# The Atomic Mass of an Unknown Metal

Background

Historically, a relative atomic mass scale for the elements was gradually assembled from many experiments leading up to Mendeleev's eventual arrangement of the known (and predicted) elements of his time into something resembling the modern periodic table. Preceding the notion of any sort of relative scale, *equivalent masses* were being determined fairly early in experiments by chemists investigating the combining power of various elements with oxygen. *Equivalent mass* at that time was defined as **the mass of an element that would react with 8 grams of oxygen**. Using calcium as an example and working backwards for CaO, the equivalent mass of calcium would be about 20. The equivalent mass for hydrogen would be 1 (think about H_2O).

In terms of getting information about elements which could be compared, a reaction with oxygen is a good idea since oxygen is a very reactive element and combines with just about every other element. Early chemists were confused, however, in their attempts to arrange elements in some manner by equivalent mass because different experiments often yielded different equivalent masses. For example, some experiments with iron and oxygen gave approximately 28 while others gave about 19.

Following Alessandro Volta's demonstration of the "electric pile" (a simple battery) around 1800, experiments with electrolysis revealed a different way to determine the equivalent mass of a metal and aided in understanding the variable results obtained for some elements. During electrolysis, electrons move through an electrical circuit enabling both oxidation and reduction in different parts of the electrolytic cell. For example, if inert electrodes are inserted into an aqueous solution of sodium sulfate and an electrical current is passed through, hydrogen gas (H_2) and oxygen gas (O_2) will be released at the different electrodes due to the oxidation and reduction of water:
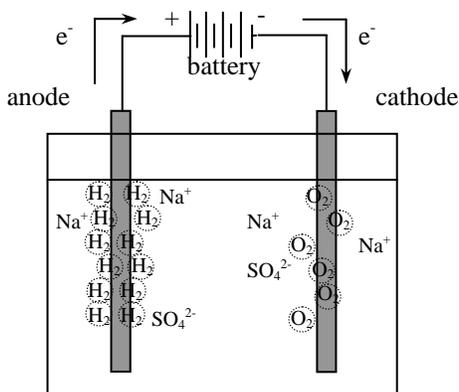

English chemists William Nicholson and Anthony Carlisle found the mass ratio of hydrogen to oxygen produced was 1:8--exactly what would be expected from water, based on equivalent masses. They also saw quite clearly that twice as much hydrogen formed as oxygen *by volume*. This discovery led to the correction of Dalton's erroneous formula for water, the *law of combining volumes* (Joseph Gay-Lussac), *Avogadro's Law*, the concept of diatomic molecules for some gaseous elements, etc.

Adapted from <u>A.P. Chemistry Syllabus</u>, Richard L. Humphery

If a second identical electrolytic cell is inserted into the electric circuit such that electrons flow first through one cell and then through the other as they complete their journey back to the power source, it must be that the same number of electrons flows through each cell. This is confirmed by equal amounts of hydrogen produced in both cells (and oxygen as well). Even if the electrolytic cells involve <u>different</u> chemical processes, the same number of electrons is available in each. Consider, then, an experiment in which water is electrolyzed in one cell and metal is plated in a second until 8 grams of oxygen have been collected in the water cell. The electrons released as water is oxidized to oxygen gas will also travel through the plating cell, available for the reduction of metal ions at the cathode of the plating cell. The mass of metal plated is thus "equivalent" to 8 g of oxygen, i.e., it is the *equivalent mass* of the metal. This mass can also be thought of in terms of the amount of hydrogen produced in the water electrolysis: 1 gram. This is, in many ways, a more convenient way of expressing experimental data of this type, as grams metal/grams hydrogen. So the equivalent mass of an element can also be thought of as the mass of material "equivalent" to 1 g of hydrogen gas (either produced by electrolysis or by direct displacement from acid or water).

Michael Faraday recognized this in 1832. As the concept of *valence* became better understood it was also clear why some experiments might yield one value for an equivalent mass and others yield a different one: many elements can have more than one valence. For example, iron in solution can be either +2 or +3. The reduction of these different ions would require different numbers of electrons which in turn could come from different amounts of oxygen (or hydrogen) in a water electrolysis cell.
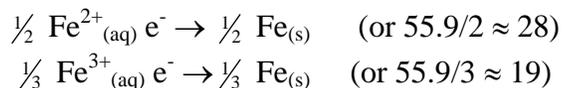
The modern definition of equivalent mass borrows from Faraday's work and reduces the question to one of electrons entirely. The transition is easy to make if we consider the reduction of water in a typical electrolysis cell on a **one mole-electron** basis:

$$H_2O_{(l)} + e^- \rightarrow \tfrac{1}{2}\ H_{2(g)} + OH^-_{(aq)}$$
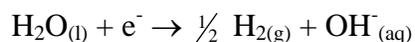
The half-reaction above shows that 1 mole of electrons will yield 0.5 moles of hydrogen gas. This much hydrogen is 1 gram. Since this is the equivalent of 8 g of oxygen in the same cell, we are back to the original standard of comparison. Thus the equivalent mass may be defined as **the mass of an element that reacts completely with 1 mole of electrons**. Returning to the earlier example of calcium in CaO, we know that the charge on calcium in the compound is +2. The reduction of that ion by 1 mole of electrons could be written as:

$$\tfrac{1}{2}\ Ca^{2+}_{(aq)}\ e^- \rightarrow \tfrac{1}{2}\ Ca_{(s)}$$
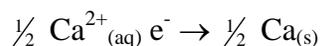
One-half mole of calcium is about 20 grams which is the equivalent mass obtained by direct combination with oxygen. In a similar way, the different equivalent masses of the iron species, Fe(II) and Fe(III), now become clear:

$$\tfrac{1}{2}\ Fe^{2+}_{(aq)}\ e^- \rightarrow \tfrac{1}{2}\ Fe_{(s)} \qquad (or\ 55.9/2 \approx 28)$$
$$\tfrac{1}{3}\ Fe^{3+}_{(aq)}\ e^- \rightarrow \tfrac{1}{3}\ Fe_{(s)} \qquad (or\ 55.9/3 \approx 19)$$

The key to unraveling the discordant iron data was an understanding that elements (metals in particular) may exist in different charged states within compounds.

That observation would only be interesting, as far as it goes, were it not for some work on the specific heats of metals done by Dulong and Petit, also around 1820. After studying many of the heavier metals they concluded that the average _molar_ *heat capacity* (the amount of heat required to raise the temperature of 1 mole of the metal by one degree) for a great number of them was about 25 J/mol·K. [Dulong and Petit would not have used the term "mole" but rather "relative atomic weight" or perhaps "gram-atomic weight"; one "gram-atomic weight" of an element is 1 mole]

The significance of this value is not immediately obvious. Consider another similar quantity, *specific heat*, the amount of heat required to raise the temperature of 1 gram of a substance by one degree. This number is *not* constant for metals and if we compare the units for the molar heat capacity with those for specific heat we can see a useful relationship emerge:

$$\frac{\text{molar heat capacity}}{\text{specific heat}} = \frac{\text{J/mol} \cdot \text{K}}{\text{J}/\text{g} \cdot \text{K}} = \frac{\text{g}}{\text{mol}}$$

When we take into account that the molar heat capacity of many heavy metals is about 25, we end up with the *law of Dulong and Petit*:
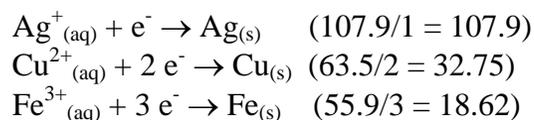
$$25 \approx \text{specific heat x atomic mass}$$

These two seemingly disconnected ideas: 1) a roughly constant molar heat capacity for many metals and 2) a relationship between equivalent mass and electrons are the basis for a method of determining the atomic mass of a metal.

Consider the earlier discussion of a metal plating cell in series with a water electrolysis cell. If the mass change of one of the plating electrodes is measured and divided by the mass of hydrogen gas produced, the equivalent mass of the metal is obtained:

$$\frac{\text{g metal plated/dissolved}}{\text{g hydrogen gas produced}} = \text{equivalent mass}$$

This equivalent mass is related to the atomic mass of the metal by an integer factor which is the *charge* on the metal ion in the plating solution. To see why, compare the following half reactions:

$$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)} \quad (107.9/1 = 107.9)$$
$$Cu^{2+}_{(aq)} + 2\ e^- \rightarrow Cu_{(s)} \quad (63.5/2 = 32.75)$$
$$Fe^{3+}_{(aq)} + 3\ e^- \rightarrow Fe_{(s)} \quad (55.9/3 = 18.62)$$

Again, this is all true because of the original definitions of equivalent mass which stretch back to 8 g of oxygen or 1 g of hydrogen (which is 0.5 mol H_2 and requires 1 mol e^- for reduction from water). But to get the atomic mass, we need the charge. How can we know that--especially if the metal is unknown?

The specific heat of a metal can be determined in the laboratory by a fairly simple procedure. A known mass of the metal is heated and dropped into a known mass of water. The initial and final temperatures of both are measured. Heat from the metal moves into the water until thermal equilibrium is reached:

$$\text{Heat lost by metal} = \text{Heat gained by water}$$

Another way of expressing this heat exchange is:

$$- \text{mass}_{metal} \text{ x } \Delta t_{metal} \text{ x } s_{metal} = + \text{mass}_{water} \text{ x } \Delta t_{water} \text{ x } s_{water}$$

where s is the specific heat of the two substances. The only unknown in the equation above is the specific heat of the metal. Once this has been calculated the law of Dulong and Petit can be applied:

$$\frac{25 \text{ J/mol} \cdot \text{K}}{\text{x J}/\text{g} \cdot \text{K}} \approx \frac{\text{g}}{\text{mol}}$$

If the metal follows the law of Dulong and Petit reasonably well, this will be a good approximation of the atomic mass. But the accuracy can be improved significantly by combining this information with the equivalent mass data from the electrolysis experiment since:

$$\frac{\text{atomic mass}}{\text{charge}} = \text{equivalent mass}$$

This relationship can be seen in the calculation of the equivalent masses of the elements shown on the previous page. The key piece of information here is that the charge <u>must</u> be an *integer*. Dividing the approximate atomic mass by the experimentally determined equivalent mass should yield a number close to an integer. Rounding to the nearest integer gives the charge of the metal ions in solution. When this rounded value is multiplied by the equivalent mass, an accurate atomic mass should be the result. In principal, with careful work and other corroborating physical evidence, this should enable a positive identification of the metal.

The Experiment

There are three parts to this experiment:

- the determination of the equivalent mass of the unknown metal
- the determination of the specific heat of the unknown metal
- the determination of the density of the unknown metal

The following non-locker materials will be provided:

- 18-volt DC power supply w/connecting cables
- 1 L (tall) beaker
- 100 mL gas measuring tube
- two stainless steel electrodes
- 6 M NaOH
- two electrodes of the unknown metal
- porcelain electrode holder for a 250 mL beaker
- plating solution containing ions of the unknown metal
- additional unknown metal in small shot form
- steam generator, stand and sample cup
- standard thermometer, -10°C to 150°C
- CBL and temperature probe
- calorimeter
- 10 mL uncalibrated pycnometer

The Chemicals

Since all of the new materials in this experiment are unknowns, specific information on their properties and hazards cannot be given. Suffice it to say that nearly all heavy metals are toxic in one form or another and while ingestion or contamination from gross metal samples is unlikely, *concentrated metal ion solutions such as those used for plating are certainly poisonous and should not be discarded down the drain*. If handled carefully to limit contamination the plating solutions can be used indefinitely and so should be returned to their respective bottles at the conclusion of the experiment.

Sodium hydroxide is commonly known as lye or caustic soda. It is a very hygroscopic white solid (absorbs water from the air rapidly) and also absorbs CO_2. It is very corrosive to vegetable and animal matter and aluminum metal, especially in the presence of moisture. Dissolving NaOH in water generates considerable heat.

Besides its use in the laboratory, sodium hydroxide is used in commercial drain cleaner preparations, to treat cellulose in the manufacture of rayon and cellophane and in the manufacture of some soaps. It is corrosive to all tissues and can be detected on skin by the "slimy" feeling associated with bases. It should be rinsed off thoroughly upon contact. It can damage delicate eye tissues and cause blindness.

Technique Discussion

The three parts of this experiment may be done in any order. The determination of the specific heat is the most subject to error due to temperature changes during the transfer of hot metal shot to the calorimeter. If possible, this determination should be repeated.

The basic procedure for determining the equivalent mass involves running electricity through a water electrolysis cell hooked together in series with a metal plating cell until a desired amount of hydrogen gas has been collected (near but not exceeding 100 mL). A correct circuit diagram for this part of the experiment is shown on the following page.
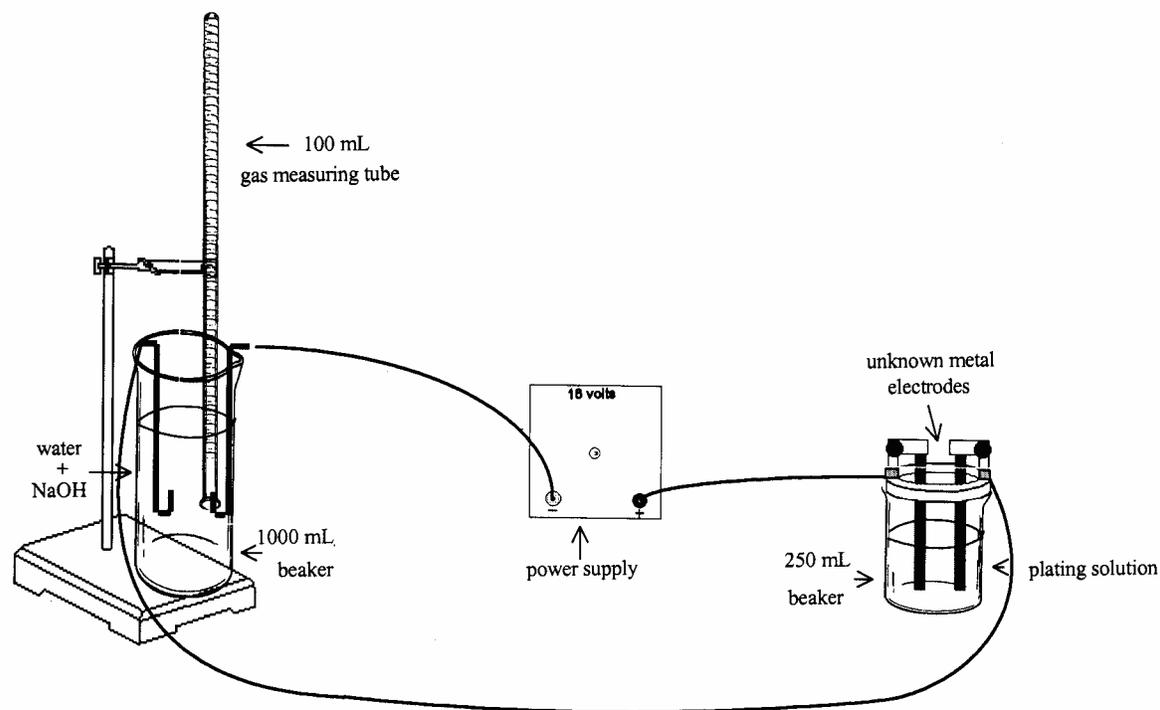
Because electrons emerge from the negative (-) terminal of a DC power supply, whichever stainless steel electrode is connected to this terminal will act as a supply of electrons to enable reduction. In water which has been "contaminated" with an electrolyte (about 20 mL 6 M NaOH) to increase conductivity and therefore rate, this will result in hydrogen gas being produced at that electrode. Thus for a correct equivalent mass determination, the gas measuring tube should be placed over this electrode. The oxygen produced at the other electrode is allowed to escape into the room.

The electrode at which hydrogen is produced should be positioned in the center of the mouth of the gas tube AND about half of the exposed metal at the "hook" on the end of the electrode should be outside the opening of the tube:
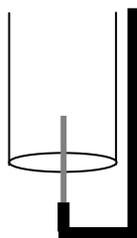
If this is **not** done the electrolysis will be very slow and it is possible not to finish the process in the available time.

After cleaning and massing the plating electrodes separately (analytical balance) they are suspended in plating solution of the same metal utilizing the porcelain electrode holder. Enough solution should be used to cover a good portion of the electrodes but not so much that there is none available for others using the same metal. Some metals have a tendency to "tree" or form dendrites which branch out toward the opposite electrode during plating. If a connection is made, the plating data will be invalid from that point so it is wise not to place the electrodes too close together. If treeing occurs, a gentle push with a stirring rod can usually prevent contact between the electrodes.

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At the conclusion of the electrolysis the unknown metal electrodes should be rinsed several times with distilled water and then dried in the oven and cooled to room temperature before remassing. The volume of hydrogen gas collected should be read only after the internal pressure has been adjusted to room pressure by leveling the inner and outer liquid levels. This means that both room pressure and room temperature must be recorded. Information on reading the barometer is found in the **Introduction to the Laboratory**.

Typical methods for determining the specific heat of a metal usually involve heating a gross sample by immersing it in boiling water and then quickly transferring the hot metal into cool water. This procedure suffers from a number of problems including knowing when the metal has reached the temperature of the boiling water and the carryover of hot water on the metal sample as it is transferred. Both of these problems contribute to significant errors since the specific heats of metals are generally small (< 1 J/g^{o}C) while that of water is quite high (4.184 J/g^{o}C).

To minimize these errors the metal can be heated dry and smaller pieces can be used to speed thermal equilibrium. Metal shot is ideal for this purpose and a steam generator fitted with a sample cup affords an easy way to heat the metal to a maximum temperature with relative ease, using the generator as essentially a boiling water bath with which the metal never comes in direct contact. There is still the problem of judging the temperature of the shot and transferring the hot metal as quickly as possible to the cool water. These are technique issues which need to be kept in mind and which are best addressed by care and repeated trials.

Sufficient dry shot should be used to prevent the standard thermometer from sitting on the bottom of the sample cup AND to completely cover the bulb of the thermometer. The mass will be considerable and so the rough balance should be used to determine the mass of the shot sample.

The sample cup should sit in the steam generator with boiling water until the temperature is at least 95°C. Meanwhile the calorimeter can be prepared with a massed amount of water (about ⅓ full). Because the water will end up above room temperature at thermal equilibrium with the shot, heat loss to the room introduces additional error. This problem can be addressed by using water that is initially *below* room temperature, preferably about as far below as it will end up above. Thus heat that leaks *into* the calorimeter from the room initially will be balanced by heat that leaks *out* afterward. Water that is about 10°C is a good first approximation. A thermometer probe connected to a CBL will be used to read the changing temperature in the calorimeter. **Be sure to bring your TI-83 calculator to lab and have the HCHEM.83G programs in memory.**

Wet metal shot should be drained as much as possible and placed in the appropriate container for drying after class.

In any density determination under ordinary laboratory conditions a number of factors must be considered. The two indispensable ones are the mass and volume of the sample! For most solids this is adequate. For liquids, the temperature is increasingly significant, while for gases the pressure is also important.

Mass can be readily determined on a balance.

The volume of a liquid can be measured in a graduated cylinder for routine work. Accurate measurement of liquid volume is made with a *pycnometer*, which is simply a container having a precisely definable volume. Some pycnometers are sold pre-calibrated. Others, such as the one used in this experiment, require calibration. Since no two pycnometers are alike, it is important to always use the same one once it has been calibrated. Our pycnometers are stored in 100 mL beakers with locker numbers on them.

Since most solids do not have a regular shape, a convenient way to determine their volume is by liquid displacement. The liquid used in such a determination should not react with or dissolve the solid. It should also not have an appreciable vapor pressure and its density should be less than that of the solid.

There is an efficient order of operations when using a pycnometer to determine the density of a solid which is not necessarily logical in terms of what measurements need to be made. Ultimately the mass of a sample of the solid which fits in the pycnometer (but does not fill it) and its volume are required for the density calculation. While the pycnometer is dry its mass should therefore be determined (analytical balance) since everything else will be measured inside of it.

Next the sample of metal should be placed in the pycnometer, typically filling about one half of the volume. Care should be exercised to select pieces of shot which actually fit through the neck of the pycnometer and will not become lodged in it. At this point there is sufficient data to determine the mass of the metal sample.

The volume of the sample is determined by displacement of water but since the pycnometer is uncalibrated, several measurements are required. The pycnometer with the metal sample in it should be filled with distilled water at room temperature (record). Pycnometers have ground-glass stoppers with a small capillary running the length of the stopper. Water should be added so that when the stopper is inserted the water is forced into the capillary and out around the stopper joint. After carefully drying the exterior of the pycnometer check that the capillary is filled. This ensures a reproducible mass.

This measurement alone cannot give the volume of the sample. The volume of the pycnometer itself must first be determined. This is done by filling the pycnometer with distilled water *only* and recording the mass. This allows a determination of the <u>mass</u> of water which fills the pycnometer at a given temperature. Water density tables can then be used to determine the volume of water (hence the volume of the pycnometer) and this information finally allows the calculation of the volume of the metal shot sample.

The Report

Your initial calculations should include:

1. The change in mass of the plating electrodes

2. The pressure of the hydrogen in the gas measuring tube
   [water vapor pressure table on following page]

3. The mass of hydrogen gas collected [recall, PV=nRT]

4. The equivalent mass of the unknown metal [g metal/g hydrogen] [relative error]

5. The specific heat of the unknown metal [specific heat of water = 4.184 J/g$^{\circ}$C]
   [relative error/best value--95% confidence (if more than one trial)]

6. Approximate atomic mass of unknown metal by Law of Dulong and Petit

7. The charge on the metal cations in the plating solution

8. The accurate atomic mass and probable identity of the metal [relative error]

9. The volume of the pycnometer [water density table on the following page]

10. The density of the metal [relative error, *propagated error uncertainty*]

      Your conclusion to this experiment should include a possible identification of your metal sample based on the data you have collected (atomic mass, likely ionic charge, color of the ion in solution, specific heat, density) with reference to a handbook or software resource. In addition, you should give the balanced equations for the reactions at <u>each</u> electrode (there are **4**) in the first part of the experiment. Discuss factors contributing to any error in your determined values. Be sure to consider which determination is likely to be the most accurate. Can you use handbook values along with some of your data to improve your results? That might indicate the relative reliability of a given determination.

Vapor pressure of water (CRC Handbook, 52nd edition)

mmHg

^{o}C	0.0	0.2	0.4	0.6	0.8
17	14.530	14.715	14.903	15.092	15.284
18	15.477	15.673	15.871	16.071	16.272
19	16.477	16.685	16.894	17.105	17.319
20	17.535	17.753	17.974	18.197	18.422
21	18.650	18.880	19.113	19.349	19.587
22	19.827	20.070	20.316	20.565	20.815
23	21.068	21.324	21.583	21.845	22.110
24	22.377	22.648	22.922	23.198	23.476
25	23.756	24.039	24.326	24.617	24.912

Absolute density of water (CRC Handbook, 52nd edition)

g/mL

^{o}C	0	1	2	3	4	5	6	7	8	9
17	**0.998**774	757	739	722	704	686	668	650	632	613
18	595	576	558	539	520	501	482	463	444	424
19	405	385	365	345	325	305	285	265	244	224
20	203	183	162	141	120	099	078	056	035	013
21	**0.997**992	970	948	926	904	882	860	837	815	792
22	770	747	724	701	678	655	632	608	585	561
23	538	514	490	466	442	418	394	369	345	320
24	296	271	246	221	196	171	146	120	095	069
25	044	018	**0.996**992	967	941	914	888	862	836	809