

Newton's "Chymistry" of Metal Solubilities

Introduction and Background

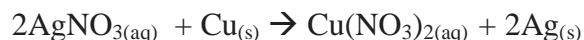
Sir Isaac Newton (1642-1727) is a famous name, of course, but few people realize that the man who discovered the law of universal gravitation, unraveled the compound nature of white light, and invented most of the mathematical techniques associated with the calculus, was also a "chymist" (seventeenth-century language for a chemist or alchemist). In fact, Newton wrote about a million words on the subject of early modern "chymistry," a subject that combined topics ranging from the refining of ores and the production of pigments to the elusive goal of transmuting metals into gold. It appears, in reality, that Newton spent more time on his alchemy than he did on his physics and math combined! Unfortunately, most of Newton's "chymical" papers were considered disreputable by his heirs because of the stigma attached to alchemy, and they remain largely unpublished to the present day. He did publish a few things on the subject though, one of which we will look at below.

The following sequence of experiments is a modern interpretation and reworking of a series of "elective affinities" taken from Query 31 of Isaac Newton's optical masterpiece, appropriately entitled the *Opticks*. In Newton's words (from the 1730 fourth edition of the *Opticks*), "And so when a Solution of Iron in *Aqua fortis* dissolves the *Lapis Calaminaris*, and lets go the Iron, or a Solution of Copper dissolves Iron immersed in it and lets go the Copper, or a Solution of Silver dissolves Copper and lets go the Silver, or a Solution of Mercury in *Aqua fortis* being poured upon Iron, Copper, Tin, or Lead, dissolves the Metal and lets go the Mercury; does not this argue that the acid Particles of the *Aqua fortis* are attracted more strongly by the *Lapis Calaminaris* than by Iron, and more strongly by Iron than by Copper, and more strongly by Copper than by Silver, and more strongly by Iron, Copper, Tin, and Lead, than by Mercury?"

In order to carry out his procedure, the first problem that we have to deal with is one of translating the archaic terminology. Newton writes *Aqua fortis* where a modern chemist would say "nitric acid" (HNO_3). He writes *Lapis Calaminaris* where we would say "calamine" (a mineral mostly made up of zinc oxide). The rest of his terminology is straightforward. The next problem is one of avoiding hazardous materials. Newton begins his series of reactions by dissolving a metal, for example iron or mercury, in nitric acid, and then putting another metal into the solution. We can easily avoid using nitric acid, which is highly corrosive and releases toxic clouds of gas upon dissolving a metal, by starting a given series of reactions with a combination of a metal and nitrate ion (NO_3). A second hazardous material is mercury, a metal with which Newton was infatuated. Since it is highly toxic, we will avoid using any mercury in this lab.

In Newton's analysis, a solution of silver nitrate will dissolve copper and "let go" (precipitate) the silver. Similarly, a solution of cupric nitrate will dissolve iron and "let go" the copper. Finally, a solution of ferrous nitrate will dissolve calamine and "let go" the iron (as iron oxide). So let's try these reactions and see what Newton was up to.

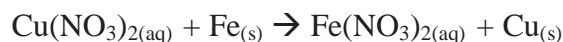
Day 1 - Weigh out 0.5g AgNO₃ and add it to 5 mL distilled water in a small glass beaker. Stir it until all solids are dissolved and a colorless solution results. (Be careful not to get this solution on your skin. It is not harmful but will **stain!**) Drop in 0.15g small copper cuttings. Allow it to sit with no agitation. Be patient! In about five minutes, the copper will begin to look silvery, as the silver begins to precipitate out and coat the copper. In ten minutes or less, the solution will start to take on a color (what color do you notice?) as more copper dissolves and more silver precipitates. Within an hour and a half, most or all of the silver will have precipitated out. When the metallic chunks (formerly copper, now silver) can be crushed with a metal spatula, the reaction is complete. The solution will now be quite colored. The reaction that has just taken place is:



Q. What ions are in solution at the beginning of the reaction? What color are these ions?

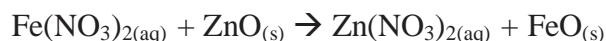
Q. What ions are in solution at the end of the reaction? What color are these ions?

Day 2 – Carefully pour off the copper nitrate solution and rinse the solid silver with water. Place the silver in a pre-weighed watchglass; remove the unreacted copper and dry before weighing. Add 0.1g of small iron shot to the copper nitrate solution. Within fifteen minutes, the solution will have begun turning a new color – what is the new color you observe? The reaction is:



It is a good idea to use a beaker that can be completely filled with solution, and to cover the top with plastic wrap in order to avoid oxidation when you leave the solution overnight.

Day 3 (Optional) – If the solution has changed its color overnight, going from greenish to brownish, there is no cause for concern. This just means that the iron(II) ion (ferrous) has gone to the iron(III) state (ferric). (This is the same color that you might observe when iron rusts.) Carefully pour off the iron nitrate solution from the solids and save the solution for the next step. Remove any unreacted iron and rinse the solid copper with water. Place the copper in a pre-weighed watchglass and dry before weighing. Add 0.1 g ZnO to the reserved iron nitrate solution. The solution will gradually go from green (or brownish) to colorless as the zinc dissolves and the iron oxide precipitates out as a greenish (or brownish) sludge. It will take a while for all of the precipitate to settle, especially if you accelerate the reaction by stirring the contents. The reaction is:



Filter the precipitate from the solution through a pre-weighed filter-paper and allow to dry completely before weighing.

Discussion

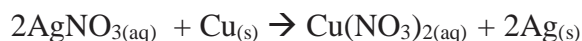
It was understood for a long time before Newton that acids could dissolve metals, but many earlier natural philosophers assumed that the metal was consumed in the process. It was in fact the alchemists who first demonstrated conclusively that the metals were not actually consumed, but remained in the solution in the form of atoms. Newton understood what we have seen in this experiment - that metals that have been dissolved in a solution can be transformed back to their original state. He also understood that the quantity of metal recovered from the solution was equal to the amount dissolved initially. Like Newton and his alchemical forebears, we now explain this in terms of atoms – the metal atoms are separated from each other in the solution but are not destroyed; the atoms recovered from solution are the same ones that were separated by dissolution so there must be the same quantity before and after.

Extension 1 – Calculations (Introductory High School)

Older students can be expected (reminded) to weigh accurately (≥ 2 decimal places) and to record the actual masses used. (The following calculations assume an initial accuracy of 3 decimal places and preserve 3 significant figures throughout.) They will then perform the calculations below with the actual masses of the reactants to determine the theoretical yield and, by comparison with the mass obtained, a percentage yield.

Day 1

First let's look at the balanced reaction equation. (Note that the reactants are in 2:1 ratio.)



Next, start by calculating the amount of reagents used. Begin with the amount of silver nitrate used.

$$(0.500 \text{ g AgNO}_3) \left(\frac{1 \text{ mol AgNO}_3}{169.88 \text{ g AgNO}_3} \right) = 0.00294 \text{ mol AgNO}_3$$

Convert this amount of silver nitrate in moles to the moles of copper that will react.

$$(0.00294 \text{ mol AgNO}_3) \left(\frac{1 \text{ mol Cu}}{2 \text{ mol AgNO}_3} \right) = 0.00147 \text{ mol Cu}$$

$$(0.00147 \text{ mol Cu}) \left(\frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}} \right) = 0.0934 \text{ g Cu}$$

Finally, we have concluded that 0.0934 g Cu is necessary to bring about this reaction to completion. Having performed these calculations with the actual mass of silver nitrate they weighed out, students can compare the mass of copper required to react fully with the actual mass used to determine which is the limiting reagent. If they use something close to the instructions, copper will be in excess.

$$0.15 \text{ g Cu used} > 0.0934 \text{ g required}$$

Therefore Cu is in excess, AgNO₃ is the limiting reagent (i.e. the amount of each of the products, copper(II) nitrate and silver, is limited by the amount of silver nitrate used, no matter how much copper is added. This point is worth emphasizing as it is not obvious to all students but relatively easy to grasp once explained.

Day 2

0.00147 mol Cu(NO₃)₂ produced by previous reaction



Therefore 0.00147 mol Fe required

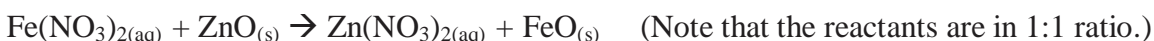
$$(0.00147 \text{ mol Fe}) \left(\frac{55.85 \text{ g Fe}}{1 \text{ mol Fe}} \right) = 0.0821 \text{ g Fe required}$$

0.1 g Fe used > 0.0821 g Fe required

Therefore Fe is in excess, and $\text{Cu}(\text{NO}_3)_2$ is the limiting reagent.

Day 3 (Optional)

Remember that 0.00147 mol $\text{Fe}(\text{NO}_3)_2$ was produced by the previous reaction



Therefore 0.00147 mol ZnO required

$$(0.00147 \text{ mol ZnO}) \left(\frac{81.41 \text{ g ZnO}}{1 \text{ mol ZnO}} \right) = 0.120 \text{ g ZnO required}$$

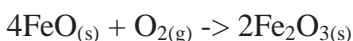
0.120 g ZnO required > 0.100 g used

Therefore ZnO is the limiting reagent, and $\text{Fe}(\text{NO}_3)_2$ is in excess.

$$(0.100 \text{ g ZnO}) \left(\frac{1 \text{ mol ZnO}}{81.41 \text{ g ZnO}} \right) \left(\frac{1 \text{ mol FeO}}{1 \text{ mol ZnO}} \right) = 0.00123 \text{ mol FeO produced}$$

Therefore 0.00123 mol FeO produced (because 1:1 stoichiometry above).

If the green iron(II) (ferrous) oxide precipitate turned red upon drying (this will almost certainly happen if it is dried completely), this means it has reacted with oxygen from the air to form iron(III) (ferric) oxide:



$$(0.00123 \text{ mol FeO}) \left(\frac{2 \text{ mol Fe}_2\text{O}_3}{4 \text{ mol FeO}} \right) \left(\frac{159.7 \text{ g Fe}_2\text{O}_3}{1 \text{ mol Fe}_2\text{O}_3} \right) = 0.0982 \text{ g Fe}_2\text{O}_3 \text{ theoretical yield}$$

Divide the actual mass obtained by the theoretical mass you calculated to obtain a percentage yield.

$$\frac{\text{actual mass}}{\text{theoretical mass}} \times 100\% = \text{percent yield}$$

Extension 2 – Redox (Advanced High School and Basic College)

While Newton believed that it was acid that kept metals in solution, we now understand the dissolution/precipitation differently. As Newton described, nitric acid is necessary for the initial dissolution of silver but what he did not realize is that the hydrogen ions that make it acidic are used up in the reaction:



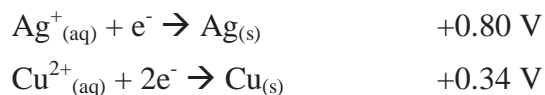
The resultant solution is actually pH neutral silver nitrate.

As you may know, solid metals are not soluble in water; however, metal ions are soluble in water. What enables the metallic copper to become soluble is that it loses electrons and gains a positive charge to become a cation. This can be made clearer by ignoring the nitrate spectator ion:

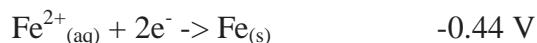


This change is called an electron transfer from one species to the other. The loss of electrons by copper here is known as **oxidation** and the gain of electrons by silver is called **reduction**. These processes occur hand-in-hand – one species can only be reduced (gain electrons) in the presence of another species that is being oxidized (losing electrons). Therefore, these reactions are usually referred to as **redox** reactions (from reduction-oxidation) since both processes must occur simultaneously.

However it is convenient to separate this coupled-change into two *half-equations* to make it explicit the change in each species:



By convention and for ease of comparison, half-equations are always written as a reduction as demonstrated above (i.e. addition of electrons). The electrical potential (in volts (V)) of this reaction is referred to as a **reduction potential**. The most common half-equations are tabulated according to their reduction potential (relative to hydrogen – this reaction is set as 0 V). This enables one to predict which species will be oxidized and which reduced; the higher the reduction potential in volts, the higher its true potential is to be reduced by another metal in a reaction. For example in the copper/silver reaction, silver has the higher reduction potential so it is the one reduced, while copper is oxidized. However, iron has a lower reduction potential than copper:



The lower reduction potential of iron explains why the copper is selectively reduced in the presence of iron (and iron oxidized in the presence of copper).

What Newton found in this experiment was that copper is more reactive than silver. He was not the first to discover this, but unlike others, he wanted to discover the quantity and character of the forces involved, just as he had done for the force of gravity. The empirical law that Newton observed was not just that metals can displace each other from

solution, but that they do so in a certain order. What Newton and other “chymists” understood as relative affinities of different metals for the acid, we now understand as relative reduction potentials compiled into what chemists now call the *Activity Series*.