

A Classification of AP Chemistry Reactions

Introduction

This classification divides all of the reactions into five major groups; simple precipitation, acids and bases, combustion, reduction and oxidation, and complexation. For each category any important special cases are presented, and then a general method for attack is outlined. Large categories (acid/base and redox) are further subdivided. Of over 150 reactions tested on AP exams since 1968, only about 20 reactions could not be classified using this scheme. If organic reactions are omitted, the number of unsolvable questions drops to a handful.

An overview of the classification scheme is presented in Figure 1. For each of the categories on the diagram, identifying characteristics of those reactions will be given, along with a brief description of the chemical principles necessary to write the equation. Sample equations from AP exams since 1968 will be shown for each category. These could be the basis for teaching materials (handouts, worksheets, or quizzes) that incorporate these principles and exercise students' equation-writing skills.

General Principles of Equation-Writing

In writing the reactants:

- Write all soluble ionic compounds in aqueous solution as their constituent ions. Never write NaCl, Ca(NO₃)₂, etc.
- Write all strong acids in water solution as H⁺ or H₂O⁺ plus the anion. Never write HCl or
- Write all strong bases as OH and the cation. Never write NaOH or LiOH.
- Consider writing water as HOH instead of H₂O, especially in acid/base reactions. Sometimes water is a reactant even if it's not explicitly stated (all "solutions" are water solutions).
- If the reaction is in "an acidified solution," H⁺ is almost sure to be a reactant, and the OH should not appear in the equation.
- Don't omit any ions unless you're absolutely sure that they'll be spectator ions. For example, although the Cl⁻ in hydrochloric acid is usually a spectator, it is sometimes a reactant.

After writing the products:

- H₂ and O₂ are almost never products of chemical reactions, except in certain special cases that will be discussed below.
- Inspect all of the ions in the products to see if there are any precipitates.
- Finally, cross out any spectator ions.

Precipitation Reactions

Many of the reactions are simple reactions that involve formation of an insoluble precipitate. These reactions generally involve mixing two solutions, but may involve hydrogen sulfide gas. Watch for the possibility of two insoluble products.

Classification based on insoluble anions; solubility rules

The soluble cation rule is: All common salts of Group 1 metals (alkali metals) and the ammonium ion are soluble. Other solubility rules are best remembered based on the solubility of certain anion. First of all, all common nitrates and acetates are soluble. Other anions are insoluble in certain cases:

Halides: CI, Br, I

The halides are generally soluble except with silver, mercury (I), and lead. Note that mercury (I) is written as Hg_2^{2+} .

Dilute hydrochloric acid is added to a dilute solution of mercury (I) nitrate. $\mathbf{Hg_2}^{2+} + \mathbf{Cl}^- \Rightarrow \mathbf{Hg_2Cl_2}$

$$Hg_2^{2+} + C\Gamma \rightarrow Hg_2Cl_2$$

Sulfates: SO₄²-

Sulfates are generally soluble except with calcium, barium, strontium, silver, mercury (I), and lead.

Dilute sulfuric acid is added to a solution of barium chloride.

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

Hydroxides: OH

Hydroxides are generally insoluble except with the soluble cations (above) and limited solubility with calcium, barium, and strontium.

A solution of copper (II) sulfate is added to a solution of barium hydroxide.

$$Cu^{2+} + SO_4^{2-} + Ba^{2+} + OH \rightarrow Cu(OH)_2 + BaSO_4$$

Sulfides: S2-

Phosphates: PO₄³
Chromates: CrO₄²
Carbonates: CO₃²

Other anions are generally insoluble except with the soluble cations (above).

- Hydrogen sulfide gas is added to a solution of cadmium nitrate.

$$H_2S + Cd^{2+} \rightarrow CdS + H^+$$

- Solutions of zinc sulfate and sodium phosphate are mixed.

$$Zn^{2+} + PO_4^{3-} \rightarrow Zn_3(PO_4)_2$$

- Solutions of silver nitrate and sodium chromate are mixed.

$$Ag^{+} + CrO_{4}^{2-} \rightarrow Ag_{2}CrO_{4}$$

Note: Although we are finished with simple precipitation, any of the following reactions may
produce insoluble salts that precipitate. Be sure to check solubility rules for the products of
every reaction.

Acid/Base Reactions

Acid/base reactions always exhibit no change in oxidation number for any of the ionic or molecular species involved in the reaction.

Special Cases

Special cases are classified based on the type of atom that exhibits special behavior: oxygen, nitrogen, hydrogen, phosphorus, aluminum, and zinc.

Oxygen: Oxides

Oxides can be either acidic or basic, depending on what happens when they are added to water. Remember, there is likely to be no change in oxidation number when an oxide dissolves in water. Oxides of non-metals are acidic:

- Sulfur trioxide gas is added to excess water.

$$SO_3 + HOH \rightarrow H_2SO_4 \rightarrow H^+ + HSO_4^-$$

Oxides of metals are basic:

- Solid sodium oxide is added to water.

$$Na_2O + HOH \rightarrow Na^+ + OH^-$$

If there is no water present, oxides can be Lewis acids and bases: they combine to form a salt as if water were present. There is no change in oxidation number for such a reaction.

- Solid calcium oxide is heated in the presence of sulfur trioxide gas.

In water, we would see:

$$CaO + HOH \rightarrow Ca^{2+} + OH$$

 $SO_3 + HOH \rightarrow H_2SO_4 \rightarrow H^+ + HSO_4$
 $Ca^{2+} + HSO_4 + OH \rightarrow CaSO_4(s) + HOH$

So, our overall reaction would be:

$$CaO + SO_3 + HOH \rightarrow CaSO_4 + HOH$$

But this can happen without the water:

$$CaO + SO_3 \rightarrow CaSO_4$$

This is the intended answer. It is helpful, however, if students see the logic of the reaction in water solution.

- Powdered magnesium oxide is added to a container of carbon dioxide gas.

$$MgO + CO_2 \rightarrow MgCO_3$$

Nitrogen

Nitrogen gas will react with some active metals to form nitride (N³-) compounds.

- Calcium metal is heated strongly in nitrogen gas.

$$Ca + N_2 \rightarrow Ca_3N_2$$

The nitride ion is very basic and pulls hydrogen from water molecules to form ammonium and hydroxide.

- Solid lithium nitride is placed in water.

$$Li_3N + HOH \rightarrow NH_3 + Li^+ + OH^-$$

Hydrogen

Hydrogen can form H ions with active metals. Such compounds, called ionic hydrides, are very basic and pull hydrogen off of water, forming hydrogen gas and hydroxide.

Water is added to a sample of pure sodium hydroxide.

$$NaH + HOH \rightarrow Na^+ + H_2 + OH^-$$

Phosphorus

Phosphorus halides form solutions of two acids when added to water. The phosphorus forms the weak oxyacid with the same oxidation number (+5 for phosphoric, +3 for phosphorus) while the halide forms the hydrogen halide acid.

Solid phosphorus pentachloride is added to excess water.

$$PCl_5 + HOH \rightarrow H_3PO_4 + H^+ + Cl^-$$

Aluminum

In water solution, aluminum ions form complexes with six ligands. When base is added to the hydrated aluminum ion, Al(H₂O)₆³⁺, some H⁺ is removed to leave Al(OH)₃(H₂O)₃, commonly written Al(OH)₃ - a precipitate. Addition of more base results in Al(OH)₄(H₂O)₂, sometimes written AlO₂ + 4H₂O. This means that aluminum hydroxide is amphoteric and will react with acid and base.

Excess concentrated sodium hydroxide is added to solid aluminum hydroxide.

$$Al(OH)_3 + OH \rightarrow Al(OH)_4$$

Zinc

Zinc ions, Zn²⁺, coordinate with only four ligands but are amphoteric in the same way as aluminum. Zinc forms $Zn(H_2O)_4^{2+}$ - $Zn(OH)_2(H_2O)_2$ (s) - $Zn(OH)_4^{2-}$.

Excess concentrated potassium hydroxide is added to a precipitate of zinc hydroxide.

$$Zn(OH)_2 + OH^- \rightarrow Zn(OH)_4^{2}$$

General Acid/Base Reaction

Strong Acids: HCl, HBr, HI, HClO₄, HClO₃, HNO₃, and H₂SO₄ (for the first H⁺). Stong Bases: LiOH, NaOh, KOH, RbOH, CsOH, Ca(OH)2, Sr(OH)2, and Ba(OH)2

Weak Acid + Strong Base (OH')

In this category a weak acid is mixed with a hydroxide. The conjugate base is produced along with water. Poly-protic acids can lose more than one H is there is excess hydroxide:

Hydrogen sulfide is bubbled through a solution of potassium hydroxide.

$$H_2S + OH \rightarrow S^2 + HOH$$

Strong Acid (H⁺) + Weak Base

In this category hydronium ions are added o a weak base. The conjugate acid is produced. More than one H⁺ can be added in poly-protic situations.

Dilute hydrochloric acid is added to a solution of potassium carbonate. $\mathbf{H}^{+} + \mathbf{CO_3}^{2-} \Rightarrow (\mathbf{H_2CO_3}) \Rightarrow \mathbf{H_2O} + \mathbf{CO_2}$

$$H^{+} + CO_{3}^{2} \rightarrow (H_{3}CO_{3}) \rightarrow H_{3}O + CO_{3}$$

Weak Acid + Weak Base

In this category a proton is transferred from the weak acid to the weak base. If both reactants are weak acids/bases, a proton must be transferred because "in all cases a reaction occurs." A household example of this is baking soda (sodium bicarbonate) plus vinegar (acetic acid):

Acetic acid solution is added to a solution of sodium hydrogen carbonate.

$$HCO_3$$
 + $CH_3COOH \rightarrow CH_3COO$ + $(H_2CO_3) \rightarrow H_2O + CO_2$ "Titration reactions"

These reaction fall into the above categories but require some thought as to Stoichiometry. A simple table to keep track of the moles of acid and base might be helpful.

A solution of sodium hydroxide is added to a solution of sodium dihydrogen phosphate until the same number of moles of each compound have been added.

$$OH^- + H_2PO_4^- \rightarrow H_2O + HPO_4^{2-}$$

Hydrolysis

In hydrolysis reactions a salt of a weak acid or weak base is added to water. Water acts as a weak acid or base itself, and a small amount of H⁺ or OH is produced.

Solid sodium cyanide is added to water.

$$CN + HOH \rightarrow HCN + OH$$

Solid aluminum nitrate is dissolved in water.

$$Al^{3+} + HOH \rightarrow Al(H_2O)_5OH^{2+} + H^+$$

Lewis Acid/Base

One classic Lewis acid/base reaction is:

- The gases boron trifluoride and ammonia are mixed.

 $BF_3 + NH_3 \rightarrow NH_3BF_3$

Combustion: Oxygen

Oxygen gas supports combustion. A standard laboratory preparation is:

- Solid potassium chlorate is heated in the presence of manganese dioxide as a catalyst.

$$KClO_3 \rightarrow KCl + O_2$$

Combustion of compounds; classification

There are some simple generalizations that can be made about combustion, depending on what atoms or ions are present in the substance to be burned:

If the compound contains:

A product will generally be:

a metal carbon the metal oxide carbon dioxide, CO₂

hydrogen sulfur

water, H₂O sulfur dioxide, SO₂

Solid copper (II) sulfide is heated strongly in oxygen gas.

 $CuS + O_2 \rightarrow CuO + SO_2$

- Carbon disulfide vapor is burned in excess oxygen.

 $CS_2 + O_2 \rightarrow CO_2 + SO_2$

- Ethanol is completely burned in air.

 $C_2H_5OH + O_2 \Rightarrow CO_2 + H_2O$

Redox Reactions

Special cases

Active Metals

Active metal, like the group 1 and 2 metals, reduce water to form hydrogen gas and hydroxide:

Sodium metal is added to water.

$$Na + HOH \rightarrow Na^+ + OH + H_2$$

Halogens

Students should recognize the following halogen diproportionation reactions:

- Chlorine gas is bubbled into a cold solution of sodium hydroxide.

$$Cl_2 + OH^- \rightarrow Cl^- + ClO^- + HOH$$

- Solutions of potassiom iodide and potassium iodate are mixed in acid solution.

$$I + IO_3 + H^+ \rightarrow I_2 + HOH$$

Hydrogen

Hydrogen gas, H₂, is an effective reducing agent for some metal oxides.

- Hydrogen gas is passed over hot copper (II) oxide.

$$CuO + H_2 \rightarrow Cu + H_2O$$

Electron Transfer Reactions

The first general type of redox reactions are simple electron-transfer equations. These do not involve oxygen or oxyanions. They usually have two reactants and two products, as electrons are transferred from one reactant to the other.

Non-oxidizing acids

Non-oxidizing acids are strong acids with anions that can't be reduced. There include HCl, HBr, and HI. They will react with more active metals to produce hydrogen gas and the metal ion. In there cases only the H^+ reacts. The E° tables given with the AP exam can be checked to see if the metal will react with H^+ .

- Calcium metal is added to a dilute solution of hydrochloric acid.

$$H^+ + Ca \rightarrow Ca^{2+} + H_2$$

E° tables

In general, the E° tables should always be checked to determine is the two species will react. Some common examples are:

- A strip of magnesium is added to a solution of silver nitrate.

$$Mg + Ag^+ \rightarrow Mg^{2+} + Ag$$

- A solution of tin (II) chloride is added to a solution of iron (III) sulfate.

$$\operatorname{Sn}^{2+} + \operatorname{Fe}^{3+} \to \operatorname{Sn}^{4+} + \operatorname{Fe}^{2+}$$

- Chlorine gas is bubbled into a solution of sodium bromide.

$$Cl_2 + Br^2 \rightarrow Cl^2 + Br_2$$

Redox with Oxygen Compounds

The second type of redox that involve oxygen-containing compounds such as nitrates, sulfates, permanganates, dichromates, etc. First of all, since these are redox reactions, one thing must be oxidized and another must be reduced. Jotting down oxidation numbers can be helpful. Second, almost all of these reactions take place in acid solution. This means that H^+ is almost sure to be a reactant and H_2O is almost sure to be a product. These types of reactions should be visually inspected to make sure all the atoms (especially oxygens) are accounted for on both sides, and that the charge could be balanced. There cannot be only negative ions on the left and only positive ions on the right. Also, check the products for precipitates.

There are four types of redox with oxygen compounds, classified by the oxidizing agent: oxidizing acids (HNO₃ and H₂SO₄), manganese compounds (MnO₄ and MnO₂), chromium compounds (Cr₂O₇²), and hydrogen peroxide (H₂O₂).

Oxidizing acids

Oxidizing acids are strong acids with anions that can be reduced. These include HNO₃ and concentrated H₂SO₄. They will react with less active metals. In this case both the H⁺ and the anion will react.

Dilute nitric acid is a good oxidizing agent and produces NO gas (colorless)

Solid silver is added to a dilute nitric acid solution.

$$H^+ + Ag + NO_3 \rightarrow Ag^+ + NO + H_2O$$

In concentrated nitric acid, brown NO₂ is produced instead.

- Zinc strips are added to a concentrated solution of nitric acid.

$$H^+ + Zn + NO_3 \rightarrow Zn^{2+} + NO_2 + H_2O$$

Concentrated sulfuric acid is also a good oxidizing agent and produces SO₂ gas:

- A strip of copper metal is added to a concentrated solution of sulfuric acid.

$$H^{+} + Cu + SO_{4}^{2-} \rightarrow Cu^{2+} + SO_{2} + H_{2}O$$

Manganese

Permanganate is MnO₄. It is a very good oxidizing agent. Mn has an oxidation number of +7, so t is a good candidate for reduction.

In acid solution, MnO₄ is reduced to Mn²⁺ ion:

- A solution of tin (II) chloride is added to an acidified solution of potassium permanganate.

$$H^{+} + MnO_{4}^{-} + Sn^{2+} \rightarrow Mn^{2+} + Sn^{4+} + H_{2}O$$

In basic solution, MnO₄ is reduced to MnO₂ (s).

A solution of potassium permanganate is mixed with an alkaline solution of sodium sulfite.

$$H_2O + MnO_4 + SO_3^2 \rightarrow MnO_2 + SO_4^2 + OH^2$$

Manganese dioxide is MnO_2 . With an oxidation number of +4, it is still a good oxidizing agent. In acid solution, MnO_2 is reduced to Mn^{2+} ion:

- A concentrated solution of hydrochloric acid is added to powdered manganese dioxide and gently heated.

$$H^+ + MnO_2 + Cl^- \rightarrow Mn^{2+} + Cl_2 + H_2O$$

Chromium

There are two chromium oxyanions with chromium in the +6 oxidation state:

Chromate: CrO₄² (yellow) Dichromate: Cr₂O₇² (orange)

We saw chromate earlier when discussing precipitates. It is not likely to appear in redox reactions on the AP exam.

Dichromate is found in redox reactions. It is a very good oxidizing agent, and is always used in acidic solution, where it forms Cr³⁺:

A solution of potassium iodide is added to an acidified solution of potassium dichromate.

$$H^+ + Cr_2O_7^{2-} + \Gamma \Rightarrow Cr^{3+} + I_2 + H_2O$$

Hydrogen Peroxide

Hydrogen peroxide, H₂O₂, has oxygen in the -1 oxidation state. H₂O₂ is an unstable compound, and it decomposes via the following reaction, in which O⁻¹ is disproportionated into O⁻² and O⁰:

A solution of hydrogen peroxide is heated.

$$H_2O_2 \rightarrow H_2O + O_2$$

Hydrogen peroxide is a good oxidizing agent. In acid solution, it forms water:

Hydrogen peroxide is added to an acidified solution of sodium bromide.

$$H^+ + H_2O_2 + Br^- \rightarrow Br_2 + H_2O$$

Hydrogen peroxide can itself be oxidized in the presence of a strong oxidizing agent (such as permanganate or dichromate). It forms oxygen gas:

Hydrogen peroxide is added to an acidified solution of potassium dichromate.

$$H^{+} + H_{2}O_{2} + Cr_{2}O_{7}^{2-} \rightarrow Cr^{3+} + O_{2} + H_{2}O$$

Complexation Reactions

Common Ligands

Ammonia, NH3

Each type of metal ion has a characteristic coordination number: Ag⁺: 2 (monodentate) ligands; Zn²⁺ and Cu²⁺: 4 ligands; Al³⁺ and Fe³⁺: 6 ligands. Complexes can be formed:

A concentrated solution of ammonia is added to a solution of copper (II) chloride.

$$Cu^{2+} + NH_3 \rightarrow Cu(NH_3)_4^{2+}$$

Also, ammonia complexes can be broken by adding acid to form the ammonia ion:

Dilute hydrochloric acid is added to a solution of diamminesilver (I) nitrate.

$$H^+ + C\Gamma + Ag(NH_3)_2^+ \rightarrow NH_4^+ + AgC1$$

Thiocyanate, SCN

Thiocyanate forms a dark red complex with iron, Fe³⁺:

A solution of ammonium thiocyanate is added to a solution of iron (III) chloride.

$$Fe^{3+} + SCN^- \rightarrow Fe(SCN)_6^{3-}$$

Thiosulfate, S₂O₃²

Thiosulfate forms complexes with any metal ions:

A solution of sodium thiosulfate is added to a precipitate of silver iodide. $AgI + S_2O_3^{2-} \rightarrow Ag(S_2O_3)_2^{3-} + \Gamma$

$$AgI + S_2O_3^2 \rightarrow Ag(S_2O_3)_2^3 + I$$