

A.P. Chemistry
Writing Chemical Reactions

Generally students do poorly on the section of the A.P. exam that deals with writing net-ionic reactions. The format of these questions changed beginning with the exam in May of 2007 and a somewhat different approach is needed.

On the actual exam in May you will have 40 minutes (calculator-free) to write three **balanced** net-ionic reactions and respond to two essay questions. Probably—although it is not yet clear—you will be able to spend whatever part of the 40 minutes you wish on the reactions. You will not be able to choose three reactions out of a larger number as in previous years. The requirement to balance is also new. In addition to writing the reactions you will have to respond to a question about each reaction. This is new.

What follows, therefore, is a best “guess”, based on reactions given in previous exams and adapted to the format that began with the May 2007 exam.

A survey of the last 10 years of A.P. exams indicates that most reactions given fall into one of these rather broad categories:

1. metathesis (double replacement)
2. single replacement
3. combustion
4. acid/base neutralization
5. combination
6. decomposition
7. reactions of anhydrides
8. organic
9. non-trivial redox
10. complex ion formation or decomposition
11. Lewis acid/base (adduct formation)

In the past these have occurred in any combination on an exam. In this course, we will break up these reactions into 7 groups and introduce a new group on each test.

Beginning at the beginning we state the "obvious": most compounds can be divided into about 6 categories:

1. acids (formulas begin with H- except for some organic acids like acetic acid which are often written with the H- at the end, as in CH₃COOH)
2. bases (formulas end in -OH except for ammonia and organic bases which are similar to ammonia and contain nitrogen)
3. metal oxides (binary compounds of a metal and oxygen)
4. non-metal oxides (binary compounds of a non-metal and oxygen)
5. salts (compounds of metals that are NEITHER bases NOR oxides)

6. other (most compounds belong here!!!!)

What should you know right now about these categories besides what is given on the previous page?

The following is a start:

ACIDS : "strong" acids (which exist largely as ions in solution rather than molecules) are few in number and should be learned: HCl, HBr and HI are the only strong binary acids; ternary acids are usually strong if the number of oxygens exceeds the number of hydrogens by two or more

BASES : "strong" bases are also few in number and should be learned: LiOH, NaOH, KOH, Ca(OH)₂, Sr(OH)₂, Ba(OH)₂

SALTS : the salts which are soluble include all of the salts of lithium, sodium, potassium and ammonium cations and of nitrate and acetate anions. All chlorides are soluble except silver, lead and mercury(I) [AP H]. All sulfates are soluble except those of calcium, lead, barium, and strontium [C PBS]. All other salts should be considered only slightly soluble unless you learn otherwise.

This is a *beginning*. Learn this **now**.

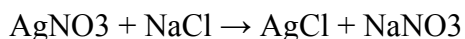
It is likely that you will need to have oxidation number rules at your mental fingertips. The reason for this has more to do with potential questions about reactions than with balancing techniques for non-trivial redox reactions. For example, some reactions students have been asked to write in the past are things they would never have seen. Whether this will remain the case is not known, but if it does, a default "fair" question about such a (redox) reaction might have to do with a change in oxidation numbers which can be determined without having any idea what the reaction behavior is like. Below is a simplified set of rules which should look familiar.

1. the oxidation number of an element is 0
2. the oxidation number of monoatomic ion is equal to its charge
3. *in compounds*: the oxidation number of hydrogen is +1 (except in metal hydrides where it is -1) the oxidation number of oxygen is -2 (except in peroxides where it is -1) the oxidation number of alkali metals is +1 the oxidation number of alkaline earth metals is +2 the oxidation number of terminal halogens is -1
4. the sum of all the oxidation numbers in a molecule or ion is equal to the charge

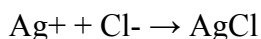
A.P. Chemistry
Metathesis Reactions

Metathesis reactions begin with two reactant compounds and produce two product compounds. They typically occur when the reactants are acids, bases or salts.

The products are predicted by simply switching the positive parts of the two reactants.



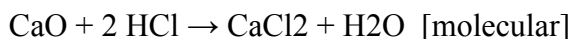
These molecular equations can be converted into net-ionic form by considering the information given in the previous handout regarding the strengths of acids and bases as well as the solubility of salts. Strong electrolytes of any type exist in water solution as separated ions. Weak electrolytes exist primarily in molecular form. The intent of the net-ionic equation is to represent reactant and product species as accurately as possible. Thus the two examples above in net-ionic form would be:

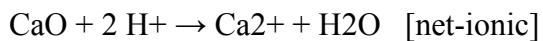


By contrast, when acetic acid is a reactant it would always be written in molecular form because it is weak and exists primarily as molecules in water solution:



While not strictly fitting the metathesis “script”, the reactions of acids with metal oxides are similar in form to those of acids and bases. A metal oxide is, in a real sense, a *basic anhydride*, i.e., a base with the water removed. For example, calcium oxide (CaO) is simply calcium hydroxide (Ca(OH)₂) with one H₂O removed from the formula. While the oxide is hardly soluble in water, a suspension of the powder is quite basic due to the formation of some calcium hydroxide. Acids therefore react with metal oxides just as if they were bases and the products of the reaction are similar:

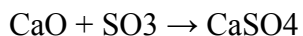




Note that the oxide, which is not soluble in water, is not broken up into ions in the net-ionic reaction. A similar reaction may be written for an *acid anhydride* (non-metal oxide) with a base.

Finally it is also possible for basic anhydrides and acid anhydrides to react directly, forming a salt.

These are typically non-aqueous reactions:



What follows are reactions taken from the old Part C of previous A.P. exams *to which have been added a potential question that might be asked about the reaction*. You should practice them when you have a chance. These kinds of reactions will be featured on your first exam.

[it is worth noting again that in the reaction section there are no "no-reactions"]

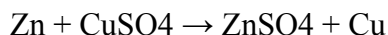
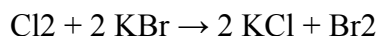
1. dilute sulfuric acid is added to a solution of barium acetate
--identify the spectator ions in this reaction; explain.
2. solutions of sodium phosphate and calcium chloride are mixed
--what is the most likely color of the final reaction mixture?; explain
3. hydrogen sulfide gas is bubbled through a solution of silver nitrate
--if a drop of the final reaction mixture is placed on litmus paper, what color will it turn?
4. manganese(II) nitrate solution is mixed with sodium hydroxide solution
--identify the spectator ions in this reaction; explain
5. solutions of zinc sulfate and sodium phosphate are mixed
--if a wire loop is dipped into the final reaction mixture and placed in a flame, what color will the flame turn?
6. sulfur trioxide gas is bubbled into a solution of sodium hydroxide
--is the temperature of the mixture likely to increase or decrease?
7. dilute solutions of lithium hydroxide and hydrobromic acid are mixed
--which of the reactant solutions will feel slippery on the skin?
8. a solution of ammonia is added to a dilute solution of acetic acid
--how does the conductivity of the final reaction mixture compare with that of either reactant?; explain
9. a solution of sulfuric acid is added to a solution of barium hydroxide
--if equimolar amounts of the two reactants are mixed, what change will be indicated by a conductivity device?



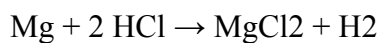
- since both products are poor electrolytes there are essentially “no” spectator ions
2. $3 \text{Ca}^{2+} + 2 \text{PO}_4^{3-} \rightarrow \text{Ca}_3(\text{PO}_4)_2$
 --white; the absence of transition metals makes this likely
 3. $\text{H}_2\text{S} + 2 \text{Ag}^+ \rightarrow 2 \text{H}^+ + \text{Ag}_2\text{S}$
 --red/pink since hydrogen ions are liberated in the reaction
 4. $\text{Mn}^{2+} + 2 \text{OH}^- \rightarrow \text{Mn}(\text{OH})_2$
 --sodium (Na^+) and nitrate ions (NO_3^-)
 5. $3 \text{Zn}^{2+} + 2 \text{PO}_4^{3-} \rightarrow \text{Zn}_3(\text{PO}_4)_2$
 --since sodium ions are spectators, they will be found in the solution and color the flame bright yellow
 6. $\text{SO}_3 + 2 \text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O}$
 --the temperature should increase as for any neutralization reaction
 7. $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$
 --lithium hydroxide will feel slippery since it is a base
 8. $\text{NH}_3 + \text{CH}_3\text{COOH} \rightarrow \text{NH}_4^+ + \text{CH}_3\text{COO}^-$
 --both reactants are weak electrolytes while the final mixture contains free ions so it should conduct
 much better
 9. $\text{H}^+ + \text{SO}_4^{2-} + \text{Ba}^{2+} + \text{OH}^- \rightarrow \text{BaSO}_4 + \text{H}_2\text{O}$
 --if equal moles are mixed “all” of the ions will be combined in either a precipitate or water and thus
 the conductivity should be essentially zero

A.P. Chemistry
 Single Replacement Reactions
 Other types of Displacement

Single replacement (or simply displacement) reactions are a type of trivial redox reaction in which an element reacts with a compound. In that compound there must be an element similar in some way to the reacting element but *less* reactive. The similarity can be as fundamental as belonging to the same chemical family, or as loose as both having the same charge polarity in compounds. In any case, the more reactive element takes the place of the less active element in the compound and the less active element is “displaced”:



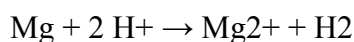
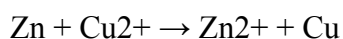
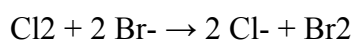
The molecular equations can be converted to net-ionic form by applying solubility rules. Note that the activity of a given element is most easily predicted with an “activity series” or a standard reduction potential table. Since there are no “no reactions” on this portion of the exam, the point is more or less moot. As a generalization, the metal with the more positive reduction potential will be replaced. For halogens, the displacement order follows the periodic table, fluorine being the most active. It should not be forgotten that hydrogen may also be produced as the “displaced” element by active metals reacting with acids:



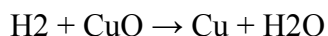
This pattern is generally true for all *dilute* acids. In the case of VERY active metals like those of Groups

I and II, hydrogen can be displaced from water (acids will also work, of course). When active metals react with nitric acid the results may be different if the acid is not dilute. In those cases little or no hydrogen may be produced and the nitric acid may instead be reduced to either NO or NO₂. Because of the potential ambiguity involved it is probable that nitric acid will be avoided. It has not appeared in this context during the past 10 years.

Examples of the above reactions in net-ionic form would be:

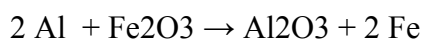


In addition to the simple element replacement reactions which follow a basic pattern there are other types of reactions—some redox and some not—which follow a similar pattern in that something is displaced or *dislodged* from a compound. The simplest of these are the *non-aqueous* replacement reactions, the most common of which are reductions of metal oxides by hydrogen gas:



Reactions like this typically take place at high temperatures. Note there is no net-ionic version since the reaction does not occur in solution.

The classic thermite reaction also fits into this category:



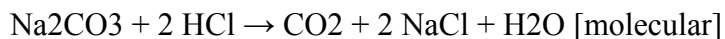
In both of the previous cases the parallel with the aqueous single replacement reaction is clear: the more “active” element (i.e., the stronger reducing agent) enters into the compound and the less “active” element is pushed out.

There is a type of reaction in which *weaker acids or bases are dislodged from compounds by stronger acids and bases*. While not redox reactions or strictly single replacements (no elements are involved) there is a kind of similarity. A simple example is the basis for a qualitative test for the presence of the ammonium ion in a compound. When a strong base, NaOH, is added to an ammonium salt, ammonia gas is liberated and can be detected by its distinctive odor:



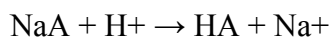


If this looks a bit odd there is a more familiar example which is again used as a qualitative test for the presence of carbonate ion:



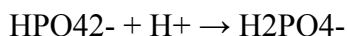
Of course, CO_2 is not an acid. However the actual unstable product of the reaction is the weak acid carbonic acid, H_2CO_3 . As we know, this spontaneously breaks down into CO_2 and H_2O .

We can generalize this process with the generic salt of a weak acid, NaA :



This can get tricky with the salts of polyprotic acids. Historically salts of phosphoric acid (H_3PO_4) have often been the subject of this kind of reaction. The object of these kinds of questions seems to be the recognition that weak polyprotic acids will only reform step-by-step, i.e., the extent to which the acid reforms depends on the amount of stronger acid added. Consider these examples:

equal volumes of equimolar solutions of sodium hydrogen phosphate and hydrochloric acid are mixed

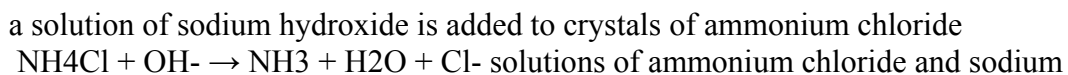


equal volumes of 0.10 M sodium hydrogen phosphate and 0.20 M hydrochloric acid are mixed

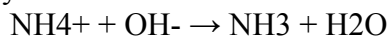


Notice that in the second case there is twice as much H^+ available so the reaction goes an additional step.

For bases the only displacement you are likely to encounter is the one with ammonia already shown above. In the past it has not been uncommon for these kinds of reactions to start with a solid salt to which aqueous acid or base is added. Compare these final forms:



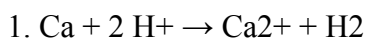
hydroxide are combined



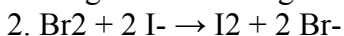
These follow the general rule that net ionic reactions should show the states in which reactants begin and products end.

Some reactions from actual previous AP exams follow. Again, questions about each reaction have been added for practice. Try them out.

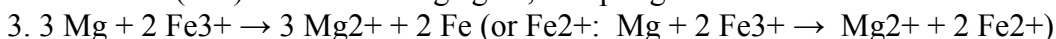
1. calcium metal is added to a dilute solution of hydrochloric acid
--give at least one visual observation for this reaction
2. liquid bromine is added to a solution of potassium iodide
--which substance is the oxidizing agent?
3. magnesium turnings are added to a solution of iron(III) chloride
--describe a color change that corresponds to the reaction you write
4. hydrogen gas is passed over hot iron(III) oxide
--which substance is reduced?
5. small chunks of solid sodium are added to water
--describe a test to confirm the gaseous product in your reaction
6. hydrobromic acid is added to a solution of potassium hydrogen carbonate
--when a gas produced by the reaction is bubbled through limewater, what visible change is expected?
7. aqueous potassium hydroxide is added to crystals of ammonium bromide
--when moistened litmus paper is held over the reaction container, what change will be observed?
8. hydrogen chloride gas is bubbled through a solution of potassium cyanide
--which species behaves as a Brønsted base?



--vigorous bubbling as hydrogen gas is produced

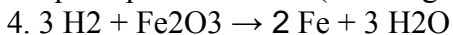


--bromine (Br_2) is the oxidizing agent, accepting electrons from the iodide ions

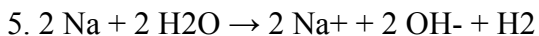


--the yellow/orange color of the mixture turns dirty looking, eventually light green (Fe^{2+}) and

perhaps to colorless ($\text{Fe} + \text{Mg}^{2+}$)

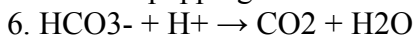


--the iron in the Fe_2O_3 is reduced to Fe

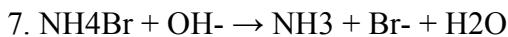


--if some of the gas is collected in a test tube of air and a lighted match brought to the mouth of the

tube a popping noise will be heard



--limewater becomes cloudy when carbon dioxide contacts it due to the formation of CaCO_3

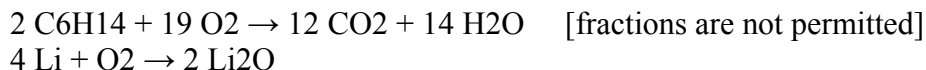


- the litmus paper will turn blue because ammonia gas is produced
8. $\text{HCl} + \text{CN}^- \rightarrow \text{HCN} + \text{Cl}^-$
- the CN^- ion behaves as a Brønsted base

A.P. Chemistry
Combustion Reactions
Combination Reactions
Decomposition Reactions

Combustion reactions can vary a good deal as soon as one steps out of the realm of hydrocarbons but the exam seldom indulges in other combustions unless they are simple combinations like the burning of a metal in air or oxygen. For the hydrocarbon combustions, the simple rule is that burning (combining with O_2) produces carbon dioxide and water. This is true whether the hydrocarbon contains oxygen or not. However, if halogens or nitrogen are present, oxides of these elements may form as well. These are difficult to predict, although in the case of nitrogen, NO or NO_2 would always be a reasonable guess.

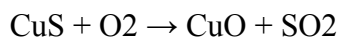
Some examples are found below:



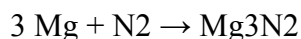
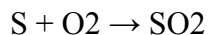
Note that net-ionic versions of these reactions really don't exist since liquid water is generally not present. The most significant hurdle with these reactions is likely to be the organic compound names. If you don't know what *propanal* is then it doesn't matter that it is easy to write the combustion reaction.

While the compounds selected are seldom complicated, some knowledge of basic organic functional group nomenclature is helpful. Stay tuned for that.

Occasionally metal sulfides are the reactants in combustion reactions. In these cases the sulfide is generally converted to the metal oxide and sulfur dioxide:

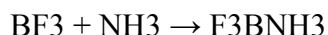


Combination reactions can refer to the very simple reaction of two elements (a redox process) to form a compound. However, some compounds also combine to form other compounds. These are sometimes less obvious. In the former case, the reaction is mostly challenging because the correct formula of the final product must be known (or guessed). Net-ionic form is usually not required because typically water would be absent:



There are many reactions in which two compounds combine to form a single product but it is difficult to generalize these. You have already seen one example in which acidic and

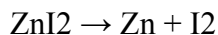
basic anhydrides react to give a salt (and no water). There is an analogue to this process which appears rather too often on the exam: the reaction of a Lewis acid with a Lewis base to form an *adduct*. Lewis acids are species which can accept electron pairs. Obvious examples are molecules with incomplete octets and even simple metal cations. Lewis bases are species which can donate electron pairs. Obvious examples are molecules with lone pairs. Historically on the exam these reactions always have taken the same form. A Group III compound reacts with a Group V compound:



It is not necessary to write the product formula as shown to get credit. The purpose of doing so is to focus attention on what is going on. There is a lone pair on the nitrogen of NH_3 and there is a pair vacancy on the boron of the BF_3 . These fit together like hand in glove and a covalent bond forms. The product (which is analogous to a salt) is called an “adduct”. Simple, if you can remember it.

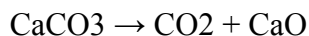
Decomposition reactions are more or less combination reactions reversed, but on the exam there are many more decompositions which do not lead directly to elements than there are combinations that do not start with elements.

Decompositions to elements are quite trivial and not common:

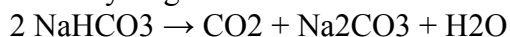


A survey of the last 10 years of exams reveals a “short” list of compound decompositions that have appeared more than once. Most are thermal decompositions, i.e., the compound is heated and partially breaks down. The ones you are likely to encounter are:

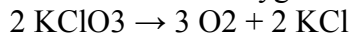
metal carbonates \rightarrow carbon dioxide + metal oxide



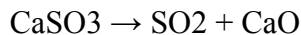
metal hydrogen carbonates \rightarrow carbon dioxide + metal carbonate + water



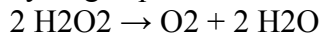
metal halates \rightarrow oxygen + metal halide



metal sulfites \rightarrow sulfur dioxide + metal oxide



hydrogen peroxide \rightarrow oxygen + water



The last reaction in the list is more often represented as the result of catalytic action (no catalyst is included in the written reaction, of course) but occasionally the H_2O_2 is simply “heated strongly”.

Here are some reactions from actual previous AP exams. Again, questions about each reaction have been added for practice. Try them out.

1. propanol is burned completely in air
--what kind of organic compound is propanol?
 2. acetic acid is burned in an excess of oxygen
--how many molecules of products are formed from the burning of 1 molecule of acetic acid?
 3. calcium metal is heated strongly in the presence of oxygen
--if the product is added to water is the resulting mixture acidic or basic?
 4. phosphine gas and boron trichloride gas are combined
--indicate which substance is the Lewis base and which is the Lewis acid
 5. solid magnesium carbonate is heated
--if the gas produced is bubbled through limewater, describe the change in appearance of the
limewater
 6. solid potassium chlorate is heated in the presence of a manganese(IV) oxide catalyst, resulting in a
change in the oxidation states of both the chlorine and the oxygen
--what is the oxidation number of chlorine before and after the reaction?
 7. a solution of hydrogen peroxide is heated
--which element changes in oxidation state? How can there be only one?
1. $2 \text{C}_3\text{H}_7\text{OH} + 9 \text{O}_2 \rightarrow 6 \text{CO}_2 + 8 \text{H}_2\text{O}$
--an alcohol
 2. $\text{CH}_3\text{COOH} + 2 \text{O}_2 \rightarrow 2 \text{CO}_2 + 2 \text{H}_2\text{O}$
--4 molecules
 3. $2 \text{Ca} + \text{O}_2 \rightarrow 2 \text{CaO}$
--basic, since CaO is the anhydride of a strong base, $\text{Ca}(\text{OH})_2$
 4. $\text{PH}_3 + \text{BCl}_3 \rightarrow \text{H}_3\text{PBCl}_3$
-- PH_3 is the Lewis base while BCl_3 is the Lewis acid
 5. $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$
--the CO_2 produced will react with the limewater to produce a cloudy white mixture containing
 CaCO_3
 6. $2 \text{KClO}_3 \rightarrow 2 \text{KCl} + 3 \text{O}_2$
--the chlorine starts as +5 and ends as -1
 7. $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$
--only oxygen changes, but it is both oxidized and reduced (from -1 to -2 and from -1 to 0)

A.P. Chemistry
Hydrolysis Reactions

Hydrolysis is generally understood as a reaction of something with water. Reaction should not be confused with dissolving. Many compounds dissolve in water and are essentially unchanged. We can count here even the ionic solids which, while they may dissociate into ions are still fundamentally the same. In a hydrolysis reaction, some new substance or species forms that is not found in the original compound.

The most common examples of hydrolysis are reactions of the anions of weak acids or the cations of weak bases with water. These are typical of the processes which occur when salts of these compounds enter water. For example, sodium acetate is the salt of a strong base and a weak acid (sodium hydroxide and acetic acid). Because of the high affinity of the acetate ion for hydrogen ions, addition of acetate ions to water actually results in some of the minuscule amounts of H⁺ present in water being grabbed by the acetate ions:



(in Brønsted form this would look like: $\text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{CH}_3\text{COOH} + \text{H}_2\text{O}$)

As you can see, this is an equilibrium process. The equilibrium lies to the left, so only a few of the acetate ions added disappear and become part of acetic acid molecules. Meanwhile, since H⁺ ions are being tied up that would otherwise establish the K_w equilibrium for water, more water begins to dissociate:



(or $2 \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$)

This results in a net excess of OH⁻ in the mixture (i.e., solutions of sodium acetate are basic). Thus the net ionic reaction for something as innocent sounding as the dissolving of sodium acetate in water becomes:



which is the sum of the two reactions that came before (plus the liberation of the sodium ion into the solution). When writing such a reaction for the exam the equilibrium arrows are not required but would be impressive.

The general form for such a reaction might be written:

anion of weak acid + water \rightleftharpoons weak acid + hydroxide ion

By a similar analysis there is a reaction that could be written for the cations of weak bases, although there is really only one common one (NH₄⁺):

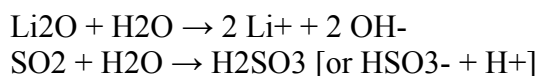
cation of weak base + water \rightleftharpoons weak base + hydrogen ion

It is possible to argue that hydrolysis reactions actually occurs with small, highly charged metal ions which form otherwise weak bases. For example, dissolving Fe(NO₃)₃ in distilled water almost always results in some reddish brown Fe(OH)₃ clouding the solution. However, this kind of example has never been featured on the exam.

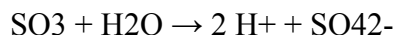
There are two other kinds of reactions with water which have been featured on the exam in the last 10 years [of course active metals react with water but this has already been covered in the second packet].

You will recall that metal and non-metal oxides are often considered as acids and bases without water.

These compounds are sometimes called acid and base *anhydrides*. When added to water there is a strong tendency for the formation of the acid or base:



The first example is fairly straightforward. You need to be careful about the solubility of the resulting base, but that's about it. The second example is more interesting. Students often ask how they are to know whether the acid formed is H₂SO₃ (sulfurous acid, by the way) or H₂SO₄ (which seems like a more familiar possibility). The answer is that the oxidation state of the non-metal does not change. In SO₂ and H₂SO₃ the oxidation state of sulfur is +4. In H₂SO₄ it is +6. Thus sulfur trioxide will form sulfuric acid:



Which brings us to a second question—why are the acids written differently? Sulfurous acid is *weak*. It has been accepted on past exams written entirely in molecular form. Because it is a polyprotic acid some people think it's better to write one hydrogen ion as coming off (hence the alternate form in square brackets). Either form is acceptable. Sulfuric acid, on the other hand, is a *strong* acid and so must be broken up.

Anyway, here are some mixed examples from actual tests of past years, again with added questions:

1. solid cesium oxide is added to water
--describe the effect of the resulting mixture on litmus paper
2. gaseous hydrogen chloride is dissolved in water
--why is the molecular compound hydrogen chloride able to dissolve in water?
3. carbon dioxide gas is bubbled through water
--describe the effect of the resulting mixture on litmus paper
4. solid sodium sulfite is added to water
--if a few drops of bromthymol blue indicator are added to the reaction mixture, what color will it be?
5. sodium phosphate crystals are added to water
--which reactant acts as a Brønsted base? explain
6. solid sodium cyanide is added to water
--give a conjugate acid-base pair in your reaction

7. solid aluminum sulfide is added to water
--describe the odor expected for the final reaction mixture
8. dinitrogen trioxide gas is bubbled through water
--if a few drops of bromthymol blue indicator are added to the reaction mixture, what color will it be?

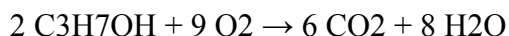
1. $\text{Cs}_2\text{O} + \text{H}_2\text{O} \rightarrow 2 \text{Cs}^+ + 2 \text{OH}^-$
--the litmus paper will turn blue because of the presence of OH^-
2. $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$ [Arrhenius version also accepted]
-- HCl is very polar as is water and thus the two molecules are attracted to one another
3. $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{H}^+$
--the litmus paper will turn red/pink because of the presence of H^+
4. $\text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow 2 \text{Na}^+ + \text{HSO}_3^- + \text{OH}^-$
--since the final mixture contains OH^- it will be basic and the indicator will turn blue
5. $\text{Na}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow 3 \text{Na}^+ + \text{OH}^- + \text{HPO}_4^{2-}$ [or H_2PO_4^-]
--the Na_3PO_4 (or the PO_4^{3-} alone) is accepting a proton from water and is thus a base
6. $\text{NaCN} + \text{H}_2\text{O} \rightarrow \text{Na}^+ + \text{HCN} + \text{OH}^-$
-- H_2O and OH^- or HCN and CN^-
7. $\text{Al}_2\text{S}_3 + 6 \text{H}_2\text{O} \rightarrow 2 \text{Al}(\text{OH})_3 + 3 \text{H}_2\text{S}$
--the H_2S should give the solution the odor of rotten eggs
8. $\text{N}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_2$
--the indicator will turn yellow since HNO_2 is a weak acid

A.P. Chemistry Organic Reactions

The subject of organic reactions is very large and rather complicated. There are hundreds of "named" reactions or reaction types which have accumulated throughout the history of modern organic chemistry, generally carrying the name of their discoverer (or explainer). These are NOT the type of things you should be worrying about at this level. There are many other names given to reactions by students but these are generally not fit to print.

In the past 10 years the scope of organic reactions on the exam has narrowed to combustions and the reaction of amines with water (analogous to the reaction of ammonia with water). For the student this is good news. The "bad" news is that the very simple combustion reactions will do you no good if you cannot translate the names of simple organic compounds into formulas. What are "simple" organic compounds? Past reactions have included alkanes, alkenes, alkynes, alcohols, ketones, aldehydes, and carboxylic acids. These compounds are generally not branched so the names are not full of numbers and punctuation.

Combustion reactions, of course, are going to result in carbon dioxide and water:



The reaction above could be the combustion of any isomer of propanol (1-propanol or 2-propanol).

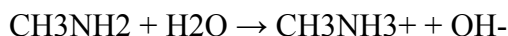
Since you are not required to show structures, the same formula works for either one although strictly speaking an organic chemist would write them differently. You could just as well write C₃H₈O. That is actually the formula for a LOT of compounds, but it doesn't matter in these questions.

More than once in the past 10 years organic bases have appeared on the exam, probably to terrorize students more than for any other reason. Why exactly amines have been picked on is anyone's guess.

It's unlikely you would encounter one in high school as the compounds smell terrible, typically fume and are generally not nice to work with. We do a small amount of work with dilute solutions of 1,2-diaminoethane (ethylenediamine) but that's it. It may be that now with only three reactions to write and no options to choose from these will "go away". Maybe.

Anyway, they *are* easy but once again the hurdle is the name. So far only methane derivatives have been used, e.g. methylamine [CH₃NH₂] and dimethylamine [(CH₃)₂NH] and so on. Notice that these compounds can be thought of as ammonia in which more and more methyl groups are substituted for the hydrogens. The nitrogen remains trivalent, so there are always only 3 groups attached unless the molecule becomes an ion (analogous to the ammonium ion, with a corresponding increase in valency to

4). In water these do exactly the same thing as ammonia:



The organic beastie on the right is the methylammonium ion (get it?). This, of course, is actually an equilibrium which we use to show why amines are bases.

Some (limited) examples follow.

1. propanone is burned completely in air
--how many total molecules of products will be produced for every molecule of propanone?
2. butanoic acid is burned in air
--what is oxidation state of the carbon in the product mixture?
3. liquid trimethylamine is dissolved in water
--when litmus paper is touched to the mixture what color is expected?

1. $\text{CH}_3\text{COCH}_3 + 4 \text{O}_2 \rightarrow 3 \text{CO}_2 + 3 \text{H}_2\text{O}$
--6 moles of products for each mole of propanone
2. $\text{C}_3\text{H}_7\text{COOH} + 5 \text{O}_2 \rightarrow 4 \text{CO}_2 + 4 \text{H}_2\text{O}$
--the C in carbon dioxide is +4

3. $(\text{CH}_3)_3\text{N} + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{NH}^+ + \text{OH}^-$
--the litmus paper will turn blue because of the presence of OH^-

A.P. Chemistry Complexation Reactions

Reactions of coordination compounds and ions are not covered in depth on the exam but you will sometimes see them in the reaction-writing section and they are easy enough to complete with a few basic principles in mind. Most can be recognized by the choice of reactants: generally a transition metal ion or compound (also occasionally the amphoteric species from Group 3A such as Al) and a source of ligands. The most common ligands involved in questions are ammonia, the hydroxide ion, and the cyanide ion. Key to recognizing such is often the word "excess", indicating that enough of the complexation agent has been added to eliminate the possibility of precipitation of lesser-coordinated species. Occasionally this word will not appear and instead "concentrated" is used to describe the added complexing agent (in that case usually an acid or base).

One of the hurdles to get over is some knowledge of the likely coordination numbers for metal ions.

Unfortunately there is no simple way to remember all of them. Some you may recognize from work done in the lab or something you read. In a pinch, it may be helpful to know that *often* the coordination number is twice the cation charge. In any case, you will seldom lose points just because you used a coordination number of 4 instead of 6.

Historically, reactions involving complex ions on the exam fall into three broad categories:

1. complexation of a soluble salt

e.g. a concentrated solution of ammonia is added to a solution of copper(II) chloride
 $4 \text{NH}_3 + \text{Cu}^{2+} \rightarrow [\text{Cu}(\text{NH}_3)_4]^{2+}$

2. complexation of an insoluble salt

e.g. excess concentrated potassium hydroxide solution is added to a precipitate of zinc hydroxide
 $2 \text{OH}^- + \text{Zn}(\text{OH})_2 \rightarrow [\text{Zn}(\text{OH})_4]^{2-}$

3. destruction of a complex by acid/base neutralization

e.g. dilute hydrochloric acid is added to a solution of diamminesilver nitrate
 $2 \text{H}^+ + \text{Cl}^- + [\text{Ag}(\text{NH}_3)_2]^+ \rightarrow \text{AgCl} + 2 \text{NH}_4^+$

Below are some examples of actual reactions from past A.P. exams along with added questions.

1. excess dilute nitric acid is added to a solution of tetramminecadmium(II) ion
--what is the coordination number of the complex ion?
2. pellets of aluminum metal are added to a solution containing an excess of sodium hydroxide
--which reactant acts as a Lewis acid? explain
3. an excess of ammonia gas is bubbled through a solution saturated with silver chloride
--which reactant acts as a Lewis base? explain
4. a concentrated solution of ammonia is added to a suspension of zinc hydroxide
--what visual change occurs in the reaction mixture?
5. a solution of ammonium thiocyanate is added to a solution of iron(III) chloride
--describe the color changes that occur during the reaction
1. $4 \text{H}^+ + [\text{Cd}(\text{NH}_3)_4]^{2+} \rightarrow \text{Cd}^{2+} + 4 \text{NH}_4^+$
--the coordination number of $[\text{Cd}(\text{NH}_3)_4]^{2+}$ is 4
2. $\text{Al} + 4 \text{OH}^- \rightarrow [\text{Al}(\text{OH})_4]^-$
--the Al accepts electron pairs from the hydroxide ions and is thus a Lewis acid
3. $2 \text{NH}_3 + \text{AgCl} \rightarrow [\text{Ag}(\text{NH}_3)_2]^+ + \text{Cl}^-$
--the NH_3 donates electron pairs to the silver ion and is thus a Lewis base
4. $4 \text{NH}_3 + \text{Zn}(\text{OH})_2 \rightarrow [\text{Zn}(\text{NH}_3)_4]^{2+} + 2 \text{OH}^-$
--the suspension starts out slightly cloudy and ends up clear
5. $\text{SCN}^- + \text{Fe}^{3+} \rightarrow [\text{FeSCN}]^{2+}$ (other species up to CN_6 accepted)
--the original solutions are nearly colorless while the product mixture is orange to blood red

A.P. Chemistry Non-trivial Redox Reactions

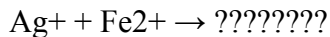
Here we are at the end of the line. We have already looked at simple reactions which involve changes in oxidation number. These include single displacement reactions and combination reactions between elements (also decomposition reactions yielding elements...). Such reactions can be completed by following simple rules. The non-trivial sort require knowledge of common oxidizer/reducer pairs or at the very least some common-sense elimination of unlikely products followed by inspired guessing. Memorizing the "common" pairs may help but you will probably get farther by trying to reason through the process since there is no guarantee that the pairs you memorize will be used on the exam.

Over the past 10 years the number of truly difficult non-trivial reactions has dwindled. There have only been 2 and those were in years when you could easily have avoided them by choosing other options. Now that there are no options and reactions must be balanced it is questionable whether these kinds of reactions will ever appear again. It is clear that monoatomic ion redox will continue to be considered fair game. Here is an example from the 2007 exam:

“A solution containing silver(I) ion (an oxidizing agent) is mixed with a solution

containing iron(II) ion
(a reducing agent)”

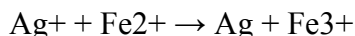
DUH. This is so transparent it is embarrassing.



At first glance this does not seem to fit any pattern you have learned. That should make you suspicious (after all, how stupid can you be after two years of chemistry?????). Iron in its intermediate oxidation state is not particularly stable. It can potentially be either oxidized to +3 or reduced to 0 (the metal itself).

The statement tells you that it behaves as a reducing agent. It will therefore be oxidized. Silver ions can really only be reduced to 0 (the metal). The statement tells you that it is an oxidizing agent and so it will, in fact, be reduced.

This is the kind of reasoning (even without the ludicrous hints) which would allow you to potentially predict probable products:



The key to monoatomic ion redox is to have some idea of what's typical (on your list of common ions?) and what's possible (minimum and maximum states).

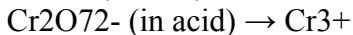
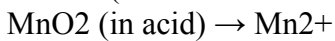
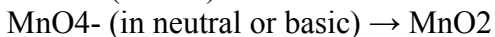
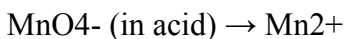
Some essential principles to keep in mind are these:

- elements in their highest positive oxidation state (same as group #, whether A or B) can ONLY be reduced
- elements in their lowest oxidation state (0 for metals, negative for non-metals, corresponding to distance from noble gases) can ONLY be oxidized
- intermediate oxidation states can go either way!!!
- if the mixture is acidic, H⁺ should be included as a reactant; water is one product
- if the mixture is basic, OH⁻ should be included as a reactant; water is one product
- occasionally the acid anion or base cation may precipitate with a product ion

The last three items on the list may be irrelevant if truly complex non-trivial processes simply die a quiet death on future exams.

For enquiring minds a list of the more common redox pairs follows:

oxidizers [remember, oxidizers will become reduced]



HNO₃ (conc.) → NO₂

HNO₃ (dilute) → NO

H₂SO₄ (hot, concentrated) → SO₂ [if not hot and conc., this acts like HCl or other normal acids] metal cations → lower charge cations or (rarely) free metals free halogens → halide ions

reducers [remember, reducers will become oxidized]

halide ions → free halogens

free metals → metal cations

SO₃²⁻ (or SO₂) → SO₄²⁻

NO₂⁻ → NO₃⁻

free halogens (dil. basic) → hypohalite ions [like XO⁻]

free halogens (conc. basic) → halate ions [like XO₃⁻]

metal cations → higher charge cations

Whew! That seems like a lot to remember for such little payback, but if you look at the list carefully you

will see that none of the species are really exotic after two years of chemistry (with the possible

exception of the hypohalite and halate ions---we did see them in the KBr/KBrO₃ lab). So the real task is

to see the changes in oxidation state as possibilities when a reaction does not fit other categories and

then use your chemical imagination: one has to go up and the other has to go down! The products should

not be weird or exotic, i.e., you should recognize them. If you don't, you probably deserve to miss the question.

What if you MUST balance a non-trivial reaction? Of course you already know a method, tedious as it

is. Old-timers often develop shortcuts for dealing with the essentials of the redox process and then do the

rest by inspection. Here is an example of a hybrid method based on *oxidation number* changes.

“a solution of potassium permanganate is mixed with an acidic solution of iron(II) sulfate”

--the potassium is junk; nothing ever happens to potassium ions

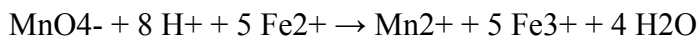
--iron(II) is probably a goner

--permanganate is a common strong oxidizer

First guess: MnO₄⁻ + H⁺ + Fe²⁺ → Mn²⁺ + Fe³⁺ + H₂O

--Mn goes from +7 to +2, Fe goes from +2 to +3
--Five Fe ions must be oxidized for each Mn that is reduced:
 $\text{MnO}_4^- + \text{H}^+ + 5 \text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + 5 \text{Fe}^{3+} + \text{H}_2\text{O}$

--now balance the oxygens and hydrogens by inspection



--Done!

Below are some reactions from past tests for you to try along with (you guessed it!) some questions.

1. a solution containing tin(II) ions is added to acidified potassium dichromate solution
--there is a color change during this reaction; which atom is most likely responsible?
explain
2. powdered iron is added to a solution of iron(III) sulfate
--which species are spectators?
3. solutions of tin(II) chloride and iron(III) chloride are mixed
--both the reactant and product mixtures are colored; which ions account for the colors?

1. $3 \text{Sn}^{2+} + 14 \text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 3 \text{Sn}^{4+} + 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$
--the chromium changes in oxidation state and is a transition metal; most transition metal compounds are colored and the color changes with oxidation state

2. $\text{Fe} + 2 \text{Fe}^{3+} \rightarrow 3 \text{Fe}^{2+}$

--the sulfate ion is a spectator

3. $\text{Sn}^{2+} + 2 \text{Fe}^{3+} \rightarrow \text{Sn}^{4+} + 2 \text{Fe}^{2+}$

--since iron is a transition metal it is likely that the colors come from Fe^{2+} and Fe^{3+}