

# Experiments

## EXPERIMENT 3

### The Law of Definite Proportions

#### 3.1. Safety

Copper sulfate pentahydrate and barium chloride dihydrate are harmful if swallowed and can cause irritation to skin, eyes and respiratory tract. At high concentrations, these compounds can affect the liver and kidneys. The anhydrous compounds are also harmful if swallowed. (We should note that 1 g is the estimated lethal dose for a human.) As usual, Bunsen burners, hot glassware, and metal ring stands can cause painful and serious burns to skin.

#### 3.2. Notebook

Read this experiment carefully before writing your notebook. This experiment is also setup in sub-experiments. However, unlike Experiment 2, this experiment can be handled within a single notebook setup using the guidelines provided. There are questions at the end of the experiment that, when answered, will help you following the notebook guidelines. However, you will need to remember to place the section headings for each notebook section.

#### 3.3. Introduction

The **law of definite proportions** states that when two or more elements combine to form a given compound, they do so in fixed proportions by mass. For example, sodium chloride contains 39.3% by mass sodium and 60.7% by mass chlorine. In these experiments, the law of definite proportions will be used to determine the *empirical formulas* of hydrated ionic salts. (An empirical formula expresses the simplest whole number ratio of atoms for each element in a compound.)

The previous two experiments have introduced basic laboratory techniques that will be used throughout the semester. This experiment represents the first laboratory involving specific chemical principles and reactions. However, before these principles can be investigated, an understanding of chemical formulas and nomenclature must first be developed.

#### 3.4. Chemical formulas

A *molecule* is defined as an electrically neutral particle consisting of two or more nonmetallic elements combine. The atoms within a molecule are bonded together by sharing electrons. This type of bond is known as a covalent bond. The actual number of each type of atom

that exists in a molecule is represented by writing the *molecular formula* of the molecule. Thus, the molecular formula for benzene, namely  $C_6H_6$ , indicates that one molecule of benzene contains 6 atoms of carbon and 6 atoms of hydrogen. *Ionic compounds* are formed when metals exchange electrons with non-metals. Thus, the atoms in an ionic compound are not electrically neutral. The force that holds ionic compounds together is a Coulomb force, ionic compounds are very different from molecular compounds. The smallest unit of an ionic compound, which is defined by the smallest whole-number ratio of the ions, is known as the *formula unit*. Thus, the compound represented by the formula  $Fe_2O_3$  has a ratio of two cations of iron to three anions of oxygen.

The mass of a single atom is difficult to measure. (For instance, the mass of a single hydrogen cation (or proton) is  $1.67 \times 10^{-24}$  g.) Therefore, the *mole* is defined as the number of  $^{12}C$  atoms in exactly 12 grams of  $^{12}C$ . Moreover, the basic unit of mass for elemental chemistry, namely the atomic mass unit (amu or dalton) is defined as  $1 \text{ amu} \equiv \frac{1}{12}$  the mass of an atom of  $^{12}C = 1.6605 \times 10^{-24}$  g. Thus,

$$1 \text{ mole} = 12 \text{ g C atoms} \times \frac{1 \text{ C atom}}{19.926 \times 10^{-24} \text{ g C atom}} = 6.022 \times 10^{23} \text{ C atoms} .$$

The constant  $6.022 \times 10^{23}$  atoms (or molecules)/mole is known as *Avogadro's number* ( $N_A$ ). Since the mole and the atomic mass unit are defined using the same scale,  $1 \text{ amu} \times N_A = 1 \text{ g/mole}$ . Thus, the masses given on the periodic table can also be expressed as the number of grams of the element per mole of element. The molar mass  $M$  of a compound is obtained by summing the mass of all of the elements in a compound and, therefore, has units of g/mol. Moreover, the definition of a mole when combined with the law of definite proportions implies that a sample of  $H_2O$  will have 2 moles of atomic hydrogen for every 1 mole of atomic oxygen, while a sample of  $MgF_2$  has a mole ratio of 1 mole of magnesium for 2 moles of atomic fluorine.

### 3.5. Chemical nomenclature

Chemical compounds are named based on their classification as molecular compounds or ionic compounds. *Acids* are the class of compounds that result from the interaction of the hydrogen cation  $H^+$  with any anion. A flow chart indicating the basic rules of nomenclature is given in Fig. 3.1 with a summary of the rules presented below. The nomenclature for acids will be given in Experiment 6.

#### 3.5.1. Molecular compounds

The numbers in the chemical formula are converted into words using the Greek prefixes of

1 → mono	6 → hexa
2 → di	7 → hepta
3 → tri	8 → octa
4 → tetra	9 → nona
5 → penta	10 → deca

The elements are named in the same order as in the chemical formula, where elements are listed in the order of increasing electronegativity. The suffix of the last element becomes *-ide*. Thus,  $N_2O_5$  is dinitrogen pentoxide, while  $ClO_2$  is monochlorine dioxide or chlorine dioxide. However,  $Na_2O$  contains a metal and, therefore, is not disodium oxide and is an ionic compound. Ionic compounds use a different set of naming rules. The acids, which are a class of covalent compounds will be discussed later. Organic compounds (i.e., compounds containing only C, H, O, N, and P) have a different nomenclature which will be covered in more detail in Organic Chemistry. Some simple compounds are more generally referred to

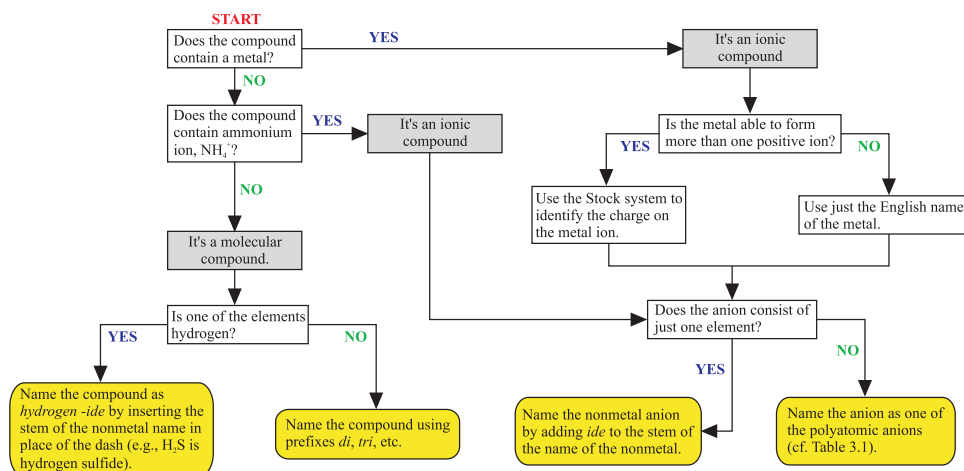


Fig. 3.1: Flow chart on chemical nomenclature, adapted from [1].

Table 3.1: Names of simple compounds important in freshman chemistry.

Formula	Common name
H <sub>2</sub> O	water ( <i>dihydrogen oxide</i> )
NH <sub>3</sub>	ammonia ( <i>azane</i> )
CH <sub>4</sub>	methane
CH <sub>3</sub> CH <sub>3</sub>	ethane
CH <sub>3</sub> OH	methanol
CH <sub>3</sub> CH <sub>2</sub> OH	ethanol
PH <sub>3</sub>	phosphane or phosphine
AsH <sub>3</sub>	arsine or arsenic trihydride

by common names. Table 3.1 gives the names of some simple compounds that you should know as a student in chemistry. Common names are in italic.

### 3.5.2. Ionic compounds

Ionic compounds are composed of charged species. Positively charged ions are cations, while negatively charged ions are anions. A neutral ionic compound must be charge balanced (i.e., the net charge on the cations must equal the next charge on the anions). Thus, the ionic compound formed by the reaction of Fe<sup>3+</sup> and Cl<sup>-</sup> must have 3 chloride anions (Cl<sup>-</sup>) for every iron(III) cation (Fe<sup>3+</sup>) in order for the compound to be neutral. This fact implies a chemical formula of FeCl<sub>3</sub>. Ionic compounds are named by naming the cation first and then the anion.

### 3.5.3. Cations

- (1) Cations from periodic table groups IA, IIA and IIIA (on some periodic tables these groups can be labeled I, II, and III) always have charges of +1, +2 and +3, respectively. Since the charge cannot vary for compounds with these cations, the unmodified metal name is used for the ion.
- (2) Silver, zinc and cadmium only form +1 cations and, therefore, are named using the unmodified metal name.

Table 3.2: Metal cation nomenclature: The Stock system in comparison to the older system.

Cation	Stock system	Older name
$\text{Cu}^+$	copper(I) ion	cuprous ion
$\text{Cu}^{2+}$	copper(II) ion	cupric ion
$\text{Fe}^{2+}$	iron(II) ion	ferrous ion
$\text{Fe}^{3+}$	iron(III) ion	ferric ion
$\text{Hg}_2^{2+}$	mercury(I) ion	mercurous ion
$\text{Hg}^{2+}$	mercury(II) ion	mercuric ion
$\text{Sn}^{2+}$	tin(II) ion	stannous ion
$\text{Sn}^{4+}$	tin(IV) ion	stannic ion

- (3) Mercury(I) ion is not stable and, therefore, always forms the cation  $\text{Hg}_2^{2+}$  in ionic compounds.
- (4) All other metal cations are named by adding a roman numeral in parentheses after the metal name to indicate the charge on the ion (known as the Stock system of nomenclature). For example,  $\text{Fe}^{3+}$  is iron(III), while  $\text{Pb}^{2+}$  is lead(II). Some of these metal compounds have an older nomenclature, which you will see on some of the reagent bottles in the laboratory. Table 3.2 gives the older system in comparison to the Stock system for metals that are important in freshman chemistry.
- (5)  $\text{NH}_4^+$ , known as the ammonium ion, behaves as a Group I metal ion although it does not contain a metallic element. Thus, the ammonium ion can act as a cation in an ionic compound.

### 3.5.4. Anions

- (1) Monoatomic anions formed from non-metal elements with sufficient extra electrons to have a rare gas configuration have names that end in *-ide*. Thus  $\text{O}^{2-}$ , which has an electron configuration similar to the rare gas Ne, is named **oxide**. Similarly,  $\text{P}^{3-}$  (having an electron configuration similar to the rare gas Ar) is named **phosphide**.

Table 3.3: The important polyatomic anions.

Formula	Name	Formula	Name
$\text{OH}^-$	hydroxide	$\text{CN}^-$	cyanide
$\text{O}_2^{2-}$	peroxide	$\text{NH}_2^-$	amide
$\text{NO}_2^-$	nitrite	$\text{NO}_3^-$	nitrate
$\text{SO}_3^{2-}$	sulfite	$\text{SO}_4^{2-}$	sulfate
$\text{PO}_3^{3-}$	phosphite	$\text{PO}_4^{3-}$	phosphate
$\text{ClO}_2^-$	chlorite	$\text{ClO}_3^-$	chlorate
$\text{CO}_3^{2-}$	carbonate	$\text{C}_2\text{H}_3\text{O}_2^-$	acetate
$\text{CrO}_4^{2-}$	chromate	$\text{Cr}_2\text{O}_7^{2-}$	dichromate
$\text{MnO}_4^-$	permanganate	$\text{SCN}^-$	thiocyanate

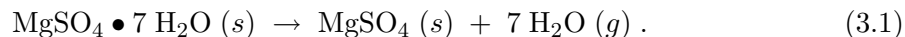
- (2) Table 3.3 lists the common polyatomic ions that are important in freshman chemistry. **It is important to know the names, formulas, and charges of these anions, therefore, this table should be memorized.**
- (3) Polyatomic anions with names ending in *-ite* are related to the *-ate* anions in Table 3.3 but have one **less** oxygen atom. The standard *-ite* anions are also given in Table 3.3.
- (4) Anions with names having the prefix *Per-* are related to the *-ate* anions in Table 3.3, but contain one **additional** oxygen atom. Thus,  $\text{ClO}_4^-$  is the perchlorate anion.
- (5) Anions with names having the prefix *Hypo-* are related to the *-ite* anions in Table 3.3, but have one **less** oxygen atom. Thus,  $\text{ClO}^-$  is the hypochlorite anion.
- (6) Anions that are formed from the combination of an anion with a charge  $> -1$  and an  $\text{H}^+$  unit are named by placing the word *hydrogen* as a prefix to the anion name. Thus,  $\text{HS}^-$  is the hydrogen sulfide ion,  $\text{HPO}_4^{2-}$  is the hydrogen phosphate ion, and  $\text{H}_2\text{PO}_4^-$  is the dihydrogen phosphate ion. An older nomenclature of compounds containing a single  $\text{H}^+$  is to use the prefix *bi-*. Thus,  $\text{HS}^-$  is also called the bisulfide anion, and  $\text{HCO}_3^-$  is most commonly known as the bicarbonate anion.

### 3.5.5. Hydrates

Hydrates are substances formed when water combines chemically in definite proportions with an ionic salt, thereby giving a constant ratio of water molecules to the ions of the salt. Hydrates are not mixtures, since the water is coordinatively bound to either the cation or anion or both in the salt. In  $\text{CuSO}_4 \bullet 5 \text{H}_2\text{O}$ , for example, the bonding involves four water molecules coordinatively bound to the  $\text{Cu}^{2+}$  ion in a square planar structure and one molecule of water bound to the sulfate ion by hydrogen bonds [cf. Fig. 3.2]. The anhydrous (without water) form of a hydrated salt is produced when all the waters of hydration are lost. Some examples of hydrates are listed below:

<u>Formula</u>	<u>Chemical name</u>	<u>Common name</u>
$(\text{CaSO}_4)_2 \bullet \text{H}_2\text{O}$	calcium sulfate hemihydrate	plaster of paris
$\text{CaSO}_4 \bullet 2 \text{H}_2\text{O}$	calcium sulfate dihydrate	gypsum
$\text{CuSO}_4 \bullet 5 \text{H}_2\text{O}$	copper (II) sulfate pentahydrate	blue vitriol
$\text{MgSO}_4 \bullet 7 \text{H}_2\text{O}$	magnesium sulfate heptahydrate	epsom salt
$\text{Na}_2\text{CO}_3 \bullet 10 \text{H}_2\text{O}$	sodium carbonate decahydrate	washing soda

Notice that hydrates are named by first naming the ionic salt and then adding *x*-hydrate, where *x* is the appropriate Greek prefix (cf. Section 3.4.1) to indicate the number of water molecules associated with the salt. The  $\bullet$  in the formula indicates a kind of chemical bond that usually can be easily broken. For example, magnesium sulfate heptahydrate can be converted to anhydrous magnesium sulfate by heating:



### 3.6. Qualitative properties of hydrates

**Efflorescence** is the process by which a hydrated salt loses water at room temperature and atmospheric pressure. On the other hand, the property of some salts to collect moisture from the air and dissolve in it is called **deliquescence**. A compound is **hygroscopic** if it absorbs water without dissolving.

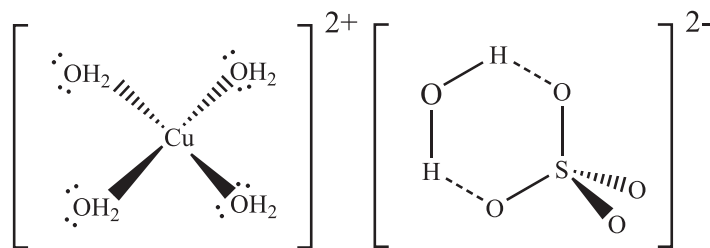


Fig. 3.2: Schematic picture of the  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  compound with the  $\text{Cu}^{2+}$  ion forming a square planar structure involving four water molecules, while the fifth water molecule is hydrogen bonded to the sulfate counter ion [i.e.,  $\text{SO}_4^{2-}$ ].

### 3.7. Experiment 3. Composition of a hydrate

In this experiment, the laboratory instructor will give you a hydrated salt chosen from copper sulfate, calcium sulfate, and sodium sulfate. The difference in the mass of the anhydride and the hydrate will then be used to determine the mass of water in the hydrate and, therefore, the empirical formula of the hydrate. The procedure, which should be performed on two samples of the same hydrate, is as follows:

- (1) Weigh a clean, dry, labeled crucible. Record the weight in your notebook.
- (2) Introduce about 1 - 2 grams of the pulverized hydrated salt. Note the appearance and color of the solid.
- (3) Weigh the crucible and contents. Record this weight in your laboratory notebook.
- (4) Setup a wire triangle on the iron ring over a bunsen burner. (Ensuring that the wire triangle will hold the crucible in an upright position.)
- (5) Heat the crucible and contents in the hottest part of the flame for 5 - 10 minutes. (The bottom of the crucible should turn a dull red during heating.) Initially, the hydrate should be heated slowly by waving the burner flame fairly rapidly under the crucible. If the material begins to boil or crackle, the heating is too intense and splattering may occur. Within approximately 1 minute, the material should become drier and stronger heat can be applied. At the end of the 5 - 10 minute period of heating, allow the crucible to cool slightly before transfer.
- (6) Using clean crucible tongs, transfer the crucible to a desiccator and allow the crucible to cool to room temperature.
- (7) When cool, weigh the dish and the anhydride and record this weight in your notebook.
- (8) Heat the crucible in the flame again for 5 minutes, place in desiccator and allow the crucible to cool. Once cool, weigh the sample again. Continue the heat/cool/weigh cycle until the mass of the sample remains constant. Be sure to record all of your measurements in your notebook.
- (9) Place a thermometer in the anhydrous salt and record the temperature.
- (10) Add water a few drops at a time to convert the anhydride back to the hydrate. Record the temperature (once the temperature is constant).

### 3.8. References

1. J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 5th ed. (Wiley, New York, 2007).

**Questions**

*These questions should be used to help you write your notebook and should be answered in some form in the notebook.*

- (1) What is the purpose of Experiment 3A?
- (2) What is the purpose of Experiment 3B?
- (3) How do you plan to determine the water content in the hydrated salt? Answer in a single if/then statement.
- (4) What materials are required for this experiment? Are any chemicals needed? Which materials must be obtained from the stockroom, which must be obtained from the instructor, and which are in your laboratory drawer?
- (5) What are the steps for determining the composition of a hydrate?
- (6) Create a table that will allow you to input the following information for both trial samples. Be sure to record all values to the appropriate units.
  - mass of the evaporating dish
  - mass of the dish and the hydrate
  - mass of the hydrate
  - mass of the dish after heating when the contents have reached constant mass
  - mass of the anhydride
  - temperature of salt before the addition of water
  - temperature of salt after the addition of water
  - color before heating
  - color after heating
  - color after adding water
- (7) Create a table that will allow you to monitor the mass of the sample during the heat/cool/weigh cycles.
- (8) Determine the amount of water in the hydrated salt for both your trial samples. To do this, answer the following questions for both samples.
  - What is the mass of water in the hydrated sample (i.e., subtract the mass of the anhydride from the mass of the hydrate)?
  - How many moles of water are in each sample? (To determine the number of moles  $n$ , divide the mass of water by the molar mass of water.)
  - How many moles of the anhydride salt are in each sample? (The number of moles of anhydride are determined by dividing the mass of the anhydride by the molar mass of the anhydride.)
  - How many moles of water are associated with a single mole of anhydride salt in each sample? (This can be determined by dividing the moles of water by the moles of anhydride.)
  - What is the average number of moles of water per mole of anhydride? What is the uncertainty?
  - What is the formula for the hydrate [i.e., anhydride •  $x$  H<sub>2</sub>O, where  $x$  is the average number of moles of water]?
- (9) What evidence of a chemical change did you observe when the sample was heated?
- (10) What evidence of a chemical change did you observe when water was added to the anhydrous sample?
- (11) For the salt that you were assigned, what is the formula for the hydrates as given from a literature search? (Remember to reference where you obtained your information.)
- (12) How does your formula compare? If this formula is not comparable, explain what might have lead to the differences.

### 3.9. Reminders

Remember to get your results signed before leaving the laboratory and to submit your laboratory notebook pages. Remember to submit your notebook pages for Experiment 2.

### 3.10. Practice problems

The problems below are excellent practice problems for the laboratory quiz and the laboratory practical. Since these problems will not be graded, the answers are given in parenthesis.

- (1) Each of the following compounds is named incorrectly. What is wrong with each name, and what is the correct name for each compound?
  - $\text{FeCl}_3$ , iron chloride (*Name does not give oxidation state of iron. iron(III) chloride*)
  - $\text{NO}_2$ , nitrogen(IV) oxide (*This is a covalent compound. nitrogen dioxide*)
  - $\text{CaO}$ , calcium(II) monoxide (*Calcium has only a single oxidation state. calcium oxide*)
  - $\text{Al}_2\text{S}_3$ , dialuminum trisulfide (*the oxidation number for Al is +3, that for sulfur is -2. aluminum sulfide*)
- (2) Write the formula or name for each.
  - chromium(VI) oxide ( $\text{CrO}_3$ )
  - $\text{HSO}_3^-$  (*bisulfite ion*)
  - sulfur difluoride ( $\text{SF}_2$ )
  - $\text{K}_2\text{HPO}_4$  (*potassium hydrogen phosphate*)
  - aluminum sulfate hexadecahydrate ( $\text{Al}_2(\text{SO}_4)_3 \bullet 16 \text{H}_2\text{O}$ )
  - $\text{KMnO}_4$  (*potassium permanganate*)
- (3) A 0.755 g sample of hydrated cobalt(II) chloride was heated carefully until it had changed completely to anhydrous cobalt(II) chloride with a mass of 0.412 g. What is the formula for the hydrated salt? ( $\text{CoCl}_2 \bullet 6 \text{H}_2\text{O}$ )
- (4) A 0.655 g sample of aluminum sulfate octadecahydrate was heated carefully until it had changed completely to anhydrous aluminum sulfate. What is the mass of the anhydrate salt sample? ( $0.346 \text{ g Al}_2(\text{SO}_4)_3$ )

### 3.11. Appendix I. Basic Stoichiometry

For most of the problems that you will encounter in general chemistry, you will begin with a known quantity (either mass or volume) and will want to go to another quantity (again either mass or volume). To go from the mass of A to the mass of B, you need a relationship between these two values. This relationship is a balanced chemical reaction such as that in eq. (3.1). However, the balanced chemical reaction gives the relationship between the moles of A and the moles of B. The molar mass of a compound is used to convert from mass to moles. For an example, let us assume that we have 0.853 g of magnesium sulfate heptahydrate. In order to determine the mass of water release during heating and the mass of anhydrous salt remaining, we must first convert the mass of magnesium sulfate heptahydrate to moles. The chemical formula for magnesium sulfate heptahydrate is  $\text{MgSO}_4 \bullet 7 \text{H}_2\text{O}$ . The molar mass  $M(\text{MgSO}_4 \bullet 7 \text{H}_2\text{O})$  is, therefore,

$$\begin{aligned}
 M(\text{MgSO}_4 \bullet 7 \text{H}_2\text{O}) &= M(\text{Mg}) + M(\text{S}) + 4 M(\text{O}) + 14 M(\text{H}) + 7 M(\text{O}) \\
 &= M(\text{Mg}) + M(\text{S}) + 11 M(\text{O}) + 14 M(\text{H}) \\
 &= 24.305 \text{ g/mol} + 32.066 \text{ g/mol} + 11 (15.999 \text{ g/mol}) + 14 (1.008 \text{ g/mol}) \\
 &= 246.472 \text{ g/mol} .
 \end{aligned}$$



Thus, the number of moles of the hydrated salt is

$$0.853 \text{ g hyd} \left( \frac{1 \text{ mole hyd}}{246.472 \text{ g hyd}} \right) = 3.46\bar{1} \times 10^{-3} \text{ mol hyd}$$

We can now use eq. (3.1), or



to convert from moles of the hydrated salt to moles of water

$$3.46\bar{1} \times 10^{-3} \text{ mol hyd} \left( \frac{7 \text{ mol H}_2\text{O}}{1 \text{ mol hyd}} \right) = 2.42\bar{3} \times 10^{-2} \text{ mol H}_2\text{O}$$

and moles of anhydrous salt

$$3.46\bar{1} \times 10^{-3} \text{ mol hyd} \left( \frac{1 \text{ mol anhyd}}{1 \text{ mol hyd}} \right) = 3.46\bar{1} \times 10^{-3} \text{ mol anhyd} .$$

Finally, we can use the molar mass of water, determined from

$$M(\text{H}_2\text{O}) = 2 M(\text{H}) + M(\text{O}) = 2 (1.008 \text{ g/mol}) + 15.999 \text{ g/mol} = 18.015 \text{ g/mol} ,$$

and the molar mass of the anhydrous salt, given by

$$\begin{aligned} M(\text{MgSO}_4) &= M(\text{Mg}) + M(\text{S}) + 4 M(\text{O}) \\ &= 24.305 \text{ g/mol} + 32.066 \text{ g/mol} + 4 (15.999 \text{ g/mol}) = 120.367 \text{ g/mol} . \end{aligned}$$

to convert from moles back to grams. Thus, the mass of water released during heating of the salt is

$$2.42\bar{3} \times 10^{-2} \text{ mol H}_2\text{O} \left( \frac{18.015 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \right) = 0.437 \text{ g H}_2\text{O} ,$$

while the mass of the anhydrous salt remaining in the container is

$$3.46\bar{1} \times 10^{-3} \text{ mol anhyd} \left( \frac{120.367 \text{ g anhyd}}{1 \text{ mol anhyd}} \right) = 0.417 \text{ g anhyd} .$$

Since, under normal laboratory conditions, mass cannot be created or destroyed, the mass of the anhydrous salt plus the mass of water released should equal the initial mass of the hydrate. Thus, to check our results,

$$m_{\text{anhyd}} + m_{\text{H}_2\text{O}} = 0.417 \text{ g anhyd} + 0.437 \text{ g H}_2\text{O} = 0.854 \text{ g} ,$$

which is indeed close to the initial value of 0.853 g of hydrated salt.

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