Electroplating

One might question the truth of that quotation, but it does have something to do with the problem at hand. Consider the men who plundered the Aztec treasure (?).

Gold-plated copper ornaments were a great disappointment to the Spaniards when melted down--and they are a surprise to us even today. Gold (along with silver) is one of the so-called "noble" metals. It is highly resistant to acid attack (only *aqua regia* is able to dissolve gold; this is a mixture of concentrated HCl and concentrated HNO_3). In order to plate gold onto copper as the Aztecs apparently did, they would need a solution of gold. But presumably they had no concentrated acids, and gold solutions do not occur in nature. They had HCl (in their stomachs) but probably didn't use it. HNO_3 was most likely unavailable.

Silver presents a similar dilemma. It will dissolve in HNO_3 (if you have some) and then the solution can be used to plate baser metals. But what if you don't have any nitric acid?

Consider a solution of nitric acid. It contains three types of ions: H^+, NO_3^- and OH^-. The $[OH^-]$ is so small we can neglect it here. Now consider a solution of more mundane materials: vinegar (which contains acetic acid) and saltpeter (saltpeter is either sodium or potassium nitrate, occurring in natural deposits). Neglecting the OH^-, four ions are present in this solution: H^+, NO_3^-, CH_3COO^-, Na^+. Notice that the building blocks of nitric acid are present, although the concentration of H^+ would be small since acetic acid is a weak acid. But left alone long enough, the silver from native ore deposits would slowly dissolve. Heating would help.

As for gold, adding ordinary table salt to the solution used to dissolve silver would provide the Cl^- ion and give the mix of ions present in *aqua regia*.

Of course, there is no way of knowing exactly how the Aztecs might have stumbled upon these processes--or even if they did. But it is important to point out that not all useful chemistry has to come off the stockroom shelves. As Pasteur said: chance favors the prepared mind.

Penny plating technique adapted from: The "Golden Penny" Demonstration, Steven H. Szczepankiewicz, Joseph F. Bieron, Mariusz Kozik, *J. Chem Educ.*, 1995, vol. 72, No. 5, p. 386

Electroplating is an important industrial process today. It is based on the concepts of redox chemistry in *electrolytic* and *galvanic* cells. Spontaneous plating is sometimes called *deposition* and produces coatings that are unsuitable for anything but arousing the curiosity of chemistry students. Plating in *electrolytic* cells can be controlled to produced tightly adhering coatings such as the chromium on car bumpers (well, old cars) or the silver on expensive flatware. Slower processes usually produce higher quality coatings, so the Aztecs--even though they undoubtedly used some sort of spontaneous process--may have gotten pretty good results simply because they had to wait since their solutions would have been so dilute!

In *electrolytic* plating operations, the **anode** is made out of the metal to be plated and the **cathode** is the object on which the plating is to be done (why?). The plating solution may be an electrolyte containing ions of the metal to be plated, but it may contain other ions as well. An external voltage is applied and the quality of results depends not only on surface preparation but also on the rate which is controlled by the current and voltage. Practical plating is something of an art as well as a science and some apparently unrelated ingredients are often added because someone once found by accident that they enhanced the quality of the final product.

Quantitatively, spontaneous plating must be a stoichiometric process since we can write balanced equations to represent what happens. For example, a piece of copper wire immersed in silver nitrate will undergo the following reaction:

$$Cu(s) + 2\ Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2\ Ag(s)$$
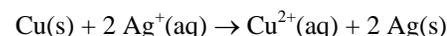
Technically this is an equilibrium reaction, but in practice it goes nearly to completion (K_c is 3.9 x 10^{38} at 25^oC !!).

Electrolytic plating is somewhat different. While mass is conserved in the example above, *charge* is also conserved and this is a key concept for understanding what happens in an electrolytic plating cell. If the anode and cathode are made out of the same material, atoms of metal dissolve at one electrode and are plated onto the other. The number of atoms that do this is related to the amount of charge that passes through the cell. Electric charge is measured in units called *coulombs*. One coulomb (C) is equal to one ampere flowing for one second:

$$charge = current \times time$$

$$Coulombs = amps \times seconds$$

Since the charge on an electron is known (1.602 x 10^{-19} C), it is possible to determine the relationship between charge and a *mole* of electrons:

$$1\ mole\ of\ electrons \Longleftrightarrow 96,500\ C$$

This number is known as the **Faraday** (*F*) and it is a very useful proportionality. Consider the example below:

A 0.500 amp current flowing for exactly one hour is passed through a solution of nickel(II) ions.

a. How many grams of nickel metal will plate out?
b. If this cell is hooked in series with another cell containing Ag^+ ions [in series the same current passes through both cells], how many grams of   Ag will plate at the same time?

First we need to know how much charge passed through the cell(s):

$$0.500 \text{ A} \times 3600 \text{ s} = 1800 \text{ C}$$

Now how many moles of electrons was that?

$$1800 \text{ C} \times \frac{1 \text{ mol e}^-}{96500 \text{ C}} = 0.0187 \text{ mole e}^-$$

Since nickel(II) has a charge of +2, one atom of nickel will require 2 e^- to plate:

$$0.0187 \text{ mole e}^- \times \frac{1 \text{ mole Ni}}{2 \text{ mole e}^-} = 0.00935 \text{ mole Ni}$$

This is **0.549 grams**.

Since silver is plated by the same amount of charge, but each atom of silver requires only one electron to plate (Ag ions are +1), we should expect twice as many moles of silver atoms to plate:

$$0.0187 \text{ mole e}^- \times \frac{1 \text{ mole Ag}}{1 \text{ mole e}^-} = 0.0187 \text{ mole Ag}$$

Thus **2.02 grams** of silver are produced. Note that the ratio based on charge affects the *moles* of silver and nickel. Their atomic masses influence the final mass plated.

Some authors (Chang, for one) call one mole of electrons a *Faraday*, but the meaning is still 96,500 C of charge.

Plating experiments are rather boring and this one is no exception. There is not much to do as the process takes place (especially if your calculator is recording the data...) and there is generally not much to look at. However, there *is* time for a fascinating diversion. You know from the activity series that zinc, which is above copper, will be displaced by copper in solution. The voltage for this process is 1.10 v as you saw in the previous experiment. The opposite process, zinc displacing copper is non-spontaneous. Or is it?

For many years chemistry teachers have done a demonstration in which they turn ordinary pennies into "gold". Traditionally the process has been done in a hot, very alkaline solution containing the ion $Zn(OH)_4^{2-}$ and some solid zinc. This combination of materials caused zinc metal to spontaneously plate on the copper. When the "silver" pennies were subsequently heated in a flame, the thin coating of zinc alloyed with the copper, producing yellow brass or "gold".

Recently a pair of chemists investigated this process more closely. Their report appeared in the *Journal of Chemical Education*. They found that the process was very different from what had been assumed. In fact, the very alkaline solution was not required at all! Copper placed in a heated solution of Zn^{2+} and a small amount of metallic zinc will become plated with zinc metal!! How is this? According to their research the process is driven by the alloying which occurs at the very surface of the copper. Due to thermal agitation in a heated solution, some zinc ions manage to work their way into the spaces between the copper atoms and form a very thin layer of brass. The voltage for zinc metal plating on brass (as opposed to copper) is positive! Thus the "silver" appearance of the penny after heating is actually a type of brass (silver brass). When heated in a flame, the silver brass is converted to yellow brass ("gold"). You can do this yourself, using the plating solution and some granular zinc.

Bring two of the shiniest (cleanest) pennies you can find. Place them in the beaker of solution provided on the hot plate and boil the solution. It takes about 10-15 minutes to plate a uniform layer of silver brass. Turning the pennies occasionally will help. When they are covered in silver brass, remove them and rinse in water. You can keep one "silver" penny and heat the other very carefully in a cool burner flame to change it to "gold". Too hot a flame will melt the brass coating, so be careful. This is just for fun, but it also points up the fact that not everything which we take for granted is happening they way we think. There are plenty of puzzles left to solve.

Be sure to keep an eye on your experiment while you do this little bit of modern alchemy!

You will be provided with the following materials:

1. two numbered zinc metal strips
2. steel wool
3. zinc plating solution (containing mainly $ZnSO_4$)
4. a power supply (set to 1.5 volts)
5. a current probe
6. 100 mL beaker and electrode holder

In addition, beakers of distilled water and acetone will be available in the lab and the oven will be on.

Design an experiment to compare the amount of electric charge flowing through a zinc plating cell with the mass loss and mass gain of the electrodes. Running the cell about 15-20 min should give sufficient mass changes to measure precisely on the balance. Measuring current each 30 seconds should be adequate.

BE SURE TO BRING YOUR TI-83/84 CALCULATOR TO CLASS FOR THIS EXPERIMENT. YOU WILL ALSO NEED A COPY OF THE HCHEM.83G FILES IN YOUR CALCULATOR MEMORY.

1. Measuring current with the CBL

The current probe consists of a small resistance shorted across the leads. Like a normal ammeter, it must be hooked in *series* with the circuit. For your plating cell the circuit would look like this:
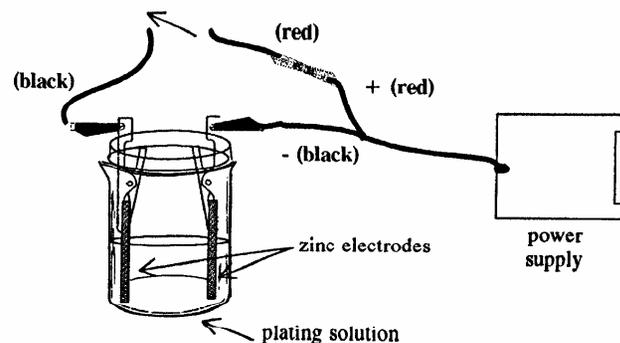
Note that the positive end of the power supply must be connected to the positive terminal of the ammeter (the red lead on the current probe). Electrons emerge from the negative terminal of the power supply and flow *through* the plating cell, through the ammeter, and back to the power supply, entering at the positive end.

Notice the level of the plating solution in the beaker. It should <u>NOT</u> touch the alligator clips that hold the electrodes. Also you should not put the numbered ends of the electrodes into the solution or the numbers will eventually disappear!

The timing function of the CBL leave something to be desired in that it does not start the moment you want it to start. Instead, there can be as many seconds as your chosen time interval before the first measurement is made. Or some other time interval! Because of this, it is necessary to watch your calculator screen very carefully. If you start with the entire circuit hooked up but do not place the electrodes in the beaker, no current will flow. When 0 seconds appears on your calculator, place the electrode assembly into the solution. The current measured at the first non-zero time interval (30 seconds) will have been flowing for 30 seconds. When you are ready to stop, remove the electrode assembly as the time you wish to stop is displayed by the calculator, then press CLEAR on the calculator. There will be another delay, but you can deal with this later (see **Analysis**).

2. Massing electrodes after plating

      The electrodes will be wet, of course, and you will want to mass them *dry*. The quickest way to do this is to gently rinse them in distilled water by dipping, followed by a similar rinse in acetone (which has a very high vapor pressure at room temperature) followed by a short stay in the oven. Be careful not to scrape off any new material adhering to the electrodes.

Analysis

1. Calculate the mass changes for the two zinc electrodes in the plating cell.
    a. How are they related? Does this seem correct? Why?
    b. Which electrode increased/decreased in mass relative to which terminal of the
       power supply (+ or -) it was connected to? Why?

2. From your current data determine the average current that flowed through the plating cell for the duration of the experiment* and use this information to determine the amount of charge (in Coulombs) which passed through the cell.

*You can determine the average current quickly. You can copy your data to the Lists on your calculator by beginning at the opening menu and selecting **3. Process data**. Look at the data (**View data**) and copy the current reading from the 30 second slot into the zero time slot. Then go to the end of the data and delete any measurements that were made after you removed the electrodes from the solution (usually some small value like 0.02 or similar). Don't forget to delete the time value for this bogus current as well. The actual duration of the experiment is now the last time entry in L_1. Now move to the empty slot at the top of L_3 and press [2nd] LIST MATH mean([2nd]L_2). The expression for this should appear across the bottom of the screen. When you press ENTER the average will appear at the top of L_3! Pretty neat, huh?

3. From the number of Coulombs, calculate the expected mass change of zinc metal and compare this to your mass change data. Comment on any difference, describing factors which you suspect may have contributed to error.