

The Chemical Interpretation of Alchemy

A Critical Review

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In the field of archeology, it is becoming increasingly common to experimentally test various hypotheses as to how ancient civilizations managed to accomplish feats that, in retrospect, seem almost miraculous (1). Can one travel across the Pacific in a crude reed boat? Could the Egyptians have built the pyramids using earthen ramps to elevate the building blocks? Were the statues on Eastern Island moved from the quarry where they were carved to their current locations using log rollers? Is it possible to accidentally discover glass by building a fire on a sandy beach? What was the source of tin used in the ancient manufacture of bronze, etc.? Rather than merely speculating on these questions, it has now become common for archeologists to experimentally test the likelihood of various proposed answers. Though such tests cannot positively prove that a proposed scenario is what actually happened, they can eliminate physically impossible suggestions from further consideration.

To a lesser degree, historians have begun to apply a similar experimental approach to various questions in the history of chemistry and especially to the evaluation of assorted recipes and processes found in the alchemical literature (2). The purpose of this review is not only to call attention to the various experimental studies and chemical speculations reported in the literature, but also to provide a critical evaluation and to suggest a few additional possibilities for future study.

Possible Aurifactions

Joseph Needham, in his epic study of technology and science in ancient China, proposed that a distinction be made between what he called *aurifaction* and *aurification* (3). Aurifaction refers to serious attempts to truly make gold via transmutation, whereas aurification refers to the making materials that mimic the appearance of gold but which are known to be imitations. Which of these labels applies depends on the beliefs of the person performing the experiments in question. Though there are ancient examples of recipes that were explicitly known by their authors to produce products having

only the appearance of gold, such as the recipes for gold-like materials found in the well-known Leyden Papyrus (4), the true alchemical literature is full of authors who thought they were performing a real aurifaction, when at best they may have unknowingly achieved only an aurification. This was possible because, as Boyle later complained, alchemists often failed to properly test their products to determine whether they really had, aside from the requisite color, the other known properties of metallic gold (5).

Since we know from the principles of modern chemistry that a true aurifaction is impossible using only chemical means, this must imply that reports of successful aurifactions, if not imaginary or cases of mistaken identity, must have relied on having, knowingly or unknowingly, introduced gold into the system at some point in the process. The traditional skeptical rationale has been that this was done on purpose and that the alchemist in question was a charlatan intent on duping a potential source of financial support – usually of the royal variety (6).

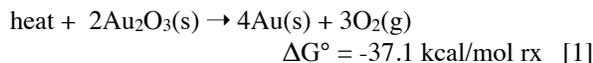
A typical example of this sort of rationale was provided by the 19th-century Scottish chemist, Thomas Thomson, in his well-known history of chemistry (7):

Sometimes [the alchemists] made use of crucibles with a false bottom. At the real bottom they put a quantity of oxide of gold or silver. This was covered with a portion of powdered crucible, glued together by a little gummed water or a little wax. The materials being put into this crucible and heat applied, the false bottom disappears, the oxide or gold or silver is reduced and, at the end of the process, is found at the bottom of the crucible and considered as the product of the operation.

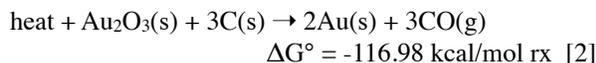
Sometimes they make a hole in a piece of charcoal and fill it with oxide of gold or silver and stop up the mouth with a little wax; or they soak charcoal in solutions of these metals, or they stir the mixtures in the crucible with hollow rods containing oxide of gold or silver within, and the bottom shut with wax. By these means the gold or silver wanted is introduced during the process and considered as a product of the operation.

Sometimes they have a solution of silver in nitric acid, or of gold in aqua regia, or an amalgam of gold or silver, which being adroitly introduced, furnishes the requisite quantity of metal. A common exhibition was to dip nails into a liquid and take them out half converted into gold. The nails consisted of one-half gold, neatly soldered to the iron and covered with something to conceal the color, which the liquid removed. Sometimes they had metals, one-half gold and the other silver, soldered together and the gold side whitened with mercury. The gold half was dipped into the transmuting liquid and then the metal heated; the mercury was dissipated and the gold half of the metal appeared.

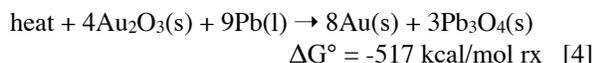
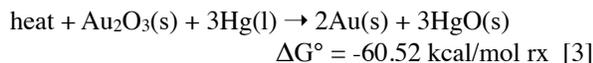
All of the reactions for oxide of gold, or digold trioxide (Au_2O_3), reported by Thomson are thermodynamically favored. Like Ag_2O and HgO , simply heating this oxide will cause it to decompose into the metal and dioxygen gas (8):



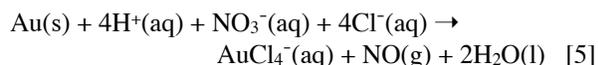
and it is easily reduced by carbon, though since we are taking about a transmutation rather than a fire assay, it is puzzling why an alchemist would put a piece of charcoal in the crucible rather than in the furnace beneath it:



Not considered in this account is the possibility that the gold oxide could also be reduced by the base metal used in the presumed transmutation:



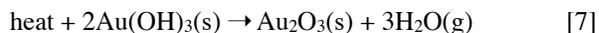
Though all of this chemistry would have been known to 18th- and 19th-century chemists, it is more questionable how much was known to the alchemists of earlier centuries. Digold trioxide cannot be made by directly reacting metallic gold with dioxygen gas and the only route to such gold compounds would have been via the reaction of gold with *aqua regia*, well known to both alchemists and early modern chemists alike. In modern terms, can be represented by the net ionic equation:



If the resulting aqueous tetrachloroaurate anion is reacted with either mild (i.e. alkali carbonates) or caustic (i.e. alkali hydroxides) alkali, it will produce a yellowish-brown precipitate of gold trihydroxide:



which, on careful drying, will yield, in turn, blackish-brown digold trioxide:



though, as one modern writer has warned, the hydroxide and oxide are poorly characterized and so similar in their properties that many so-called samples may in fact be mixtures of the two or of various hydroxyoxides (9).

Based on two well-known 17th-century reports of supposedly successful transmutations – one by the Flemish iatrochemist, Jan Baptist van Helmont (1580-1644), and the other by the Dutch-German physician, Johann Helvetius (1625-1709), I would like to suggest a possible alternative to Thomson's account in which a different gold compound was, in all likelihood, unknowingly used to perform a supposedly successful transmutation (10). The route of introduction was not via hidden compartments or disguised gold samples, but rather via samples of the so-called philosopher's stone. This was provided in both cases by a mysterious stranger, so neither van Helmont or Helvetius would have necessarily known that it was a compound of gold.

Van Helmont described this substance as “of a color, such as is in Saffron in its Powder, yet weighty, and shining like unto powdered Glass,” whilst Helvetius described it as “resembling glass or pale sulfur.” Both of these descriptions are consistent with the known color of hydrogen tetrachloroaurate (figure 1), the primary product obtained by evaporation of the resulting solution in reaction 5, as well as with the colors of other closely related gold compounds (Table 1), whereas the reference to an appearance like powdered glass suggests that the material in question was most



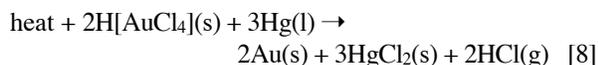
Figure 1. A tube of crystalline hydrogen tetrachloroaurate tetrahydrate. Was this the philosopher's stone?

Table 1. Various Gold Compounds and their Colors.

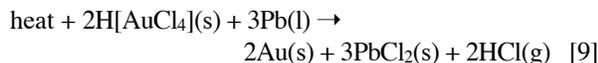
Compound	Color
Au_2O_3	brown
$\text{Au}(\text{OH})_3$	brown
$\text{H}[\text{AuCl}_4]$	light yellow
$\text{K}[\text{AuCl}_4]$	light yellow
$\text{Na}[\text{AuCl}_4]$	orange yellow
Au_2Cl_6	orange red

likely in the form of a crystalline powder.

In van Helmont's account this powder was added to heated mercury in order to affect the transmutation, presumably leading to the generation of metallic gold via the reaction (8):



whereas in Helvetius' account it was added to molten lead, leading to the analogous reaction:



Unhappily I have been unable to locate any free energy data for the tetrachloroaurates that would allow one to quantitatively verify that these reactions are both thermodynamically favored. However, given the notoriously unstable nature of most simple gold compounds, the ease with which they are reduced to metallic gold by a wide variety of reducing agents, and the thermodynamic stabilities of the various byproducts, it is highly probable that both have the required negative free energy values (6). It is also of note that both van Helmont and Helvetius reported observing an effervescence on adding the powder to the liquid base metal, most likely due to the escaping gaseous hydrogen chloride byproduct postulated in these equations.

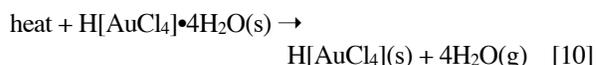
There are, however, several pertinent objections to



Figure 2. An ampoule of digold hexachloride.

this proposal. The first is that not all alchemists agreed that the philosopher's stone had a yellow color. Thus the 14th-century alchemist, Nicolas Flamel (1340-1418), claimed that it was red, rather than yellow. This problem was actually noted by Helvetius, but the mysterious stranger who showed him the light yellow "stone" replied that "the color makes no difference, and that the substance was sufficiently mature for all practical purposes" (7). This refers to the alchemical belief that the philosopher's stone was prepared by a progressive maturing process, each stage of which was characterized by a specific color – red or ruby being the final or fully matured product, though this was often preceded by a yellow or citron stage.

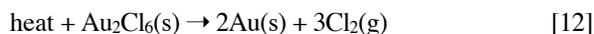
Consistent with this color sequence is the fact that yellow hydrogen tetrachloroaurate tetrahydrate can be converted into red digold hexachloride (figure 2) by careful heating. Differential thermal analysis shows that this occurs in several stages: below 130.7°C the tetrachloroaurate first loses its water of hydration:



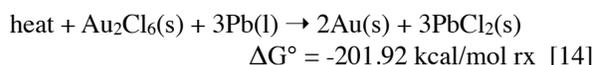
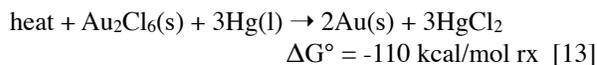
whereas between 130.7 and 186.8°C it further decomposes into red digold hexachloride and hydrogen chloride:



and, finally, at yet higher temperatures, into metallic gold and dichlorine gas (11):



Once formed through controlled thermolysis, the red digold hexachloride, like the yellow hydrogen tetrachloroaurate in reactions 8 and 9, can react with either metallic mercury or molten lead to produce metallic gold, and the proposed reactions can both be thermodynamically evaluated due to the availability of the necessary free energy data for digold hexachloride (6):



The second objection is more serious. Reactions 8, 9, 13 and 14 would produce only a small amount of gold due to the small amount of the philosopher's stone used in the so-called transmutation and this gold would have to be separated from the bulk of unreacted base metal via scorification. However, both van Helmont

and Helvetius reported that the entire masses of the mercury and lead, both of which were many times greater than the mass of powder used, were instantly transformed into gold and that this gold was properly tested and found to be authentic (12). The alloys of gold with both mercury and lead are white or gray, rather than gold, in appearance and neither would pass for gold in a conventional assay test.

Of course I am not the first person to propose that the so-called philosopher's stone might actually have been an easily decomposable compound of gold. Indeed, several alchemists hinted as much. Thus Eirenaeus Philalethes (aka George Starkey, 1628-1665) described the stone as "a species of gold" and Michal Sendivogius (1566-1636) admitted that it was "nothing other than gold digested to the highest degree." In 1987 John Schroeder suggested, based on the color sequence often quoted for the preparation of the philosopher's stone (13):

black → white → yellow → red → violet

that the stone was actually digold oxide (Au_2O), which has been described as having a grayish-violet color (9). Like the gold (III) compounds discussed above, there is little doubt that this compound would easily form metallic gold upon heating or upon reduction by either metallic mercury or lead. However, Schroeder further implies that this oxide was made by heating gold in air, which, as already noted for the case of the trioxide, is not chemically possible. Indeed, more recent reviews of gold chemistry claim that there is still no definitive evidence for the existence of this oxide, which, even if it does exist, is likely to be extremely unstable.

In any case, though thermodynamically favored, both reactions 8 and 9 and reactions 13 and 14 still await experimental verification by someone lucky enough to be able to afford the present-day cost of the necessary gold compounds needed to determine whether the reactions in question are also kinetically labile.

Aurifictions

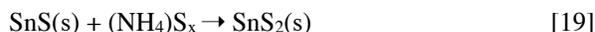
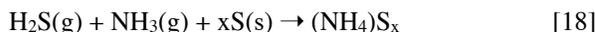
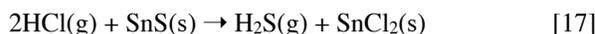
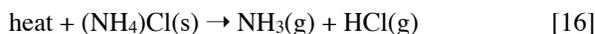
Moving on to tested examples of known aurifictions rather than proposed tests of presumed aurifactions, attention should first be called to the studies of Anthony Butler, Christopher Glidewell, Joseph Needham and coworkers in the 1980s (14, 15, 22, 24, 26). In a 1985 paper these authors examined two alchemical recipes for the preparation of tin disulfide (SnS_2) – one European and one Chinese (14, 15). As older chemists who have taken an undergraduate course in qualitative analysis know, this compound has a golden yellow color (figure 3) (16), and was thus known to European al-



Figure 3. The appearance of tin disulfide when precipitated in the standard qual scheme.

chemists as "mosaic gold" or *aurum musivum*. Though European recipes for its preparation date back as far as the 14th century, the authors fail to directly quote a specific example but rather summarize the ingredients given in a 1678 book by Johann Kunkel involving the heating of a mixture of tin amalgam, ammonium chloride, and sulfur in a crucible.

Since heating a simple mixture of tin and sulfur produces only blackish tin sulfide (SnS), the pertinent question is why the presence of ammonium chloride allows the oxidation of the tin to proceed all the way to the disulfide stage. After experimentally verifying that the recipe works using metallic tin rather than tin amalgam, and that other ammonium halides can be substituted in place of the chloride, the authors proceeded to postulate a rather elaborate reaction sequence to rationalize these results:

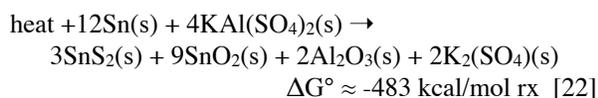


This proposal is unsatisfactory for a number of reasons, not the least of which is that steps 18 and 19 remain unbalanced and employ an incorrect formula for ammonium polysulfide, which should be written as $(\text{NH}_4)_2\text{S}_x$, since most polysulfide anions are known to carry a 2- charge. Without thermodynamic evaluation, it is also not obvious why the polysulfide anion, but not elemental sulfur, is able to oxidize tin from the II to the

IV oxidation state, presumably via the half reactions:



In the case of China, the authors quote an English translation of a circa 300 AD recipe from a text by an alchemist named Ko Hung. After first pointing out that several of the ingredients were mistranslated and arguing that a previously unknown term stands for ammonium chloride, the authors proceeded to experimentally verify that it works. The modern equivalent involves heating a mixture of tin filings, dried alum, and ammonium chloride in a crucible sealed inside an iron bomb for five days at 500°C. Here the alum acts as the oxidizing agent in accord with the proposed equation:



Though reduction of sulfur from VI to II- may at first seem thermodynamically improbable, this reaction is probably driven by the high thermodynamic stabilities of the various oxide byproducts (17). The role of the ammonium chloride in this process is indirect, the authors noting only that the process works without it, but that, when present, it improves crystal formation of the tin disulfide product.

More recently Opferkuch has called attention to several classes of metallurgical reactions for the indirect synthesis of various copper alloys having a gold-like appearance that may have been accidentally stum-

Table 2. Copper Alloys Produced by Roasting Oxide/Sulfide Mixtures

Oxide	Sulfide	Product	Color
CuO	PbS	Cu ₆₅ Pb	Copper
Cu ₂ O	As ₄ S ₄	Cu _{7.5} AsS _{0.5}	Silver-Gray
CuO	Ag ₂ S	CuAg _{1.1}	Gold
Cu ₂ O	Ag ₂ S	Cu _{1.6} Ag	Gold
CuO	Sb ₂ S ₃	Cu ₁₀ SbS _{0.3}	Bright Copper
PbO	CuS	CuPb _{20.7}	Gray
Cu ₂ O	SnS	Cu ₁₇ SnS _{0.3}	Yellow-Copper

bled upon by alchemists, though he cites no original recipes to confirm this hypothesis (18). The first class involves roasting mixtures of various metallic oxides and sulfides to produce the results summarized in Table 2.

The second class involves reacting the oxides of copper with various thiosalts, all of which are found as naturally occurring minerals that were accessible to early alchemists, to give the results in Table 3.

Table 3. Copper Alloys Produced by Roasting with Various Thiosalt Minerals

Oxide	Sulfide	Product	Color
CuO	AgSbS ₂	Cu _{6.2} Ag _{2.2} Sb	Gold
CuO	Ag ₈ SbS ₆	Cu ₃ Ag ₂	Bright Gold
Cu ₂ O	AgSbS ₂	Cu _{1.5} Ag ₂ S	Gold

The third class involves reacting either copper oxide or copper sulfide with various arsenates and stibinates, all of which could have been made by alchemists by reacting the naturally occurring oxides and/or sulfides of arsenic or antimony with either liver of sulfur (calcium polysulfide) or caustic soda.

Table 4. Copper Alloys Made via Roasting with Various Arsenates and Stibinates

Oxide	Sulfide	Product	Color
CuO	Na ₃ AsS ₄	Cu ₇ AsS	Golden Yellow
CuO	Na ₃ SbS ₄	Cu ₁₆ SbS	Golden Yellow
Ag ₃ AsO ₄	CuS	Cu _{1.3} AgS	Golden Yellow

In 1987 Glidewell briefly mentioned a recipe for aurification found in yet another book by the 4th-century Chinese alchemist Ko Hung (15). This was affected by adding to molten lead a purple powder made by heating a mixture of potassium nitrate, hematite (Fe₂O₃), sulfur, mercury sulfide, lead amalgam, and malachite (basic copper carbonate). Experimental replication revealed that the resulting powder was more red than purple in color, and that it did indeed impart a brilliant metallic gold sheen to the surface of the molten lead provided that the surface was first freed from all contaminants. This color was found to be only surface deep and was attributed to the formation of a micro, semi-transparent, surface film of yellow lead ox-

ide, the metallic appearance being due to sheen of the underlying molten lead. This was further assumed to be the result of the oxidation of the freshly exposed surface by the nitrate in the mixture:



the function of the remaining ingredients of the red powder remaining, in Glidewell's words, "obscure."

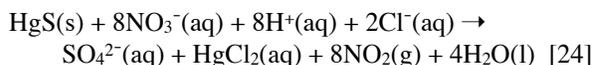
In 1976 Schwartz and Kauffman published a two-part article entitled "Experiments in Alchemy" outlining a series of simple laboratory experiments for use in a history of chemistry course (19). Despite the title, virtually all of these experiments were based on the early technological literature rather than the true alchemical literature. The only aurifictions discussed involved 19th-century alchemists and are therefore beyond the scope of this review. In any case, the authors either merely summarized the claims of these modern alchemists or reported, sans details, that their personal attempts at replication were a failure.

From the relevant and only slightly relevant, we now move to the improbable. In 1974 R. J. Gillespie and coworkers reported the synthesis of a mercury hexafluoroarsenate having the compositional formula $\text{Hg}_{2.86}(\text{AsF}_6)$ that was found to contain infinitely-extended polycationic mercury chains (20). This compound formed crystals having a metallic gold color and Gillespie, perhaps in jest, implied that a past encounter with this material by ancient alchemists might account for some of their naive reports of having successfully transmuted mercury into gold. Later the corresponding antimony analog, $\text{Hg}_{2.81}(\text{SbF}_6)$, was also synthesized and was found to have a similar metallic gold appearance (21). Why I have labeled this suggestion improbable is because these compounds were made by condensing either AsF_6 or SbF_6 onto elemental mercury in liquid SO_2 at -196°C – reactants and reaction conditions hardly available to your average alchemist.

Associated Processes

Alchemical recipes other than those dealing with aurifictions have also been the subject of modern experimental studies. Thus in 1980 Butler *et al* published a study of an anonymous 6th-century AD Chinese recipe for the solubilization of cinnabar (HgS) (15, 22). This was an important process for Chinese alchemists because of the supposed medicinal properties of mercury compounds. Based on an earlier English translation by Needham and coworkers (23), this called for mixing the cinnabar with a vinegar solution of copper sulfate and potassium nitrate and letting the mixture sit a buried porcelain jar for 30 days.

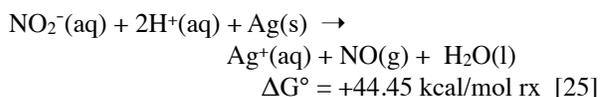
The authors found that significant dissolution occurred only if they used concentrated acetic acid and halide ions were also present, leading them to postulate the net reaction:



despite their failure to mention observing any red NO_2 fumes. The absence of chloride as an explicit ingredient in the recipe was rationalized by the fact that a Chinese alchemist would have used naturally occurring nitre as his source of potassium nitrate and this is almost always contaminated with potassium chloride. A source of concentrated acetic acid was much harder to explain. Though mentioning that it might have been concentrated by freezing, as the ancient Chinese had done in the case of ethanol (24), they did not experimentally test this hypothesis. However, in 1980 Butler and Needham, using modern models of ancient stills, further investigated whether the required concentration could have been obtained instead via distillation of vinegar, but found that the ability these stills to fractionate acetic acid-water solutions was quite poor, so an ancient source of concentrated acetic acid still remains a mystery (25).

Lastly, the authors' experiments also suggested that the role of the copper sulfate in the recipe was catalytic. However, they failed to rationalize why the original recipe also reported that the final solution was red, implying that it may not have been a solution at all but rather a suspension of the red cinnabar in water (or was this color due to dissolved NO_2 fumes?).

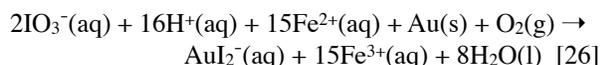
In 1987 Butler, Glidewell and coworkers explored several other recipes from the same 6th-century Chinese book, this time dealing with the dissolution of gold and silver in vinegar solutions of potassium nitrate (15, 26). In these cases the anonymous Chinese author indicated that the dissolutions in question should be carried out in lacquered bamboo tubes with reaction times of between 30 and 100 days. For the dissolution of silver, the authors postulated that the organic matter in the bamboo first reduced some of the nitrate anion to nitrite and that this, via a complex reaction mechanism involving the generation of a NO^+ intermediate, then oxidized the silver via the net overall reaction:



However, as may be seen from my thermodynamic evaluation, this reaction is not thermodynamically fa-

vored under standard conditions, though it might still be driven sufficiently to the right via a Le Chatelier shift due to the escaping NO gas, and, in keeping with this, the authors did indeed report that silver does dissolve in acetic acid solutions of potassium nitrate carried out in glass, but only if some nitrite anion is also added.

For the dissolution of gold, the corresponding recipe also specified the addition of green vitriol or iron sulfate heptahydrate to the mixture. However the authors found that the recipe worked only if iodide anion was added as well. Since potassium iodide is not found as a contaminant in naturally occurring nitre but potassium iodate sometimes is, the authors further assumed that the function of the iron sulfate in the recipe was to reduce the iodate to iodide. When coupled with reduction of dioxygen gas in the air, the resulting sequence of intermediate steps sums to give the following, rather complex, overall reaction, leading to the dissolution of gold as a diiodaurate (I) complex:

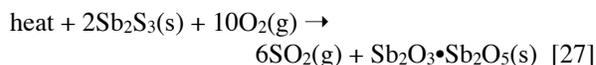


This could not be thermodynamically evaluated due to the absence of free energy data for the resulting gold complex.

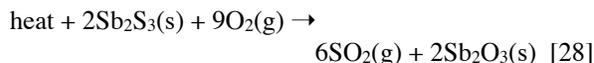
As may be seen from the above examples, the presence or absence of certain impurities in the ingredients used in many alchemical recipes plays a key role in determining whether the recipe will or will not work when attempts are made to replicate it in the modern laboratory. This same point was the focus of an article by Lawrence Principe, also published in 1987 (27), in which he experimentally evaluated several recipes taken from Basil Valentine's famous 1604 book, *The Triumphal Chariot of Antimony* (28).

Though Valentine was supposedly a 15th-century Benedictine Monk and alchemist, historians of chemistry have long suspected that no such alchemist ever existed and that the works attributed to him were all written in the 16th and 17th century by a variety of anonymous authors under this common *nom de plume*. Indeed, many suspect that the book under consideration was actually the work of its first publisher – a German salt maker named Johann Thölde. In addition, it is somewhat misleading to characterize this book as alchemical (see note 1). Though it contains some of the usual alchemical rhetoric in the introductory sections, most of it is concerned with the supposed medicinal benefits of antimony and its compounds and it is therefore more accurately described as iatrochemical, rather than alchemical, in its emphasis.

In this article Principe attempted to replicate Valentine's recipe for the making of so-called antimony glass, followed by an extraction of the glass to produce a "tincture of antimony" for medical use. Unlike some of the previous authors, Principe fully quotes the original recipe, but fails to give the details of his own experiments beyond stating their final results. The recipe begins by first calcining or oxidizing natural occurring diantimony trisulfide or stibnite (Sb_2S_3) to a "white ash" – a reaction which Principe represents as:



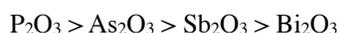
In fact, this is probably incorrect. Differential thermal analysis (DTA) of the oxidation of Sb_2S_3 shows that between 283–478°C one obtains, in keeping with Valentine's description, only white diantimony trioxide and sulfur dioxide as the primary products (29):



In contrast, the mixed-valence oxide in equation 27, now written as Sb_2O_4 , is actually yellow rather than white in color, as is the pentaoxide, Sb_2O_5 – both of which are obtained upon heating the trioxide to higher temperatures (30).

The next step is to fuse the white ash so as to produce a golden yellow glass. However, initially Principe was unable to get this step to work. Success was obtained only after following up a hint found in the writings of the 19th-century chemist, Jean Baptiste Dumas (1800–1884), that the addition of a little SiO_2 , leached from the wall of the crucible, was necessary for successful glass formation. Principe also noted that the Hungarian stibnite specified by Valentine is generally intermixed with a small percentage of silica, though in his own experiments he added silica directly to the molten Sb_2O_3 in order to successfully form the glass.

These results are in keeping with the modern literature on glass chemistry. Thus Rawson states that the glass-forming ability of the Group V trioxides follows the order (31):

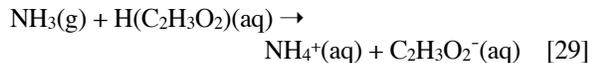


Indeed, Bi_2O_3 will not form a glass on its own and Sb_2O_3 only with difficulty and extremely rapid cooling. However the binary system SiO_2 - Bi_2O_3 does form a glass and presumably the same is true of a SiO_2 - Sb_2O_3 system. In general, even today, the question of whether a given mixture of oxides will or will not form a glass

cannot be predicted theoretically and must instead be tested empirically.

The next step in Valentine's recipe was to leech the finely ground glass with distilled vinegar, followed by evaporation of the vinegar and dissolution of the remaining residue in ethanol to produce a red "tincture of antimony." Once again Principe could not get the recipe to work, the powdered glass remaining inert to freshly distilled wine vinegar. Only when he guessed that the vinegar had been "sharpened" prior to distillation via the addition *Salmiac* (a mixture of ammonium chloride and carbonate) did the extraction steps work. However, when the final alcoholic tincture was analyzed, it was found to contain, not antimony, as Valentine had assumed, but rather iron! This was rationalized either by the fact that the Hungarian stibnite used in the first step was found to be associated with minute amounts of hematite or by the fact that Valentine had used an iron rod to stir his molten glass, though Principe failed to make a decision one way or another on this point.

Why the extraction worked after addition of *Salmiac* is because these ammonium salts give off ammonia gas on being heated to dryness and this would pass over into the receiver where it would react with the vinegar distillate to produce ammonium acetate:



Unlike weakly dissociated acetic acid, this salt is completely dissociated in aqueous solution and would generate a sufficiently high concentration of free acetate ion to extract the iron in the glass as red basic iron acetate. This contains a heterocatenated complex ion (figure 4) having the composition $\text{Fe}_3[\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3]^+$ (where AcO stands for acetate) that is known to be soluble in ethanol.

Since, when Sb_2O_3 is introduced into either the phosphate or borate glasses used for bead tests in blowpipe analysis (32), the resulting beads are either white or colorless, it is unlikely that a pure $\text{SiO}_2\text{-Sb}_2\text{O}_3$ glass would be yellow. Thus the question of the origin of the yellow color in Valentine's product remains to be answered. The most obvious choice is that the yellow color is due to the iron (III) impurities in the glass. However, iron (III) normally colors oxide glasses either green or brown or, at best, a yellowish brown. (33). Though the latter color, at low concentrations, might be charitably interpreted as a golden yellow, there is yet another possible choice, since, if heated to a sufficiently high temperature during the fusion process, some of the white Sb_2O_4 may be further oxidized to give the yellow mixed valence oxide, $\text{Sb}_2\text{O}_4 - \text{a}$

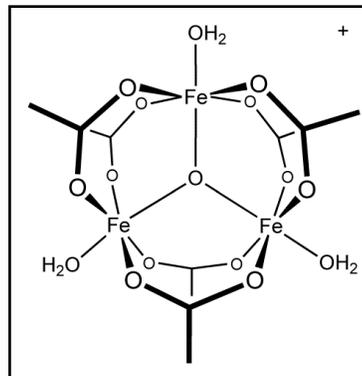


Figure 4. The structure of the red $\text{Fe}_3[\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3]^+$ complex ion found in basic iron acetate.

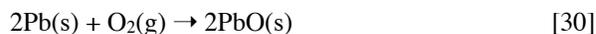
process that DTA shows will occur between 595-610°C. Which of these rationales actually applies is a subject for future investigation.

As our final example, we cite a 1997 paper by Rodygin (34) on the modeling of an alchemical recipe for the production of acetone attributed to the 15th-century English alchemist, George Ripley (1415-1490), or rather on a rationalization of this recipe given by Jean-Baptiste Dumas in his 1839 volume on the history of chemistry (35). This paper is unsatisfactory for a number of reasons. Thus neither Rodygin nor Dumas directly quote the original recipe and neither references its original source (36). Given that the terminology used by Ripley was apparently highly allegorical (and therefore far more typically alchemical than the example used by Principe), there is also the problem that no explanation is provided as to how Dumas translated the recipe into a set of concrete modern ingredients or whether his apparent French paraphrases of Ripley's allegorical names are reasonable.

According to these authors, the recipe begins by heating something called *mecure des philosophers* to first produce *lion vert* and then *lion rouge*:

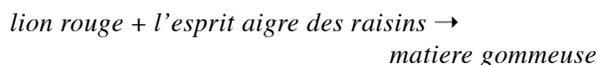


which they interpret as:

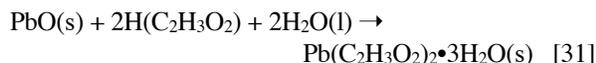


As required, PbO is red. However the nature of *lion vert* remains obscure, since the only other known polymorph of PbO is yellow rather than green in color.

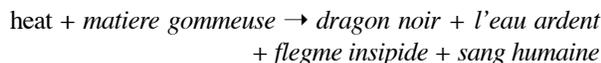
The *lion rouge* is then reacted with *l'esprit aigre des raisins* to produce a *matiere gommeuse*:



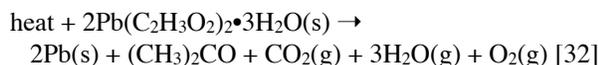
which the authors interpret as the reaction between lead oxide and vinegar to produce lead acetate trihydrate:



Finally, the *matiere gummeuse* is strongly heated in a retort to give *dragon noir* and three liquid fractions described as *l'eau ardent*, *flegme insipide*, and an oil called *sang humaine*:



With the exception of *sang humaine*, this reaction can be represented as (37):



in which *l'eau ardent* is interpreted as acetone, *flegme insipide* as water, and *dragon noir* as finely powdered pyrophoric lead, as the recipe calls for setting this on fire to reform *lion vert* and then repeating the entire process. Interestingly, the use of this reaction to produce pyrophoric lead was rediscovered by Böttger in the 19th century and is still used to prepare this material for demonstrations in freshman chemistry (38). As a side bar, the term *l'eau ardent* was traditionally used in alchemy to denote ethanol (24), but since it translates as “burning water,” it is not unreasonable that it might also have been applied to acetone.

As noted by Dumas, unlike modern chemists, Ripley apparently had little interest in the acetone product. Rather it was the red liquid byproduct, or *sang humaine*, that fascinated him and which, because of its color, he identified with the long sought *elixir d'sages*. It was the purpose of Rodygin's note to discover the nature of this liquid fraction. However, his description of his experimental results is so terse that it is unclear whether he actually prepared this fraction using reaction 32 and then analyzed it using “gas-liquid chromatography, IR and UV spectroscopy, and both ^1H and ^{13}C NMR,” or whether he analyzed a mixture modeled on what he thought it contained based on a search of the chemical literature. In any case, he concluded that it was a solution of lead bis(acetylacetonate) in a mixture of acetic acid and acetylacetone and that the red color might be due to polycondensation products of the latter compound.

Conclusions

This review reveals that attempts to replicate recipes

and processes found in the true alchemical literature are plagued by three recurring problems:

1. Proper identification of the necessary ingredients and reaction conditions.
2. The hidden role of impurities.
3. The pervasive, but imprecise, use of color as the sole means of characterizing reactants and products.

The first of these problems is much more serious when dealing with European versus Chinese alchemical recipes. As Needham has emphasized, the latter are usually straight forward, whereas the former are often obscured by the pervasive use of allegory, as illustrated by the Ripley recipe for acetone. Nevertheless, the Chinese recipe for mosaic gold did contain a previously unknown term for ammonium chloride and several of the recipes for the dissolution of minerals and metals in vinegar-nitre solutions failed to explicitly mention one or the other of these two ingredients – their presence being inferred instead from the nature of the surrounding recipes. In yet other cases, such as the addition of *Salmiac* to the distilled vinegar used to prepare tincture of antimony, the replicator simply had to guess that something was missing. As for reaction conditions, most modern replicators, lacking the patience to let a process proceed for 30-100 days, have been forced to use much shorter reaction times. Other problems have been glossed over, such as, for example, the proper temperature setting for a heating mantel if one is trying to duplicate the heating effects of a dung bath.

The often critical role of impurities for the success of a given recipe was amply illustrated by several examples in this review. Sometimes the impurity was present in the starting materials, as in the case of KCl in the recipe for the solubilization of cinnabar or $\text{K}(\text{IO}_3)$ in the case of the recipe for the dissolution of gold, whereas in other instances the necessary impurity was extracted from the chemical apparatus used in the process, such as silica from the crucible wall in the case of the recipe for antimony glass, or iron (III) from an iron stirring rod in the case of the recipe for tincture of antimony, or the organic reducing agents from the wall of the bamboo tubes used for the Chinese recipes for the dissolution of metals.

Less often noted is the third problem. That color played a central role in alchemical thought has been known since the pioneering work of Hopkins at the beginning of the 20th century (39). Indeed, it was the red colors of the so-called tincture of antimony in Valentine's recipe and of the *sang humaine* in the Ripley

recipe that caused their original authors to focus on these two incidental products rather than the products of interest to the modern chemist (i.e. antimony glass and acetone). Of all the properties that can be used to characterize a material, color – unless quantified via modern spectroscopy – is the least dependable. The visual color of a given substance is known to vary with such circumstances as the presence of impurities, its degree of hydration, and its degree of subdivision. Due to oxidation or exposure to chemical fumes, the surface may have a color different from the bulk material, etc. And of course, not only do individuals vary widely in their ability to visually identify colors, different cultures do as well. Are the colors recognized by the ancient Chinese identical to those recognized by medieval Europeans? At what point did these two cultures distinguish between orange and red or between ruby red and violet, etc.? I am unaware that the implications of these questions for the study of the alchemical literature have ever been explicitly confronted.

Applications to the History of Modern Chemistry

In closing I cannot resist briefly noting that the experimental approach to historical questions in the history of alchemy is being increasingly applied to questions in the history of modern chemistry as well, most notably by the late Melvyn Usselman. These include replication of some of William Hyde Wollaston's micro electrochemical apparatus (40); of Wollaston's and Thomas Thomson's analyses of various carbonates and oxalates, often quoted as the first important experimental confirmations of Dalton's then recently formulated law of multiple proportions (41); and a reconstruction of Liebig's original apparatus for organic combustion analysis and replication of many of his analyses (42).

References and Notes

1. D. Ingersoll, J. E. Yellen, W. Macdonald, Eds., *Experimental Archeology*, Columbia University Press: New York, NY, 1977.
2. In this article I use the term alchemy as it has been used by historians for the past 300 years to denote either attempts to transmute base metals into gold or discover the elixir of life. I am fully aware that Newman and Principe have declared this usage incorrect and have instead named the first of these practices *chrysopoeia* and argued that the term alchemy should be used as a blanket descriptor for all early chemical practice, be it technological, metallurgical, pharmaceutical, or iatrochemical in nature. Their primary argument is that this is how the term was used in the past by many of its actual European practitioners. However, I am unaware that the term *chrysopoeia* was ever widely used by European alchemists nor that most of the distinctive technological,

metallurgical or pharmaceutical literature ever explicitly identified itself with alchemy (the case of iatrochemistry is less clear cut). Also this argument from period usage would logically preclude use of an Arabic term to describe alchemical practices in ancient China, India, and Egypt. I personally prefer to use the less provocative term "protochemistry" as a blanket descriptor for pre-modern chemical practice and to retain the traditional historical use of the term alchemy for the above two practices so as not to produce an unnecessary discontinuity with earlier scholarship.

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5. L. M. Principe, *The Aspiring Adept: Robert Boyle and his Alchemical Quest*, Princeton University Press: Princeton, NJ, 1998, Appendix 1. This is an attempt, albeit highly biased, to reconstruct Boyle's unpublished dialog on "The Transmutation and Melioration of Metals."
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9. The best review of the basic inorganic chemistry of simple gold compounds is still J. W. Laist, "Gold" in M. C. Sneed, J. L. Maynard, R. C. Brasted, Eds., *Comprehensive Inorganic Chemistry*, Vol. 2, Van Nostrand: New York, NY, 1954, Chapter 3. This is because more recent reviews of gold chemistry focus instead almost exclusively on the organometallic chemistry of gold.
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12. See reference 5. Boyle spends considerable space attempting to rationalize how it was possible for a small amount of the philosopher's stone to completely transform a

much larger amount of base metal.

13. J. C. Schroeder, "A Chemical Interpretation of Alchemy," *J. Chem. Educ.*, **1987**, *64*, 994-995.
14. A. R. Butler, C. Glidewell, J. Needham, S. Pritchard, "Mosaic Gold in Europe and China," *Chem. Brit.*, **1983**, *19*, 132-136.
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16. C. H. Sorum, *Introduction to Semiquantitative Chemical Analysis*, 4th ed., Prentice-Hall: Englewood Cliffs, NJ, 1967, Chapter 4.
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