

# CHEM1110: CHEMISTRY FOR THE LIFE SCIENCES I

A Supplementary Textbook to the On-Line Lecture Notes

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To Roya and Mina, my inspirations



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## Preface

At the University of Lethbridge, the first year undergraduate course Chem1110 (Chemistry for the Life Sciences I) is a general chemistry course tailor designed for those students who fit some or all of the following definitions:

- Having very limited high school chemistry and mathematics background
- Not considering to major in Chemistry or Biochemistry in university
- Not considering to enter medical, dental, or engineering schools

The intention of this course is to equip students with some fundamental understanding of chemistry before they enter the work force or take a few more chemistry-related courses such as Chem2120 (Chemistry for the Life Sciences II) in order to fulfill the requirement of their respective degree programs.

I have chosen to arrange the topics of this course around two important themes in today's world: water and energy. I have written this book in a story-telling style in the hope that, as the story unfolds, the students will gradually adopt a chemist's perspective in viewing the world around us. I have also written this book in a question-and-answer style so that the readers may acquire a critical-thinking attitude and learn the various problem-solving skills as they take part in answering each question.

This course is delivered using a combination of the following teaching/learning tools:

- Lecture (including Powerpoint online lecture notes)
- Laboratory experiments
- Small group tutorials
- Interactive online practices
- Interactive molecular modeling visualization tools
- Supplementary textbook (this coursepack)

As you can see from the above list, this textbook is only one of the many tools used in this course to facilitate the teaching/learning process. It contains most of the basic concepts we introduce in this course but **does not** cover everything we discuss during lectures, labs and tutorials. It does not contain a large number of exercises and data tables as those are accessible online. To succeed in this course the students are advised to study all materials introduced to them via the above combination of teaching/learning tools.

For those who are genuinely interested in having a glimpse of the chemistry language, this book hopes to be an informative but easy and fun read.

Ying Zheng

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## Introduction to Scientific Thinking

*Thinking scientifically is an acquired habit. The training of scientific thinking begins when you start working in a science laboratory.*

**W**hen you work in a science laboratory, you will need to think scientifically, talk scientifically, and write scientifically.

Compare these two situations:

**To make a cup of salt water at home:** add a spoonful of table salt to a drinking glass half-filled with water, stir and drink.

**To make 500.0 mL of a 0.1000 M sodium chloride solution in a lab:**

To complete this seemingly simple job in a scientifically correct way, you need to have some scientific knowledge, and more specifically, some chemistry knowledge. To mention a few:

- Table salt is sodium chloride.
- The molecular formula of sodium chloride is NaCl. How does this relate to the amount of NaCl needed?
- What does 0.1000 M mean and how much NaCl is needed to obtain this number?
- What measurement tool to use to measure the amount of NaCl and how accurate should you be? Accurate to a gram or a milligram?
- What does 500.0 mL mean and how would you measure this amount; by using a balance, a beaker, a graduated cylinder or a pipet?

By the way, no eating and drinking in a laboratory.

This course will enable you to accomplish the above simple tasks and much more. Let's start with **units**.

## 1.1 Units of Measurement

A unit must always be included when reporting a measurement. For example, 5.0 m indicates a quantity of 5.0 metres. Without the unit, we would not know the system of measurement used to obtain the number 5.0 (5.0 feet, 5.0 kilometres, or 5.0 inches) and therefore, a unit is required to complete the measurement reported.

### Question 1.

Read points *a* to *e* on the previous page and identify the words or symbols that are units of measurement. Also indicate the type of measurement the units are used for.

### Answer:

M (as in 0.1 M), gram, milligram, and mL are units. M is the symbol of molarity, a measurement of concentration. The words "gram" and "milligram" are for the measurement of weights or masses. The symbol mL means milliliter and is used as a unit for volume measurement.

Different systems of units have been developed in different parts of the world. However, in the scientific world, it is first the **metric system** and then the **SI** (Système International) units that have been adopted worldwide. Table 1 summarizes these two systems and also compares them with the imperial units which are still in use in North America.

**Table 1. Units of Measurement**

Measurement	Metric	SI	Imperial
Length	Meter (m)	Meter (m)	Foot
Volume	Liter (L)	Cubic meter (m <sup>3</sup> )	Quart
Mass	Gram (g)	Kilogram (kg)	Pound (lb)
Time	Second (s)	Second (s)	Second (s)
Temperature	Celsius (°C)	Kelvin (K)	Fahrenheit (°F)
Pressure	mmHg, atm, bar	Pascal (Pa)	
Energy	Calorie (cal)	Joule (J)	

meter is equivalent to 100 centimeters; one kilogram is equivalent to 1000 grams, et cetera.

It is easier for us to relate to numbers that are relatively close to a value of 1 (i.e. we have difficulty comprehending numbers such as 1000000000000). Therefore, for larger and smaller measurements, prefixes are attached in front of the standard unit. Some prefixes such as kilo are used for larger quantities; other prefixes such as milli are used for smaller quantities. The most common prefixes are listed in Table 2.

Table 2. Some Common Prefixes Used in the Metric System

Prefix	Symbol	Meaning	Exponent
giga	G	1000000000	$10^9$
mega	M	1000000	$10^6$
kilo	k	1000	$10^3$
deci	d	0.1 (1/10)	$10^{-1}$
centi	c	0.01 (1/100)	$10^{-2}$
milli	m	0.001 (1/1000)	$10^{-3}$
micro	$\mu$	0.000001 (1/1000000)	$10^{-6}$
nano	n	0.000000001 (1/1000000000)	$10^{-9}$
pico	p	0.000000000001 (1/1000000000000)	$10^{-12}$

A specific word is used to indicate the change of quantity in multiples of 10. For example, centimeter (cm) is 100<sup>th</sup> of a meter (m), and kilogram (kg) is 1000 times a gram (g). Comparing the last two columns in Table 2, one can appreciate the clarity as a result of using exponents to express very large or very small numbers. This is the usefulness of **Scientific Notation**.

## 1.2 Scientific Notation

As shown in Table 2, scientific notation is a way to express the number of zeros before or after a decimal point as a power of 10. This not only reduces the labor in writing down all the zeros but also helps prevent possible errors in counting the zeros. More importantly, using scientific notation greatly facilitates various scientific calculations, as you will see later.

### Question 2.

Write 0.00000023 and 4500000000.0 in scientific notation.

### Definition and Strategy:

In scientific notation the number is written such that only a single positive integer (called a *coefficient*) precedes the decimal. Moving the decimal to the left results in a positive power of 10. The exponent is the number of places the decimal had to be moved to result in the correct representation of scientific notation. A number smaller than one (i.e. the decimal equivalent of a fraction) is written in scientific notation by moving the decimal to the right. This results a negative power of 10, i.e. the exponent is a negative number.

For example, to write 0.00000023 in scientific notation we move the decimal point to the **right** seven digits to obtain the coefficient **2.3**, then we multiply 2.3 by  $10^{-7}$ . The power is **negative** because the original number is less than one.



Every measurement made is really an approximation. When we measure the length, volume, or mass of an object, the numbers we report are called **measured numbers**. Suppose you got on a scale this morning and saw that you weighed 145 lb. The scale is a measuring tool and your weight is a measured number. Each time we use a measuring tool to determine a quantity; the result is a measured number.

The accuracy to which you can report your measured numbers is dependent on the measuring device you use.

### Accurate vs Approximate Quantities

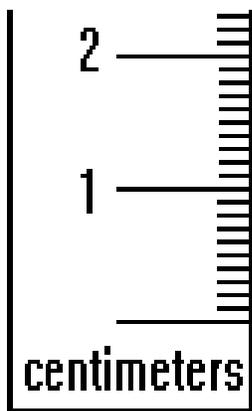
In many cases, it is not necessary to accurately measure the exact quantity of a material. If an experiment calls for **about** 3 g of a reagent, it is not necessary to weigh it on the analytical balance to exactly 3.0000 g. If however, the directions call for 3 g to the nearest 0.0001 g then measuring the mass on an analytical balance is in order. It does not mean the mass should be exactly 3.0001 g but rather the mass should be known to 1/10,000 of a gram.

### Accurate vs Precision

While **accuracy** measures how close your measurement is to the real thing, **precision** tells how close the repeated measurements (of one thing) are to each other. For example, you set out to clone a monkey, but repeatedly getting identical rabbits, then you have a good precision (identical rabbits) but very bad accuracy (no monkeys).

When working in a science laboratory, how you record your data reflects how you make your measurements. In other words, your data should reflect just the right accuracy offered by the tool you use for the measurement. Incorrect data recording can misrepresent the accuracy of the tool you use; sometimes too accurate to be true, other times an accurate measurement might be taken as a rough one simply because you did not write down the **correct number of digits**.

The scientific way to record your data is to *only* write down the correct number of significant figures. The **significant figures** are **all the numbers** you can **read clearly** plus **one estimated digit**.



For example, when using the ruler shown to measure the wing-span of the butterfly image next to the ruler, we can be certain that the measurement is between 1.1 and 1.2. We can also tell that it is roughly in the middle of 1.1 and 1.2 so we write 1.15 cm as the result of the measurement. This number has **3** significant figures and it implies the best accuracy this particular ruler can offer. If we only write 1.1 cm, we would be downgrading the accuracy capacity of the ruler. On the other hand, if we write down the measurement as 1.150 cm, adding a zero randomly, we would be exaggerating the accuracy of the measurement. Either too many or too few significant figures can lead to incorrect representation of the accuracy of a measurement.

Since the “5” in the number 1.15 is estimated, this datum implies an uncertainty at the 0.01 cm level. Repeating the measurement two or three times can help determine how reliable the first measurement is. This is the precision issue and is an important one. **Only good precision can ensure good accuracy.**

For example, two students were asked to measure the wing-span of the butterfly image as shown above. They used the same ruler; each made three measurements, and reported their data as follows:

	<u>Student A</u>	<u>Student B</u>
Trial 1:	1.15 cm	1.15 cm
Trial 2:	1.17 cm	1.20 cm
Trial 3:	1.14 cm	1.11 cm

Student A’s data are clearly closer to each other (more precise) than student B’s. This also implies that student A is perhaps more careful in making the measurements. Equipped with such basic understanding, we can be more critical in analyzing certain lab data. To make a really long stretch, if you were the employer looking for someone to work in a physics lab or a health care clinic, would you hire student A or student B? **Sometimes a tiny error can be detrimental.**

Suppose students C and D also used the same ruler, each made three measurements of the wing-span of the butterfly image, and reported their data as follows:

	<u>Student C</u>	<u>Student D</u>
Trial 1:	1.1 cm	1.1500 cm
Trial 2:	1.0 cm	1.1600 cm
Trial 3:	1.2 cm	1.1500 cm

What can you say about the data if you are marking the lab reports?

Knowing that the ruler chosen can afford **3** and **only 3** significant figures in accuracy, both students C and D had problems with significant figures and should lose partial marks. Student D had apparently worked very carefully to obtain the measurements. His or her data had very good precision. But he or she added extra zeros to make the data “more accurate”. This actually exposed the fact that the student did not quite understand the rules for significant figures.

Sometimes we don’t know what tools are used for a certain reported data. In such cases the number of significant figures (provided that they are correctly recorded) can shed light on the accuracy capacity of the tool. Let’s look at the data from students F and G, each was asked to measure the wing-span of the butterfly image with a tool of their choice.

<u>Student F</u>	<u>Number of Sig. Fig.</u>	<u>Student G</u>	<u>Number of Sig. Fig.</u>
Trial 1: 1.1 cm	2	Trial 1: 1.1579 cm	5
Trial 2: 1.0 cm	2	Trial 2: 1.1580 cm	5
Trial 3: 1.2 cm	2	Trial 3: 1.1576 cm	5

With trained eyes, one can tell that the tool student F used to measure the length is a rough one, whereas student G apparently used a very fine instrument to measure the length. Both students can be doing the right thing as long as the accuracy provided by the tool matches the expected accuracy of the data. This example again illustrates the importance of recording the **correct** number of significant figures when you perform a measurement.

### Question 3.

Write 0.005600 mL in scientific notation.

**Answer:** We should write the answer as

$$0.005600 \text{ mL} = 5.600 \times 10^{-3} \text{ mL} \quad \text{not} \quad 5.60 \times 10^{-3} \text{ mL} \quad \text{nor} \quad 5.6 \times 10^{-3} \text{ mL}$$

This is because the two zeros after the number “6” are placed there by the experimenter to indicate that the instrument used to measure the volume can be accurate to 0.001 mL. Writing the volume as  $5.60 \times 10^{-3} \text{ mL}$  or  $5.6 \times 10^{-3} \text{ mL}$  by dropping the zeros without a reason will compromise the good effort being put into the data collection.

So when to count a zero as a significant figure?

### Counting Significant Figures

1. All zeros between other digits in a number are significant. For example: 5.255, 3005, 650.2. Each of these numbers has four significant figures.
2. Zeros to the left of the first nonzero digit (leading zeros) are used to locate the decimal point and are not significant. Thus 0.025 has only two significant figures.
3. Zeros both to the right of the last nonzero digit, and to the right of the decimal point are significant if there is a whole, nonzero number to the left of the decimal, for they would not have been included except to express precision. For example, 2.250 has four significant figures while 0.025 has only two and 0.002500 has four.

4. Zeros to the right of the last nonzero digit, but to the left of the decimal, as in the numbers 200, 550 and 6000 **may** or **may not** be significant. For example 6000 as a measured value might be good to the nearest 100, 10 or 1. Intended precision may be shown by adding a decimal at the end if all are significant such as 200., but a better way of expressing this is by using scientific notation such that  $200 = 2.00 \times 10^2$ ,  $550 = 5.50 \times 10^2$  and  $6000 = 6.000 \times 10^3$  as any digit in the coefficient of a number written in scientific notation is significant. If in each case only two digits were significant then this can be represented as such:  $2.0 \times 10^2$ ,  $5.5 \times 10^2$  and  $6.0 \times 10^3$ . Zeros to the right of a decimal that are preceded by a whole nonzero integer are significant. Thus 25.0 has three significant figures while 0.025 has only two.
5. All fractional numbers should be written with a zero before the decimal point (0.50 g and not .50g) as a safety precaution against the possible misprint of the decimal point. For example, if the decimal point fails to print in the number written as 0.25 g, the result will be 0 25 g and the obvious blank space provides a clear warning of the misprinted decimal point. If the number were written in the form .25 g and the decimal point failed to print, the result would read 25 g without any sign of misprint. If you were conducting an experiment that required 0.25 g of a reagent but with the missing decimal it appeared the recipe needed 25 g there would be a significant difference in the success of the reaction. Now imagine if an experiment used a reagent that was safe at 0.25 g but at 25 g it was explosive, what the potential outcome might be.

**Remember:**

All digits of the coefficient in a number written in scientific notation **are** significant,

E.g.  $5.600 \times 10^{-3}$  (4 sig. fig.)

What do we do when we need to calculate an average of the Trial 1 data from the following three students?

Student C

Trial 1: 1.1 cm

Student D

Trial 1: 1.1500 cm

Student E

Trial 1: 1.15 cm

How many significant figures should we retain in our answer? There are certain rules to follow concerning **significant figures in calculations**.

## 1.4 Significant Figures in Calculations

The result of multiplication, division, or other mathematical manipulation cannot be more precise than the least precise measurement used in the calculation. Suppose an object weighs 2.55 pounds

and you want to know the mass in grams. The multiplication of 2.55 lbs by the conversion factor 453.6 g/lb results in an answer of 1156.68 g. This value is not an accurate representation of the degree of precision of the measuring instrument. The conversion factor used has four significant figures and the measured value has only three. Therefore to accurately represent the degree of accuracy of the result, the answer can only have three significant figures. The value must be rounded off to 1,160 g. Again, the answer is more correctly reported in **Scientific Notation** as  $1.16 \times 10^3$  g.

**Rule for multiplication/division:** the final answer should retain the **same** number of **significant figures as the** measurement with the **fewest** significant figures.

#### Question 4.

With a calculator, find the answer of  $25.0 \times 5.600 \div 4.1$ , then write the final answer in scientific notation.

**Answer:** When you use a calculator, it doesn't matter how you input the numbers. Whether you punch in exactly  $25.0 \times 5.600 \div 4.1$  or  $25 \times 5.6 \div 4.1$ , the calculator displays 34.14634146 as the result. It is up to you to decide how to write down the final answer correctly. According to the rule for multiplication/division, the final answer should only retain **2** significant figures because the least accurate number, 4.1, has only 2 significant figures. Therefore you should take 34 and "abandon" everything after the decimal point. In scientific notation, the final answer is

$$25.0 \times 5.600 \div 4.1 = 34 = 3.4 \times 10^1 \text{ (It is not necessary to write the exponent "1")}$$

Did you see how the less accurate number 4.1 ruins the good accuracy of the number 5.600? This is a lesson to be learned when designing your experiments. It is sensible to use measurement tools that afford **similar** accuracy (giving the same number of significant figures).

#### Question 5.

Using a calculator, find the answer for  $5 \times 5.5 \div 0.5$  and write the final answer in scientific notation with **4** significant figures.

**Answer:** The calculator displays 55 as the result. In scientific notation this is  $5.5 \times 10$ . To have 4 significant figures in the final answer we need to add two zeros after 5.5. The final answer is  $5.500 \times 10$ . In this case we intentionally **added zeros** to reflect the accuracy of the measurement, as requested in the question.

**Rule for addition/subtraction:** the final answer should retain the **same** number of **decimal places as the** measurement with the **fewest** decimal places.

#### Question 6.

Calculate  $25.0 + 5.600 + 4.10$  and write the final answer in scientific notation.

**Answer:**

When you input  $25 + 5.6 + 4.1 =$ , the calculator displays 34.7 as the result. Since the number with the fewest decimal places is 25.0 which has only **1** decimal place, the final answer can only retain **1** decimal place. The number 34.7 satisfies this rule and is the correct final answer. In scientific notation, the answer is  $3.47 \times 10$ .

**Question 7.**

Calculate  $25.00 + 5.500 - 4.5$  and write the final answer in scientific notation.

**Answer:**

The calculator would display 26 as the result of  $25 + 5.5 - 4.5$ . However you should write down 26.0 because the least accurate number, 4.5, has one decimal place. In scientific notation, the answer is  $2.60 \times 10$ .

**1.5 The Rule for Rounding Off**

Usually there are fewer significant figures in the measured numbers used in a calculation than there are digits that appear in the answer. Therefore, we adjust the calculator result by rounding off. If the first number to be dropped is less than 5, it and all following numbers are dropped and the value of the last retained number remains the same. If the first number to be dropped is 5 or greater, the numbers are dropped and the value of the last retained digit is increased by 1. Thus if in the number 54.25563 we wanted to round to the third decimal place, we would drop the digits 6 and 3 and increase the five to a six for a final answer of 54.256.

When you round a large, whole number the correct magnitude is retained by replacing the dropped digits with the placeholder zeros. For example, 4325 rounded to two significant figures would appear as 4300 with zeros being added to replace the two and five and to maintain the magnitude. If we just dropped the last two digits without adding place-holder zeros our answer would appear as 43 rather than 4300 which is significantly different in magnitude and value (think of \$43 vs \$4300). Thus, when a whole number appears in the answer zeros may be added to achieve the right number of significant figures and maintain the integrity of the number.

**Question 8.**

Round off the following numbers to 3 significant figures.

25.04562,    5.600345,    0.003467241

**Answer:**

25.04562 = 25.0,    5.600345 = 5.60,    0.003467241 = 0.00347

In the examples above, the bold digits are to be rounded off. We look at the underlined digit in each number. If the underlined digit is less than 5, we abandon all bold digits and keep the rest of the numbers as they are. We did this for 25.04562 and 5.600345.

If the underlined digit is greater than 5, we add “1” to the digit immediately before the underlined digit and abandon all bold digits. We did this for 0.003467241.

**Rule for rounding off (with regard to the underlined digit):**

Abandon anything less than 5; carry over 1 for anything 5 and above.

Normally calculations have to be performed with *one more figure than is significant* in order to exclude the possibility of round-off error in the calculation. For example, if the least significant data are observed to three significant figures, then the calculations have to be carried out using at least four figures. The resultant calculation is, however, only precise to three significant figures, and it must therefore be rounded off and recorded with three significant figures.

## 1.6 Conversion Factors

You have been using conversion factors since the day you knew **1 dollar is 4 quarters** or earlier. When this relationship is written as a ratio,  $\frac{4 \text{ quarters}}{1 \text{ dollar}}$  or  $\frac{1 \text{ dollar}}{4 \text{ quarters}}$ , it is a **conversion factor**. We use conversion factors to convert between units.

### Question 9.

How many quarters are there in 25 dollars?

#### Answer:

Using the conversion factor  $\frac{4 \text{ quarters}}{1 \text{ dollar}}$ , we have

$$25 \text{ dollars} \times \frac{4 \text{ quarters}}{1 \text{ dollar}} = 25 \times 4 \text{ quarters} = 100 \text{ quarters}.$$

### Question 10.

How many dollars are equal to 2500 quarters?

#### Answer:

Using the conversion factor  $\frac{1 \text{ dollar}}{4 \text{ quarters}}$ , we have

$$2500 \text{ quarters} \times \frac{1 \text{ dollar}}{4 \text{ quarters}} = 2500 \div 4 \text{ dollars} = 625 \text{ dollars.}$$

The above two examples show that

When choosing a conversion factor, the **numerator** should be in the **same unit** wanted for the **final answer**.

In a science laboratory, almost daily we encounter the need to convert “milligrams” to “grams” or “meters” to “centimeters” or “milliliters” to “liters”. It is very useful to be familiar with some common conversion factors as listed in Table 3.

**Table 3. Some Common Conversion Factors in the Metric (SI) System**

Length	Volume	Mass	Time
1 m = 1000 mm	1 L = 1000 mL	1 kg = 1000 g	1 hr = 60 min
1 m = 10 <sup>9</sup> nm	1 dL = 100 mL	1 g = 1000 mg	1 min = 60 s
1 cm = 10 mm	1 mL = 1 cc = 1 cm <sup>3</sup>	—	1 s = 10 <sup>6</sup> μs

The units “mL”, “cc”, and “cm<sup>3</sup>” are used interchangeably to indicate the same amount of volume.

Sometimes we need to use two or more conversion factors to get the desired unit for the final answer.

### Question 11.

A certain vitamin tablet contains 17 mg of iron per tablet. For a patient who needs 30 mg of iron supplement per day, how many tablets does the patient need for one month (assuming a 30 day month)?

### Answer:

Several conversion factors are needed to figure out the final answer. These are:

$$\frac{1 \text{ tablet}}{17 \text{ mg}} \text{ or } \frac{17 \text{ mg}}{1 \text{ tablet}}$$

$$\frac{30 \text{ mg}}{1 \text{ day}} \text{ or } \frac{1 \text{ day}}{30 \text{ mg}}$$

$$\frac{30 \text{ day}}{1 \text{ month}} \text{ or } \frac{1 \text{ month}}{30 \text{ day}}$$

The final answer needs to be in the unit  $\frac{\text{tablet}}{\text{month}}$ . So we need to use conversion factors that can have all other units canceled out and leave only the unit “tablet” in the numerator and the unit “month” in the denominator. The equation shown as follows serves this purpose.

$$\frac{1 \text{ tablet}}{17 \text{ mg}} \times \frac{30 \text{ mg}}{1 \text{ day}} \times \frac{30 \text{ day}}{1 \text{ month}} = (900 \div 17) \frac{\text{tablet}}{\text{month}} = 53 \frac{\text{tablet}}{\text{month}}$$

## 1.7 Conversions in Temperature

Not all conversion factors come in simple ratios. Conversions in temperature units are good examples of such cases. As shown in Table 1 (page 2) there are three units for temperature: Celsius ( $^{\circ}\text{C}$ ) in metric system, Kelvin (K) in SI, and Fahrenheit ( $^{\circ}\text{F}$ ) in imperial system. The conversion between these units employs two equalities:

### Celsius to Kelvin

$$T \text{ K} = T \text{ }^{\circ}\text{C} + 273.15$$

and

### Celsius to Fahrenheit

$$T \text{ }^{\circ}\text{F} = 1.8 \times T \text{ }^{\circ}\text{C} + 32$$

This gives the definition that

$0 \text{ }^{\circ}\text{C} = 273.15 \text{ K} = 32 \text{ }^{\circ}\text{F}$
---

There are **negative temperatures** in both Celsius and Fahrenheit scales but **not in the Kelvin scale** because **0 K** has been defined as the **absolute zero** in temperature.

### Question 12.

What is the temperature in  $^{\circ}\text{C}$  at 0 K?

#### Answer:

Rearranging the equation  $T \text{ K} = T \text{ }^{\circ}\text{C} + 273.15$ , we have  $T \text{ }^{\circ}\text{C} = 0 \text{ K} - 273.15 = -273.15 \text{ }^{\circ}\text{C}$ .

### Question 13.

What is the temperature in  $^{\circ}\text{C}$  at  $-10 \text{ }^{\circ}\text{F}$ ?

#### Answer:

Rearranging the equation  $T \text{ }^{\circ}\text{F} = 1.8 \times T \text{ }^{\circ}\text{C} + 32$ , we have  $T \text{ }^{\circ}\text{C} = \frac{-10^{\circ}\text{F} - 32}{1.8} = -23 \text{ }^{\circ}\text{C}$ .

## Practice and Review for Chapter 1

Define (in your own words) the following terms:

Unit: \_\_\_\_\_

Metric System: \_\_\_\_\_

SI: \_\_\_\_\_

Scientific Notation: \_\_\_\_\_

Significant Figure: \_\_\_\_\_

Accuracy: \_\_\_\_\_

Precision: \_\_\_\_\_

Conversion Factor: \_\_\_\_\_

### Short-Answer Questions:

1. What is the chemical name for table salt? \_\_\_\_\_
2. What is the rule for retaining significant figures in multiplication/division?
3. What is the rule for retaining significant figures in addition/subtraction?
4. What types of zeros are significant and what are not?
5. How do you convert temperatures in degrees Celsius to degrees Fahrenheit?
6. How do you convert temperatures in degrees Celsius to Kelvin?
7. Is it possible to have -25 K? Explain your answer.

## The Chemistry Language

*To do well in Chemistry you need to know the chemistry language. You need to be able to read it, speak it, think with it, and write with it. When you do, your life will be filled with “good chemistry”.*

The alphabet in Chemistry is the periodic table. The first periodic table was developed by **Dmitri Mendeleev** in the 1800s (Google “Dmitri Mendeleev and the periodic table” to read more on this). The first periodic table contains **63** known elements at that time. Today a typical periodic table contains 103 elements and a total of **118** elements are currently known. A comparison of the two numbers (63 and 118) would show us that about 200 years after the first periodic table, scientists have discovered almost twice as many elements (some man-made).

For the purpose of this course, Table 4 (below) is the periodic table you need to know well. As it is, the elements are given in their **atomic symbols**. The elements are arranged in a special way to reflect their periodic properties. The reason for this arrangement will become clear to you soon.

**Table 4. The Simplified Periodic Table**

<i>H</i>																	<i>He</i>
<i>Li</i>	<i>Be</i>											<i>B</i>	<i>C</i>	<i>N</i>	<i>O</i>	<i>F</i>	<i>Ne</i>
<i>Na</i>	<i>Mg</i>											<i>Al</i>	<i>Si</i>	<i>P</i>	<i>S</i>	<i>Cl</i>	<i>Ar</i>
<i>K</i>	<i>Ca</i>	<i>Sc</i>	<i>Ti</i>	<i>V</i>	<i>Cr</i>	<i>Mn</i>	<i>Fe</i>	<i>Co</i>	<i>Ni</i>	<i>Cu</i>	<i>Zn</i>	<i>Ga</i>	<i>Ge</i>	<i>As</i>	<i>Se</i>	<i>Br</i>	<i>Kr</i>
<i>Rb</i>	<i>Sr</i>	<i>Y</i>	<i>Zr</i>	<i>Nb</i>	<i>Mo</i>	<i>Tc</i>	<i>Ru</i>	<i>Rh</i>	<i>Pd</i>	<i>Ag</i>	<i>Cd</i>	<i>In</i>	<i>Sn</i>	<i>Sb</i>	<i>Te</i>	<i>I</i>	<i>Xe</i>
<i>Cs</i>	<i>Ba</i>	<i>La</i>	<i>Hf</i>	<i>Ta</i>	<i>W</i>	<i>Re</i>	<i>Os</i>	<i>Ir</i>	<i>Pt</i>	<i>Au</i>	<i>Hg</i>	<i>Tl</i>	<i>Pb</i>	<i>Bi</i>	<i>Po</i>	<i>At</i>	<i>Rn</i>

### 2.1 Chemical Symbols

A special feature of the chemistry language is that it uses symbols most of the time. An atomic symbol is a one- or two-letter abbreviation for the name of an element.



It is beyond my expertise to understand how the “bytes” are put together to make a video full of sound and image. However, I do know what most of the “atoms” are and how they combine to make things. This is the foundation of Chemistry.

Everything is made of atoms.

Each element in the periodic table is made of a special atom. At the time when Dalton (1766-1844) developed his atomic theory atoms were thought to be indestructible. However, now we know that atoms are made of subatomic particles.

Atoms are made of protons, neutrons, and electrons.

The proton has a positive charge (+), and the electron carries a negative charge (-). As suggested by its name, the neutron is a neutral particle. Since atoms are neutral, it requires that the number of protons and electrons be equal so the overall charge is zero. Thus we have this relationship:

In an atom, # of protons = # of electrons

The assigned atomic number of an element is equal to the number of protons in the atom.

Thus we also have this relationship:

Atomic number = # of protons = # of electrons

The hydrogen atom is made of one proton and one electron (0 neutrons). This is why it is the No. 1 element (Atomic number = # of protons = 1). Every time a proton is added to make a new atom, an electron must also be added in order to keep the atom neutral. Thus the helium (He) atom is made of two electrons and two protons.

### Question 15.

Fill in each blank cell in the table below with the correct answer. Please try to do it yourself before reading the answer on next page.

Name	Symbol	Atomic Number	Number of Protons	Number of Electrons
Aluminum		13		
	Ca			20
Oxygen	O		8	

**Answer to Question 15:**

Name	Symbol	Atomic Number	Number of Protons	Number of Electrons
Aluminum	Al	13	13	13
Calcium	Ca	20	20	20
Oxygen	O	8	8	8

It was in 1911 Ernest Rutherford proposed, based on the results of his famous gold-foil experiment, the spatial arrangement of the three subatomic particles within an atom. He believed that the protons and neutrons are located at the center of the atom, the nucleus, while the electrons move about the nucleus like a cloud. He also concluded that the mass of the atom is mainly due to the combined mass of the protons and the neutrons. The mass of the electrons is so tiny that it is negligible in calculating the atomic mass.

**Question 16.**

The mass of a proton is  $1.67 \times 10^{-24}$  g, and the mass of a neutron is about the same. Nitrogen has 7 neutrons. What is the atomic mass of nitrogen?

**Answer:**

The atomic number of nitrogen (N) is 7, therefore it has 7 protons.  $7 \text{ proton} + 7 \text{ neutron} = 14$ . Thus the atomic mass of nitrogen is  $14 \times 1.67 \times 10^{-24} \text{ g} = 23.4 \times 10^{-24} \text{ g} = 2.34 \times 10^{-23} \text{ g}$ .

To make things easier chemists decided to call the mass of a proton one atomic mass unit (amu), that is, 1 amu is defined as equal to  $1.67 \times 10^{-24}$  g. The unit for amu is “u”. By doing so we have a choice of saying that the atomic mass of nitrogen is 14 u, instead of the exact mass of  $2.34 \times 10^{-23}$  g. This number, 14 u, is called the **mass number of nitrogen**.

The mass number of any atom is defined as equal to the sum of proton number and neutron number. Below is a common way to write an atomic symbol where both mass number (upper left) and atomic number (bottom left) are shown.



You can see that the mass number is twice the atomic number. This is true only for elements without isotopes, as will be discussed in Question 18.

**Question 17.**

Fill in each blank cell in the table below with the correct answer. Please try to do it yourself before reading the answer on next page.

Name	Symbol	Atomic Number	Mass Number	# of Neutrons	# of Protons	# of Electrons
	${}_{13}^{27}\text{Al}$		27			13
Calcium				22		20
Oxygen		8		10		

**Question 18.**

Is it true that, for a given element, the proton number, neutron number and electron number are always the same?

**Answer:**

This is true for proton number and electron number. However, some elements can have one or more atoms with **different number of neutrons**. Such atoms are called the **isotopes** of the element. For example, the element carbon (C) has three naturally occurring isotopes, as shown below.



These isotopes behave exactly the same. They all have 6 protons and 6 electrons each, but carbon-12 or C-12 has 6 neutrons whereas C-13 and C-14 have 7 and 8 neutrons, respectively. The different number of neutrons causes the isotopes to weigh differently. Thus the mass numbers of C-12, C-13, and C-14 are 12, 13, and 14, respectively.

The isotopes of an element coexist in certain proportions. The size of the portion of each isotope is usually expressed as a percentage (**abundance**). In ordinary conditions the element carbon is made up of 98.93% C-12 and 1.07% C-13. The chance of finding a C-14 atom is one in a million (1 ppm). In the periodic table there is only one space for carbon. To indicate that this carbon is not only the C-12 atom, the atomic mass of carbon is reported as a *weighted average* of the two most abundant isotopes (C-12 and C-13). The calculation is shown below.

$$\text{Weighted average atomic mass of carbon} = 12.00 \times 0.9893 + 13.00 \times 0.0107 = 12.01 \text{ u}$$

This is why the atomic masses of all elements in the periodic table are different from the respective mass numbers, or more than twice the atomic numbers.

**Answer to Question 17:**

Name	Symbol	Atomic Number	Mass Number	# of Neutrons	# of Protons	# of Electrons
Aluminum	${}_{13}^{27}\text{Al}$	13	27	14	13	13
Calcium	${}_{20}^{42}\text{Ca}$	20	42	22	20	20
Oxygen	${}_{8}^{18}\text{O}$	8	18	10	8	8

## 2.3 Chemical Quantities

### The Concept of Mole

Imagine that you need to know how many eggs there are in a truck-load of dozen-egg cartons packed in equal-sized corrugated boxes; how are you going to count? Most likely you will count the number of boxes and the number of cartons in one box, and then you can find the total number of eggs by

$$\# \text{ of boxes} \times \# \text{ of cartons} \times 12$$

Aren't you glad that you do not have to count the eggs one by one? The fact that **one dozen equals 12** greatly simplifies the daunting task.

Chemists also use a number known as **Avogadro's number** ( $6.022 \times 10^{23}$ ) to "pack" atoms and molecules in "cartons" for the ease of counting. Recall that the atomic masses of atoms are expressed in atomic mass unit and  $1 \text{ u} = 1.67 \times 10^{-24} \text{ g}$ . The magic of the **Avogadro's number** is that

$$6.022 \times 10^{23} \times 1 \text{ u} = 6.022 \times 10^{23} \times 1.67 \times 10^{-24} \text{ g} = 1.00 \text{ g}$$

This means that the mass of  $6.022 \times 10^{23}$  protons together is one gram. This also means that if we pack  $6.022 \times 10^{23}$  atoms of an element together and measure the mass, we will get the mass in grams that has the same number as the atomic mass in u for that element.

For example,  $6.022 \times 10^{23}$  C-12 atoms together would weigh 12.00 g. If we consider the weighted average atom of carbon, then  $6.022 \times 10^{23}$  carbon atoms together would weigh 12.01 g. This number  $6.022 \times 10^{23}$  is indeed very magical because it gives us a bridge between the masses of tiny particles, such as protons and atoms, and masses measurable in the lab.

Just as the quantity 12 is conveniently called "a dozen," Avogadro's number is called a **mole**. So instead of saying that  $6.022 \times 10^{23}$  carbon atoms weigh 12.01 g, we just say that **one mole** of carbon weigh **12.01 g**. This number "12.01" is called the **molar atomic mass** of carbon and has the unit **g/mol**, or **g mol<sup>-1</sup>**. The following two conversion factors are very useful in converting among *mass, number of moles, and number of atoms* of an element:

$$\frac{1 \text{ mole of an element}}{\text{molar atomic mass of that element}(g)} \text{ and } \frac{6.022 \times 10^{23} \text{ atoms of that element}}{1 \text{ mole of an element}}$$

In fact, the concept of “mole” can be applied to anything, be it atoms, molecules, eggs, people, or cars. It is just that we rarely have the need to count eggs and cars in bunches of  $6 \times 10^{23}$ . However, we do frequently need to count molecules in “moles.” Thus we have the following two general conversion factors that are very useful in converting among *mass, number of moles, and number of molecules* of a substance:

$$\frac{1 \text{ mole of a substance}}{\text{molar molecular mass of that substance}(g)}$$

and

$$\frac{6.022 \times 10^{23} \text{ molecules of that substance}}{1 \text{ mole of a substance}}$$

## 2.4 Molar (Molecular) Mass

### Question 19.

How much does one mole of water molecules weigh? In other words, what is the molar molecular mass of water?

**Answer:** The molecular formula of water is  $\text{H}_2\text{O}$ . Thus the mass of one mole of water is the sum of the masses of two moles of H and one mole of O:

$$\text{Mass of one mole of water} = 2 \times 1.008 \text{ g/mol} + 1 \times 15.9994 \text{ g/mol} = 18.02 \text{ g/mol}$$

The mass in grams of one mole of any pure substance is called the molar (molecular) mass of that substance. Thus the molar mass of water is 18.02 g/mol. How many water molecules does it take to weigh this much? The answer is one mole, or to be exact,  $6.022 \times 10^{23}$  water molecules.

### Question 20.

How many water molecules are there in 500.0 g of water (about a can of water)?

**Answer:** Applying two conversion factors as shown below we get:

$$\begin{aligned} \text{Number of water molecules} &= 500.0\text{g} \times \frac{1 \text{ mole of water}}{18.02 \text{ g}} \times \frac{6.022 \times 10^{23} \text{ water molecules}}{1 \text{ mole of water}} \\ &= 1.671 \times 10^{25} \end{aligned}$$

**Question 21.**

How many water molecules are there in 500.0 cc water ( $d = 1.00 \text{ g/mL}$ )?

**Answer:**

To solve this question as we did in **Question 20**, we need to know the mass of the 500.0 cc water. This brings us to the concept of **density**.

**Density**

For any substance, we measure its quantity by measuring its volume or mass. If we know the **density** ( $d$ ) of the substance, we can also calculate the volume from the mass data or vice versa. The relationship of the three quantities is given below.

$$d = \frac{\text{mass of substance}}{\text{volume of substance}}$$

This equation is also the definition of **density**—a measure of how much mass is packed into a single unit of volume. The more densely packed a substance, the higher its density. Since every substance packs in its own way, density is a physical property that is different for different substances.

For a given substance, density changes with temperature. A perfect example would be the different densities exhibited by water vapor, water, and ice. Clearly the density of water vapor is smaller than that of the water. Interestingly, contrary to most other common examples, the density of ice is smaller than that of water. This is why ice cubes float in water. Normally, a substance would pack more densely in its solid state than in its liquid state. We will explain the water-ice density anomaly a little later.

In the metric system, the densities of solids and liquids are usually expressed as grams per cubic centimeter ( $\text{g/cm}^3$ ) or grams per milliliter ( $\text{g/mL}$ ), respectively. The density of gases is usually stated as grams per liter ( $\text{g/L}$ ).

By rearranging the density formula above, for 500.0 cc of water, we have

$$\text{Mass of water} = \text{volume} \times d = 500.0 \text{ cc} \times \frac{1 \text{ mL}}{1 \text{ cc}} \times 1.00 \frac{\text{g}}{\text{mL}} = 5.00 \times 10^2 \text{ g}$$

In **Question 20** we already found out that there are  $1.671 \times 10^{25}$  molecules in 500.0 g of water. We can apply the same answer here. Since the density of water is only given in three sig. fig., we should give our answer here as  $1.67 \times 10^{25}$ .

## 2.5 The Mole Relationship

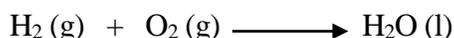
Chemistry would be boring if it is all about writing atomic symbols and calculating molar masses. The more exciting part of chemistry is about how things are made and how to make new things via *chemical reactions*. Before we move on to those topics, however, we will apply the “mole” concept (while it is fresh) in understanding the quantitative aspects of chemical reactions.

### Question 22.

Hydrogen burns explosively in the presence of oxygen. Water is formed as a result of this chemical reaction. Write a *balanced equation* for this reaction.

### Answer:

When we say that “hydrogen burns explosively in the presence of oxygen,” we are talking about molecules of hydrogen and oxygen, not the atomic hydrogen and oxygen. A molecule of hydrogen is composed of two moles of hydrogen atoms, and a molecule of oxygen is composed of two moles of oxygen atoms. So we write the equation as follows.



Thinking in terms of “moles,” this equation says that one mole of hydrogen gas reacts with one mole of oxygen gas to form one mole of liquid water.

The equation as written is not balanced because the moles of individual atoms are not equal on both sides of the equation. We start with 2 moles of the hydrogen atom and 2 moles of the oxygen atom, and end up with 2 moles of the hydrogen atom but only 1 mole of the oxygen atom. Where did the other 1 mole of oxygen atom go? **Atoms do not form or disappear in chemical reactions.**

To balance the number of oxygen atoms on both sides of the equation, we add a coefficient, 2, in front of the water molecule. When we add a coefficient to a molecule, all atoms in that molecule are affected. So we now have 4 moles of H atoms on the product side, to balance that we add a coefficient (2) in front of the hydrogen molecule on the reactant side. Now all atoms are accounted for on both sides of the equation, as shown below.



This balanced equation provides us with a **mole relationship** among the reactants and products. In this case it says that we *always* need **2** moles of hydrogen molecules to completely react with **1** mole of oxygen molecules, and **2** moles of water molecules shall be formed. Such mole relationships are very useful in chemical calculations, as demonstrated in the next section.

## 2.6 Stoichiometry of Chemical Reactions

**Stoichiometry** is the application of **mole relationships** from balanced reaction equations to calculate, for example, how much of the reactants are required, how much of the products are formed, what the yield of the reaction is, etc. We will use several questions to introduce a few important types of stoichiometric calculations.

### Calculating the Amount of Reactants and Products

#### Question 23.

How many grams of oxygen are needed to completely react with 2.00 g of hydrogen?

#### Answer:

This chemical reaction is described by the following balanced equation. From the equation we know that the **mole relationship** between  $H_2$  and  $O_2$  is 2:1. To apply this mole relationship, first we need to convert all masses from grams to moles.



Using the conversion factor between mass, molar mass and # of moles, we have

$$\# \text{ of moles of } H_2 = \text{mass (g)} \times \frac{1 \text{ mole of } H_2}{\text{molar mass of } H_2} = 2.00 \text{ g} \times \frac{1 \text{ mole of } H_2}{2.016 \text{ g}} = 0.992 \text{ mol}$$

The mole relationship gives us this conversion factor:

$$\frac{1 \text{ mol } O_2}{2 \text{ mol } H_2}$$

Now we can calculate the number of moles of oxygen needed,

$$\# \text{ of moles of } O_2 = \# \text{ of moles of } H_2 \times \frac{1 \text{ mol } O_2}{2 \text{ mol } H_2} = 0.992 \text{ mol } H_2 \times \frac{1 \text{ mol } O_2}{2 \text{ mol } H_2} = 0.496 \text{ mol}$$

To give the answer in grams, we convert moles to grams as follows:

$$\text{Mass of } O_2 = \# \text{ of moles of } O_2 \times \frac{\text{molar mass of } O_2}{1 \text{ mol } O_2} = 0.496 \text{ mol} \times 32.00 \text{ g/mol} = 15.9 \text{ g}$$

**Limiting Reactant****Question 24.**

How many grams of water may be formed from the reaction of 2.00 g of hydrogen and 30.0 g of oxygen?

**Answer:**

From the answer to **Question 23** we know that it only takes 15.9 g of O<sub>2</sub> to completely burn 2.00 g of H<sub>2</sub>. If 30.0 g of oxygen is used, 14.1 g of oxygen will be left after the reaction. The reactant hydrogen in this case is called the **limiting reactant** because its amount, not the amount of oxygen, limits how much of the products can be formed from this reaction.

We can always use the mole relationship provided by the balanced reaction equation to determine the limiting reactant. Again, first we convert all masses from grams to moles. Note that we simplified the equation by not fully writing out the conversion factors.

$$\# \text{ of moles of H}_2 = \frac{\text{mass of H}_2}{\text{molar mass of H}_2} = \frac{2.00 \text{ g}}{2.016 \text{ g/mol}} = 0.992 \text{ mol}$$

$$\# \text{ of moles of O}_2 = \frac{\text{mass of O}_2}{\text{molar mass of O}_2} = \frac{30.0 \text{ g}}{32.00 \text{ g/mol}} = 0.938 \text{ mol}$$

To determine which reactant is the limiting reactant, we use the mole ratios from the equation to find out which reactant is in excess,

# of moles of O<sub>2</sub> needed for 0.992 mol of hydrogen

$$= \# \text{ of moles of H}_2 \times \frac{1 \text{ mol O}_2}{2 \text{ mol H}_2} = 0.992 \text{ mol H}_2 \times \frac{1 \text{ mol O}_2}{2 \text{ mol H}_2} = 0.496 \text{ mol} < 0.938 \text{ mol O}_2 \text{ available}$$

Whereas

# of moles of H<sub>2</sub> needed for 0.938 mol of oxygen

$$= \# \text{ of moles of O}_2 \times \frac{2 \text{ mol H}_2}{1 \text{ mol O}_2} = 0.938 \text{ mol O}_2 \times \frac{2 \text{ mol H}_2}{1 \text{ mol O}_2} = 1.88 \text{ mol} \gg 0.992 \text{ mol H}_2 \text{ available}$$

Clearly oxygen cannot be the limiting reactant because there is not enough hydrogen to completely use up the 30.0 g of oxygen. Using H<sub>2</sub> as the limiting reactant and the conversion factor from the reaction equation we have

$$\# \text{ of moles of H}_2\text{O} = \# \text{ of moles of H}_2 \times \frac{2 \text{ mol H}_2\text{O}}{2 \text{ mol H}_2} = 0.992 \text{ mol} \times \frac{2 \text{ mol H}_2\text{O}}{2 \text{ mol H}_2} = 0.992 \text{ mol}$$

$$\text{Mass of H}_2\text{O} = \# \text{ of moles of H}_2\text{O} \times \text{molar mass of H}_2\text{O} = 0.992 \text{ mol} \times 18.02 \text{ g/mol} = 17.9 \text{ g}$$

## Percent Yield

In **Question 24** we saw that when all 2.00 g of the limiting reactant ( $\text{H}_2$ ) is used up, 17.9 g of water is produced. This is the highest possible amount to be produced in this reaction and is called the **theoretical yield** for the product. In reality we can never “harvest” exactly this amount of product. Usually we get less due to experimental errors. The actual amount of product gathered in the laboratory is called the **actual yield** and **percent yield** is defined as

$$\text{Percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 \%$$

To calculate a percent yield, we need the actual yield from weighing our product and the theoretical yield from calculations involving steps similar to those performed in **Questions 23 and 24**. We will show how this is done in the following question.

### Question 25.

Chromium can be made by heating chromium oxide,  $\text{Cr}_2\text{O}_3$ , with aluminum. Aluminum oxide,  $\text{Al}_2\text{O}_3$ , is the other product. When 18.7 g of  $\text{Cr}_2\text{O}_3$  were heated with excess aluminum, 10.8 g of chromium were isolated from the products. What was the percent yield of chromium?

### Answer:

We first write the balanced equation:



To find the percent yield of chromium we must first find the theoretical yield, that is, the mass of Cr that will be produced according to the balanced equation. We do this by using three conversion factors in one step as follows:

$$\begin{aligned} \text{Mass of Cr} &= (\text{Mass of } \text{Cr}_2\text{O}_3 \times \frac{1 \text{ mol } \text{Cr}_2\text{O}_3}{\text{molar mass of } \text{Cr}_2\text{O}_3}) \times (\frac{2 \text{ mol Cr}}{1 \text{ mol } \text{Cr}_2\text{O}_3}) \times (\frac{\text{molar mass Cr}}{1 \text{ mol Cr}}) \\ &\quad \uparrow \qquad \qquad \qquad \uparrow \qquad \qquad \qquad \uparrow \\ &\quad \text{grams to mole} \qquad \text{mole relationship} \qquad \text{mole to grams} \\ &= 18.7 \text{ g } \text{Cr}_2\text{O}_3 \times \frac{1 \text{ mol } \text{Cr}_2\text{O}_3}{152.0 \text{ g } \text{Cr}_2\text{O}_3} \times \frac{2 \text{ mol Cr}}{1 \text{ mol } \text{Cr}_2\text{O}_3} \times \frac{52.00 \text{ g Cr}}{1 \text{ mol Cr}} = 12.8 \text{ g Cr} \end{aligned}$$

This mass of Cr is the theoretical yield. What actually isolated was 10.8 g. The percent yield is

$$\text{Percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{10.8 \text{ g}}{12.8 \text{ g}} \times 100\% = 84.4\%$$

## Practice and Review for Chapter 2

Define (in your own words) the following terms:

Periodic Table: \_\_\_\_\_

Element: \_\_\_\_\_

Atom: \_\_\_\_\_

Atomic Symbol: \_\_\_\_\_

Atomic Number: \_\_\_\_\_

Proton Number: \_\_\_\_\_

Electron Number: \_\_\_\_\_

Neutron Number: \_\_\_\_\_

Mass Number: \_\_\_\_\_

amu: \_\_\_\_\_

Isotope: \_\_\_\_\_

Abundance: \_\_\_\_\_

ppm: \_\_\_\_\_

Density: \_\_\_\_\_

The Mole: \_\_\_\_\_

Avogadro's Number: \_\_\_\_\_

Molar Mass: \_\_\_\_\_

Mole Relationship: \_\_\_\_\_

Limiting Reactant: \_\_\_\_\_

Theoretical Yield: \_\_\_\_\_

Actual Yield: \_\_\_\_\_

Percent Yield: \_\_\_\_\_

## The Root of All Chemistry

*Why atoms combine the way they do? Reveal me the mystery of all chemistry.*

While the nucleus of an atom carries all the weight, the electrons carry all the chemistry.

Although the periodic table is arranged in increasing order of the atomic number (or proton number, or electron number), the peculiar way that the elements are grouped in columns and rows is totally the work of electrons. It would be impossible to understand the organization of the periodic table and to make good use of the table without the knowledge of **electron configurations**—a map of the electrons' locations.

### 3.1 Electron Configurations and the Four Quantum Numbers

According to quantum mechanics (also known as wave mechanics), electrons reside in “orbitals.” Since each orbital can accommodate a maximum of two electrons, many orbitals would be needed to accommodate, for example, the 20 electrons of calcium (Ca) or the 53 electrons of iodine (I). It turns out that the orbitals are quite like the rooms in an apartment building. They can be on different floors, in different units (one-bedroom, two-bedroom, etc.), and priced differently. The higher the floor number, the larger (more bedrooms) the unit, more expensive the rooms are. In quantum mechanics language, the currency is energy, not dollars. Therefore the more expensive rooms are simply the orbitals with higher energy. Also in quantum mechanics language, the floors are called “main levels” and the units are called “sublevels.”

As chemists we are most interested in the **energy state** of a particular electron. This is like knowing the address of a person. To reach that person, the address should be specific to that person. In quantum mechanics we use **four quantum numbers** to give specific information about the **energy state** of a particular electron. These are:

$n$ , the **principle quantum number**, representing the floor level (main energy level)

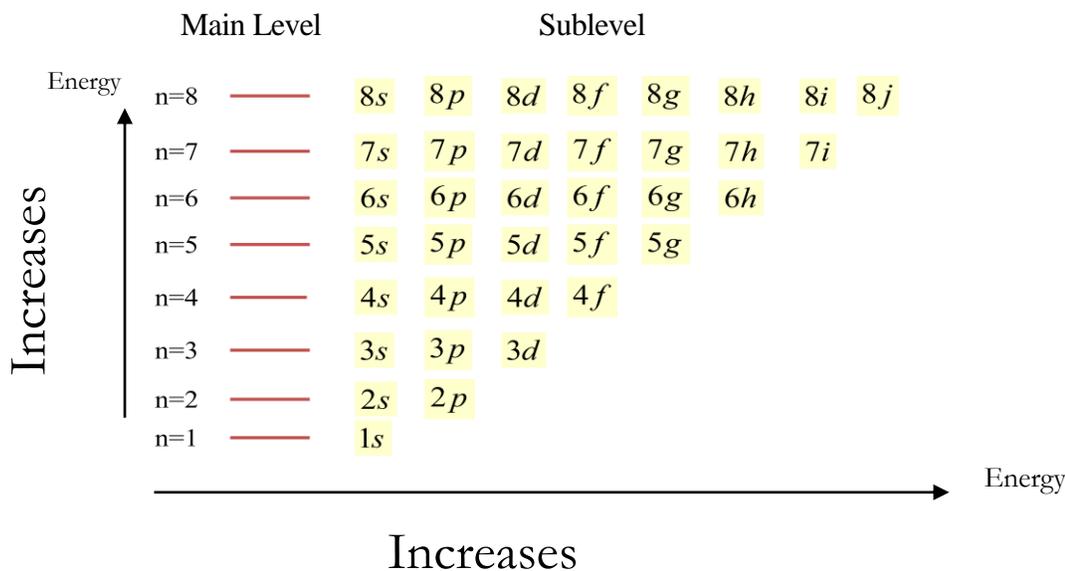
$l$ , the **angular quantum number**, representing the type of unit (sublevel)

$m_l$ , the **magnetic quantum number**, representing the type of room (orbital)

$m_s$ , the **electron spin quantum number**, representing the direction of the electron's spin, either “up” or “down”.

An electron configuration is a list of the addresses of all the electrons of a particular atom. To be able to write a correct electron configuration for any atom, we need to know what kind of rooms (or should I say “orbitals”) are available for the electrons. Let's take a look at the **building plan** provided by quantum mechanics calculations.

### Possible Energy Levels for Electrons



The main levels are numbered by the **principle quantum number** “ $n$ ”. The number  $n$  **starts** from **1** and can go on beyond 8. We will soon realize that it is not necessary to go all the way up to the 8<sup>th</sup> floor because a seven-floor building already provides enough rooms for over 100 electrons.

An inspection of the “building plan” above will allow us to draw two conclusions:

1. The main level number ( $n$ ) dictates how many sublevels a main level can have. In other words, you cannot have **three** sublevels on the **second** floor.
2. The sublevels (units) are labeled as  $s, p, d, f$ , etc.

**Question 26.**

Mathematically, what is the relationship between the principle quantum number “ $n$ ” and the angular quantum number “ $l$ ”? How are the different units labeled?

**Answer:**

Mathematically, for every “ $n$ ” there are only “0, 1, 2... $n-1$ ” possible values of “ $l$ ”, as illustrated below:

<u>When <math>n</math> is</u>	<u><math>l</math> can be</u>	<u>Type of Units</u>	<u>Label</u>
<b>1</b>	0	1	$s$
<b>2</b>	0, 1	2	$s (l = 0), p (l = 1)$
<b>3</b>	0, 1, 2	3	$s (l = 0), p (l = 1), d (l = 2)$

And so on...

**Question 27.**

What are the meanings of a “1s orbital”, a “2p orbital”, and a “3d orbital”?

**Answer:**

The specific energy state of a particular electron can be described by a four-quantum-number address. From the labels “1s”, “2p”, “3d” and etc. we can extract the values of two quantum numbers, some examples are listed below.

<u>Label of Orbital</u>	<u>Quantum Numbers</u>
$1s$	$n = 1, l = 0$
$2s$	$n = 2, l = 0$
$2p$	$n = 2, l = 1$
$3p$	$n = 3, l = 1$
$3d$	$n = 3, l = 2$

**Question 28.**

What determines the number of rooms (orbitals) a particular unit (sublevel) can have?

**Answer:**

This is where the magnetic quantum number “ $m_l$ ” comes into play. The subscript “ $l$ ” indicates that the values of “ $m$ ” are dependent on the values of “ $l$ ”.

Mathematically, for every “ $l$ ” there are “ $-l \dots -2, -1, 0, +1, +2 \dots +l$ ” possible values of “ $m_l$ ”, as illustrated below:

When $l$ is	$m_l$ can be	number of orbitals
<b>0</b> ( $s$ unit)	0	1
<b>1</b> ( $p$ unit)	-1, 0, +1	3
<b>2</b> ( $d$ unit)	-2, -1, 0, +1, +2	5
<b>3</b> ( $f$ unit)	-3, -2, -1, 0, +1, +2, +3	7

And so on...

The different values of “ $m_l$ ” represent different orientations of the orbitals, quite like different rooms in a unit have windows facing different directions. For the  $s$  ( $l = 0$ ) unit since there is only one value for  $m_l$  ( $= 0$ ), there is also only one room that is shaped like a sphere (with a  $360^\circ$  panoramic window!). For the  $p$  ( $l = 1$ ) unit, however, there are three values for  $m_l$  ( $= -1, 0, +1$ ), so there should be three rooms each with a window facing a different direction. In a three-dimensional world represented by the Cartesian coordinates, these three directions are the  $(x,y,z)$  axes. Similarly, the  $d$  sublevel is a 5-room unit and the  $f$  sublevel is a 7-room unit.

### Question 29.

How do orbitals look like and do I need to know how to draw the  $s$  and  $p$  orbitals?

#### Answer:

The “ $s$ ” orbitals are spherically shaped. The “ $p$ ” orbitals are shaped like a dumb-bell. The shapes of the orbitals in the  $d$  and  $f$  sublevels are very exotic. We will show some to you in class from the website <http://winter.group.shef.ac.uk/orbitron/> which has a collection of orbital shapes obtained using quantum mechanics calculations.

To understand most of the everyday chemistry we only need to be familiar with the characteristics of the  $s$  and  $p$  orbitals. Therefore you do need to know how to draw the simplest  $s$  and  $p$  orbitals. Take out your pencil and let's practice.

First draw a set of Cartesian axes, as shown below (Figure A). The center of the coordinates would be the nucleus of the atom.

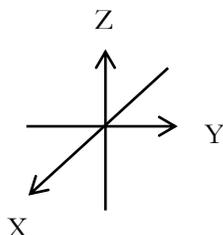


Figure A. The Cartesian Axes

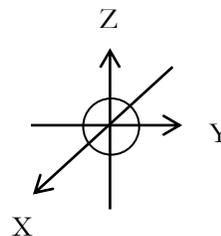


Figure B. The  $1s$  orbital

Now draw a circle around the center (Figure B), this shows the cross-section of a  $1s$  orbital. For an electron to be called a  $1s$  electron (given the address as “ $1s$ ”), it should be found at least 90% of the time residing within the boundaries defined by the shape of the  $1s$  orbital.

The size of the  $s$  orbitals increases as the principle quantum number  $n$  increases. Thus the size of the circle for a  $2s$  orbital should be drawn larger than the one for a  $1s$  orbital. In other words,  $1s$  electrons “live” very close to the nucleus whereas electrons “living” on higher “floors” are farther away from the nucleus.

Figure C below illustrates two of the three  $2p$  orbitals. If the orbital is drawn around the X axis, it is called the  $2p_x$  orbital. Can you draw the third  $2p$  orbital ( $p_y$ )? You can use Figure A or create your own axes.

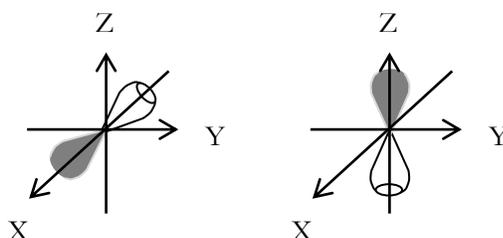


Figure C. The  $2p_x$  and  $2p_z$  orbitals

Note that we have drawn the  $p$  orbitals with different “phases”. We have drawn the half that goes around the positive region of the axis as a solid shape and the other half as an open shape. The choice of “solid for positive” versus “open for negative” is arbitrary. You just need to know that  $p$  orbitals have two phases.

The correspondence between the directions ( $x$ ,  $y$  or  $z$ ) and the three values of “ $m_l$ ” is also undefined. You just need to know that the three orientations of the  $p$  orbitals correspond to the three  $m_l$  values.

The three  $p$  orbitals have the same energy so often we just use  $p$  sublevel to represent all three  $p$  orbitals, without specifying the directions ( $x$ ,  $y$  or  $z$ ).

We have strayed a bit far from our task at hand. Our job here is to learn how to write electron configurations for any atom in the periodic table. In other words, we need to give an address to each electron in that atom. We can do this by making a “head-count” of all electrons in all occupied rooms using the “building plan”, starting from the first floor, bearing in mind that on the same main level, units with a higher “ $l$ ” value have higher energy. For example, on the third floor, electrons in  $3d$  orbitals have higher energy than those in  $3p$  orbitals.

### Question 30.

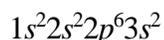
Give the electron configuration for the sulfur (S) atom.

**Answer:**

Sulfur has a total of 16 electrons. You can get this information from the periodic table. Starting from the  $n = 1$  floor and moving up, we will count two electrons per room until all sixteen electrons are located. While counting we keep our records by writing down the number of electrons in each unit (sublevel). For the 2 electrons “living” in the “1s” orbital, we write down “ $1s^2$ .”

The next lowest energy unit is  $2s$  so we write down “ $2s^2$ .” The next sublevel to count is the  $2p$  sublevel. Since there are three  $p$  orbitals, we need to count up 6 electrons. We do this by writing down “ $2p^6$ .”

We still have to locate the rest of the 6 electrons. So we move on to the  $3s$  orbital and write down “ $3s^2$ .” At this moment our electron configuration for sulfur looks like this

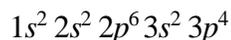


For the last 4 electrons, we know that they are in the  $3p$  unit. We can write down “ $3p^4$ .” What we are curious to know is the way they take up the three rooms. There are two ways to distribute them:



Electrons living “single” are called unpaired electrons. Those sharing a room are called paired electrons. An orbital with two electrons is called a filled orbital. An orbital with only one electron is called a half-filled orbital. An orbital with zero electrons is called an empty orbital. It turns out that **electrons prefer to live “single” if possible.**

For the understanding of the periodic table, however, writing down  $3p^4$  is sufficient. So the complete electron configuration for sulfur is



Add all superscript numbers up to see if the sum is 16. If not, check to see if every sublevel (unit) is assigned the maximum number of electrons it can accommodate. Only the last sublevel (the highest energy unit) can have fewer electrons than the allowed maximum. The maximum comes from filling all rooms in a unit (except the last unit) with two electrons each, as listed below.

<u>Unit (sublevel)</u>	<u>Maximum Number of Electrons</u>
$s$	2
$p$	6
$d$	10
$f$	14

**Question 31.**

Do I have to know how to write electron configurations for all the elements in the periodic table?

**Answer:**

For the scope of this course, you should know up to atomic number 36.

**3.2 Electron Configurations and the Periodic Table**

We have mentioned before that the organization of the periodic table is fundamentally related to electron configurations. Now we will see why this is so. First, let's look at the electron configurations for the first 18 elements in the periodic table.

Row 1	<i>H</i> $1s^1$							<i>He</i> $1s^2$
Row 2	<i>Li</i> $1s^2 2s^1$	<i>Be</i> $1s^2 2s^2$	<i>B</i> $1s^2 2s^2 2p^1$	<i>C</i> $1s^2 2s^2 2p^2$	<i>N</i> $1s^2 2s^2 2p^3$	<i>O</i> $1s^2 2s^2 2p^4$	<i>F</i> $1s^2 2s^2 2p^5$	<i>Ne</i> $1s^2 2s^2 2p^6$
Row 3	<i>Na</i> $1s^2 2s^2 2p^6 3s^1$	<i>Mg</i> $1s^2 2s^2 2p^6 3s^2$	<i>Al</i> $1s^2 2s^2 2p^6 3s^2 3p^1$	<i>Si</i> $1s^2 2s^2 2p^6 3s^2 3p^2$	<i>P</i> $1s^2 2s^2 2p^6 3s^2 3p^3$	<i>S</i> $1s^2 2s^2 2p^6 3s^2 3p^4$	<i>Cl</i> $1s^2 2s^2 2p^6 3s^2 3p^5$	<i>Ar</i> $1s^2 2s^2 2p^6 3s^2 3p^6$
	Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7	Column 8

What do we notice? We have the following interesting observations:

1. The elements lined up in a column all have the same number of electrons in the highest main level. For example, nitrogen has 5 electrons in main level 2 ( $2s^2 2p^3$ ) and phosphorous also has 5 electrons in main level 3 ( $3s^2 3p^3$ ).
2. The column number is the same as the number of electrons in the highest main level. That is, for column 1 there is 1 electron in the highest main level and for column 2 there are 2 electrons in the highest main level, and so on.
3. Elements with the same highest main level are lined up in a row. For example, in Row 2 the highest main level is the second level ( $n = 2$ ) and in Row 3 the highest main level is the third level ( $n = 3$ ), and so on.
4. The row number is the highest main level number (the highest  $n$ ), or, the row number is the same as the number of main levels there are.
5. Elements in Column 8 all have a fully-filled highest main level.

When we say that *electrons carry all the chemistry* we are not exaggerating. The elements in Column 1, namely Li and Na (H is an exception), have very similar chemical properties,

simply because they all have only one electron in an  $s$  orbital. The elements in Column 7, namely F and Cl, also have very similar chemical properties, because they all have seven electrons in the highest main level.

So this is the root of all “chemistry.” **It is the electrons, how many and where they are, that dictates the chemical behavior of an atom.**

Now we know why the table of elements is called the periodic table and why it is organized in such a fashion—it arranges the elements purposely to reflect the similarity (in a column or group) and the periodic change (in rows or periods that begins and ends with similarly behaved elements) in chemical behavior.

Period 1	$H$ $1s^1$						$He$ $1s^2$	
Period 2	$Li$ $1s^2 2s^1$	$Be$ $1s^2 2s^2$	$B$ $1s^2 2s^2 2p^1$	$C$ $1s^2 2s^2 2p^2$	$N$ $1s^2 2s^2 2p^3$	$O$ $1s^2 2s^2 2p^4$	$F$ $1s^2 2s^2 2p^5$	$Ne$ $1s^2 2s^2 2p^6$
Period 3	$Na$ $1s^2 2s^2 2p^6 3s^1$	$Mg$ $1s^2 2s^2 2p^6 3s^2$	$Al$ $1s^2 2s^2 2p^6 3s^2 3p^1$	$Si$ $1s^2 2s^2 2p^6 3s^2 3p^2$	$P$ $1s^2 2s^2 2p^6 3s^2 3p^3$	$S$ $1s^2 2s^2 2p^6 3s^2 3p^4$	$Cl$ $1s^2 2s^2 2p^6 3s^2 3p^5$	$Ar$ $1s^2 2s^2 2p^6 3s^2 3p^6$
	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII

### 3.3 The Noble Gas Notation

You will notice that the part of the electron configuration before the highest main level is exactly the same as the electron configuration of the last element of the previous period, i.e. an element in Group VIII.

The truth is that all elements in Group VIII rarely participate in any chemical reactions. So they are sometimes called the “noble gas elements” and other times the “inert elements.” As far as chemistry is concerned, we can come to the following observations:

An atom with a full electron configuration is a **stable** atom (not chemically active).

And

Electrons occupying fully filled main levels are usually not active in chemical reactions.

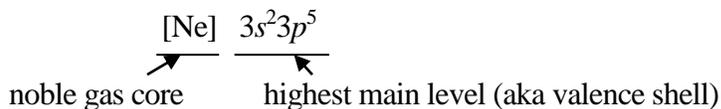
This means that if we write the electron configuration of Na as  $[Ne] 3s^1$ , we do not risk making wrong predictions of the chemical behavior of Na. After all, the electrons represented by the notation  $[Ne]$  ( $= 1s^2 2s^2 2p^6$ ) do not get involved in most chemical reactions of sodium, so they behave more like the electrons of Neon.

This simplified way of writing electron configurations is called the **Noble Gas Notation**. Writing electron configuration in noble gas notation has another advantage: it tells us how





The electron configurations given under each group of the **main group elements** are the electron configuration of the highest main levels. They represent the electrons not included in the **noble gas core**, as illustrated below for chlorine (Cl).



For any element, the electrons included in the noble gas core behave like the electrons of the noble gas, i.e. they don't usually participate in chemical reactions. The electrons outside the noble gas core, i.e. the electrons in the highest main level, have the highest energy. They constantly seek opportunities to lower their energy (to be more stable). These electrons provide all the chemistry for the atoms to which they belong. They are called **valence electrons**. The highest main level is called the **valence shell**.

#### Question 34.

Give the number of valence electrons to all the elements in period 2.

#### Answer:

From Li to F, the number of valence electrons for each element is, respectively: 1, 2, 3, 4, 5, 6, and 7.

#### Question 35.

Neon is also an element in period 2, why didn't you give its valence electron number in the answer to **Question 34**?

#### Answer:

Neon has a fully filled highest main level with **8** electrons. The fact that they belong to a noble gas element indicates that they are not actively seeking changes (chemical reactions). In other words, they don't behave like valence electrons. In fact, as we will see in the next chapter, it is the mission of every element (other than the noble gas elements) to try to have **8** electrons in the **highest main level**. This is called the **octet rule**. We will discuss more about octet rule in Chapter 4.

#### Question 36.

What is the relationship between the group number and the valence electron number?

**Answer:**

An inspection of the table on Page 37 shows that

For any main group element, its valence electron number = its group number.

You should be able to tell how many valence electrons any main group element has by looking up its position in the periodic table. This is a very important skill that will be useful throughout this and other chemistry courses.

### 3.4 The Orbital Box Notation and Magnetic Properties

Elements with unpaired valence electrons exhibit paramagnetic behavior in a magnetic field. How can we find out whether or not an element has unpaired valence electrons? The orbital box notation is one way to help us do just that.

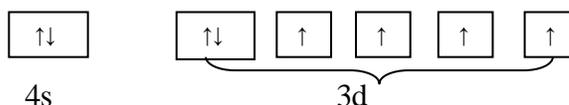
#### Question 37.

Give the valence electron configuration of Fe in orbital box notation.

**Answer:**

The valence electron configuration for Fe is  $4s^23d^6$ .

If we just look at the superscript numbers, it appears that all electrons are paired: one pair in the  $s$  sublevel and three pairs in the  $d$  sublevel. However, if we lay out the orbitals in each sublevel, we have



We have mentioned previously that electrons prefer to “live single” if possible. This preference results in **four unpaired valence electrons** for iron. This renders iron highly paramagnetic. So much so that iron exhibits magnetic behavior even in the absence of magnetic fields—a phenomenon known as **ferromagnetism**.

Note that in laying out the orbitals in a sublevel, we do not differentiate the orientation of the orbitals. We treat all orbitals in the same sublevel as if they all have the same energy.

## Practice and Review for Chapter 3

Define (in your own words) the following terms:

Electron Configuration:

---

Main (Energy) Level:

---

Sublevel: \_\_\_\_\_

Orbital: \_\_\_\_\_

Noble Gas Notation:

---

Orbital Box Notation:

---

Valence Electron:

---

### Short-Answer Questions:

1. How are the elements arranged in the periodic table in terms of atomic number?
2. What are the three subatomic particles inside the atom?
3. What are the charges carried by each of the three subatomic particles inside the atom?
4. Why is the mass of electrons not included in the calculation of the mass of the atom?
5. What are the symbols for the “four quantum numbers?”
6. How many sublevels are there in the  $n = 2$  main level?

7. What are the shapes of the  $s$  and  $p$  orbitals?
  
8. What is the relationship between the number of valence electrons and the group number for the main group elements?
  
9. Sketch and label a periodic table that shows the 3 blocks, the 8 main groups, and the transition elements. Give the valence shell electron configuration and the number of valence electrons to the 8 main groups.

## Some Important Periodic Properties

*Electrons have a life-long mission: to be in the lowest possible energy state.*

No wonder human beings are constantly seeking changes. It is the electrons in us that are never satisfied with where they are.

Elements carrying **valence electrons** participate in chemical reactions, sometimes voluntarily, other times not, to be transformed into a more stable existence.

### 4.1 Metals Form Cations

A major characteristic of that happy noble gas state is to have **8** electrons in the highest main level, sometimes referred to as the “outermost shell” or the “valence shell.” This observation is known as the **octet rule**. More accurately, however, it should be called the “**noble electron configuration rule**” because for helium (He) its valence shell only takes 2 electrons to be full ( $1s^2$ ) and it still offers a stable existence chased after by Lithium and Beryllium.

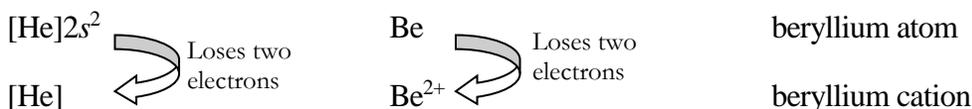
#### Question 38.

How do Lithium and Beryllium transform themselves into a helium-like existence?

#### Answer:

Li and Be have these electron configurations, respectively,  $[\text{He}]2s^1$  and  $[\text{He}]2s^2$ . Both voluntarily **give up** their valence electrons to be in a more stable existence. With this change also come a new symbol and a new name, as shown below.

<u>Electron Configuration</u>	<u>Symbol</u>	<u>Name</u>
$[\text{He}]2s^1$	Li	lithium atom
$[\text{He}]$  Loses one electron	Li <sup>+</sup>  Loses one electron	lithium cation (A positively charged ion)

**Question 39.**

Why do Li and Be carry positive charges after they are transformed from atoms to ions?

**Answer:**

We have been so excited about electrons and their importance in bringing about chemical reactions that we have, to this point, ignored the existence of protons and neutrons in the atom. It is OK to ignore the neutrons when atomic masses are not concerned. However, since protons carry positive charges we need to indicate how the charge balance is also changed after the valence electrons are lost.

Let's do some charge counting here.

<u>E. C.</u>	<u>Symbol</u>	<u>Name</u>	<u># of protons</u>	<u># of electrons</u>	<u>Net Charge</u>
$[\text{He}]2s^1$	Li	lithium atom	3	3	0
$[\text{He}]$	$\text{Li}^+$	lithium cation	3	2	+1
$[\text{He}]2s^2$	Be	beryllium atom	4	4	0
$[\text{He}]$	$\text{Be}^{2+}$	beryllium cation	4	2	+2

The **net charges** carried by the metal ions are called **oxidation numbers** of the elements. Thus Li has an oxidation number +1 and Be has an oxidation number +2.

To describe the transformation of lithium atom to lithium ion, we write the following half-equation:



It reads as “a lithium atom loses one electron to become a positively charged lithium ion.” When an atom loses electrons, we say that the atom is **oxidized**. The half-equation is called an **oxidation half-equation**. It is called a half-equation because it does not indicate where the lost electron goes.

All “s block **metals**” prefer to **lose** their **valence electrons** to form cations. Thus it is not entirely unfair to call metals “losers.” However, to *charge them positively*, let's just say that they are a very generous bunch. Such generosity, though, is aimed at gaining stability for **themselves**. No loss, no gain. Good strategy.

A half-equation is, after all, half a reaction. Without the other half, there will be no reaction. We need some voluntary takers to accept the electrons given up by the metals. Who are they? As we will see below, some atoms do pick up electrons to become more stable.

## 4.2 Non-Metals Form Anions

Consider the choices that the oxygen atom has. To become more stable, it can either lose all 6 valence electrons to become Helium-like, or pick up 2 electrons to become Neon-like.



This is hardly a dilemma. Gaining two is obviously easier than losing all six electrons. Thus oxygen almost never chooses to lose electrons. Its preferred chemical behavior can be described by the following half-equation:



It reads as “an oxygen atom gains two electrons to become a negatively charged oxygen ion.” When an atom gains electrons, we say that the atom is **reduced**. The half-equation is called a **reduction half-equation**. A negatively charged ion is called an **anion**.

Oxygen is not the only element that almost never chooses to lose electrons. Typically the **non-metal** elements with more than 4 electrons in their highest main level prefer to **gain** electrons to form anions. This is particularly true for fluorine (and the other Group VII elements Cl, Br, and I). Together, fluorine and oxygen are referred to as “**the most electron hungry elements**” in the periodic table.

The anion formed from a non-metal takes on a very different name. Below are some examples. The charge counting is also listed.

<u>E. C.</u>	<u>Symbol</u>	<u>Name</u>	<u># of protons</u>	<u># of electrons</u>	<u>Net Charge</u>
[He]2s <sup>2</sup> 2p <sup>3</sup>	N	nitrogen	7	7	0
[He]2s <sup>2</sup> 2p <sup>6</sup>	N <sup>3-</sup>	nitride	7	7+3=10	-3
[He]2s <sup>2</sup> 2p <sup>4</sup>	O	oxygen	8	8	0
[He]2s <sup>2</sup> 2p <sup>6</sup>	O <sup>2-</sup>	oxide	8	8+2=10	-2
[He]2s <sup>2</sup> 2p <sup>5</sup>	F	fluorine	9	9	0
[He]2s <sup>2</sup> 2p <sup>6</sup>	F <sup>-</sup>	fluoride	9	9+1=10	-1

The **net charges** carried by the non-metal ions are also called **oxidation numbers**. Thus the oxidation number of N is -3, the oxidation number of O is -2, and the oxidation number of F is -1.



**Question 43. (Give it a try before checking the answer on next page.)**

Fill in the blank cells in the table with correct answers.

Name	Symbol	Atomic Number	Mass Number	Number of Protons	Number of Neutrons	Number of Electrons
	${}_{13}^{27}\text{Al}$					
calcium ion			42			
oxide ion			18			

**4.3 The Formation of Diatomic Molecules****Question 44.**

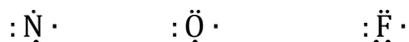
What do N, O, and F atoms have in common as far as electrons are concerned?

**Answer:**

They are the most electron-grabbing atoms in the periodic table. They will grab any electrons available to satisfy the octet rule.

That is not an exaggeration! In fact these atoms are so restless on their own that they make arrangements to help each other to stay calm. They do this by **sharing** their valence electrons to help each other acquiring the **octet** status. To make this easier to understand, we need to introduce what is called an **electron-dot structure**.

An **electron-dot structure** shows the number of valence electrons around the atomic symbol, as shown below. It also shows which valence electrons are paired in an orbital, and which electrons are alone in an orbital.

**Question 45.**

How do I know how many electrons are paired and how many are unpaired?

**Answer to Question 43:**

Name	Symbol	Atomic Number	Mass Number	Number of Protons	Number of Neutrons	Number of Electrons
aluminum	${}_{13}^{27}\text{Al}$	13	27	13	14	13
calcium ion	${}_{20}^{42}\text{Ca}^{2+}$	20	42	20	22	18
oxide ion	${}_{8}^{18}\text{O}^{2-}$	8	18	8	10	10

**Answer to Question 45:**

You need to write the electron configuration in orbital box notation, as shown below.

<u>Element</u>	<u>Highest Main Level</u>	<u>Orbital Box Notation</u>	<u>#of Unpaired Electrons</u>
N	$2s^2 2p^3$	<div style="display: inline-block; border: 1px solid black; padding: 2px; margin-right: 10px;">↑↓</div> <div style="display: inline-block; border: 1px solid black; padding: 2px; margin-right: 10px;">↑</div> <div style="display: inline-block; border: 1px solid black; padding: 2px; margin-right: 10px;">↑</div> <div style="display: inline-block; border: 1px solid black; padding: 2px;">↑</div>	3
O	$2s^2 2p^4$	<div style="display: inline-block; border: 1px solid black; padding: 2px; margin-right: 10px;">↑↓</div> <div style="display: inline-block; border: 1px solid black; padding: 2px; margin-right: 10px;">↑↓</div> <div style="display: inline-block; border: 1px solid black; padding: 2px; margin-right: 10px;">↑</div> <div style="display: inline-block; border: 1px solid black; padding: 2px;">↑</div>	2
F	$2s^2 2p^5$	<div style="display: inline-block; border: 1px solid black; padding: 2px; margin-right: 10px;">↑↓</div> <div style="display: inline-block; border: 1px solid black; padding: 2px; margin-right: 10px;">↑↓</div> <div style="display: inline-block; border: 1px solid black; padding: 2px; margin-right: 10px;">↑↓</div> <div style="display: inline-block; border: 1px solid black; padding: 2px;">↑</div>	1

Remember that there are three orbitals in the  $p$  sublevel and each orbital can accommodate a maximum of two electrons. Also remember that electrons prefer to occupy empty orbitals first before pairing up with another electron in one orbital.

The following illustration shows how the fluorine atoms help each other to become a more stable entity.



The shared pair can be counted in the octet by both F atoms.

Because of this a fluorine atom almost never stays alone. Stable fluorine gases are made of such diatomic entities, formally known as **molecules**.

A **molecule** is a combination of atoms. Such combinations are not random. Atoms in a molecule are held together by special glues called **bonds**. In the fluorine molecule the two fluorine atoms form a **covalent bond** by **sharing one pair of electrons**. The newborn molecule also needs a new symbol—a molecular formula. The **molecular formula** should indicate clearly what kinds

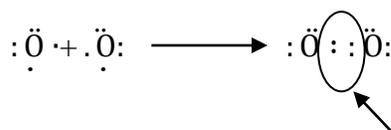
of atoms and how many of each kind are in the molecule. For fluorine, the molecular formula is  $F_2$ .

Once a bond is formed, it will take a chemical reaction to break it. The number of bonds needed to hold two atoms together depends on the number of electron pairs needed to be shared between the two atoms for each to achieve the octet status.

### Question 46.

Use the electron-dot structure to show how an oxygen molecule is formed and how many covalent bonds are formed.

#### Answer:



The shared pairs can be counted in the octet by both O atoms

To give an octet to each oxygen atom, two pairs of electrons must be shared. Therefore two covalent bonds are formed between the two oxygen atoms in order to form an oxygen molecule. The molecular formula for the oxygen molecule is  $O_2$ .

### Question 47. (Try to do this one on your own before looking at the answer on next page.)

Using the electron-dot structure, show how a nitrogen molecule is formed and how many covalent bonds there are in the molecule.

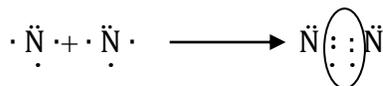
Three covalent bonds are formed between the two nitrogen atoms in order to form a nitrogen molecule. The molecular formula for the nitrogen molecule is  $N_2$ .

It is easier to break one bond than to break two or three bonds. This is why the nitrogen molecule is very stable. It is the major component (about 78%) of the air we breathe. The next major but more important component of air is the oxygen molecule (about 21%). We know that it does not take much to break the two bonds in oxygen molecule from the speed at which iron rusts and freshly cut apples turn brown. These are examples of the tricks played on us by the ubiquitous oxygen molecule getting involved in various chemical reactions.

Other elements in the periodic table that choose to exist as **diatomic** molecules include hydrogen (H), chlorine (Cl), bromine (Br), and iodine (I). Can you figure out the molecular formula for each element and the number of bonds formed in each molecule?

A more important use of the periodic table is to predict and compare chemical behavior of different elements. This is possible because certain properties show periodic variation with electron configuration. That is, certain trends are observed going across a period or down a group. Three of such properties are discussed below.

**Answer to Question 47:**



The shared pairs can be counted in the octet by both N atoms

## 4.4 Ionization Energy

We know by now that all metals can lose their valence electrons to form cations. The willingness to lose, however, varies from metal to metal. This willingness can actually be quantified by measuring the **ionization energy** of the element. It is the energy required to remove **one** valence electron from a gaseous atom of any element (including non-metals).

Experimental data indicate that ionization energy increases going up a Group and increases going across a Period from Group I to VIII, as illustrated below, using only the first 18 elements.

<i>H</i> 1s <sup>1</sup>							<i>He</i> 1s <sup>2</sup>
<i>Li</i> 1s <sup>2</sup> 2s <sup>1</sup>	<i>Be</i> 1s <sup>2</sup> 2s <sup>2</sup>	<i>B</i> 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>1</sup>	<i>C</i> 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup>	<i>N</i> 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>3</sup>	<i>O</i> 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>4</sup>	<i>F</i> 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup>	<i>Ne</i> 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup>
<i>Na</i> 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>1</sup>	<i>Mg</i> 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup>	<i>Al</i> 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>1</sup>	<i>Si</i> 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>2</sup>	<i>P</i> 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>3</sup>	<i>S</i> 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>4</sup>	<i>Cl</i> 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>5</sup>	<i>Ar</i> 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup>

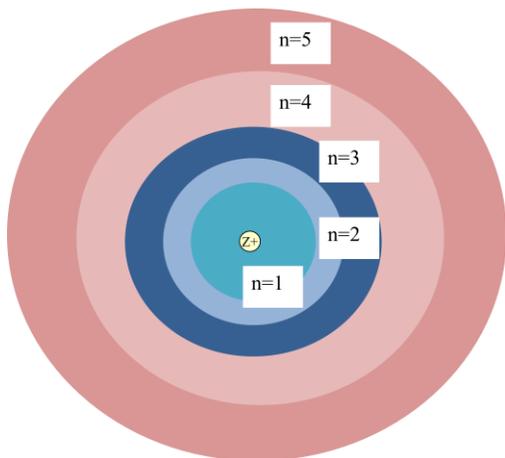
Ionization Energy increases  $\longrightarrow$

By using such trends in ionization energy, we can explain why it is easier for metals to lose their valence electrons. We can even predict that sodium (Na) will be more reactive than lithium (Li) in chemical reactions because it is easier for Na to lose its valence electron.

But how do we explain such trends?

## 4.5 The Shell Model

Compared to the quantum mechanical description of the whereabouts of electrons in an atom (main energy level, sublevel and orbitals), the **shell model** (shown below) provides satisfactory explanations to the periodical changes in properties such as ionization energy in a more common-sense fashion.



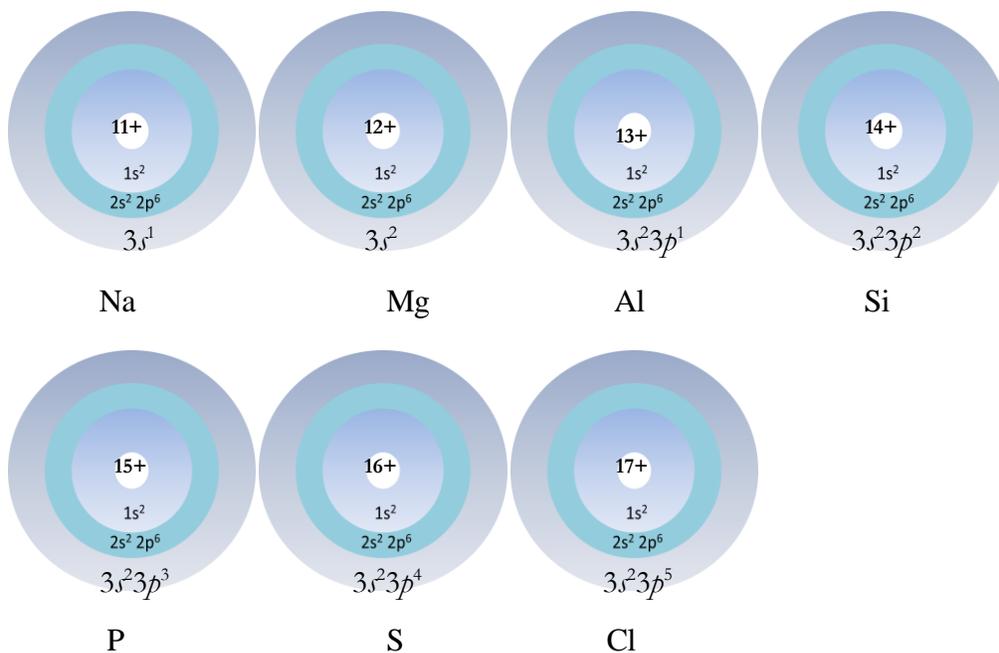
The shell model treats electron clouds around the nucleus (carrying  $Z+$  charges,  $Z$  = atomic number = # of protons) as layers of shells. The first shell is the  $n = 1$  main energy level, the second shell is the  $n = 2$  main energy level, and so on. The sublevels ( $s$ ,  $p$ ,  $d$ ,  $f$ , etc.) and orbitals are all treated as being contained in the shell they belong. The shells are positioned farther away from the nucleus as  $n$  value increases. The highest main shell is called the **valence shell** as it contains the valence electrons. Knowing that the orbitals all have different shapes, this treatment is certainly very inaccurate. However, it serves our

purpose reasonably well when used to explain general trends in the periodic table.

### Question 48.

Explain why ionization energy increases going across the 3<sup>rd</sup> period from Na to Cl.

**Answer:** Using the shell model, we can depict the atoms of the 3<sup>rd</sup> period as follows.



As the atomic number increases, going from Na to Cl, the number of protons and the number of electrons also increase. Two factors impact the force of attraction felt by the valence electrons: 1) the distance from the nucleus and 2) the core charge.

The **core charge** is equal to the atomic number  $Z$  minus the total number of electrons in the inner shells.

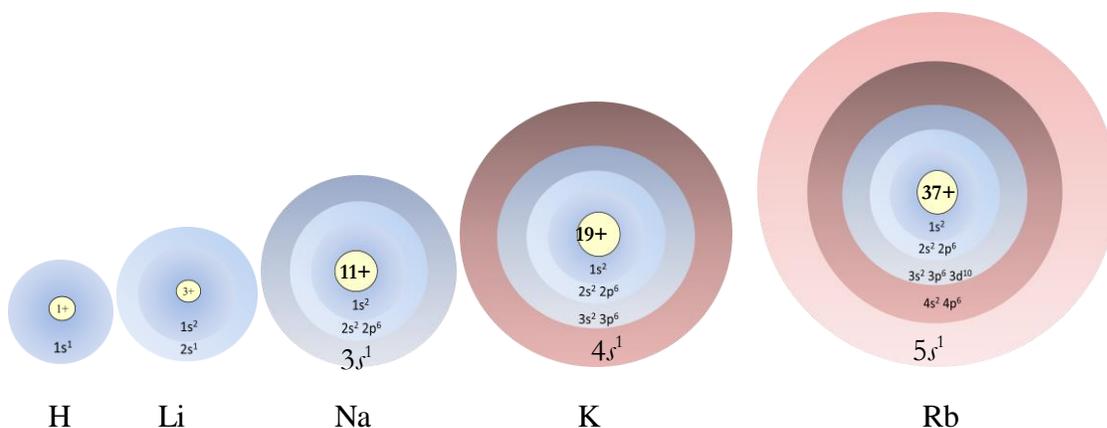
Since the number of inner-shell electrons is the same ( $2 + 8 = 10$ ) for all seven elements in the 3<sup>rd</sup> period, the core charge increases from **1** ( $11$  minus  $10$ ) to **7** ( $17$  minus  $10$ ) while the distance between the valence electrons and the nucleus remains roughly the same. Therefore the force of attraction between the nucleus and the valence electrons increases gradually with the increase of the core charge. From sodium to chlorine the ionization energy becomes higher and higher as it gets harder and harder to remove one valence electron.

### Question 49.

Explain why ionization energy decreases going down Group I from hydrogen (H) to Rubidium (Rb).

### Answer:

Using the shell model, we can depict the atoms of Group I as follows.



Let's again look at the two factors impacting the force of attraction felt by the valence electrons, i.e. the distance from the nucleus and the core charge. A simple calculation shows that the core charge for all five elements is  $+1$ ! The distance between the nucleus and the valence electron, on the other hand, increases significantly. From hydrogen to rubidium the ionization energy becomes lower and lower as it gets easier and easier to remove one valence electron.

*This trend in ionization energy parallels the trend of the reactivity of metals in any group. For example, potassium is more reactive than sodium and calcium, sodium is more reactive than lithium and magnesium, whereas calcium is more reactive than magnesium, and so on.*

Knowledge of such periodic variations allows us to predict and compare the chemical behavior of different elements simply by locating the elements in the periodic table. Two other important periodic properties are introduced below.

## 4.6 Sizes of Atoms

The size of an atom is determined by the position of the valance shell.

### Question 50.

Does the size of the atoms increase going down a group as depicted by the shell model above for the Group I elements?

#### Answer:

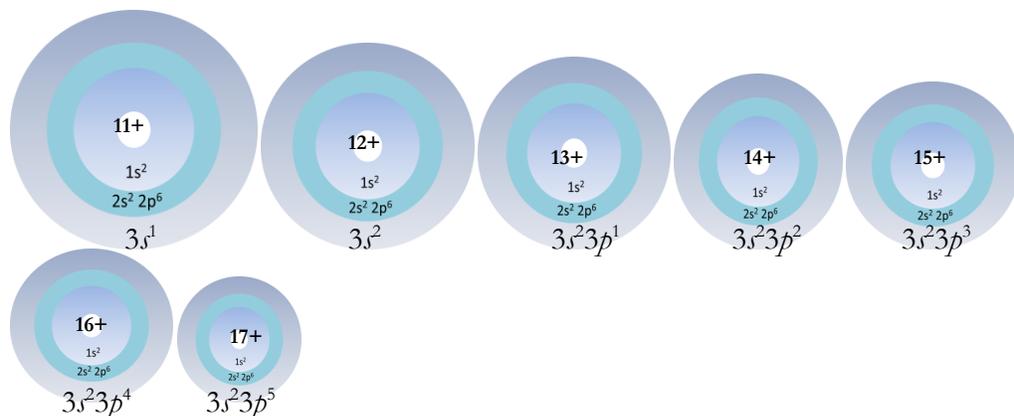
Yes. The size of the atom indeed increases as the distance between the valance shell and the nucleus increases.

### Question 51.

Does the size of the atoms remain the same going across a period as depicted for the elements in the 3<sup>rd</sup> period in Question 48?

#### Answer:

No. Actually the size of the atom decreases going across a period, as illustrated below for the elements in the 3<sup>rd</sup> period. This is due to the increase in the core charges. As the core charge increases gradually from, for example, Na to Cl, the valance electrons are pulled closer and closer toward the nucleus, so that the atoms decrease in size from left to right across a period. This further explains why the ionization energy of chlorine (Cl) is so much higher than that of sodium (Na).



## 4.7 Electronegativity

Rather than talking about how reluctant the non-metals are to lose their valence electrons, as exhibited by the high ionization energies, more often we talk about how much they “like” to get some “extra” electrons. One measure of such electron affinity is **electronegativity**.

Values of electronegativity are available for most known elements in the periodic table. These show periodic variation as illustrated by the values given for the first three periods of elements below. Electronegativity increases going up a Group and increases going across a Period from Group I to VII. Understandably, the noble gas elements do not show measurable affinity toward extra electrons.

The numbers also support our previous claim that fluorine and oxygen are the most electron-hungry elements in the periodic table.

<i>H</i> 2.20							<i>He</i> -
<i>Li</i> 0.98	<i>Be</i> 1.57	<i>B</i> 2.04	<i>C</i> 2.55	<i>N</i> 3.04	<i>O</i> 3.44	<i>F</i> 3.98	<i>Ne</i> -
<i>Na</i> 0.93	<i>Mg</i> 1.31	<i>Al</i> 1.61	<i>Si</i> 1.90	<i>P</i> 2.19	<i>S</i> 2.58	<i>Cl</i> 3.16	<i>Ar</i> -

Electronegativity increases  →

## Practice and Review for Chapter 4

Define (in your own words) the following terms:

Octet Rule: \_\_\_\_\_

Cation: \_\_\_\_\_

Anion: \_\_\_\_\_

Oxidation Number: \_\_\_\_\_

Electron-Dot Structure: \_\_\_\_\_

Molecule: \_\_\_\_\_

Molecular Formula: \_\_\_\_\_

Coefficient: \_\_\_\_\_

Covalent Bond: \_\_\_\_\_

Ionization Energy: \_\_\_\_\_

Valence Shell: \_\_\_\_\_

Core Charge: \_\_\_\_\_

Electronegativity: \_\_\_\_\_

**Short-Answer Questions:**

1. Give an example of an oxidation half-equation:
2. Give an example of an reduction half-equation:
3. Name the two “most electron-hungry” elements in the periodic table. \_\_\_\_\_
4. What is the oxidation number for any neutral atoms? \_\_\_\_\_
5. How many paired and unpaired electrons are there in the valence shell of the element phosphorus (P)?  
\_\_\_\_\_
6. List all diatomic molecules in the periodic table.
7. List the names of all cations and anions formed from the first 20 elements in the periodic table.

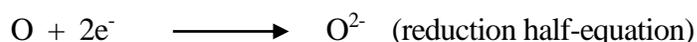
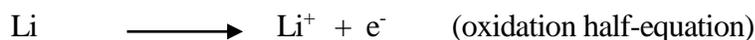
## Chemical Reactions

*When gaining equals losing, it is a balanced world.*

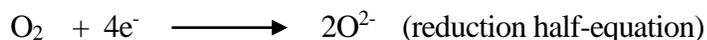
What happens when we put a metal and a non-metal together? The desire to lose meets the desire to gain. Well, you get chemistry!

### 5.1 Introducing Reaction Equations

Recall the two half-equations that led to the formation of the lithium cation and the oxide anion.



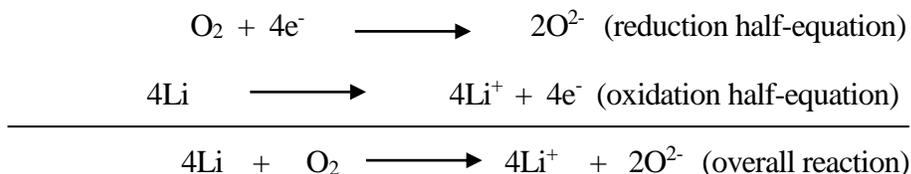
Now that we know oxygen exists as a diatomic molecule, we should rewrite its reduction half-equation as



We can satisfy oxygen's need for 4 electrons by coupling its reduction half-equation with lithium's oxidation half-equation. Only we need to rewrite the half-equation as follows in order to produce 4 electrons.



Now we can add the two sides of the half-equations to obtain an overall equation, as shown below.



Note that in the addition process; the electrons gained and lost are canceled out, indicating that the electrons given are exactly taken. Elements oxidized are balanced by elements reduced. The overall reaction above is a **balanced** equation for an oxidation-reduction reaction.

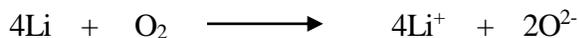
The balanced equation shows that it takes **4** lithium atoms to lose a total of **4** electrons to meet the need of **4** electrons for **1** oxygen **molecule** ( $\text{O}_2$ ). The numbers in front of the symbols for lithium, lithium cation, and the oxide anion are called **coefficients**. We have to account for the numbers of individual atoms before and after a reaction. If four lithium atoms participate in the reaction, then four lithium cations should be produced.

Atoms never appear or disappear during a chemical reaction. They are only transformed from one form of existence to another.

An equation that has all atoms accounted for on both sides of the reaction arrow ( $\rightarrow$ ) is called a **balanced equation**. The process of adding coefficients to obtain a balanced equation is called **balancing the equation**. A balanced equation should also have **zero net charges** on both sides of the equation.

## 5.2 Ionic Compounds

Let's take another look at the oxidation-reduction reaction between lithium and oxygen:



What makes this reaction go? We know that lithium, being a Group I metal, is very eager to lose its 1 valence electron to become Helium-like, i.e. more stable. However, in the oxygen molecule each oxygen atom already satisfies its octet need by forming two covalent bonds. Why does the oxygen molecule break the  $\text{O}=\text{O}$  bond to form the oxide ion?

There is only one explanation. It does so to become something even more stable!

Look what are formed on the right side of the equation: positive and negative ions! Opposite charges attract. The lithium cations and the oxide anions can now be “glued” together by a strong electrical force called the **ionic bond**. Ionic bonds are much stronger than covalent bonds.

The breaking of old bonds is always accompanied by the formation of **stronger** new bonds.

Again the formation of such ionic bonds is not random. Each oxide ion should be glued to two lithium ions in order to balance out the opposite charges. The combination formed as such is called an **ionic compound**. This new born compound also has a new formula:  $\text{Li}_2\text{O}$ . As in all cases, the formula has to indicate clearly what atoms and how many of them are used to make the compound.

### 5.3 Naming Ionic Compounds

Ionic compounds are named by saying the names of the cations and the anions in the same order as they are written in the ionic formula. Recall that the cations (formed from most metals) retain their elemental name while anions (formed from most non-metals) are turned into xxx-ide.

Here are some examples.

<u>Compound</u>	<u>Cation</u>	<u>Anion</u>	<u>Name</u>
$\text{Li}_2\text{O}$	$\text{Li}^{+1}$ (Lithium)	$\text{O}^{2-}$ (Oxide)	Lithium Oxide
$\text{NaF}$	$\text{Na}^{+1}$ (Sodium)	$\text{F}^{-}$ (Fluoride)	Sodium Fluoride

#### Question 52.

Aluminum has an oxidation number of +3. When aluminum is oxidized by oxygen (molecule), what are the formula and name of the ionic compound formed?

#### Answer:

The name would be aluminum oxide. This part is easy. To figure out the formula, we need to know how to balance electrons lost by aluminum and gained by oxygen. The short way is to find the smallest common multiple of the two oxidation numbers, 3+ for aluminum and 2- for oxygen, in this case. Thus the smallest common multiple would be  $2 \times 3 = 6$ . This means a total of 6 electrons are transferred from the “loser” to the “taker.”

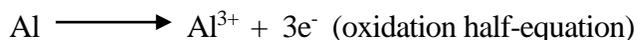
It will take 3  $\text{O}^{2-}$  ions to accept the 6 electron given by 2  $\text{Al}^{3+}$  ions. Thus the formula is  $\text{Al}_2\text{O}_3$ . Write the metal first, then the non-metal. The number of atoms for each element is written as a subscript next to the element.

#### Question 53.

Write a balanced equation for the formation of aluminum oxide.

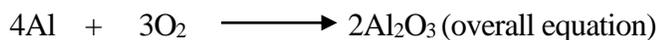
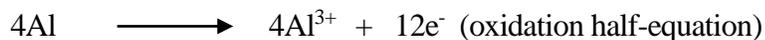
**Answer:**

Since there are electrons transferred in the formation of aluminum oxide, the reaction must be an oxidation-reduction reaction. We can write out a half-equation for each element, and then combine the half-equations to get the balanced equation, as shown below.



Before adding the half-equations, we need to adjust the coefficients (some are 1 at the moment and are not written out) to make electrons lost equal to electrons gained.

We adjust the half-equations as shown below by finding the smallest common multiple of +4 and -3. It is 12. So we multiply 3 to all coefficients in the reduction half-equation and multiply 4 to all coefficients in the oxidation half-equation. Then we add the half-equations.



Note that the straightforward addition of the right sides gives  $\text{Al}_4\text{O}_6$  as the product formed. We know from the previous question, however, that the formula of the ionic compound formed is  $\text{Al}_2\text{O}_3$ . Therefore we changed the answer to  $2\text{Al}_2\text{O}_3$ , meaning that two molecules of the compound are formed.

Even if we do not know the answer from the previous question, the common practice is to give the **simplest atomic ratio as the formula** of an ionic compound. Thus  $\text{Al}_4\text{O}_6$  would need to be simplified to  $2\text{Al}_2\text{O}_3$ .

Most ionic compounds are composed of at least one cation and one anion, just like in sodium chloride,  $\text{NaCl}$ , the table salt. Therefore ionic compounds are also called salts. In the formula of the salt the positive **charges** from the cation must be **balanced** by the negative charges from the anion.

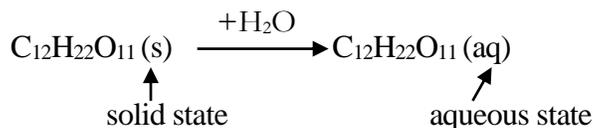
The naming of salts is similar to the naming of  $\text{NaCl}$ , sodium chloride. The cation gets named first and gets to keep its elemental name while the anion gets a name derived from its corresponding acid. The following are a few examples of salts and their names.

<u>Base</u>	<u>Acid</u>	<u>Anion</u>	<u>Salt</u>
KOH	H <sub>2</sub> SO <sub>4</sub> (sulfuric acid)	SO <sub>4</sub> <sup>2-</sup> (sulfate)	K <sub>2</sub> SO <sub>4</sub> (potassium sulfate)
NaOH	HNO <sub>3</sub> (nitric acid)	NO <sub>3</sub> <sup>-</sup> (nitrate)	NaNO <sub>3</sub> (sodium nitrate)
Mg(OH) <sub>2</sub>	HBr (hydrobromic acid)	Br <sup>-</sup> (bromide)	MgBr <sub>2</sub> (magnesium bromide)
Ca(OH) <sub>2</sub>	H <sub>2</sub> CO <sub>3</sub> (carbonic acid)	CO <sub>3</sub> <sup>2-</sup> (carbonate)	CaCO <sub>3</sub> (calcium carbonate)
NH <sub>3</sub>	HCl (hydrochloric acid)	Cl <sup>-</sup> (chloride)	NH <sub>4</sub> Cl (ammonium chloride)

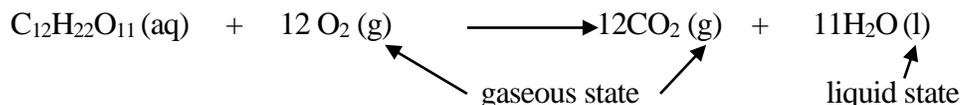
## 5.4 Chemical Reactions vs. Physical Changes

A chemical reaction must involve the breaking of old bonds and the formation of new bonds. In other words, a chemical reaction must involve the transformation of one molecule/compound to another.

Dissolving table sugar crystals (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>) in water is not a chemical reaction because the sugar molecule is not broken, i.e. the atoms remain bonded together in the same way in the crystal and in the water solution. The dissolving process is a **physical change**. An equation for such a change would be written like this,



If the sugar water is consumed, the sugar molecules would be turned into carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O), inside our body. Those sugar molecules are said to have gone through a series of **chemical** (or more precisely **biochemical**) **reactions** as they move through the digestive paths. The overall reaction also involves oxygen and is thus called a **respiration reaction**. An equation for such a transformation would be written like this:



This is an example of a **well written equation**. A well written equation must include all participating compounds, also called **reactants**, and all **products**. The physical state of each compound must be shown (in brackets), and the equation must be **balanced**.

**Question 54.**

In the equation above, why is the physical state of water indicated as (l), not (aq)?

**Answer:**

The notation (aq) following a molecule/ion indicates that the molecule/ion is surrounded by many water molecules. To write H<sub>2</sub>O (aq) will be redundant whereas H<sub>2</sub>O (l) indicates that the water molecule is in a liquid state, as oppose to solid (ice) or gaseous (steam) states.

**5.5 Types of Chemical Reactions**

You have been introduced to oxidation-reduction reactions. As you will see from the following examples, most reactions are oxidation-reduction reactions. We do, however, have more specific names for certain chemical changes.

**Combination Reactions**

When **two elements** combine to form **one compound**, this chemical change is called a **combination reaction**. Most metals, including transition metals, can react with most non-metals to form an ionic compound. Thus, by looking at the periodic table, we should be able to give many examples of combination reactions.

**Question 55.**

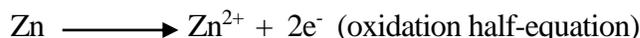
Write a balanced equation for the combination reaction between Zinc and Chlorine.

**Answer:**

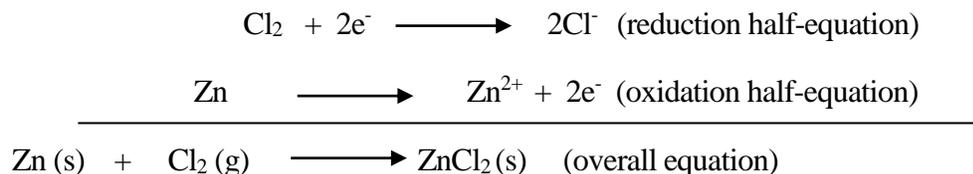
Remember that chlorine is one of the elements that exist as diatomic molecules. The Group VII element usually forms a -1 anion in chemical reactions. Thus we have a half equation as follows:



The electron configuration of Zn in noble gas notation is [Ar]3d<sup>10</sup>4s<sup>2</sup>. The valence shell is the 4s sublevel and Zn usually loses its two 4s electrons to form a 2+ cation, as shown below.



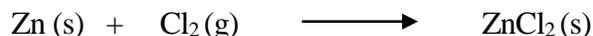
As the electrons lost and gained in these two half-equations are the same, there is no need to make any adjustment to the coefficients. We can add the half-equations as they are.



Note that it takes two  $\text{Cl}^-$  to charge-balance the one  $\text{Zn}^{2+}$ . Also note that we added the physical states to the reactants and the product in the overall equation, in order to give a well-written equation.

### Question 56.

Is this an oxidation-reduction reaction? What is the oxidizing agent and what is the reducing agent?



### Answer:

Since we build this full equation from two half-equations, as shown in the previous question, we know that there is electron transfer involved—electrons “transferred” from Zn to Cl. We also know that Zn is oxidized and Cl is reduced from the two half-equations. So we can conclude that this indeed is an oxidation-reduction reaction. We call Zn the **reducing agent** because without it the reduction half-reaction (reducing a chlorine atom to a chloride ion) would not occur. Similarly, the chlorine molecule plays the role of an **oxidizing agent** because without it the oxidation half-reaction (oxidizing a Zn atom to a  $\text{Zn}^{2+}$  ion) would not occur.

### Remember:

The element that gives up electrons acts as a reducing agent while itself is oxidized.

The element that receives electrons acts as an oxidizing agent while itself is reduced.

There is an easier way to tell whether or not a reaction is an oxidation-reduction reaction. It can be done by analyzing the changes in oxidation numbers of the elements involved. We will introduce this method while continuing to introduce other types of chemical reactions.

### Decomposition Reactions

A **decomposition reaction** describes the formation of two or more products from one reactant.

For example, the reverse reaction of the combination reaction between zinc and chlorine is a decomposition reaction



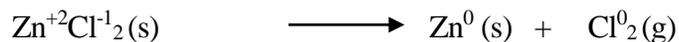
### Question 57.

How can we tell whether or not the above decomposition reaction is an oxidation-reduction reaction without writing out half-equations? What is the oxidizing agent and what is the reducing agent?

**Answer:**

We follow these simple steps to find the answer:

1. Assign oxidation numbers to all elements in the equation, as shown below.

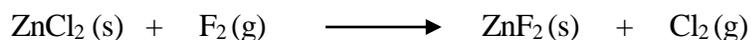


2. Compare the oxidation numbers of the same element before and after the reaction. If the oxidation number is decreased, from +2 to 0 in Zn's case, then the element is reduced. If the oxidation number is increased, from -1 to 0 in Cl's case, then the element is oxidized.
3. If a chemical reaction involves such oxidation number changes, it is an oxidation-reduction reaction.
4. The compound containing the element that is oxidized is the reducing agent and the compound containing the element that is reduced is the oxidizing agent.
5. In this case  $\text{ZnCl}_2$  (Zinc Chloride) contains both the oxidized element (Cl) and the reduced element (Zn) so it is acting as both a reducing agent and oxidizing agent.

**Single Replacement Reactions**

Sometimes a more reactive element takes the place of a less reactive element in an already-formed compound.

Example:

**Question 58.**

How can you explain the replacement reaction above?

**Answer:**

Let's look at the periodic table:

Fluorine is more electronegative than chlorine. This means that it is more eager to form the fluoride ion than chlorine is to form the chloride ion. Thus it can replace chlorine as shown in the reaction above.

**Double Replacement Reactions**

Sometimes two compounds simply switch partners, as shown in the example below. There are different reasons for such "switching" to occur. In this example it is the formation of a solid compound (called a **precipitate**) that acts as the driving force for the reaction.

Example:



**Question 59.**

Is the above reaction an oxidation-reduction reaction?

Answer:

As introduced previously (**Question 57**), we follow these simple steps to find out:

1. Assign oxidation numbers to all elements in the equation, as shown below. Remember that each compound should be neutral (total positive charges = total negative charges) and the reaction equation should be neutral.



Note that silver **always** forms the  $\text{Ag}^{+1}$  cation. This can be easily understood by looking at its electron configuration:  $[\text{Kr}]4d^{10}5s^1$ . It can easily lose its one valence electron. The electron configuration of the cation  $\text{Ag}^{+1}$  has a fully filled  $d$  sublevel—resembling an octet—but with 10 electrons. This is why we don't apply octet rule to transition metals. However the same idea applies: transition metals form cations to be in a more stable existence.

Also note that we treat  $\text{NO}_3$  as one ion (one of many polyatomic ions that will be introduced in the next section). As an ion  $\text{NO}_3$  always carries a -1 charge ( $+5 - 6 = -1$ ). So it is written as  $\text{NO}_3^-$ .

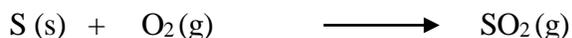
2. Compare the oxidation numbers of the same element before and after the reaction. In this case no element is oxidized or reduced (no changes found in oxidation numbers). Thus this is not an oxidation-reduction reaction.

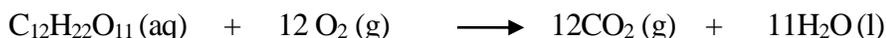
Double replacement reactions are one of the few types of reactions that are **not** oxidation-reduction reactions.

**Combustion Reactions**

This group of reactions is dedicated to showcase the oxidizing power of oxygen—one of the most electronegative elements in the periodic table. Most substances can burn (with or without flames) in the presence of oxygen. Thus the special name, **combustion reaction**, is given to those reactions where  $\text{O}_2$  is involved as a reactant.

Examples:





We can see that in all three cases oxygen is reduced from  $\text{O}^0$  to  $\text{O}^{-2}$ , thus acting as an oxidizing agent.

These three examples also show that it is not just metals that are easily oxidized—willingly or forced to surrender valence electrons to oxygen. Non-metals also can carry positive oxidation numbers, i.e. become cation-like, in the presence of oxygen. Typical examples of such cases can be found in a group of very common anions, called **oxoanions**.

## 5.6 Polyatomic Ions

The name polyatomic ion refers to an ion that is composed of more than two atoms. For example, the hydroxide ion ( $\text{OH}^-$ ) and the cyanide ion ( $\text{CN}^-$ ) are not polyatomic ions but the ammonium ion ( $\text{NH}_4^+$ ) is.

There are a group of polyatomic ions that are only composed of one nonmetal atom and different numbers of oxygen atoms (sometimes hydrogen atoms are present too). These are specially called oxoanions. The name **oxoanion** also indicates that these ions carry one or more negative charges. The nonmetals in these oxoanions all have positive oxidation numbers. The difference, in such cases, is that the valence electrons of the nonmetals are not completely lost to oxygen, but are **shared between the nonmetal and oxygen**. In these oxoanions, the atoms are “glued” together not by ionic bonds, but by **covalent bonds**.

It will greatly facilitate your learning later on if you become well acquainted with the following oxoanions.

Name	Formula	<u>Group</u> Charge	Name	Formula	<u>Group</u> Charge
Nitrate	$\text{NO}_3^-$	-1	Nitrite	$\text{NO}_2^-$	-1
Chlorate	$\text{ClO}_3^-$	-1	Chlorite	$\text{ClO}_2^-$	-1
Sulfate	$\text{SO}_4^{2-}$	-2	Sulfite	$\text{SO}_3^{2-}$	-2
Phosphate	$\text{PO}_4^{3-}$	-3	Phosphite	$\text{PO}_3^{3-}$	-3
Carbonate	$\text{CO}_3^{2-}$	-2	Hydrogen carbonate	$\text{HCO}_3^-$	-1

### Question 60.

What is the oxidation number of chlorine in chlorate?

### Answer:

In all oxoanions, the oxidation number of oxygen is invariably **-2**. The other nonmetal has a positive oxidation number because it is *oxidized* by oxygen (as oxygen is more electronegative).

In chlorate there are three oxygen atoms, each carries a charge of -2, this gives a total charge of -6.

Let the oxidation number of chlorine be  $x$ , since the charge of the group is -1, we have

$$x + (-6) = -1$$

$$x = +5$$

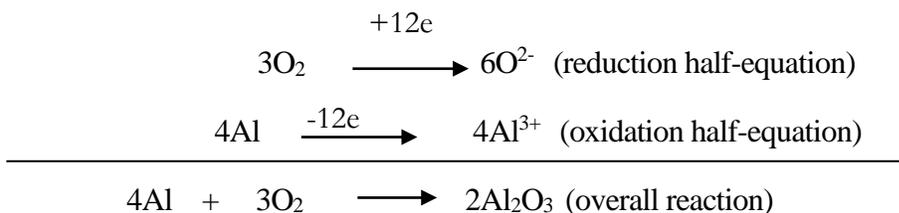
As a good exercise, try figure out the oxidation number of the nonmetal in each of the oxoanions listed on the previous page.

Polyatomic ions form ionic compounds with ions of opposite charge in the same way as  $\text{Li}^+$  and  $\text{Cl}^-$  combine to form  $\text{LiCl}$ . The naming of such compounds follows the same rule as well. For example, when  $\text{Li}^+$  and  $\text{ClO}_3^-$  combine to form  $\text{LiClO}_3$ , the compound is called lithium chlorate. Treating an oxoanion as one entity greatly simplifies the dealing of chemical reactions where these oxoanions are involved.

We have discussed previously, in Chapter 4, the formation of one covalent bond between two F atoms to form the diatomic molecule  $\text{F}_2$ . We have also discussed above the polyatomic ions formed with covalent bonds. In fact there are many types of molecules in which atoms are “glued” together by covalent bonds. These molecules are called **covalent compounds**.

## 5.7 Application of Redox Reactions: Electrochemical Cells

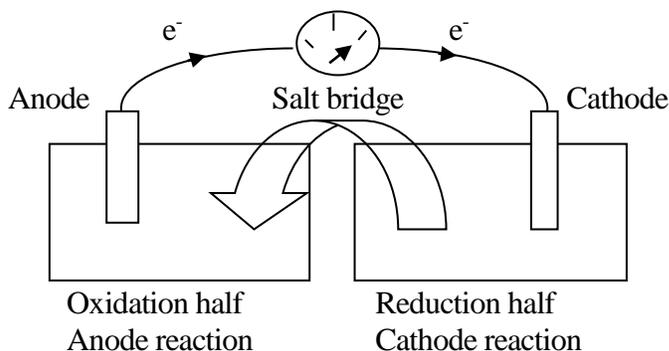
As discussed in 5.5, any oxidation-reduction reaction can be divided into two half reactions: an oxidation half, and a reduction half. As an example, let’s look at the reaction between aluminum and oxygen.



In this Redox reaction, twelve moles of electrons are transferred from 4 moles of aluminum to 3 moles of oxygen. Can we “feel” the electron flow and even make use of the electron flow to get an electric current? Yes, we can.

We make use of a proper set up called an **electrochemical cell**, also known as **voltaic cell**, or **galvanic cell**. We will call it a cell for short. In a cell there are four parts: one for the reduction half reaction (cathode), one for the oxidation half reaction (anode), one for electron transfer (wire

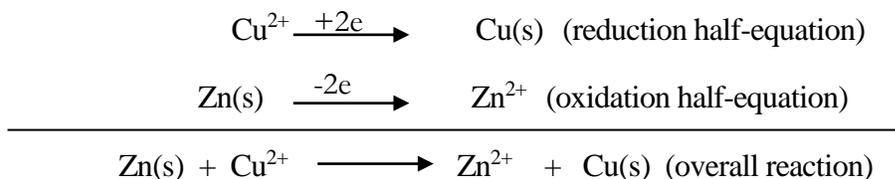
from anode to cathode) and one for ion transfer (salt bridge). Below is a sketch of a cell configuration.



The cell configuration separates the two half reactions, so the electrons lost from the oxidation half reaction do not go immediately to the reduction half reaction. Instead, the electrons flow through a conductive wire, forming an electric current that can be actually measured with a volt meter, before reaching the reduction half reaction. The function of the **salt bridge** is to allow only certain ions to flow from one side to the other in order to maintain charge balance. Thus salt bridges are usually made of conductive electrolytes and some porous material that only allow the passing through of certain ions.

The **anode** and **cathode** are usually two different pieces of metal, chosen for their good electrical conductivity, their capability in oxidation-reduction reactions, and easy of handling. Obviously the reaction between aluminum and oxygen (gaseous) would need more elaborate set up to be used as an electrochemical cell.

In undergraduate laboratories a zinc-copper cell is often used for experimental or demonstration purposes. Thus in the set up above, the anode would be a piece of Zn metal and the cathode would be a piece of Cu metal. These are dipped in ZnSO<sub>4</sub> and CuSO<sub>4</sub> solutions, respectively. The cell reactions are:



The sulfate ions are not included in the reaction equations because they are spectator ions. When the Cu<sup>2+</sup> ions are reduced to Cu at the cathode, there will be “unpaired” SO<sub>4</sub><sup>2-</sup> ions left in the CuSO<sub>4</sub> solution. The originally neutral solution is now in danger of being negatively charged. Fortunately, at the same time Zn gets oxidized at the anode, electrons flow through the wire while Zn<sup>2+</sup> ions diffuse into the ZnSO<sub>4</sub> solution. These “unpaired” Zn<sup>2+</sup> ions **draw** the “unpaired” SO<sub>4</sub><sup>2-</sup> ions at the cathode **over** through the salt bridge. And the neutrality of the solutions for both the anode and the cathode is maintained.

An easier way to represent a cell, instead of doing the detailed drawing, is to write a **cell diagram**. For the zinc-copper cell, the cell diagram would be



In the diagram the single vertical line separates the electrode from the solution with which it is in contact, and the double vertical lines indicate a salt bridge. The anode—the electrode at which oxidation occurs—is on the left and the cathode—the electrode at which reduction occurs—is on the right.

Since the sulfate ions are spectators in the cell, we can further simplify the cell diagram as



## 5.8 Cell Potentials

Like water, electrons flow from higher places to lower places. When electrons flow from the anode to the cathode, we say that it is because the anode has a higher **cell potential** and the cathode has a lower cell potential. The difference in potential is measured in **volts (V)** and is often called the **voltage** of the cell.

The potential difference (voltage) of a cell tells us how much work can be expected from the cell. Thus batteries with higher voltage can do more work than those with lower voltage. If 1 J of work is done by moving a charge of 1 C (coulomb) through a potential difference, the potential difference is 1 V:

$$1 \text{ V} = 1 \text{ J C}^{-1}$$

The symbol for cell potential is  $E_{cell}$  and the unit is V.

For a given cell reaction the cell potential depends on the concentrations of the ions in the cell, the temperature, and the partial pressures of any gases that might be involved in the cell reactions. When all the concentrations are 1 mol L<sup>-1</sup>, all partial pressures of gases are 1 atm, and the temperature is 25 °C, the cell potential is called the **standard cell potential**,  $E_{cell}^{\circ}$ .

For an electrochemical cell the reaction employed is an oxidation-reduction reaction, the overall cell potential is then the sum of the two half-cell potentials:

$$E_{cell}^{\circ} = E_{ox}^{\circ} + E_{red}^{\circ}$$

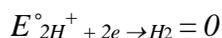
Potential of the oxidation half reaction
Potential of the reduction half reaction

## 5.9 Standard Reduction (Electrode) Potentials

An oxidation half reaction will not occur by itself; so is a reduction half reaction. Only when two halves are together, we have an oxidation-reduction reaction. Similarly, it would not be possible to measure any  $E_{ox}$  and  $E_{red}$  values separately because we can only measure the sum,  $E_{cell}$ , of the two half potentials.

Arbitrarily we have assigned a particular reduction half reaction to have a cell potential of 0 V. This allows us to obtain values of  $E_{ox}$  or  $E_{red}$  by measuring  $E_{cell}$  of an oxidation-reduction reaction involving the chosen half reaction.

This **chosen one** is the **hydrogen half cell**, with



### Question 61.

A zinc-hydrogen cell has a standard cell potential of 0.76 V. Find the cell potential for the zinc half cell.

#### Answer:

The two half reactions are:



Since  $E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red} = 0.76$

then  $E^\circ_{ox} = E^\circ_{cell} - E^\circ_{red} = 0.76 - 0 = 0.76 \text{ V}$

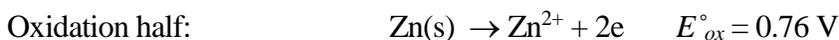
*Note: The value listed in Data table gives  $E^\circ_{red} = -0.76 \text{ V}$ .*

### Question 62.

A zinc-copper cell has a standard cell potential of 1.10 V. Find the cell potential for the copper half cell given that  $E^\circ_{Zn(s) \rightarrow Zn^{2+} + 2e} = 0.76 \text{ V}$ .

#### Answer:

The two half reactions are:



Since  $E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red} = 1.10$

Then  $E^\circ_{red} = E^\circ_{cell} - E^\circ_{ox} = 1.10 - 0.76 = 0.34 \text{ V}$

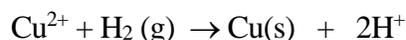
**Question 63.**

A copper-hydrogen cell has a standard cell potential of 0.34 V. Find the cell potential for the copper half cell.

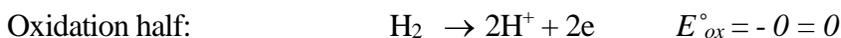
**Answer:**

Both the hydrogen half cell and the copper half cell act as the reduction half reaction in the above two examples. Which of them will act as the oxidation half reaction in this cell?

Experimentally we know that copper does not spontaneously react with dilute acids. In other words, the reverse reaction, shown below, would occur spontaneously.



For this reaction, the half reactions are:



Since  $E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red} = 0.34$

Then  $E^\circ_{red} = E^\circ_{cell} - E^\circ_{ox} = 0.34 - 0 = 0.34 \text{ V}$

This example shows that, by combining any half-cell with a hydrogen cell, we can determine the value of the standard half-cell potential for any half reactions except the reduction reaction of hydrogen (for which  $E^\circ_{red} = 0$ ). Some of these potentials are for oxidation reactions, and others are for reduction reactions. For convenience, in commonly seen Data tables all standard half-cell potentials are listed as reductions and are called **standard reduction potentials**. When values from such tables are used, it is important to know whether the half-cell is acting as cathode or anode. If it is acting as cathode, the value of  $E^\circ_{red}$  can be used directly. If the half-cell is acting as anode, then since  $E^\circ_{ox} = -E^\circ_{red}$ , the sign of the value should be reversed.

## Practice and Review for Chapter 5

Define (in your own words) the following terms:

Reaction Equation: \_\_\_\_\_

Coefficient: \_\_\_\_\_

Ionic Bond: \_\_\_\_\_

Ionic Compound: \_\_\_\_\_

Simplest Atomic Ratio: \_\_\_\_\_

Chemical Change: \_\_\_\_\_

Oxidizing Agent: \_\_\_\_\_

Reducing Agent: \_\_\_\_\_

Oxidation-Reduction Reaction: \_\_\_\_\_

Oxoanions: \_\_\_\_\_

Covalent Bond: \_\_\_\_\_

Covalent Compound: \_\_\_\_\_

Electrochemistry: \_\_\_\_\_

Electrochemical Cell:  
\_\_\_\_\_

Cell Potential: \_\_\_\_\_

Voltage: \_\_\_\_\_

Standard Cell Potential:  
\_\_\_\_\_

Standard Reduction Potential:  
\_\_\_\_\_

**Short-Answer Questions:**

1. What are the two requirements for an equation to be “balanced” (in terms of atoms and charges)?
- 

2. Give an example of a well-written equation for an oxidation-reduction reaction.

3. Give an example of an oxoanion.

4. Give an example of a polyatomic ion that is not an oxoanion.

5. Sketch a diagram for an electrochemical cell. Label all components.

6. Write the cell diagram for a zinc-copper cell.

7. What is the hydrogen half cell and what are the values of  $E^{\circ}_{ox}$  and  $E^{\circ}_{red}$  for this cell?

## Water Science I: Dissolving and Solving for Solutions

*Like dissolves like, but why?*

We started this book with two situations where making salt waters means two very different tasks at home and in a laboratory. In this chapter we are going to eventually make the salt water. But first we need to learn about solutions.

Scientifically speaking, the process of making salt water is the process of making a **solution**. A solution is a homogeneous mixture of two or more substances; these can be all gases, all liquids, all solids, or a mixture of substances in different physical states. The most common solutions we make at home and in a laboratory are the ones similar to the salt water where a solid substance (**solute**) is put into a liquid (**solvent**). We say that the solute is being **dissolved** in the solvent and that the solute is **soluble** in the solvent. When the solvent is water, the solution formed is called an **aqueous solution**.

### 6.1 Solubility in Water

Water is the most ubiquitous solvent in the world. Many things are soluble in water. Blood is an aqueous solution. It carries the dissolved oxygen and many other nutrients and delivers them to where they are needed in the body. The oxygen dissolved in rivers, lakes and oceans is needed by fishes and other creatures.

Some things, however, do not dissolve in water at all. A well known example would be the oil and water mixture where it is clearly visible that the two substances form a boundary between each other. Vinegar, on the other hand, mixes well with water in any proportions. Liquids that are soluble in each other are said to be **miscible**. Liquids that are not soluble (insoluble) in each other

are said to be **immiscible**. More specifically, substances that are soluble in water are said to be **hydrophilic** (like water). Substances that are insoluble in water are said to be **hydrophobic** (dislike water).

How well a substance dissolves in water can be measured by its **solubility** (in water). The amount of a substance that is dissolved in a given amount of water is defined as the **concentration** of the solution.

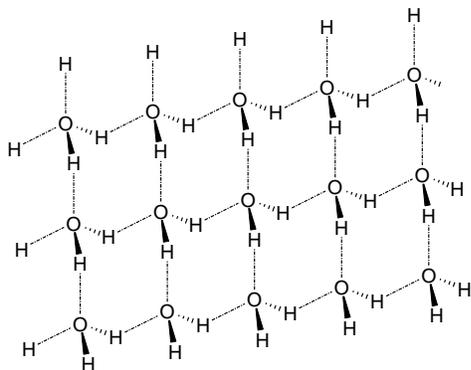
A solution with a relatively small concentration is said to be **dilute**. A solution having a large concentration of solute is said to be **concentrated**. In the case of fruit drinks made from concentrated juices, the latter must have come from originally dilute juices. The dilute juices, freshly squeezed out of the fruits, are usually evaporated via some industrial means, boiling or freeze-drying, to get rid of most of the water (the solvent), to become concentrated juices. If freeze-drying is used, the juices are actually turned into powders of the solutes. Such processes provide convenience for preservation and transportation of this important ingredient in making fruit juices.

The maximum amount of a solute that can be dissolved in a given amount of water is called the **solubility** of the solute in water. The solubility of a solid substance in water usually increases with the increase of temperature and is often expressed in grams of solute per 100 g of solvent, or, alternatively, in grams of solute per liter (or milliliter) of solution.

A solution that contains the maximum amount of a solute at a given temperature is said to be **saturated**. If we make a saturated solution of a solute at a high temperature, then cool the solution down to a much lower temperature, due to the lowered solubility of the solute at the lower temperature, some solute will come out of the solution. A laboratory technique that employs this principle for purification purposes is called **recrystallization**. This name suggests that the substance to be purified exists as **crystals** before being dissolved at a high temperature and forms crystals again once being “pushed” out of the solution at a lower temperature. So what are crystals?

## 6.2 Three Types of Crystals

We have seen ice crystals forming on winter days. If you haven’t observed a snow flake closely, you should do so at the next opportunity to make up for the missed “wow” moment. We use salt crystals every day. From time to time we get glimpses of the “shine” from a diamond ring. All of these are crystals but each represents a different kind of crystal.



The ice crystals represent the type of solids called **molecular solids**. These solids are made of covalent molecules held together by intermolecular forces. In the case of ice, the formation of H-bonds is the key factor for its structure, as shown by the drawing to the left.

Molecular solids melt at very low temperatures because of the relatively weak strength of the intermolecular forces. For example, ice melts at 0 °C under ambient conditions. Three commonly seen molecular solids at room temperature and pressure are the iodine (I<sub>2</sub>), sulfur (S<sub>8</sub>) and phosphorus (P<sub>4</sub>) crystals, each having a formula that represents the **smallest structural unit** in the molecular solid.

### Question 64.

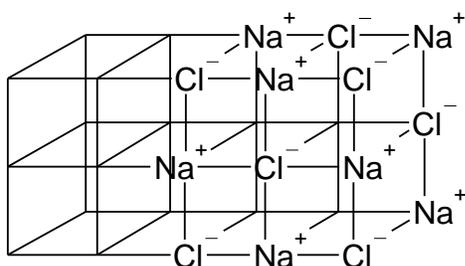
Is dry ice (CO<sub>2</sub> in its solid state) a molecular solid? What holds the CO<sub>2</sub> molecules together in dry ice?

### Answer:

CO<sub>2</sub> is a non-polar, covalent molecule. Therefore dry ice is a molecular solid. The only intermolecular forces exist among CO<sub>2</sub> molecules are London forces. This is why dry ice forms only at temperatures below -78 °C at 1 atmospheric (atm) pressure. At -78 °C or higher temperatures dry ice transforms directly into gaseous CO<sub>2</sub>. Liquid CO<sub>2</sub> can only be obtained under pressure.

When a substance goes from its solid state directly into a gaseous state, it is said to **sublime**. The process is called **sublimation**.

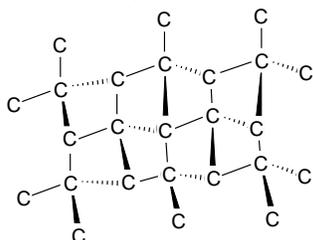
The crystals of NaCl represent another type of solid known as **3D-network solids**. In these solids the regular arrangement of ions extends indefinitely in three dimensions and no individual molecules can be recognized. The ions are held together by **ionic bonds** in a fashion that ensures that each ion is bonded (attracted) to as many ions of opposite charge as possible. Below is a drawing that shows the network arrangement of the ions in NaCl (not all ions are shown).



In the extended network each Na<sup>+</sup> is bonded to six Cl<sup>-</sup> and each Cl<sup>-</sup> is bonded to six Na<sup>+</sup> so the simplest unit formula is NaCl. Ions in such 3D-network solids are held together by real bonds (ionic bonds), not intermolecular forces. Thus such solids have very high melting points and even higher boiling points. For example, sodium chloride melts at 801 °C and boils at 1465 °C.

Clearly the best way to make the NaCl crystals “disappear” would be to dissolve them in water.

Diamond crystals, on the other hand, melt at 3600 °C and boil at 4800 °C. They also do not dissolve in water. What makes them so strong?



Diamond is yet another type of 3D-network crystals. Only here the smallest unit is the carbon atom and the atoms are held together by

**covalent bonds**. We shall call such crystals **covalent network solids** as compared to **ionic network solids** (e.g. NaCl).

Carbon is a Group IV element. It has 4 valence electrons. In the diamond network each carbon atom is bonded to four other carbon atoms. The four bonds arrange around the central carbon in a perfect tetrahedral arrangement (shown by the drawing on the previous page), just like in CH<sub>4</sub> (see the answer to **Question 68** on page 79), except that diamond is made of pure carbon atoms.

The study of solids is an important branch of Chemistry. Like photographers that take pictures, some scientists, known as X-ray crystallographers, take “photos” of the detailed arrangement inside crystals. Their camera is a piece of very sophisticated machine called an X-ray diffractometer.

### 6.3 Electrolytes and Non-electrolytes

Finally I have my 500.0 mL of salt water and I know that there are  $3.012 \times 10^{22}$  Na<sup>+</sup> cations and equal number of Cl<sup>-</sup> anions swimming inside the 500.0 mL solution, each surrounded by a layer of water molecules. Get the picture? This is a “charged” solution although the net electrical charge is zero. A “charged” solution like this can conduct electricity.

Substances that dissolve in water and result in “charged” solutions are called **electrolytes**. NaCl is an electrolyte and in fact a **strong electrolyte** because once dissolved NaCl only exists as ions in water.

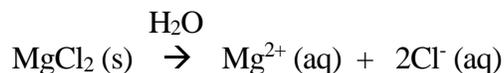
Other soluble ionic compounds dissolve in a similar way. For these compounds we can always write a net ionic equation just like the one for NaCl.

#### Question 65.

Magnesium chloride is soluble in water. Write a net ionic equation for its dissolving process.

#### Answer:

Magnesium is a Group II metal and forms a 2+ cation, Mg<sup>2+</sup>. The balanced net ionic equation would be:

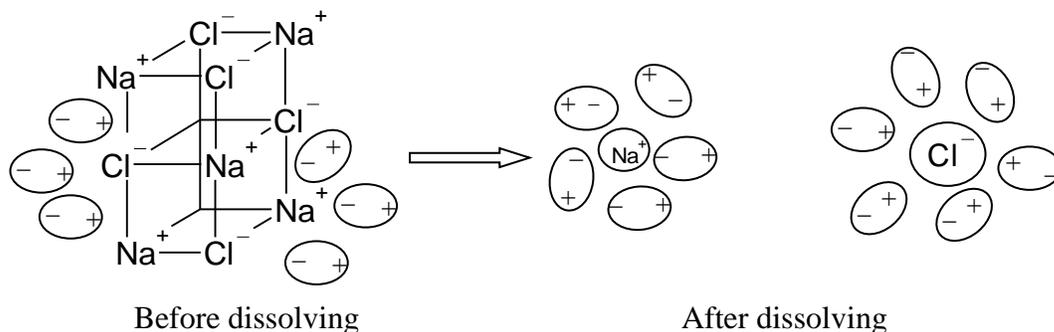


Note that both the number of atoms and the charges should be balanced.

Not all compounds that dissolve in water are strong electrolytes. Some are **weak electrolytes** and some are **non-electrolytes**. We will explain this in the next question.

## 6.4 The Dissolving Process

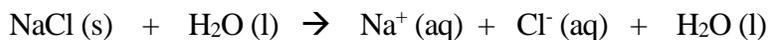
The drawing on the next page shows how a chunk of NaCl crystal is being dissolved. The polar water molecule is depicted as a dipole. At the boundary between the crystal and the water, the water dipoles arrange themselves in a fashion that maximizes the electrostatic attractive force between opposite charges.



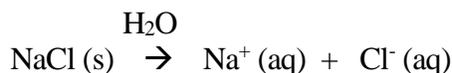
The numbers of water molecules surrounding the ions are not exact. The drawing is only for illustration purposes. Note that the sodium cation (electron configuration  $[\text{He}]2s^22p^6$ ) should be considerably smaller in size than the chloride anion (electron configuration  $[\text{Ne}]3s^23p^6$ ); because the chloride ion has an  $n = 3$  valence shell whereas the sodium ion has an  $n = 2$  valence shell.

When the “pull” from the water dipoles becomes strong enough to break the ionic bond between the  $\text{Na}^+$  and the  $\text{Cl}^-$  ions, the ion is pulled away from the crystal. One by one the water army eats away the ions in the ionic network, and the salt crystals gradually disappeared (dissolved) into the solution.

In the solution each ion is surrounded by water molecules. We say that the ions are **aqueous** or **hydrated**. The layer of water prevents the  $\text{Na}^+$  ions and the  $\text{Cl}^-$  ions from being attracted to each other again. An equation describing this dissolving process would be



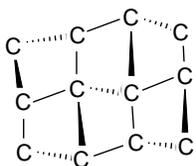
The solution is said to have a molar concentration of 0.0001 M in **both**  $\text{Na}^+$  and  $\text{Cl}^-$ . That is,  $[\text{Na}^+] = [\text{Cl}^-] = 0.0001 \text{ M}$ . This is a very dilute solution. Because the water molecules outnumber the salt ions significantly, we can consider that there is almost no change in the concentration of water. This allows us to cancel the water on both sides of the above equation, and we simply write:



An equation like this is called a **net ionic equation**.

**Question 66.**

Why do diamond crystals not dissolve in water?

**Answer:**

The diamond crystals are 3D network covalent solids (structure shown on the left) and are non-polar covalent substance. There is not a positive or negative center that can attract the dipole of water molecules. Thus there is no way that the water molecules can “eat away” the carbon atoms from the 3D network. There might be London forces between the carbon atoms and the water molecules in close proximity but the forces are too weak to break the covalent bonds between the carbon atoms. Thus diamond crystals do not dissolve in water.

The above two questions illustrate the key factor that determines the solubility of a substance in water.

The substance must be able to attract the dipoles of the water molecules. This attractive force must be great enough to overcome the original forces that hold the molecules, or ions, or atoms of the substance together.

In other words, only polar substances are soluble in water, the most polar solvent. Non-polar substances are not soluble in (or do not mix well with) water. Thus the saying goes: *like dissolves like*. This saying implies that non-polar substances would be soluble in non-polar solvents. And this is very true.

**Compounds that have N—H, O—H, and F—H bonds are particularly hydrophilic (very soluble in water) because they can form H-bonds with water.**

## 6.5 The Molarity

To make 500.0 mL of a 0.1000 M sodium chloride solution in the lab, we should use the measurement tools that offer an accuracy of at least four significant figures. But what does 0.1000 M mean?

The concentration of a solution can be expressed in several ways. The concentration of commercial products is usually indicated by **mass percentage**, or **volume percentage**. These are defined as follows:

$$\text{Mass percentage} = \frac{\text{mass of solute (g)}}{\text{mass of solute (g)} + \text{mass of solvent (g)}} \times 100\%$$

$$\text{Volume percentage} = \frac{\text{volume of solute (mL)}}{\text{volume of solute (mL)} + \text{volume of solvent (mL)}} \times 100\%$$

For example, a beer can be listed as having a 5% ABV (alcohol by volume) or a 4% ABW (alcohol by weight). It is easy to convert between these two.  $ABW = 0.8 \times ABV$ .

In the laboratory the most commonly encountered concentration expression is **Molarity**. It is defined as follows:

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Liters of solution}}$$

The units of molarity are thus moles per liter ( $\text{mol L}^{-1}$ ), or moles per cubic decimeter ( $\text{mol dm}^{-3}$ ). The symbol for molarity is M.  $M = \text{mol L}^{-1}$  or  $\text{mol dm}^{-3}$ .

Molar concentration (Molarity) is another convenient way to relate the mass of a solute to its molar mass and the number of molecules, as discussed in Chapter 2.

### Question 67.

How many grams of NaCl crystals are needed to make 500.0 mL of a 0.1000 M sodium chloride solution?

### Answer:

First change the unit of volume from mL to L, thus  $500.0 \text{ mL} = 0.5000 \text{ L}$ . Next find the number of moles of NaCl needed by rearranging the molarity equation as follows:

$$\begin{aligned} \text{Moles of NaCl} &= \text{Molarity} \times \text{Liters of solution} \\ &= 0.1000 \frac{\text{mol}}{\text{L}} \times 0.5000 \text{ L} = 0.05000 \text{ mol} \end{aligned}$$

Now we need to relate the number of moles to grams by using the mole-mass-molar mass relationship:

$$\begin{aligned} \text{Mass of NaCl (g)} &= \text{mol} \times \text{molar mass of NaCl} \\ &= 0.05000 \text{ mol} \times \left( 22.99 \frac{\text{g}}{\text{mol}} + 35.45 \frac{\text{g}}{\text{mol}} \right) \\ &= 0.05000 \text{ mol} \times 58.44 \frac{\text{g}}{\text{mol}} = 2.922 \text{ g} \end{aligned}$$

By using an analytical balance in the laboratory, we can measure the mass of NaCl needed to 4 significant figures.

### Question 68.

How many molecules of NaCl are there in 2.922 g of NaCl (assuming 100% purity)?

**Answer:**

The conversion factor for number of molecules and number of moles is this:  $\frac{6.023 \times 10^{23}}{1 \text{ mol}}$ . From **Question 73** we know that 2.922 g NaCl is 0.05000 moles. So the number of NaCl molecules contained in 2.922 g of NaCl would be as follows:

$$\# \text{ of molecules of NaCl} = 0.05000 \text{ mol} \times \frac{6.023 \times 10^{23}}{1 \text{ mol}} = 3.012 \times 10^{22}$$

Since the NaCl crystals are ionic network crystals the more accurate way of saying this would be that there are  $3.012 \times 10^{22}$  **sodium cations** and  $3.012 \times 10^{22}$  **chloride anions** in 2.922 g NaCl crystals.

**Question 69.**

How many water molecules are there in 500.0 mL of pure water at 22.0 °C?

**Answer:**

The density of water changes slightly with temperature. In most labs we can find a density table for water and we can read that at 22.0 °C  $d_{\text{water}} = 0.9978 \text{ g/cm}^3$ .

In most everyday situations we can say that  $d_{\text{water}} = 1.00 \text{ g/cm}^3$  at ambient temperatures (from 0 °C to 40 °C) and it would be quite accurate. However, since we are working with an accuracy of 4 significant figures we should find the density that is also accurate to 4 significant figures, if possible.

The mass of 500.0 mL pure water is (always remember that 1 mL = 1 cm<sup>3</sup>)

$$500.0 \text{ mL} \times 0.9978 \frac{\text{g}}{\text{cm}^3} = 498.9 \text{ g}$$

Next we find the number of water molecules in one step as follows:

$$\begin{aligned} \# \text{ of water molecules} &= \frac{\text{mass of water (g)}}{\text{molar mass of water } (\frac{\text{g}}{\text{mol}})} \times \frac{6.023 \times 10^{23}}{1 \text{ mol}} \\ \frac{498.9 \text{ g}}{18.02 \frac{\text{g}}{\text{mol}}} \times \frac{6.023 \times 10^{23}}{1 \text{ mol}} &= 27.69 \text{ mol} \times \frac{6.023 \times 10^{23}}{1 \text{ mol}} = 1.668 \times 10^{25} \end{aligned}$$

**Question 70.**

When we put 2.992 g of NaCl crystals in 500.0 mL of pure water, how many water molecules are there for each sodium cation or chloride anion?

**Answer:**

The total number of ions in 2.992 g of NaCl crystals is

$$3.012 \times 10^{22} \text{Na}^+ + 3.012 \times 10^{22} \text{Cl}^- = 6.024 \times 10^{22}$$

The total number of water molecules in 500.0 mL of water is  $1.668 \times 10^{25}$ . So for every ion in NaCl there are

$$\frac{1.668 \times 10^{25}}{6.024 \times 10^{22}} = 276.9 = 277 \text{ water molecules}$$

Obviously the water molecules outnumber the  $\text{Na}^+$  and  $\text{Cl}^-$  ions enormously. So how do the water molecules attack and “dissolve” the NaCl crystals?

Well, it is going to be an electrifying, fully charged battle! Let’s watch how the battle unfolds.

## Practice and Review for Chapter 6

**Define (in your own words) the following terms:**

Solution: \_\_\_\_\_

Solute: \_\_\_\_\_

Solvent: \_\_\_\_\_

Miscible: \_\_\_\_\_

Immiscible: \_\_\_\_\_

Hydrophilic: \_\_\_\_\_

Hydrophobic: \_\_\_\_\_

Solubility: \_\_\_\_\_

Recrystallization: \_\_\_\_\_

Molecular Solids: \_\_\_\_\_

Ionic Network Solids: \_\_\_\_\_

Covalent Network Solids: \_\_\_\_\_

Molarity: \_\_\_\_\_

Strong Electrolyte: \_\_\_\_\_

Weak Electrolyte: \_\_\_\_\_

Non-electrolyte: \_\_\_\_\_

Hydronium Ion: \_\_\_\_\_

**Short-Answer Questions:**

1. Draw the dissolving process for a small NaCl crystal.
2. Why anions are larger than cations when both are formed from elements in the same period?
3. Write a net ionic equation for the dissolving of KCl in water.
4. What is the key factor that determines the solubility of a substance in water?

## Covalent Compounds

*It is in us to give and take. It is also in us to share.*

Although the periodic table is dominantly populated by **metals** (the “**losers**”), it is the few non-metals that form the basis of life, as attested by the data below. In this sense, it is not entirely without substantiation that we declare the non-metals “**winners**” in the circle of life.

Human Body Composition (*by mass*):

Oxygen	( <u>  O  </u> , 65%)
Carbon	( <u>  C  </u> , 18.3%)
Hydrogen	( <u>  H  </u> , 10%)
Nitrogen	( <u>  N  </u> , 3.3%)
Calcium	( <u>  Ca  </u> , 1.7%)
Phosphorous	( <u>  P  </u> , 1%)

These non-metals, more specifically, oxygen, carbon, hydrogen and nitrogen, make up about 97% of a human body. They form an enormously wide variety of covalent compounds by sharing their valence electrons with each other. To know these covalent compounds and their chemical behavior is to understand the chemistry of life. Organic chemistry, as will be introduced in Chem2120, is a branch of science dedicated to such topics. Before we move on to

organic chemistry, however, we need to acquire some more basic skills covered in this course.

### 7.1 Writing and Naming Covalent Compounds

We learned how to write the simplest covalent compounds when we talked about the formation of diatomic molecules (Chapter 4). For example, the formation of the N<sub>2</sub> molecule can be represented by the following equation.



An easier way to represent the shared electron pairs is to use a line “—” for a pair. In this way the N<sub>2</sub> molecule can be written as



This representation is called the **Lewis structure** of the nitrogen molecule. It is so named to honor the chemist, Gilbert Lewis, who invented the electron-dot symbols.

When a Group I metal reacts with a non-metal, there is only one formula for the final product. For example, Li only reacts with  $N_2$  to form  $Li_3N$  (remember N has an oxidation number of -3), with  $O_2$  to form  $Li_2O$  (O has an oxidation number of -2), and with  $F_2$  to form  $LiF$  (F has an oxidation number of -1). This is because Li (and other main group metals) only can form one cation.

When non-metals form covalent compounds with each other, however, there could be more than one formula for the final product. For example, carbon can react with oxygen to form both  $CO$  and  $CO_2$ . Nitrogen forms several products with oxygen, such as  $NO$ ,  $N_2O$ ,  $NO_2$ ,  $N_2O_3$ ,  $N_2O_4$ , and  $N_2O_5$ . Thus it becomes a little more complicated to predict what and how many covalent compounds can be formed between two or more non-metal elements. For the purpose of this course, you will always be given the formula of a covalent compound, and you need to be able to do the following simple things with the formula.

1. Name the compound
2. Figure out the oxidation states of each of the elements in the compound
3. Write the Lewis structure for the compound

We will use the group of covalent compounds formed between nitrogen and oxygen to illustrate how to do these, as shown below.

<u>Formula</u>	<u>Oxidation State of N</u>	<u>Name</u>	<u>Physical State at 25 °C</u>
$N_2O$	+1	Dinitrogen monoxide	Colorless gas
$NO$	+2	Nitrogen monoxide	Colorless gas (automobile exhaust)
$N_2O_3$	+3	Dinitrogen trioxide	Deep blue liquid (-80°C)
$NO_2$	+4	Nitrogen dioxide	Brown gas (part of smog)
$N_2O_4$	+4	Dinitrogen tetraoxide	White solid
$N_2O_5$	+5	Dinitrogen pentaoxide	White solid

We can see that the naming of covalent compounds is similar to that of ionic compounds, only more specific. The first element is named like a cation, while the second element is named like an anion. The number of atoms of each element in the compound is clearly named by using prefixes such as mono- (1), di- (2), tri- (3), tetra- (4), penta- (5), hexa- (6), hepta- (7), octa- (8), and so on.

To determine the oxidation states of the elements, we need to compare the electronegativities of the elements involved. The more electronegative element will have a negative oxidation number and the less electronegative element will have a positive oxidation number. Thus it is a good idea to be familiar with the following table and the general trends of electronegativity variation in the periodic table.

Electronegativity increases ↑	<i>H</i> 2.20						
	<i>Li</i> 0.98	<i>Be</i> 1.57	<i>B</i> 2.04	<i>C</i> 2.55	<i>N</i> 3.04	<i>O</i> 3.44	<i>F</i> 3.98
	<i>Na</i> 0.93	<i>Mg</i> 1.31	<i>Al</i> 1.61	<i>Si</i> 1.90	<i>P</i> 2.19	<i>S</i> 2.58	<i>Cl</i> 3.16
	Electronegativity increases →						

Since oxygen has the second highest electronegativity in the periodic table, all metals and most non-metals (except F) will have positive oxidation numbers when forming covalent bonds with the oxygen atom. As the *p* block non-metals typically have 3 to 7 valence electrons in the valence shell, they can have several positive oxidation numbers depending on how many valence electrons are “lost” to the more electronegative element. It is a much simpler situation when the non-metals form anions, in which case they **only** have **one** negative oxidation state that is equal to the number of electrons needed to achieve the octet status.

Two facts help make it easier for us to figure out the oxidation number of an element in a compound formed with oxygen and/or hydrogen.

Remember:

**Oxygen** usually has an oxidation number of **-2** (except in peroxides and superoxides).

**Hydrogen** usually has an oxidation number of **+1** (except in hydrides).

### Question 71.

Why is the oxidation number of nitrogen in  $N_2O_4$  +4?

Answer:

$N_2O_4$  is a neutral compound so the net charge of the molecule should be zero. Knowing that oxygen's oxidation number is -2, and let the oxidation number of nitrogen be  $x$ , we have

$$4(-2) + 2(x) = 0$$

$$x = +4$$

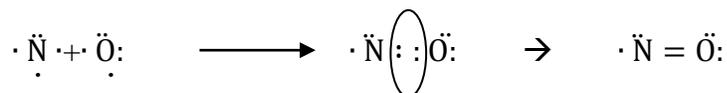
For practice, can you check the oxidation numbers for nitrogen in different oxide compounds listed on the previous page?

**Question 72.**

Give the Lewis structure for NO.

**Answer:**

We envision the formation of the NO molecule as follows.



The **Lewis structure** of the NO molecule shows that, while oxygen achieves the octet status by sharing two electrons with nitrogen, there is still an unpaired electron on the nitrogen atom. Atoms or molecules with unpaired electrons are called **free radicals**. Free radicals are not stable as they are still seeking to achieve the octet status.

More often, however, we need to write Lewis structures for covalent compounds with more than two atoms. A more general procedure for writing Lewis structures is discussed in the next section.

## 7.2 Lewis Structures of Covalent Compounds

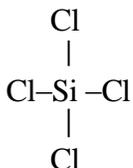
**Question 73.**

Draw the Lewis structure for silicon tetrachloride.

**Answer:**

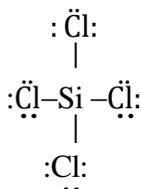
First we need to translate the name silicon tetrachloride to the formula  $\text{SiCl}_4$ . Then we follow these steps:

1. Arrange the molecule so that the element (except H) with only one atom in the molecule is at the **center** and is connected by **one covalent bond** each to all atoms of the other element(s). The atom at the center is called the **central atom**. For  $\text{SiCl}_4$  Si is the central atom.



2. Calculate the total number of valence electrons for the molecule. In this case it is  $4(7) + 4 = 32$ . Remember that the number of valence electrons of an element is the same as the group number of the element.

3. Since we used **8** electrons to form the **4 covalent bonds** between Si and the **4** Cl atoms, we have  $32 - 8 = 24$  electrons left to distribute among the elements that do not have octet status. In this case, we give 6 electrons to each of the 4 chlorine atoms.



4. Finally we check to see if all elements have achieved the octet status. If yes, then we have completed the drawing of the Lewis structure for the given compound. If not, we need to help the elements satisfy the octet requirement by forming multiple bonds.

To determine where and how many multiple bonds need to be formed, we should first figure out the **formal charge** on each atom in the compound.

### 7.3 Formal Charge

The concept of **formal charge** on an atom in a Lewis structure is **different from** the concept of **oxidation states** of an element. To calculate formal charge for any covalently bonded atom, we have

Formal charge = # of valence electrons – # of unshared electrons – # of bonds
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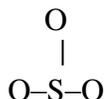
#### Question 74.

Draw the Lewis structure for sulfur trioxide.

#### Answer:

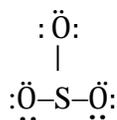
First we need to translate the name sulfur trioxide to the formula  $\text{SO}_3$ . Then we follow these steps.

1. Arrange the molecule as shown below.

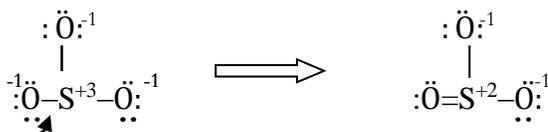


2. The total number of valence electrons for the molecule is  $3(6) + 6 = 24$ .
3. Since we used **6** electrons to form the **3 covalent bonds** between S and the **3** O atoms, we have  $24 - 6 = 18$  electrons left to distribute among the elements that do not have octet status. We start

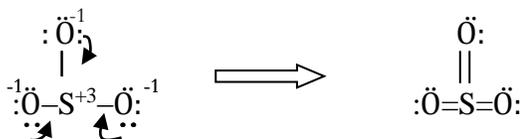
with the more electronegative elements. In this case, we just have enough to give 6 electrons to each of the 3 oxygen atoms.



- Now we check to see if all elements have achieved the octet status and we find that although all oxygen atoms have the octet status, the sulfur atom is in need of one more pair of electrons.
- This is the moment when we need to calculate the **formal charges** on each atom in the compound. Using the formula for formal charge calculation given above, we get, for the sulfur atom, a formal charge of  $6 - 0 - 3 = +3$ ; for each of the oxygen atom,  $6 - 6 - 1 = -1$ .
- We rewrite the Lewis structure with formal charges shown (below). A Lewis structure with formal charge separation such as this is less desirable than one with fewer or no formal charge separation. It is only natural that the electron density will “flow” from the electron “rich” atom to the electron “needy” atom. We envision this as a lone pair that “**flows**” from one oxygen atom to **become a second bond** between the oxygen and the sulfur atom, thus eliminating one pair of charge separation, as illustrated below.



- In fact the Lewis structure for the  $\text{SO}_3$  molecule is better written as a Lewis structure with no formal charge separation. So we form one bond for each pair of charge separation, as illustrated below.



The use of the **curved arrow** to indicate the direction of flow of electrons will be extensively applied in the study of organic chemistry. The curved arrows used here are called the “lone pair to bond” arrows as they represent the formation of one bond from one pair of unshared electrons (the lone pair of electrons). The arrows always start from high electron density and point to low electron density. A full arrow head ( $\rightarrow$ ) indicates the flow of **2** electrons whereas a half arrow head ( $\curvearrowright$ ) indicates the flow of **1** electron.

When looking at the finished Lewis structure for the  $\text{SO}_3$  molecule, are you quick to realize that now sulfur has more than achieved its octet status? Indeed, the octet rule is mainly obeyed by the second period elements. For elements in the 3<sup>rd</sup> and higher periods, they

sometimes can accommodate more than 8 electrons in their valence shell (just like the transition metals). To understand this we only need to write out the orbitals available in, for example, the 3<sup>rd</sup> valence shell. They are: one 3s, three 3p, and five 3d. A total of nine orbitals are available to accommodate up to 18 shared valence electrons.

## 7.4 Lewis Structures for Polyatomic Ions

**Polyatomic ions** are covalent molecules with an electric charge. When writing Lewis structures for polyatomic ions, we use formal charge calculation to determine which atom(s) would carry the charge of the ion.

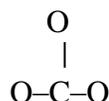
### Question 75.

Draw the Lewis structure for the CO<sub>3</sub><sup>2-</sup> ion.

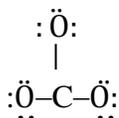
### Answer:

We follow these steps.

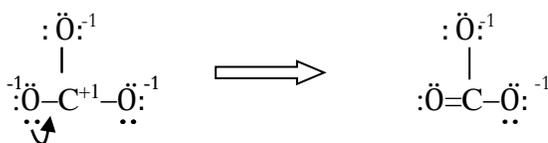
1. Arrange the molecule as shown below.



2. The total number of valence electrons for the ion is  $3(6) + 4 + 2 = 24$ . Remember we need to include the ionic charges in the calculation.
3. Since we used **6** electrons to form the **3 covalent bonds** between C and the **3** O atoms, we have  $24 - 6 = 18$  electrons left to distribute among the elements that do not have octet status. We start with the more electronegative elements. In this case, we just have enough to give 6 electrons to each of the 3 oxygen atoms.



4. All oxygen atoms have the octet status, but the carbon atom is in need of one more pair of electrons.
5. We calculate the **formal charges** on each atom and get, for the carbon atom, a formal charge of  $4 - 0 - 3 = +1$ ; for each of the oxygen atom,  $6 - 6 - 1 = -1$ .
6. We mark the formal charges on the atoms in the Lewis structure. Then we form one bond to eliminate one pair of charge separation, as illustrated below.



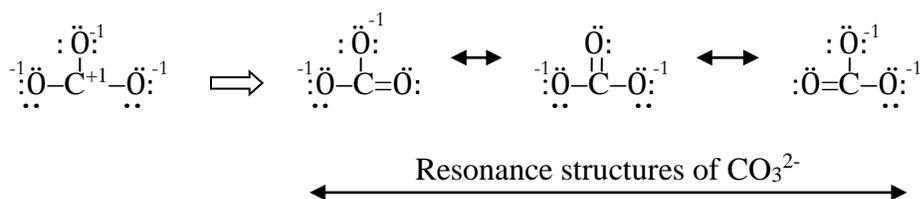
7. Since there is no more charge separation (no more positive charges to be neutralized by negative charges), and all atoms have achieved octet status, we accept this as a correct Lewis structure for the  $\text{CO}_3^{2-}$  polyatomic ion.

This Lewis structure tells us that the two negative charges carried by this ion are located on two of the oxygen atoms. Thus we have

The charge of the polyatomic ion = the sum of the formal charges in the Lewis structure

At this point you might ask: does it matter which oxygen form the double bond in the  $\text{CO}_3^{2-}$  ion?

Indeed we can't discriminate among the oxygen atoms. They all have equal rights to share their valence electrons with carbon. To be fair, we write out all possibilities:



We call all of these possible (and correct) Lewis structures the **resonance structures** of the  $\text{CO}_3^{2-}$  ion. We use the word **resonance** to describe the situation where we cannot use **only one** Lewis structure to adequately represent a covalent molecule. In reality the molecule should be viewed as a “**hybrid**” of all resonance structures. How can we **view** a molecule and what does it look like?

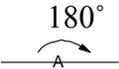
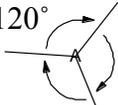
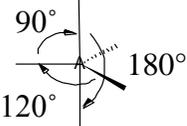
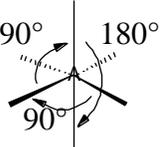
## 7.5 Shapes of Covalent Molecules

The first step of drawing a Lewis structure for a covalent molecule is to “**arrange**” all other atoms around the central atom. Is there a rule for this “arranging game?” Yes there is and once again it has to do with the electrons. It is important to know how to do the arrangement correctly because the shape of the covalent molecule depends on the arrangement.

When we are doing the arrangement, we are spacing the bonds around the central atom. So what we are actually arranging are the **electron pairs** in the **valence shell** of the central atom. These electron pairs need not all be bonding pairs. They can be lone pairs, too. We

shall call them “electron groups” in general. For molecules with double or triple bonds, each double or triple bond is counted as one electron group.

The electron groups all carry negative charges. Because “*opposites attract and likes repel*,” these electron groups would want to stay as far apart from each other as possible. This understanding forms the basis of the **VSEPR** (the Valence Shell Electron Pair Repulsion) model. According to this model the geometric arrangements below would best minimize the repulsion among the electron groups around the central atom (A). The shape adopted by the molecule according to this geometry is called the **ideal shape**.

<u># of Electron Groups</u>	<u>Preferred Geometry and Bond Angle</u>	<u>Ideal Shape</u>
2		Linear
3		Trigonal planar
4		Tetrahedral
5		Trigonal bipyramidal
6		Octohedral

For geometries involving more than three electron groups the drawings are done in 3-D. To do so we have employed the convention of using **wedge/dash bonds**. A wedge bond () is a bond pointing out of the paper plane toward you and a dash bond () is a bond pointing inward of the paper plane away from you. The line bond “—” lies in the same plane as the paper plane.

## 7.6 Bond Polarity

So far we have introduced two types of bonds: ionic bonds and covalent bonds. Some compounds only contain ionic bonds. For example, the table salt sodium chloride, NaCl, contains only ionic bonds between the  $\text{Na}^+$  cations and the  $\text{Cl}^-$  anions. Most compounds, however, contain both types of bonds. For example, the baking soda sodium bicarbonate,  $\text{NaHCO}_3$ , contains ionic bonds between  $\text{Na}^+$  and the oxoanion  $\text{HCO}_3^-$ , the latter containing covalent bonds between H and C, C and O.

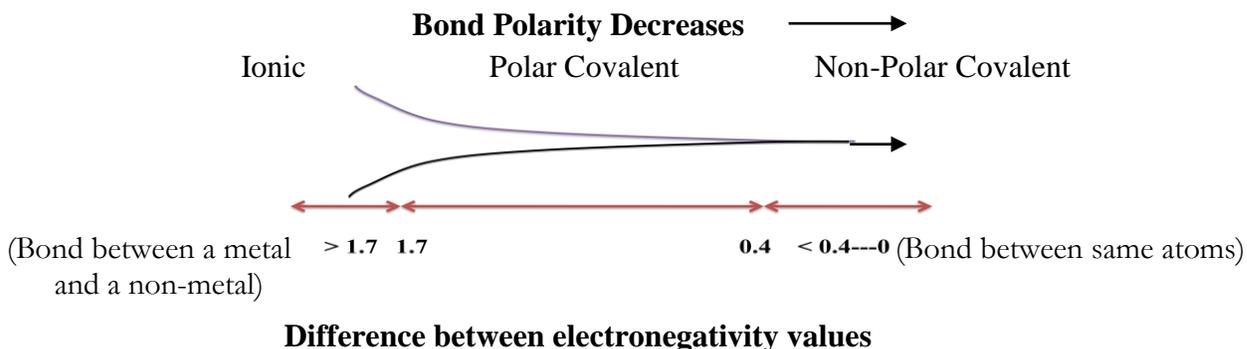
The difference between an ionic bond and a covalent bond lies in the difference between the electronegativity of the two atoms that form the bond. When the two atoms are of different electronegativity, the more electronegative element will pull the shared electron pair closer to its core, causing it to bear a little more negative charge than the less electronegative atom at the other end of the bond. Consequently the less electronegative atom would appear to be carrying a little positive charge. A polarized bond like this is being compared to a dipole—consisting two separated, equal, and opposite charges. We use a **dipole arrow** such as the one shown below to clearly indicate the polarization of the bond.



Positive end    Negative end

A dipole is described quantitatively by its **dipole moment**. A dipole moment is an experimentally measurable quantity and has a symbol “ $\mu$ .” The dipole moment  $\mu$  is defined as the product of the magnitude of the charge,  $Q$ , at each end of the dipole and the distance,  $r$ , between the charges:  $\mu = Qr$ . In SI units the charge  $Q$  is measured in coulombs; the distance  $r$  is measured in meters. So the dipole moment is measured in coulomb meters, C m. The understanding of dipole moments will become useful in the next section.

We use the concept of **bond polarity** to discuss the degree of polarization of any bond formed between two atoms. The greater the difference in the electronegativity values of these two atoms, the more polar the bond is, as illustrated below.



An ionic bond is, therefore, an extreme case of bond polarization—a complete separation of the positive and the negative end. When this happens, the dipole arrow is no longer appropriate in describing the ionic bond because the force of attraction between cations and anions is **non-directional**.

For covalent compounds, on the other hand, it is very important to draw each dipole arrow correctly because the sum of the individual dipoles gives rise to the net dipole for the molecule, the **molecular dipole**. Since the dipoles have directions, the summation of the individual dipoles is not simple addition but follows the rules for the addition of **vectors**. A vector is a quantity that has both a magnitude and a direction.

## 7.7 Polar and Non-Polar Molecules

We all know that oil does not mix with water. Why? Because water is polar and oil is non-polar, therefore they do not mix well. But this raises several questions:

How do you know water is polar and oil is non-polar?

How do we determine if any molecule is polar or not?

Why polar compounds and non-polar compounds do not mix well?

We will attempt to answer the first two questions here and will leave the third question to the next chapter.

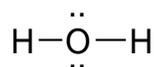
### Question 76.

Is water a polar molecule? Explain your answer.

### Answer:

To determine whether or not water is a polar molecule, we need to know if it has a non-zero molecular dipole moment. To add the individual dipoles correctly, we need to know the direction of the dipoles, hence the shape of the molecule. Here is how we proceed.

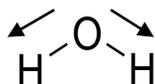
We first draw the Lewis structure for the water molecule, as shown below. The total number of valence electrons for water is  $2(1) + 6 = 8$ . Since we used **4** electrons to form the **2 covalent bonds** between O and the **2** H atoms, we have  $8 - 4 = 4$  electrons left to distribute among the elements that do not have octet status. We start with the more electronegative element and, in this case, it is oxygen. So we give the 4 electrons (2 pairs) to the oxygen atom.



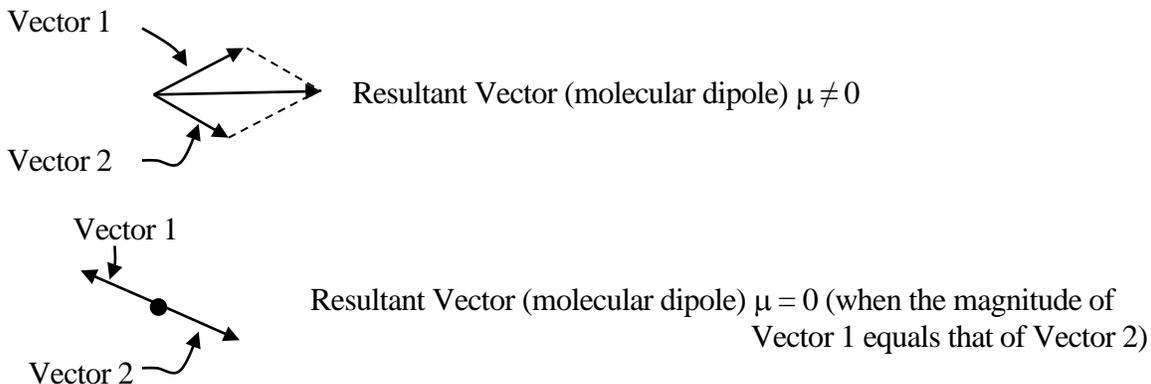
Now we count the total number of electron pairs and bonds around O, the central atom. Note that the answer is not 2, but **4**. This leads to a **tetrahedral** arrangement. When the four bonds around the central atom are identical, the molecular shape is a perfect tetrahedral with bond angles of  $109.5^\circ$ . However, in the water molecule, there are two covalent bonds and two lone pairs around the central atom O, so the actual arrangement of the electron pairs deviates from the ideal arrangement, also shown below. In the actual arrangement the lone pairs are drawn as two “puffy” electron clouds to stress the fact that they do occupy more space around the central atom than the bonding electron pairs. As a result the two bond pairs are somewhat pushed toward each other so the actual bond angle is measured to be  $104^\circ$ , smaller than in the ideal arrangement.



The water molecule as depicted above has two polar bonds, forming a  $104^\circ$  angle. It is commonly known as having a “**bent**” shape. For the purpose of finding the molecular dipole, we redraw the molecule and the individual dipoles as follows:

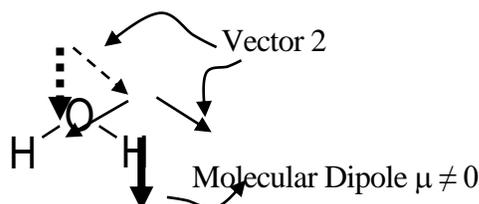


The molecular dipole comes from the **vector addition** of the two individual dipoles. A commonly used method for vector addition is the parallelogram method, as illustrated below.



A molecule with a non-zero molecular dipole moment is a polar molecule. When the molecular dipole moment is zero (opposite dipoles canceled each other, as shown above), the molecule is non-polar even if it contains polar bonds.

Below we illustrate how we find the molecular dipole for water. Since the water molecule has a non-zero dipole moment, it is a polar molecule.



### Question 77.

How polar is water?

#### Answer:

Molecular dipole moments can be experimentally measured. A comparison of the dipole moments of a few compounds is given below.

<u>Molecule</u>	<u>Dipole Moment (Units of <math>10^{-30}</math> C m)</u>
HF	6.36
H <sub>2</sub> O	6.17
SO <sub>2</sub>	5.42
NH <sub>3</sub>	4.88
HCl	3.43
H <sub>2</sub> S	3.12
BCl <sub>3</sub>	0
CO <sub>2</sub>	0

The data indicate that water is indeed a very polar molecule. This high polarity has made water a precious gift in the circle of life. We will dedicate the next few chapters to water. For now, we still have one more question to answer.

### Question 78.

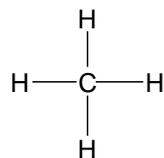
Why is oil non-polar?

#### Answer:

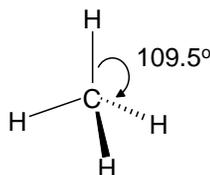
Oil is a general name for a wide range of fatty acid compounds. We will leave the discussion of the structures and properties of fatty acids to organic chemistry. For the moment, it will suffice to say that a major portion of the structures of most oil has a polarity that is similar to a very simple

covalent compound,  $\text{CH}_4$ , the methane molecule. Let's analyze the polarity of methane as a simple and reasonably acceptable way to answer our question.

The Lewis structure of  $\text{CH}_4$  renders it the perfect example of the ideal tetrahedral arrangement—four identical C—H bonds around the C central atom, with no lone pairs, as shown below.

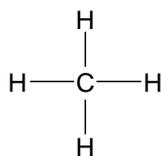


Lewis structure

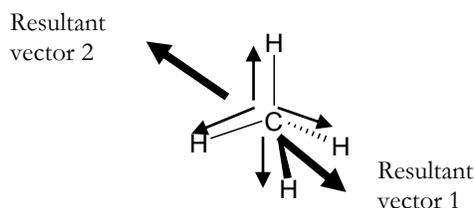


Molecular shape

Although each C—H bond is polar the resultant dipoles from any two pairs of individual dipoles are equal but pointing to opposite directions, thus canceling each other. We get the same result by using either the Lewis structure (flat) or the actual molecular shape (3-D), as shown below.



Lewis structure



Molecular shape

Molecular Dipole Moment  $\mu = 0$

Since the molecular dipole moment is zero, the methane molecule is non-polar.

To summarize, here is how we predict whether any covalent molecule is polar or non-polar.

1. Draw the Lewis structure (in 3-D to be more accurate).
2. Draw the individual dipoles.
3. Find a resultant dipole for each pair of individual dipoles by vector addition. Do not use an individual dipole twice in the calculations.
4. Find the molecular dipole from the resultant dipoles by vector addition.
5. If the resultant dipoles do not cancel out, the molecule is polar; otherwise non-polar.

## Practice and Review for Chapter 7

Define (in your own words) the following terms:

Lewis Structure: \_\_\_\_\_

Free Radical: \_\_\_\_\_

Formal Charge: \_\_\_\_\_

Curved Arrow: \_\_\_\_\_

Polyatomic Ion: \_\_\_\_\_

Resonance Structures: \_\_\_\_\_

VSEPR: \_\_\_\_\_

Wedge/Dash Bonds: \_\_\_\_\_

Dipole: \_\_\_\_\_

Dipole Arrow: \_\_\_\_\_

Bond Polarity: \_\_\_\_\_

Dipole Moment: \_\_\_\_\_

Molecular Shape: \_\_\_\_\_

Individual Dipole: \_\_\_\_\_

Vector Addition: \_\_\_\_\_

Resultant Dipole: \_\_\_\_\_

Molecular Dipole: \_\_\_\_\_

## Water Science II: The Hydrogen Bond

*Opposites attract. It's only natural.*

**I**n **Question 21** we found that there are  $1.67 \times 10^{25}$  water molecules in 500.0 cc of water. How do the water molecules arrange themselves in the container (maybe a 600.0 mL beaker)? Every day we see water in all three physical states (gaseous, liquid and solid). What is the reason behind this magical transformation?

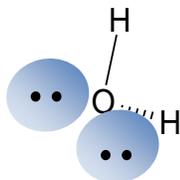
In an ionic molecule, it is the ionic bond (electrical attractions between opposite charges) that holds the ions together. In a covalent molecule, it is the covalent bond (formed by the sharing of electrons) that holds the atoms together. What holds the molecules together? To answer this question, we need to look at the interaction among molecules. What “intermolecular forces” hold the molecules together?

There are several types of **intermolecular forces**. **The most important one is called the Hydrogen bond.**

### 8.1 The Hydrogen Bond

What and how many intermolecular forces can we find among water molecules? To find the answer we need to dive back into the world of atoms and molecules and, most importantly, the world of electrons. It is time for day-dreaming.

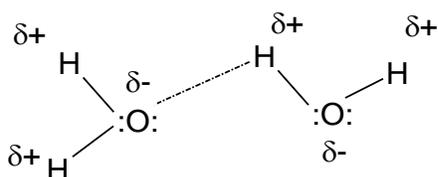
OK, I see the bent water molecule now, with the “puffy” lone pairs on the oxygen atom. I even see the individual dipoles. H atoms are the positive ends and O is the negative end.



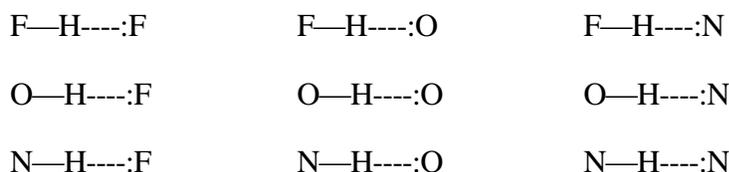
The polarization of charges within a molecule is the key to understanding intermolecular forces.

Remember that hydrogen has only one electron around its nucleus. Now that this electron is “pulled away” by the oxygen atom, we almost can see the “naked” nucleus of hydrogen—a small, positive “dot.”

What happens, when you put two water molecules together, is only natural. Opposites attract. The “naked” H nucleus is inevitably attracted to the “puffy” lone pairs of a nearby oxygen atom. This attraction is so strong that it is considered to be quite like a bond, specifically named **hydrogen bond**, and depicted by a dashed line, as shown below.



The hydrogen bond is the strongest of all intermolecular forces. It is much weaker, however, when compared to the real bonds—ionic and covalent bonds. Hydrogen bonds are **only** formed between **H** and the three most electronegative elements in the periodic table, namely, **F**, **O**, and **N**. By far the most common hydrogen bonds are therefore the following combinations:



H—bonds that give the double helix shape of DNA

## 8.2 Other Intermolecular Forces

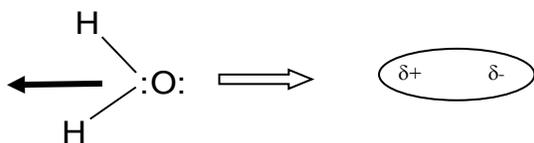
So far we have seen three major types of interactions among atoms, molecules, and ions. Whether we describe them as covalent bonds, ionic bonds, or intermolecular forces such as hydrogen bonds, they all result from **electrostatic attractions** and **repulsions** between positive nuclei and negative electrons.

Such electrostatic attractions can be seen in yet two more forms—two other types of forces that are much weaker than the three “bonds” but nevertheless play important roles in holding molecules together.

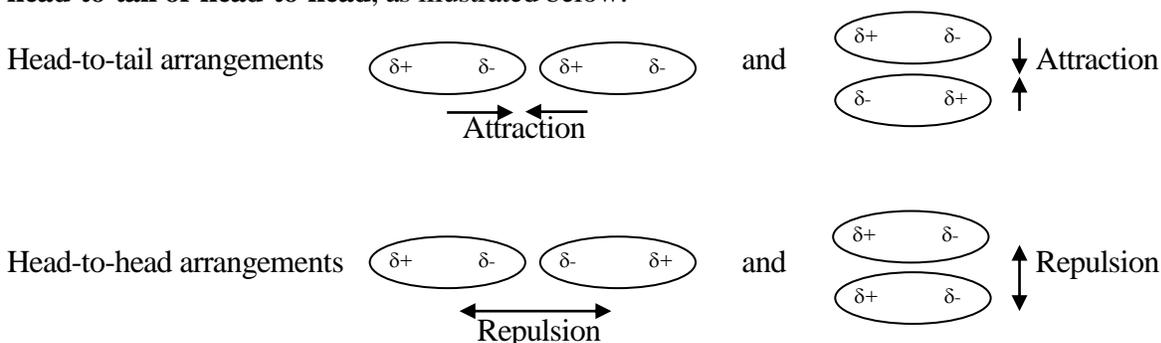
### Dipole-Dipole Forces

Polar covalent molecules have non-zero dipole moments. Thus each of them can be viewed as a dipole, as shown below using the water molecule as an example. The direction of the dipole is the

direction of the molecular dipole—the resultant dipole from the vector addition of the individual dipoles.



When two of such dipoles are put together, there are only two ways in which they align themselves, **head-to-tail or head-to-head**, as illustrated below.



The head-to-tail arrangements have a lower energy and therefore, more common, than the head-to-head arrangements. So there is an **overall attraction** between the polar molecules. This is called the **dipole-dipole (intermolecular) forces**.

Dipole-dipole forces exist in all polar molecules. When the dipoles are far apart, however, the attractions and repulsions almost cancel each other. So dipole-dipole forces are only significant when the dipoles are close together.

### London (Dispersion) Forces

#### Question 79.

Nitrogen is a non-polar molecule. What holds the nitrogen molecules together in liquid nitrogen?

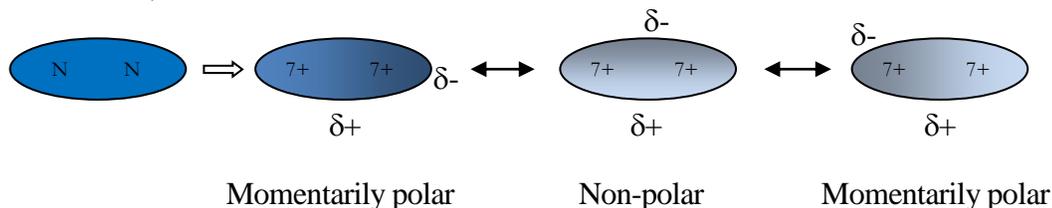
#### Answer:

Have we made the claim earlier that all forces are electrostatic in nature? Have we used many examples to show that “opposites attract” is the single thread that holds all things together? Yes we did and we stand by our words. So where would the “opposite charges” come from in a non-polar molecule? The best example is the  $N_2$  molecule. It does not have a net dipole!

But it is also a fact that  $N_2$  molecules can stick together in a liquid state found at very low temperatures. How do we explain this? The popular saying goes: engineers do, scientists explain. We need to **propose an explanation** for this natural phenomenon. This daunting task was

undertaken in 1926 by German physicist Fritz London (1900-1954). Here is how he saw it and I think it makes total sense.

Let's look at the nitrogen molecule in detail. It has two nuclei, each carries 7 positive charges. It has a total of 14 electrons. Remember that the electrons are constantly moving around, such that while the positive centers in the molecule are relatively fixed in position, the negative centers shift from moment to moment, as illustrated below.



Thus although the nitrogen molecules appear to be non-polar on average, at any one instant each is momentarily polar and has an **instantaneous dipole moment**. These momentarily polar molecules also choose the head-to-tail arrangement when put together, creating an overall attractive force—called **London force**.

This is why even non-polar molecules such as  $N_2$  attract each other.

London forces are different in different molecules. What factors affect the strength of London forces?

### 8.3 Polarizability

Now it is a good time to introduce the concept of **polarizability**. We see in the previous section how nitrogen molecules form instant dipoles (two opposite and equal charges) because of the movement of the electrons within the molecule. The magnitude of such instant dipole moments is directly proportional to the distance between the two opposite charges. The easier it is for the electrons to move around, the farther away the negative center might be from the positive center, thus the greater the distance between the opposite charges, and the greater the instantaneous dipole moments.

Polarizability is a measure of the ease with which a molecule creates instant dipoles. Simply put, if a non-polar molecule can easily polarize itself, it has a good polarizability.

In the same way non-polar molecules polarize instantaneously, atoms also polarize momentarily. Different atoms also have different polarizability.

In an atom, the electrons that move around most are the valence electrons. They are the most far from the nucleus and are held less strongly than the other electrons. They make the greatest contribution to the polarizability of the atom. In the periodic table, when we go down any group, the valence electrons of the elements locate farther and farther from the nucleus of the respective elements. Since the core charge is constant in any given group, we expect **polarizability to increase as atomic size increases** from top to bottom within a group.

In a molecule a dipole is induced in each atom, and the total induced-dipole moment is the resultant of all these small dipoles. Hence a large molecule with many atoms has larger polarizability than a small molecule.

The polarizability of a molecule increases with both increasing **size** and increasing **number** of the atoms in the molecule. Greater polarizability means stronger London forces. Thus molecules with more atoms and larger atoms have greater London forces. We can also say:

The greater the molar mass of the molecule, the greater the London forces.

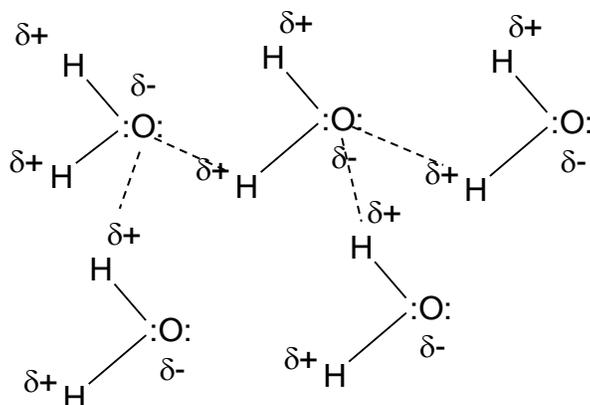
London forces exist among all molecules and are particularly important for larger molecules. They are quite often stronger than the dipole-dipole forces between polar molecules. In summary, whenever we want to know what holds molecules together, we should always consider these three intermolecular forces: **H-bonds, dipole-dipole forces, and London forces.**

### Question 80.

Illustrate how do the water molecules arrange themselves in a sample of pure water?

#### Answer:

The best picture I can think of would be like this (in two dimensions):



The water molecules would arrange themselves to maximize all intermolecular forces. Since each oxygen atom has two lone pairs, it can form two H-bonds with two nearby “almost naked” hydrogen atoms.

## 8.4 The Vapor, the Water, and the Ice; It's All about Freedom

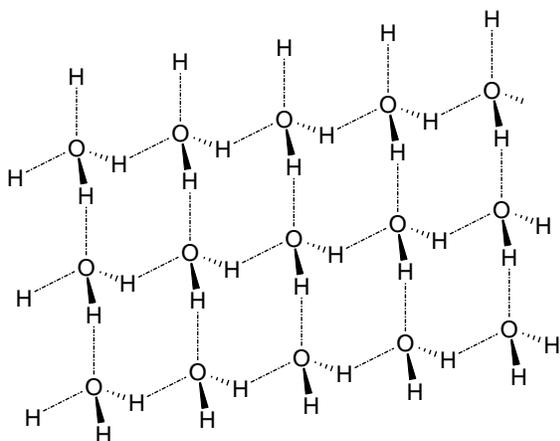
### Question 81.

How can you explain the three forms of water and the fact that ice floats in water?

**Answer:**

Water boils at 100 °C and freezes at 0 °C under 1 atm and at sea level. Clearly the temperature of water is the key factor behind water's magical power of transformation. Temperature is a measure of the **kinetic energy** (the energy to move) of the molecules in any substance. The higher the temperature, the greater the kinetic energy the molecules have.

Let's start from the solid state. At 0 °C and below, the water molecules have very low kinetic energy, so they don't move around much. In fact they stay in such a position that the molecules form a regular array that gives the structure of ice and the **rigidity** of ice. The best picture I can think of would be like this (in three dimensions):



Each water molecule is surrounded by a tetrahedral arrangement of four other water molecules to which it is bound by hydrogen bonds. Each oxygen atom forms two covalent bonds with two hydrogen atoms within the water molecule, and two hydrogen bonds with another two hydrogen atoms of neighboring water molecules.

When the temperature is increased, the kinetic energy of the water molecules increase and they move around more freely. Some of the H-bonds are broken and the ice structure collapses. The ice melts into water.

For most substances the density of their solids is greater than that of their liquids. This is because the molecules usually pack more closely together in the solid form than in the liquid form. However, ice floats in water. This means that the density of ice is smaller than that of water. This is the result of the special ice structure. Although very strong and rigid, the ice has a very open structure. There are plenty of empty spaces (hence low density). When ice melts, water molecules are able to pack more closely together so the density of water is greater than that of ice.

As the temperature continues to increase, the kinetic energy of each water molecule also continues to increase; more water molecules are able to move around more and more freely, thus more and more H-bonds are broken, and more and more dipole-dipole forces and London-forces are weakened. When a water molecule moves farther enough away from other water molecules, it is free of attractive forces from other water molecules, it escapes into the atmosphere (evaporates). At 100 °C all water molecules have enough kinetic energy to “travel” far away from other water molecules, the water turns into vapor.

The above explanation can be applied to the **phase changes** (switching between different physical states) of most substances. From solid to liquid and to gaseous state, temperature is the “freedom fighter” that helps to liberate molecules from intermolecular forces.

## Practice and Review for Chapter 8

Define (in your own words) the following terms:

Hydrogen Bond: \_\_\_\_\_

Intermolecular Forces: \_\_\_\_\_

Dipole-Dipole Forces: \_\_\_\_\_

London (Dispersion) Forces: \_\_\_\_\_

Instantaneous Dipole Moment: \_\_\_\_\_

Polarizability: \_\_\_\_\_

Phase Changes: \_\_\_\_\_

### Short-Answer Questions:

1. Use drawings to illustrate the head-to-tail and head-to-head arrangement of dipoles.
2. How does polarizability change going from top to bottom in a group?
3. What is the most important intermolecular force in water? Use drawings to illustrate the intermolecular interaction among water molecules.
4. What is special about the structure of ice? Explain why ice floats in water.

## How to Shift a Chemical Equilibrium

*Stress can be relieved by reacting to restore the balance.*

All chemical reactions carried out in a *closed system* eventually reach a state of dynamic equilibrium in which the concentrations of all the reactants and products do not change with time. A system is *closed* if the total mass of the reactants and the products remains constant. In other words, the system has no exchange with the outside world whatsoever. Since we can view every reaction as in an equilibrium state, it would be useful to learn some important skills in dealing with equilibria.

### 9.1 The Equilibrium Constant and the Reaction Quotient

For any chemical equilibrium we can write a **balanced** general equation as this



where the coefficients for the reactants and products are represented by lower case letters.

Once the equilibrium is reached, the concentrations of the products and the reactants remain constant. This has led to the establishment of a quantity called the **equilibrium constant**. The capital letter K is used as the symbol for the equilibrium constant.

In general, the equilibrium constant for any reaction is written as the product of the concentrations of all products divided by the product of the concentrations of all reactants. If there is a coefficient in front of a participant, the coefficient should be used as a power of the concentration of that participant.

For the above general equation, the equilibrium constant expression is written as

$$K = \left( \frac{[C]^c [D]^d}{[A]^a [B]^b} \right)_{\text{eq}}$$

Note that it is the products over reactants.

All concentrations in the equilibrium constant expression are equilibrium concentrations.

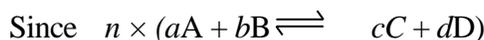
We can write a similar relationship for the concentrations of all participants at any given time of the reaction. Such a relationship is called the **reaction quotient, Q**.

For the general equation on the previous page, the reaction quotient expression is written as

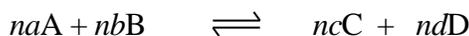
$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

At a given temperature, the equilibrium constant is a constant for a given reaction. However, the reaction quotient can be different at any moment before the reaction reaches equilibrium. By comparing the value of the reaction quotient with the equilibrium constant, we can predict the direction of a reaction.

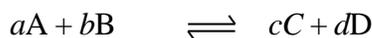
Because the coefficients are raised as powers in the equilibrium constant expression, when we multiply the equation by a constant,  $n$ , we need to also raise the equilibrium constant  $K$  to a power of  $n$ , as shown below.



equals

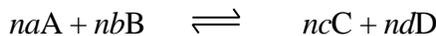


therefore, if for



$$K = \left( \frac{[P]^p[Q]^q[R]^r}{[A]^a[B]^b[C]^c} \right)_{\text{eq}}$$

Then for



$$K_{\text{new}} = \left( \frac{[C]^c[D]^d}{[A]^a[B]^b} \right)_{\text{eq}} = \left( \frac{[C]^c[D]^d}{[A]^a[B]^b} \right)_{\text{eq}}^n = K^n$$

## 9.2 Simultaneous Reactions

Sometimes one observed overall reaction is the final outcome of several reactions taking place at the same time. For example, the following three reactions occur simultaneously,





For the overall reaction which is the sum of the three reactions above



we can write

$$K_{\text{overall}} = K_1 \times K_2 \times K_3 = \left( \frac{[P]^p [Q]^q}{[A]^a [B]^b} \right)_{\text{eq}} \times \left( \frac{[R]^r}{[Q]^q [C]^c} \right)_{\text{eq}} \times \left( \frac{[S]^s}{[D]^d [R]^r} \right)_{\text{eq}} = \left( \frac{[P]^p [S]^s}{[A]^a [B]^b [C]^c [D]^d} \right)_{\text{eq}}$$

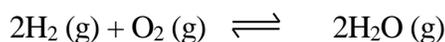
The important point to remember is:

When we **add** several **reactions** to obtain an overall reaction, we **multiply** their **equilibrium constants** to obtain the equilibrium constant for the overall reaction.

### 9.3 The Position of Equilibrium

The value of equilibrium constant can be used to predict the position of equilibrium.

For example, the formation of H<sub>2</sub>O from H<sub>2</sub> and O<sub>2</sub>,

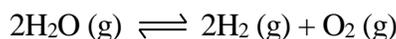


has the equilibrium constant

$$K = \left( \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2 [\text{O}_2]} \right)_{\text{eq}} = 5.9 \times 10^{40}$$

This equilibrium constant is so large that we consider the formation reaction goes to completion.

On the other hand, the equilibrium constant for the decomposition of water,



has the expression

$$K_{\text{decomp}} = \left( \frac{[\text{H}_2]^2 [\text{O}_2]}{[\text{H}_2\text{O}]^2} \right)_{\text{eq}}$$

which is the reciprocal of the K for the formation of water.

$$K_{\text{decomp}} = \left( \frac{[\text{H}_2]^2 [\text{O}_2]}{[\text{H}_2\text{O}]^2} \right)_{\text{eq}} = \frac{1}{K} = \frac{1}{5.9 \times 10^{40}} = 1.7 \times 10^{-41}$$

This equilibrium constant is so tiny that we consider it impossible for water to voluntarily decompose into H<sub>2</sub> and O<sub>2</sub>.

This example shows that, in general:

The equilibrium constant for a reaction as written from **right to left** is the **reciprocal** of the equilibrium constant for the reaction written from **left to right**, or,  $K_{\text{forward}} = \frac{1}{K_{\text{backward}}}$

## 9.4 Heterogeneous Equilibria

So far we have been mostly talking about chemical reactions occurring in aqueous solution, a homogenous system. However, many equilibria involve solids and gases, solids and liquids, or liquids and gases. These equilibria are called **heterogeneous equilibria**.

An example is the decomposition of calcium carbonate, which when heated gives calcium oxide and carbon dioxide:



The equilibrium constant for this reaction is,

$$K = \left( \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]} \right)_{\text{eq}}$$

But CaCO<sub>3</sub> and CaO are pure solids. For solids the term concentration does not apply. The number of molecules or ions in a given volume of a pure solid is fixed (measured by density) and cannot vary. Thus the “concentration” of a pure solid, the number of moles per liter, is constant and is independent of the amount of the pure solid that is present. So both [CaCO<sub>3</sub>] and [CaO] are constant.

The concentration of CO<sub>2</sub>, however, does vary and is dependent on the partial pressure of CO<sub>2</sub> in the system (the proportion of CO<sub>2</sub> in the “air”). We can rearrange the above equilibrium constant expression to give

$$K_{\text{new}} = K \times \frac{[\text{CaCO}_3]}{[\text{CaO}]} = [\text{CO}_2]_{\text{eq}}$$

This equilibrium constant shows that, in a closed system, the decomposition of CaCO<sub>3</sub> will reach equilibrium when the proportion of CO<sub>2</sub> in the “air” inside the system reaches [CO<sub>2</sub>]<sub>eq</sub>. However, if the reaction is carried out in the open air, the CO<sub>2</sub> diffuses away and its concentration in air will never reach [CO<sub>2</sub>]<sub>eq</sub>. So the decomposition will keep going until all the CaCO<sub>3</sub> is turned into CaO and CO<sub>2</sub>.

The same consideration can be applied to pure liquids in heterogeneous equilibria. In general we can state:

The pure solids and liquids taking part in heterogeneous equilibria are not included in the equilibrium constant expression.

## 9.5 Le Châtelier's Principle

The example of the decomposition of  $\text{CaCO}_3$  into  $\text{CaO}$  and  $\text{CO}_2$  in the open air illustrates one of several ways to shift the position of a chemical equilibrium towards producing more products—by **reducing the concentration of the products**.

We now introduce how to predict the direction of a reaction by comparing the reaction quotient,  $Q$ , with the equilibrium constant,  $K$ .

For any equilibrium,



We have

$$K = \left( \frac{[C]^c [D]^d}{[A]^a [B]^b} \right)_{\text{eq}} \quad \text{and} \quad Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{at any time of the reaction}$$

If we want to shift the equilibrium towards producing more products, we should make sure that  $Q < K$ . If we want to shift the equilibrium towards producing more reactants, we should make sure that  $Q > K$ .

In other words, there are two ways to shift the position of equilibrium forward:

- Add more reactants, or
- Remove products.

By constantly adding more reactants or removing products, the equilibrium will be forced to shift forward until the completion of the reaction.

Similarly, there are also two ways to shift the position of equilibrium backward:

- Reduce the amount of reactants, or
- Add products.

Such manipulations of the position of any equilibrium are possible because of a fundamental property associated with any equilibrated system:

**If any of the conditions affecting a system at equilibrium is changed, the position of the equilibrium shifts so as to minimize the change.**

In other words,

**When the balance of an equilibrated system is disturbed, the system reacts to restore the balance.**

This is called **Le Châtelier's principle**.

In terms of concentration change, Le Châtelier's principle can be restated as:

When the concentrations of any of the reactants or products in a reaction at equilibrium are changed, the position of the equilibrium shifts so as to reduce the change in concentration that was made.

Since the equilibrium constant is dependent on temperature, changing the temperature at which to carry out the reaction can also shift the equilibrium. If we know the equilibrium constants at both temperatures before and after the change, we can quantitatively predict the direction of the shift.

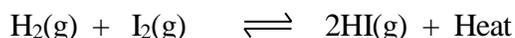
Sometimes we can apply Le Châtelier's principle to qualitatively predict the effect of temperature on the position of equilibrium. To do this we need to know whether the reaction is exothermic or endothermic. An **exothermic reaction** gives out heat whereas an **endothermic** reaction takes in heat.

### **Question 82.**

The formation of hydrogen iodide from hydrogen and iodine is an exothermic reaction. Predict how increasing or decreasing the temperature of the reaction will shift the equilibrium.

### **Answer:**

We write the reaction equation, including heat:



For this reaction increasing temperature is the same as adding a product, according to Le Châtelier's principle, the equilibrium will shift to the reactants side in order to reduce the stress from added heat.

On the other hand, reducing the temperature of the reaction is equivalent to removing a product. This will shift the equilibrium to the product side in order to make up for the heat lost.

If a high yield of HI is expected from this reaction, the reaction should be carried out under cooling conditions where the heat produced as a byproduct of the reaction can be constantly removed.

## Practice and Review for Chapter 9

Define (in your own words) the following terms:

Closed System: \_\_\_\_\_

Heterogeneous Equilibria: \_\_\_\_\_

Le Châtelier's Principle: \_\_\_\_\_

Exothermic Reaction: \_\_\_\_\_

Endothermic Reaction: \_\_\_\_\_

### Short-Answer Questions:

1. Write the equilibrium constant for a general chemical equilibrium.
2. State Le Châtelier's principle in terms of concentration change.
3. State Le Châtelier's principle in terms of temperature change.

## Water Science III: Formation of Water from Acids and Bases

*When opposites neutralize, you get salt water, too.*

### Question 83.

Hydrogen chloride (HCl) and hydrogen fluoride (HF) are both polar covalent compounds. When equal moles of HCl and HF are separately dissolved in water, experiments show that the HCl solution has a much higher electrical conductivity. Why?

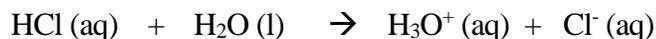
### Answer:

HCl and HF are both gaseous at room temperature and pressure. They dissolve in water easily because they are very polar molecules. The dipole-dipole attraction between these molecules and the water dipoles is strong enough to “pull” them into water. In fact, once in water, the attraction between the lone pairs on the oxygen atoms in water and the positive  $H^{\delta+}$  centers in these compounds is so strong that an O—H covalent bond is formed, as illustrated below for HCl. One



of oxygen’s lone pairs is turned into the O—H covalent bond and the pair of electrons forming the H—Cl bond is “pushed” to the chlorine atom, giving it a complete octet, forming the  $Cl^-$  anion. The **curved arrows** are used to indicate the electron movement.

We can write a net ionic equation for this process as follows:

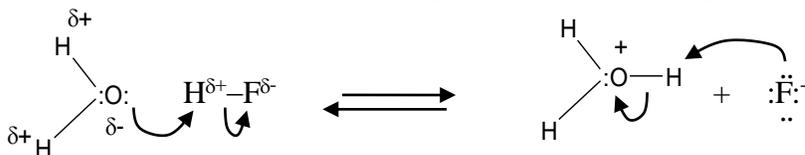


This equation is also called the **ionization equation** for HCl (aq). It shows how HCl **ionizes** in water. The experimental observation that the HCl solution has a very good electrical conductivity shows that HCl is a strong electrolyte. It ionizes completely in water. In other words, the above equation represents a **reaction that goes to complete** in the direction of the equation arrow.

The newly formed cation  $\text{H}_3\text{O}^+$  is called the **hydronium ion**. The positive charge is the formal charge located on the oxygen atom (draw the Lewis structure to see for yourselves). We can consider that the hydronium ion is formed from a water molecule and a “naked” hydrogen atom—the cation,  $\text{H}^+$ , formed after H loses its one and only electron.

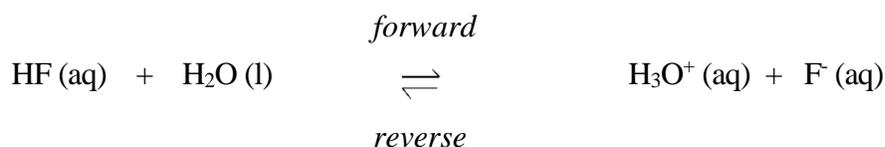
The  $\text{H}^+$  cation is in fact the “naked” proton of the hydrogen atom. Thus the  **$\text{H}^+$  ion** is often called the **proton**. When HCl dissolves in water, the H in HCl is given to water to form the product (the hydronium). This type of process is called “**proton transfer**.”

HF dissolves in water in the same way as does HCl. The only difference is that the lone pairs of



the fluoride ion are also strongly attracted to the positive  $\text{H}^{\delta+}$  centers in the hydronium ion. So a reverse reaction occurs between the hydronium ion and the fluoride ion to form water and HF, as indicated by the reversed reaction arrow in the illustration above.

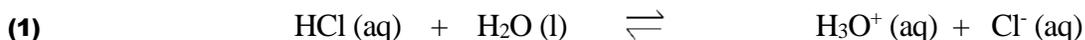
There appears to be a fight for “proton” between the  $\text{H}_2\text{O}$  and the HF molecules. The forward reaction transfers the proton from HF to  $\text{H}_2\text{O}$ . The reverse reaction transfers the proton from the hydronium ion to the fluoride ion. We write the net ionic equation for such processes as follows:



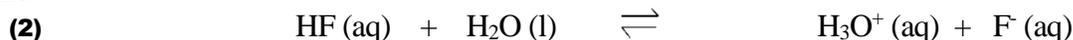
The double arrow “ $\rightleftharpoons$ ” is used to indicate that the forward and the reverse reactions is taking place simultaneously. In the beginning of the dissolving process, there are very little of  $\text{H}_3\text{O}^+$  and  $\text{F}^-$  ions in the solution, so the reverse reaction is going slower than the forward reaction. Gradually as the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{F}^-$  increase, the rate of the reverse reaction also increases. At the same time the rate of the forward reaction decreases as the concentrations of the reactants decrease. Eventually the **rate of the reverse reaction** becomes **the same** as the **rate of the forward reaction**, the system is said to be in a state of **equilibrium**.

It is important to see that equilibrium like this is a “**dynamic**” equilibrium. The forward and the reverse reactions are constantly going on. It is just that the numbers of molecules being formed and used up are **the same** so the **concentrations at equilibrium stay unchanged**.

Essentially every reaction can be treated as an equilibrium reaction. Compare these two equilibrium reactions:



And



Since experiments show that the HCl solution has a high electrical conductivity, we can say that at equilibrium, the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{Cl}^-$  must be much higher than the concentration of HCl in reaction (1). In other words, the equilibrium “lies” heavily toward the forward direction. Even though the reverse reaction in (1) is constantly going on the equilibrium concentration of HCl is so small that the forward reaction is considered a complete reaction. That is why HCl is considered a strong electrolyte.

Note that because water is the solvent we have been assuming that the concentration of water remains constant throughout the reaction.

For reaction (2), on the other hand, since experiments show that the HF solution has a low electrical conductivity, we can conclude that at equilibrium, the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{F}^-$  must be quite low. The equilibrium “lies” heavily toward the reverse direction.

A polar covalent compound that dissolves in water but does not ionize completely is called a **weak electrolyte**. HF is a weak electrolyte.

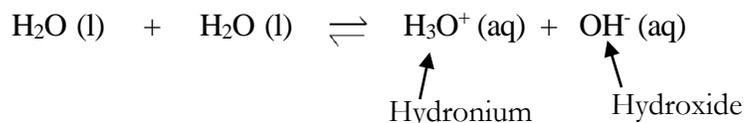
If strong electrolytes ionize completely in water, weak electrolytes ionize only slightly in water, then **non-electrolytes** must be those compounds that do not ionize at all in water.

How about water itself? Pure water does not conduct electricity. Does this mean that water does not ionize?

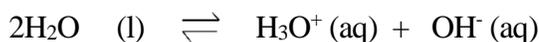
**W**ater does ionize. It is called self-ionization or **autoprotolysis**.

## 10.1 The Self-Ionization of Water

We can write the ionization equation for water as follows:



Or simply:



Because pure water does not conduct electricity at an observable scale, the concentrations of the hydronium ion and the **hydroxide ion** must be very small. How small are they?

**Question 84.**

At 25 °C, it has been found that  $[H_3O^+] = [OH^-] = 1.00 \times 10^{-7} \text{ mol L}^{-1}$ . What is the equilibrium constant for the self-ionization of water at 25 °C?

**Answer:**

For the self-ionization equilibrium of water



The equilibrium constant for the forward reaction is written as follows:

$$K = \left( \frac{[H_3O^+][OH^-]}{[H_2O]^2} \right)_{eq}$$

We can use this expression to calculate the equilibrium constant of water at 25 °C. However, a simplified treatment has been commonly used. This treatment is based on the fact that, in any dilute solution (including pure water), the concentration of water can be considered as nearly constant, this allows us to multiply K by  $[H_2O]^2$  to give a new constant,  $K_w$ , called the **ionic product constant of water**.

$$K_w = K \times [H_2O]^2 = ([H_3O^+][OH^-])_{eq}$$

$$\begin{aligned} \text{At } 25 \text{ }^\circ\text{C,} \quad K_w &= [H_3O^+] \times [OH^-] = (1.00 \times 10^{-7})(1.00 \times 10^{-7}) \\ &= 1.00 \times 10^{-14} \end{aligned}$$

This equilibrium constant,  $K_w$ , applies not only to pure water but also to the self-ionization of water in **any** aqueous solution. That is, the product of the concentrations of the hydronium ion and the hydroxide ion is always  $1.00 \times 10^{-14}$ , at 25 °C, in any aqueous solution that has reached equilibrium.

**Question 85.**

At 25 °C, it has been found that, in an aqueous solution, the initial concentration of  $H_3O^+$  is  $5.00 \times 10^{-5} \text{ mol L}^{-1}$ , and the initial concentration of  $OH^-$  is  $3.20 \times 10^{-4} \text{ mol L}^{-1}$ . Is the solution at equilibrium? If not, what will be the direction of the reaction?

**Answer:**

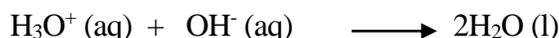
We calculate the reaction quotient and compare it with the  $K_w$  of water at 25 °C, which is  $1.00 \times 10^{-14}$ .

Assume that the concentration of water is constant, thus

$$\begin{aligned} Q_w &= Q \times [\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+][\text{OH}^-] \\ &= (5.00 \times 10^{-5})(3.20 \times 10^{-4}) \\ &= 1.60 \times 10^{-8} \end{aligned}$$

Since  $Q_w \gg K_w$ , the solution is not in equilibrium and the reaction will proceed in the direction that will reduce the concentrations of the  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  until  $Q_w = K_w$ .

The reaction before reaching equilibrium would be



In general, if we know the initial concentrations of the reactants and the products, we can predict the direction in which a reaction will proceed, as follows (provided that  $K$  is known):

- If  $Q < K$ , the concentrations of the products will increase and the concentrations of the reactants will decrease until equilibrium is reached.
- If  $Q > K$ , the concentrations of the reactants will increase and the concentrations of the products will decrease until equilibrium is reached.
- If  $Q = K$ , the reactants and the products are at equilibrium, and there will be no change in the concentrations of the reactants or the products.

## 10.2 The pH Scale

Most of us might know that in everyday life acids (such as vinegar and lemon juice) taste sour and bases (such as baking soda) taste bitter. In the laboratory we often use **pH paper** strips to identify if a solution is acidic or basic (alkaline). **Red litmus paper** and **blue litmus paper** are two examples of pH papers. A basic solution will turn **red litmus paper** blue whereas an acidic solution will turn **blue litmus paper** red. Some **pH paper** can be used to determine the pH of a solution to at least two significant figures. What is this pH scale?

The definition is

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$$

So for pure water at 25 °C,  $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = -\log_{10}[\underline{1.00} \times 10^{-7}] = \underline{7.000}$

Not an indication of accuracy

3 sig. fig.                      3 decimal places

Note that pH has no units. Also note that because pH is a logarithmic scale, the number before the decimal point should not be included in counting significant numbers. Thus the pH value usually has **one more digit** than the concentration value, as indicated above.

### Question 86.

At 25 °C, an aqueous solution has been found to turn red litmus paper blue and has a  $[\text{OH}^-] = 3.20 \times 10^{-4} \text{ mol L}^{-1}$ . Is the solution acidic or basic? What is the pH of the solution?

#### Answer:

We know that at 25 °C,  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}$ . For a solution with  $[\text{OH}^-] = 3.20 \times 10^{-4} \text{ mol L}^{-1}$ , it must have

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{3.20 \times 10^{-4}} = 3.13 \times 10^{-11}$$

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = -\log_{10}[3.13 \times 10^{-11}] = 10.5.$$

The solution is basic and has a pH of 10.5.

### Question 87.

What is pOH and what is the relationship between pH and pOH?

#### Answer:

pOH is defined similarly as is pH. So is  $\text{p}K_w$ . Therefore

$$\text{pOH} = -\log_{10}[\text{OH}^-] \quad \text{and} \quad \text{p}K_w = -\log_{10}K_w$$

Since at 25 °C,  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$ , we have

$\text{p}K_w = \text{pH} + \text{pOH} = 14$
---

This is a very useful relationship. Note that **14** is an exact number here.

All acidic solutions give a pH value less than 7 ( $[\text{H}_3\text{O}^+] > 10^{-7}$ ). All basic solutions give a pH value greater than 7 ( $[\text{H}_3\text{O}^+] < 10^{-7}$ ). The concentration of the hydronium ion plays a key role in defining the nature (acidic or basic) of a solution.

## 10.3 Acids

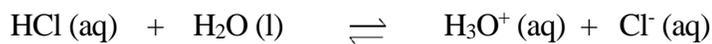
In **Question 83** (page 111) we saw the birth of the hydronium ion. It is formed when a substance, upon dissolving in water, donates its protons to the water molecules. In the same question we also

saw the difference between the HCl and the HF molecules. The former ionizes completely in water while the latter only ionizes to a small degree.

When a compound causes the formation of the hydronium ion, it increases the  $[\text{H}_3\text{O}^+]$  of the solution to greater than  $10^{-7} \text{ mol L}^{-1}$ . Such a solution will have a  $\text{pH} < 7$  and will behave like an acid. The more the increase in  $[\text{H}_3\text{O}^+]$ , the stronger the acid is. Thus HCl (aq) is a strong acid and HF (aq) is a weak acid.

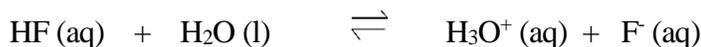
We mentioned in the answer to **Question 83** (page 112) that if we treat the ionization of HCl and HF both as equilibrium reactions, the one for HCl lies heavily on the product side and the one for HF lies heavily on the reactant side. We now can use the concept of equilibrium constant to quantitatively describe the strength of these acids.

We write the equilibrium constants for the two equilibria as follows:



$$K (\text{HCl}) = \left( \frac{[\text{H}_3\text{O}^+][\text{Cl}^-]}{[\text{HCl}][\text{H}_2\text{O}]} \right)_{\text{eq}}$$

And



$$K (\text{HF}) = \left( \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}][\text{H}_2\text{O}]} \right)_{\text{eq}}$$

In both cases if we again assume that  $[\text{H}_2\text{O}]$  is constant in dilute solutions, we can obtain new constants, respectively, as follows:

$$K_a(\text{HCl}) = K (\text{HCl}) \times [\text{H}_2\text{O}] = \left( \frac{[\text{H}_3\text{O}^+][\text{Cl}^-]}{[\text{HCl}]} \right)_{\text{eq}}$$

And

$$K_a(\text{HF}) = K (\text{HF}) \times [\text{H}_2\text{O}] = \left( \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} \right)_{\text{eq}}$$

The new equilibrium constant,  $K_a$ , is called the **acid dissociation constant** of an acid. Like any equilibrium constants, acid dissociation constants only change with temperature. Thus the value, once measured accurately for an acid at a given temperature, can be used in any aqueous solutions involving that acid at that temperature.

**As  $K_a$  is directly proportional to  $[\text{H}_3\text{O}^+]$ , it is a measure of the strength of the acid. The larger the  $K_a$ , the stronger the acid is.**

For really strong acids such as the HCl solution, at equilibrium the product of  $[\text{H}_3\text{O}^+]$  and  $[\text{Cl}^-]$  is so large and the  $[\text{HCl}]$  is so small (almost zero) that  $K_a$  becomes a very large value, as shown below:

$$K_a(\text{HCl}) = \left( \frac{[\text{H}_3\text{O}^+][\text{Cl}^-]}{[\text{HCl}]} \right)_{\text{eq}} = \left( \frac{\text{very large}}{\sim 0} \right)_{\text{eq}} \sim \text{very large}$$

In such cases we consider that the acid completely dissociates in the solution and  $[\text{H}_3\text{O}^+] = [\text{Cl}^-]$  according to the reaction stoichiometry. The amount of  $\text{H}_3\text{O}^+$  from the self-ionization of water is usually negligible compared to that formed from the strong acid.

There are only a few commonly encountered strong acids. These are **HCl** (hydrochloric acid), **HBr** (hydrobromic acid), **HI** (hydroiodic acid), **HNO<sub>3</sub>** (nitric acid), **H<sub>2</sub>SO<sub>4</sub>** (sulfuric acid), and **HClO<sub>4</sub>** (perchloric acid). Most acids have the magnitude of  $K_a$  values ranging from  $10^{-2}$  to  $10^{-13}$ . Below is a list of a few commonly encountered weak acids and their  $K_a$  values at 25 °C.

Name	Proton Transfer Reaction	$K_a$	$\text{p}K_a$
Phosphoric acid	$\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^-$	$7.5 \times 10^{-3}$	2.12
Hydrofluoric acid	$\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$	$3.5 \times 10^{-4}$	3.45
Acetic acid	$\text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$	$1.8 \times 10^{-5}$	4.74
Carbonic acid	$\text{CO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCO}_3^-$	$4.3 \times 10^{-7}$	6.37

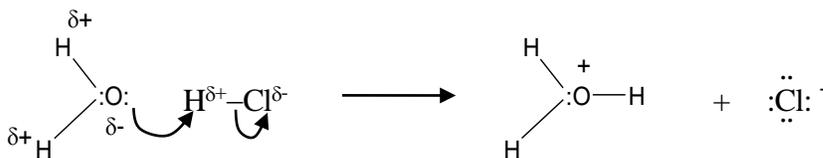
The  $\text{p}K_a$  values in the last column are obtained by doing the following calculation, for example

$$\text{p}K_a(\text{HF}) = -\log_{10}K_a(\text{HF}) = -\log_{10}(3.5 \times 10^{-4}) = 3.45$$

When comparing the strength of acids, it is easier to compare the  $\text{p}K_a$  values than the  $K_a$  values, for the same reason as the use of pH values to compare the acidity of aqueous solutions.

The larger the  $\text{p}K_a$ , the weaker the acid is.

To define an acid from a structural point of view, let's look at the dissociation of HCl in water one more time.



There are two ways to interpret this “proton transfer” process. One is to say that HCl donates a proton to water. The other is to say that HCl accepts a pair of unshared electrons from water. These two interpretations have led to two definitions for acids, as given below.

**The Brønsted-Lowry acids** are those compounds that **donate** one or more protons in a reaction. For example, HCl is a **proton donor** and therefore a Brønsted-Lowry acid. The general symbol for a Brønsted-Lowry acid is **HA**.

**The Lewis acids** are any compounds that **accept** a pair of unshared electrons in a reaction. For example, HCl is an **electron pair acceptor** and therefore a Lewis acid.

The Lewis definition of acids is a more general one and is very useful in Organic Chemistry. The Brønsted-Lowry acids can be considered a special group of Lewis acids that is commonly encountered in Inorganic Chemistry and Analytical Chemistry.

## 10.4 Bases

Both definitions of acids require a partner to make the acid ACID. This partner is called the **base**, as defined below.

**The Brønsted-Lowry bases** are those compounds that **accept** one or more protons in a reaction. They are **proton acceptors**. The general symbol for a Brønsted-Lowry base is **B**.

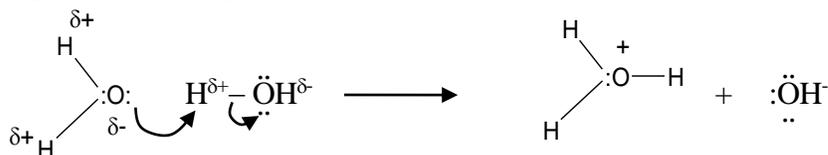
**The Lewis bases** are any compounds that **donate** a pair of unshared electrons in a reaction. They are **electron pair donors**.

### Question 88.

Use Lewis structures to illustrate the proton transfer process in the self-ionization of water. Is water an acid or a base?

#### Answer:

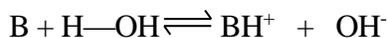
The proton transfer process can be illustrated as follows:



It shows that water is **both an electron pair donor** and an **electron pair acceptor**. Therefore water can act as both a Lewis base and a Lewis acid. Water is also a Brønsted-Lowry acid and a Brønsted-Lowry base. This is the **amphoteric** nature of water. That is, **water can act as both a weak acid and a weak base**.

Water is not the only covalent molecule that is amphoteric. It is important to bear in mind that when a compound usually acts as a Lewis acid, it does not mean that the compound can never act as a Lewis base.

When a base reacts with water, water acts as an acid, the proton donor. A general reaction can be written as



The base is said to be **protonated**. The production of the **hydroxide ion** is the general result of a base dissolving in water. This causes an increase of  $[OH^-]$  in the solution and consequently a decrease of  $[H_3O^+]$  as the system tries to satisfy the requirement that

$$[H_3O^+] \times [OH^-] = 1.00 \times 10^{-14} \text{ (at } 25^\circ\text{C)}$$

The decrease of  $[H_3O^+]$  leads to an increase of the pH of the solution. That's why alkaline solutions usually have pH values  $> 7$ .

The strength of bases can be quantitatively measured by the equilibrium constants for the reaction of the base with water (on previous page). Thus we have

$$K_b(B) = K(B) \times [H_2O] = \left( \frac{[BH^+][OH^-]}{[B]} \right)_{eq}$$

The equilibrium constant,  $K_b$ , is called the **base dissociation constant** of a base. **The larger the  $K_b$ , the stronger the base is.**

Like strong acids, strong bases are essentially completely converted to  $OH^-$  in water and they have very large dissociation constants. Weak bases have dissociation constants that are less than 1.0. Below is a list of a few commonly encountered weak bases and their  $K_b$  and  $pK_b$  values at  $25^\circ\text{C}$ .

<u>Name</u>	<u>Proton Transfer Reaction</u>	<u><math>K_b</math></u>	<u><math>pK_b</math></u> (= $-\log_{10}K_b$ )
Sulfide ion	$S^{2-} + H_2O \rightleftharpoons HS^- + OH^-$	$7.7 \times 10^{-2}$	1.11
Phosphate ion	$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^- + OH^-$	$4.8 \times 10^{-2}$	1.32
Carbonate ion	$CO_3^{2-} + H_2O \rightleftharpoons OH^- + HCO_3^-$	$2.1 \times 10^{-4}$	3.68
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	$1.8 \times 10^{-5}$	4.74

The larger the  $pK_b$ , the weaker the base is.

Note that when ammonia,  $NH_3$ , gets protonated, the product is a positive ion called ammonium ion,  $NH_4^+$ . At  $25^\circ\text{C}$  ammonia is a gas. In the laboratory we usually find the aqueous solution of ammonia. When aqueous ammonia participates in chemical reactions, it behaves like the base ammonium hydroxide,  $NH_4OH$ .

## 10.5 Hydroxides of Group I and II Metals

A special group of strong inorganic bases are the ionic compounds formed between the  $\text{OH}^-$  and the metal ions from the Group I and II metals. Group I metals form  $\text{M}^+$  ions so the bases formed are  $\text{LiOH}$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{RbOH}$ ,  $\text{CsOH}$  and  $\text{FrOH}$ . These are the strongest inorganic bases. That is why these metals are also called **alkali metals**. Among these **NaOH** (sodium hydroxide) and **KOH** (potassium hydroxide) are commonly used in undergraduate laboratories. They dissolve easily in water and dissociate completely, as shown below.



Or simply



Group II metals form  $\text{M}^{2+}$  ions so the bases formed are  $\text{Be}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$ ,  $\text{Ba}(\text{OH})_2$ , and  $\text{Ra}(\text{OH})_2$ . Group II metals are sometimes referred to as **alkaline earth metals**. Among them  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ , and  $\text{Ba}(\text{OH})_2$  are frequently encountered in inorganic laboratories.

These hydroxides can be formed from the reaction of the metals with water, as shown by the general equations below.



And



In all cases hydrogen gas is produced. Most of these reactions are highly exothermic. To avoid reactions with the moisture in the air, samples of these metals are usually kept in oil solvents (hydrophobic) that can keep the moisture away.

The hydroxides can also be formed from the reaction of the metal oxides with water, as shown by the general equations below.



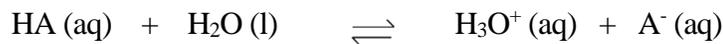
And



Hydrogen gas is not a product in these reactions.

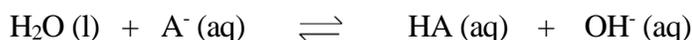
## 10.6 Conjugate Acid-Base Pairs

For any acid in water, we have



$$K_a(\text{HA}) = \left( \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \right)_{\text{eq}}$$

We expect the anion produced,  $\text{A}^-$ , to behave like a Lewis base, and we have



$$K_b(\text{A}^-) = \left( \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} \right)_{\text{eq}}$$

This shows that there is a **base** in any **acid** and, for any **base**, there is a corresponding **acid**. This “destined couple” is called a **conjugate acid-base pair**.

There is something very interesting about conjugate acid-base pairs. Let’s multiply  $K_a(\text{HA})$  by  $K_b(\text{A}^-)$  and see what happens.

$$\begin{aligned} K_a(\text{HA}) \times K_b(\text{A}^-) &= \left( \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \right)_{\text{eq}} \times \left( \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} \right)_{\text{eq}} \\ &= [\text{H}_3\text{O}^+] \times [\text{OH}^-] = K_w = 1.00 \times 10^{-14} \text{ (at } 25^\circ\text{C)} \end{aligned}$$

Are you amazed by what happened to the concentrations of HA and its conjugate base  $\text{A}^-$ ? Who would have thought that the “product” of “multiplication” would turn out to be “elimination?” Mathematics certainly played a big trick on the conjugate acid-base pair here.

Chemists, on the other hand, make a very good use of this special relationship. We can turn it into

$pK_a(\text{HA}) + pK_b(\text{A}^-) = pK_w = 14$
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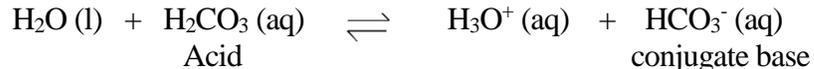
This “locked in” relationship not only allows us to calculate  $pK_a$  or  $pK_b$  when the other one is known but also gives us a way to compare the strength of acids and their conjugate bases, as shown in the following examples.

### Question 89.

The  $pK_a$  of  $\text{H}_2\text{CO}_3$  is 3.7. What is the dissociation constant of its conjugate base?

### Answer:

The dissociation equilibrium for  $\text{H}_2\text{CO}_3$  is



$$\text{pK}_b = 14 - \text{pK}_a = 14 - 3.7 = 10.3$$

$$\text{K}_b = 10^{-10.3} = 5.01 \times 10^{-11}$$

**Question 90.**

The values of  $\text{pK}_a$  for  $\text{H}_2\text{CO}_3$  and  $\text{HF}$  are 3.7 and 3.2, respectively. Which one is a stronger base,  $\text{HCO}_3^-$  or  $\text{F}^-$ ?

**Answer:**

$\text{HCO}_3^-$  is the conjugate base of  $\text{H}_2\text{CO}_3$  and  $\text{F}^-$  is the conjugate base of  $\text{HF}$ . Since  $\text{pK}_b + \text{pK}_a = 14$ , the **larger the  $\text{pK}_a$** , the smaller the  $\text{pK}_b$ . The smaller the  $\text{pK}_b$ , the larger the  $\text{K}_b$ , and **the stronger the base** is. Therefore  $\text{HCO}_3^-$  is a stronger base than  $\text{F}^-$ .

This example leads us to a very important observation:

**The larger the  $\text{pK}_a$  of an acid, the stronger its conjugate base is.**

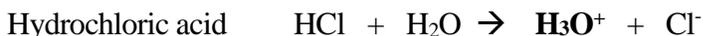
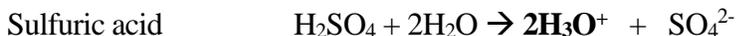
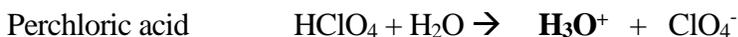
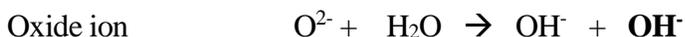
**Or**

**The weaker the acid is, the stronger its conjugate base is, and vice versa.**

Values of  $\text{pK}_a$  are available for an extensive group of compounds. We can use these values to predict the direction of acid-base reactions. *Stronger acids will react with stronger bases to produce weaker acids and weaker bases.*

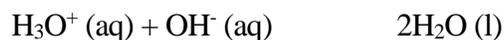
**10.7 The Leveling Effect of Water**

Strong acids and strong bases are all completely ionized in dilute aqueous solutions. Below we give a list of such ionization reactions.

**Strong acids:****Strong bases:**







When the reaction is complete, the amount of  $\text{H}_3\text{O}^+$  (aq) and  $\text{OH}^-$  (aq) in solution is governed by the self-ionization equilibrium of water, thus the **resultant salt water** will have

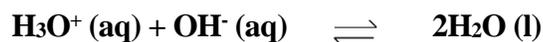
$$\text{pH} = \text{pOH} = 7.00$$

This observation leads us to another important conclusion:

**The reactions between any Brønsted-Lowry acids and bases are simply the reaction of  $\text{H}_3\text{O}^+$  (aq) and  $\text{OH}^-$  (aq) to form water.**

**Or**

**Any Brønsted-Lowry acid-base reactions can be represented by this net ionic equation**



Reactions between **strong** Brønsted-Lowry **acids** and **bases** are often called **neutralization reactions** because the result of the reaction gives a neutral ( $\text{pH} = 7$ ) solution. Other types of acid-base reactions will not necessarily produce neutral salt water, as we shall see in the next chapter.

## Practice and Review for Chapter 10

**Define (in your own words) the following terms:**

Autoprotolysis: \_\_\_\_\_

Equilibrium Constant: \_\_\_\_\_

Reaction Quotient: \_\_\_\_\_

$K_w$ : \_\_\_\_\_

pH: \_\_\_\_\_

pOH: \_\_\_\_\_

$\text{pK}_a$ : \_\_\_\_\_

$\text{pK}_b$ : \_\_\_\_\_

Brønsted-Lowry Acids and Bases:

---

Lewis Acids and Bases: \_\_\_\_\_

Amphoteric Nature of Water: \_\_\_\_\_

Proton Transfer: \_\_\_\_\_

Protonation and Deprotonation: \_\_\_\_\_

Conjugate Acid-Base Pair: \_\_\_\_\_

The Leveling Effect of Water: \_\_\_\_\_

Spectator Ions: \_\_\_\_\_

Hydronium Ion: \_\_\_\_\_

**Short-Answer Questions:**

1. List the six common strong acids.
2. List the four common weak acids.
3. List all alkali metals.
4. List all alkaline earth metals.
5. List the five common hydroxides.
6. What are the products of any acid base reaction?
7. Write a net ionic equation for any neutralization reaction.



## Water Science IV: pH of Salt Waters

*The strong one wins the pHight.*

Most aqueous solutions are some kind of salt solution. Mineral water contains some metal ions. Water in the swimming pools contains some anions formed from using  $\text{Cl}_2$  as a disinfectant. The pH values of these waters are never at exactly 7.00. The measurement and control of the pH of any solution require some basic understanding of the acid-base properties of the salts.

### 11.1 Are All Salt Waters Neutral?

**Salt** is the general name for compounds formed from acid-base reactions. Water is the other product. For example, table salt  $\text{NaCl}$  is a product of the reaction between  $\text{HCl}$  and  $\text{NaOH}$ .

Recall that ammonia,  $\text{NH}_3$ , when used as an aqueous solution, behaves like **ammonium hydroxide**,  $\text{NH}_4\text{OH}$ . We can write the acid-base reaction equation as



Because  $\text{NH}_4\text{OH} = \text{NH}_3 + \text{H}_2\text{O}$ .

Note that in this chapter we will not be writing the states for compounds in a reaction equation for simplicity. It is understood that all ions are hydrated.

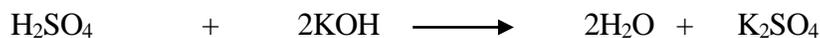
When salts dissolve in water, we can use the following rules of thumb to estimate the pH of the solution:

- Salts formed from strong acids and strong bases give neutral solutions,  $\text{pH} \sim 7$
- Salts formed from strong acids and weak bases give acidic solutions,  $\text{pH} < 7$
- Salts formed from weak acids and strong bases give basic solutions,  $\text{pH} > 7$

Between the acid and base involved in forming the salt, the **stronger one controls** the pH of the salt water. For example, let's take a look at the salts formed between the following acids and bases.

<u>Strong Acid</u>	<u>Strong Base</u>	<u>Weak Acid</u>	<u>Weak Base</u>
H <sub>2</sub> SO <sub>4</sub>	KOH	H <sub>3</sub> PO <sub>4</sub> (pK <sub>a</sub> = 2.12)	NH <sub>3</sub> (pK <sub>b</sub> = 4.74)

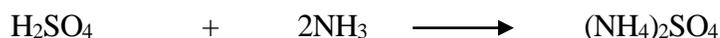
Assuming complete reaction:



Strong acid + Strong base  $\longrightarrow$  Neutral salt water

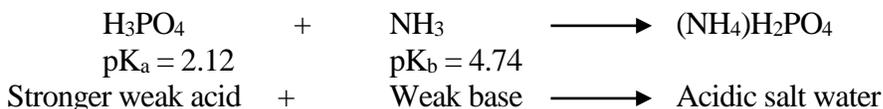


Weak acid + Strong base  $\longrightarrow$  Basic salt water



Strong acid + Weak base  $\longrightarrow$  Acidic salt water

For salts formed from weak acids and weak bases, such as the one below, we will have to compare the pK<sub>a</sub> value of the acid with the pK<sub>b</sub> value of the base to make a prediction, as shown below.



### Question 92.

How do you decide which one is stronger, H<sub>3</sub>PO<sub>4</sub> or NH<sub>3</sub>?

### Answer:

When a salt is formed from a weak acid and a weak base, such as (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub>, the situation is a bit complicated. There are two equilibriums coexisting in the salt solution, one of NH<sub>4</sub><sup>+</sup> and H<sub>2</sub>O, the other of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and H<sub>2</sub>O, as shown below.



Since there are equal moles of  $\text{NH}_4^+$  and  $\text{H}_2\text{PO}_4^-$  in the solution, one can estimate, without going into lengthy calculations, that at equilibrium there should be more  $\text{H}_3\text{O}^+$  than  $\text{OH}^-$  because  $K_a$  is larger than  $K_b$ . This means that the solution would be slightly acidic.

This agrees with the prediction based on the  $\text{p}K_a$  value of the acid and the  $\text{p}K_b$  value of the base.

It is less complicated to calculate the exact pH values for solutions of salts formed from either a strong acid and a weak base or a weak acid and a strong base. We will take you through these calculations in the following examples.

## 11.2 Calculating the pH of a Salt Solution

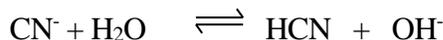
### Question 93.

Calculate the pH of a 0.200 M solution of sodium cyanide;  $\text{p}K_b(\text{CN}^-) = 4.70$  at  $25^\circ\text{C}$ .

### Answer:

First we need to realize that this is a salt formed from a weak acid (HCN) and a strong base (NaOH). HCN is a weak acid simply because it is not one of the six strong acids. So we predict that the pH should be greater than 7.

When sodium cyanide, NaCN, dissolves in water, it completely dissociates into  $\text{Na}^+$  and  $\text{CN}^-$  ions. Thus the initial concentrations for both ions are 0.200 M. The  $\text{CN}^-$  ions, however, immediately set up equilibrium with water, as all weak acids and bases do, as follows:



This equilibrium produces more  $\text{OH}^-$  and therefore makes the solution basic. If we find the  $[\text{OH}^-]$  at equilibrium, we can find the pH of the solution. Note that  $\text{Na}^+$  here is a spectator ion.

We find the equilibrium concentrations by making use of the equilibrium constant expression and the  $\text{p}K_b$  value given, assuming that the reaction takes place at  $25^\circ\text{C}$ .

Since  $\text{p}K_b = 4.70$ ,  $K_b = 2.0 \times 10^{-5}$ . Let  $[\text{OH}^-]_{\text{eq}}$  be  $x$

	$\text{CN}^- + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{HCN}$	+	$\text{OH}^-$
Initial concentrations	0.200		0		0
Equilibrium concentrations	$0.200 - x$		$x$		$x$

Thus we have

$$K_b = \left( \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} \right)_{\text{eq}} = \frac{x^2}{0.200 - x} = 2.0 \times 10^{-5}$$

To make solving the equation easier, we assume that  $x \ll 0.200$ , so  $0.200 - x \approx 0.200$ . This allows us to simplify the equation into

$$\frac{x^2}{0.200} = 2.0 \times 10^{-5}$$

and

$$x^2 = 0.200 \times 2.0 \times 10^{-5} = 4.0 \times 10^{-6}$$

$$x = 2.0 \times 10^{-3} \text{ mol L}^{-1} = [\text{OH}]_{\text{eq}}$$

The concentration  $2.0 \times 10^{-3}$  is indeed much smaller than 0.200 so we can say that our initial assumption, that  $x \ll 0.200$ , is valid.

Therefore

$$\text{pH} = 14 - \text{pOH} = 14 - (-\log 2.0 \times 10^{-3}) = 11.30$$

↑
↑
↑

Treated as an exact number    2 sig. fig.    2 decimal places

The pH of the solution is greater than 7 as we predicted using the rules of thumb on page 123.

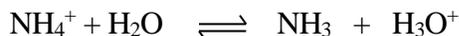
#### Question 94.

Calculate the pH of a 0.10 M solution of  $\text{NH}_4\text{Cl}$ ;  $\text{pK}_a(\text{NH}_4^+) = 9.2$  at  $25^\circ\text{C}$ .

#### Answer:

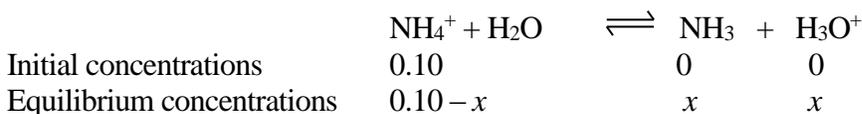
$\text{NH}_4\text{Cl}$  is formed from a strong acid (HCl) and a weak base ( $\text{NH}_4\text{OH}$ ). So we predict that the pH should be less than 7.

When  $\text{NH}_4\text{Cl}$  dissolves in water, it completely dissociates into  $\text{NH}_4^+$  and  $\text{Cl}^-$  ions. Thus the initial concentrations for both ions are 0.10 M. The  $\text{NH}_4^+$  ions, being the conjugate acid of the weak base  $\text{NH}_3$ , however, immediately set up equilibrium with water as follows:



This equilibrium produces more  $\text{H}_3\text{O}^+$  and therefore makes the solution acidic. If we find the  $[\text{H}_3\text{O}^+]$  at equilibrium, we can find the pH of the solution.

Since  $\text{pK}_a = 9.2$ ,  $K_a = 6 \times 10^{-10}$ . Let  $[\text{H}_3\text{O}^+]_{\text{eq}}$  be  $x$



Thus we have

$$K_a = \left( \frac{[NH_3][H_3O^+]}{[NH_4^+]} \right)_{eq} = \frac{x^2}{0.10-x} = 6 \times 10^{-10}$$

Assume that  $x \ll 0.10$ , so  $0.10 - x \approx 0.10$ . We have

$$\frac{x^2}{0.10} = 6 \times 10^{-10}$$

and

$$x^2 = 0.10 \times 6 \times 10^{-10} = 6 \times 10^{-11}$$

$$x = 8 \times 10^{-6} = [H_3O^+]_{eq}$$

The concentration  $8 \times 10^{-6}$  is much smaller than 0.10 so we can say that our initial assumption, that  $x \ll 0.10$ , is valid.

Therefore

$$\text{pH} = -\log 8 \times 10^{-6} = 5.1$$

$\uparrow$                        $\uparrow$   
 1 sig. fig.    1 decimal place

The pH of the solution is less than 7 as we predicted.

### 11.3 Buffer Solutions

The above two examples show that different salts, except those formed from strong acids and strong bases, can give salt solutions of different values of pH. The pH given by a particular salt is only dependent on the equilibrium between the anion and its conjugate weak acid (**Question 90**) or the cation and its conjugate weak base (**Question 91**). Using the expression from **Question 91**, we can obtain a general expression between  $K_a$ ,  $[H_3O^+]_{eq}$ , and the equilibrium concentrations of any conjugate weak acid-base pairs as follows:

$$K_a = \left( \frac{[NH_3][H_3O^+]}{[NH_4^+]} \right)_{eq} \iff K_a = \left( \frac{[base][H_3O^+]}{[acid]} \right)_{eq} = [H_3O^+] \left( \frac{[base]}{[acid]} \right)_{eq}$$

Taking negative logarithms of both sides of the general expression, we obtain

$$-\log K_a = -\log[H_3O^+] - \log \left( \frac{[base]}{[acid]} \right)_{eq}$$

That is

$$\text{p}K_a = \text{pH} - \log \left( \frac{[base]}{[acid]} \right)_{eq}$$

or

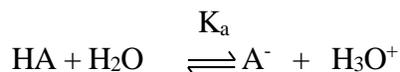
$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)_{\text{eq}}$$

We have seen in **Question 90** and **Question 91** that the equilibrium concentrations of the weak acid and base can usually be assumed to be the same as the initial concentrations ( $x$  is usually much smaller), so we can write

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)_{\text{initial}}$$

This relationship is called the **Henderson-Hasselbalch equation** and it allows us to calculate the pH of **any** salt solutions.

The most important application of the Henderson-Hasselbalch equation is in making **buffer solutions**. Let's look at the following general weak acid-base equilibrium.



If **extra  $\text{H}_3\text{O}^+$**  is added to the equilibrium, it will react with  $\text{A}^-$  to **form some extra HA and water**. If **extra  $\text{OH}^-$**  is added to the equilibrium, it will react with HA to **form some extra  $\text{A}^-$  and water**. As long as



the ratio  $\left(\frac{[\text{base}]}{[\text{acid}]}\right)_{\text{initial}}$  stays unchanged and **pH of the solution** stays unaffected. Thus a solution made by **mixing a weak base and its conjugate acid** is called a **buffer solution**, meaning that it has a **buffering capacity** to withstand small changes in  $[\text{H}_3\text{O}^+]$  or  $[\text{OH}^-]$  without changing the pH of the solution.

From the Henderson-Hasselbalch equation we can also see that, if we mix equal amounts of a weak base and its conjugate acid in water ( $[\text{base}] = [\text{acid}]$  and  $\frac{[\text{base}]}{[\text{acid}]} = 1$ ), we will get a solution with a  $\text{pH} = \text{pK}_a$  of the weak acid-base pair, as shown below.

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)_{\text{initial}} = \text{pK}_a + \log(1) = \text{pK}_a$$

This means that we can make buffer solutions of any desired pH simply by choosing the conjugate weak acid-base pair that has the right  $\text{pK}_a$ .

Not all buffer solutions are made with equal amounts of a weak acid and its conjugate base.

However, a buffer solution with  $\frac{[\text{base}]}{[\text{acid}]} = 1$  will have the best buffering capacity. Sometime several buffer systems are required to maintain a delicate pH balance. For example, the constant pH of

blood (7.40) is maintained by several conjugate acid-base pairs including  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ , and  $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ .

### Question 95.

Blood has a pH of 7.40. Use the Henderson-Hasselbalch equation to calculate the ratio of hydrogen carbonate ion,  $\text{HCO}_3^-$ , to carbonic acid,  $\text{H}_2\text{CO}_3$ , in blood;  $\text{pK}_a(\text{H}_2\text{CO}_3) = 6.37$ .

### Answer:

The Henderson-Hasselbalch equation for this buffer system is

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]} = \text{pK}_a + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

To solve for the ratio we rearrange the equation to

$$\log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \text{pH} - \text{pK}_a = 7.40 - 6.37 = 1.03$$

Therefore

$$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 10^{1.03} = 10.7 = 11$$

Since both ions are in the same solution (hence have the same volume), the mole ratio of  $\text{HCO}_3^-$  to  $\text{H}_2\text{CO}_3$  must also be **11 to 1**.

## 11.4 Indicators

Most chemical reactions are acid-base reactions. Depending on the nature of the acid and the base, solutions of different pH are obtained at the completion of the acid-base reaction. Sometimes an **indicator** is added to the solution to help signal the end of the reaction.

To function as an indicator, the compound must be a weak acid of an easily detectable color. More importantly, its conjugate base must have a different color so that a **color change** can be observed as pH changes.

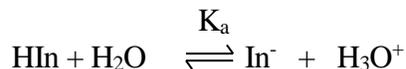
One of the most commonly used indicators is litmus. Its basic form has a blue color and its acidic form has a red color. When we dip a red litmus paper into a basic solution, the base reacts with the acidic form and turns it to the blue basic form. We see a color change from red to blue. When we dip a blue litmus paper into an acidic solution, the acid reacts with the basic form and turns it to the red acidic form. We see a color change from blue to red.

Another most commonly used indicator is phenolphthalein. Its basic form has a pink color and its acidic form is colorless. When the pH changes from acidic to basic, the colorless solution turns to

pink. This is a very detectable color change. Thus phenolphthalein is almost always used as an indicator for neutralization (acid-base titration) reactions.

When choosing an indicator, it is important to know at what pH range a color change occurs. As we are dealing with a conjugate acid-base pair, we can use the Henderson-Hasselbalch equation for this purpose.

We write a general acid-base equilibrium for any indicator HIn.



Using the Henderson-Hasselbalch equation we have

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{In}^-]}{[\text{HIn}]}\right)_{\text{eq}}$$

We can see that, when  $\frac{[\text{In}^-]}{[\text{HIn}]} = 1$ , that is, in the middle of the indicator's color change, we have  $\text{pH} = \text{p}K_a$ . This means we can choose a suitable indicator for a desired pH range by looking at the  $\text{p}K_a$  of the indicator. For the sensitivity of our eyes, a visible color change occurs over a range that is usually

$$\text{pH} = \text{p}K_a(\text{HIn}) \pm 1$$

The following are a few common indicators and their properties.

<u>Name</u>	<u>pK<sub>a</sub></u>	<u>pH Range</u>	<u>Acid Form</u>	<u>Color</u> <u>Base Form</u>
Methyl orange	4.2	3.1-4.4	Red	Yellow
Methyl red	5.2	4.2-6.2	Red	Yellow
Bromothymol blue	7.1	6.0-7.8	Yellow	Blue
Phenolphthalein	9.5	8.3-10.0	Colorless	Red

When using indicators, we should use the smallest amount that will give a clearly observable color. The color change should be detected at the earliest moment possible.

In most laboratories we use strips of pH paper to detect different pH by observing different color changes within a wide pH range, sometimes as wide as from  $\text{pH} = 1$  to 14. Such pH paper is impregnated with a solution called a **universal indicator**. The universal indicator is a mixture of several indicators that give several color changes within the defined pH range.

## 11.5 Polyprotic Acids

An acid that can donate more than one proton to a base is called a **polyprotic acid**. So far we have encountered a few polyprotic acids. For example,  $\text{H}_2\text{CO}_3$  and  $\text{H}_2\text{SO}_4$  are both diprotic acid.  $\text{H}_3\text{PO}_4$  is a triprotic acid.

For strong acids such as  $\text{H}_2\text{SO}_4$  (the **only** polyprotic acid indeed), the dissociation of both protons are complete reactions. We can write the ionization equation for  $\text{H}_2\text{SO}_4$  as follows:



For every mole of  $\text{H}_2\text{SO}_4$ , two moles of  $\text{H}_3\text{O}^+$  are produced.

For weak polyprotic acids such as  $\text{H}_3\text{PO}_4$ , however, the dissociation of protons is stepwise and each step is an equilibrium equation, as shown below.



$$K_{a1}(\text{H}_3\text{PO}_4) = \frac{[\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{PO}_4]} = 7.1 \times 10^{-3}$$



$$K_{a2}(\text{H}_3\text{PO}_4) = K_a(\text{H}_2\text{PO}_4^-) = \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]} = 6.2 \times 10^{-8}$$



$$K_{a3}(\text{H}_3\text{PO}_4) = K_a(\text{HPO}_4^{2-}) = \frac{[\text{PO}_4^{3-}][\text{H}_3\text{O}^+]}{[\text{HPO}_4^{2-}]} = 4.4 \times 10^{-13}$$

If we compare the equilibrium constants for the three steps, we can see that the dissociation of the proton becomes more difficult in step 2 and much more difficult in step 3. In other words, it is easy for the neutral  $\text{H}_3\text{PO}_4$  to donate one proton but it is harder for the negatively charged  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  to donate their protons. The more negatively charged the ion, the harder it is to give up a proton.

In a solution of  $\text{H}_3\text{PO}_4$  there always exists a combination of these species:  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ , and  $\text{H}_3\text{O}^+$ . By using the Henderson-Hasselbalch equation, however, we can manipulate the ratio of the species and obtain buffer solutions of different pH values that correspond to different values of  $\text{pK}_a$ , as shown below:

<u>Conjugate acid-base pair</u>	<u>Ratio</u>	<u><math>K_a</math></u>	<u><math>\text{pH} = \text{pK}_a</math></u>
---------------------------------	--------------	-------------------------	---

$\frac{[H_2PO_4^-]}{[H_3PO_4]}$	1	$7.1 \times 10^{-3}$	2.15
$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$	1	$6.2 \times 10^{-8}$	7.20
$\frac{[HPO_4^{2-}]}{[PO_4^{3-}]}$	1	$4.4 \times 10^{-13}$	12.36

We can see that the  $H_2PO_4^-/HPO_4^{2-}$  pair is an excellent buffer for maintaining a pH of 7.20. This is a buffer solution that is commonly used in biological sciences.

## 11.6 Dilutions

**Dilution** is a frequently used technique in most laboratories. Often it means adding water to a concentrated solution to make it less concentrated. The new concentration of the diluted solution can be calculated based on this understanding:

**The number of the solute molecules stays the same before and after the dilution.**

### Question 96.

Jimmy was given a stock solution that contains 55.85 ppm of  $Fe^{2+}$ . His job was to prepare five standard solutions, each with a different dilution. In his lab report he submitted the following table. The table indicates that he prepared the solutions by transferring, for example for solution 1, 10.00 mL of the stock solution into a 100.00 mL volumetric flask, and then diluting the stock solution by adding water to the 100.00 mL volume mark. He prepared solutions 2 to 5 similarly. He reported the concentrations of the diluted solutions in Table 1 but didn't include a sample calculation to show that he indeed performed the calculations himself. For this he would suffer a deduction of marks even if his values were all correct.

Show the calculations for the concentrations of solutions 1 and 2.

**Table 1. The Preparation of Standard  $Fe^{2+}$  Solutions**

Solution	Volume of Stock Solution (mL)	Total Volume of Diluted Solution (mL)	Concentration [ $Fe^{2+}$ ] (ppm)
1	10.00	100.00	5.585
2	5.00	100.00	2.79
3	3.00	100.00	1.68
4	2.00	100.00	1.12
5	1.00	100.00	0.559

**Answer:**

The unit **ppm** means parts per million, or more specifically **grams per 1 million milliliters**. It is a convenient unit for very dilute solutions. Jimmy's stock solution contains 55.85 grams of the  $\text{Fe}^{2+}$  ions in one million mL of solution. The total grams of  $\text{Fe}^{2+}$  ions in 10.00 mL of the stock solution can be calculated as follows:

$$\frac{55.85 \text{ grams}}{10^6 \text{ mL}} \times 10.00 \text{ mL}$$

After dilution, the total volume becomes 100.00 mL. Let the diluted concentration be  $x$ , the total grams of  $\text{Fe}^{2+}$  ions in 100.00 mL of the diluted solution can be calculated as follows:

$$\frac{x \text{ grams}}{10^6 \text{ mL}} \times 100.00 \text{ mL}$$

Since the total grams of  $\text{Fe}^{2+}$  ions do not change before and after dilution, we have

$$\frac{55.85 \text{ grams}}{10^6 \text{ mL}} \times 10.00 \text{ mL} = \frac{x \text{ grams}}{10^6 \text{ mL}} \times 100.00 \text{ mL}$$

Solving for  $x$ , we get

$$\frac{55.85 \text{ grams}}{10^6 \text{ mL}} \times 10.00 \text{ mL} = \frac{x \text{ grams}}{10^6 \text{ mL}} \times 100.00 \text{ mL}$$

$$x = \frac{55.85}{100.00} \times 10.00 = 5.585 \text{ ppm}$$

The sample calculation Jimmy should have included in his lab report could look like this

$$\text{Sample calculation: } M_2 = \frac{M_1 V_1}{V_2} = \frac{55.85 \text{ ppm} \times 10.00 \text{ mL}}{100.00 \text{ mL}} = 5.585 \text{ ppm}$$

Where  $M_1$  is the concentration of the stock solution,  $M_2$  is the concentration of the diluted solution,  $V_1$  is the volume of the stock solution, and  $V_2$  is the volume of the diluted solution.

The equation  $M_1 V_1 = M_2 V_2$  is the mathematical expression for this sentence:

**The number of the solute molecules stays the same before and after the dilution.**

Using the same equation we can calculate the concentration for solution 2 as follows:

$$M_2 = \frac{M_1 V_1}{V_2} = \frac{55.85 \text{ ppm} \times 5.00 \text{ mL}}{100.00 \text{ mL}} = 2.79 \text{ ppm}$$

Note that now the volume is only accurate to 3 significant figures. So the final answer can only retain 3 significant figures.

Can you verify if Jimmy's values of the concentrations for solutions 3 to 5 are correct?

Generally we can use the expression  $M_1V_1 = M_2V_2$  for calculations of **any dilution**. As long as three of the four variables are known, the fourth can be calculated. This expression also allows the use of different units for concentration and volume, as long as  $M_1$  and  $M_2$  are of the same unit and  $V_1$  and  $V_2$  are of the same unit. The following are a few common variations of this expression:

$$C_1V_1 = C_2V_2 \text{ (C in mol L}^{-1} \text{ and V in L)}$$

$$C_1v_1 = C_2v_2 \text{ (C in mol L}^{-1} \text{ and v in mL)}$$

$$m_1V_1 = m_2V_2 \text{ (m in g L}^{-1} \text{ and V in L or mL)}$$

$$\%_1v_1 = \%_2v_2 \text{ (% is any percent concentration and v in mL)}$$

You get the idea.

## 11.7 Acid-Base Titrations

**Titration** is a technique frequently used to accurately determine the concentration of one solution by reacting it with another solution for which the concentration is accurately known. For the reaction between colorless compounds, an indicator must be used to signal the completion of the reaction, or the arrival of the **equivalence point**. The equivalence point is the point during the titration at which just **enough of one compound has been added to completely react with the other compound of a given amount**.

For example, in the case of the titration of a strong base such as NaOH with a strong acid such as HCl, the titration is carried out by following these steps until the earliest color change is detected.

1. Add a very small amount of the acid from a buret to a measured volume of the base in an Erlenmeyer flask
2. Mix (swirl the flask) to allow for complete consumption of the added acid
3. Check for color change expected from the indicator used
4. Repeat steps 1 to 3 until the first faint color change persists longer than 15 seconds, indicating the completion of the reaction

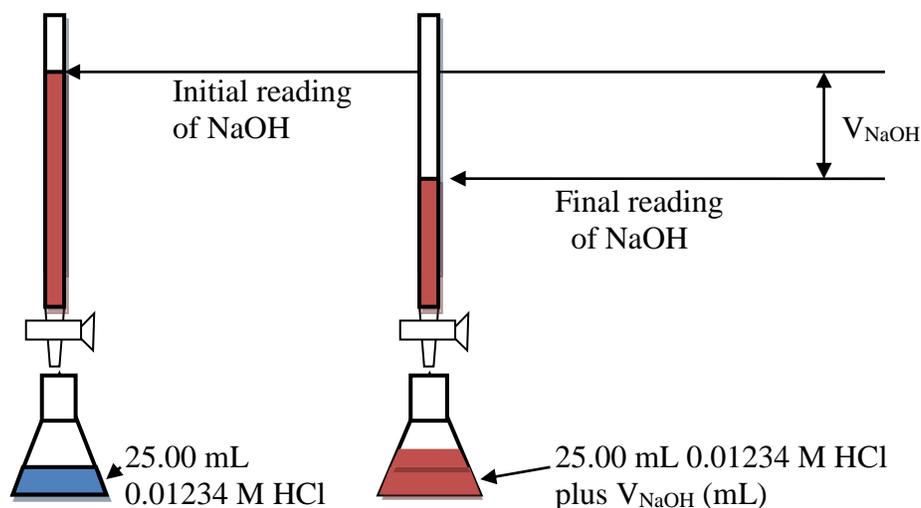
When phenolphthalein is used as indicator ( $pK_a = 9.5$ ), the color change occurs within the pH range of 8.3 to 10.0. In the beginning of the titration, the color of the NaOH solution is red as the solution is basic. At the equivalence point, when all of the NaOH have been neutralized by HCl, pH is 7 as a neutral salt, NaCl, is produced. The solution is still red (faint pink) at this exact moment.

The addition of a very small aliquot of HCl, however, changes the pH to acidic. As there is no more NaOH to neutralize, the HCl now reacts with the basic form of the indicator and turn the indicator to

its acidic form, and the solution turns from pink to colorless. This process is inevitably associated with experimental error in the detection of the equivalence point, even if the titration is carried out by a skilled chemist. To minimize experimental error, care should be taken to use the smallest amount of indicator and to slow down the pace of steps 1 to 3 when the equivalence point is approaching. Good titration results can be obtained by students who take time to practice adding the smallest possible aliquots of HCl around the equivalence point.

We can try to minimize human error by titrating an acid with a base, hence a color change from **colorless to pink** is expected; as it is easier to detect the appearance of the faint pink color from an originally colorless solution.

We will show you how to process typical titration data in **Question 94**. A drawing of the titration set up for the question is shown below.



**Question 97.**

Betty performed three trials of an acid-base titration, using the set up shown on the previous page. In her lab report she submitted the following table.

**Table 1: Data for the Titration of Three 25.00 mL 0.01234 M HCl Solutions with the Unknown NaOH Solution**

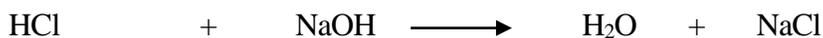
Trial	1	2	3
Initial Volume (mL)	0.00	10.50	0.00
Final Volume (mL)	23.00	32.00	21.68
V of NaOH Added (mL)	23.00	21.50	21.68

The **initial** volume is the reading before a titration begins and the **final** volume is the reading at the equivalence point. It is not necessary to always begin a titration with 0.00 mL as the initial volume. The total volume used can be easily calculated from the difference between the final volume and the initial volume, as she did for trial 2.

Using Betty's data, calculate the concentration of the unknown NaOH solution.

**Answer:**

First we need to write the balanced reaction equation as shown below.



In each of the three 25.00 mL 0.01234 M HCl solutions, the total moles of HCl can be calculated as follows:

$$\text{Moles HCl} = \text{Molarity} \times \text{volume} = 0.01234 \frac{\text{mol}}{\text{L}} \times 25.00 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 3.085 \times 10^{-4} \text{ mol}$$

At the equivalence point, the total moles of NaOH used can be calculated as follows:

$$\text{Moles NaOH} = \text{Molarity} \times \text{volume} = M_{\text{NaOH}} \frac{\text{mol}}{\text{L}} \times V \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}$$

As the balanced reaction equation suggests a 1:1 molar relationship between HCl and NaOH, we have

$$\text{Moles NaOH} = \text{Moles HCl}$$

Thus

$$M_{\text{NaOH}} \frac{\text{mol}}{\text{L}} \times V \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 3.085 \times 10^{-4} \text{ mol}$$

Solving for  $M_{\text{NaOH}}$ , we get

$$M_{\text{NaOH}} = 3.085 \times 10^{-4} \text{ mol} \div \left( V \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \right)$$

By using the V value for each trial, we get

$$\text{For trial 1: } M_{\text{NaOH}} = 3.085 \times 10^{-4} \text{ mol} \div \left( 23.00 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \right) = 0.01341 \frac{\text{mol}}{\text{L}}$$

$$\text{For trial 2: } M_{\text{NaOH}} = 3.085 \times 10^{-4} \text{ mol} \div \left( 21.50 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \right) = 0.01435 \frac{\text{mol}}{\text{L}}$$

$$\text{For trial 3: } M_{\text{NaOH}} = 3.085 \times 10^{-4} \text{ mol} \div \left( 21.68 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \right) = 0.01423 \frac{\text{mol}}{\text{L}}$$

The concentration of the unknown NaOH solution can be calculated by finding the average of the above three concentrations

$$\bar{M}_{NaOH} = (0.01341 + 0.01435 + 0.01423) \div 3 = 0.01340 \frac{mol}{L}$$

Although the concentration from trial 1 is quite a bit different from those from trials 2 and 3, it is not valid to exclude trial 1 value in the calculation of the average unless an error was noted during the performance of the trial 1 titration.

The above example shows that, **at the equivalence point of any acid-base titration**, we have

Moles OH <sup>-</sup> = Moles H <sub>3</sub> O <sup>+</sup>
---

In the case of NaOH and HCl, the molar relationship between the acid and the base is 1:1, the follow expression can be used to calculate the concentration of the unknown acid or base:

$$C_{base}V_{base} = C_{acid}V_{acid} \text{ (C in mol L}^{-1} \text{ and V in mL)}$$

In the case of NaOH and H<sub>2</sub>SO<sub>4</sub>, it takes two NaOH to neutralize every H<sub>2</sub>SO<sub>4</sub>, the molar relationship between the acid and the base is 1:2, and the follow expression can be used to calculate the concentration of the unknown acid or base:

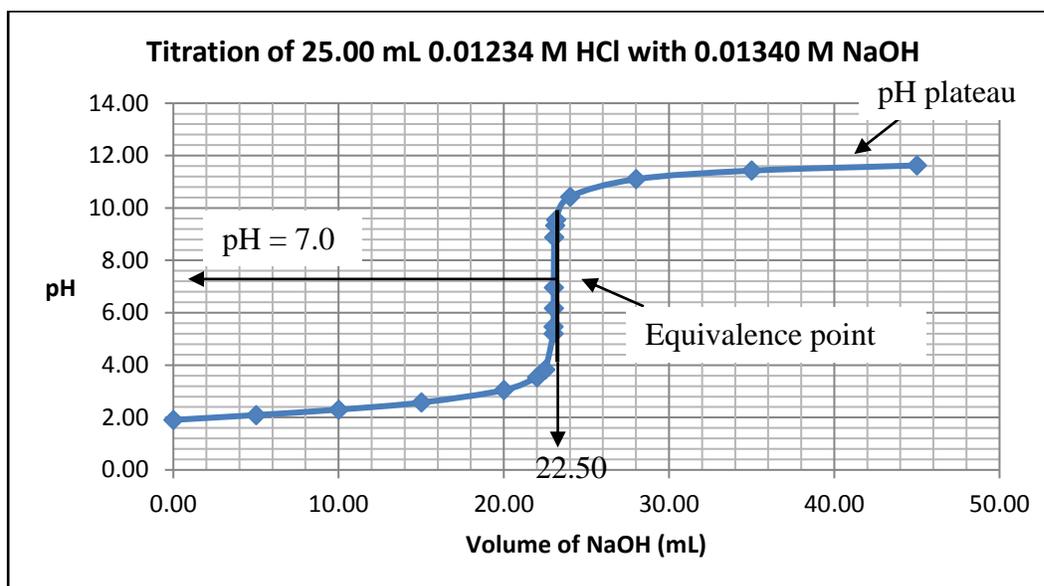
$$C_{base}V_{base} = 2C_{acid}V_{acid} \text{ (C in mol L}^{-1} \text{ and V in mL)}$$

## 11.8 pH Curve for Strong Acid-Strong Base Titration

Another way to determine the equivalence point of an acid-base reaction is by constructing a **titration curve** or **pH curve**. As an example, we will construct the titration curve for the same titration discussed in **Question 94**, that is, for the titration of 25.00 mL 0.01234 M HCl with 0.01340 M NaOH (the average molarity of NaOH found in **Question 94**).

The titration process is similar to a titration by hand. However, instead of waiting for the color change from the indicator to signal the completion of the reaction, a pH meter is used to read the pH of the solution after every addition of the NaOH. The titration continues until there is no longer an obvious pH change.

The pH titration curve can then be constructed by plotting pH readings vs. the volume of NaOH added, as shown below. The equivalence point is the midpoint of the straight vertical region where a sharp pH jump is observed. For this particular titration, the equivalence point was reached when 22.50 mL of NaOH was added. The pH at the equivalence point was 7.0 because the salt formed, NaCl, is a neutral salt.



This is a typical titration curve for the titration of a strong acid with a strong base. There is very little pH change before or after the equivalence point. However, around the equivalence point, the addition of small volume as little as 0.01 mL NaOH can cause a sharp jump in pH. For students performing the titration, such pH jumps are signals of the approach or arrival of the equivalence point. To construct a well-defined titration curve, the student should try to add very small amounts of NaOH during this period. Once the pH values start to show no obvious change, the student can increase the volume of each addition. The titration can be stopped once an obvious plateau is observed.

A pH curve can also be constructed by calculating the pH of the solution after each addition of NaOH. Spreadsheet software such as Microsoft Excel is convenient to use for this purpose. Below is an Excel worksheet set up for the **theoretical** titration of 25.00 mL 0.01234 M HCl with 0.01340 M NaOH.

**Data Table for the Titration of 25.00 mL 0.01234 M HCl with 0.01340 M NaOH**

$M_{\text{NaOH}} = 0.01340 \text{ mol L}^{-1}$			$M_{\text{HCl}} = 0.01234 \text{ mol L}^{-1}$			
Volume of NaOH Added (mL)	Volume of Total Solution (mL)	Moles of NaOH Added (mol)	Moles of Initial HCl (mol)	Moles of Leftover HCl (mol)	$[\text{H}_3\text{O}^+]$ ( $\text{mol L}^{-1}$ )	pH
0.00	25.00	0.000E+00	3.085E-04	3.085E-04	1.234E-02	1.91
5.00	30.00	6.700E-05	3.085E-04	2.415E-04	8.050E-03	2.09
10.00	35.00	1.340E-04	3.085E-04	1.745E-04	4.986E-03	2.30
15.00	40.00	2.010E-04	3.085E-04	1.075E-04	2.688E-03	2.57
20.00	45.00	2.680E-04	3.085E-04	4.050E-05	9.000E-04	3.05

22.00	47.00	2.948E-04	3.085E-04	1.370E-05	2.915E-04	3.54
22.50	47.50	3.015E-04	3.085E-04	7.000E-06	1.474E-04	3.83
23.00	48.00	3.082E-04	3.085E-04	3.000E-07	6.250E-06	5.20
23.01	48.01	3.083E-04	3.085E-04	1.660E-07	3.458E-06	5.46
23.02	48.02	3.085E-04	3.085E-04	3.200E-08	6.664E-07	6.18
23.022	48.022	3.085E-04	3.085E-04	5.200E-09	1.083E-07	6.97
				Moles of Extra NaOH (mol)	[OH <sup>-</sup> ] (mol L <sup>-1</sup> )	
23.05	48.05	3.089E-04	3.085E-04	3.700E-07	7.700E-06	8.89
23.10	48.10	3.095E-04	3.085E-04	1.040E-06	2.162E-05	9.33
23.15	48.15	3.102E-04	3.085E-04	1.710E-06	3.551E-05	9.55
24.00	49.00	3.216E-04	3.085E-04	1.310E-05	2.673E-04	10.43
28.00	53.00	3.752E-04	3.085E-04	6.670E-05	1.258E-03	11.10
35.00	60.00	4.690E-04	3.085E-04	1.605E-04	2.675E-03	11.43
45.00	70.00	6.030E-04	3.085E-04	2.945E-04	4.207E-03	11.62

Sample calculations for the columns are as follows:

Moles of initial HCl = Molarity  $\times$  volume

$$= 0.01234 \frac{\text{mol}}{\text{L}} \times 25.00 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 3.085 \times 10^{-4} \text{ mol}$$

When  $V_{\text{NaOH}} = 15.00 \text{ mL}$ ,

Moles NaOH added = Molarity  $\times$  volume

$$= 0.01340 \frac{\text{mol}}{\text{L}} \times 15.00 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 2.010 \times 10^{-4} \text{ mol}$$

Moles of leftover HCl = Moles of initial HCl - Moles NaOH added

$$= 3.085 \times 10^{-4} \text{ mol} - 2.010 \times 10^{-4} \text{ mol} = 1.075 \times 10^{-4} \text{ mol}$$

$$[\text{H}_3\text{O}^+] = \frac{\text{moles of leftover HCl}}{\text{volume of total solution}} = \frac{1.075 \times 10^{-4} \text{ mol}}{40.00 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} = 2.688 \times 10^{-3} \text{ mol L}^{-1}$$

$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(2.688 \times 10^{-3}) = 2.57$  (we choose to keep only 2 sig. fig. here)

Note that with Betty's titration set up (page 134) it would be impossible to add a volume that is 23.022 mL. This volume is only chosen to show you that it only takes an addition of as little as 0.002 mL of NaOH to make the pH jump from 6.18 (at  $V_{\text{NaOH}} = 23.02 \text{ mL}$ ) to 6.97 (at  $V_{\text{NaOH}} = 23.022 \text{ mL}$ ).

At pH = 6.97 when  $V_{\text{NaOH}} = 23.022 \text{ mL}$ ,  $[\text{H}_3\text{O}^+] = 1.083 \times 10^{-7} \text{ mol L}^{-1}$ . The solution essentially has the pH of pure water. Experimentally the equivalence point was observed between  $V_{\text{NaOH}} = 22.00 \text{ mL}$  to  $23.05 \text{ mL}$  (labeled as 22.50 on the titration curve on page 137).

After the equivalence point, any additional NaOH added would cause the solution to have an  $[\text{OH}^-]$  greater than  $1.0 \times 10^{-7} \text{ mol L}^{-1}$ . The solution becomes basic after that. For example, we can find the pH of the solution by doing the following calculation.

When  $V_{\text{NaOH}} = 23.15 \text{ mL}$ ,

$$\begin{aligned} \text{Moles NaOH added} &= \text{Molarity} \times \text{volume} \\ &= 0.01340 \frac{\text{mol}}{\text{L}} \times 23.15 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 3.102 \times 10^{-4} \text{ mol} \end{aligned}$$

Moles of extra NaOH = Moles NaOH added - Moles of initial HCl

$$= 3.102 \times 10^{-4} \text{ mol} - 3.085 \times 10^{-4} \text{ mol} = 1.710 \times 10^{-6} \text{ mol}$$

$$[\text{OH}^-] = \frac{\text{moles of extra NaOH}}{\text{volume of total solution}} = \frac{1.710 \times 10^{-6} \text{ mol}}{48.15 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} = 3.551 \times 10^{-5} \text{ mol L}^{-1}$$

$$\text{pH} = 14 - \text{pOH} = 14 + \log[\text{OH}^-] = 14 + \log(3.551 \times 10^{-5}) = 9.55$$

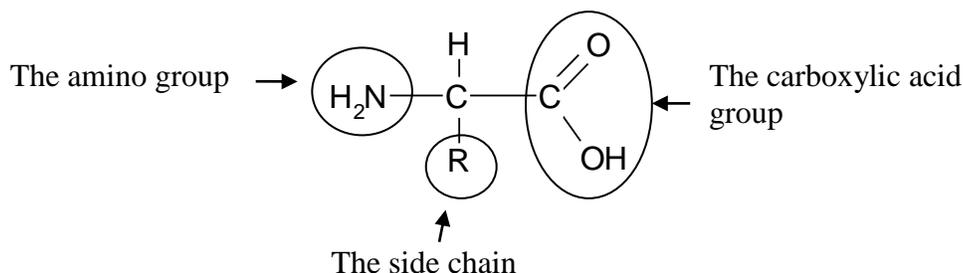
If we plot pH against the volume of NaOH added, we get a titration curve (pH curve) just like the one on page 137.

When a weak acid is titrated with a strong base or a weak base with a strong acid, the titration curves look similar to the typical HCl-NaOH titration curve. The only difference is that the pH jumps are not as sharp and the pH at the equivalence point is not 7.0. This is because at the equivalence point the salts formed are no longer neutral salts. A strong acid-weak base salt will have at equivalence point a  $\text{pH} < 7$  while a weak acid-strong base salt will have at equivalence point a  $\text{pH} > 7$ .

For calculation of pH values during such titrations you will need to take into account of the weak acid-weak base equilibria. We will not go into the details here.

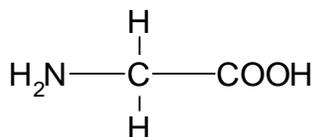
## 11.9 Amino Acids and pH

Amino acids are the building blocks of proteins. There are 20 amino acids found in proteins, and they all have the same structural frame, as shown below.



It is the difference in the side chain R that makes the 20 amino acids different from each other. The similarity in their structural frame, however, gives them some very important common properties. One of these, the structural dependence on pH, will be discussed here.

The simplest amino acid is glycine (Gly, when R = H), shown below, which will be our example for all amino acids.



Glycine can behave as an acid because the  $-\text{COOH}$  group can donate a proton to become  $-\text{COO}^-$ . It can also behave as a base because the  $-\text{NH}_2$  group can donate a lone pair of electrons on the nitrogen atom to a proton, or, the  $-\text{NH}_2$  group can be protonated to become  $-\text{NH}_3^+$ . Thus amino acids are amphoteric species (**ampholytes**).

Similar to acetic acid ( $\text{CH}_3\text{COOH}$ ,  $\text{pK}_a = 4.8$ ) and ammonia ( $\text{NH}_3$ ,  $\text{pK}_a(\text{NH}_4^+) = 9.2$ ), in any amino acid, the carboxylic group is a weak acid and the amine group is a weak base. The strength of each can be measured by their  $\text{pK}_a$  values.

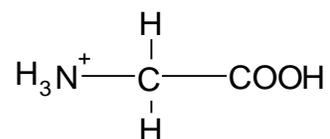
When an amino acid is dissolved in solution, the amine group ( $-\text{NH}_2$ ) and the carboxylic acid group ( $-\text{COOH}$ ) are either **protonated** or **deprotonated**, depending on the pH of the solution. We will discuss this dependency in the following examples.

### Question 98.

Draw the structure of glycine in a  $\text{pH} = 2$  solution, given that  $\text{pK}_a(-\text{COOH}) = 2.2$  and  $\text{pK}_a(-\text{NH}_3^+) = 9.7$ .

**Answer:**

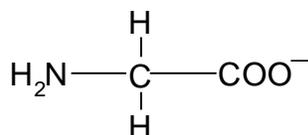
A solution of pH 2 is a strong acidic solution. Since pH of the solution is less than both  $pK_a(-\text{COOH})$  and  $pK_a(-\text{NH}_3^+)$ , the solution is acidic enough to make both the COOH group and the  $\text{NH}_2$  group exist in their acidic forms (protonated, as shown in the structure below). The amino acid glycine has the following structure and is a positively charged ion.

**Question 99.**

Draw the structure of glycine in a pH = 10 solution, given that  $pK_a(-\text{COOH}) = 2.2$  and  $pK_a(-\text{NH}_3^+) = 9.7$ .

**Answer:**

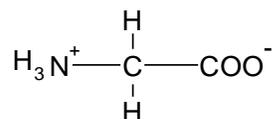
A solution of pH 10 is a strong basic solution. Since pH of the solution is greater than both  $pK_a(-\text{COOH})$  and  $pK_a(-\text{NH}_3^+)$ , the solution is basic enough to make both the COOH group and the  $\text{NH}_2$  group exist in their basic forms (deprotonated, as shown in the structure below). The amino acid glycine has the following structure and is a negatively charged ion.

**Question 100.**

Draw the structure of glycine in a pH = 6 buffer solution, given that  $pK_a(-\text{COOH}) = 2.2$  and  $pK_a(-\text{NH}_3^+) = 9.7$ .

**Answer:**

A near neutral solution of pH 6 is basic enough to deprotonate the  $-\text{COOH}$  group ( $\text{pH} > pK_a(-\text{COOH})$ ) but not basic enough to deprotonate the  $-\text{NH}_3^+$  group ( $\text{pH} < pK_a(-\text{NH}_3^+)$ ). Thus the  $-\text{COOH}$  group will exist in its basic form ( $-\text{COO}^-$ ) and the  $-\text{NH}_2$  group will exist in its acidic form ( $-\text{NH}_3^+$ ). The amino acid has the following structure and is a dipolar ion (**zwitterion**). The amino acid glycine carries zero net charge.



In fact glycine can exist as a dipolar ion in solutions of pH ranging from 2.2 to slightly lower than 9.7. That is why we write amino acids generally as dipolar ions in most solutions except in strong acids or strong bases. As dipolar ions, amino acids have solubility properties similar to salts in aqueous solutions.

Some amino acids have an acidic side chain or a basic side chain. In those cases a **pI** calculation can help decide at what pH they exist as dipolar ions. pI is called the **isoelectric point**. It is the pH at which the amino acid has zero net charge.

For amino acids with neutral side chain, such as glycine,

$$\text{pI} = \frac{pK_a(-\text{COOH}) + pK_a(-\text{NH}_3^+)}{2} = \frac{2.2+9.7}{2} = 6.0$$

For amino acids with an acidic side chain,

$$\text{pI} = \frac{pK_{a1}(-\text{COOH}) + pK_{a2}(-\text{COOH})}{2} \sim 3$$

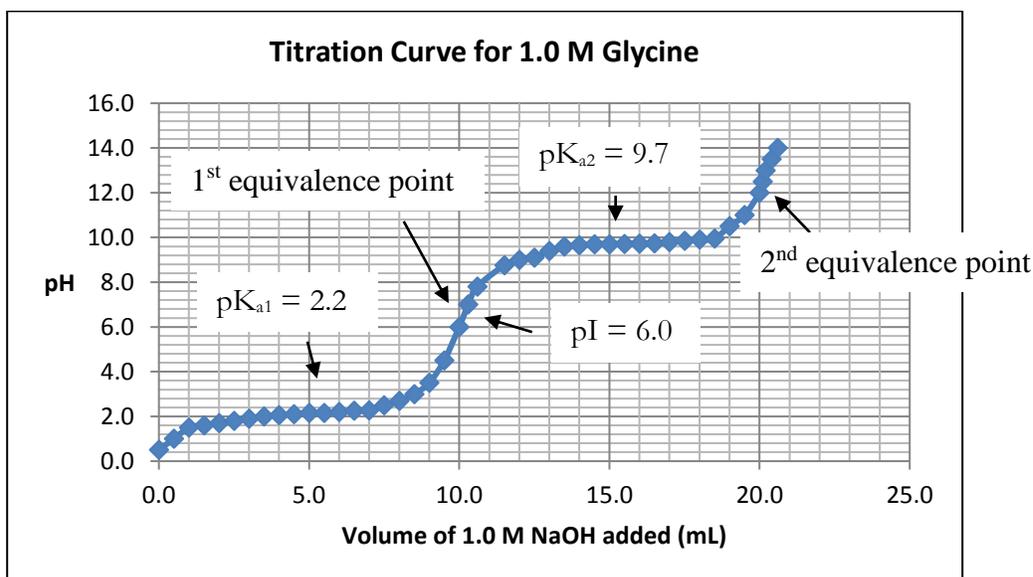
For amino acids with a basic side chain,

$$\text{pI} = \frac{pK_{a1}(-\text{NH}_3^+) + pK_{a2}(-\text{NH}_3^+)}{2} > 7$$

The structural dependency of amino acids on pH means that it is possible to manipulate the pH of a solution of a mixture of amino acids to “turn” some amino acids into positive ions, some into negative ions and some neutral species. An experimental technique called **electrophoresis** makes use of this principle to achieve the separation of amino acids and protein fragments in biochemical research. **Proteins** are long chain molecules made up of amino acids and have similar structural dependency on pH.

## 11.10 Titration Curve for Amino Acids

The structural dependency of an amino acid on pH can be visually observed from the titration curve for the amino acid. Shown below is a titration curve for glycine, constructed by titrating 10.0 mL of a 1.0 M glycine solution with a 1.0 M NaOH solution. A pH meter was used to read the pH values after each addition of aliquots of NaOH. The glycine solution was initially acidified with concentrated HCl so that the pH of the starting solution was at 0.5. At this pH glycine is fully protonated. As pH increases during the titration process, we expect to observe the neutralization (or more accurately deprotonation) of both the  $-\text{COOH}$  group and the  $-\text{NH}_3^+$  group.



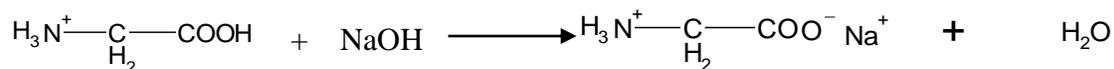
The titration curve provides us with several pieces of important information. We will show you how to make use of the titration curve in the following examples.

### Question 101.

Referring to the titration curve for glycine, write the reaction equations for the two equivalence points. How do you know that the pH at the 1<sup>st</sup> equivalence point is pI? What are the net charges on glycine at the two equivalence points?

#### Answer:

Two pH jumps are observed on the titration curve, thus two equivalence points can be found. The first one corresponds to this neutralization reaction:



Remember that initially at pH = 0.5, glycine exists as a fully protonated, positively charged ion. When 10.0 mL of 1.0 M NaOH is added to the 10.0 mL 1.0 M glycine solution, the carboxylic acid group is completely neutralized to form salt and water.

At this time glycine is a dipolar ion with zero net charge, so the pH at this point is also pI for glycine. From the titration curve we can read that pI = 6.0.

The second pH jump corresponds to this neutralization reaction:



This jump occurs at  $V_{\text{NaOH}} = 20.0$  mL because another 10.0 mL of 1.0 M NaOH is needed to completely deprotonate the  $-\text{NH}_3^+$  group in the 10.0 mL 1.0 M glycine solution. At this point glycine exists as a fully deprotonated, negatively charged ion. It has a -1 net charge.

### Question 102.

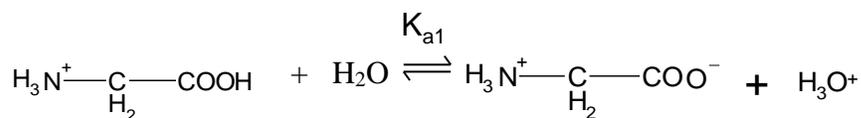
Referring to the titration curve for glycine, how do you find that  $\text{pK}_a(-\text{COOH}) = 2.2$  and  $\text{pK}_a(-\text{NH}_3^+) = 9.7$ ? Where are the two buffer regions?

#### Answer:

Two buffer regions are observed. A **buffer region** is the horizontally flat part of the curve. Within the buffer region the pH remains relatively constant even though more and more NaOH is being added.

The **first buffer region** on the titration curve can be found around  $V_{\text{NaOH}} = 5.0$  mL. When 5.0 mL of 1.0 M NaOH is added to the 10.0 mL 1.0 M glycine solution, half of the carboxylic acid group is neutralized to form salt and water.

At this exact moment we have the following acid-base equilibrium between the carboxylic group and its conjugate base and we know that  $\frac{[\text{A}^-]}{[\text{HA}]} = 1$ :



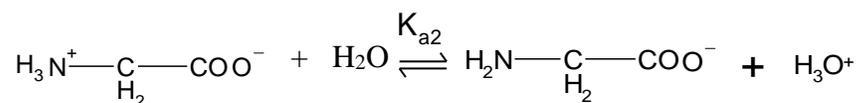
By applying the Henderson-Hasselbalch equation

$$\text{pH} = \text{pK}_{a1} + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)_{\text{eq}}$$

we get that when  $\frac{[\text{A}^-]}{[\text{HA}]} = 1$ ,  $\text{pH} = \text{pK}_a$ . Therefore we find  $\text{pK}_{a1}(-\text{COOH}) = 2.2$  from the titration curve at  $V_{\text{NaOH}} = 5.0$  mL. This is indeed the midpoint between the beginning of the titration and the 1<sup>st</sup> equivalence point. This is also the midpoint of the 1<sup>st</sup> buffer region. This shows that dipolar glycine and its positively charged form can be used to make buffer solutions for pH around 2.

The **second buffer region** on the titration curve can be found around  $V_{\text{NaOH}} = 15.0$  mL.

At this moment we have the following acid-base equilibrium between the  $-\text{NH}_3^+$  group and its conjugate base and we know that  $\frac{[-\text{NH}_2]}{[-\text{NH}_3^+]} = 1$ :



By applying the Henderson-Hasselbalch equation

$$\text{pH} = \text{p}K_{a2} + \log\left(\frac{[-\text{NH}_2]}{[-\text{NH}_3^+]}\right)_{\text{eq}}$$

we get that when  $\frac{[-\text{NH}_2]}{[-\text{NH}_3^+]} = 1$ ,  $\text{pH} = \text{p}K_{a2}$ . Therefore we find  $\text{p}K_{a2}(-\text{NH}_3^+) = 9.7$  from the titration curve at  $V_{\text{NaOH}} = 15.0$  mL. This is indeed the midpoint between the 1<sup>st</sup> equivalence point and the 2<sup>nd</sup> equivalence point. This is also the midpoint of the 2<sup>nd</sup> buffer region. This shows that the dipolar glycine and its negatively charged form can be used to make buffer solutions for pH around 9.7.

## Practice and Review for Chapter 11

Define (in your own words) the following terms:

Salt: \_\_\_\_\_

Buffer Solution: \_\_\_\_\_

Acid-Base Indicator: \_\_\_\_\_

Phenolphthalein: \_\_\_\_\_

Polyprotic Acid: \_\_\_\_\_

Titration: \_\_\_\_\_

Equivalence Point: \_\_\_\_\_

Titration Curve: \_\_\_\_\_

Amino Acid: \_\_\_\_\_

Ampholyte: \_\_\_\_\_

pI: \_\_\_\_\_

Zwitterion: \_\_\_\_\_

Electrophoresis: \_\_\_\_\_

Protein: \_\_\_\_\_

Buffer Region: \_\_\_\_\_

**Short-Answer Questions:**

1. Use Henderson-Hasselbalch equation to calculate the pH of the buffer solution made by mixing 50.0 mL 0.50 M  $\text{Na}_2\text{CO}_3$  with 50.0 mL 0.50 M  $\text{NaHCO}_3$ , given that  $\text{pK}_a(\text{HCO}_3^-) = 10.2$ .
2. What is the concentration of a 0.25 M NaOH solution after a 100 times dilution?
3. Draw a typical titration curve for an amino acid. Label the buffer region, the  $\text{pK}_a$  and  $\text{pI}$  values and the equivalence points.

## Thermodynamics I: Energy Expressions

*What goes around comes around; maybe in different forms.*

Although most chemical reactions can be treated as equilibrium reactions, the magnitude of the equilibrium constants vary so much that some reactions can be considered as going to completion while others never seem to start. What is the reason behind all this?

If I have taught you well, you would say “it is all about the electrons wanting to be at the lowest energy level,” and that would make my day. You are absolutely on the right track.

But what exactly is **energy**?

On an energetic day, you get more work done; energy is spent to do work. On a hot day, you turn on the air conditioner; energy is spent to remove the heat in your room. When you are hungry, you eat, food is turned into energy. When you eat too much, the extra energy (Calories) is turned into fat. So I think we can give a simple but scientific definition to energy:

**Energy is the capacity to do work or to transfer heat.**

We also have scientific definitions for **work** and **heat**.

When a hockey player hits a puck, the player uses a **force,  $F$** , to **displace** an object (the puck) to a certain **distance,  $d$** . We say that **work** is done on the object and the amount of work done,  $w$ , can be calculated from:

$$w = F \times d$$

These quantities all have units. In SI *force* is measured in **Newton** and *distance* in **meter** so the SI unit for *work* is **Newton meter** (N m) which is called a joule (J):

$$1 \text{ J} = 1 \text{ N m} = 1 \text{ kg m S}^{-2} \times \text{m} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

**Heat,  $q$** , is energy that is transferred as the result of a temperature difference. Heat always **flows** from a warmer object to a colder object. Heat has the same unit as work.

There is a whole branch of science dedicated to the study of work, heat, and the transformation of energy in general. It is called **thermodynamics**. Learning about thermodynamics will help us understand the reason behind the direction of chemical reactions.

## 12.1 First Law of Thermodynamics

A chemical reaction is usually carried out in a container of some sort. In a laboratory we often use test tubes and beakers as the container. In thermodynamics the reaction confined in the container is called the **system**, and everything outside the container (including the experimenter) is called the **surroundings**.

If the reaction container is sealed and insulated to prevent **any exchange** with its surroundings, the system is called an **isolated system**. This is not the case for most chemical reactions. If a reaction being carried out in an Erlenmeyer flask is exothermic, we can feel the warmth of the flask, heat is being transferred from the system to its surroundings. If the reaction is endothermic, we can feel the “coldness” of the flask and sometimes even observe the condensation of moisture from the air on the flask. In these cases there is clearly energy exchange between the system and its surroundings.

How much energy is being exchanged is governed by the **first law of thermodynamics**. It is based on the understanding that **energy can neither be created nor destroyed but only changed from one form to another (law of conservation of energy)**. If a system loses heat to its surroundings, the system will have lower energy after the exchange. If a system gains energy from the surroundings, being heated up for example, the system will have higher energy after the exchange. How much lower or higher energy the system would contain should equal to the heat (energy) lost or gained.

We use  $E_{initial}$  and  $E_{final}$  to represent the energy of the system (internal energy) before and after the energy exchange, and the difference between  $E_{initial}$  and  $E_{final}$  is given the symbol  $\Delta E$ . Mathematically we can write

$$E_{final} - E_{initial} = \Delta E = w + q$$

where  $w + q$  is the **total energy** being exchanged with the surroundings.

### Question 103.

How do you state the first law of thermodynamics in words?

**Answer:**

The first law of thermodynamics states that if an amount of heat  $q$  flows into a system from the surroundings and the surroundings do an amount of work  $w$  on the system, it will cause the system to have an internal energy change that equals  $w + q$ .

**Question 104.**

What are kinetic energy and potential energy? How are they related to the internal energy of a system?

**Answer:**

**Kinetic energy** and **potential energy** are two fundamentally different forms of energy. Simply put, **kinetic energy** is related to **motion** of the system whereas **potential energy** is related to the **position** of the system in relation to another system that is interacting with the system.

The **internal energy** of a system is the **sum of the kinetic and potential energies** of all the particles in the system.

**Question 105.**

What is a state function? Are all the energies involved in the first law of thermodynamics state functions?

**Answer:**

A **state function** is *any property of a system that depends only on the state of the system and not on how that state is reached*. In the first law of thermodynamics,  $\Delta E = w + q$ ,  $\Delta E$  is a state function but  $w$  and  $q$  are not.

For example, cooling a cup of water from 25 °C to 0 °C lowers the internal energy of the water from  $E_{25\text{ }^\circ\text{C}}$  to  $E_{0\text{ }^\circ\text{C}}$ .  $\Delta E = E_{0\text{ }^\circ\text{C}} - E_{25\text{ }^\circ\text{C}}$ . We can achieve this amount of internal energy change in several ways. We can simply cool the 25 °C water down by submerging the cup in an ice-water bath (0 °C). We can also heat the 25 °C water up to 60 °C and then submerging the cup in an ice-water bath. In either ways  $\Delta E = E_{0\text{ }^\circ\text{C}} - E_{25\text{ }^\circ\text{C}}$ .

Heat and work,  $w$  and  $q$ , are not state functions because their amounts are directly related to how the work is done and how the heat is transferred.

## 12.2 Enthalpy

We have used the words **exothermic** and **endothermic** to describe chemical reactions that give out heat or take in heat. An exothermic reaction is exothermic whether it happens at home or in a laboratory. So is an endothermic reaction. In other words, the heat given out (or taken in) by a

certain chemical reaction appears to be a state function. But we just said that heat and work are not state functions!

To avoid further confusion, we introduce a new term to describe the “heat” given out (taken in) by exothermic (endothermic) reactions. This “heat” is called the **enthalpy change** and is given the symbol  $\Delta H$ .

For a chemical reaction, the enthalpy change is given by the equation

$$\Delta H = \text{total } H_{\text{products}} - \text{total } H_{\text{reactants}}$$

There is **an enthalpy for every compound**. In an exothermic reaction, the system loses enthalpy; the sum of the enthalpies of the products is less than the sum of the enthalpies of reactants;  $\Delta H$  is *negative*. In an endothermic reaction, the system gains enthalpy; the sum of the enthalpies of the products is more than the sum of the enthalpies of reactants;  $\Delta H$  is *positive*.

In other words, we have

if  $\Delta H < 0$ , the reaction is exothermic;

if  $\Delta H > 0$ , the reaction is endothermic.

For any chemical reaction,  $\Delta H$  can be measured experimentally by carrying out the reaction in a **calorimeter**.

Since enthalpy is a state function, its value is dependent on the condition under which the measurement is made. Chemists commonly use a set of enthalpy changes measured at a **pressure of 1 atm and at 25 °C**. These are called the **standard enthalpies** of reactions and are given the symbol  $\Delta H^\circ$ .

When a chemical reaction is carried out at 1 atm and 25 °C, the reactants and products are said to be in their **standard states**. Common laboratory conditions are quite close to this standard condition, so values of  $\Delta H^\circ$  are frequently used in place of  $\Delta H$ . However, chemical reactions taking place inside our body, for example, are not under standard conditions; at least the temperature is not 25 °C but 37 °C. In those cases we need to be careful in choosing the proper  $\Delta H$  values to use.

## 12.3 Bond Energies

When we carry out the following reaction in a calorimeter, we obtain a value of

$\Delta H^\circ = 436.0 \text{ kJ mol}^{-1}$  for this reaction.



That is to say, it takes 436.0 kJ of energy to break one mole of hydrogen molecules into hydrogen atoms! In other words, we just measured the **strength of the H—H bond**. This enthalpy change is called the **bond dissociation enthalpy**, or **bond enthalpy** of the hydrogen molecule. A more commonly used, although less specific, term for bond enthalpy is **bond energy (BE)**. For 1 mole of hydrogen molecules, we can write

$$\text{BE}(\text{H—H}) = 436.0 \text{ kJ mol}^{-1}$$

Bond energies have been measured for many common bonds. These values are useful because

**Bond energy for a given bond does not vary from substance to substance.**

In other words, a C—C bond has the same energy whether it is in diamond or graphite or alcohol.

Since a chemical reaction basically involves breaking some old bonds and forming some new bonds, we can estimate the enthalpy change of a reaction by using bond energies of the reactants and the products. The formula is

$$\Delta H^\circ = \text{total BE}_{\text{reactants}} - \text{total BE}_{\text{products}}$$

or

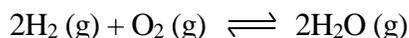
$$\Delta H^\circ = \text{total BE (bonds broken)} - \text{total BE (bonds formed)}$$

### Question 106.

Is the formation reaction of water exothermic or endothermic? Given that  $\text{BE}(\text{H—H}) = 436.0 \text{ kJ mol}^{-1}$ ,  $\text{BE}(\text{O=O}) = 498.0 \text{ kJ mol}^{-1}$ , and  $\text{BE}(\text{O—H}) = 463.0 \text{ kJ mol}^{-1}$ .

### Answer:

The formation of  $\text{H}_2\text{O}$  from  $\text{H}_2$  and  $\text{O}_2$  takes place according to the following balanced equation:



Using the reaction stoichiometry, we know that 2 H—H bonds and 1 O=O bond are broken and 4 O—H bonds (each water has 2 O—H bonds) are formed. Under standard condition,

$$\begin{aligned}\Delta H^\circ &= \text{total BE (bonds broken)} - \text{total BE (bonds formed)} \\ &= (2 \times 436.0 + 498.0) - (4 \times 463.0) = 1370 - 1892 = -482.0 \text{ kJ}\end{aligned}$$

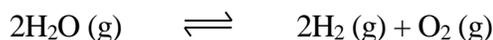
Since  $\Delta H < 0$ , the formation reaction of water is exothermic.

### Question 107.

Is the decomposition reaction of water exothermic or endothermic? Given that  $\text{BE}(\text{H—H}) = 436.0 \text{ kJ mol}^{-1}$ ,  $\text{BE}(\text{O=O}) = 498.0 \text{ kJ mol}^{-1}$ , and  $\text{BE}(\text{O—H}) = 463.0 \text{ kJ mol}^{-1}$ .

### Answer:

The decomposition reaction of water is the reverse of the formation of  $\text{H}_2\text{O}$ . The equation is:



Four O—H bonds are broken and 2 H—H bonds and 1 O=O bond are formed. Under standard condition,

$$\begin{aligned}\Delta H^\circ &= \text{total BE (bonds broken)} - \text{total BE (bonds formed)} \\ &= (4 \times 463.0) - (2 \times 436.0 + 498.0) = 1852 - 1370 = 482.0 \text{ kJ}\end{aligned}$$

Since  $\Delta H > 0$ , the decomposition reaction of water is endothermic.

These two examples show that the enthalpy of a forward reaction equals in value the enthalpy of the same reaction when going backward; only the signs (“+” or “-”) are reversed.

## 12.4 Hess's Law

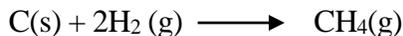
The fact that enthalpy is a state function implies that we can find the enthalpy change of a reaction through different paths. As long as we arrive at the same destination, it is not important where we start and how we proceed. This is the essence of **Hess's Law**. It states that

**The enthalpy change in a reaction is the same regardless of the path by which the reaction occurs.**

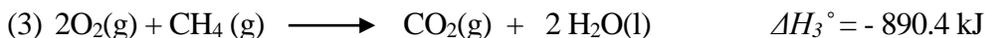
The following example will show you how we apply Hess's Law.

**Question 108.**

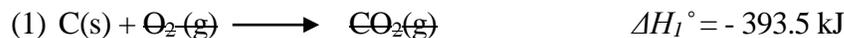
Calculate the enthalpy change for the formation of methane from carbon and hydrogen,



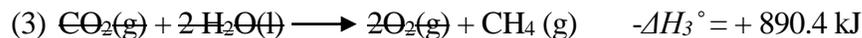
given that the enthalpy changes for the following reactions are known:

**Answer:**

We need to manipulate the three known reactions in such a way that we end up with the desired formation reaction of methane. By inspecting the reactants and products, we see that the following addition of the three reactions will serve our purpose.



And reverse (3) (remember to also reverse the sign of  $\Delta H^\circ$ )



After canceling common items on both sides of the equation we get the desired reaction equation. We add the enthalpy changes exactly the same way as we add the reactions and we get the enthalpy change for the formation of methane,

$$\begin{aligned} \Delta H^\circ &= \Delta H_1^\circ + \Delta H_2^\circ + (-\Delta H_3^\circ) = (-393.5 \text{ kJ}) + (-571.6 \text{ kJ}) + (+890.4 \text{ kJ}) \\ &= -74.7 \text{ kJ} \end{aligned}$$

We can use Hess's Law to calculate enthalpy changes for reactions for which it is hard to measure the enthalpy change experimentally. Or we can check the accuracy of our experiments by comparing the results calculated from Hess's Law to those measured experimentally.

## 12.5 Standard Enthalpies of Formation

What we found in **Question 105** is the enthalpy change for the formation of methane from the elements carbon and hydrogen. This introduces us to another thermodynamic concept, namely, the **standard enthalpy of formation,  $\Delta H_f^\circ$** .

The standard enthalpy of formation,  $\Delta H_f^\circ$ , for any compound is the enthalpy change for the reaction in which the **compound is formed from its elements in their most stable standard states**.

For most elements their most stable form of existence is the most commonly seen form. For example, the most stable elemental form of oxygen is  $\text{O}_2(\text{g})$ , hydrogen is  $\text{H}_2(\text{g})$ , and bromine is  $\text{Br}_2(\text{l})$ , etc. For elements that exist in different solid forms (allotropes), we must specify the form of the element on which standard enthalpies of formation are based. For example, for carbon, its graphite form of existence is chosen as the most stable standard state, not its diamond form.

**The standard enthalpy of formation for any element in its most stable standard state is zero.**

The values of  $\Delta H_f^\circ$  are known for many compounds. We can make use of these values in the same way we use bond energies. Thus we have

$$\Delta H^\circ = \text{total } \Delta H_f^\circ \text{ products} - \text{total } \Delta H_f^\circ \text{ reactants}$$

When using  $\Delta H_f^\circ$  values, it is important to choose the value that corresponds to the physical state. For example, the  $\Delta H_f^\circ$  for liquid water is  $-285.8 \text{ kJ mol}^{-1}$  whereas for gaseous water it is  $-241.8 \text{ kJ mol}^{-1}$ .

One important application of  $\Delta H_f^\circ$  data is to gain a sense of stability of the compound. Essentially what a  $\Delta H_f^\circ$  value tells us is how much chemical energy is stored in a compound. If the standard enthalpy of formation of a compound is negative, the compound contains less stored energy than the elements from which it is formed. If  $\Delta H_f^\circ$  is positive, the compound contains more stored energy than the elements from which it is formed.

For example,  $\Delta H_f^\circ$  for  $\text{CO}_2(\text{g})$  is  $-393 \text{ kJ mol}^{-1}$ , we say that  $\text{CO}_2$  contains less stored energy than the sum of the energy stored in  $\text{C}(\text{graphite})$  and  $\text{O}_2(\text{g})$ . More often we say that  $\text{CO}_2$  is more stable than  $\text{C}(\text{graphite})$  and  $\text{O}_2(\text{g})$ .

In line with the idea that electrons prefer to stay in the lowest possible energy state, compounds participate in chemical reactions to lose their stored energy to become more stable. Based on this understanding, we say

**A more stable compound is chemically less reactive.**

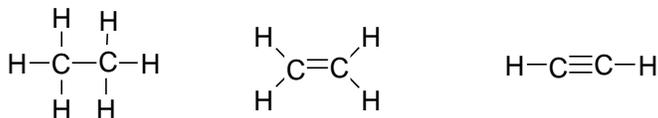
**A less stable compound is chemically more reactive.**

**Question 109.**

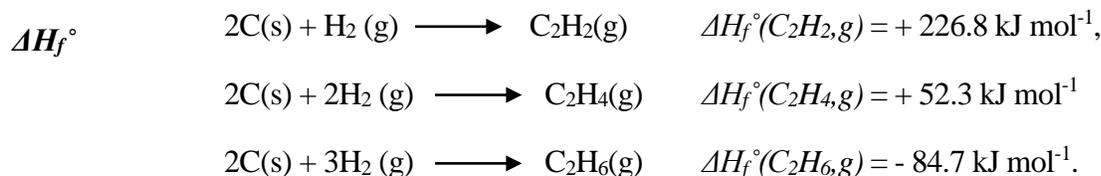
Draw the Lewis structures for ethyne ( $C_2H_2$ ), ethene ( $C_2H_4$ ), and ethane ( $C_2H_6$ ). Compare their chemical stability, given that  $\Delta H_f^\circ(C_2H_2, g) = +226.8 \text{ kJ mol}^{-1}$ ,  $\Delta H_f^\circ(C_2H_4, g) = +52.3 \text{ kJ mol}^{-1}$  and  $\Delta H_f^\circ(C_2H_6, g) = -84.7 \text{ kJ mol}^{-1}$ .

**Answer:**

The Lewis structures are:

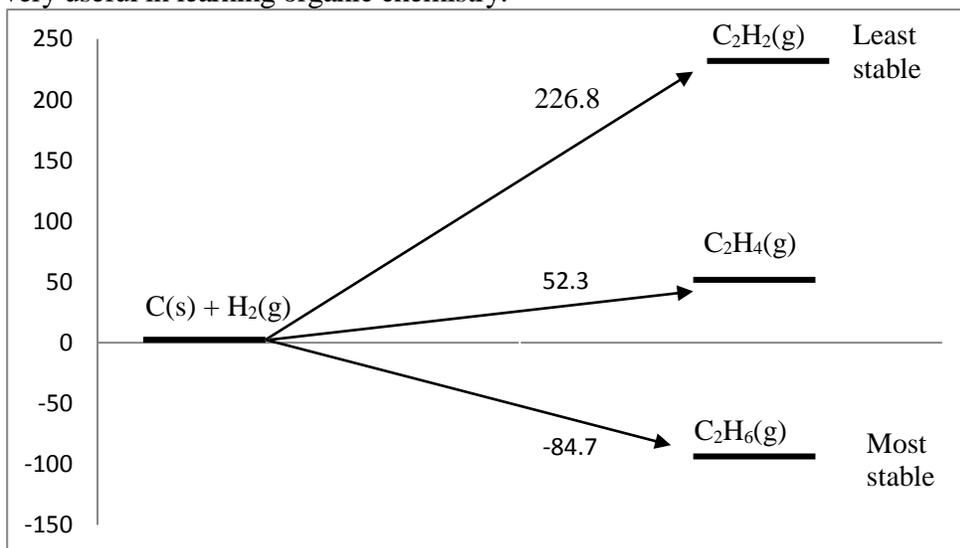


For the formation reactions we have



All three compounds are formed from elemental carbon and hydrogen. Therefore the values of  $\Delta H_f^\circ$  can be used as a measure of their relative stability. We can graphically compare these values as shown on the graph below.

The graph clearly shows that the system  $C_2H_6(g)$  has the lowest stored energy, which makes it the most stable compound on the chart.  $C_2H_2(g)$  has the highest stored energy, which makes it the least stable compound on the chart. Chemically, we say that  $C_2H_2(g)$  is more reactive than  $C_2H_4(g)$ , and  $C_2H_4(g)$  is more reactive than  $C_2H_6(g)$ . In other words, a compound containing a triple bond is more reactive than one containing a double bond, and a compound containing a double bond is more reactive than one containing only single bonds. This understanding will be very useful in learning organic chemistry.



## Practice and Review for Chapter 12

Define (in your own words) the following terms:

Energy: \_\_\_\_\_

Work: \_\_\_\_\_

Heat: \_\_\_\_\_

Force: \_\_\_\_\_

System: \_\_\_\_\_

Surroundings: \_\_\_\_\_

Isolated System: \_\_\_\_\_

First Law of Thermodynamics:

\_\_\_\_\_

Kinetic Energy: \_\_\_\_\_

Potential Energy: \_\_\_\_\_

Internal Energy: \_\_\_\_\_

State Function: \_\_\_\_\_

Enthalpy: \_\_\_\_\_

Exothermic: \_\_\_\_\_

Endothermic: \_\_\_\_\_

Calorimeter: \_\_\_\_\_

Standard Enthalpy: \_\_\_\_\_

Standard State: \_\_\_\_\_

Bond Energy: \_\_\_\_\_

Hess's Law: \_\_\_\_\_

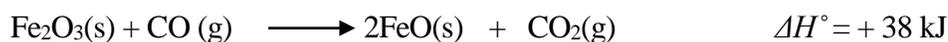
Standard Enthalpy of Formation:

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**Short-Answer Questions:**

1. Give the chemical symbols for the following elements in their most stable elemental form: carbon, hydrogen, chlorine, bromine, oxygen, nitrogen, iodine, mercury, sodium, calcium.

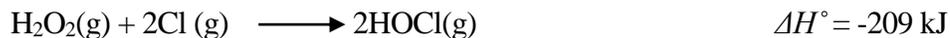
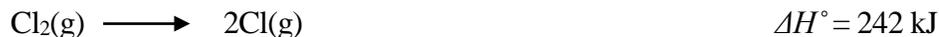
2. Calculate  $\Delta H^\circ$  for the reduction of FeO(s) to Fe(s) by CO(g), given that



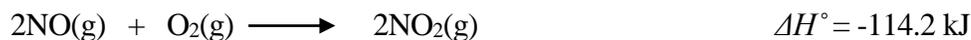
3. It has been proposed that the following reaction might occur in the stratosphere:



Calculate  $\Delta H^\circ$  for this reaction from the following data:



4. Calculate  $\Delta H_f^\circ$  for  $\text{N}_2\text{O}_4(\text{g})$  from the following data:



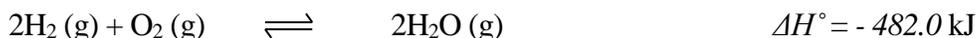
5. For  $\text{H}_2(\text{g})$ ,  $\text{N}_2(\text{g})$ ,  $\text{O}_2(\text{g})$ ,  $\text{F}_2(\text{g})$ , and  $\text{Cl}_2(\text{g})$ , but not for  $\text{Br}_2(\text{g})$  and  $\text{I}_2(\text{g})$ , the standard enthalpies of formation are  $0 \text{ kJ mol}^{-1}$ . Explain why. In what physical states are the standard enthalpies of formation of bromine and iodine  $0 \text{ kJ mol}^{-1}$ , respectively?

# Chapter 13

## Thermodynamics II: The Direction of Chemical Reactions

*Nothing is free. But nature has free energy to do work.*

In chapter 12 (**Question 103**) we have seen that the formation reaction of water is an exothermic reaction:



But the reaction is not spontaneous. When water is left in an open container, however, it spontaneously evaporates, even though the vaporization of water is an endothermic process:



So losing or gaining **only enthalpy** does not seem to make a process go or not go.

It is time to bring in the other player.

### 13.1 Entropy and the Second Law of Thermodynamics

This so-far-hidden player is called **entropy** and is given the symbol  $S$ . Like enthalpy, **entropy is also a state function**. Its value depends only on the conditions that determine the state of the system, such as composition, temperature, and pressure.

Entropy is a **measure of the disorder** of the particles (atoms and molecules) that make up **the system** and the dispersal of energy associated with these particles. If the first law of thermodynamics is the law for energy, then **the second law of thermodynamics** is the law for entropy. It states that:

**In any spontaneous process the total entropy of a system and its surroundings increases.**

In other words, going from order to disorder is spontaneous. It is only *natural*. Mathematically we can write the second law of thermodynamics as:

$$S_{final} - S_{initial} = \Delta S > 0$$

It is almost ironic that we don't see entropy at play when everything in our life seems to be following the second law of thermodynamics!

Our rooms are always messy unless we do “work” to tidy things up. Toys of my kids disappear until I spend time and energy digging in every corner of the house to find them and put them back in place. Try not to groom yourself for a couple of days and I guarantee that you will be a mess! Entropy of the universe is increasing every second. It is the law.

## 13.2 Standard Molar Entropies

Is there that perfect world where there is no disorder? Believe it or not, there is. It is said that **at 0 K** (-273.15 °C), the **entropy of any pure crystalline substance is zero**. Imagine that, all atoms and molecules stay absolutely still in their crystal lattice, not a single movement, no disorder.

To illustrate how entropy of a system varies, let's again use the ice-water-vapor transformation as an example. Here we have a system with fixed composition (only water molecules) and, let's assume, that the pressure is 1 atm. This allows us to just look at the dependency of entropy on temperature.

Imagine the ice crystal at 0K when every atom stays perfectly still and every water molecule has zero kinetic energy. Then slowly we raise the temperature. As the temperature increases, the water molecules gain increased kinetic energy; they vibrate about their positions (although still tied up in the ice network) and they vibrate faster and faster as the temperature goes higher and higher. Disorder increases during the process. When the temperature warms up to above 0 °C, the ice melts and the water molecules move more freely in the liquid state (although still tied up by many H-bonds), causing more and more disorder. When the temperature goes above 100 °C, the water molecules start to move away from the liquid state (evaporate), and the increase of the entropy of the system continues as the temperature continues to rise.

This example shows that in general gases have larger entropies than liquids and liquids have larger entropies than solids.

It is possible to have absolute values of the entropies of any substances at any temperature. The standard molar entropy,  $S^\circ$ , is the entropy of 1 mol of the substance in its standard state—that is, at 1 atm pressure—and at 25 °C. The units of entropy are joules per Kelvin per mol,  $\text{JK}^{-1} \text{mol}^{-1}$ . Note that unlike enthalpy values, entropy values are normally given in joules, not kilojoules.

The values of  $S^\circ$  are known for many compounds. We can make use of these values in the same way we use enthalpy values. Thus we have, for any chemical reaction,

$$\Delta S^\circ = \text{total } S^\circ_{\text{products}} - \text{total } S^\circ_{\text{reactants}}$$

### 13.3 Gibbs Free Energy

Now we are ready to talk about the direction of chemical reactions. A new **state function** that shows the combined effort of enthalpy and entropy in determining the direction of a reaction is called **Gibbs free energy, G**. At constant temperature and pressure the intricate play between enthalpy and entropy is expressed as

$$\Delta G = \Delta H - T\Delta S$$

Here is how we use  $\Delta G$  to determine the direction of a reaction.

**When  $\Delta G < 0$ , the reaction is spontaneous.**

**When  $\Delta G > 0$ , the reaction is not spontaneous (but spontaneous in the reverse direction).**

**When  $\Delta G = 0$ , the reaction is at equilibrium.**

Like enthalpy and entropy, we can calculate the **standard free energy change,  $\Delta G^\circ$** , for any reaction, from the **standard free energies of formation,  $\Delta G_f^\circ$** , of the reactants and products.

$$\Delta G^\circ = \text{total } \Delta G_f^\circ_{\text{products}} - \text{total } \Delta G_f^\circ_{\text{reactants}}$$

**$\Delta G_f^\circ$  of the elements in their standard states are taken as zero, as for  $\Delta H_f^\circ$  values.**

Recall in Chapter 9 we introduced how to predict the shift of equilibrium by comparing the reaction quotient and the equilibrium constant as follows:

- If  $Q < K$ , the concentrations of the products will increase and the concentrations of the reactants will decrease until equilibrium is reached.
- If  $Q > K$ , the concentrations of the reactants will increase and the concentrations of the products will decrease until equilibrium is reached.
- If  $Q = K$ , the reactants and the products are at equilibrium, and there will be no change in the concentrations of the reactants or the products.

The relationship between  $\Delta G$ , the reaction quotient (Q) and the equilibrium constant (K) is defined by

$$\Delta G = RT \ln\left(\frac{Q}{K}\right)$$

Or

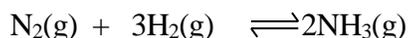
$$\Delta G = RT \ln Q - RT \ln K$$

Where  $R$  is called gas constant and has the value of  $8.314 \text{ JK}^{-1}$ .  $T$  is temperature in Kelvin.

This equation shows that we can arrive at the same conclusion regarding the direction of a reaction by using either  $\Delta G$ , or the reaction quotient ( $Q$ ) and the equilibrium constant ( $K$ ).

### Question 110.

A reaction vessel contains 10 atm  $\text{N}_2$ , 10 atm  $\text{H}_2$ , and 1 atm  $\text{NH}_3$ . Predict the direction of the reaction at 298 K given that  $K_p = 5.68 \times 10^5 \text{ atm}^{-2}$ .  $K_p$  is the equilibrium constant when partial pressures (not concentrations) are used in the expression.



### Answer:

First we write the reaction quotient. Since all reactants and products are in gaseous state, we use their partial pressures in place of concentrations.

$$Q = \frac{(p_{\text{NH}_3})^2}{(p_{\text{N}_2})(p_{\text{H}_2})^3} = \frac{1^2}{10 \times 10^3} = 1 \times 10^{-4}$$

Since  $Q \ll K_p$ , we predict that the equilibrium will shift to the reactants side. We can also calculate

$$\begin{aligned} \Delta G &= RT \ln\left(\frac{Q}{K}\right) = (8.314 \text{ JK}^{-1})(298\text{K})\left(\ln\frac{1 \times 10^{-4}}{5.68 \times 10^5}\right) \\ &= (8.314 \text{ JK}^{-1})(298\text{K})(-22.5) = -55719 \text{ J} = -60 \text{ kJ} \end{aligned}$$

Since  $\Delta G < 0$ , the reaction is spontaneous from left to right.

In summary, in this chapter we have introduced three new thermodynamics concepts, namely, enthalpy change ( $\Delta H$ ), entropy change ( $\Delta S$ ), and Gibbs free energy change ( $\Delta G$ ). For most people the concept of enthalpy change is not so hard to grasp, as most of the time we can think of  $\Delta H$  in terms of heat released or taken in by a system.

What escape our common sense are the concepts of  $\Delta G$  and  $\Delta S$ . Here I will try to put a human perspective into the two important, but not-so-obvious, state functions. We can compare  $G$ , the free energy, to cash in someone's hand. When you have cash, spending it is spontaneous, and you always end up having less ( $\Delta G < 0$ ). In fact most people would keep spending until rock bottom ( $\Delta G = 0$ ). It is this same "natural force" that drives a reaction towards a certain direction.

A chemical reaction takes place so that the **system** ends up with **less** free energy.

On the other hand, we can compare  $S$ , the entropy, to the human desire to possess material things (catching up with the Joneses). One's desire to have more forever grows ( $\Delta S > 0$ ). Now you can blame it on the *chemistry in us*.

## 13.4 Gibbs Free Energy and Work

Spending is not always a bad thing, especially if the money is well spent. In fact nature is not at all as wasteful and careless as we are, in spending its free energy. Most of the time, the free energy change is harvested to do work. For example, our body gets energy from the metabolic oxidation reaction of glucose,



By digesting 1 mol (180.2 g) of glucose, 686 kilocalories of free energy are produced and are available to do work.

For a healthy working adult, 2000 to 2500 kcal is the amount of energy needed daily from diet. If we overeat, we take in more calories than needed. If we are less active (sitting and watching TV all day), we need even less than 2000 kcal to maintain our day. Ideally we should never overeat. When we do, the body's way to deal with the extra free energy is to store it (as fat) for future use. Thus we gain weight. No free energy is wasted; this is as good as nature gets.

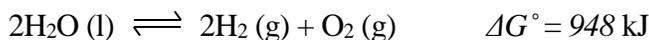
Now we know why  $G$  is called **free energy**. It means the amount of energy a system can **spare** to do work, or the maximum work obtainable from a chemical reaction. At constant temperature and pressure we can write

$$w_{\max} = -\Delta G$$

If a chemical reaction is not spontaneous in the desired direction,  $\Delta G$  provides us with the estimation as to how much minimal amount of work is needed to make the reaction proceed as desired. This is a very useful aspect of  $\Delta G$ .

### Question 111.

How much work is needed to decompose 1 mol of water at 298 K and 1 atm? Given that



### Answer:

The free energy change given for the above reaction ( $\Delta G^\circ = 948 \text{ kJ} > 0$ ) means that under standard conditions the decomposition of water is not a spontaneous process and it will take at least 948 kJ of energy to decompose 2 moles of water. Therefore it will take 474 kJ of work to decompose 1 mol of water at 298 K and 1 atm.

Industrially this has been done by passing an electric current through water in order to produce hydrogen and oxygen. Reversely, if a spontaneous reaction is an oxidation-reduction reaction, then there will be electron transfer between the reactants. If we can keep the electron transfer going continuously in one direction, we have an **electric current**. This is the thinking behind

**electrochemistry**, a branch of chemistry that studies the electron flow in oxidation-reduction reactions and the application of such reactions.

## 13.5 Coupled Reactions

Since  $\Delta G$  is a state function just like  $\Delta H$ , we can apply Hess's Law to obtain  $\Delta G_{\text{overall}}$  for an overall reaction in the same way as we find  $\Delta H_{\text{overall}}$ .

When we deliberately combine two or more reactions to obtain a  $\Delta G_{\text{overall}}$  that is negative, we are trying to **drive** a non-spontaneous reaction to go forward. That is, to make a non-spontaneous reaction go by combining the reaction with another reaction that **has a greater and negative  $\Delta G$**  (so that  $\Delta G_{\text{overall}} < 0$ ). This strategy is called **reaction coupling**.

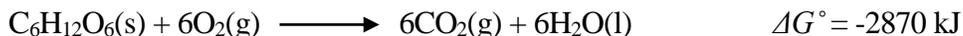
Again nature does it better. The coupling of reactions has been a key strategy in the body's metabolic system.

### Question 112.

At body temperature (37 °C), the hydrolysis of ATP occurs as follows, to produce ADP.



To convert 1 mol of ADP back to ATP, 30 kJ of energy is needed. If the oxidation reaction of glucose is coupled to provide the energy, how many moles of ATP can be produced from the oxidation of 1 mol of glucose? Given that



### Answer:

To convert ADP back to ATP, the reaction is



Since the oxidation of 1 mol of glucose can provide 2870 kJ of free energy,  $\frac{2870}{30} = 95$  moles of ATP can be produced by coupling the oxidation reaction of glucose with this reaction.

Note that in reality only 38 moles of ATP are generated for each mol of glucose oxidized. This is because the actual coupling is a multistep process and inevitably some energy is being used elsewhere and some is lost as heat.

I wonder how our bodies would feel if they found out that some of us get *paid* for work done using the body's "free energy."

### 13.6 Direction of Oxidation-Reduction Reactions

The availability of half-cell potential values for a wide range of half reactions provides us with another way to predict the direction of chemical reactions. Indeed the three methods of prediction, namely, by Gibbs free energy ( $\Delta G$ ), by reaction quotient ( $Q$ ) and equilibrium constant ( $K$ ), and by cell potential ( $E_{cell}$ ) are quantitatively related. The relationship is

$$\Delta G = -n F E_{cell} = -RT \ln(K/Q)$$

Or, if all substances are in their standard states (hence  $Q = 1$ ),

$$\Delta G^\circ = -n F E^\circ_{cell} = -RT \ln K$$

Where  $n$  is the number of moles of electrons and  $F$  is the Faraday constant. 1 F is the charge of 1 mol electrons.

$$1 F = (6.0221 \times 10^{23} \text{ electrons mol}^{-1})(1.6022 \times 10^{-19} \text{ coulomb electron}^{-1}) = 96485 \text{ C mol}^{-1}$$

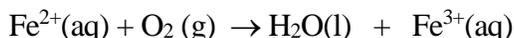
$$\text{or} \quad = 96485 \text{ J/(V mol)}$$

#### Question 113.

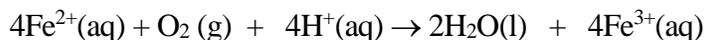
Calculate  $\Delta G^\circ$  and  $K$  to find out if  $\text{Fe}^{2+}(\text{aq})$  can be spontaneously oxidized by the oxygen in air? Given that for oxygen  $E^\circ_{red} = 1.23 \text{ V}$  and for  $\text{Fe}^{3+}$   $E^\circ_{red} = 0.77 \text{ V}$ .

#### Answer:

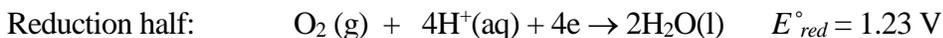
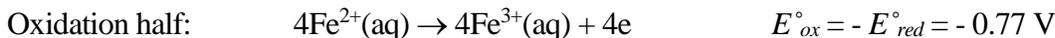
The reaction in question is



After balancing both charges and atoms, the reaction is



For this reaction, the half reactions are:



$$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red} = -0.77 + 1.23 = 0.46 \text{ V}$$

The positive cell potential indicates that the reaction in question is a spontaneous reaction.

This can be confirmed by calculating  $\Delta G^\circ$ , assuming that all substances are in their standard states,

$$\Delta G^\circ = -n F E^\circ_{cell} = -(4 \text{ mol})(96485 \text{ C mol}^{-1})(0.46 \text{ J C}^{-1}) = -177532 \text{ J} = -180 \text{ kJ}$$

The large negative value of  $\Delta G^\circ$  indicates that the reaction is spontaneous from left to right.

Since 
$$\Delta G^\circ = -n F E^\circ_{cell} = -RT \ln K$$

We have

$$\ln K = -\frac{\Delta G^\circ}{RT} = -\frac{-180\,000 \text{ J mol}^{-1}}{(8.31 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 73$$

$$K = e^{-\frac{\Delta G^\circ}{RT}} = 5 \times 10^{31}$$

This is a very large equilibrium constant and it again indicates that the position of the equilibrium lies far to the right and the reaction will go to completion from left to right.

### 13.7 Nonstandard Conditions: The Nernst Equation

The values of standard reduction potential can still be useful in nonstandard conditions, that is, when all substances are not in 1 M and all partial pressures of gases are not 1 atm. We can calculate cell potentials under nonstandard conditions by making use of the **Nernst equation**:

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln Q$$

Using this equation, we can calculate the cell potential of any cell if we know the concentrations of the reactants and the standard cell potential,  $E^\circ$ .

Since  $R$  and  $F$  are constants, if we let  $T = 298 \text{ K}$  ( $25^\circ \text{C}$ ), we can simplify the Nernst equation as follows:

$$E_{cell} = E^\circ_{cell} - \frac{(8.31 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{n(96485 \text{ C mol}^{-1})} \ln Q = E^\circ_{cell} - \frac{0.0257 \text{ J C}^{-1}}{n} \ln Q$$

$E_{cell} = E^\circ_{cell} - \frac{0.0257}{n} \ln Q \quad (\text{at } 25^\circ \text{C})$
---

#### Question 114.

At  $25^\circ \text{C}$ , a zinc-copper cell started to operate with  $[\text{Zn}^{2+}] = [\text{Cu}^{2+}] = 1.00 \text{ M}$ . After a certain time the concentrations had changed so that  $[\text{Zn}^{2+}] = 1.90 \text{ M}$  and  $[\text{Cu}^{2+}] = 0.10 \text{ M}$ . Calculate the cell potential at these new concentrations. Given that  $E^\circ_{cell} = 1.10 \text{ V}$ .

**Answer:**

The overall reaction for the zinc-copper cell is



For this reaction  $n = 2$  and

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \quad (\text{remember that solids are not included in the expression of } Q)$$

Thus

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0257}{n} \ln Q = 1.10 - \frac{0.0257}{2} \ln \frac{1.9}{0.1} = 1.10 - 0.038 = 1.06 \text{ V}$$

We can see that the cell potential decreased from 1.10 V to 1.06 V. As the reaction continues, the concentrations will change more and the cell potential will decrease more. Gradually the cell potential will decrease to zero and the cell will stop to produce an electric current. If the cell is a battery, then we say that the battery is dead.

## Practice and Review for Chapter 13

**Define (in your own words) the following terms:**

Entropy: \_\_\_\_\_

The Second Law of Thermodynamics:

\_\_\_\_\_

Standard Molar Entropy:

\_\_\_\_\_

Gibbs Free Energy: \_\_\_\_\_

Hess's Law for Free Energy Changes:

\_\_\_\_\_

Faraday Constant: \_\_\_\_\_

**Short-Answer Questions:**

1. How is Gibbs free energy related to the equilibrium constant and the reaction quotient?
2. How is Gibbs free energy related to work?
3. How is Gibbs free energy change related to the direction of chemical reactions?
4. What is the relationship between the values of  $E_{cell}$ ,  $\Delta G$ , reaction quotient  $Q$  and equilibrium constant  $K$ ?
5. How many ways do we have to predict the direction of chemical reactions? List the criteria for a) a spontaneous reaction; b) a non-spontaneous reaction; and c) a reaction at equilibrium in terms of the values of  $E_{cell}$ ,  $\Delta G$ , reaction quotient  $Q$  and equilibrium constant  $K$ ?
6. Give the Nernst equation at 25 °C.