CHEMICAL REACTIONS IN SOLUTION
AND NET IONIC EQUATIONS

Chemical reactions that occur in solution fall into two broad categories:

- Oxidation-reduction reactions: reactions in which ion charges change
- Metathesis reactions: reactions in which ion charges do not change

In Chem 101A, we will deal exclusively with metathesis reactions; oxidation-reduction reactions are covered in Chem 101B.

In any metathesis reaction, two ions come together to form a new substance, either a compound or a larger ion. The most important categories of metathesis reactions for our purposes are:

- Precipitation reactions: positive and negative ions combine to form an insoluble solid
- Acid-base reactions: H⁺ combines with a negative ion to form a stable substance

This handout will introduce you to these two types of reactions and show you how to write chemical equations for these reaction types.

PRECIPITATION REACTIONS

In a precipitation reaction, two aqueous ions come together to form a solid compound. This will only happen if the product is insoluble in water. For example, if you mix an aqueous solution of AgNO₃ with an aqueous solution of NaI, the mixture instantly becomes cloudy yellow as solid AgI forms. You can predict whether a precipitation reaction will occur as follows:

Step 1: Write the formulas of the individual ions that are present when you mix the solutions.
Step 2: Look for a combination of positive and negative ions that is insoluble in water. If you find one, that is your product. If all possible combinations are water-soluble, no precipitation reaction will occur.

To do step 2, you need to know which combinations are water-soluble and which are not. Here is a table showing the behavior of common combinations of ions.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Cations that give soluble compounds</th>
<th>Cations that give insoluble compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₃⁻</td>
<td>All cations</td>
<td>None</td>
</tr>
<tr>
<td>Cl⁻, Br⁻, I⁻</td>
<td>Most cations</td>
<td>Ag⁺, Pb⁺²⁺, Hg⁺²⁺</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>Most cations</td>
<td>Ag⁺, Pb⁺²⁺, Hg⁺²⁺, Ca⁺²⁺, Sr⁺²⁺, Ba⁺²⁺</td>
</tr>
<tr>
<td>CO₃²⁻, PO₄³⁻</td>
<td>Na⁺⁺, K⁺⁺, NH₄⁺⁺</td>
<td>Most cations</td>
</tr>
<tr>
<td>OH⁻, O²⁻</td>
<td>Na⁺⁺, K⁺⁺, NH₄⁺⁺, Ba⁺²⁺</td>
<td>Most cations</td>
</tr>
<tr>
<td>S²⁻</td>
<td>Na⁺⁺, K⁺⁺, NH₄⁺⁺ All group 2A ions</td>
<td>All other cations with +1 or +2 charges (primarily transition metals)</td>
</tr>
</tbody>
</table>

Note: Soluble metal oxides react with water as they dissolve, forming the corresponding metal hydroxides.
This table only covers the most common anions and cations; it does not, for instance include $F^-$, $CrO_4^{2-}$, $Li^+$, and $Be^{2+}$, among others. You will not be expected to know the properties of ions not listed in this table.

Once we have identified an insoluble product, we write a **net ionic equation** to represent what actually happens in a precipitation reaction. For instance, when you mix solutions of $AgNO_3$ and $NaI$, only the $Ag^+$ and $I^-$ ions react, so the net ionic equation is:

$$Ag^+ (aq) + I^- (aq) \rightarrow AgI(s)$$

The $NO_3^-$ and $Na^+$ ions play no part in the reaction. We refer to them as **spectator ions**.

Here are some examples that illustrate how you can predict precipitation reactions and write net ionic equations to represent them.

**Example 1:** mixing aqueous solutions of $ZnCl_2$ and $K_2CO_3$

Step 1: The ions that are actually present are $Zn^{2+}$, $Cl^-$, $K^+$, and $CO_3^{2-}$. These ions are totally independent of one another in aqueous solution; there is no bond between $Zn^{2+}$ and $Cl^-$, or between $K^+$ and $CO_3^{2-}$.

Step 2: In principle, there are six possible combinations of ions, but actually we only need to consider two possibilities. Only combinations that contain a cation and an anion need be considered, because ions with like charges repel each other. In addition, we do not need to consider the original compounds ($Zn^{2+}$ combining with $Cl^-$, or $K^+$ combining with $CO_3^{2-}$). Therefore, **the only possible compounds that could form are $ZnCO_3$ (combining $Zn^{2+}$ with $CO_3^{2-}$) and $KCl$ (combining $K^+$ with $Cl^-$)**.

To determine whether either of these compounds will actually form, we check the solubility rules. We see that the combination of $Cl^-$ with $K^+$ is water-soluble, but the combination of $CO_3^{2-}$ with $Zn^{2+}$ is insoluble. Therefore, the two solutions will react, and the product will be solid $ZnCO_3$.

Finally, we write the net ionic equation for the reaction. The only thing that is happening here is zinc ions combining with carbonate ions, so the net ionic equation is:

$$Zn^{2+}(aq) + CO_3^{2-}(aq) \rightarrow ZnCO_3(s)$$

**Example 2:** mixing aqueous solutions of $(NH_4)_3PO_4$ and $CuSO_4$

Step 1: The ions that are actually present are $NH_4^+$, $PO_4^{3-}$, $Cu^{2+}$, and $SO_4^{2-}$.

Step 2: The only compounds that could form are $(NH_4)_2SO_4$ (by combining $NH_4^+$ and $SO_4^{2-}$ ions) and $Cu_3(PO_4)_2$ (by combining $Cu^{2+}$ and $PO_4^{3-}$ ions). Consulting the solubility rules, we see that only $Cu_3(PO_4)_2$ is insoluble, so that is our product.

The net ionic equation is:

$$3 Cu^{2+}(aq) + 2 PO_4^{3-}(aq) \rightarrow Cu_3(PO_4)_2$$

*Note that the equation must be balanced. A common error is to omit the coefficients on the left side of the net ionic equation.*
Example 3: mixing aqueous solutions of MgBr₂ and FeSO₄

Step 1: The ions that are actually present are Mg²⁺, Br⁻, Fe²⁺, and SO₄²⁻.

Step 2: The only compounds that could form are MgSO₄ (by combining Mg²⁺ and SO₄²⁻) and FeBr₂ (by combining Fe²⁺ and Br⁻). Consulting the solubility rules, we see that both of these compounds are water-soluble. Therefore, no reaction will occur in this case, and there is no chemical equation to write.

Final note: It isn’t obvious from the solubility table, but it’s worth remembering that all compounds that contain Na⁺, K⁺, or NH₄⁺ are water-soluble.

ACID-BASE REACTIONS

In an acid-base reaction, H⁺ becomes attached to a negative ion or (occasionally) an electrically neutral molecule. Sorting out acid-base chemistry is more complicated than dealing with precipitation reactions, so we will limit ourselves to situations where H⁺ becomes bonded to OH⁻, CO₃²⁻, or HCO₃⁻.

Even with this restriction, we must deal with the annoying fact that most acids do not dissociate much when they are dissolved in water. For example, compare NaC₂H₃O₂ with HC₂H₃O₂. When we dissolve NaC₂H₃O₂ (sodium acetate) in water, the resulting solution only contains Na⁺ ions and C₂H₃O₂⁻ ions. On the other hand, when we dissolve HC₂H₃O₂ (acetic acid) in water, the solution contains primarily HC₂H₃O₂ molecules, with very small amounts of H⁺ ions and C₂H₃O₂⁻ ions. Only a few acids dissociate completely, and you just need to learn the five common ones:

<table>
<thead>
<tr>
<th>Strong acids (100% dissociated in water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
</tr>
</tbody>
</table>

When we want to predict an acid-base reaction, we use the same general procedure that we used for precipitation reactions: identify the substances that are actually present, and then figure out what will combine with what. However, we do not use the solubility rules to predict what will happen with combinations that involve H⁺. Instead, we use the fact that H⁺ will always bond to OH⁻, CO₃²⁻, or HCO₃⁻, even when it starts out bonded to something else. Here are some examples.

REATIONS INVOLVING A STRONG ACID

Example 1: mixing aqueous solutions of HCl and Na₂CO₃

Step 1: HCl is one of our strong acids and is 100% dissociated in water, so the actual substances that are present are H⁺, Cl⁻, Na⁺, and CO₃²⁻.
Step 2: The possible products are NaCl (by combining Na\(^+\) and Cl\(^-\)) and HCO\(_3\)\(^-\) (by combining H\(^+\) and OH\(^-\)). NaCl is water-soluble, so it will not form. However, H\(^+\) will bond to CO\(_3\)\(^2-\) whenever the two are put together, so our product is HCO\(_3\)\(^-\). The net ionic equation is:
\[ \text{H}^+(aq) + \text{CO}_3^{2-}(aq) \rightarrow \text{HCO}_3^-(aq) \]

"Why didn’t we make H\(_2\)CO\(_3\)?" In acid-base reactions, only one H\(^+\) ion becomes attached to the base at a time. When we mix the reactants, each CO\(_3\)\(^2-\) bonds to one H\(^+\) ion until all of the CO\(_3\)\(^2-\) ions are used up. If we have excess H\(^+\) ions, they will react with HCO\(_3\)\(^-\), but that is a separate reaction. We’ll look at that situation in a bit.

**Example 2:** mixing aqueous solutions of H\(_2\)SO\(_4\) and KOH

Step 1: H\(_2\)SO\(_4\) is one of our strong acids and is 100% dissociated in water, but it dissociates into H\(^+\) and HSO\(_4\)^\(^-\), not two H\(^+\) and SO\(_4\)^\(^2-\). The actual substances that are present are therefore H\(^+\), HSO\(_4\)^\(^-\), K\(^+\), and OH\(^-\).

Step 2: The possible products are KHSO\(_4\) (by combining K\(^+\) and HSO\(_4\)^\(^-\)) and H\(_2\)O (by combining H\(^+\) and OH\(^-\)). KHSO\(_4\) is water-soluble, so it will not form. However, H\(^+\) will bond to OH\(^-\) whenever the two are put together, so our product is H\(_2\)O. The net ionic equation is:
\[ \text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l) \]

*Note that when water is involved in an aqueous reaction, it is always written H\(_2\)O(l), not H\(_2\)O(aq).*

**REACTIONS INVOLVING A WEAK ACID**

**Example 3:** mixing aqueous solutions of HF and NaOH

Step 1: HF is a weak acid, so most of the HF molecules remain undissociated. We are looking for the principal reaction, so we ignore the tiny amounts of H\(^+\) and F\(^-\) ions that are also present. The primary substances that are present are HF, Na\(^+\), and OH\(^-\).

Step 2: At first glance, it looks like nothing should happen. However, even though HF doesn’t dissociate very much on its own, the H\(^+\) ion can come off if it is pulled off by a different anion. In this case, H\(^+\) is strongly attracted to OH\(^-\), so it will leave the F\(^-\) ion and stick to the OH\(^-\) ion.

To write the net ionic equation, it helps to list the substances that are present before and after the reaction between HF and OH\(^-\):

*Before:* HF and OH\(^-\) (H\(^+\) is bonded to F\(^-\))
*After:* F\(^-\) and H\(_2\)O (H\(^+\) is bonded to OH\(^-\))

Therefore, the net ionic equation is:
\[ \text{HF}(aq) + \text{OH}^-(aq) \rightarrow \text{F}^-(aq) + \text{H}_2\text{O}(l) \]

*Note that the reaction is not H\(^+\)(aq) + OH\(^-\)(aq) → H\(_2\)O(l). H\(^+\) is not an independent ion here; it is bonded to F\(^-\), and must be pulled off.*

**Example 4:** mixing aqueous solution of H\(_3\)PO\(_4\) and K\(_2\)CO\(_3\)
Step 1: H₃PO₄ is a weak acid, so the primary substances that are present are H₃PO₄, K⁺, and CO₃²⁻.

Step 2: H⁺ can be pulled off by CO₃²⁻, forming HCO₃⁻. H₃PO₄ loses one H⁺ ion and becomes H₂PO₄⁻. The net ionic equation is:

\[
\text{H}_3\text{PO}_4(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{H}_2\text{PO}_4^{-}(\text{aq}) + \text{HCO}_3^{-}(\text{aq})
\]

This reaction is an excellent illustration of the fact that acid-base reactions are always 1:1, with one H⁺ ion moving from the acid to the base.

**Example 5:** mixing aqueous solutions of H₂C₄H₄O₄ (succinic acid) and Ba(OH)₂

Step 1: H₂C₄H₄O₄ is a weak acid, so most of the H₂C₄H₄O₄ molecules remain undissociated. The primary substances that are present are H₂C₄H₄O₄, Ba²⁺, and OH⁻.

Step 2: H⁺ can be pulled off by OH⁻, forming H₂O. H₂C₄H₄O₄ loses one H⁺ ion and becomes HC₄H₄O₄⁻. The net ionic equation is:

\[
\text{H}_2\text{C}_4\text{H}_4\text{O}_4(\text{aq}) + \text{OH}^{-}(\text{aq}) \rightarrow \text{HC}_4\text{H}_4\text{O}_4^{-}(\text{aq}) + \text{H}_2\text{O}(\text{l})
\]

**Example 6:** what happens if we add excess Ba(OH)₂ in the previous example?

Step 1: After the reaction in example 5, we were left with HC₄H₄O₄⁻ ions and Ba²⁺ ions in the solution. Adding more Ba(OH)₂ solution means that we now have some OH⁻ ions, so the primary substances that are present are HC₄H₄O₄⁻, Ba²⁺, and OH⁻.

Step 2: HC₄H₄O₄⁻ can lose one more H⁺ ion, and OH⁻ can pull it off. Removing H⁺ from HC₄H₄O₄⁻ leaves us with C₄H₄O₄²⁻, and we also make a molecule of H₂O. The net ionic equation is:

\[
\text{HC}_4\text{H}_4\text{O}_4^{-}(\text{aq}) + \text{OH}^{-}(\text{aq}) \rightarrow \text{C}_4\text{H}_4\text{O}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})
\]

**REACTIONS OF ACIDS WITH INSOLUBLE OXIDES AND HYDROXIDES**

Both OH⁻ and O²⁻ are powerfully attracted to H⁺. This attraction is so strong that OH⁻ and O²⁻ will bond to H⁺ even if the anion is initially bonded to a metal ion. For example, Mg(OH)₂ is insoluble in water, but it reacts with any acid, strong or weak. Reactions with weak acids tend to be rather complicated, so we will only consider strong acids in Chem 101A. With any strong acid, the reaction is:

\[
\text{Mg(OH)}_2(s) + 2 \text{H}^+(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})
\]

In all cases, the products are water and a metal ion.

**Example 7:** adding solid ZnO to a solution of HNO₃

Step 1: The primary substances that are present are solid ZnO, aqueous H⁺ ions, and aqueous NO₃⁻ ions. HNO₃ is a strong acid, so it dissociates completely, but ZnO cannot dissociate, because it does not dissolve in water.
Step 2: $H^+$ will bond to $O^{2-}$, forming water and pulling the $O^{2-}$ off the zinc ion. It takes two $H^+$ ions to form $H_2O$, so the net ionic equation is:

$$\text{ZnO(s)} + 2 \text{H}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{H}_2\text{O(l)}$$

**REATIONS OF ACIDS WITH BICARBONATE IONS**

$\text{HCO}_3^-$ can bond to $H^+$, forming $\text{H}_2\text{CO}_3$. However, $\text{H}_2\text{CO}_3$ is unstable; only tiny amounts of $\text{H}_2\text{CO}_3$ can exist in a solution. Whenever a reaction makes a significant amount of $\text{H}_2\text{CO}_3$, the $\text{H}_2\text{CO}_3$ breaks down into $\text{H}_2\text{O}$ and gaseous $\text{CO}_2$ as quickly as it is formed. The $\text{CO}_2$ bubbles out of the solution, giving a “fizzing” effect like a carbonated beverage that has been shaken.

**Example 8:** mixing solutions of $\text{NaHCO}_3$ and $\text{HCl}$

Step 1: The substances that are present are $\text{Na}^+$, $\text{HCO}_3^-$, $\text{H}^+$, and $\text{Cl}^-$

Step 2: $\text{NaCl}$ will not form (because it is water-soluble). However, $\text{H}^+$ ions will combine with $\text{HCO}_3^-$ ions. As described above, the final products of this combination are $\text{H}_2\text{O}$ and $\text{CO}_2$, so the net ionic equation is:

$$\text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{O(l)} + \text{CO}_2(\text{g})$$

**Example 9:** mixing solutions of $\text{KHCO}_3$ and $\text{H}_3\text{PO}_4$

Step 1: The primary substances that are present are $\text{K}^+$, $\text{HCO}_3^-$, and $\text{H}_3\text{PO}_4$. Note that $\text{H}_3\text{PO}_4$ is a weak acid, so most of the $\text{H}_3\text{PO}_4$ molecules are not dissociated.

Step 2: $\text{HCO}_3^-$ is attracted to $\text{H}^+$ and can pull it off the $\text{H}_3\text{PO}_4$ molecule. When $\text{H}_3\text{PO}_4$ loses one $\text{H}^+$ ion, we are left with $\text{H}_2\text{PO}_4^-$. The $\text{H}^+$ combines with $\text{HCO}_3^-$ to form $\text{H}_2\text{O}$ and $\text{CO}_2$, so the net ionic equation is:

$$\text{HCO}_3^-(\text{aq}) + \text{H}_3\text{PO}_4(\text{aq}) \rightarrow \text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_2\text{O(l)} + \text{CO}_2(\text{g})$$

**DISSOLVING INSOLUBLE METAL CARBONATES IN ACIDS**

Insoluble compounds that contain $\text{CO}_3^{2-}$ are similar to insoluble compounds containing $\text{OH}^-$ or $\text{O}^{2-}$, in that all of them can be dissolved in solutions that contain acids. For insoluble carbonates (like $\text{CaCO}_3$ or $\text{Ag}_2\text{CO}_3$), the $\text{H}^+$ ions from the acid bond to the $\text{CO}_3^{2-}$ ions, forming $\text{HCO}_3^-$. Since metal bicarbonates are water-soluble, this reaction forms a clear solution. However, in general we use excess acid to speed up the dissolving process. In excess acid, the $\text{HCO}_3^-$ ions gain an additional $\text{H}^+$, producing $\text{H}_2\text{O}$ and $\text{CO}_2$. Here is the net ionic equation for the reaction that occurs when $\text{CaCO}_3$ dissolves in excess aqueous $\text{HCl}$:

$$\text{CaCO}_3(\text{s}) + 2 \text{H}^+(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + \text{H}_2\text{O(l)} + \text{CO}_2(\text{g})$$

Here is the net ionic equation for the reaction that occurs when $\text{Ag}_2\text{CO}_3$ dissolves in excess aqueous $\text{HNO}_3$:

$$\text{Ag}_2\text{CO}_3(\text{s}) + 2 \text{H}^+(\text{aq}) \rightarrow 2 \text{Ag}^+(\text{aq}) + \text{H}_2\text{O(l)} + \text{CO}_2(\text{g})$$
SUMMARY OF ACID-BASE REACTION TYPES YOU SHOULD LEARN

Strong acid reacting with a water-soluble hydroxide or carbonate:

\[ \text{H}^+ (aq) + \text{OH}^- (aq) \rightarrow \text{H}_2\text{O}(l) \]
\[ \text{H}^+ (aq) + \text{CO}_3^{2-} (aq) \rightarrow \text{HCO}_3^- (aq) \]

Weak acid reacting with a water-soluble hydroxide or carbonate (using HX, H$_2$X, etc. to represent weak acids):

\[ \text{HX}(aq) + \text{OH}^- (aq) \rightarrow \text{H}_2\text{O}(l) + X^- (aq) \quad \text{(for an acid that contains one H}^+\text{)} \]
\[ \text{HX}(aq) + \text{CO}_3^{2-} (aq) \rightarrow \text{HCO}_3^- (aq) + X^- (aq) \]
\[ \text{H}_2\text{X}(aq) + \text{OH}^- (aq) \rightarrow \text{H}_2\text{O}(l) + \text{HX}^- (aq) \quad \text{(for an acid that contains two H}^+\text{)} \]
\[ \text{H}_2\text{X}(aq) + \text{CO}_3^{2-} (aq) \rightarrow \text{HCO}_3^- (aq) + \text{HX}^- (aq) \]

Successive steps if a diprotic acid reacts with excess hydroxide:

\[ \text{H}_2\text{X}(aq) + \text{OH}^- (aq) \rightarrow \text{H}_2\text{O}(l) + \text{HX}^- (aq) \quad \text{(initial reaction)} \]
\[ \text{HX}^- (aq) + \text{OH}^- (aq) \rightarrow \text{H}_2\text{O}(l) + X^{2-} (aq) \quad \text{(second reaction)} \]

Note: A triprotic acid (H$_3$X) can undergo three reactions.

Strong acid reacting with a water-soluble bicarbonate:

\[ \text{H}^+ (aq) + \text{HCO}_3^- (aq) \rightarrow \text{H}_2\text{O}(l) + \text{CO}_2(g) \]

Weak acid reacting with bicarbonate:

\[ \text{HX}(aq) + \text{HCO}_3^- (aq) \rightarrow X^- (aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \]
\[ \text{H}_2\text{X}(aq) + \text{HCO}_3^- (aq) \rightarrow \text{HX}^- (aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \]

Strong acid reacting with an insoluble hydroxide or oxide (using M to represent the metal):

\[ \text{H}^+ (aq) + \text{MOH}(s) \rightarrow \text{M}^+(aq) + \text{H}_2\text{O}(l) \quad \text{(for a +1 metal ion)} \]
\[ 2 \text{H}^+ (aq) + \text{M}_2\text{O}(s) \rightarrow 2 \text{M}^+(aq) + \text{H}_2\text{O}(l) \]
\[ 2 \text{H}^+ (aq) + \text{M(OH)}_2(s) \rightarrow \text{M}^{2+}(aq) + 2 \text{H}_2\text{O}(l) \quad \text{(for a +2 metal ion)} \]
\[ 2 \text{H}^+ (aq) + \text{MO}(s) \rightarrow \text{M}^{2+}(aq) + \text{H}_2\text{O}(l) \]
\[ 3 \text{H}^+ (aq) + \text{M(OH)}_3(s) \rightarrow \text{M}^{3+}(aq) + 3 \text{H}_2\text{O}(l) \quad \text{(for a +3 metal ion)} \]
\[ 6 \text{H}^+ (aq) + \text{M}_2\text{O}_3(s) \rightarrow 2 \text{M}^{3+}(aq) + 3 \text{H}_2\text{O}(l) \]

Strong acid reacting with an insoluble carbonate:

\[ 2 \text{H}^+ (aq) + \text{M}_2\text{CO}_3(s) \rightarrow 2 \text{M}^+(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \quad \text{(for a +1 metal ion)} \]
\[ 2 \text{H}^+ (aq) + \text{MCO}_3(s) \rightarrow \text{M}^{2+}(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \quad \text{(for a +2 metal ion)} \]