new aspect of balancing chemical equations. Well, it's not really new. Here's what I said in Chapter 6.

"All equations must be "balanced"... There are <u>two</u> aspects of balancing an equation: atom count must be balanced and charges must be balanced. Right now, we'll stick with neutral compounds of zero charge; this means we won't need to cover charge balance until later. "

Later is now. We have to start worrying about charge balance because net ionic equations may not be neutral.

Charge balance is simple: the sum of all charges for all reactants on the left must equal the sum of all charges for all products on the right. Go back to the net ionic equation above.

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2$$

On the left we have a 1– anion and a 1+ cation for a charge sum of zero. On the right we have only neutrals, which are zero charges. Overall, the charge sums are zero left and zero right. Everything's balanced. Everything's fine. Although the charge sum is zero in this example, that's not required. The charge sum could be any number, as long as it's the same number left and right.

Unfortunately, the term "charge balance" is a bit indirect. Charge balance is really <u>electron balance</u>. This is a very important aspect which I am pointing out now, but which I will explain later in Chapters 13 and 14. That's when it will matter even more so.

RECAP. Let me summarize the essential features of our two types of balanced equations for aqueous reactions.

- ✓ The undissociated equation shows all reactants and products as whole, neutral compounds.
- ✓ The net ionic equation shows dissociated ions as such; also, it shows only those chemical units which are undergoing a change in the reaction. There are no spectator ions listed.

There are three points which you must keep in mind regarding net ionic equations.

- Dissociated ions are written by their ion formulas. (This applies to HCO<sub>3</sub><sup>-</sup> and H<sup>+</sup> in the equation above.)
- 2. Insoluble solids cannot be dissociated since they are not significantly dissolved. These must be written by their full, neutral formulas. (We'll see examples of this later.)
- 3. Covalent, molecular compounds which are not substantially dissociated are also written as their neutral formulas. This will include H<sub>2</sub>O itself, all gases, and some solutes. (In the equation above, H<sub>2</sub>O and CO<sub>2</sub> are shown by their molecular formulas.)

Circle these three points. I'll send you back here later.

OK, this concludes this section. Now, we are ready to dive deep into the water world of reactions. Over this and the next three Chapters, we will cover four specific types: precipitation, neutralization, gasforming and oxidation-reduction. These are very important and very common types of reactions in chemistry. Technically, they are not restricted to aqueous reactions and they can occur under other conditions, too, but, as I said in the beginning of Chapter 10, I'm not covering every kind of reaction.

### 11.2 Precipitation: background

As a noun, the word "precipitate" means an insoluble solid which forms as the product of a reaction between soluble reactants. As a verb, to "precipitate" means to form the insoluble compound. A compound which is able to precipitate is "precipitable". The reaction itself is called a "precipitation reaction" or just "precipitation". For our purposes here, we will limit the discussion to ionic precipitates; some covalent compounds can also precipitate but this is less common.

Here's the picture. You have two separate solutions of soluble compounds. You mix them together. A reaction occurs and one of the products forms as an insoluble solid (the precipitate). Typically, this forms as a powder which can eventually settle to the bottom of the container. Less typically but sometimes possible, crystals of the ionic compound form slowly. These can look fairly impressive when done properly.

In order to understand precipitation, you have to understand the meaning of insoluble except you have to understand it from a different viewpoint. For this part, we will follow up on the discussion from last Chapter in terms of the strength of hydration versus the strength of ionic bonding. (We're still not doing the entropy part yet.) As introduced in Section 10.3, A COMPOUND CAN BE INSOLUBLE WHEN HYDRATION IS NOT STRONG ENOUGH TO DISSOLVE AND DISSOCIATE THE IONS. Now, let's turn it around: A COMPOUND CAN BE INSOLUBLE BECAUSE ITS IONIC BONDS CANNOT BE OVERCOME BY HYDRATION. There's an important consequence to this: if those ions do somehow run into each other in solution, then ionic bonding will overcome hydration and the ionic network solid will form. As more and more hydrated ions come onto the scene, these also join in on the ionic bonding. This is the process of precipitation. Note a key concept: ALL PRECIPITATES ARE INSOLUBLE COMPOUNDS AND ALL INSOLUBLE COMPOUNDS ARE PRECIPITABLE COMPOUNDS.

We've actually been working with a precipitation reaction since Chapter 9, except we weren't able to call it that back then. Here's how I presented it in Section 9.3.

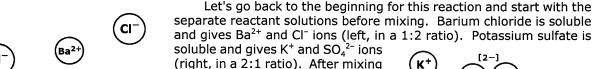
For this we'll use the reaction of barium chloride with potassium sulfate to produce barium sulfate and potassium chloride.

$$BaCl_2 + K_2SO_4 \rightarrow BaSO_4 + 2 KCI$$

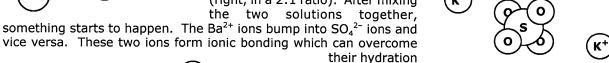
Both reactants are soluble in water, so both of their solutions are homogeneous. One product, potassium chloride, is also soluble in water, but barium sulfate is not. Thus, the reaction produces a cloud of very fine particles of solid BaSO<sub>4</sub>, which eventually settle to the bottom of the pot. This is then a heterogeneous mixture. I can describe this with words, like I just did. Or I can say it with phases.

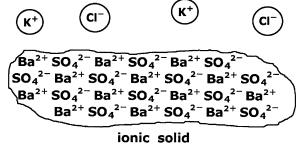
$$BaCl_2(aq) + K_2SO_4(aq) \rightarrow BaSO_4(s) + 2 KCl(aq)$$

Here in this Chapter, we can now identify this as a precipitation reaction and we identify barium sulfate as the precipitate. The above equation is written in the undissociated format.



something starts to happen. The  $Ba^{2+}$  ions bump into  $SO_4^{2-}$  ions and





interactions; thus, they stick with each other as ionic bonding kicks in. They're joined by other Ba<sup>2+</sup> ions and by other SO<sub>4</sub><sup>2-</sup> ions to form the ionic network solid (depicted at left), which precipitates from solution. So what about the other ions? The Cl<sup>-</sup> ions are still there and the K<sup>+</sup> ions are still there, just swimming around, still dissociated. Since they don't do anything, they are spectator ions. The grand tally for everything happening in the pot is the following.

$$Ba^{2+} + 2 Cl^{-} + 2 K^{+} + SO_{4}^{2-} \rightarrow BaSO_{4} + 2 Cl^{-} + 2 K^{+}$$

Now, drop the spectators (cancel them out) to get the net ionic equation.

$$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$$

While we're at it, I'll throw in phases.

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

Notice that  $BaSO_4$  is written as the whole, neutral compound. That's because it's insoluble and therefore not dissociated.

For emphasis when dealing with precipitation reactions, I want to repeat what I said above.

... A COMPOUND CAN BE INSOLUBLE WHEN HYDRATION IS NOT STRONG ENOUGH TO DISSOLVE AND DISSOCIATE THE IONS. Now, let's turn it around: A COMPOUND CAN BE INSOLUBLE BECAUSE ITS IONIC BONDS CANNOT BE OVERCOME BY HYDRATION. There's an important consequence to this: if those ions do somehow run into each other in solution, then ionic bonding will overcome hydration and the ionic network solid will form. As more and more hydrated ions come onto the scene, these also join in on the ionic bonding. This is the process of precipitation. Note a key concept: ALL PRECIPITATES ARE INSOLUBLE COMPOUNDS AND ALL INSOLUBLE COMPOUNDS ARE PRECIPITABLE COMPOUNDS.

This part is <u>really</u> important for understanding precipitation. Given this information, you can predict whether a precipitation can occur when two solutions are mixed. All you have to do is determine whether an insoluble (precipitable) compound can be formed from the combination of the ions which are present.

There's a catch here. In order for this to work, you need to know whether a compound is soluble or insoluble. How do you do that? Well, it's not exactly straightforward.

There is a huge number of combinations for ionic compounds of different cations with different anions. There are no universal <u>rules</u> for knowing in advance whether certain ionic compounds will be soluble or not. But there are at least some general solubility <u>trends</u> to go by, although these will have exceptions. Different lists of trends have evolved over many years, and the different lists are used by different instructors. Here is a list of trends which has evolved from I-don't-know-where. The way to use this list is to go down the list until you find a trend which fits the compound you are considering, and that is the trend you go with. Even if a later trend in the sequence might also apply for that compound, you still go with the first trend which applies. Thus, these are listed as a hierarchy or priority scheme.

#### **SOLUBILITY TRENDS**

- 1. Compounds containing a Group 1 metal cation or ammonium tend to be SOLUBLE.
- 2. Compounds containing nitrate, acetate, chlorate or perchlorate tend to be SOLUBLE.
- 3. Silver, lead and copper(I) compounds tend to be INSOLUBLE.
- 4. Chlorides, bromides, and iodides tend to be SOLUBLE.
- 5. Sulfates tend to be SOLUBLE except those of calcium, strontium and barium.
- 6. Compounds with anions of 2- or 3- charge tend to be INSOLUBLE.
- 7. Hydroxides tend to be INSOLUBLE except for those of calcium, strontium and barium.

We'll use this list although your instructor may provide you with a different one to better fit their approach. That is their prerogative. Again, there will be exceptions to any list. They're trends and they're not rules. Use them as trends.

The general approach here is that you are given some compound and you need to decide whether that compound will be a soluble or insoluble compound. Again, just start with Trend #1 and go from there: the first trend which applies will determine the outcome. Here are some examples.

- $K_3PO_4$  Potassium is a Group 1 metal cation, so Trend #1 applies and we conclude the compound is soluble. Even though other phosphates may not be soluble due to Trend #6, we go with Trend #1.
- AgNO<sub>3</sub> Trend #2 tells us nitrates tend to be soluble, so that is what we go with. Although other silver compounds may not be soluble as suggested by Trend #3, we go with #2.
- PbCl<sub>2</sub> The first Trend to apply is #3 for lead compounds, and this says insoluble. This takes priority over other chloride compounds given in Trend #4.
- ZnSO<sub>4</sub> The first Trend to apply is #5 for sulfates, and this says soluble.
- CoCO<sub>3</sub> The first Trend to apply is #6 which includes carbonates; this says insoluble.

That's all there is to that. Again, this is set up as a priority system: go with the first Trend which applies. Here, you try a few. Are the following compounds soluble or insoluble?

NiBr <sub>3</sub>	Cu(OH) <sub>2</sub>
NH <sub>4</sub> ClO <sub>4</sub>	AIPO <sub>4</sub>

Two are soluble and two are insoluble.

OK, with this background, we can proceed to predicting the products of a precipitation reaction.

### 11.3 Precipitation: putting it together

Here's what we've got so far. The setup for a precipitation reaction will begin with separate solutions of ionic compounds. Upon mixing the two solutions, all ions scramble and collide with one another, which means all combinations of cations and anions are possible. If any combination makes a precipitable (insoluble) compound, then that compound will precipitate.

Let's illustrate the whole process, including balanced equations.

You have a solution of iron(II) nitrate and a solution of ammonium oxalate. You add them together. What precipitate will result? Write the balanced, undissociated equation for the process. Also, write the balanced, net ionic equation. Identify the spectator ions.

Notice that I said  $\underline{solutions}$  of each reactant. "Solution"  $\underline{always}$  means everything's dissolved, so that automatically tells you that the reactants are soluble by themselves. Let's identify what ions are present in each reactant solution.

The solution of  $Fe(NO_3)_2$  will contain separated  $Fe^{2+}$  cations and  $NO_3^-$  anions.

These will be in a 1:2 ratio but for now we are just listing the ions.

The solution of  $(NH_4)_2C_2O_4$  will contain separated  $NH_4^+$  cations and  $C_2O_4^{2-}$  anions.

These will be in a 2:1 ratio but for now we are just listing the ions.

Upon mixing the two solutions into one pot, all four ions would be available. List these.

$$Fe^{2+}$$
  $NO_3^ NH_4^+$   $C_2O_4^{2-}$ 

Once the various ions start bumping into each other, what new cation/anion combinations are possible?

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NH_4^+ and NO_3^- ions could combine to give NH_4NO_3. Fe^{2+} and C_2O_4^{2-} ions could combine to give FeC_2O_4.
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In order to have a precipitate, there must be a combination which gives an insoluble compound. Bring in the Solubility Trends.

 $NH_4NO_3$ : The Solubility Trends tell you that this is a soluble compound, so it will stay dissolved and it will not precipitate.

 $FeC_2O_4$ : The Solubility Trends tell you that this is an insoluble (precipitable) compound, so it will precipitate.

So now we've identified  $FeC_2O_4$  as the precipitate in this reaction. Now let's turn to the balanced equation, beginning with the undissociated format. Start with the reactants.

$$Fe(NO_3)_2 + (NH_4)_2C_2O_4 \rightarrow$$

The products include the FeC<sub>2</sub>O<sub>4</sub> precipitate

$$Fe(NO_3)_2 + (NH_4)_2C_2O_4 \rightarrow FeC_2O_4$$

along with the  $NH_4^+$  and  $NO_3^-$  ions which remain dissolved in the solution. For the undissociated equation, we represent these as the compound  $NH_4NO_3$ .

$$Fe(NO_3)_2 + (NH_4)_2C_2O_4 \rightarrow FeC_2O_4 + NH_4NO_3$$

Balance this to get the final answer for the undissociated equation.

$$Fe(NO_3)_2 + (NH_4)_2C_2O_4 \rightarrow FeC_2O_4 + 2 NH_4NO_3$$

Now we derive the net ionic equation. By the discussion so far, we already know that  $Fe^{2+}$  and  $C_2O_4^{2-}$  react to form insoluble  $FeC_2O_4$  and we can construct the net ionic equation directly from that information.

But, as a more general method, I will break this down into several steps starting from the undissociated equation. This parallels the approach which was used for the sodium bicarbonate/hydrochloric acid reaction early in the Chapter, and it will work for other kinds of reactions down the road.

Start with the reactants from the above equation.

$$Fe(NO_3)_2 + (NH_4)_2C_2O_4 \rightarrow$$

Both of these are soluble, so they'll be dissolved and dissociated. Bust them up into their separate ions.

$$\overbrace{\text{Fe}^{2^{+}} + 2 \text{ NO}_{3}^{-}}^{\text{Fe}(\text{NO}_{3})_{2}} + \underbrace{(\text{NH}_{4})_{2}\text{C}_{2}\text{O}_{4}}_{\text{NH}_{4}^{+}} + \text{C}_{2}\text{O}_{4}^{2^{-}} \rightarrow$$

Now you need to keep track of the number of ions involved. Notice that there are two  $NO_3^-$  from one formula unit of  $Fe(NO_3)_2$  and there are two  $NH_4^+$  from one formula unit of  $(NH_4)_2C_2O_4$ . We didn't need those numbers above because we only need a list of ions in order to identify the precipitate. For balancing the net ionic equation, however, we have to take the numbers into consideration.

Bring in the products.

$$\frac{\text{Fe(NO}_3)_2}{\text{Fe}^{2+} + 2 \text{ NO}_3^-} + \frac{(\text{NH}_4)_2 \text{C}_2 \text{O}_4}{2 \text{ NH}_4^+ + \text{C}_2 \text{O}_4^{2-}} \rightarrow \text{FeC}_2 \text{O}_4 + 2 \text{ NH}_4 \text{NO}_3$$

 $FeC_2O_4$  is insoluble and it is written undissociated. On the other hand,  $NH_4NO_3$  is soluble and dissociated, so write it in as dissociated ions.

$$\overbrace{\text{Fe}^{2^{+}} + 2 \text{ NO}_{3}^{-}}^{\text{Fe}(\text{NO}_{3})_{2}} + \underbrace{(\text{NH}_{4})_{2}\text{C}_{2}\text{O}_{4}}_{\text{NH}_{4}^{+}} + \text{C}_{2}\text{O}_{4}^{2^{-}} \rightarrow \underbrace{\text{Fe}\text{C}_{2}\text{O}_{4}}_{\text{Fe}\text{C}_{2}\text{O}_{4}} + \underbrace{2 \text{ NH}_{4}\text{NO}_{3}}_{\text{NH}_{4}^{+}} + 2 \text{ NO}_{3}^{-}$$

Notice that there are two  $NH_4^+$  and there are two  $NO_3^-$  because there are two formula units of  $NH_4NO_3$  in the balanced, undissociated equation.

Now, cancel what you can from both sides, namely the  $2 \text{ NH}_4^+$  and the  $2 \text{ NO}_3^-$ . Those do not react which means they are spectator ions. Look at what's left.

$$Fe^{2+} + C_2O_4^{2-} \rightarrow FeC_2O_4$$

Now you're down to net ionic level and now you're done. Go back to the three points which you circled earlier for net ionic equations; we've fulfilled #1 and #2 although #3 doesn't apply for this reaction.

Let me add a point here for deriving net ionic equations. Sometimes, you can end up with coefficients which are not smallest, whole numbers (Section 6.2), so you must divide through by some number to finish it off. That's not the case presently, but it can happen.

All done. If you want phases, remember that a precipitate is always (s) while solubles are always (aq).

$$Fe(NO_3)_2(aq) + (NH_4)_2C_2O_4(aq) \rightarrow FeC_2O_4(s) + 2 NH_4NO_3(aq)$$
  
 $Fe^{2+}(aq) + C_2O_4^{2-}(aq) \rightarrow FeC_2O_4(s)$ 

OK, there were several parts to all that. The first part involved identifying the precipitate; then, deriving a balanced undissociated equation; and, then, developing a balanced, net ionic equation. We'll cover more about balancing equations, including net ionics, for this and other kinds of reactions. For now, let me just summarize the steps for identifying the precipitate.

- Step 1. Determine the dissociated ions which are present in each reactant solution.
- Step 2. Upon mixing the reactant solutions, the separate ions mix among each other. Identify the ionic compounds which can be produced from new combinations of cations and anions.
- Step 3. For each new ionic product which is possible, determine whether each is soluble or insoluble. If a new ionic combination gives an insoluble compound, then that is the precipitate.

Go back to the beginning of this problem and see how these Steps fit in.

Let's do a different one. This time, you fill things in.

<b>Example.</b> A solution of lead(II) perchlorate and a solution of sodium chromate are mixed togeth Identify the precipitate formed. Write the undissociated equation, write the net ionic equation, a identify the spectator ions.	and
List the ions present in each reactant solution.	•
The solution of Pb(ClO <sub>4</sub> ) <sub>2</sub> will have and ions.	
The solution of $Na_2CrO_4$ will have and ions.	
After mixing the solutions together, the ions can form new combinations of ionic compounds. What n combinations of cations and anions are possible as products?	ew
Possible ionic products: and	
Are these soluble or insoluble?	
Which is the precipitate?	
Now construct the full, undissociated equation. I've entered the reactants below. You list products and then fill in the coefficients as necessary for balance.	the
$\_$ Pb(ClO <sub>4</sub> ) <sub>2</sub> + $\_$ Na <sub>2</sub> CrO <sub>4</sub> $\rightarrow$ $\_$ $\_$ $\_$ + $\_$ $\_$	
That finishes that part. Now we'll go to the net ionic equation. Bust up everybody that's soluble a dissociated; leave the precipitate intact. I'll do the reactants again.	and
$Pb^{2+} + 2 CIO_4^- + 2 Na^+ + CrO_4^{2-} \rightarrow $ + + + + precipitate	_
What are the spectator ions? and	
Take the spectators out of the equation, check your coefficients, make sure everything is fine and danger and write out the final equation here.	dy,
I won't give you the answers directly but, if you want to be sure that you have the identity and form of the precipitate correct, then here's a clue: it's the chrome yellow pigment mentioned in Chapter 4	

Before closing this section, I want to point out that precipitation will not happen every time two solutions are mixed. If all possible combinations of ions give soluble compounds, then everything stays in solution. I actually covered this possibility when I first opened this Chapter: I gave an example of mixing a solution of NaCl with a solution of  $KNO_3$ . Everybody stays soluble and all ions stay dissociated. You can only have precipitation when a new combination gives a precipitable (insoluble) compound.

Enough precipitation for now. Let's go to the next type of reaction: neutralization. First, we need some background.

#### 11.4 Acids and bases

Neutralization reactions are also called acid-base reactions and these reactions are just what they sound like: a reaction between an acid and a base. Acids and bases are chemical opposites, so one will "neutralize" the effect of the other.

Historically, the classification of compounds as acids and bases is an oldie. Furthermore, numerous acid-base classifications exist because the definitions for acids and bases have evolved over many years. Your instructor may describe some of these variations. I am presently emphasizing the water world, but definitions for acids and bases nowadays also include nonaqueous solutions and even gas and solid phases. Here, we'll stick with introductory definitions for aqueous solutions.

For now, our working definitions for acids and bases depend on how compounds behave when they dissolve in water:

An acid is any compound which dissolves in water and forms H<sup>+</sup> (protonated water).

A base is any compound which dissolves in water and forms OH<sup>-</sup>.

This is all we need right now. We will greatly expand on this beginning in Chapter 54.

Here's something you should note. The reaction between H<sup>+</sup> and OH<sup>-</sup> always gives water.

$$H^+ + OH^- \rightarrow H_2O$$

Many (but not all) acid-base reactions involve this process. Since water is considered neutral, this is where the sense of "neutralization" can come in.

Many people are familiar with many examples of acids and bases. Acetic acid is the primary acid in vinegar. (It's also the biggest part of vinegar's smell.) Hydrochloric acid is the powerful acid in your stomach. Vitamin C is ascorbic acid. Lye is a base, sodium hydroxide. Ammonia is also a base.

We talked about hydrochloric acid in Chapter 10. We described how water molecules can help to break the covalent bond of hydrogen chloride to give a solution of hydrochloric acid.

$$HCI \rightarrow H^{+} + CI^{-}$$

This is the stuff which Nature uses in your stomach to start breaking down your foods. It's strong stuff and it's also very common industrially and commercially in a variety of applications. You can buy a jug of it in a hardware or home improvement store, but they may not call it hydrochloric acid; it's often called "muriatic acid". (Muriate is a very old name for some kinds of chlorine compounds.) Hydrochloric acid is very strong. Very corrosive. It will eat rust and many metals. It will also eat skin. Since it dissociates in water to give H<sup>+</sup>, it is an acid by the definition above.

Sodium hydroxide is one of the most common bases used in all sorts of things commercially and industrially. It's also powerful stuff and it's very hazardous in only modest concentration. They use solutions of NaOH in many (not all) drain cleaners which you can buy in the store. Read the label. The compound itself is an ionic compound with an extreme tenacity for water. In fact, if you leave solid NaOH open to air with moderate or high humidity, it will absorb enough moisture out of the air to dissolve itself. In any aqueous solution of NaOH, dissociation occurs to Na<sup>+</sup> and OH<sup>-</sup> ions.

Since it dissolves and dissociates to give OH-, it is a base by the definition above.

A base does not have to be a compound with a hydroxide anion. Ionic metal oxide compounds which can dissolve in water will also produce hydroxide ions, because the oxide ions react with water. The following is a net ionic equation for this process.

$$O^{2-} + H_2O \rightarrow 2 OH^{-}$$

Thus, these kinds of compounds are also bases. An example is sodium oxide.

$$Na_2O + H_2O \rightarrow 2 Na^+ + 2 OH^-$$

Notice that I said metal oxide compounds which can <u>dissolve</u> in water. Most metal oxide compounds cannot dissolve in water (to a significant extent); therefore, their oxide ions cannot dissociate and cannot react to produce hydroxide. These compounds would not fit this category.

Although some <u>ionic</u> oxides dissolve in water and are bases, many <u>covalent</u> oxides do the exact opposite: they react with water and produce  $H^+(aq)$ . That means that they are acids. Carbon dioxide is an excellent example.  $CO_2$  dissolves only slightly in water. A very small fraction (<1%) of the dissolved  $CO_2$  molecules react with water to form carbonic acid,  $H_2CO_3$ .

$$CO_2 + H_2O \rightarrow H_2CO_3$$

Water molecules can pull apart some of the molecules of H<sub>2</sub>CO<sub>3</sub>, producing bicarbonate and H<sup>+</sup>.

$$H_2CO_3 \rightarrow H^+ + HCO_3^-$$

Since  $CO_2$  stays mostly intact as  $CO_2$  in water, and since the small amount of carbonic acid doesn't really dissociate much anyway, then there's not a lot of  $H^+$  obtained in this manner. However, it's still very important in Nature, biologically, geologically and environmentally.

A related example is another gas,  $SO_2$ . This one is much more soluble in water than is  $CO_2$ . Unlike  $CO_2$  forming  $H_2CO_3$ , however, there's no proof that  $H_2SO_3$  even exists in aqueous solution. Thus,  $SO_2$  reacts directly with water to form  $H^+$ .

$$SO_2 + H_2O \rightarrow H^+ + HSO_3^-$$

This dissociation happens much more readily than does the dissociation for  $CO_2$  and  $H_2CO_3$ , but most of the original molecules of  $SO_2$  which dissolve are still  $SO_2$  molecules and not  $HSO_3^-$  ions.

A really good acid is sulfuric acid,  $H_2SO_4$ , which is produced when sulfur trioxide gas dissolves in water.  $SO_3$  dissolves a lot into water and it reacts very vigorously with water.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Water completely dissociates sulfuric acid: you get bisulfate along with H+.

$$H_2SO_4 \rightarrow H^+ + HSO_4^-$$

 $H_2CO_3$  and  $H_2SO_4$  are acids since they are dissociated by water to give  $H^+$ . We can also say that  $CO_2$ ,  $SO_2$ , and  $SO_3$  are acids according to our working definition; this is true because they lead to the production of some  $H^+$ . As an aside, these things are all part of acid rain. Nature puts a huge amount of  $CO_2$  into the atmosphere, along with an occasional belch of volcanic  $SO_2$ , and Nature has developed the means over the eons to deal with these. But humans also put large amounts of  $CO_2$  and  $SO_2$  and  $SO_3$  (and other covalent oxides) into the atmosphere, leading to extensive environmental problems. These things are part of your world. Unfortunately.

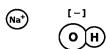
I need to introduce some terminology here.

It is common to call acids and bases "strong" or "weak", but these terms have a specific chemical definition. The terms do not refer to concentration nor do they refer to toxicity or hazards. The terms instead refer to how many of the dissolved chemical units actually produce  $H^+$  or  $OH^-$ . In the case of "strong", virtually all of the dissolved chemical units (acid or base) give  $H^+$  or  $OH^-$  ions. In the case of "weak", only some of the dissolved chemical units (acid or base) give  $H^+$  or  $OH^-$  ions. I want to point something out to you here: the term "weak" is typically an understatement. Many "weak" acids or bases give only 10% or 1% or 0.1% or even fewer ions. So the term "weak" is putting it mildly: "pitiful" or "lousy" would be a better description.

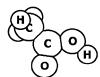
I've already described for you an example of a strong acid and a strong base. Hydrochloric acid (below) is a strong acid because virtually all of the molecules of hydrogen chloride gas which are dissolved



will be pulled apart by water molecules to give H<sup>+</sup> and Cl<sup>-</sup> ions. Sodium hydroxide (right) is a strong base because virtually all formula units of the ionic compound are dissociated in water.



Notice that I keep saying "virtually all" instead of just "all". "All" is fine at low or moderate concentrations but, when the concentration gets high enough, the dissociation may not be completely 100.0%. This is a minor point and I will not keep saying "virtually" all the time.



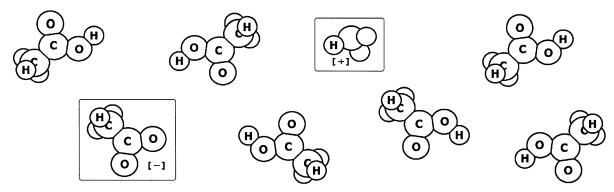
Now let's compare this strong behavior to some weak cases. Acetic acid (the vinegar smell) is a weak acid. Its formula is  $\text{CH}_3\text{CO}_2\text{H}$ ; a molecule is shown at left. Acetic acid is a covalent compound. Notice that there is an OH bond in this molecule; this bond is very polar. Do you remember the significance of this? I talked about this in the last Chapter.

Dissociation is primarily limited to a very small fraction of covalent compounds in general. By far, most cases of this small fraction have a hydrogen atom in a very polar covalent bond. Why does hydrogen matter? There are two reasons, one involving the cost of breaking the covalent bond and one involving the payback from the hydration of ions. \*\*

Acetic acid has a bond which fits this description but the situation is not completely favorable in terms of cost. For this reason, a water molecule has a hard time pulling H<sup>+</sup> off an acetic acid, and a struggle results. This has major consequences. Yes, when dissolved in water, water can dissociate some acetic acid molecules to form protonated water and acetate ions,

$$CH_3CO_2H \rightarrow H^+ + CH_3CO_2^-$$

but not many of the acetic acid molecules actually allow this to happen. The fact is, few are dissociated at any given period of time. The molecules which lose H<sup>+</sup> will even take them back, so there's a constant trade off: one molecule might be dissociated in one second and then undissociated in the next second. The overall result is that there will be some <u>average fraction of dissociated molecules at any time</u>. This average varies immensely with different concentrations (and also for different compounds). For acetic acid, typically less than 10% of the molecules are dissociated. What that means is that <u>most of the acetic acid in the solution is still neutral, undissociated molecules</u>. Only a few (on average at any given time) are dissociated and separated at any given time (outlined figuratively below).



The grand conclusion for all of this is that acetic acid is a weak acid. It's still an acid, since some  $H^+$  is indeed produced, but it's weak because only some of the molecules are actually dissociated at any given time.

For clarification, I want to point out that one molecule of acetic acid has four H's in it but only one of them can dissociate. That H is the one H which is bonded to O. The other three are bonded to C. As noted in Chapter 10, OH bonds are much more prone to dissociate than are CH bonds and the CH bonds in acetic acid do not dissociate.

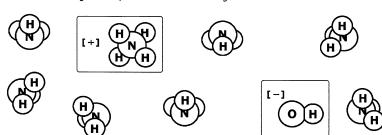
OK, let's do a weak base. By far, the most common is ammonia. No other weak base comes close in use or importance. Like hydrogen chloride, ammonia by itself is a gas and it dissolves very well in water. Contrary to hydrogen chloride, ammonia is a base. That's because it can react with the water molecules but with a twist.

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

This process involves role reversal. For acids, water dissociates the solute but, here, ammonia dissociates the water. The products are ammonium cation and hydroxide ion. Because of this combination of products, aqueous solutions of ammonia are often called "ammonium hydroxide". In fact, the bottles of ammonia solution in many laboratories are labeled with that name. What's strange about this is that  $NH_4OH$  cannot be made as a pure compound by itself. It can only exist in small amounts in solution.

We have another problem here with some parallel to the acetic acid case above. Most of the ammonia molecules in solution are just neutral  $NH_3$ . Only a few of the  $NH_3$  molecules react with water

molecules to form  $\mathrm{NH_4}^+$  and  $\mathrm{OH^-}$  ions. The neutral  $\mathrm{NH_3}$  molecules and the  $\mathrm{NH_4}^+$  ions trade off with each other and overall there is some average amount of ions. How many? Like acetic acid above, this will depend on concentration but it turns out again to be typically less than 10%.



So here's the grand result: ammonia is classified as a base, since some hydroxide ions are produced when it dissolves in water. It's further classified as weak, because only some of the ammonia molecules actually do this.

The strong/weak distinction for acids and bases is extremely important to many aspects of chemistry and also to biology. Nature uses a multitude of weak acids and weak bases in biological organisms and very few strong ones. (Stomach acid is one of the rare examples of a strong acid used in biology.) You

must understand the terms strong/weak as defined in this usage. These are NOT the usual dictionary definitions. Let me repeat what I said above.

The terms do not refer to concentration nor do they refer to toxicity or hazards. The terms instead refer to how many of the dissolved chemical units actually produce H<sup>+</sup> or OH<sup>-</sup>.

Remember this. It's important.

A common question at this point is how to know which acids or bases are strong and which are weak. This is not easy at this stage of the game and it is best to just memorize a few things. Based only on numbers, there are far more weaks than strongs, but this is not a good thing to go by on an exam. I'll list some things for our purposes here, but your instructor may have a different way of setting this up.

STRONG VERSUS WEAK ACIDS. There are six strong acids that are commonly encountered in chemistry and these can simply be memorized as strong. These six are the following.

Hydrochloric acid, HCl Nitric acid, HNO₂ Hydrobromic acid, HBr Perchloric acid, HClO<sub>4</sub>

Hydroiodic acid, HI Sulfuric acid, H<sub>2</sub>SO<sub>4</sub>

Although there are many other strong acids, they are not nearly as common. Most other acids are weak and you can assume this unless told otherwise.

STRONG VERSUS WEAK BASES. By far, the most common strong bases are the soluble metal hydroxides. Less common, but still strong, are the soluble metal oxides. For weak bases, ammonia is by far the most common and it should be memorized as such. There are still many others, but they are not as common at this stage of the game.

Let me add a comment about the strong bases. To be a strong base, the compound must dissociate completely to produce OH<sup>-</sup>. If the compound is not soluble, then it cannot dissolve (to a significant extent) and therefore it cannot dissociate (to a significant extent). This eliminates most ionic hydroxides and oxides from being strong bases, since most are not soluble. On a practical basis, the soluble cases mostly involve the ionic hydroxides and oxides of Group 1 and Group 2, except for Be and Mg. Here are some examples.

LiOH K<sub>2</sub>O CsOH

Ca(OH)<sub>2</sub>

SrO

Ba(OH)<sub>2</sub>

Actually, even  $Ca(OH)_2$  is running into borderline solubility. Some instructors might consider  $Ca(OH)_2$  to be a strong base and other instructors might not consider it a strong base due to its poor solubility. The bottom line for you is to be clear with how your instructor is handling this.

Historically, the terms "alkali" and "alkaline" have referred to a basic substance or mixture. Thus, NaOH is an alkali and a solution of NaOH is alkaline. These terms also connect to the names of two Groups in the Periodic Table: the alkali metals for Group 1 metals and the alkaline earth metals for Group 2. Keep these terms in mind.

Notice that acids and bases give ions in solution, so these are electrolytes. The terms strong and weak also apply to electrolytes, so we can say HCl and NaOH are strong electrolytes while  $CH_3CO_2H$  and  $NH_3$  are weak electrolytes. Strong electrolytes also include soluble ionic compounds such as NaCl.

There's one final point which I want to make before closing this section. We set up acids and bases as compounds which give H<sup>+</sup> and OH<sup>-</sup> ions, but other ions are also part of the picture. An acid loses H<sup>+</sup> to water and it also forms an anion. For example, hydrochloric acid gives H<sup>+</sup> cation and chloride anion; acetic acid gives H<sup>+</sup> cation and acetate anion. On the other hand, a base gives OH<sup>-</sup> and a cation. Sodium hydroxide gives sodium cation and hydroxide anion; ammonia gives ammonium cation and hydroxide anion. You will see, especially in the next Chapter, why this is important.

#### **Problems**

- 1. True or false.
  - a. H<sub>2</sub>O never appears in a net ionic equation.
  - b. In the reaction of LiI with AgNO<sub>3</sub>, I<sup>-</sup> is a spectator ion.
  - c. When HBr dissolves in water, most of the molecules stay neutral and undissociated.
  - d. HClO<sub>2</sub> dissociates completely in water.

e. Barium hydroxide is a strong electrolyte.
True or false.
a. Spectator ions are left out of a net ionic
b. $\mathrm{AI^{3+}}$ and $\mathrm{PO_4^{3-}}$ ions cannot be kept apart

2.

- equation.
- by water.
- c. When HF dissolves in water, water pulls apart all of the molecules of HF.

MgSO<sub>4</sub>

- d. When 0.02 mole of HNO<sub>3</sub> dissolves in 4.0 L water, 0.04 moles of separate ions are obtained.
- e. Ammonia dissociates completely when dissolved in water.
- Which of the following compounds are insoluble?

 $Co(CH_3CO_2)_2$ K<sub>3</sub>PO<sub>4</sub> Al(OH)3 Ba(ClO<sub>3</sub>)<sub>2</sub> CuCl CaC<sub>2</sub>O<sub>4</sub>

Which of the following compounds are soluble?

Fe(NO<sub>3</sub>)<sub>3</sub>

5.

For each of the following, what is the formula of the precipitate which is formed upon mixing the two solutions?

CuClO<sub>4</sub>

K<sub>2</sub>SeO<sub>3</sub>

CrAsO<sub>₄</sub>

- a.  $(NH_4)_2SO_4(aq) + Ca(ClO_4)_2(aq)$
- b.  $Co(NO_3)_2(aq) + Na_2CO_3(aq)$

NH₄CN

- c. copper(II) chloride(aq) + potassium oxalate(aq)
- d. lithium chromate(aq) + nickel(II) nitrate(aq)
- Write the undissociated equation and the net ionic equation for the reaction of AqNO<sub>3</sub>(aq) with  $ZnBr_2(aq)$ .
- Write the undissociated equation and the net ionic equation for the reaction of  $(NH_4)_2CO_3(aq)$  with  $Mg(CH_3CO_2)_2(aq)$ .
- Write the undissociated equation and the net ionic equation for the reaction of mercury(II) perchlorate(aq) with potassium sulfide(aq).
- 1.00 L each of separate solutions of 0.3 M KCl, 0.1 M AgClO<sub>4</sub> and 0.1 M Pb(NO<sub>3</sub>)<sub>2</sub> are mixed into one container.
  - a. Give the formula(s) of the precipitate(s) formed.
  - b. Give the formula(s) of the spectator ion(s).
- 10. Which of the following are strong acids and which are weak acids?

**HCIO** ΗI HNO<sub>2</sub> H<sub>2</sub>SO<sub>4</sub> HBr H<sub>3</sub>PO<sub>4</sub> CH<sub>3</sub>CO<sub>2</sub>H

- 11. Consider a solution of  $HNO_3(aq)$ . What ions (if any) are present in the solution?
- 12. Consider a solution of  $HClO_2(aq)$ . What ions (if any) are present in the solution? What neutral molecules (if any, other than water) are present in the solution?