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

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.

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

- Lecture (PowerPoint lecture notes are posted on Moodle)
- Applied Cases and Tutorials (ACT)
- Online homework and quizzes
- Free and open educational resources (this coursepack and the ACT manual)

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. Treat this book as an exercise book, work or at least think through each question before taking in the answer. This way you will get the most out of this book.

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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Chapter 1

Introduction to Scientific Thinking

Thinking scientifically is an acquired habit.

You can think scientifically, talk scientifically, and write scientifically, if needed.

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, swirl to dissolve the salt.

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:

a. Table salt is sodium chloride.

b. The molecular formula of sodium chloride is NaCl. How does this relate to the amount of NaCl needed?

c. What does 0.1000 M mean and how much NaCl is needed to obtain this number?

d. What measurement tool to use to measure the amount of NaCl and how accurate should you be? Accurate to a gram or a milligram?

e. 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?

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.

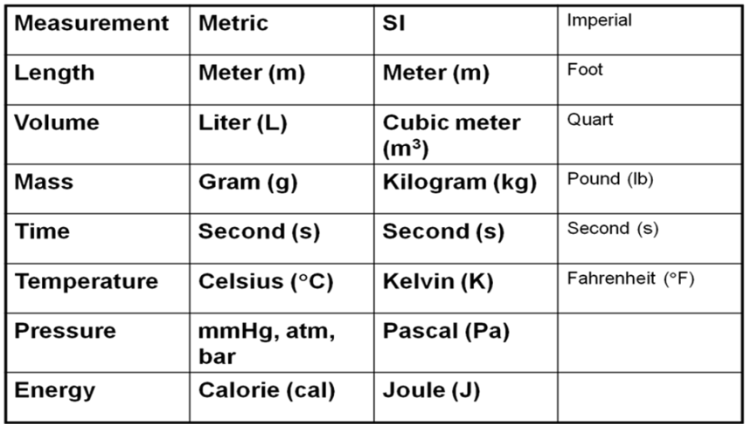
Read points "*a*" to "*e*" on the previous page and identify the words or symbols that are units of measurement. Also indicate the type of measurement the units are used for.

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^3)	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)	

The metric system is a decimal system in which measurements of each type are related by factors of 10. For example, one centimeter is equivalent to 10 millimeters; one 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	µ	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 100th 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.

To write 4500000000.0 in scientific notation we move the decimal point to the **left** nine digits to obtain the coefficient **4.5**, then we multiply 4.5 by 10^9. The power is **positive** because the original number is greater than one.

Answer:

negative power

$0.00000023 = 2.3 \times 10^{-7}$,

Decimal point moves to the *right*

positive power

$4500000000.0 = 4.5 \times 10^{9}$

Decimal point moves to the *left*

To convert a scientific notation to a standard number, we simply reverse the direction in moving the decimal point, as illustrated below.

Negative power

$2.3 \times 10^{-7} = 0.00000023$,

Decimal point moves to the *left seven digits*

Positive power

$4.5 \times 10^{9} = 4500000000.0$

Decimal point moves to the *right nine digits*

When we want to write 0.005600 mL in scientific notation, what do we do with the two zeros after the number 6?

First we move the decimal point to the right **3** digits to obtain the coefficient 5.6. This gives a negative power of 10, 10^{-3}. Now do we keep or drop the two zeros after the number 6? That is, whether

0.005600 mL $= 5.600 \times 10^{-3}$ mL or $= 5.60 \times 10^{-3}$ mL or $= 5.6 \times 10^{-3}$ mL?

The three choices above would represent three types of accuracy. Therefore a correct decision cannot be made without the knowledge of **significant figures**.

1.3 Accuracy and Significant Figures

Measured and Exact Numbers

Exact numbers are obtained when we count objects. Suppose you counted 5 beakers in your laboratory drawer. The number 5 is an exact number. You did not use a measuring tool such as a graduated cylinder or a balance to obtain the number, you counted them exactly. Exact numbers are also found in the numbers that define a relationship between two metric units. For example, the numbers in the following definitions are exact: 1 metre is equal to 100 cm; 1000 mL is equal to 1 L.

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

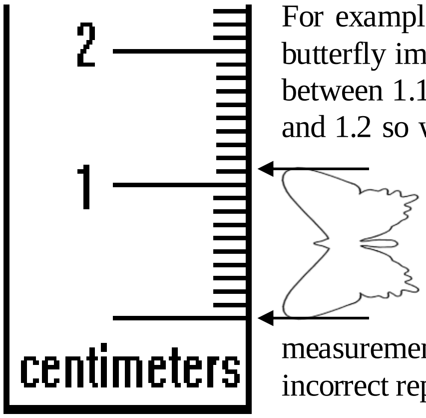
In many cases, it is not necessary to accurately measure the exact quantity of a material. If an experiment calls for **about** 3 g of a reagent, it is not necessary to weigh it on the analytical balance to exactly 3.0000 g. If however, the directions call for 3 g to the nearest 0.0001 g then measuring 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 wingspan 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 wingspan of the butterfly image as shown above. They used the same ruler; each made three measurements, and reported their data as follows:

	Student A	Student B
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 wingspan of the butterfly image, and reported their data as follows:

	Student C	Student D
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 wingspan of the butterfly image with a tool of their choice.

Student F	Number of Sig. Fig.	Student G	Number of Sig. Fig.
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 mL = 5.600×10^{-3} mL **not** 5.60×10^{-3} mL **nor** 5.6×10^{-3} 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 5.60×10^{-3} mL or 5.6×10^{-3} 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 = 2.00×10^2, 550 = 5.50×10^2 and 6000 = 6.000×10^3 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: 2.0×10^2, 5.5×10^2 and 6.0×10^3. 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. 5.600×10^{-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	Student D	Student E
Trial 1: 1.1 cm	Trial 1: 1.1500 cm	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 1.16×10^3 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 × 5.600 ÷ 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 × 5.600 ÷ 4.1 or 25 × 5.6 ÷ 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

$25.0 \times 5.600 \div 4.1 = 34 = 3.4 \times 10^1$ (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 × 5.5 ÷ 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 × 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 × 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 × 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 × 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:

25.0**4562** = 25.0, 5.60**0345** = 5.60, 0.00346**7241**= 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 25.0**4562** and 5.60**0345**.

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 0.003467**241**.

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, $\frac{\textbf{4 quarters}}{\textbf{1 dollar}}$ or $\frac{\textbf{1 dollar}}{\textbf{4 quarters}}$, 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 $\frac{\textbf{4 quarters}}{\textbf{1 dollar}}$, we have

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

Question 10.

How many dollars are equal to 2500 quarters?

Answer:

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

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

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 = 10^9 nm	1 dL = 100 mL	1 g = 1000 mg	1 min = 60 s
1 cm = 10 mm	1 mL = 1 cc = 1 cm^3	—	1 s = 10^6 μs

The units "mL", "cc", and "cm^3" 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:

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

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

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

The final answer needs to be in the unit $\frac{tablet}{month}$. 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.

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

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 (˚C) in metric system, Kelvin (K) in SI, and Fahrenheit (˚F) in imperial system. The conversion between these units employs two equalities:

Celsius to Kelvin		Celsius to Fahrenheit
$T\ K = T\ ^\circ C + 273.15$	and	$T\ ^\circ F = 1.8 \times T\ ^\circ C + 32$

This gives the definition that

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

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 ˚C at 0 K?

Answer:

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

Question 13.

What is the temperature in ˚C at -10 ˚F?

Answer:

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

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.

Chapter 2

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

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

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.

Question 14.

Give the chemical symbol for the elements hydrogen, oxygen, aluminum, carbon, and helium.

<u>Answer:</u>

The corresponding symbols are, respectively, H, O, Al, C, and He.

Every element is assigned an **atomic number**. The periodic table below has the atomic numbers filled in for the first 36 elements.

$_{1}$H																	$_{2}$He
$_{3}$Li	$_{4}$Be											$_{5}$B	$_{6}$C	$_{7}$N	$_{8}$O	$_{9}$F	$_{10}$Ne
$_{11}$Na	$_{12}$Mg											$_{13}$Al	$_{14}$Si	$_{15}$P	$_{16}$S	$_{17}$Cl	$_{18}$Ar
$_{19}$K	$_{20}$Ca	$_{21}$Sc	$_{22}$Ti	$_{23}$V	$_{24}$Cr	$_{25}$Mn	$_{26}$Fe	$_{27}$Co	$_{28}$Ni	$_{29}$Cu	$_{30}$Zn	$_{31}$Ga	$_{32}$Ge	$_{33}$As	$_{34}$Se	$_{35}$Br	$_{36}$Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Below is one feature of the periodic table:

The elements are arranged in increasing order of atomic numbers

from left to right, top to bottom.

One thing you need to be able to do, when given a simplified periodic table such as Table 4 (page 15), is to fill in the atomic numbers. Can you fill in the atomic numbers for the rest of the elements in the table above?

How were the atomic numbers assigned to the elements? What makes hydrogen (H) the "No. 1" element? There are many reasons that I can give to show that hydrogen is indeed a very important element. However, what makes hydrogen the very first element in the periodic table has to do with the **structure of the atoms**.

2.2 Atomic Theory

Let's take a look at the following comparison.

Item	Size	Smallest unit
A two-hour video clip	700 MB	byte
Anything we know	any size	atom

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 1.67×10^{-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 proton + 7 neutron = 14. Thus the atomic mass of nitrogen is $14 \times 1.67 \times 10^{-24}$ g = 23.4×10^{-24} g = 2.34×10^{-23} 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 1.67×10^{-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 2.34×10^{-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.

$$^{12}_{6}\mathrm{C}$$

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
	${}^{27}_{13}\mathbf{Al}$		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.

$$ {}^{12}_{6}\mathrm{C} \qquad {}^{13}_{6}\mathrm{C} \qquad {}^{14}_{6}\mathrm{C} $$

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.

Weighted average atomic mass of carbon $= 12.00 \times 0.9893 + 13.00 \times 0.0107 = 12.01$ 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	$^{27}_{13}\mathrm{Al}$	13	27	14	13	13
Calcium	$^{42}_{20}\mathrm{Ca}$	20	42	22	20	20
Oxygen	$^{18}_{8}\mathrm{O}$	8	18	10	8	8

2.3 Chemical Quantities

The Concept of Mole

Imaging 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 (6.022×10^{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 $1\ \mathrm{u} = 1.67 \times 10^{-24}$ g. The magic of the **Avogadro's number** is that

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

This means that the mass of 6.022×10^{23} protons together is one gram. This also means that if we pack 6.022×10^{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, 6.022×10^{23} C-12 atoms together would weigh 12.00 g. If we consider the weighted average atom of carbon, then 6.022×10^{23} carbon atoms together would weigh 12.01 g. This number 6.022×10^{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 6.022×10^{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^{-1}**. The following two conversion factors are very useful in converting among *mass, number of moles, and number of atoms* of an element*:*

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

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 × 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*:*

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

$$and$$

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

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 H_2O. Thus the mass of one mole of water is the sum of the masses of two moles of H and one mole of O:

Mass of one mole of water = **2** × 1.008 g/mol + **1** × 15.9994 g/mol = 18.02 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 × 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:

$$\text{Number of water molecules} = 500.0\text{g} \times \frac{1\ mole\ of\ water}{18.02\ g} \times \frac{6.022 \times 10^{23} water\ molecules}{1\ mole\ of\ water}$$

$$= 1.671 \times 10^{25}$$

Question 21.

How many water molecules are there in 500.0 cc water (d = 1.00 g/mL)?

<u>**Answer:**</u>

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.

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

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 (g/cm^3) or grams per milliliter (g/mL), respectively. The density of gases is usually stated as grams per liter (g/L).

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

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

In **Question 20** we already found out that there are 1.671×10^{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 1.67×10^{25}.

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: ____

Chapter 3

Water Science I: Dissolving and Solving for Solutions

Like dissolves like!

We started this book with a simple task: making salt water. 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 are the ones 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**.

3.1 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.

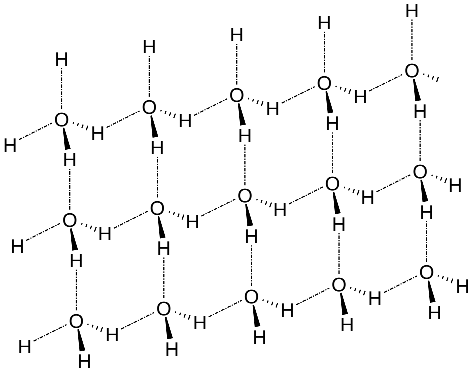
A solution with a relatively small concentration is said to be **dilute**. A solution having a large concentration of solute is said to be **concentrated**. In the case of fruit drinks made from concentrated juices, the latter must have come from originally dilute juices. The dilute juices, freshly squeezed 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?

3.2 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_2), sulfur (S_8) and phosphorus (P_4) crystals, each having a formula that represents the **smallest structural unit** in the molecular solid.

Question 22.

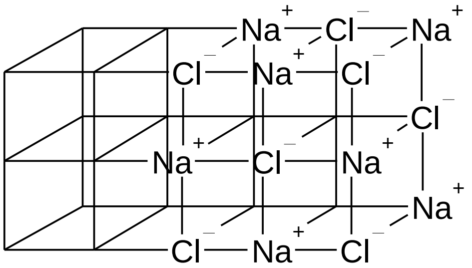
Is dry ice (CO_2 in its solid state) a molecular solid? What holds the CO_2 molecules together in dry ice?

Answer:

CO_2 is a non-polar, covalent molecule. Therefore dry ice is a molecular solid. The only intermolecular forces exist among CO_2 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_2. Liquid CO_2 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**.

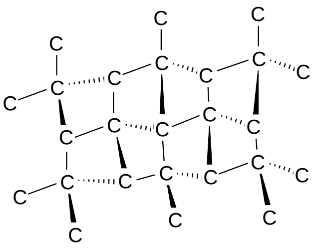
The crystals of NaCl represent another type of solid known as **3D-network solids**. In these solids the regular arrangement of ions extends indefinitely in three dimensions and no individual molecules can be recognized. The ions are held together by **ionic bonds** in a fashion that ensures that each 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^+ is bonded to six Cl^- and each Cl^- is bonded to six Na^+ 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?



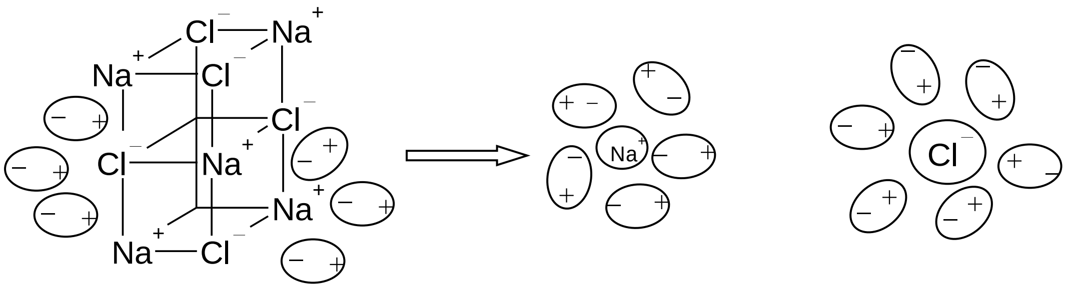
Diamond is yet another type of 3D-network crystals. Only here the smallest unit is the carbon atom and the atoms are held together by

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

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.

3.3 The Dissolving Process

The drawing below 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.



Before dissolving After dissolving

The numbers of water molecules surrounding the ions are not exact. The drawing is only for illustration purposes. Note that the sodium cation is drawn as smaller in size than the chloride anion. The reason for this will be discussed in Chapter 6.

When the "pull" from the water dipoles becomes strong enough to break the ionic bond between the Na^+ and the Cl^- ions, the ions are 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** (aq) or **hydrated**. The layer of water prevents the Na^+ ions and the Cl^- ions from being attracted to each other again. An equation describing this dissolving process would be

$$NaCl\,(s) \;+\; H_2O\,(l) \;\rightarrow\; Na^+\,(aq) \;+\; Cl^-\,(aq) \;+\; H_2O\,(l)$$

If we made the solution to have a molar concentration of 0.0001 M, then $[Na^+] = [Cl^-] = 0.0001$ 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:

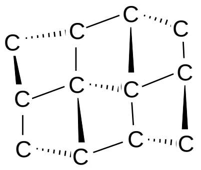
$$\mathrm{NaCl\ (s)} \xrightarrow{H_2O} \mathrm{Na^+\ (aq)} + \mathrm{Cl^-\ (aq)}$$

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

Question 23.

Why diamond crystals do 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.

3.4 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:

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

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

For example, a beer can be listed as having a 5% ABV (**a**lcohol **b**y **v**olume) or a 4% ABW (**a**lcohol **b**y **w**eight). It is easy to convert between these two. ABW = 0.8 × ABV.

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

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

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

Question 24.

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

Answer:

This questions requires us to find mass (in grams) from a given volume and a given molar concentration. This can be done in several small steps, or in one step using several conversion factors (dimensional analysis). We will demonstrate both methods below.

The step by step method:

1) Find the number of moles of NaCl (note: the unit of volume must be changed from mL to L, thus 500.0 mL = 0.5000 L)

$$\text{Moles of NaCl} = Molarity\ \times Liters\ of\ solution$$

$$= 0.1000\ \frac{mol}{\cancel{L}} \times 0.5000\ \cancel{L} = 0.05000\ \text{mol}$$

2) Turn moles to grams by using molar mass of NaCl:

$$\text{Molar mass of NaCl} = 22.99\ \frac{g}{mol} + 35.45\ \frac{g}{mol} = 58.44\ \frac{g}{mol}$$

$$\text{Mass of NaCl (g)} = moles\ \times molar\ mass\ of\ NaCl$$

$$= 0.05000\ \cancel{\text{mol}} \times 58.44\ \frac{g}{\cancel{mol}} = 2.922\ \text{g}$$

The one-step dimensional analysis method:

Mass of NaCl (g)

= $Molarity(\frac{moles}{L}) \times volume(mL) \times (\frac{1L}{1000mL}) \times molar\ mass\ of\ NaCl(\frac{g}{1\ mole})$

= 0.1000 $\frac{\cancel{moles}}{\cancel{L}} \times 500.0\cancel{mL} \times (\frac{1\cancel{L}}{1000\cancel{mL}}) \times 58.44\ \frac{g}{\cancel{1\ mole}}$ = 2.922 g

It is strongly recommended that you learn to master the dimensional analysis method.

The required amount of NaCl has **4** significant figures. To achieve such accuracy we need to use an analytical balance in the laboratory.

The relationships among mole, molar mass, mass, and number of molecules are very important in quantitative chemistry. We will do some more example questions to illustrate these relationships.

Question 25.

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: $\frac{6.023 \times 10^{23} molecules}{1\ mol}$. Using the dimensional analysis method, we can write:

# of molecules of NaCl = 2.922 $\cancel{g} \times 58.44\ \frac{1mol}{58.44\ \cancel{g}} \times \frac{6.023 \times 10^{23}}{\cancel{1\ mol}}$ = 3.012×10^{22}

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

Question 26.

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

Answer:

This question requires us to find the mass of water (g) from its volume (mL) and density. In most everyday situations we can use $d_{water} = 1.00\ g/cm^3$ 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 available.

The density of water changes slightly with temperature. At 22.0 ˚C $d_{water} = 0.9978\ g/cm^3$.

Using the dimensional analysis method, we calculate:

$$\#\text{ of water molecules} = 500.0\ \cancel{\text{mL}} \times 0.9978\ \frac{\cancel{g}}{\cancel{cm^3}} \times \left(\frac{1\ \cancel{cm^3}}{1\ \cancel{\text{mL}}}\right) \times \frac{1 mol}{18.02 \cancel{g}} \times \frac{6.023 \times 10^{23}}{\cancel{1\ mol}} = 1.668 \times 10^{25}$$

Question 27.

When we dissolve 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

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

The total number of water molecules in 500.0 mL of water is 1.668×10^{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 Na^+ and Cl^- ions enormously.

3.5 Electrolytes and Non-electrolytes

Now imagine the 3.012×10^{22} Na^+ cations and equal number of Cl^- anions swimming inside the 500.0 mL solution, each surrounded by a layer of water molecules. 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 there is no such thing as a sodium chloride molecule. There are only hydrated sodium cations and hydrated chloride anions.

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 28.

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

Answer:

Magnesium forms a 2+ cation, Mg^{2+}. The balanced net ionic equation would be:

$$MgCl_2\,(s) \xrightarrow{H_2O} Mg^{2+}\,(aq) + 2Cl^{-}\,(aq)$$

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**.

Practice and Review for Chapter 3

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: ____

Short-Answer Questions:

1. Draw the dissolving process for a small NaCl crystal.

2. Write a net ionic equation for the dissolving of KCl in water.

3. What is the key factor that determines the solubility of a substance in water?

Chapter 4

Chemical Reactions

It is all about balance.

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!

4.1 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 ($C_{12}H_{22}O_{11}$) 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,

$$C_{12}H_{22}O_{11}\underset{\underset{\text{solid state}}{\uparrow}}{(s)} \xrightarrow{+H_2O} C_{12}H_{22}O_{11}\underset{\underset{\text{aqueous state}}{\nearrow}}{(aq)}$$

If the sugar water is consumed, the sugar molecules would be turned into carbon dioxide (CO_2) and water (H_2O), 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:

$$C_{12}H_{22}O_{11}(aq) + 12\,O_2\underset{\nwarrow}{(g)} \longrightarrow 12CO_2\underset{\nearrow}{(g)} + 11H_2O\underset{\underset{\text{liquid state}}{\nearrow}}{(l)}$$

gaseous state

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**.

An equation that has all atoms accounted for on both sides of the reaction arrow (→) 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.

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

Question 29.

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_2O (aq) will be redundant whereas H_2O (l) indicates that the water molecule is in a liquid state, as oppose to solid (ice) or gaseous (steam) states.

4.2 Types of Chemical Reactions

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 30.

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

Answer:

Chlorine is one of the elements that exist as diatomic molecules. It forms a -1 anion in chemical reactions. Zn forms a 2+ cation. It takes two Cl^- to charge-balance one Zn^{2+}. By including the physical states to the reactants and the product the balanced reaction equation would be:

$$\text{Zn (s)} + \text{Cl}_2\text{ (g)} \longrightarrow \text{ZnCl}_2\text{ (s)}$$

Question 31.

Is this an oxidation-reduction reaction? Which reactant is the oxidizing agent and which is the reducing agent?

$$Zn\,(s) + Cl_2\,(g) \longrightarrow ZnCl_2\,(s)$$

Answer:

Yes this is an oxidation-reduction reaction. Metals usually act as reducing agents. So zinc is the **reducing agent** and chlorine is the **oxidizing agent**.

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

$$ZnCl_2\,(s) \longrightarrow Zn\,(s) + Cl_2\,(g)$$

Single Replacement Reactions

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

Example:

$$ZnCl_2\,(s) + F_2\,(g) \longrightarrow ZnF_2\,(s) + Cl_2\,(g)$$

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:

$$CaCl_2\,(aq) + 2AgNO_3\,(aq) \longrightarrow Ca(NO_3)_2\,(aq) + 2AgCl\,(s)$$

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. 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 O_2 is involved as a reactant.

Examples:

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

$$C_{12}H_{22}O_{11}(aq) + 12\,O_2(g) \longrightarrow 12CO_2(g) + 11H_2O(l)$$

These three examples also show that it is not just metals that can act as reducing agents, i.e. being oxidized. Many elements are easily oxidized by oxygen. In the presence of oxygen, some non-metals are forced to carry positive charges, i.e. become cation-like. Typical examples of such cases can be found in a group of very common anions, called **oxoanions**.

4.3 Polyatomic Ions

The name polyatomic ion refers to an ion that is composed of more than two atoms. For example, the hydroxide ion (OH^-) and the cyanide ion (CN^-) are not polyatomic ions but the ammonium ion (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 but they are not cations. The positively charged nonmetal and the negatively charged oxygen 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	Charge	Name	Formula	Charge
Nitrate	NO_3^-	-1	Nitrite	NO_2^-	-1
Chlorate	ClO_3^-	-1	Chlorite	ClO_2^-	-1
Sulfate	SO_4^{-2}	-2	Sulfite	SO_3^{-2}	-2
Phosphate	PO_4^{-3}	-3	Phosphite	PO_3^{-3}	-3
Carbonate	CO_3^{-2}	-2	Hydrogen carbonate	HCO_3^-	-1

Question 32.

What is the positive charge (aka oxidation number) of chlorine in the chlorate anion?

Answer:

In all common oxoanions, the oxidation number of oxygen is **-2**. Knowing this will help us to figure out the oxidation number of the "cation-like" nonmetal by simple algebra method. In chlorate there are three oxygen atoms, each carries a charge of -2.

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

$$x + 3\times(-2) = -1$$

$$x = +5$$

As a good exercise, try figure out the oxidation number of the nonmetal in each of the oxoanions listed on the previous page. Treating an oxoanion as one entity greatly simplifies the dealing of chemical reactions where these oxoanions are involved.

4.4 Naming Ionic Compounds

Most ionic compounds are composed of at least one cation and one anion, just like in sodium chloride, 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.

When naming ionic compounds, the metal cations retain their elemental names while anions (mostly formed from non-metals) are called xxx-ide. When polyatomic anions are involved, use their respective name.

Here are some examples.

Compound	Cation	Anion	Name
Li_2O	Li^{+1} (Lithium)	O^{2-} (Oxide)	Lithium Oxide
NaF	Na^{+1} (Sodium)	F^- (Fluoride)	Sodium Fluoride
$LiClO_3$	Li^{+1} (Lithium)	ClO_3^- (Chlorate)	Lithium Chlorate
K_2SO_4	K^{+1} (Potassium)	SO_4^{2-} (Sulfate)	Potassium Sulfate
NH_4Cl	NH_4^+ (ammonium)	Cl^- (Chloride)	Ammonium Chloride

The ammonium cation NH_4^+ is one example of not many positively charged polyatomic ions.

Question 33.

When aluminum reacts with oxygen (gas), it forms a cation with an oxidation number of +3. What are the formula and the 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 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 $2 \times 3 = 6$.

It will take three O^{2-} ions to charge balance the two Al^{3+} ions. Thus the formula is Al_2O_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.

4.5 The Mole Relationship

A balanced chemical equation reveals the quantitative aspects of chemical reactions.

Question 34.

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. One mole of hydrogen molecule contains two moles of hydrogen atoms, and one mole of oxygen molecule contains two moles of oxygen atoms. So the balanced equation should be:

$$2H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O\,(l)$$

This balanced equation provides us with a **mole relationship** among the reactants and products. In this case it says that **2** moles of hydrogen molecules are required to completely react with **1** mole of oxygen molecules, and **2** moles of water molecules shall be formed. All quantitative chemical calculations must be based on such mole relationships.

4.6 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 Amounts of Reactants Used and the Amounts of Products Formed

Question 35.

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.

$$2H_2\,(g) \;+\; O_2\,(g) \longrightarrow 2H_2O\,(l)$$

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

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

The mole relationship gives us this conversion factor:

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

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

$$\#\text{ of moles of } O_2 = \#\text{ of moles of } H_2 \times \frac{1\ mol\ O_2}{2\ mol\ H_2} = 0.992\ \cancel{\text{mol H}_2} \times \frac{1\ mol\ O_2}{2\ \cancel{mol\ H_2}} = 0.496\text{ mol}$$

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

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

Alternatively, the above small steps can be combined in a one-step dimensional analysis:

$$\text{Mass of } O_2 = 2.00\cancel{g} \times \frac{1\ \cancel{mole\ of\ H_2}}{2.016\ \cancel{g}} \times \frac{1\ \cancel{mol}\ O_2}{2\ \cancel{mol\ H_2}} \times \frac{32.00 g O_2}{1\ \cancel{mol}\ O_2} = 15.9\text{ g}$$

Limiting Reactant

When calculating the amounts of products formed, we usually encounter two scenarios.

Scenario 1: The amount of one reactant is given, and the other reactant is said to be in excess. In this scenario the amount of product formed can be calculated based on the reactant whose amount is known.

Scenario 2: The amounts of both reactants are given. It is possible that one will be used up and the other might have left over. Which amount should be used to calculate the reaction yield, i.e. the amounts of products formed? In this scenario we need to determine the **limiting reagent**.

In a chemical reaction where not both reactants are used up, the one being used up is called the **limiting reactant,** because its amount, not the amount of the reactant in excess, limits how much of the products can be formed from this reaction.

Here are the steps we use to figure out which reactant is the limiting reagent based on a balanced equation.

Consider the reaction between **A** and **B**.

1. Assuming **A** (randomly chosen) will be used up, do a calculation to find out how much of **B** would be required.

2. Compare the answer with what is provided for **B**.

    a. If the provided amount is more than the calculated amount, then **A** is the limiting reagent;

    b. If the provided amount is less than the calculated amount, then **B** is the limiting reagent.

Question 36.

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

Answer:

This is scenario 2 where we need to determine the limiting reagent.

Pretending that we don't know the answer from **Question 35**, we will follow the two steps to figure out which one is the limiting reagent.

1. Assuming that hydrogen will be used up, calculate how much oxygen would be needed.

   Mass of O_2 needed to use up 2.00 g of hydrogen

$$= 2.00\cancel{g} \times \frac{1\cancel{mol}H_2}{2.016\ \cancel{g}} \times \frac{1\ \cancel{mol}\ O_2}{2\ \cancel{mol}\ H_2} \times \frac{32.00g\ O_2}{1\ \cancel{mol\ O_2}} = 15.9\text{ g}$$

2. 15.9 g < 30.0 g O_2 available, therefore hydrogen is the limiting reagent.

Using H_2 as the limiting reactant and the conversion factors from the balanced reaction equation we have

$$\text{Mass of } H_2O = 2.00\cancel{g} \times \frac{1\cancel{mol}H_2}{2.016\ \cancel{g}} \times \frac{2\ mol\ H_2O}{2\ mol\ H_2} \times 18.02\text{ g/}\cancel{\text{mol}} = 17.9\text{ g}$$

Percent Yield

In **Question 36** we saw that when all 2.00 g of the limiting reactant (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

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

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 35 and 36**. We will show how this is done in the following question.

Question 37.

Chromium can be made by heating chromium oxide, Cr_2O_3, with aluminum. Aluminum oxide, Al_2O_3, is the other product. When 18.7 g of Cr_2O_3 were heated with excess aluminum, 10.8 g of chromium were isolated from the products. What was the percent yield of chromium?

<u>Answer:</u>

We first write the balanced equation:

$$Cr_2O_3\ (s) \ +\ 2Al\ (s) \longrightarrow 2Cr\ (s) + Al_2O_3\ (s)$$

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:

$$\text{Mass of Cr} = (\text{Mass of } Cr_2O_3 \times \underset{\substack{\uparrow \\ \text{grams to mole}}}{\frac{1\ mol\ Cr_2O_3}{molar\ mass\ of\ Cr_2O_3}}) \times (\underset{\substack{\uparrow \\ \text{mole relationship}}}{\frac{2\ mol\ Cr}{1\ mol\ Cr_2O_3}}) \times (\underset{\substack{\uparrow \\ \text{mole to grams}}}{\frac{molar\ mass\ Cr}{1\ mol\ Cr}})$$

$$= 18.7\text{ g } Cr_2O_3 \times \frac{1\ mol\ Cr_2O_3}{152.0\ g\ Cr_2O_3} \times \frac{2\ mol\ Cr}{1\ mol\ Cr_2O_3} \times \frac{52.00\ g\ Cr}{1\ mol\ Cr} = 12.8\text{ g Cr}$$

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

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

Practice and Review for Chapter 4

Define (in your own words) the following terms:

Reaction Equation: ____

Coefficient: ____

Ionic Bond: ____

Ionic Compound: ____

Simplest Atomic Ratio: ____

Chemical Change: ____

Oxidizing Agent: ____

Reducing Agent: ____

Oxoanions: ____

Covalent Bond: ____

Limiting Reactant: ____

Theoretical Yield: ____

Actual Yield: ____

Percent Yield: ____

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.

Chapter 5

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.

5.1 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)**

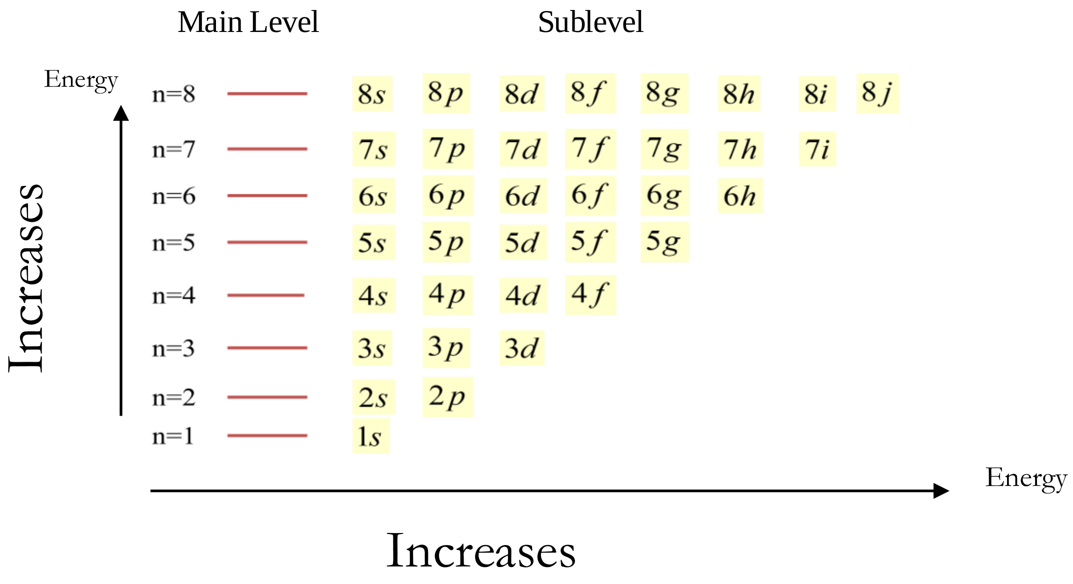
l, the **angular quantum number, representing the type of unit (sublevel)**

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 8th 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 38.

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:

When *n* is	*l* can be	Type of Units	Label
1	0	1	*s*
2	0, 1	2	*s* ($l = 0$), *p* ($l = 1$)
3	0, 1, 2	3	*s* ($l = 0$), *p* ($l = 1$), *d* ($l = 2$)

And so on…

Question 39.

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

Answer:

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

Label of Orbital	Quantum Numbers
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 40.

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 “$-l$… -2, -1, 0, +1, +2… $+l$” possible values of “m_l”, as illustrated below:

When l is	m_l can be	number of orbitals
0 (*s* unit)	0	1
1 (*p* unit)	-1, 0, +1	3
2 (*d* unit)	-2, -1, 0, +1, +2	5
3 (*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 360º 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 41.

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.

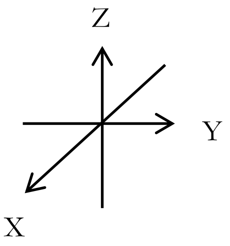


Figure A. The Cartesian Axes

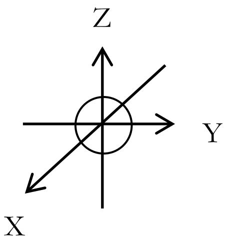


Figure B. The 1*s* orbital

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

The size of the *s* orbitals increases as the principle quantum number *n* increases. Thus the size of the circle for a 2*s* orbital should be drawn larger than the one for a 1*s* orbital. In other words, 1*s* 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 2*p* orbitals. If the orbital is drawn around the X axis, it is called the $2p_x$ orbital. Can you draw the third 2*p* orbital (p_y)? You can use Figure A or create your own axes.

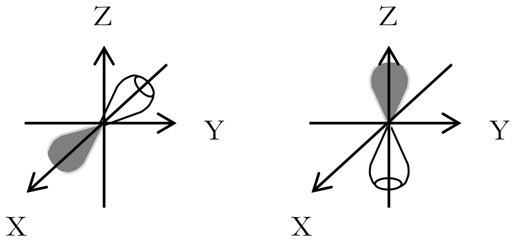


Figure C. The $2p_x$ and $2p_z$ orbitals

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 3*d* orbitals have higher energy than those in 3*p* orbitals.

Question 42.

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

$$1s^2 2s^2 2p^6 3s^2$$

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:

$$3p_x^2\ 3p_y^1\ 3p_z^1 \qquad \text{or} \qquad 3p_x^2\ 3p_y^2\ 3p_z^0$$

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

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$$

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.

Unit (sublevel)	**Maximum Number of Electrons**
s	*2*
p	*6*
d	*10*
f	*14*

Question 43.

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.

5.2 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	***H*** $1s^1$							***He*** $1s^2$
Row 2	***Li*** $1s^22s^1$	***Be*** $1s^22s^2$	***B*** $1s^22s^22p^1$	***C*** $1s^22s^22p^2$	***N*** $1s^22s^22p^3$	***O*** $1s^22s^22p^4$	***F*** $1s^22s^22p^5$	***Ne*** $1s^22s^22p^6$
Row 3	***Na*** $1s^22s^22p^63s^1$	***Mg*** $1s^22s^22p^63s^2$	***Al*** $1s^22s^22p^63s^23p^1$	***Si*** $1s^22s^22p^63s^23p^2$	***P*** $1s^22s^22p^63s^23p^3$	***S*** $1s^22s^22p^63s^23p^4$	***Cl*** $1s^22s^22p^63s^23p^5$	***Ar*** $1s^22s^22p^63s^23p^6$
	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 ($2s^22p^3$) and phosphorous also has 5 electrons in main level 3 ($3s^23p^3$).

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

5.3 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 many electrons are available for reaction. For example, when we look at the electron configuration of sodium, [Ne] $3s^1$, we can tell that one 3s electron will participate in the chemical reactions of sodium.

Question 44.

Give the electron configurations of N, Cl and Fe in noble gas notation.

Answer:

N, $1s^22s^22p^3$, can be written as [He] $2s^22p^3$.

Cl, $1s^22s^22p^63s^23p^5$, can be written as [Ne] $3s^23p^5$.

Fe has a total of 26 electrons. We know the first 18 electrons can be represented by [Ar]. What about the rest of the 8 electrons?

According to the building plan (page 29), we should now start filling 3*d* orbitals. It turns out that the ensuing 4*s* orbital has lower energy than the 3*d* orbitals (for quantum mechanics reasons). So we should fill the 4*s* orbital first and then start filling the 3*d* orbitals. We get [Ar] $4s^23d^6$ as the electron configuration for Fe in noble gas notation.

Writing the electron configuration for Fe brings us to the part of the periodic table that we have not been talking about, the shaded block of elements. Table 5 below is a shortened periodic table, listing only 36 elements. We notice that the 4th period now contains 18 elements. Ten of them are inserted between Ca and Ga and are shaded. What is the reason for this arrangement?

Table 5. The Shortened Periodic Table

Period 1	*H*																	*He*
Period 2	*Li*	*Be*											*B*	*C*	*N*	*O*	*F*	*Ne*
Period 3	*Na*	*Mg*											*Al*	*Si*	*P*	*S*	*Cl*	*Ar*
Period 4	*K*	*Ca*	*Sc*	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Co*	*Ni*	*Cu*	*Zn*	*Ga*	*Ge*	*As*	*Se*	*Br*	*Kr*

Question 45.

Give the complete electron configurations for the elements K to Zn in the 4th period. Also give the electron configurations in noble gas notation.

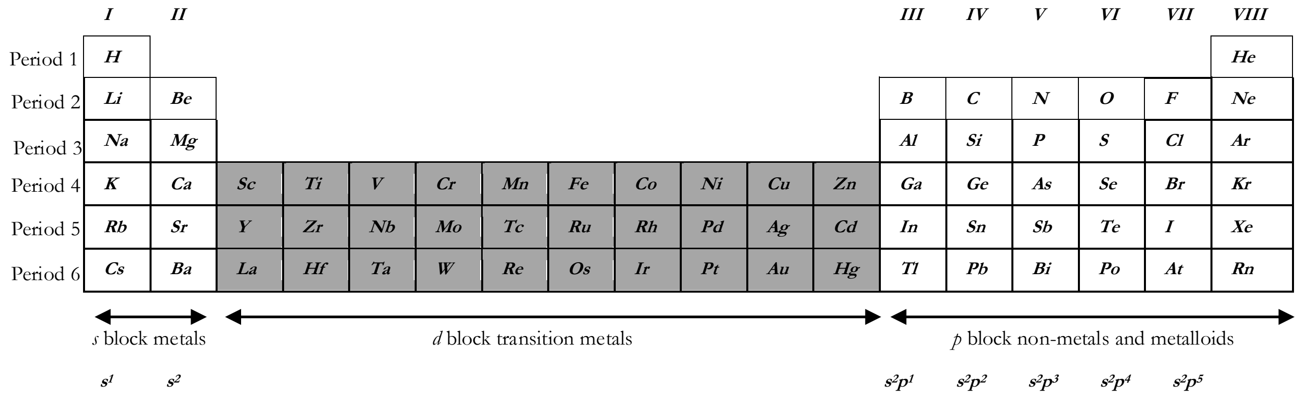
Answer:

As in the example for Fe above, when it is time to start filling 3*d* and 4*s* orbitals, we should fill 4*s* first, then 3*d*. Thus we have:

K, $1s^22s^22p^63s^23p^64s^1$	[Ar] $4s^1$			
Ca, $1s^22s^22p^63s^23p^64s^2$	[Ar] $4s^2$			
Sc, $1s^22s^22p^63s^23p^64s^2\,3d^1$	[Ar] $4s^23d^1$			
Ti, $1s^22s^22p^63s^23p^64s^2\,3d^2$	[Ar] $4s^23d^2$			
V, $1s^22s^22p^63s^23p^64s^2\,3d^3$	[Ar] $4s^23d^3$			
Cr, $1s^22s^22p^63s^23p^64s^1\,3d^5$	[Ar] $4s^13d^5$	**NOT**	[Ar] $4s^23d^4$	because half- and fully-
Mn, $1s^22s^22p^63s^23p^64s^2\,3d^5$	[Ar] $4s^23d^5$			filled sublevels are more
Fe, $1s^22s^22p^63s^23p^64s^2\,3d^6$	[Ar] $4s^23d^6$			stable (lower in energy)
Co, $1s^22s^22p^63s^23p^64s^2\,3d^7$	[Ar] $4s^23d^7$			than empty ones.
Ni, $1s^22s^22p^63s^23p^64s^2\,3d^8$	[Ar] $4s^23d^8$			
Cu, $1s^22s^22p^63s^23p^64s^1\,3d^{10}$	[Ar] $4s^13d^{10}$	**NOT**	[Ar] $4s^23d^9$	for the same reason
Zn, $1s^22s^22p^63s^23p^64s^2\,3d^{10}$	[Ar] $4s^23d^{10}$			as above

An inspection of the above electron configurations immediately tells us that the shaded elements have one thing in common: they all have *d* electrons. Since there are five *d* orbitals (remember that *d* is a 5-orbital unit), it takes 10 elements to completely populate the *d* sublevel. Having *d* electrons makes these 10 elements behave in a very similar fashion, that is why they are shaded together as a special group, known as the "**transition elements**." The shaded block is called the "***d* block**." All other elements not in the "*d* block" are called "**main group elements**" or "**representative elements**."

Below is a more complete periodic table. The Roman numerals in the top row are **group numbers**.



	I	*II*											*III*	*IV*	*V*	*VI*	*VII*	*VIII*
Period 1	*H*																	*He*
Period 2	*Li*	*Be*											*B*	*C*	*N*	*O*	*F*	*Ne*
Period 3	*Na*	*Mg*											*Al*	*Si*	*P*	*S*	*Cl*	*Ar*
Period 4	*K*	*Ca*	*Sc*	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Co*	*Ni*	*Cu*	*Zn*	*Ga*	*Ge*	*As*	*Se*	*Br*	*Kr*
Period 5	*Rb*	*Sr*	*Y*	*Zr*	*Nb*	*Mo*	*Tc*	*Ru*	*Rh*	*Pd*	*Ag*	*Cd*	*In*	*Sn*	*Sb*	*Te*	*I*	*Xe*
Period 6	*Cs*	*Ba*	*La*	*Hf*	*Ta*	*W*	*Re*	*Os*	*Ir*	*Pt*	*Au*	*Hg*	*Tl*	*Pb*	*Bi*	*Po*	*At*	*Rn*

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).

$$\underbrace{[\mathrm{Ne}]}_{\text{noble gas core}}\quad\underbrace{3s^{2}3p^{5}}_{\text{highest main level (aka valence shell)}}$$

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 46.

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

<u>Answer:</u>

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

Question 47.

Neon is also an element in period 2, why didn't you give its valence electron number in the answer to **Question 46**?

<u>Answer:</u>

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 6.

Question 48.

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

<u>Answer:</u>

An inspection of the table on Page 54 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.

5.4 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.

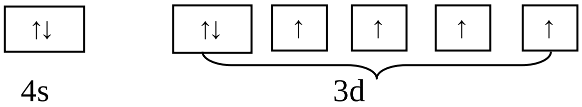
Question 49.

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

Answer:

The valence electron configuration for Fe is $4s^2 3d^6$.

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 5

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.

Chapter 6

Periodic Properties and Electrochemistry

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.

6.1 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.

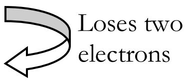
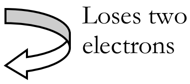
Question 50.

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

Answer:

Li and Be have these electron configurations, respectively, $[He]2s^1$ and $[He]2s^2$. 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.

Electron Configuration		Symbol		Name
$[He]2s^1$	Loses one electron	Li	Loses one electron	lithium atom
$[He]$		Li^+		lithium cation (A positively charged ion)

$[He]2s^2$		Be		beryllium atom
[He]		Be^{2+}		beryllium cation

Question 51.

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.

E. C.	Symbol	Name	# of protons	# of electrons	Net Charge
$[He]2s^1$	Li	lithium atom	3	3	0
[He]	Li^+	lithium cation	3	2	+1
$[He]2s^2$	Be	beryllium atom	4	4	0
[He]	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:

$$Li \longrightarrow Li^+ + e^-$$

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.

6.2 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.

$$O^{2-} \xleftarrow{+2e} O \xrightarrow{-6e} O^{+6}$$

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:

$$O + 2e^- \longrightarrow O^{2-}$$

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.

E. C.	Symbol	Name	# of protons	# of electrons	Net Charge
$[He]2s^22p^3$	N	nitrogen	7	7	0
$[He]2s^22p^6$	N^{3-}	nitride	7	7+3=10	-3
$[He]2s^22p^4$	O	oxygen	8	8	0
$[He]2s^22p^6$	O^{2-}	oxide	8	8+2=10	-2
$[He]2s^22p^5$	F	fluorine	9	9	0
$[He]2s^22p^6$	F^-	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 52.

What is the difference between metals and non-metals in the treatment of their valence electrons?

Answer:

Metals lose their valence electrons and non-metals “grab” valence electrons from other atoms.

Question 53.

What is the motivation for an element to “lose” or “gain” a certain number of electrons?

Answer:

The element aims at acquiring an **octet** of electrons in the highest main level of its electron configuration. The motivation is to be more stable, to be in a lower energy state.

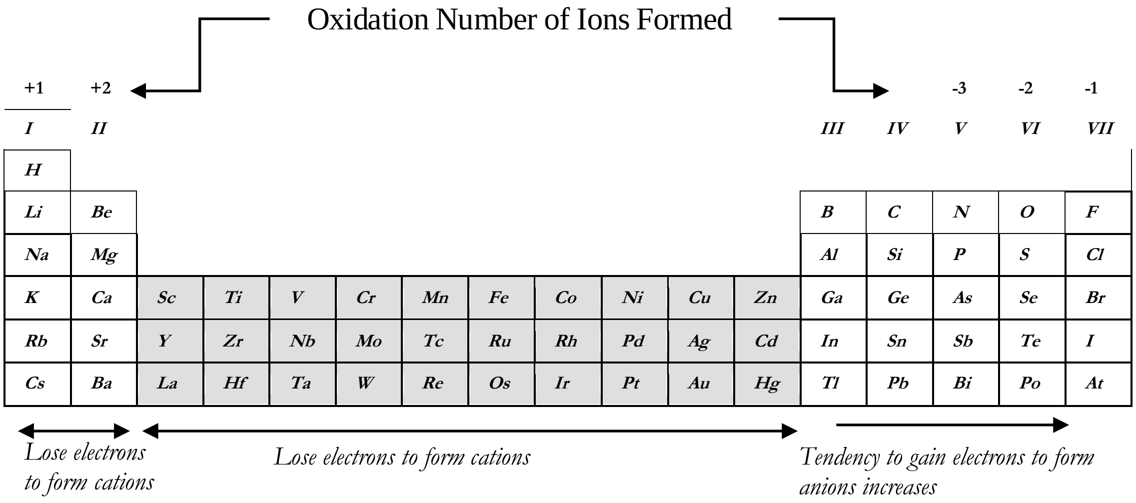
Question 54.

What is the difference between metals and non-metals in the change of their names after they become ions?

Answer:

A metal retains its atomic name but a non-metal replaces half of its atomic name with “ide.” For example, ***sodium*** remains ***sodium*** ion whereas chlor***ine*** becomes chlor***ide***.

You should be very familiar with the chemical behavior of main group metals and non-metals, i.e. what type of ions they become and what charges they carry (summarized below). For an element in its natural state (on its own), we assign its oxidation number as “zero” because its valence shell has lost or gained “zero” electrons.



Question 55. **<u>(Give it a try before checking the answer on next page.)</u>**

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
	$^{27}_{13}\mathrm{Al}$					
calcium ion			42			
oxide ion			18			

6.3 The Formation of Diatomic Molecules

Question 56.

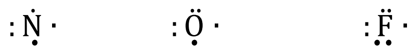
What do N, O, and F atoms have in common as far as electrons are concerned?

<u>Answer:</u>

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.



$:\underset{\cdot}{\dot{\mathrm{N}}}\cdot \qquad :\underset{\cdot}{\ddot{\mathrm{O}}}\cdot \qquad :\underset{\cdot\cdot}{\ddot{\mathrm{F}}}\cdot$

Question 57.

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

Answer to Question 55:

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

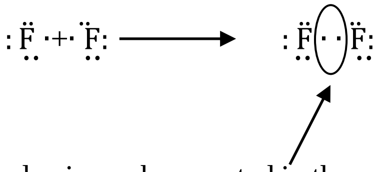
Answer to Question 57:

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

Element	Highest Main Level	Orbital Box Notation	#of Unpaired Electrons
N	$2s^22p^3$	$\boxed{\uparrow\downarrow}\quad\boxed{\uparrow}\,\boxed{\uparrow}\,\boxed{\uparrow}$	3
O	$2s^22p^4$	$\boxed{\uparrow\downarrow}\quad\boxed{\uparrow\downarrow}\,\boxed{\uparrow}\,\boxed{\uparrow}$	2
F	$2s^22p^5$	$\boxed{\uparrow\downarrow}\quad\boxed{\uparrow\downarrow}\,\boxed{\uparrow\downarrow}\,\boxed{\uparrow}$	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**.

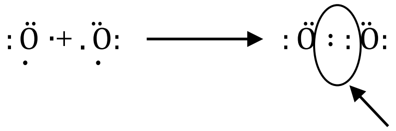
A **molecule** is a combination of atoms. Such combinations are not random. Atoms in a molecule are held together by special glues called **bonds**. In the fluorine molecule the two fluorine atoms form **a covalent bond** by **sharing one pair of electrons**. The newborn molecule also needs a new symbol—a 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 58.

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 59. **(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.

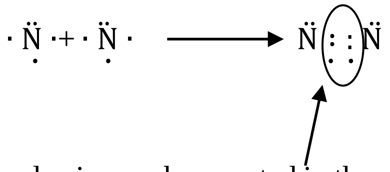
Three covalent bonds are formed between the two nitrogen atoms in order to form a nitrogen molecule. The molecular formula for the nitrogen molecule is N_2.

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 59:



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

6.4 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** valance 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.

Ionization Energy increases ↑

H $1s^1$							***He*** $1s^2$
Li $1s^22s^1$	***Be*** $1s^22s^2$	***B*** $1s^22s^22p^1$	***C*** $1s^22s^22p^2$	***N*** $1s^22s^22p^3$	***O*** $1s^22s^22p^4$	***F*** $1s^22s^22p^5$	***Ne*** $1s^22s^22p^6$
Na $1s^22s^22p^63s^1$	***Mg*** $1s^22s^22p^63s^2$	***Al*** $1s^22s^22p^63s^23p^1$	***Si*** $1s^22s^22p^63s^23p^2$	***P*** $1s^22s^22p^63s^23p^3$	***S*** $1s^22s^22p^63s^23p^4$	***Cl*** $1s^22s^22p^63s^23p^5$	***Ar*** $1s^22s^22p^63s^23p^6$

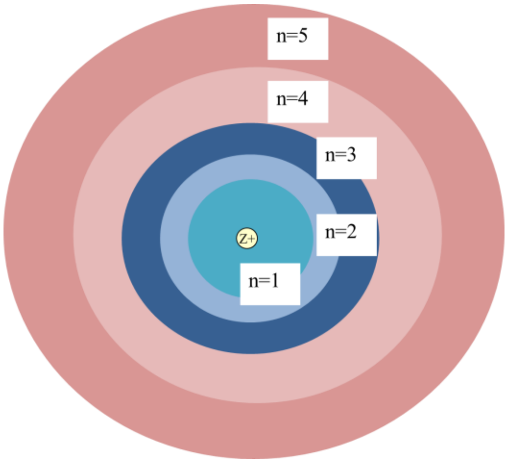
Ionization Energy increases →

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?

6.5 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.

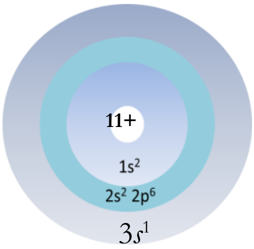


The shell model treats electron clouds around the nucleus (carrying Z+ charges, Z = atomic number = # of protons) as layers of shells. The first shell is the *n* = 1 main energy level, the second shell is the *n* = 2 main energy level, and so on. The sublevels (*s*, *p*, *d*, *f*, etc.) and orbitals 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.

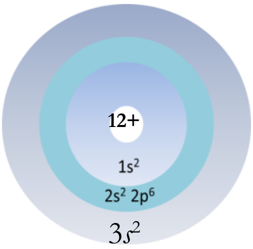
Question 60.

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

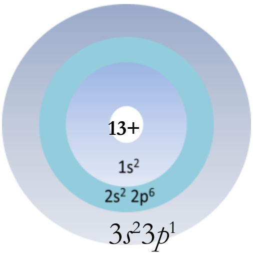
Answer: Using the shell model, we can depict the atoms of the 3rd period as follows.



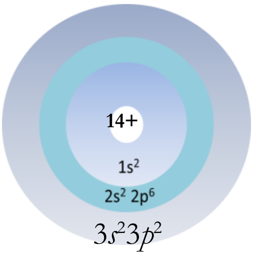
Na



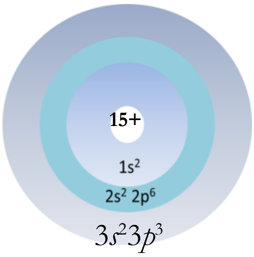
Mg



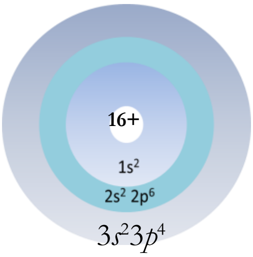
Al



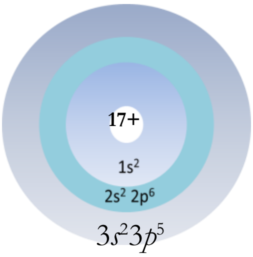
Si



P



S



Cl

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.

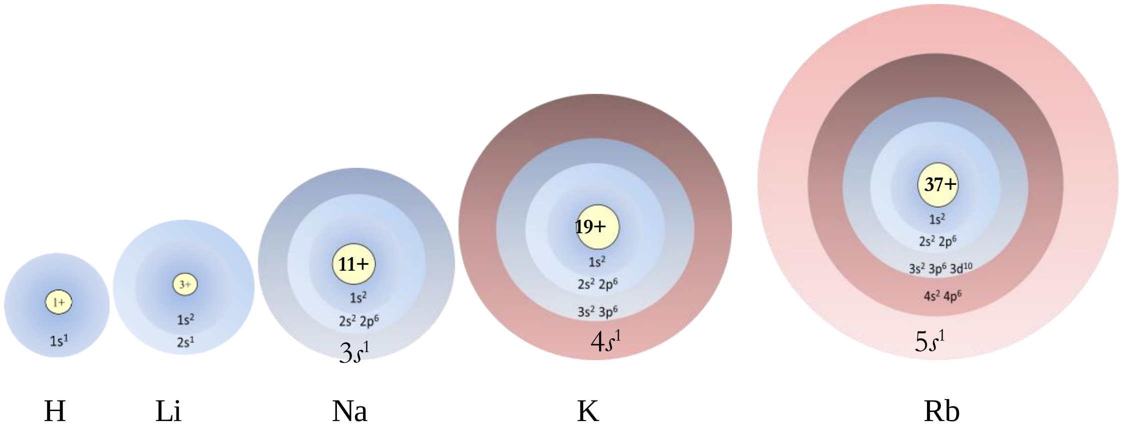
Since the number of inner-shell electrons is the same (2 + 8 = 10) for all seven elements in the 3rd period, the core charge increases from **1** (11 minor 10) to **7** (17 minors 10) while the distance between the valence electrons and the nucleus remains roughly the same. Therefore the force of attraction 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 61.

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.

6.6 Sizes of Atoms

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

Question 62.

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

Answer:

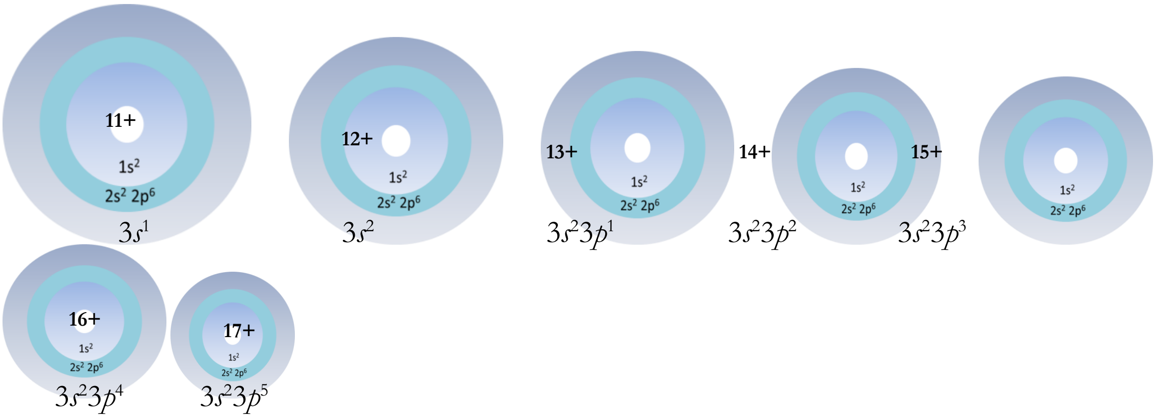
Yes. The size of the atom indeed increases as the distance between the valence shell and the nucleus increases.

Question 63.

Does the size of the atoms remain the same going across a period as depicted for the elements in the 3rd 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 3rd period. This is due to the increase in the core charges. As the core charge increases gradually from, for example, Na to Cl, the valence 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).



6.7 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.

Electronegativity increases

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

Electronegativity increases

6.8 Application of Redox Reactions: Electrochemical Cells

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.

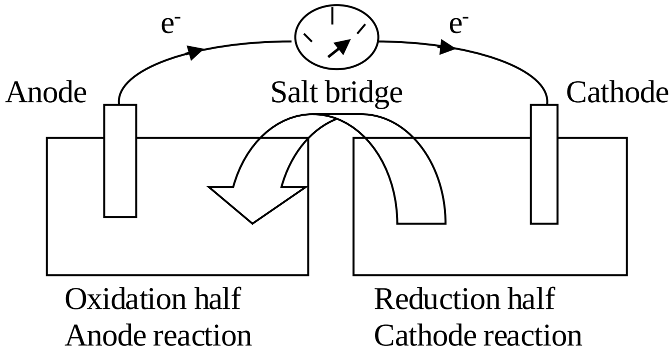
$$3O_2 \xrightarrow{+12e} 6O^{2-} \quad \text{(reduction half-equation)}$$

$$4Al \xrightarrow{-12e} 4Al^{3+} \quad \text{(oxidation half-equation)}$$

$$4Al + 3O_2 \longrightarrow 2Al_2O_3 \quad \text{(overall reaction)}$$

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 $ZnSO_4$ and $CuSO_4$ solutions, respectively. The cell reactions are:

$$\begin{array}{rcl} Cu^{2+} & \xrightarrow{+2e} & Cu(s) \text{ (reduction half-equation)} \\ Zn(s) & \xrightarrow{-2e} & Zn^{2+} \text{ (oxidation half-equation)} \\ \hline Zn(s) + Cu^{2+} & \longrightarrow & Zn^{2+} + Cu(s) \text{ (overall reaction)} \end{array}$$

The sulfate ions are not included in the reaction equations because they are spectator ions. When the Cu^{2+} ions are reduced to Cu at the cathode, there will be “unpaired” SO_4^{2-} ions left in the $CuSO_4$ 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^{2+} ions diffuse into the $ZnSO_4$ solution. These “unpaired” Zn^{2+} ions ***draw*** the “unpaired” SO_4^{2-} 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

$$Zn(s)|ZnSO_4(aq)||CuSO_4(aq)|Cu(s)$$

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

$$Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$$

6.9 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:

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

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^{-1}, 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}.

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:

$$E^o_{cell} = \underset{\swarrow}{E^o_{ox}} + \underset{\searrow}{E^o_{red}}$$

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

6.10 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

$$E^{\circ}_{2H^{+} + 2e \rightarrow H_2} = 0$$

Question 64.

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:

Oxidation half: $Zn(s) \rightarrow Zn^{2+} + 2e \quad E^{\circ}_{ox} = ?$

Reduction half: $2H^{+} + 2e \rightarrow H_2 \quad E^{\circ}_{red} = 0$

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

then $E^{\circ}_{ox} = E^{\circ}_{cell} - E^{\circ}_{red} = 0.76 – 0 = 0.76\ V$

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

Question 65.

A zinc-copper cell has a standard cell potential of 1.10 V. Find the cell potential for the copper half cell given that $E^{\circ}_{Zn(s) \rightarrow Zn2+ + 2e} = 0.76\ V$.

Answer:

The two half reactions are:

Oxidation half: $Zn(s) \rightarrow Zn^{2+} + 2e \quad E^{\circ}_{ox} = 0.76\ V$

Reduction half: $Cu^{2+} + 2e \rightarrow Cu(s) \quad E^{\circ}_{red} = ?$

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

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

Question 66.

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.

$$Cu^{2+} + H_2\ (g) \rightarrow Cu(s) \quad + \quad 2H^+$$

For this reaction, the half reactions are:

Oxidation half: $H_2 \rightarrow 2H^+ + 2e$ $E^\circ_{ox} = -0 = 0$

Reduction half: $Cu^{2+} + 2e \rightarrow Cu(s)$ $E^\circ_{red} = ?$

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

Then $E^\circ_{red} = E^\circ_{cell} - E^\circ_{ox} = 0.34 - 0 = 0.34$ 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°_{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 6

Define (in your own words) the following terms:

Cation: ____

Anion: ____

Octet Rule: ____

Valence Shell: ____

Covalent Bond: ____

Oxidation Number: ____

Electron-Dot Structure: ____

Core Charge: ____

Ionization Energy: ____

Electronegativity: ____

Electrochemistry: ____

Electrochemical Cell: ____

Cell Potential: ____

Voltage: ____

Standard Cell Potential: ____

Standard Reduction Potential: ____

Short-Answer Questions:

1. What is the oxidation number for any neutral atoms? ________________________________
2. How many paired and unpaired electrons are there in the valence shell of the element phosphorus (P)?
   ____
3. List all diatomic molecules in the periodic table.
4. Name the two "most electron-hungry" elements in the periodic table.____________________
5. Give an example of an oxidation half-equation:
6. Give an example of an reduction half-equation:
7. Sketch a diagram for an electrochemical cell. Label all components.
8. Write the cell diagram for a zinc-copper cell.
9. What is the hydrogen half cell and what are the values of E°_{ox} and E°_{red} for this cell?

Chapter 7

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.

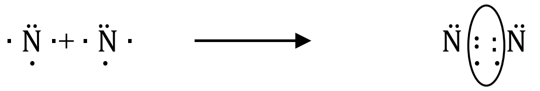
Human Body Composition (*by mass*):

Oxygen	(O, 65%)
Carbon	(C, 18.3%)
Hydrogen	(H, 10%)
Nitrogen	(N, 3.3%)
Calcium	(Ca, 1.7%)
Phosphorous	(P, 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_2 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_2 molecule can be written as

$$\ddot{N} \equiv \ddot{N}$$

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.

Formula	Oxidation State of N	Name	Physical State at 25 ˚C
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

H 2.20						
Li 0.98	*Be* 1.57	*B* 2.04	*C* 2.55	*N* 3.04	*O* 3.44	*F* 3.98
Na 0.93	*Mg* 1.31	*Al* 1.61	*Si* 1.90	*P* 2.19	*S* 2.58	*Cl* 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 67.

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

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

$$x = +4$$

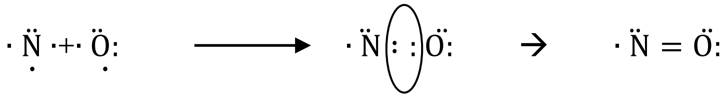
For practice, can you check the oxidation numbers for nitrogen in different oxide compounds listed on the previous page?

Question 68.

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

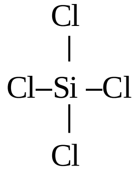
Question 69.

Draw the Lewis structure for silicon tetrachloride.

Answer:

First we need to translate the name silicon tetrachloride to the formula $SiCl_4$. Then we follow these steps:

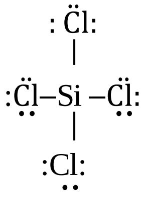
1. Arrange the molecule so that the element (except H) with only one atom in the molecule is at the **center** and is connected by **one covalent bond** each to all atoms of the other element(s). The atom at the center is called the **central atom**. For $SiCl_4$ Si is the central atom.



$$\begin{array}{c} \text{Cl} \\ | \\ \text{Cl–Si–Cl} \\ | \\ \text{Cl} \end{array}$$

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.



$$\begin{array}{c} :\ddot{Cl}: \\ | \\ :\underset{\cdot\cdot}{\ddot{Cl}}-Si-\underset{\cdot\cdot}{\ddot{Cl}}: \\ | \\ :\underset{\cdot\cdot}{Cl}: \end{array}$$

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

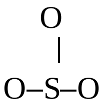
Question 70.

Draw the Lewis structure for sulfur trioxide.

Answer:

First we need to translate the name sulfur trioxide to the formula SO_3. Then we follow these steps.

1. Arrange the molecule as shown below.

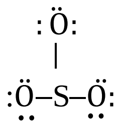


$$\begin{array}{c} O \\ | \\ O-S-O \end{array}$$

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.

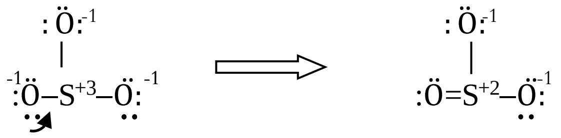


$$\begin{array}{c} :\ddot{O}: \\ | \\ :\ddot{O}-S-\ddot{O}: \end{array}$$

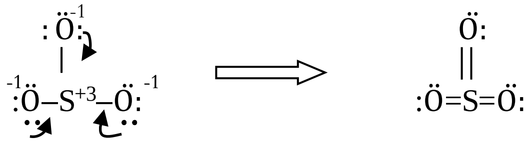
4. Now we check to see if all elements have achieved the octet status and we find that although all oxygen atoms have the octet status, the sulfur atom is in need of one more pair of electrons.

5. 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.

6. 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.



7. In fact the Lewis structure for the 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 (→) indicates the flow of **2** electrons whereas a half arrow head (⇀) indicates the flow of **1** electron.

When looking at the finished Lewis structure for the 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 3rd 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 3rd valence shell. They are: one 3*s*, three 3*p*, and five 3*d*. 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 71.

Draw the Lewis structure for the CO_3^{2-} ion.

<u>Answer:</u>

We follow these steps.

1. Arrange the molecule as shown below.

   O
   |
   O–C–O

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.

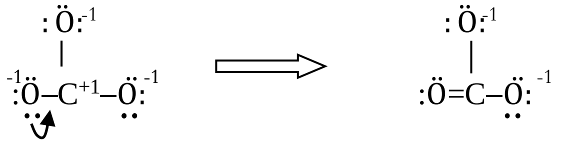
3. Since we used **6** electrons to form the **3 covalent bonds** between C and the **3** O atoms, we have 24 – 6 = 18 electrons left to distribute among the elements that do not have octet status. We start with the more electronegative elements. In this case, we just have enough to give 6 electrons to each of the 3 oxygen atoms.

   : Ö:
   |
   :Ö–C–Ö:
   ••   ••

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.



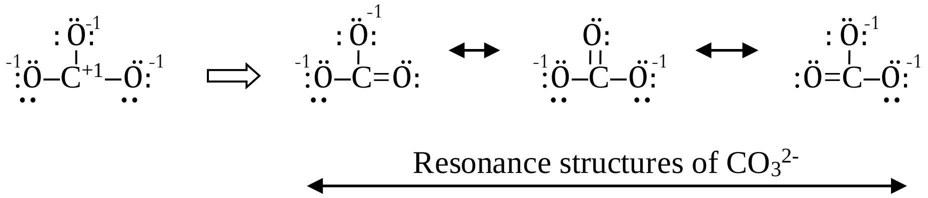
7. Since there is no more charge separation (no more positive charges to be neutralized by negative charges), and all atoms have achieved octet status, we accept this as a correct Lewis structure for the CO_3^{2-} polyatomic ion.

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 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:



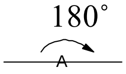
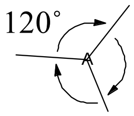
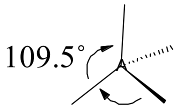
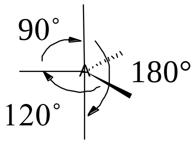
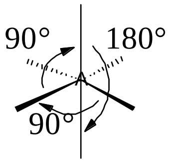
We call all of these possible (and correct) Lewis structures the **resonance structures** of the CO_3^{2-} ion. We use the word **resonance** to describe the situation where we cannot use **only one** Lewis structure to adequately represent a covalent molecule. In reality the molecule should be viewed 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**.

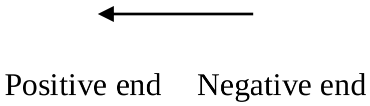
# of Electron Groups	Preferred Geometry and Bond Angle	Ideal Shape
2		Linear
3		Trigonal planar
4		Tetrahedral
5		Trigonal bipyramidal
6		Octohedral

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

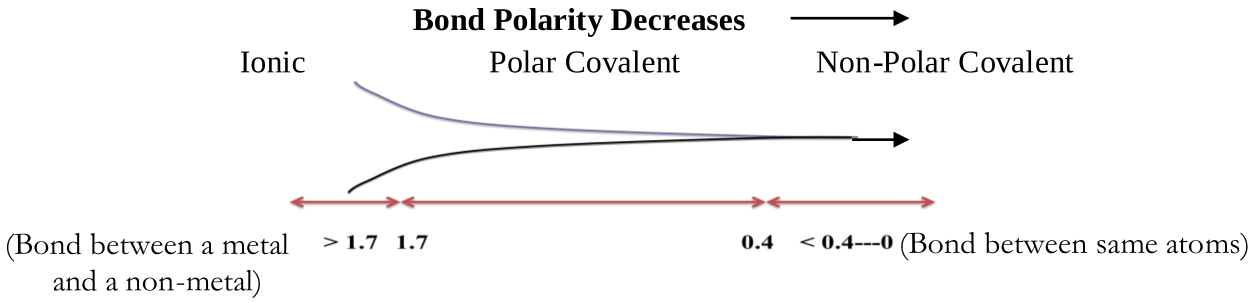
So far we have introduced two types of bonds: ionic bonds and covalent bonds. Some compounds only contain ionic bonds. For example, the table salt sodium chloride, NaCl, contains only ionic bonds between the Na^+ cations and the Cl^- anions. Most compounds, however, contain both types of bonds. For example, the baking soda sodium bicarbonate, $NaHCO_3$, contains ionic bonds between Na^+ and the oxoanion 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.



A dipole is described quantitatively by its **dipole moment**. A dipole moment is an experimentally measureable quantity and has a symbol "μ." The dipole moment μ 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.



Difference between electronegativity values

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.

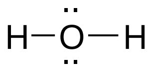
Question 72.

Is water a polar molecule? Explain your answer.

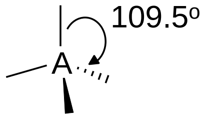
Answer:

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.

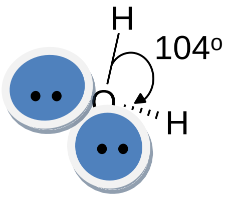
We first draw the Lewis structure for the water molecule, as shown below. The total number of valence electrons for water is 2 (1) + 6 = 8. Since we used **4** electrons to form the **2 covalent bonds** between O and the **2** H atoms, we have 8 – 4 = 4 electrons left to distribute among the elements 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°. 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°, smaller than in the ideal arrangement.

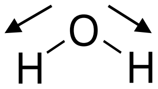


Ideal arrangement

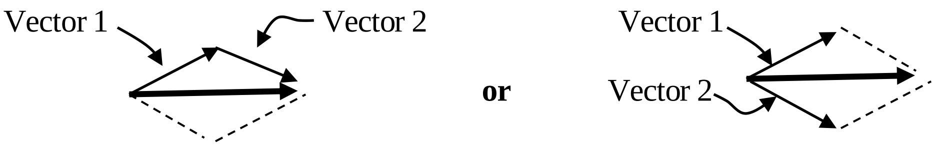


Actual arrangement

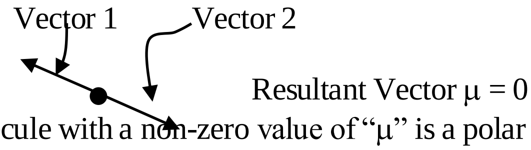
The water molecule as depicted above has two polar bonds, forming a 104° angle. It is commonly known as having a "**bent**" shape. For the purpose of finding the molecular dipole, we redraw the molecule and the individual dipoles as follows:



The molecular dipole can be calculated by doing **vector addition** of the two individual dipoles. The sum of two vectors is called the resultant vector, as illustrated below, in two kinds of vector arrangements. Two dashed lines are used to help make each pattern the shape a parallelogram. Therefore this commonly used method for vector addition is called the parallelogram method.

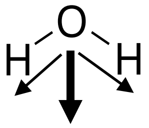


The resultant vector, the thicker vector, is the molecular dipole, denoted "μ". In situations where two individual dipoles point towards opposite directions and their magnitudes are equal, they would cancel each other and the resultant vector would be zero.



A molecule with a non-zero value of "μ" is a polar molecule. When μ = 0, the molecule is non-polar even if it contains polar bonds (because the polar bonds can cancel each other if their directions are opposite).

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



Molecular Dipole $\mu \neq 0$

Question 73.

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.

Molecule	Dipole Moment (Units of 10^{-30} C m)
HF	6.36
H_2O	6.17
SO_2	5.42
NH_3	4.88
HCl	3.43
H_2S	3.12
BCl_3	0
CO_2	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.

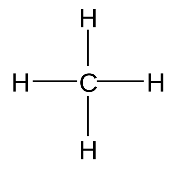
Question 74.

Why is oil non-polar?

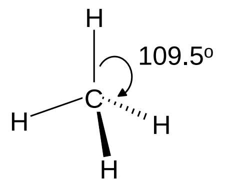
Answer:

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, 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 CH_4 is 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.

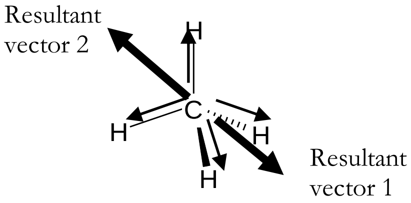


Lewis structure



Molecular shape

Although each C—H bond is polar, the resultant dipoles from any two pairs of individual dipoles, resultant 1 and resultant 2, are equal but pointing to opposite directions, thus canceling each other, as illustrated below. This renders the net molecular dipole moment zero. Bear in mind that this vector addition should be done based on the 3D molecular geometry.



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: ____

Chapter 8

Water Science II: The Hydrogen Bond

Opposites attract. It's only natural.

In **Question 21** we found that there are 1.67×10^{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?

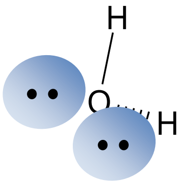
In an ionic molecule, it is the ionic bond (electrical attractions between opposite charges) that holds the ions together. In a covalent molecule, it is the covalent bond (formed by the sharing of electrons) that holds the atoms together. What holds the molecules together? To answer this question, we 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.

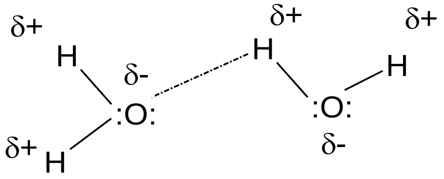
OK, I see the bent water molecule now, with the "puffy" lone pairs on the oxygen atom. I even see the individual dipoles. H atoms are the positive ends and O is the negative end.



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:

F—H----:F F—H----:O F—H----:N

O—H----:F O—H----:O O—H----:N

N—H----:F N—H----:O N—H----:N

H—bonds that give the double helix shape of DNA

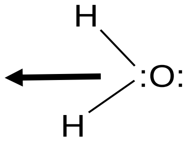
8.2 Other Intermolecular Forces

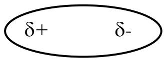
So far we have seen three major types of interactions among atoms, molecules, and ions. Whether we describe them as covalent bonds, ionic bonds, or intermolecular forces such as hydrogen bonds, they all result from **electrostatic attractions** and **repulsions** between positive nuclei and negative 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, represented by an oval shape with two oppositely charged ends, as shown on the next page using the water molecule as an example. The locations of the positive end and the negative end follows the vector direction of water's molecular dipole—the positive end is where the arrow points to.

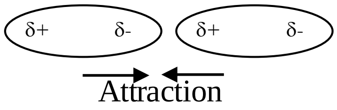




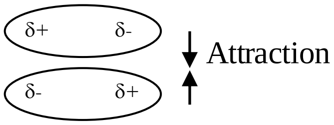
the water dipole

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.

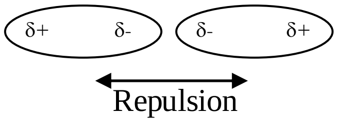
Head-to-tail arrangements



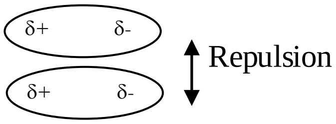
or



Head-to-head arrangements



or



The head-to-tail arrangements have a lower energy and therefore, more common, than the head-to-head arrangements. There is an **net 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 all diminish. So dipole-dipole forces are only significant when the dipoles are close together.

London (Dispersion) Forces

Question 75.

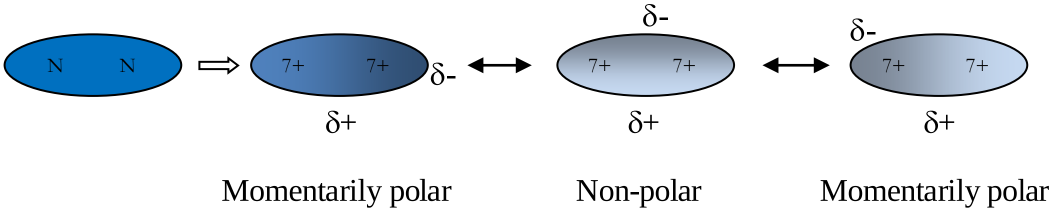
Nitrogen is a non-polar molecule. What holds the nitrogen molecules together in liquid nitrogen?

__**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.

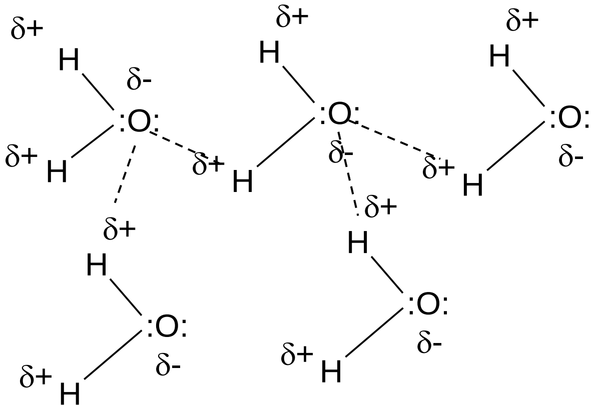
London forces exist among all molecules and are particularly important for larger molecules. They are quite often stronger than the dipole-dipole forces between polar molecules. In summary, whenever we want to know what holds molecules together, we should always consider these three intermolecular forces: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

Question 76.

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

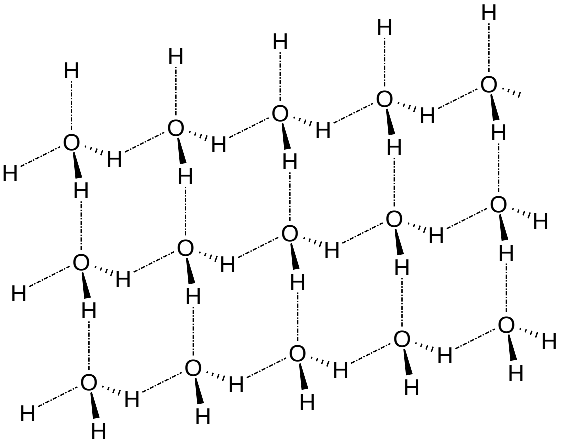
Question 77.

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.

Chapter

9

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

$$aA + bB \rightleftharpoons cC + dD$$

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

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

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.

$$\text{Since} \quad n \times (a\text{A} + b\text{B} \rightleftharpoons cC + d\text{D})$$

equals

$$na\text{A} + nb\text{B} \rightleftharpoons nc\text{C} + nd\text{D}$$

therefore, if for $a\text{A} + b\text{B} \rightleftharpoons cC + d\text{D}$

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

Then for $na\text{A} + nb\text{B} \rightleftharpoons nc\text{C} + nd\text{D}$

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

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,

$$a\text{A} + b\text{B} \rightleftharpoons p\text{P} + q\text{Q} \qquad K_1 = \left(\frac{[P]^p[Q]^q}{[A]^a[B]^b}\right)_{\text{eq}}$$

$$qQ + cC \rightleftharpoons rR \qquad K_2 = \left(\frac{[R]^r}{[Q]^q[C]^c}\right)_{eq}$$

$$rR + dD \rightleftharpoons sS \qquad K_3 = \left(\frac{[S]^s}{[D]^d[R]^r}\right)_{eq}$$

For the overall reaction which is the sum of the three reactions above

$$aA + bB + cC + dD \rightleftharpoons pP + sS$$

we can write

$$K_{overall} = K_1 \times K_2 \times K_3 = \left(\frac{[P]^p\cancel{[Q]^q}}{[A]^a[B]^b}\right)_{eq} \times \left(\frac{\cancel{[R]^r}}{\cancel{[Q]^q}[C]^c}\right)_{eq} \times \left(\frac{[S]^s}{[D]^d\cancel{[R]^r}}\right)_{eq} = \left(\frac{[P]^p[S]^s}{[A]^a[B]^b[C]^c[D]^d}\right)_{eq}$$

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_2O from H_2 and O_2,

$$2H_2\,(g) + O_2\,(g) \rightleftharpoons 2H_2O\,(g)$$

has the equilibrium constant

$$K = \left(\frac{[H_2O]^2}{[H_2]^2[O_2]}\right)_{eq} = 5.9 \times 10^{40}$$

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,

$$2H_2O\,(g) \rightleftharpoons 2H_2\,(g) + O_2\,(g)$$

has the expression

$$K_{decomp} = \left(\frac{[H_2]^2[O_2]}{[H_2O]^2}\right)_{eq}$$

which is the reciprocal of the K for the formation of water.

$$K_{decomp} = \left(\frac{[H_2]^2[O_2]}{[H_2O]^2}\right)_{eq} = \frac{1}{K} = \frac{1}{5.9 \times 10^{40}} = 1.7 \times 10^{-41}$$

This equilibrium constant is so tiny that we consider it impossible for water to voluntarily decompose into H_2 and O_2.

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, o**r, $K_{\text{forward}} = \frac{1}{K_{backward}}$

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:

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

The equilibrium constant for this reaction is,

$$K = \left(\frac{[CaO][CO_2]}{[CaCO_3]}\right)_{eq}$$

But $CaCO_3$ 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 $[CaCO_3]$ and [CaO] are constant.

The concentration of CO_2, however, does vary and is dependent on the partial pressure of CO_2 in the system (the proportion of CO_2 in the "air"). We can rearrange the above equilibrium constant expression to give

$$K_{new} = K \times \frac{[CaCO_3]}{[CaO]} = [CO_2]_{eq}$$

This equilibrium constant shows that, in a closed system, the decomposition of $CaCO_3$ will reach equilibrium when the proportion of CO_2 in the "air" inside the system reaches $[CO_2]_{eq}$. However, if the reaction is carried out in the open air, the CO_2 diffuses away and its concentration in air will never reach $[CO_2]_{eq}$. So the decomposition will keep going until all the $CaCO_3$ is turned into CaO and CO_2.

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 $CaCO_3$ into CaO and 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,

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons cC + d\mathrm{D}$$

We have

$$K = \left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)_{eq} \quad \text{and} \quad Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{at any time of the reaction}$$

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 78.

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:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) + \text{Heat}$$

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.

Chapter 10

Water Science III: Formation of Water from Acids and Bases

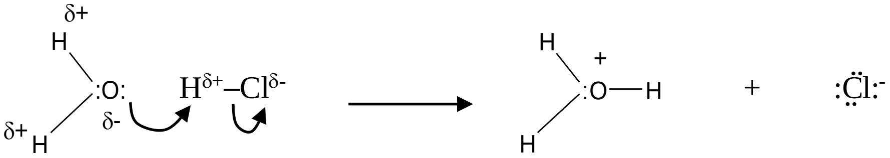
When opposites neutralize, you get salt water, too.

Question 79.

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:

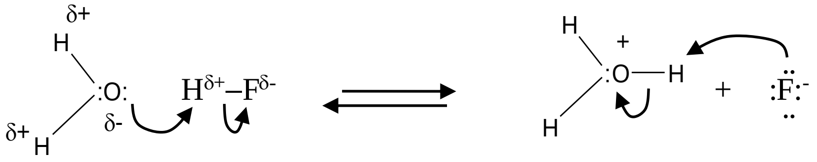
$$HCl\ (aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + Cl^-\ (aq)$$

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 H_3O^+ 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, H^+, formed after H loses its one and only electron.

The H^+ cation is in fact the "naked" proton of the hydrogen atom. Thus the **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 $H^{\delta+}$ 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 H_2O and the HF molecules. The forward reaction transfers the proton from HF to H_2O. 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:

$$HF\,(aq) \quad + \quad H_2O\,(l) \quad \underset{\textit{reverse}}{\overset{\textit{forward}}{\rightleftharpoons}} \quad H_3O^+\,(aq) \;+\; F^-\,(aq)$$

The double arrow "⇋" 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 H_3O^+ and F^- ions in the solution, so the reverse reaction is going slower than the forward reaction. Gradually as the concentrations of H_3O^+ and 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:

(1) $$HCl\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + Cl^-\ (aq)$$

And

(2) $$HF\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + F^-\ (aq)$$

Since experiments show that the HCl solution has a high electrical conductivity, we can say that at equilibrium, the concentrations of H_3O^+ and 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 H_3O^+ and 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?

Water 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:

$$H_2O\ (l) + H_2O\ (l) \rightleftharpoons \underset{\text{Hydronium}}{\underset{\uparrow}{H_3O^+}}\ (aq) + \underset{\text{Hydroxide}}{\underset{\uparrow}{OH^-}}\ (aq)$$

Or simply:

$$2H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + OH^-\ (aq)$$

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 80.

At 25 ˚C, it has been found that $[H_3O^+] = [OH^-] = 1.00 \times 10^{-7}$ 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

$$2H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + OH^-\ (aq)$$

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**.

$$K_w = K \times [H_2O]^2 = ([H_3O^+][OH^-])_{eq}$$

At 25 ˚C, $K_w = [H_3O^+] \times [OH^-] = (1.00 \times 10^{-7})\ (1.00 \times 10^{-7})$

$= 1.00 \times 10^{-14}$

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 1.00×10^{-14}, at 25 ˚C, in any aqueous solution that has reached equilibrium.

Question 81.

At 25 ˚C, it has been found that, in an aqueous solution, the initial concentration of H_3O^+ is 5.00×10^{-5} mol L^{-1}, and the initial concentration of OH^- is 3.20×10^{-4} 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 1.00×10^{-14}.

Assume that the concentration of water is constant, thus

$$Q_w = Q \times [H_2O]^2 = [H_3O^+][OH^-]$$

$$= (5.00 \times 10^{-5})\,(3.20 \times 10^{-4})$$

$$= 1.60 \times 10^{-8}$$

Since $Q_w >> K_w$, the solution is not in equilibrium and the reaction will proceed in the direction that will reduce the concentrations of the H_3O^+ and OH^- until $Q_w = K_w$.

The reaction before reaching equilibrium would be

$$H_3O^+ (aq) + OH^- (aq) \longrightarrow 2H_2O (l)$$

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

$$pH = -\log_{10}[H_3O^+]$$

Not an indication of accuracy

So for pure water at 25 ˚C, $pH = -\log_{10}[H_3O^+] = -\log_{10}[\underbrace{1.00}_{\text{3 sig. fig.}} \times 10^{-7}] = 7.\underbrace{000}_{\text{3 decimal places}}$

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 82.

At 25 ˚C, an aqueous solution has been found to turn red litmus paper blue and has a $[OH^-] = 3.20 \times 10^{-4}$ mol L^{-1}. Is the solution acidic or basic? What is the pH of the solution?

Answer:

We know that at 25 ˚C, $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ mol^2 L^{-2}. For a solution with $[OH^-] = 3.20 \times 10^{-4}$ mol L^{-1}, it must have

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{3.20 \times 10^{-4}} = 3.13 \times 10^{-11}$$

$$pH = -\log_{10}[H_3O^+] = -\log_{10}[3.13 \times 10^{-11}] = 10.5.$$

The solution is basic and has a pH of 10.5.

Question 83.

What is pOH and what is the relationship between pH and pOH?

Answer:

pOH is defined similarly as is pH. So is pK_w. Therefore

$$pOH = -\log_{10}[OH^-] \text{ and } pK_w = -\log_{10}K_w$$

Since at 25 ˚C, $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$, we have

$$\boxed{pK_w = pH + pOH = 14}$$

This is a very useful relationship. Note that **14** is an exact number here.

All acidic solutions give a pH value less than 7 ($[H_3O^+] > 10^{-7}$). All basic solutions give a pH value greater than 7 ($[H_3O^+] < 10^{-7}$). 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 $[H_3O^+]$ of the solution to greater than 10^{-7} mol L^{-1}. Such a solution will have a pH < 7 and will behave like an acid. The more the increase in $[H_3O^+]$, 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 79** (page 106) 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 equilibriums as follows:

$$HCl\ (aq) \quad + \quad H_2O\ (l) \quad \rightleftharpoons \quad H_3O^+\ (aq) \ + \ Cl^-\ (aq)$$

$$K\ (HCl) = \left(\frac{[H_3O^+][Cl^-]}{[HCl][H_2O]}\right)_{eq}$$

And

$$HF\ (aq) \quad + \quad H_2O\ (l) \quad \rightleftharpoons \quad H_3O^+\ (aq) \ + \ F^-\ (aq)$$

$$K\ (HF) = \left(\frac{[H_3O^+][F^-]}{[HF][H_2O]}\right)_{eq}$$

In both cases if we again assume that $[H_2O]$ is constant in dilute solutions, we can obtain new constants, respectively, as follows:

$$K_a(HCl) = K\ (HCl) \times [H_2O] = \left(\frac{[H_3O^+][Cl^-]}{[HCl]}\right)_{eq}$$

And

$$K_a(HF) = K\ (HF) \times [H_2O] = \left(\frac{[H_3O^+][F^-]}{[HF]}\right)_{eq}$$

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 $[H_3O^+]$, 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 $[H_3O^+]$ and $[Cl^-]$ is so large and the [HCl] is so small (almost zero) that K_a becomes a very large value, as shown below:

$$K_a(HCl) = \left(\frac{[H_3O^+][Cl^-]}{[HCl]}\right)_{eq} = \left(\frac{very\ large}{\sim 0}\right)_{eq} \sim \text{very large}$$

In such cases we consider that the acid completely dissociates in the solution and $[H_3O^+] = [Cl^-]$ according to the reaction stoichiometry. The amount of H_3O^+ 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_3** (nitric acid), **H_2SO_4** (sulfuric acid), and **$HClO_4$** (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	pK_a
Phosphoric acid	$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$	7.5×10^{-3}	2.12
Hydrofluoric acid	$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	3.5×10^{-4}	3.45
Acetic acid	$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$	1.8×10^{-5}	4.74
Carbonic acid	$CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^-$	4.3×10^{-7}	6.37

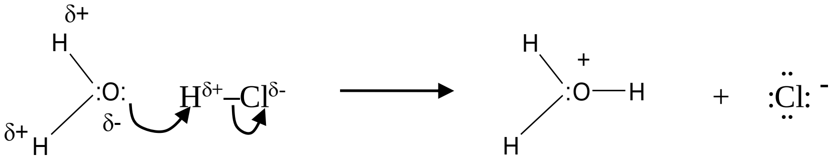
The pK_a values in the last column are obtained by doing the following calculation, for example

$$pK_a(HF) = -\log_{10}K_a(HF) = -\log_{10}(3.5 \times 10^{-4}) = 3.45$$

When comparing the strength of acids, it is easier to compare the pK_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 pK_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**.

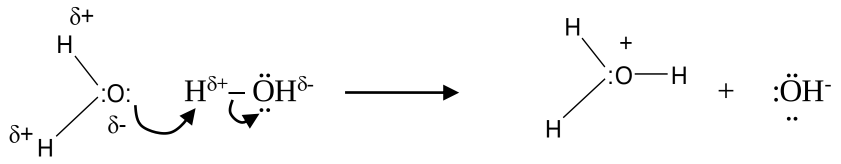
The Lewis bases are any compounds that **donate** a pair of unshared electrons in a reaction. They are **electron pair donors**.

Question 84.

Use Lewis structures to illustrate the proton transfer process in the self-ionization of water. Is water an acid or a base?

<u>**Answer:**</u>

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

$$B + H\text{—}OH \rightleftharpoons BH^+ + OH^-$$

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

$$[H_3O^+] \times [OH^-] = 1.00 \times 10^{-14} \text{ (at 25 ˚C)}$$

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 ˚C.

Name	Proton Transfer Reaction	K_b	pK_b (= - $\log_{10}K_b$)
Sulfide ion	$S^{2-} + H_2O \rightleftharpoons HS^- + OH^-$	7.7×10^{-2}	1.11
Phosphate ion	$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^- + OH^-$	4.8×10^{-2}	1.32
Carbonate ion	$CO_3^{2-} + H_2O \rightleftharpoons OH^- + HCO_3^-$	2.1×10^{-4}	3.68
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-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 ˚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 OH^- and the metal ions from the Group I and II metals. Group I metals form M^+ ions so the bases formed are LiOH, NaOH, KOH, RbOH, CsOH and 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.

$$H_2O\,(l) + NaOH\,(s) \longrightarrow Na^+\,(aq) + OH^-\,(aq) + H_2O\,(l)$$

Or simply

$$NaOH\,(s) \longrightarrow Na^+\,(aq) + OH^-\,(aq)$$

Group II metals form M^{+2} ions so the bases formed are $Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$, and $Ra(OH)_2$. Group II metals are sometimes referred to as **alkaline earth metals**. Among them $Mg(OH)_2$, $Ca(OH)_2$, and $Ba(OH)_2$ 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.

<u>Group I metals</u>: $2M\,(s) + 2H_2O\,(l) \longrightarrow 2M^+(aq) + 2OH^-\,(aq) + H_2\,(g)$

And

<u>Group II metals</u>: $M\,(s) + 2H_2O\,(l) \longrightarrow M^{2+}\,(aq) + 2OH^-\,(aq) + H_2\,(g)$

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.

<u>Group I metals</u>: $M_2O\,(s) + H_2O\,(l) \longrightarrow 2M^+(aq) + 2OH^-\,(aq)$

And

<u>Group II metals</u>: $MO\,(s) + H_2O\,(l) \longrightarrow M^{2+}(aq) + 2OH^-\,(aq)$

Hydrogen gas is not a product in these reactions.

10.6 Conjugate Acid-Base Pairs

For any acid in water, we have

$$\text{HA (aq)} \quad + \quad \text{H}_2\text{O (l)} \quad \rightleftharpoons \quad \text{H}_3\text{O}^+ \text{ (aq)} \quad + \quad \text{A}^- \text{ (aq)}$$

$$K_a(\text{HA}) = \left(\frac{[H_3O^+][A^-]}{[HA]}\right)_{\text{eq}}$$

We expect the anion produced, A^-, to behave like a Lewis base, and we have

$$\text{H}_2\text{O (l)} \quad + \quad \text{A}^- \text{ (aq)} \quad \rightleftharpoons \quad \text{HA (aq)} \quad + \quad \text{OH}^- \text{ (aq)}$$

$$K_b(\text{A}^-) = \left(\frac{[HA][OH^-]}{[A^-]}\right)_{\text{eq}}$$

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.

$$K_a(\text{HA}) \times K_b(\text{A}^-) = \left(\frac{[H_3O^+][\cancel{A}^-]}{[\cancel{HA}]}\right)_{\text{eq}} \times \left(\frac{[\cancel{HA}][OH^-]}{[\cancel{A}^-]}\right)_{\text{eq}}$$

$$= [\text{H}_3\text{O}^+] \times [\text{OH}^-] = K_w = 1.00 \times 10^{-14} \text{ (at 25 °C)}$$

Are you amazed by what happened to the concentrations of HA and its conjugate base 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

$$\boxed{pK_a(\text{HA}) + pK_b(\text{A}^-) = pK_w = 14}$$

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 85.

The pK_a of H_2CO_3 is 3.7. What is the dissociation constant of its conjugate base?

Answer:

The dissociation equilibrium for H_2CO_3 is

$$\underset{\text{Acid}}{H_2O\,(l) + H_2CO_3\,(aq)} \rightleftharpoons \underset{\text{conjugate base}}{H_3O^+\,(aq) + HCO_3^-\,(aq)}$$

$pK_b = 14 - pK_a = 14 - 3.7 = 10.3$ $K_b = 10^{-10.3} = 5.01 \times 10^{-11}$

Question 86.

The values of pK_a for H_2CO_3 and HF are 3.7 and 3.2, respectively. Which one is a stronger base, HCO_3^- or F^-?

Answer:

HCO_3^- is the conjugate base of H_2CO_3 and F^- is the conjugate base of HF. Since $pK_b + pK_a = 14$, the **larger the pK_a**, the smaller the pK_b. The smaller the pK_b, the larger the K_b, and **the stronger the base** is. Therefore HCO_3^- is a stronger base than F^-.

This example leads us to a very important observation:

The larger the 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 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:

Perchloric acid $HClO_4 + H_2O \rightarrow \mathbf{H_3O^+} + ClO_4^-$

Sulfuric acid $H_2SO_4 + 2H_2O \rightarrow \mathbf{2H_3O^+} + SO_4^{2-}$

Hydrochloric acid $HCl + H_2O \rightarrow \mathbf{H_3O^+} + Cl^-$

Strong bases:

Oxide ion $O^{2-} + H_2O \rightarrow OH^- + \mathbf{OH^-}$

Amide ion	$NH_2^- + H_2O \rightarrow NH_3 + \mathbf{OH^-}$
Hydride ion	$H^- + H_2O \rightarrow H_2 + \mathbf{OH^-}$

These examples show that whatever the strong acid or base is, it is inevitably converted into either the **hydronium ion** or the **hydroxide ion**. Thus in aqueous solutions

There is no base stronger than OH^- and there is no acid stronger than H_3O^+.

This "wiping out all difference" action is called the **leveling effect of water**. When used in organic solvents, strong bases such as the amide ion (NH_2^-) and the hydride ion (H^-) are much stronger bases than the hydroxide ion (OH^-). They are powerful Lewis bases commonly used in organic synthesis. However, if water is chosen as the solvent, they will react with water first and will not be able to serve as the intended Lewis base.

10.8 Acid-Base Reactions in Aqueous Solution

I hope you still remember that electrons are the "root" of all chemistry. Based on this understanding we can divide most chemical reactions into two major categories:

When one or more **electrons** are **lost** by one reactant **and gained** by another reactant, the reaction is an **oxidation-reduction** reaction;

When one **pair of unshared electrons** is **donated** by one reactant and **accepted** by another reactant, the reaction is an **acid-base** reaction. Most acid-base reactions involve "**proton transfer**" from one reactant to another reactant.

Let's see what happens when we put a strong acid and a strong base together.

Question 87.

What are the values of pH of a 500.0 mL 0.0010 M HCl solution and a 500.0 mL 0.0010 M NaOH solution, respectively? What is the pH of the solution obtained by completely mixing these two solutions?

Answer:

HCl is a strong acid and NaOH is a strong base. Both **completely** dissociate in water. So before mixing, these are the ions existing in each solution and their concentrations:

In HCl solution: $$\underset{}{H_2O\,(l)} + HCl\,(aq) \longrightarrow \underset{0.0010\text{ M}}{\mathbf{H_3O^+\,(aq)}} + \underset{0.0010\text{ M}}{\mathbf{Cl^-\,(aq)}}$$

$$\mathbf{pH = -\log [H_3O^+] = -\log 0.0010 = 3.00\ (acidic)}$$

The actual number of moles of H_3O^+ (aq) and Cl^- (aq) can be calculated as follows:

Since Molarity = $\frac{moles}{volume\,(L)}$

$$\text{Moles} = \text{Molarity} \times \text{volume (L)} = 0.0010\ \frac{mol}{\cancel{L}} \times 0.5000\ \cancel{L} = 5.0 \times 10^{-4}\ \text{mol}$$

In NaOH solution: $\text{NaOH (aq)} \longrightarrow \underset{0.0010\ \text{M}}{\mathbf{Na^+ (aq)}} + \underset{0.0010\ \text{M}}{\mathbf{OH^- (aq)}}$

$pH = 14 – pOH = 14 – (-\log [OH^-]) = 14 – 3.00 = 11.00$ (basic)

The actual number of moles of Na^+ (aq) and OH^- (aq) can be calculated as follows:

$$\text{Moles} = \text{Molarity} \times \text{volume (L)} = 0.0010\ \frac{mol}{\cancel{L}} \times 0.5000\ \cancel{L} = 5.0 \times 10^{-4}\ \text{mol}$$

When we completely mix these two solutions together, we get the following reaction equation:

$$H_3O^+ (aq) + Cl^- (aq) + Na^+ (aq) + OH^- (aq) \rightleftharpoons 2H_2O (l) + Cl^- (aq) + Na^+ (aq)$$

Before mixing 5.0 × 10^{-4} mol of each ion $\quad\quad \uparrow \quad\quad \nwarrow \quad \nearrow$

After mixing $\quad\quad 2 \times 5.0 \times 10^{-4}$ mol $\quad 5.0 \times 10^{-4}$ mol

Note that we have ignored the amount of H_3O^+ (aq) and OH^- (aq) from the autoprotolysis of water as they are over 1000 times smaller than the H_3O^+ (aq) and OH^- (aq) from HCl and NaOH.

What we get is a solution equivalent to the one we can obtain by dissolving NaCl in water, the **salt water** we set out to make in the beginning of this book! Coincidence or not, we draw a very important conclusion from this result:

When an acid reacts with a base, salt (like NaCl) and water are formed.
Or
The result of an acid-base reaction is salt (like NaCl) and water.

Since 5.0 × 10^{-4} mol of H_3O^+ (aq) completely react with 5.0 × 10^{-4} mol of OH^- (aq), according to the balanced reaction equation, 2 × 5.0 × 10^{-4} mol = 1.0 × 10^{-3} mol of water is formed.

Notice that Cl^- and Na^+ are left alone in the solution on both sides of the equation. They are called **spectator ions** and can be canceled from both sides of the equation:

$$H_3O^+ (aq) + \cancel{Cl^- (aq)} + \cancel{Na^+ (aq)} + OH^- (aq) \rightleftharpoons 2H_2O (l) + \cancel{Cl^- (aq)} + \cancel{Na^+ (aq)}$$

And we get

$$\rightleftharpoons$$

$$H_3O^+ (aq) + OH^- (aq) \qquad\qquad 2H_2O (l)$$

When the reaction is complete, the amount of H_3O^+ (aq) and OH^- (aq) in solution is governed by the self-ionization equilibrium of water, thus the **resultant salt water** will have

$$pH = pOH = 7.00$$

This observation leads us to another important conclusion:

The reactions between any Brønsted-Lowry acids and bases are simply the reaction of H_3O^+ (aq) and OH^- (aq) to form water.

Or

Any Brønsted-Lowry acid-base reactions can be represented by this net ionic equation

$$\mathbf{H_3O^+ (aq) + OH^- (aq) \rightleftharpoons 2H_2O (l)}$$

Reactions between **strong** Brønsted-Lowry **acids** and **bases** are often called **neutralization reactions** because the result of the reaction gives a neutral (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: ______________________________

pK_a: ______________________________

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.

8. Write an ionization equation for HBr in water.

9. Using drawings to illustrate the process of proton transfer for the equation given for question 5.

Chapter

11

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 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 NaCl is a product of the reaction between HCl and NaOH.

Recall that ammonia, NH_3, when used as an aqueous solution, behaves like **ammonium hydroxide, NH_4OH**. We can write the acid-base reaction equation as

$$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$$

Or simply $HCl + NH_3 \longrightarrow NH_4Cl$

Because $NH_4OH = NH_3 + H_2O$.

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, pH ~ 7**
- **Salts formed from strong acids and weak bases give acidic solutions, pH < 7**
- **Salts formed from weak acids and strong bases give basic solutions, 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.

Strong Acid	Strong Base	Weak Acid	Weak Base
H_2SO_4	KOH	H_3PO_4 ($pK_a = 2.12$)	NH_3 ($pK_b = 4.74$)

Assuming complete reaction:

$H_2SO_4 + 2KOH \longrightarrow 2H_2O + K_2SO_4$

Strong acid + Strong base ⟶ Neutral salt water

$H_3PO_4 + KOH \longrightarrow H_2O + KH_2PO_4$

Weak acid + Strong base ⟶ Basic salt water

$H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4$

Strong acid + Weak base ⟶ Acidic salt water

For salts formed from weak acids and weak bases, such as the one below, we will have to compare the pK_a value of the acid with the pK_b value of the base to make a prediction, as shown below.

$H_3PO_4 + NH_3 \longrightarrow (NH_4)H_2PO_4$
$pK_a = 2.12$ $pK_b = 4.74$
Stronger weak acid + Weak base ⟶ Acidic salt water

Question 88.

How do you decide which one is stronger, H_3PO_4 or NH_3?

Answer:

When a salt is formed from a weak acid and a weak base, such as $(NH_4)H_2PO_4$, the situation is a bit complicated. There are two equilibriums coexisting in the salt solution, one of NH_4^+ and H_2O, the other of $H_2PO_4^-$ and H_2O, as shown below.

$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^-$ $pK_b = 11.9$ $K_b = 1.3 \times 10^{-12}$

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ $pK_a = 9.2$ $K_a = 6.3 \times 10^{-10}$

Since there are equal moles of NH_4^+ and $H_2PO_4^-$ in the solution, one can estimate, without going into lengthy calculations, that at equilibrium there should be more H_3O^+ than 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 pK_a value of the acid and the pK_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 89.

Calculate the pH of a 0.200 M solution of sodium cyanide; pK_b (CN^-) = 4.70 at 25 ˚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 Na^+ and CN^- ions. Thus the initial concentrations for both ions are 0.200 M. The CN^- ions, however, immediately set up equilibrium with water, as all weak acids and bases do, as follows:

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

This equilibrium produces more OH^- and therefore makes the solution basic. If we find the $[OH^-]$ at equilibrium, we can find the pH of the solution. Note that Na^+ here is a spectator ion.

We find the equilibrium concentrations by making use of the equilibrium constant expression and the pK_b value given, assuming that the reaction takes place at 25 ˚C.

Since $pK_b = 4.70$, $K_b = 2.0 \times 10^{-5}$. Let $[OH^-]_{eq}$ be x

	$CN^- + H_2O$	$\rightleftharpoons$	HCN	+	OH^-
Initial concentrations	0.200		0		0
Equilibrium concentrations	$0.200 - x$		x		x

Thus we have

$$K_b = \left(\frac{[HCN][OH^-]}{[CN^-]}\right)_{eq} = \frac{x^2}{0.200-x} = 2.0 \times 10^{-5}$$

To make solving the equation easier, we assume that $x << 0.200$, 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

$$x^2 = 0.200 \times 2.0 \times 10^{-5} = 4.0 \times 10^{-6}$$

$$x = 2.0 \times 10^{-3} \text{ mol L}^{-1} = [OH^-]_{eq}$$

The concentration 2.0×10^{-3} is indeed much smaller than 0.200 so we can say that our initial assumption, that $x << 0.200$, is valid.

Therefore

$$\mathrm{pH} = 14 - \mathrm{pOH} = \underset{\nearrow}{14} - (-\log \underset{\nwarrow}{\underline{2.0}} \times 10^{-3}) = 11.\underset{\uparrow}{\underline{30}}$$

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 124.

Question 90.

Calculate the pH of a 0.10 M solution of NH_4Cl; pK_a (NH_4^+) = 9.2 at 25 ˚C.

<u>Answer:</u>

NH_4Cl is formed from a strong acid (HCl) and a weak base (NH_4OH). So we predict that the pH should be less than 7.

When NH_4Cl dissolves in water, it completely dissociates into NH_4^+ and Cl^- ions. Thus the initial concentrations for both ions are 0.10 M. The NH_4^+ ions, being the conjugate acid of the weak base NH_3, however, immediately set up equilibrium with water as follows:

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

This equilibrium produces more H_3O^+ and therefore makes the solution acidic. If we find the $[H_3O^+]$ at equilibrium, we can find the pH of the solution.

Since $pK_a = 9.2$, $K_a = 6 \times 10^{-10}$. Let $[H_3O^+]_{eq}$ be x

	$NH_4^+ + H_2O$ ⇌	NH_3 +	H_3O^+
Initial concentrations	0.10	0	0
Equilibrium concentrations	$0.10 - x$	x	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 $x << 0.10$, 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 8×10^{-6} is much smaller than 0.10 so we can say that our initial assumption, that $x << 0.10$, is valid.

Therefore

$$pH = -\log \underset{\substack{\uparrow \\ \text{1 sig. fig.}}}{\underline{8}} \times 10^{-6} = 5.\underset{\substack{\uparrow \\ \text{1 decimal place}}}{\underline{1}}$$

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 86**) or the cation and its conjugate weak base (**Question 87**). Using the expression from **Question 87**, 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:

$$K_a = \left(\frac{[NH_3][H_3O^+]}{[NH_4{}^+]}\right)_{eq} \Longrightarrow K_a = \left(\frac{[base][H_3O^+]}{[acid]}\right)_{eq} = [H_3O^+]\left(\frac{[base]}{[acid]}\right)_{eq}$$

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

$$pK_a = pH - \log\left(\frac{[base]}{[acid]}\right)_{eq}$$

or

$$pH = pK_a + \log(\frac{[base]}{[acid]})_{eq}$$

We have seen in **Question 86** and **Question 87** 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

$$\boxed{pH = pK_a + \log(\frac{[base]}{[acid]})_{initial}}$$

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.

$$HA + H_2O \overset{K_a}{\rightleftharpoons} A^- + H_3O^+$$

If **extra H_3O^+** is added to the equilibrium, it will react with A^- to **form some extra HA and water**. If **extra OH^-** is added to the equilibrium, it will react with HA to **form some extra A^- and water**. As long as

extra HA << original HA or **extra A^- << original A^-**

the ratio $(\frac{[base]}{[acid]})_{initial}$ 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 $[H_3O^+]$ or $[OH^-]$ 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 ([base] = [acid] and $\frac{[base]}{[acid]} = 1$), we will get a solution with a pH = pK_a of the weak acid-base pair, as shown below.

$$\mathbf{pH} = pK_a + \log(\frac{[base]}{[acid]})_{initial} = pK_a + \log(1) \mathbf{= pK_a}$$

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 pK_a.

Not all buffer solutions are made with equal amounts of a weak acid and its conjugate base. However, a buffer solution with $\frac{[base]}{[acid]} = 1$ 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 $H_2PO_4^-/HPO_4^{2-}$, and H_2CO_3/HCO_3^-.

Question 91.

Blood has a pH of 7.40. Use the Henderson-Hasselbalch equation to calculate the ratio of hydrogen carbonate ion, HCO_3^-, to carbonic acid, H_2CO_3, in blood; pK_a (H_2CO_3) = 6.37.

Answer:

The Henderson-Hasselbalch equation for this buffer system is

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[base]}{[acid]} = \mathrm{p}K_a + \log\frac{[\mathrm{HCO_3}^-]}{[\mathrm{H_2CO_3}]}$$

To solve for the ratio we rearrange the equation to

$$\log\frac{[\mathrm{HCO_3}^-]}{[\mathrm{H_2CO_3}]} = \mathrm{pH} - \mathrm{p}K_a = 7.40 - 6.37 = 1.03$$

Therefore

$$\frac{[\mathrm{HCO_3}^-]}{[\mathrm{H_2CO_3}]} = 10^{1.03} = 10.7 = 11$$

Since both ions are in the same solution (hence have the same volume), the mole ratio of HCO_3^- to H_2CO_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.

$$\mathrm{HIn} + \mathrm{H_2O} \overset{K_a}{\rightleftharpoons} \mathrm{In^-} + \mathrm{H_3O^+}$$

Using the Henderson-Hasselbalch equation we have

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[In^-]}{[HIn]}\right)_{eq}$$

We can see that, when $\frac{[In^-]}{[HIn]} = 1$, that is, in the middle of the indicator's color change, we have pH = $\mathrm{p}K_a$. This means we can choose a suitable indicator for a desired pH range by looking at the $\mathrm{p}K_a$ of the indicator. For the sensitivity of our eyes, a visible color change occurs over a range that is usually

$$\mathrm{pH} = \mathrm{p}K_a(\mathrm{HIn}) \pm 1$$

The following are a few common indicators and their properties.

			Color	
Name	$\mathrm{p}K_a$	pH Range	Acid Form	Base Form
Methyl organge	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 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, H_2CO_3 and H_2SO_4 are both diprotic acid. H_3PO_4 is a triprotic acid.

For strong acids such as H_2SO_4 (the **only** polyprotic acid indeed), the dissociation of both protons are complete reactions. We can write the ionization equation for H_2SO_4 as follows:

$$H_2SO_4 + 2H_2O \longrightarrow 2H_3O^+ + SO_4^{2-}$$

For every mole of H_2SO_4, two moles of H_3O^+ are produced.

For weak polyprotic acids such as H_3PO_4, however, the dissociation of protons is stepwise and each step is an equilibrium equation, as shown below.

Step 1: $H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$

$$K_{a1}(H_3PO_4) = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4\ \ ]} = 7.1 \times 10^{-3}$$

Step 2: $H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$

$$K_{a2}(H_3PO_4) = K_a(H_2PO_4^-) = \frac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-]} = 6.2 \times 10^{-8}$$

Step 3: $HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$

$$K_{a3}(H_3PO_4) = K_a(HPO_4^{2-}) = \frac{[PO_4^{3-}][H_3O^+]}{[HPO_4^{2-}]} = 4.4 \times 10^{-13}$$

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 H_3PO_4 to donate one proton but it is harder for the negatively charged $H_2PO_4^-$ and 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 H_3PO_4 there always exists a combination of these species: H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, and H_3O^+. 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 pK_a, as shown below:

Conjugate acid-base pair	Ratio	K_a	$pH = pK_a$
$\frac{[H_2PO_4^-]}{[H_3PO_4\ \ ]}$	1	7.1×10^{-3}	2.15
$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$	1	6.2×10^{-8}	7.20
$\frac{[HPO_4^{2-}]}{[PO_4^{3-}]}$	1	4.4×10^{-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 92.

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 Fe^{2+} ions in one million mL of solution. The total grams of Fe^{2+} ions in 10.00 mL of the stock solution can be calculated as follows:

$$\frac{55.85\ grams}{10^6\ mL} \times 10.00\ mL$$

After dilution, the total volume becomes 100.00 mL. Let the diluted concentration be x, the total grams of Fe^{2+} ions in 100.00 mL of the diluted solution can be calculated as follows:

$$\frac{x\ grams}{10^6\ mL} \times 100.00\ mL$$

Since the total grams of Fe^{2+} ions do not change before and after dilution, we have

$$\frac{55.85\ grams}{10^6\ mL} \times 10.00\ mL = \frac{x\ grams}{10^6\ mL} \times 100.00\ mL$$

Solving for x, we get

$$\frac{55.85\ \cancel{grams}}{\cancel{10^6\ mL}} \times 10.00\ \cancel{mL} = \frac{x\ \cancel{grams}}{\cancel{10^6\ mL}} \times 100.00\ \cancel{mL}$$

$$x = \frac{55.85}{100.00} \times 10.00 = 5.585\ ppm$$

The sample calculation Jimmy should have included in his lab report could look like this

Sample calculation: $M_2 = \frac{M_1V_1}{V_2} = \frac{55.85ppm \times 10.00mL}{100.00mL} = 5.585ppm$

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 $M_1V_1 = M_2V_2$ 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:

$$M_2 = \frac{M_1V_1}{V_2} = \frac{55.85ppm \times 5.00mL}{100.00mL} = 2.79ppm$$

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 $\mathbf{M_1V_1 = M_2V_2}$ 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:

$$\mathbf{C_1V_1 = C_2V_2 \text{ (C in mol L}^{-1}\text{ and V in L)}}$$

$$\mathbf{C_1v_1 = C_2v_2 \text{ (C in mol L}^{-1}\text{ and v in mL)}}$$
$$\mathbf{m_1V_1 = m_2V_2 \text{ (m in g L}^{-1}\text{ and V in L or mL)}}$$

$$\mathbf{\%_1v_1 = \%_2v_2 \text{ (\% is any percent concentration and v in mL)}}$$

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.

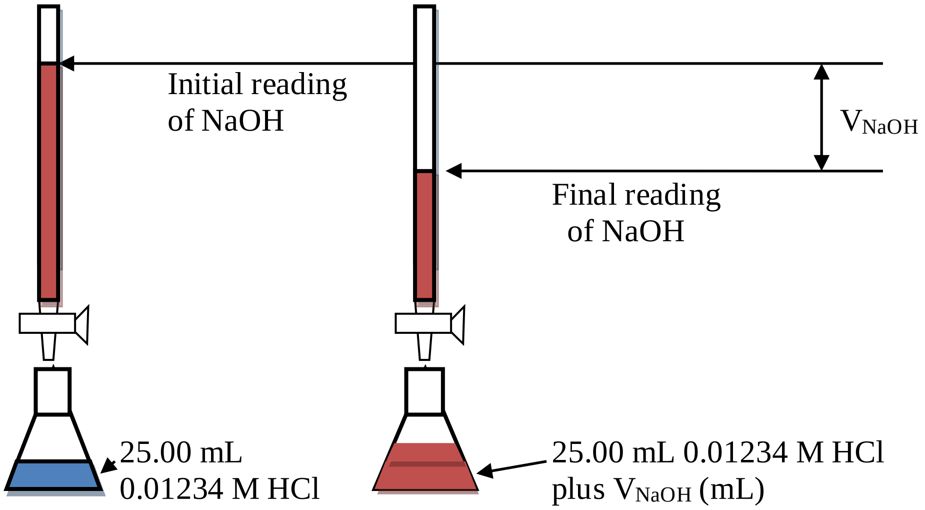
1. Add a very small amount of the acid from a buret to a measured volume of the base in an Erlenmeyer flask
2. Mix (swirl the flask) to allow for complete consumption of the added acid
3. Check for color change expected from the indicator used
4. Repeat steps 1 to 3 until the first faint color change 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 93**. A drawing of the titration set up for the question is shown below.



Question 93.

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.

$$\mathrm{HCl} \quad + \quad \mathrm{NaOH} \longrightarrow \mathrm{H_2O} \quad + \quad \mathrm{NaCl}$$

In each of the three 25.00 mL 0.01234 M HCl solutions, the total moles of HCl can be calculated as follows:

$$\text{Moles HCl} = \text{Molarity} \times \text{volume} = 0.01234\ \frac{mol}{\cancel{L}} \times 25.00\ \cancel{mL} \times \frac{1\ \cancel{L}}{1000\ \cancel{mL}} = 3.085 \times 10^{-4}\ \text{mol}$$

At the equivalence point, the total moles of NaOH used can be calculated as follows:

$$\text{Moles NaOH} = \text{Molarity} \times \text{volume} = M_{NaOH}\frac{mol}{\cancel{L}} \times V\ \cancel{mL} \times \frac{1\ \cancel{L}}{1000\ \cancel{mL}}$$

As the balanced reaction equation suggests a 1:1 molar relationship between HCl and NaOH, we have

$$\text{Moles NaOH} = \text{Moles HCl}$$

Thus

$$M_{NaOH}\frac{mol}{\cancel{L}} \times V\ \cancel{mL} \times \frac{1\ \cancel{L}}{1000\ \cancel{mL}} = 3.085 \times 10^{-4}\ \text{mol}$$

Solving for M_{NaOH}, we get

$$M_{NaOH} = 3.085 \times 10^{-4}\ \text{mol} \div (\text{V}\ \cancel{\text{mL}} \times \frac{1\ L}{1000\ \cancel{mL}})$$

By using the V value for each trial, we get

For trial 1: $M_{NaOH} = 3.085 \times 10^{-4}\ \text{mol} \div (23.00\ \cancel{\text{mL}} \times \frac{1\ L}{1000\ \cancel{mL}}) = 0.01341\frac{mol}{L}$

For trial 2: $M_{NaOH} = 3.085 \times 10^{-4}\ \text{mol} \div (21.50\ \cancel{\text{mL}} \times \frac{1\ L}{1000\ \cancel{mL}}) = 0.01435\frac{mol}{L}$

For trial 3: $M_{NaOH} = 3.085 \times 10^{-4}\ \text{mol} \div (21.68\ \cancel{\text{mL}} \times \frac{1\ L}{1000\ \cancel{mL}}) = 0.01423\frac{mol}{L}$

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^- = Moles H_3O^+

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:

$$\mathbf{C_{base}V_{base} = C_{acid}V_{acid}\ (C\ in\ mol\ L^{-1}\ and\ V\ in\ mL)}$$

In the case of NaOH and H_2SO_4, it takes two NaOH to neutralize every H_2SO_4, 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:

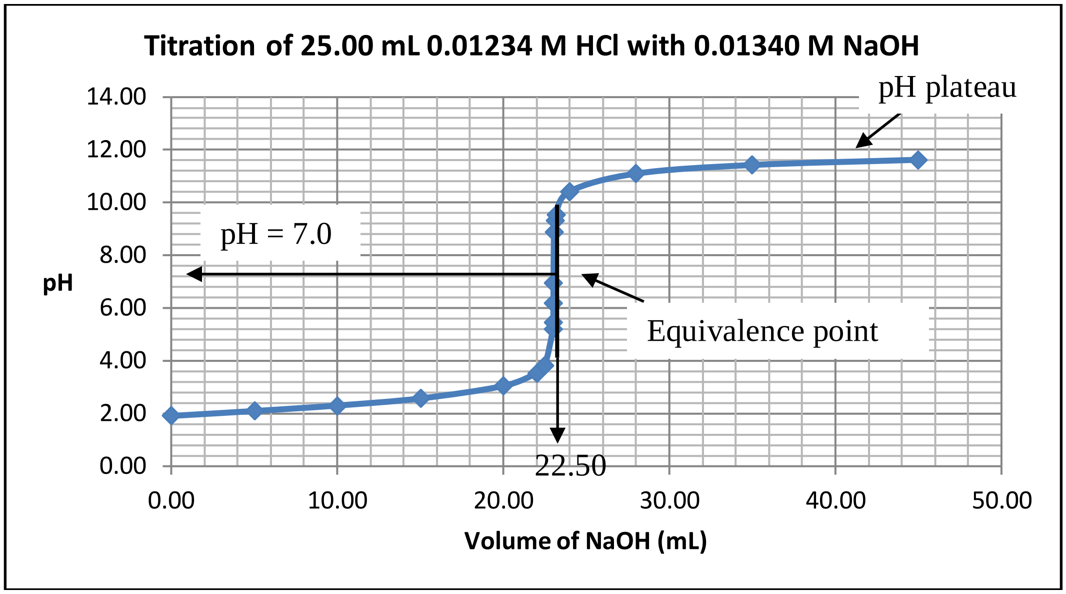
$$\mathbf{C_{base}V_{base} = 2C_{acid}V_{acid}\ (C\ in\ mol\ L^{-1}\ and\ V\ in\ mL)}$$

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 93**, 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 93**).

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_{NaOH} = 0.01340 mol L^{-1}			M_{HCl} = 0.01234 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)	$[H_3O^+]$ (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$^-$] (mol L^{-1})	
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 × volume

$$= 0.01234\ \frac{mol}{\cancel{L}} \times 25.00\ \cancel{mL} \times \frac{1\ \cancel{L}}{1000\ \cancel{mL}} = 3.085 \times 10^{-4}\ \text{mol}$$

When V_{NaOH} = 15.00 mL,

Moles NaOH added = Molarity × volume

$$= 0.01340\ \frac{mol}{\cancel{L}} \times 15.00\ \cancel{mL} \times \frac{1\ \cancel{L}}{1000\ \cancel{mL}} = 2.010 \times 10^{-4}\ \text{mol}$$

Moles of leftover HCl = Moles of initial HCl - Moles NaOH added

$$= 3.085 \times 10^{-4}\ \text{mol} - 2.010 \times 10^{-4}\ \text{mol} = 1.075 \times 10^{-4}\ \text{mol}$$

$$[H_3O^+] = \frac{moles\ of\ leftover\ HCl}{volume\ of\ total\ solution} = \frac{1.075 \times 10^{-4}\ mol}{40.00\ \cancel{mL}} \times \frac{1000\cancel{mL}}{L} = 2.688 \times 10^{-3}\ \text{mol L}^{-1}$$

pH = $-\log[H_3O^+] = -\log(2.688 \times 10^{-3}) = 2.57$ (we choose to keep only 2 sig. fig. here)

Note that with Betty's titration set up (page 136) 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_{NaOH} = 23.02 mL) to 6.97 (at V_{NaOH} = 23.022 mL).

At pH = 6.97 when V_{NaOH} = 23.022 mL, $[H_3O^+] = 1.083 \times 10^{-7}$ mol L^{-1}. The solution essentially has the pH of pure water. Experimentally the equivalence point was observed between V_{NaOH} = 22.00 mL to 23.05 mL (labeled as 22.50 on the titration curve on page 139).

After the equivalence point, any additional NaOH added would cause the solution to have an $[OH^-]$ greater than 1.0×10^{-7} 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_{NaOH} = 23.15 mL,

Moles NaOH added = Molarity × volume

$$= 0.01340\ \frac{mol}{\cancel{L}} \times 23.15\ \cancel{mL} \times \frac{1\ \cancel{L}}{1000\ \cancel{mL}} = 3.102 \times 10^{-4}\ \text{mol}$$

Moles of extra NaOH = Moles NaOH added - Moles of initial HCl

$$= 3.102 \times 10^{-4}\ \text{mol} - 3.085 \times 10^{-4}\ \text{mol} = 1.710 \times 10^{-6}\ \text{mol}$$

$$[OH^-] = \frac{moles\ of\ extra\ NaOH}{volume\ of\ total\ solution} = \frac{1.710 \times 10^{-6}\ mol}{48.15\ \cancel{mL}} \times \frac{1000 \cancel{mL}}{L} = 3.551 \times 10^{-5}\ \text{mol L}^{-1}$$

$$pH = 14 - pOH = 14 + \log[OH^-] = 14 + \log(3.551 \times 10^{-5}) = 9.55$$

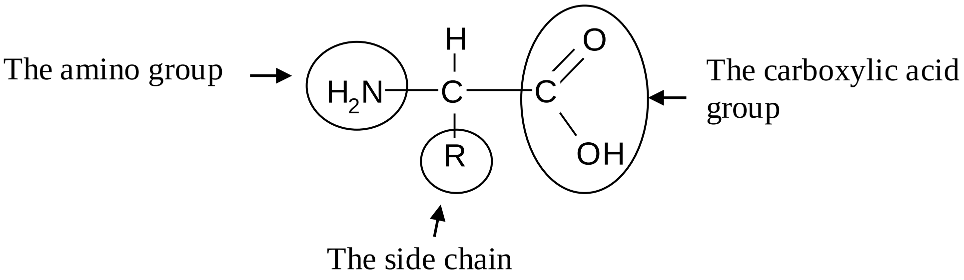
If we plot pH against the volume of NaOH added, we get a titration curve (pH curve) just like the one on page 139.

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 pH < 7 while a weak acid-strong base salt will have at equivalence point a 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.

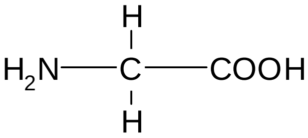
11.9 Amino Acids and pH

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.



$$H_2N-\overset{H}{\underset{H}{C}}-COOH$$

Glycine can behave as an acid because the –COOH group can donate a proton to become –COO^-. It can also behave as a base because the $–NH_2$ group can donate a lone pair of electrons on the nitrogen atom to a proton, or, the $–NH_2$ group can be protonated to become $–NH_3^+$. Thus amino acids are amphoteric species (**ampholytes**).

Similar to acetic acid (CH_3COOH, $pK_a = 4.8$) and ammonia (NH_3, $pK_a(NH_4^+) = 9.2$), 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 pK_a values.

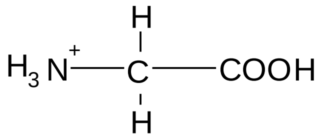
When an amino acid is dissolved in solution, the amine group ($–NH_2$) and the carboxylic acid group (–COOH) are either **protonated** or **deprotonated**, depending on the pH of the solution. We will discuss this dependency in the following examples.

Question 94.

Draw the structure of glycine in a pH = 2 solution, given that $pK_a(\text{-COOH}) = 2.2$ and $pK_a(\text{-NH}_3^+) = 9.7$.

Answer:

A solution of pH 2 is a strong acidic solution. Since pH of the solution is less than both pK_a(-COOH) and pK_a($-NH_3^+$), the solution is acidic enough to make both the COOH group and the 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.



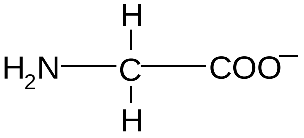
$$H_3\overset{+}{N}-\underset{H}{\overset{H}{C}}-COOH$$

Question 95.

Draw the structure of glycine in a pH = 10 solution, given that pK_a(-COOH) = 2.2 and pK_a($-NH_3^+$) = 9.7.

Answer:

A solution of pH 10 is a strong basic solution. Since pH of the solution is greater than both pK_a(-COOH) and pK_a($-NH_3^+$), the solution is basic enough to make both the COOH group and the 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.



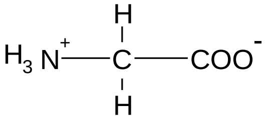
$$H_2N-\underset{H}{\overset{H}{C}}-COO^-$$

Question 96.

Draw the structure of glycine in a pH = 6 buffer solution, given that pK_a(-COOH) = 2.2 and pK_a($-NH_3^+$) = 9.7.

Answer:

A near neutral solution of pH 6 is basic enough to deprotonate the –COOH group (pH > pK_a(-COOH)) but not basic enough to deprotonate the $-NH_3^+$ group (pH < pK_a($-NH_3^+$)). Thus the –COOH group will exist in its basic form ($-COO^-$) and the $-NH_2$ group will exist in its acidic form ($-NH_3^+$). The amino acid has the following structure and is a dipolar ion (**zwitterion**). The amino acid glycine carries zero net charge.



$$H_3\overset{+}{N}-\underset{H}{\overset{H}{C}}-COO^-$$

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,

$$\text{pI} = \frac{pK_a(-COOH) + pK_a(-NH_3{}^+)}{2} = \frac{2.2+9.7}{2} = 6.0$$

For amino acids with an acidic side chain,

$$\text{pI} = \frac{pK_{a1}(-COOH) + pK_{a2}(-COOH)}{2} \sim 3$$

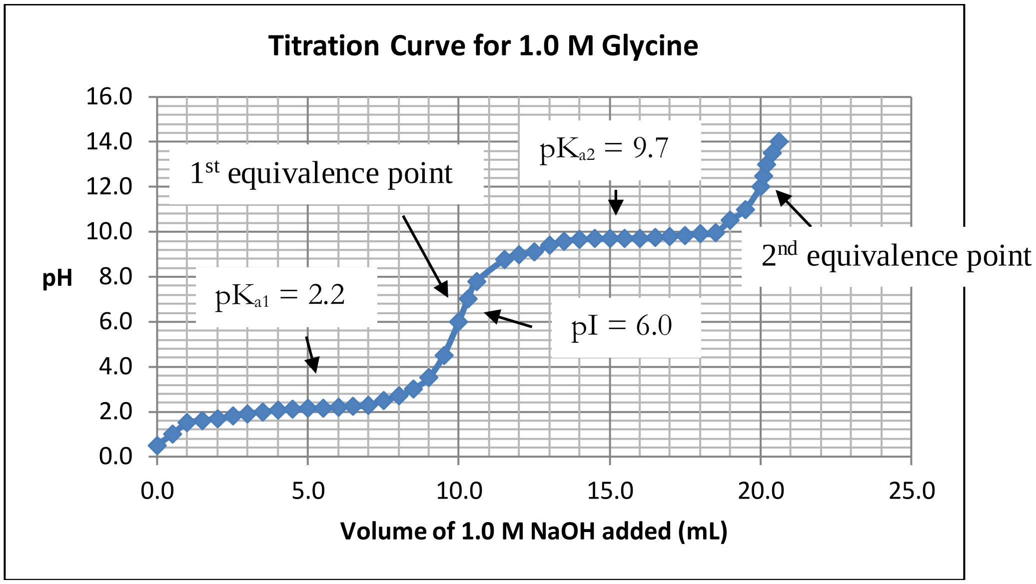
For amino acids with a basic side chain,

$$\text{pI} = \frac{pK_{a1}(-NH_3{}^+) + pK_{a2}(-NH_3{}^+)}{2} > 7$$

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 –COOH group and the $-NH_3{}^+$ group.



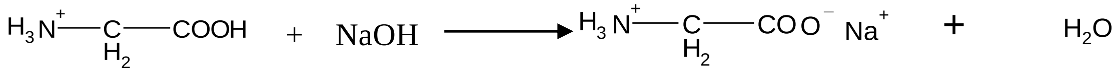
The titration curve provides us with several pieces of important information. We will show you how to make use of the titration curve in the following examples.

Question 97.

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 1st 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:

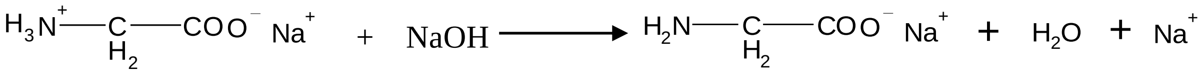


$$H_3\overset{+}{N}-\underset{H_2}{C}-COOH + NaOH \longrightarrow H_3\overset{+}{N}-\underset{H_2}{C}-COO^- \; Na^+ + H_2O$$

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:



$$H_3\overset{+}{N}-\underset{H_2}{C}-COO^- \; Na^+ + NaOH \longrightarrow H_2N-\underset{H_2}{C}-COO^- \; Na^+ + H_2O + Na^+$$

This jump occurs at V_{NaOH} = 20.0 mL because another 10.0 mL of 1.0 M NaOH is needed to completely deprotonate the $–NH_3^+$ 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 98.

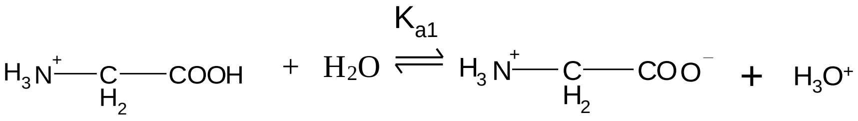
Referring to the titration curve for glycine, how do you find that $pK_a(-COOH) = 2.2$ and $pK_a(-NH_3^+) = 9.7$? Where are the two buffer regions?

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_{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 $\frac{[A^-]}{[HA]} = 1$:



$$H_3\overset{+}{N}-\underset{H_2}{C}-COOH + H_2O \overset{K_{a1}}{\rightleftharpoons} H_3\overset{+}{N}-\underset{H_2}{C}-COO^- + H_3O^+$$

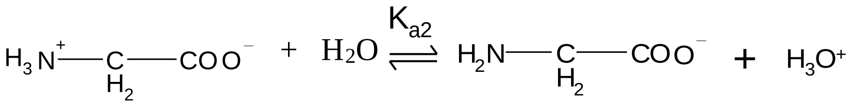
By applying the Henderson-Hasselbalch equation

$$pH = pK_{a1} + \log(\frac{[A^-]}{[HA]})_{eq}$$

we get that when $\frac{[A^-]}{[HA]} = 1$, pH = pK_a. Therefore we find $pK_{a1}(-COOH) = 2.2$ from the titration curve at V_{NaOH} = 5.0 mL. This is indeed the midpoint between the beginning of the titration and the 1st equivalence point. This is also the midpoint of the 1st 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_{NaOH} = 15.0 mL.

At this moment we have the following acid-base equilibrium between the $–NH_3^+$ group and its conjugate base and we know that $\frac{[-NH_2]}{[-NH_3{}^+]} = 1$:



$$H_3\overset{+}{N}-\underset{H_2}{C}-COO^- + H_2O \overset{K_{a2}}{\rightleftharpoons} H_2N-\underset{H_2}{C}-COO^- + H_3O^+$$

By applying the Henderson-Hasselbalch equation

$$pH = pK_{a2} + \log\left(\frac{[-NH_2]}{[-NH_3{}^+]}\right)_{eq}$$

we get that when $\frac{[-NH_2]}{[-NH_3{}^+]} = 1$, pH = pK_{a2}. Therefore we find $pK_{a2}(-NH_3^+) = 9.7$ from the titration curve at $V_{NaOH} = 15.0$ mL. This is indeed the midpoint between the 1st equivalence point and the 2nd equivalence point. This is also the midpoint of the 2nd 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 Na_2CO_3 with 50.0 mL 0.50 M $NaHCO_3$, given that $pK_a(HCO_3^-) = 10.2$.

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 pK_a and pI values and the equivalence points.

Chapter 12

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):

$$1\ \mathrm{J} = 1\ \mathrm{N\ m} = 1\ \mathrm{kg\ m\ S^{-2}} \times \mathrm{m} = 1\ \mathrm{kg\ m^2\ s^{-2}}$$

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 ΔE. 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 99.

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 100.

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 101.

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, $\Delta E = w + q$, ΔE 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 $E_{25\,^\circ\mathrm{C}}$ to $E_{0\,^\circ\mathrm{C}}$. $\Delta E = E_{0\,^\circ\mathrm{C}} - E_{25\,^\circ\mathrm{C}}$. 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 $\Delta E = E_{0\,^\circ\mathrm{C}} - E_{25\,^\circ\mathrm{C}}$.

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 ΔH.

For a chemical reaction, the enthalpy change is given by the equation

$$\Delta \mathbf{H} = \textit{total } \mathbf{H}_{products} - \textit{total } \mathbf{H}_{reactants}$$

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; *ΔH 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; *ΔH 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, ΔH 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 ΔH°**.**

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 ΔH° are frequently used in place of ΔH**.** 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 ΔH 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.

$$H_2(g) \longrightarrow 2H(g)$$

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

$$\text{BE(H—H)} = 436.0 \text{ kJ mol}^{-1}$$

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 102.

Is the formation reaction of water exothermic or endothermic? Given that BE(H—H) = 436.0 kJ mol^{-1}, BE(O=O) = 498.0 kJ mol^{-1}, and BE(O—H) = 463.0 kJ mol^{-1}.

Answer:

The formation of H_2O from H_2 and O_2 takes place according to the following balanced equation:

$$2H_2\text{ (g)} + O_2\text{ (g)} \rightleftharpoons 2H_2O\text{ (g)}$$

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,

$$\Delta H^\circ = \text{total BE (bonds broken)} - \text{total BE (bonds formed)}$$

$$= (2 \times 436.0 + 498.0) - (4 \times 463.0) = 1370 - 1892 = -482.0 \text{ kJ}$$

Since $\Delta H < 0$, the formation reaction of water is exothermic.

Question 103.

Is the decomposition reaction of water exothermic or endothermic? Given that BE(H—H) = 436.0 kJ mol^{-1}, BE(O=O) = 498.0 kJ mol^{-1}, and BE(O—H) = 463.0 kJ mol^{-1}.

Answer:

The decomposition reaction of water is the reverse of the formation of H_2O. The equation is:

$$2H_2O\ (g) \rightleftharpoons 2H_2\ (g) + O_2\ (g)$$

Four O—H bonds are broken and 2 H—H bonds and 1 O=O bond are formed. Under standard condition,

$$\Delta H^\circ = \text{total BE (bonds broken)} - \text{total BE (bonds formed)}$$

$$= (4 \times 463.0) - (2 \times 436.0 + 498.0) = 1852 - 1370 = 482.0 \text{ kJ}$$

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 104.

Calculate the enthalpy change for the formation of methane from carbon and hydrogen,

$$C(s) + 2H_2\,(g) \longrightarrow CH_4(g)$$

given that the enthalpy changes for the following reactions are known:

(1) $C(s) + O_2\,(g) \longrightarrow CO_2(g)$ $\qquad \Delta H_1{}^\circ = -\,393.5\text{ kJ}$

(2) $O_2(g) + 2H_2\,(g) \longrightarrow 2\,H_2O(l)$ $\qquad \Delta H_2{}^\circ = -\,571.6\text{ kJ}$

(3) $2O_2(g) + CH_4\,(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$ $\qquad \Delta H_3{}^\circ = -\,890.4\text{ kJ}$

<u>Answer:</u>

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.

$$(1)\;\; C(s) + \cancel{O_2\,(g)} \longrightarrow \cancel{CO_2(g)} \qquad \Delta H_1{}^\circ = -\,393.5\text{ kJ}$$

$$(2)\;\; \cancel{O_2(g)} + 2H_2\,(g) \longrightarrow \cancel{2\,H_2O(l)} \qquad \Delta H_2{}^\circ = -\,571.6\text{ kJ}$$

And reverse (3) (remember to also reverse the sign of ΔH°)

$$(3)\;\; \cancel{CO_2(g)} + \cancel{2\,H_2O(l)} \longrightarrow \cancel{2O_2(g)} + CH_4\,(g) \qquad -\Delta H_3{}^\circ = +\,890.4\text{ kJ}$$

$$C(s) \;+\; 2H_2\,(g) \longrightarrow CH_4\,(g) \;\;\text{(Result of Addition)}$$

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,

$$\Delta H^\circ = \Delta H_1{}^\circ + \Delta H_2{}^\circ + (-\Delta H_3{}^\circ) = (-\,393.5\text{ kJ}) + (-\,571.6\text{ kJ}) + (+\,890.4\text{ kJ})$$

$$= -\,74.7\text{ kJ}$$

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**, ΔH_f°.

The standard enthalpy of formation, ΔH_f°, 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 $O_2(g)$, hydrogen is $H_2(g)$, and bromine is $Br_2(l)$, 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 ΔH_f° 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 ΔH_f° values, it is important to choose the value that corresponds to the physical state. For example, the ΔH_f° for liquid water is -285.8 kJ mol^{-1} whereas for gaseous water it is -241.8 kJ mol^{-1}.

One important application of ΔH_f° data is to gain a sense of stability of the compound. Essentially what a ΔH_f° 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 ΔH_f° is positive, the compound contains more stored energy than the elements from which it is formed.

For example, ΔH_f° for $CO_2(g)$ is -393 kJ mol^{-1}, we say that CO_2 contains less stored energy than the sum of the energy stored in C(graphite) and $O_2(g)$. More often we say that CO_2 is more stable than C(graphite) and $O_2(g)$.

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.

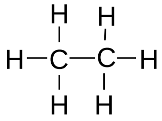
A less stable compound is chemically more reactive.

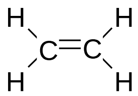
Question 105.

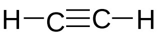
Draw the Lewis structures for ethyne (C_2H_2), ethene (C_2H_4), and ethane (C_2H_6). Compare their chemical stability, given that $\Delta H_f^\circ(C_2H_2,g) = +226.8\ \text{kJ mol}^{-1}$, $\Delta H_f^\circ(C_2H_4,g) = +52.3\ \text{kJ mol}^{-1}$ and $\Delta H_f^\circ(C_2H_6,g) = -84.7\ \text{kJ mol}^{-1}$.

Answer:

The Lewis structures are:







For the formation reactions we have

ΔH_f°

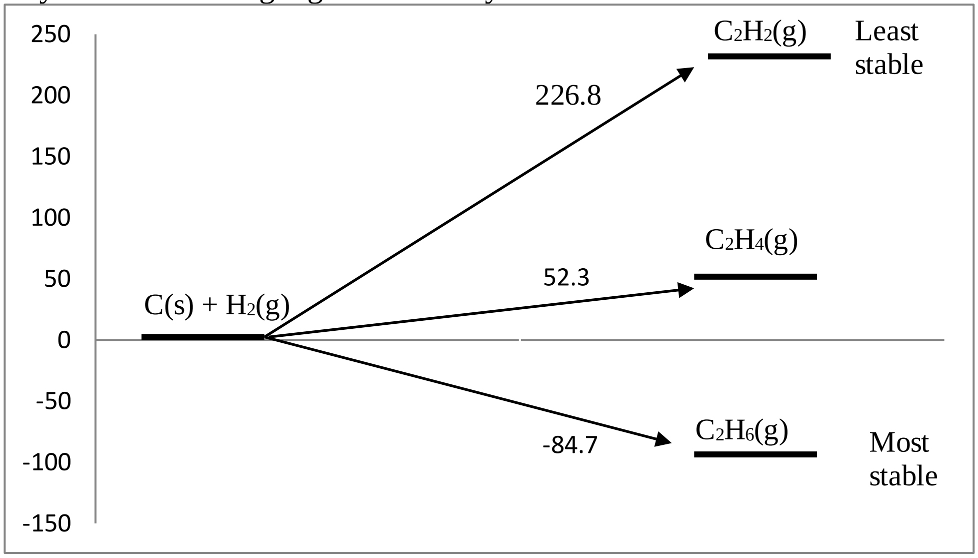
$$2C(s) + H_2(g) \longrightarrow C_2H_2(g) \qquad \Delta H_f^\circ(C_2H_2,g) = +226.8\ \text{kJ mol}^{-1},$$

$$2C(s) + 2H_2(g) \longrightarrow C_2H_4(g) \qquad \Delta H_f^\circ(C_2H_4,g) = +52.3\ \text{kJ mol}^{-1}$$

$$2C(s) + 3H_2(g) \longrightarrow C_2H_6(g) \qquad \Delta H_f^\circ(C_2H_6,g) = -84.7\ \text{kJ mol}^{-1}.$$

All three compounds are formed from elemental carbon and hydrogen. Therefore the values of ΔH_f° 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:

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 ΔH˚ for the reduction of FeO(s) to Fe(s) by CO(g), given that

$Fe_2O_3(s) + CO(g) \longrightarrow 2FeO(s) + CO_2(g)$ $\qquad \Delta H^\circ = +38$ kJ

$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$ $\qquad \Delta H^\circ = -28$ kJ

3. It has been proposed that the following reaction might occur in the stratosphere:

$HO(g) + Cl_2(g) \longrightarrow HOCl(g) + Cl(g)$

Calculate ΔH˚ for this reaction from the following data:

$Cl_2(g) \longrightarrow 2Cl(g)$ $\qquad \Delta H^\circ = 242$ kJ

$H_2O_2(g) \longrightarrow 2HO(g)$ $\qquad \Delta H^\circ = 134$ kJ

$H_2O_2(g) + 2Cl(g) \longrightarrow 2HOCl(g)$ $\qquad \Delta H^\circ = -209$ kJ

4. Calculate ΔH_f° for $N_2O_4(g)$ from the following data:

$N_2(g) + O_2(g) \longrightarrow 2NO(g)$ $\qquad \Delta H^\circ = 180.6$ kJ

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ $\qquad \Delta H^\circ = -114.2$ kJ

$2NO_2(g) \longrightarrow N_2O_4(g)$ $\qquad \Delta H^\circ = -58.0$ kJ

5. For $H_2(g)$, $N_2(g)$, $O_2(g)$, $F_2(g)$, and $Cl_2(g)$, but not for $Br_2(g)$ and $I_2(g)$, the standard enthalpies of formation are 0 kJ mol^{-1}. Explain why. In what physical states are the standard enthalpies of formation of bromine and iodine 0 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 102**) we have seen that the formation reaction of water is an exothermic reaction:

$$2H_2\ (g) + O_2\ (g) \rightleftharpoons 2H_2O\ (g) \qquad \Delta H^\circ = -\ 482.0\ \text{kJ}$$

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:

$$H_2O\ (l) \rightarrow H_2O\ (g) \qquad \Delta H^\circ = 44.0\ \text{kJ mol}^{-1}$$

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°, 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, JK^{-1} mol^{-1}. Note that unlike enthalpy values, entropy values are normally given in joules, not kilojoules.

The values of S° 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 ΔG 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, ΔG°,** for any reaction, from the **standard free energies of formation, ΔG_f°,** of the reactants and products.

$$\Delta G^\circ = \text{total } \Delta G_f^\circ{}_{\text{products}} - \text{total } \Delta G_f^\circ{}_{\text{reactants}}$$

ΔG_f° of the elements in their standard states are taken as zero, as for ΔH_f° 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 ΔG, 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 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 ΔG, or the reaction quotient (Q) and the equilibrium constant (K).

Question 106.

A reaction vessel contains 10 atm N_2, 10 atm H_2, and 1 atm NH_3. Predict the direction of the reaction at 298 K given that $K_p = 5.68 \times 10^5$ atm^{-2}. K_p is the equilibrium constant when partial pressures (not concentrations) are used in the expression.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

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.

$$Q = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3} = \frac{1^2}{10 \times 10^3} = 1 \times 10^{-4}$$

Since Q << K_p, we predict that the equilibrium will shift to the reactants side. We can also calculate

$$\Delta G = RT \ln(\frac{Q}{K}) = (8.314\ JK^{-1})(298K)(\ln\frac{1 \times 10^{-4}}{5.68 \times 10^5})$$

$$= (8.314\ JK^{-1})(298K)(-22.5) = -55719\ J = -60 kJ$$

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 (ΔH), entropy change (ΔS), and Gibbs free energy change (ΔG). For most people the concept of enthalpy change is not so hard to grasp, as most of the time we can think of ΔH in terms of heat released or taken in by a system.

What escape our common sense are the concepts of ΔG and ΔS. 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,

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta G^\circ = -2870 \text{ kJ} = -686 \text{ kcal}$$

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, ΔG 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 ΔG**.**

Question 107.

How much work is needed to decompose 1 mol of water at 298 K and 1 atm? Given that

$$2H_2O\ (l) \rightleftharpoons 2H_2\ (g) + O_2\ (g) \qquad \Delta G^\circ = 948 \text{ kJ}$$

Answer:

The free energy change given for the above reaction ($\Delta G^\circ = 948$ 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 ΔG is a state function just like ΔH, we can apply Hess's Law to obtain $\Delta G_{overall}$ for an overall reaction in the same way as we find $\Delta H_{overall}$.

When we deliberately combine two or more reactions to obtain a $\Delta G_{overall}$ 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 ΔG** (so that $\Delta G_{overall} < 0$). 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 108.

At body temperature (37 ˚C), the hydrolysis of ATP occurs as follows, to produce ADP.

$$\text{ATP} + \text{H}_2\text{O} \longrightarrow \text{ADP} + \text{H}_2\text{PO}_4^- \qquad \Delta G^\circ = -30 \text{ kJ}$$

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

$$\text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g) \longrightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \qquad \Delta G^\circ = -2870 \text{ kJ}$$

<u>**Answer:**</u>

To convert ADP back to ATP, the reaction is

$$\text{ADP} + \text{H}_2\text{PO}_4^- \longrightarrow \text{ATP} + \text{H}_2\text{O} \qquad \Delta G^\circ = +30 \text{ kJ}$$

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 (ΔG), 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.

$$1\ F = (6.0221 \times 10^{23} \text{ electrons mol}^{-1})(1.6022 \times 10^{-19} \text{ coulomb electron}^{-1}) = 96485 \text{ C mol}^{-1}$$

$$\text{or} \qquad = 96485 \text{ J/(V mol)}$$

Question 109.

Calculate ΔG° and K to find out if $Fe^{2+}(aq)$ can be spontaneously oxidized by the oxygen in air? Given that for oxygen $E^{\circ}_{red} = 1.23$ V and for Fe^{3+} $E^{\circ}_{red} = 0.77$ V.

Answer:

The reaction in question is

$$Fe^{2+}(aq) + O_2\,(g) \rightarrow H_2O(l) \quad + \quad Fe^{3+}(aq)$$

After balancing both charges and atoms, the reaction is

$$4Fe^{2+}(aq) + O_2\,(g) \ + \ 4H^{+}(aq) \rightarrow 2H_2O(l) \quad + \quad 4Fe^{3+}(aq)$$

For this reaction, the half reactions are:

Oxidation half: $4Fe^{2+}(aq) \rightarrow 4Fe^{3+}(aq) + 4e$ $\qquad E^{\circ}_{ox} = - E^{\circ}_{red} = - 0.77$ V

Reduction half: $O_2\,(g) \ + \ 4H^{+}(aq) + 4e \rightarrow 2H_2O(l)$ $\qquad E^{\circ}_{red} = 1.23$ V

$$E^{\circ}_{cell} = E^{\circ}_{ox} + E^{\circ}_{red} = -0.77 + 1.23 = 0.46 \text{ V}$$

The positive cell potential indicates that the reaction in question is a spontaneous reaction.

This can be confirmed by calculating ΔG°, assuming that all substances are in their standard states,

$$\Delta G^\circ = - n\,F\,E^\circ_{cell} = - (4\ \cancel{\text{mol}})(96485\ \cancel{\text{C}}\ \cancel{\text{mol}^{-1}})(0.46\ \text{J}\ \cancel{\text{C}^{-1}}) = -177532\ \text{J} = -180\ \text{kJ}$$

The large negative value of ΔG° indicates that the reaction is spontaneous from left to right.

Since $\Delta G^\circ = - n\,F\,E^\circ_{cell} = - RT \ln K$

We have

$$\ln K = -\frac{\Delta G^\circ}{RT} = -\frac{-180\,000\ \cancel{J\ mol^{-1}}}{(8.31\ \cancel{J\ mol^{-1} K^{-1}})(298\cancel{K})} = 73$$

$$K = e^{-\frac{\Delta G^\circ}{RT}} = 5 \times 10^{31}$$

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°.

Since R and F are constants, if we let T = 298 K (25 ˚C), we can simplify the Nernst equation as follows:

$$E_{cell} = E^\circ_{cell} - \frac{(8.31\ \cancel{J\ mol^{-1} K^{-1}})(298\cancel{K})}{n(96485\ \cancel{\text{C}}\ \cancel{\text{mol}^{-1}})} \ln Q = E^\circ_{cell} - \frac{0.0257\ JC^{-1}}{n} \ln Q$$

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{0.0257}{n} \ln Q \qquad \text{(at 25 ˚C)}}$$

Question 110.

At 25 ˚C, a zinc-copper cell started to operate with $[Zn^{2+}] = [Cu^{2+}] = 1.00$ M. After a certain time the concentrations had changed so that $[Zn^{2+}] = 1.90$ M and $[Cu^{2+}] = 0.10$ M. Calculate the cell potential at these new concentrations. Given that $E^\circ_{cell} = 1.10$ V.

Answer:

The overall reaction for the zinc-copper cell is

$$Cu^{2+} + Zn(s) \rightarrow Zn^{2+} + Cu(s) \qquad E^{\circ}_{cell} = 1.10\ V$$

For this reaction $n = 2$ and

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$ (remember that solids are not included in the expression of Q)

Thus

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0257}{n} \ln Q = 1.10 - \frac{0.0257}{2} \ln \frac{1.9}{0.1} = 1.10 - 0.038 = 1.06\ V$$

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}, ΔG, 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}, ΔG, reaction quotient Q and equilibrium constant K?

6. Give the Nernst equation at 25 ˚C.