

The "Golden Penny" Demonstration

An Explanation of the Old Experiment and the *Rational Design* of the New and Simpler Demonstration

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The demonstration referred to as "Striking It Rich" (1) and "Copper to Silver to Gold" (2), or more commonly as the "Golden Penny Experiment" is popular among general chemistry teachers and is described in the two widely used chemistry texts cited above. Both of these texts, however, present an insufficient or incorrect explanation for the major part of the experiment. This paper reports a series of electrochemical measurements that lead to a logical explanation for this demonstration and to a simplified design that makes it safer.

In the popular version of this experiment granular zinc is placed in 3M NaOH solution and heated until the liquid boils. A copper penny is then placed in the beaker and the heating continues. After a short time the copper coin becomes silvery (zinc deposits on copper). The silvery coin is subsequently heated in the cold part of a Bunsen burner flame and the coin turns golden (1, 2).

The experiment, as presented above, consists of three separate chemical processes:

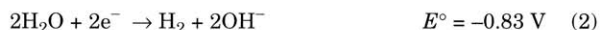
Step A. Granular zinc dissolves in NaOH solution, forming a zincate anion, $[\text{Zn}(\text{OH})_4]^{2-}$.

Step B. Zincate ion becomes reduced to metallic zinc on the surface of the copper penny.

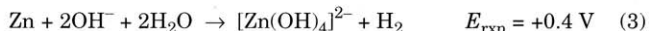
Step C. Zinc and copper, when heated in the Bunsen burner flame, form brass.

Of the three chemical processes presented above, steps A and C are easy to explain (1, 2).

In step A metallic zinc dissolves in NaOH solution because of the following reduction potentials:



Therefore, if reaction 1 is reversed and combined with reaction 2, the net reaction 3 takes place as the result of 0.4 V of the driving force:



Step C of this experiment is a typical example of a high-temperature alloy formation and does not require any special explanation.

None of the cited references present, however, a satisfactory explanation for step B in the experiment. The question one needs to address is why does zincate anion become reduced to zinc (from +2 oxidation state to 0)? What is the reducing agent? It cannot be water, because it is shown above that water will actually oxidize zinc at the pH of the experiment. The same argument excludes hydrogen gas as a possible reducing agent. Metallic copper is also ruled out, because copper is a much poorer reducing agent than zinc at any pH. Besides, the solution remains colorless, indicating that no oxidation of copper takes place.

We will show below that the reducing agent is zinc itself, and the driving force is related to the difference in the re-

duction potentials of zincate ion on different surfaces due to low-temperature alloy formation, but first we will present the explanations proposed in the literature.

Suggested Explanations in the Literature

Both of the sources cited above make an attempt to explain the chemistry behind the mysterious reduction of zinc.

A concentration cell was proposed as a source of the driving force for step B by Shakhshiri (2). He found that zinc can be deposited on a copper electrode in an electrochemical cell consisting of a zinc plate in NaOH solution in one half-cell, and copper in sodium zincate solution in the second half-cell. In this cell, zincate ions are reduced to zinc at the copper cathode and zinc is oxidized to zincate ions at the zinc anode. The net reaction is driven then by the difference in concentration of zincate ions in the two half cells. A similar concentration gradient was proposed by Shakhshiri to exist in this demonstration. Our experimental work confirms Shakhshiri's assignment of the reducing agent (zinc metal), but clearly excludes the concentration gradient as the driving force for the reaction.

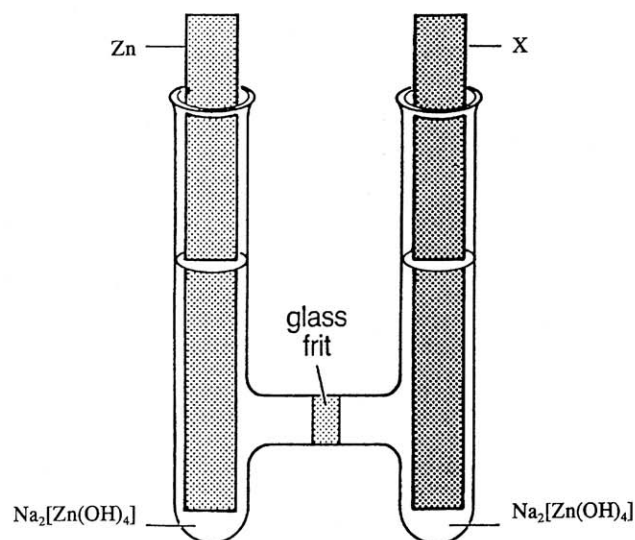
The Teacher's Guide for reference 1 (3) simply states that the reason for the reduction to zinc taking place is that zincate ion can react to plate zinc metal on the copper surface. This explanation does *not* identify the reducing agent. In addition, it creates an impression that the presence of zinc complexed by hydroxide ions (zincate) is necessary for this process to take place. In fact, this convenient explanation is used by high school teachers when they present this experiment to students. However, our electrochemical measurements, *vide infra*, clearly show that complexation of zinc with *hydroxide ions* is *not* necessary for the reduction of zinc to take place.

An Explanation Based on the Reduction Potentials Determined in This Work

In order to definitely exclude the possibility that copper itself could be a reducing agent we determined the amount of deposited zinc on the plate and compared it to the amount of copper in solution. Both metals were determined by AA spectroscopy. Copper was measured in the solution used for zinc deposition, and zinc was determined after digestion from the copper plate with 1.0 M HCl solution. (The two solutions had equal volumes.) The molar ratio of Zn to Cu was found to be more than 20:1. (The level of copper was below detection limit by AA.) This clearly excludes copper as a possible reducing agent.

Next, we constructed the electrochemical cell similar to the cell designed by Shakhshiri, but consisting of 1 M sodium zincate solution in *both* half cells. See the figure. Note that there is *no* concentration gradient in the cell. The voltage in this cell was determined to be 1.1 V. Therefore, a very large driving force exists for the redox reaction in which zincate is reduced to zinc on copper and the zinc plate is oxidized to zincate. Zinc indeed does deposit on copper in this cell when the electrodes are connected by an

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An electrochemical cell used to explain the chemistry behind the classical "golden penny" experiment, involving 3M NaOH solution. X=Cu, Pt, Ag, Fe, Cd and C_{graphite}.

external wire (2 minutes when the solutions are hot, and ~1 hour in cold solutions).

Therefore, we have shown that

$$E([\text{Zn}(\text{OH})_4]^{2-}/\text{Zn}_{\text{Cu}}) - E([\text{Zn}(\text{OH})_4]^{2-}/\text{Zn}_{\text{Zn}}) = 1.1 \text{ V} \quad (4)$$

and the net reaction for the process of the zinc deposition on copper is



We have independently confirmed this result by measuring the potentials of $[\text{Zn}(\text{OH})_4]^{2-}/\text{Zn}_{\text{Cu}}$ and $[\text{Zn}(\text{OH})_4]^{2-}/\text{Zn}_{\text{Zn}}$ versus standard calomel electrode. The difference between those two measurements was again 1.1 V. The subscript in the symbolism used above identifies the surface on which the reduction takes place. Table 1 presents the results of similar measurements for other surfaces.

The measurements presented in Table 1 show that the reduction potential of the zincate ion is very strongly affected by the surface on which the reduction takes place. Zincate being reduced to zinc on copper (or on several other surfaces) is much more favorable than zincate being reduced to zinc on zinc. We concluded that an increase in the reduction potentials is caused by the fact that zinc atoms diffuse into the lattice of the more noble metal (or graphite) forming an alloy of zinc and the more noble metal at the surface or an intercalation compound with graphite. (The intercalation compounds of zinc with graphite have been reported in the literature (4).)

The following two observations supply additional proof that the diffusion rate of zinc is sufficiently high for alloy formation at the conditions applied in the demonstration.

1. When the concentration of zinc-containing electrolyte is lowered to 0.01 M, the copper plate changes color to gold *in solution*, and the heating in the flame is not necessary to visually detect an alloy.
2. The silvery plates obtained from more concentrated solutions become gold if kept at room temperature for a prolonged amount of time (2–4 days).

We have been able to plate zinc on graphite and all the metals presented in Table 1, except cadmium. In all cases the thickness of the zinc layer is very small (less than 0.03 μm as determined by AA). As the metallic zinc deposits on the surface of the metal the voltage of the cell drops to almost zero. The large drop of the potential is in fact the best way to determine that zinc has deposited on the surface, because in many cases the colors of zinc and the other met-

Table 1. Voltages of the Electrochemical Cells Assembled from the Following Two Half Cells Separated by a Glass Frit.

Anodic half cell: Zn metal in 1 M $\text{Na}_2[\text{Zn}(\text{OH})_4]$.
Cathodic half cell: X (another metal or graphite) in 1 M $\text{Na}_2[\text{Zn}(\text{OH})_4]$.

The net reaction	E_{rxn}, V
$\text{Zn}_{\text{Zn}} + [\text{Zn}(\text{OH})_4]^{2-} \rightarrow \text{Zn}(\text{OH})_4^{2-} + \text{Zn}_{\text{Cu}}$	1.1
$\text{Zn}_{\text{Zn}} + [\text{Zn}(\text{OH})_4]^{2-} \rightarrow \text{Zn}(\text{OH})_4^{2-} + \text{Zn}_{\text{Pt}}$	1.2
$\text{Zn}_{\text{Zn}} + [\text{Zn}(\text{OH})_4]^{2-} \rightarrow \text{Zn}(\text{OH})_4^{2-} + \text{Zn}_{\text{Ag}}$	1.6
$\text{Zn}_{\text{Zn}} + [\text{Zn}(\text{OH})_4]^{2-} \rightarrow \text{Zn}(\text{OH})_4^{2-} + \text{Zn}_{\text{C(graphite)}}$	1.5
$\text{Zn}_{\text{Zn}} + [\text{Zn}(\text{OH})_4]^{2-} \rightarrow \text{Zn}(\text{OH})_4^{2-} + \text{Zn}_{\text{Fe}}$	0.75
$\text{Zn}_{\text{Zn}} + [\text{Zn}(\text{OH})_4]^{2-} \rightarrow \text{Zn}(\text{OH})_4^{2-} + \text{Zn}_{\text{Cd}}$	0.3

al are indistinguishable. There was no appreciable potential drop in the cell containing zinc and cadmium electrodes. All of the metals on which we were able to deposit zinc are known to form alloys with zinc. Cadmium is the only metal of those tested in this work that does not form any intermetallic compounds with zinc (5).

The nature of the silvery color of the deposit on the surface of Cu requires further explanation. In the chemical eq 5 we show the product of the reaction being Zn_{Cu} , the intermetallic compound of zinc and copper = brass. However, the color of the deposit is silvery. The color becomes golden only when the coin is heated in the flame or when the concentration of Zn-containing compound in solution is very small ($\approx 0.01 \text{ M}$). The explanation requires a consideration of various types and colors of known brasses. The color of brass changes depending on the Zn content. One form, α -brass, with the zinc content less than 35% is golden in color, while γ -brass with a zinc content of more than 45% is silvery-gray. Therefore, the meaning of Zn_{Cu} in eq 5 is different depending on the duration of the experiment. At the very beginning it is the α -brass that forms at the surface. However, as time progresses, owing to the slow diffusion of metal atoms at temperatures less than 100°C the content of Zn in the deposit is increasing and the consequent layers eventually become γ -brass. Therefore, the observed color of the deposit is silvery. This also explains why the deposition of Zn stops after a short time or is very significantly slowed down. The reduction potential of $[\text{Zn}(\text{OH})_4]^{2-}/\text{Zn}_{\text{Cu}}(\alpha\text{-brass})$ is much larger (close to 1 V) than $[\text{Zn}(\text{OH})_4]^{2-}/\text{Zn}_{\text{Cu}}(\gamma\text{-brass})$, which is approximately 0.01 V. Therefore, the voltage of the cell from the figure drops to almost zero ($\approx 10 \text{ mV}$) when the copper plate becomes silvery. However, when the γ -brass on the surface is transformed into α -brass (by heating in the flame), the deposition process continues and the plate becomes silvery again!

The Rational Design of a Simpler "Golden Penny" Experiment

A new electrochemical cell was constructed where 1M solution of ZnCl_2 was substituted for $\text{Na}_2[\text{Zn}(\text{OH})_4]$ in the figure. The measured voltage was 0.70 V and zinc plated on copper again (after several hours at room temperature). Therefore,

$$E(\text{Zn}^{2+}(\text{aq})/\text{Zn}_{\text{Cu}}) - E^\circ(\text{Zn}^{2+}(\text{aq})/\text{Zn}_{\text{Zn}}) = 0.70 \text{ V} \quad (5)$$

or

$$E([\text{Zn}(\text{H}_2\text{O})_6]^{2+}/\text{Zn}_{\text{Cu}}) - E^\circ([\text{Zn}(\text{H}_2\text{O})_6]^{2+}/\text{Zn}_{\text{Zn}}) = 0.70 \text{ V} \quad (6)$$

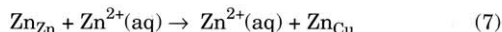
Clearly, there is no need to include a highly corrosive concentrated NaOH solution in the demonstration. A much

Table 2. Voltages of the Electrochemical Cells Assembled from the Following Two Half Cells Separated by a Glass Frit.

Anodic half cell: Zn metal in 1 M ZnCl₂.
Cathodic half cell: X (another metal or graphite) in 1 M ZnCl₂.
ZnCl₂ solution was slightly acidified in order to prevent hydrolysis.

The net reaction	E_{rxn}, V
$\text{Zn}_{\text{Zn}} + [\text{Zn}(\text{H}_2\text{O})_6]^{2+} \rightarrow [\text{Zn}(\text{H}_2\text{O})_6]^{2+} + \text{Zn}_{\text{Cu}}$	0.7
$\text{Zn}_{\text{Zn}} + [\text{Zn}(\text{H}_2\text{O})_6]^{2+} \rightarrow [\text{Zn}(\text{H}_2\text{O})_6]^{2+} + \text{Zn}_{\text{Pt}}$	1.2
$\text{Zn}_{\text{Zn}} + [\text{Zn}(\text{H}_2\text{O})_6]^{2+} \rightarrow [\text{Zn}(\text{H}_2\text{O})_6]^{2+} + \text{Zn}_{\text{Ag}}$	1.0
$\text{Zn}_{\text{Zn}} + [\text{Zn}(\text{H}_2\text{O})_6]^{2+} \rightarrow [\text{Zn}(\text{H}_2\text{O})_6]^{2+} + \text{Zn}_{\text{C(graphite)}}$	1.2
$\text{Zn}_{\text{Zn}} + [\text{Zn}(\text{H}_2\text{O})_6]^{2+} \rightarrow [\text{Zn}(\text{H}_2\text{O})_6]^{2+} + \text{Zn}_{\text{Fe}}$	0.8
$\text{Zn}_{\text{Zn}} + [\text{Zn}(\text{H}_2\text{O})_6]^{2+} \rightarrow [\text{Zn}(\text{H}_2\text{O})_6]^{2+} + \text{Zn}_{\text{Cd}}$	0.2

safer solution of ZnCl₂ is sufficient. In the new demonstration granular zinc is placed in 1 M ZnCl₂ solution and heated until the liquid boils. A copper penny is then placed in the beaker and the heating continues. After a short time of continued boiling (≈ 2 min) the copper coin becomes silvery. The net reaction in the new demonstration is



The next step (α -brass formation) is carried out in the same way as in the original experiment.

Table 2 presents more reduction potentials for $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ determined by us on other surfaces.

Literature Search

We performed two separate literature searches, one before and one after our data were collected. The first search did not reveal any previous work related to the zinc deposition on copper. However, after we realized that alloy formation was the driving force for the reaction, the new literature search quickly revealed that this phenomenon was discussed first in 1873 by Raoult (6), who showed that several active metals (zinc, tin, and cadmium) could be deposited on gold and silver (less active or more noble metals) by the same procedure as described in this paper. Raoult's interpretation of the phenomenon was that the more active metals become less active after diffusion into the less active metal's lattice. Raoult also made the analogy between vapor pressure lowering of a solvent in solution and the lowering of activity of zinc in the zinc/gold alloy (a solid solution). Therefore, Zn_{Au} is less active than pure Zn and the reaction 7 becomes a simple activity series displacement reaction. In 1935 Plotnikow and Zosimowicz (7) measured the voltages for the cell presented in the figure with zinc anode, copper cathode, and ZnCl₂ electrolyte at various temperatures as a function of time. At room temperature their data agree with ours within 0.1 V. They also observed that the voltage slowly decreases to zero after zinc deposits on copper and they identified by X-ray the presence of alpha, beta, and gamma brass on the surface.

The general phenomenon of alloy formation by electrodeposition and, more specifically, the shift of reduction potentials for the case of alloy formation were reviewed more recently by Brenner (8). He reported that the deposition of brass coatings by the process described in this paper has been the subject of several patents. The first patent concerning production of brass coatings on copper objects or on iron objects coated with copper, by immersion in a hot solution of ZnCl₂ containing zinc particles in suspension, was granted to Elkington and Barratt in 1838 (9). This plating process was later proposed by the American Chemical Paint Company (10) during World War II as a coating for steel shell casings and steel pennies. Items were copper plated and then immersed in a 70% solution of zinc chloride at 150 °C. Zinc shot was kept in suspension in the bath. Both the inside and outside of the shell casings could be coated by this means.

Conclusions

Owing to surface alloy formation the reduction potentials of $[\text{Zn}(\text{OH})_4]^{2-}$ or $\text{Zn}^{2+}(\text{aq})$ ions to metallic zinc are very strongly dependent on the surface where the reduction process takes place. This leads to the deposition of a very thin layer of zinc (in the form of an alloy) on some surfaces in the presence of metallic zinc and Zn^{2+} species. Neither complexation of zinc with hydroxide ions nor a concentration gradient is necessary in the explanation of the "golden penny" experiment.

The phenomena described in this paper have been known since the 1830's. Therefore one might ask why we did all these experiments if an explanation already appears in the literature. In hindsight, good chemical explanations always appear so clear and orderly but chemical research is much more chaotic. Computer-based literature searches can be very efficient if one has the correct search strategy. At the beginning of our search, we did not appreciate the importance of alloy formation. Only after many experiments did it become a key term in our literature search and all pieces of the puzzle fell into place. We also believe that the measurements presented in this paper could be used in the general chemistry laboratory.

Acknowledgement

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