Chapter 1: Chemistry and Measurement

Chemistry (noun): *a science studying the composition, characteristics, properties, and transformations of all matter in the known universe*.

Most modern textbooks start their coverage of chemistry with a discussion of why chemistry is so important to modern life, how it is relevant, why it is the "central science", blah, blah, blah.

Here is the truth; chemistry is important ***to you*** because a group of professionals decided that you must study chemistry in order to earn the degree in your major, or to gain admission to a particular kind of professional school. Whether you agree with their decision or not is irrelevant: you have chosen your major, and your major requires you to study chemistry.

If you don't want to study chemistry, then choose a different major. You don't have to be a chemist, (or a biologist, or a physician, or whatever) in order to be happy and successful. You won't hurt my feelings if you choose to be an artist or a business executive. I would prefer you to be a happy and successful business executive, and not know any chemistry at all, than to have you study a subject you detest. Just don't expect me to justify to you why you should study chemistry; I don't owe you a justification, and neither does science in general nor chemistry in particular.

The above definition of chemistry says it all: all matter, anything you can touch or that can touch you, is within the scope of chemistry. Any type or kind of physical substance you can name or describe is subject to the laws of chemistry.

Normally, the next topic would be a lengthy discussion of the scientific method, hypotheses, theories, laws, and so on. I'm not going to indulge in this waste of paper; instead I'll give you two relatively simple definitions and consider this topic finished.

Theory (noun): *a detailed and elaborate explanation for a set of apparently unrelated facts or observations*.

Scientific law (noun): *a principle or pattern observed in nature, and commonly expressed mathematically*.

An example of a scientific law is the ***law of conservation of mass,*** which tells us that, in a closed system, the total mass is constant. This law is expressed mathematically as:

$$mass_{(initial,total)} = mass_{(final,total)}$$

An example of a theory is ***Atomic theory***, which tells us that all of the different types of matter present in nature are explained as the combination of small particles of individual elements, called ***atoms***. These combinations occur in specific ratios: 1 atom of oxygen for 2 atoms of hydrogen to produce water. Atoms are not permanently changed when they are combined, although the properties of the matter produced by the atoms may be very different from the properties of the original atoms.

Scientific laws and scientific theories are different kinds of knowledge. They are **never** interconverted, and a law is **NOT** a theory that has been "promoted" to a higher level, despite what non-science educated people may believe to the contrary.

Classification of matter

There are three general classes of matter distinguished by their bulk physical properties:

Solid – has a fixed shape, fixed volume, and fixed mass.

Liquid - has no fixed shape, but has fixed volume, and fixed mass.

Gas – has no fixed shape, and no fixed volume, but has fixed mass.

Sometimes the word ***vapor*** is used as a synonym for gas. Sometimes people talk about a fourth phase of matter – ***plasma***. Plasma is an electrically charged gas. While it has many of the properties of ordinary gas, the electric charge gives the plasma some unique properties. Nevertheless, we generally ignore plasmas in introductory chemistry courses.

There are many other ways to organize and classify matter. One important organization is based on the composition of matter.

Element – any substance that can't be broken down by chemical processes into two or more simpler substances. There are currently 114 elements on the periodic table. Each element has a unique **atomic number**, and a unique chemical symbol. The atomic number tells us the number of protons present in the **nucleus** (center) of an atom of the element. The tiniest individual particle of an element, having the same chemical properties as the bulk element, is called an ***atom***. Combining individual atoms of these elements in specific proportions produces all other types of matter.

Compound – a substance composed of two or more elements, chemically combined. For the time being, we won't worry about how atoms "chemically combine". For our purposes, a compound has a fixed and definite ratio of atoms of individual elements, and this ratio is shown in the substances ***chemical formula***. Here are some chemical formulas for ordinary substances:

Water – H_2O	Sugar – $C_6H_{12}O_6$
Table salt – NaCl	Ammonia – NH_3

In all cases, the chemical formulas list the specific elements making up the substance. The subscripted numbers following the element symbols indicate the number of atoms of that element present in one ***molecule*** of the compound. In water, there are 2 hydrogen atoms and 1 oxygen atom combined together to make a water molecule. In sugar, there are 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms combined together to make a sugar molecule.

A molecule is a particle made up of individual atoms, chemically combined, functioning as a whole, independent unit of matter. A molecule can be made from atoms of one element (not particularly common) or from atoms of different elements (very common).

Compounds follow the ***law of definite proportions*** (also known as the ***law of constant composition***): a pure compound has a fixed and definite ratio, by weight, of individual elements, regardless of the source. Water is 88.81% oxygen by weight, and 11.19% hydrogen by weight. It doesn't matter if the water came from rain, snow, an iceberg, sweat, or from outer space: all water has the same composition by weight.

Elements and compounds are examples of pure matter. If two or more kinds of pure matter are physically combined, then we have a ***mixture.*** There are two general types of mixtures: ***homogeneous*** and ***heterogeneous.*** If a mixture has a single phase, and all substances are uniformly distributed throughout the mixture, then the mixture is called homogeneous. Southern style sweet tea, wine, mayonnaise, white gold, and vanilla ice cream are examples of homogenous mixtures.

If the mixture has two or more phases, and the substances are not uniformly distributed throughout the mixture, then the mixture is heterogeneous. Vegetable soup, Italian salad dressing, rice pudding, and chocolate chip cookies are examples of heterogeneous mixtures.

Figure 1.1 summarizes the classification of matter based on its composition.

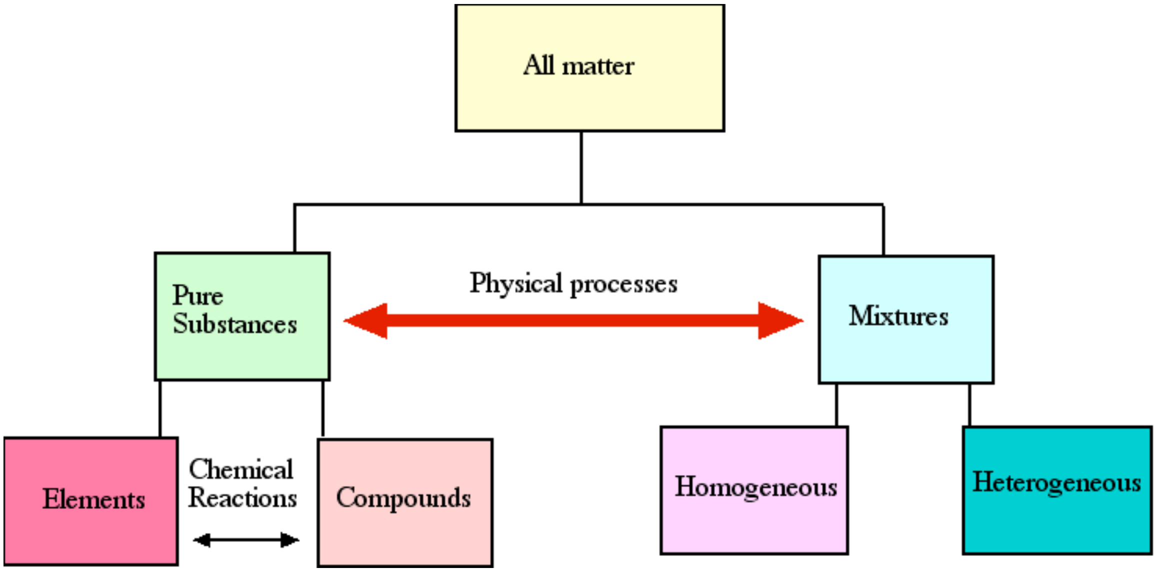


Figure 1.1. Classification of matter based on composition.

Measurements and units

Chemistry is measurement intensive, and the measuring system used by all chemists is the metric system.

It is hardly believable that anyone studying freshman chemistry has not been exposed to the metric system in elementary or high school courses. I am not going to waste time with a long description of the metric system, nor am I going to waste time covering metric-English conversions. You will become comfortable and familiar with the metric system by using the metric system, just as you became comfortable and familiar with the English measuring system by using it.

Scientists use the metric system for two reasons; it is simple and easy to use.

There are seven fundamental units used to measure basic properties. These units are independent from each other, and all other measurement units are derived from these fundamental units. Table 1.1 lists the fundamental units.

Basic Property	Metric Unit
Length	meter (m)
Mass	kilogram (kg)
Time	second (s)
Temperature	kelvin (K)
Electric current	ampere (A)
Amount of substance	mole (mol)
Luminous intensity	candela (cd)

Table 1.1. Fundamental metric units and the properties they measure.

You probably won't use electric current and luminous intensity in general chemistry, and will only rarely use time. The other four properties (length, mass, temperature, amount of substance) are used regularly.

Every other unit is derived from the base units and appropriate mathematics. One unit that is commonly used, but isn't fundamental, is a unit for volume. Consider the box shown below (Figure 1.2.). If we want to find the volume of this box, we multiply the width (W) times the length (L) times the height (H) to get the volume: V = L x W x H. The volume unit would be cubic units of distance: if the length, width, and height were measured in meters, then the volume unit would be meter x meter x meter = meter^3. Volume is a *derived unit*, and you will encounter many other derived units as you progress through this course.

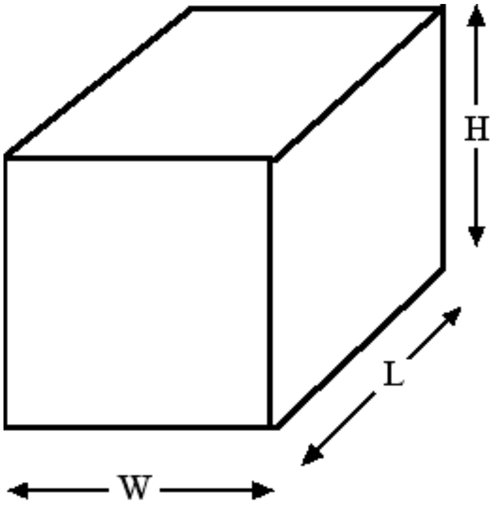


Figure 1.2. A box.

In general, volumes of m^3 are inconveniently large. Instead we use a smaller volume unit, the liter (L). One liter is equal to 1000 cm^3 (cubic centimeter) or 1000 mL (milliliter).

All measured quantities must have the unit included with the measured value. Saying that something is "3.47" is not informative, but saying that something is "3.47 meters" gives me a great deal of information. The unit tells me that the basic property being measured is length, that the metric system is being used, and that the measurement was made to the nearest centimeter (1 cm = 0.01m). Most students develop the habit of dropping off units, and in response most teachers develop the habit of subtracting points from test answers that don't have units.

When calculations are made using base metric units, we commonly derive units that are simple combinations of the base units. For example, if we want a unit to express the idea of *speed* (the distance traveled per unit of time), the unit is meters/second (m/s), where the diagonal line indicates a division. An object traveling 35 meters in 12 seconds is travelling 35/12 = 2.92 m/s.

You might also see this unit in a more "traditional" fraction format such as $\frac{m}{s}$.

Occasionally, a "simpler" metric unit is substituted for a combination of base units. The metric unit for energy is the joule (J), with 1 J equal to 1 $kg\text{-}m^2/s^2$. (The dash "-" in this unit does NOT indicate subtraction. It simply separates one metric unit from another for clarity.)

All measuring systems must be able to handle values ranging from the very small to the very large. The metric system accomplishes this using a set of constant value prefixes to indicate how the units have been increased/decreased in size. Table 1.2 lists these prefixes and their affects on the unit.

Notice that the abbreviation for the prefix is typically one letter (deka and micro are exceptions). Upper case letters are typically used for large units, while lower case letters are used for small units (kilo, hecto, and deka are exceptions). You must use the proper case for the proper unit: zeta (Z) can be easily misunderstood for zepto (z) if you aren't careful! The three most important prefixes are given in bold, and you should definitely learn these.

Prefix name	Affect on unit
yotta (Y)	unit x 10^{24}
zetta (Z)	unit x 10^{21}
exa (E)	unit x 10^{18}
peta (P)	unit x 10^{15}
tera (T)	unit x 10^{12} (1,000,000,000,000)
giga (G)	unit x 10^{9} (1,000,000,000)
mega (M)	unit x 10^{6} (1,000,000)
kilo (k)	**unit x 10^{3} (1000)**
hecto (h)	unit x 10^{2} (100)
deka (deca) (da)	unit x 10
deci (d)	unit ÷ 10
centi (c)	**unit ÷ 100**
milli (m)	**unit ÷ 10^{3} (1000)**
micro (μ)	unit ÷ 10^{6} (1,000,000)
nano (n)	unit ÷ 10^{9} (1,000,000,000)
pico (p)	unit ÷ 10^{12} (1,000,000,000,000)
femto (f)	unit ÷10^{15}
atto (a)	unit ÷10^{18}
zepto (z)	unit ÷10^{21}
yocto (y)	unit ÷10^{24}

Table 1.2. Metric prefixes and the affect on the unit.

Significant figures

The proper use of significant figures is always frustrating for students, so I have adopted a very simple approach: for all calculated values, show 3 non-zero digits (or 3 digits total if one is a "trapped" zero). Consider the following examples:

A. Your calculator shows a value of 19.35467669. Report this as 19.4.

B. A value of 527,988,365,216,363 should be reported as 5.28 x 10^{14}.

C. You calculate an answer of 0.309427867; report this as 0.309. In this case, we have a "trapped" zero separating the 3 and the 9.

D. Your calculator gives a value of 0.000000000224; report this as 2.24×10^{-10}.

E. You have a value of 100,000,000. This should be reported as 1.00×10^{8}.

The last example is a special case – just go with it.

I am not saying that the proper use of significant figures isn't important. It is very important in scientific and engineering calculations. However, it is not one of the most important things for you to learn in general chemistry. If I have to choose between fooling around for one lecture with significant figures, or spend that time teaching something more important, I know what I will choose.

Dimensional analysis and conversion factors

Dimensional analysis is a calculation procedure allowing us to express calculated values with proper units. You have already seen an example of how new units are produced in the previous section. Basically, units follow the same rules of arithmetic that numbers follow.

For addition and subtraction, the units of the quantities being added or subtracted **MUST BE IDENTICAL**. Subtracting 4 apples from 9 apples gives us 5 apples:

9 apples – 4 apples = 5 apples

Subtracting 4 apples from 9 oranges is a meaningless operation.

Sometimes we will be given values having identical units; other times we will have to change the units of one or more values before we can add or subtract. We can change units using ***conversion factors***. A conversion factor is the ratio of two equivalent quantities. For example, 1 kilogram is equal to 1000 grams. Whether we measure mass in kilograms, or in grams, we can change from grams to kilograms or kilograms to grams using the proper conversion factor.

From any pair of exactly equivalent quantities, two conversion factors can be written: 1-kilogram/1000 grams or 1000 grams/1-kilogram. Both of these conversion factors are equally correct. Which conversion factor do we use in a problem? The choice depends on the units of the quantity we want to convert. If I want to convert 7 kilograms into grams, the conversion factor I use is 1000 grams/1 kilogram. I perform the following calculation:

$$7 \text{ kilograms} \times \frac{1000 \text{ grams}}{1 \text{ kilogram}} = 7000 \text{ grams}$$

This example shows the most important idea in using conversion factors: select the conversion factor that has the desired units on top. Then, when you multiply your starting quantity by the conversion factor, the desired units will carry through the calculation.

Sometimes, several conversion factors must be used before the final result is determined. For example: I have 5.0 kilograms of iron. If I want to express this amount of iron in milligrams, I need to use two conversion factors: 1000 grams/1 kilogram and 1000-milligrams/1 gram. I then perform the following calculation:

$$5.0 \text{ kilograms x } \frac{1000 \text{ grams}}{1 \text{ kilogram}} \text{ x } \frac{1000 \text{ milligrams}}{1 \text{ gram}} = 5{,}000{,}000 \text{ milligrams } (5.00 \text{ x } 10^6 \text{ mg})$$

For multiplication and division, units multiply together or divide each other. We have seen that units of length are multiplied together in calculating volume. Units that aren't the same also multiply together; under some circumstances we can have units of kilograms multiplied by meters to get kilogram-meter (kg x m = kg-m). Notice again that the dash is a separator for clarity; it does NOT indicate that meters are being subtracted from kilograms. In division, units are written using a diagonal slash showing a ratio of units. Speed has units of meter/second (m/s) and is read as "meters per second". The joule (J) can also be written as kg-m^2/s^2, which is read as "kilogram-meter squared per second squared".

If identical units are divided, then the units disappear; they are said to "cancel out". This is exactly what happens with our conversion factors. Consider the earlier example of converting 7 kilograms into grams. The conversion factor we choose is 1000 grams/1 kilogram. The detailed calculation is shown below:

$$7 \text{ kilograms} \times \frac{1000 \text{ grams}}{1 \text{ kilogram}} = \frac{7000 \text{ kilogram-grams}}{1 \text{ kilogram}} = 7000 \text{ grams}$$

Notice that the intermediate unit is kilogram-grams/kilogram. Units of kilogram and gram were multiplied together to create a new unit (kilogram-grams), and then the new unit was divided by kilogram to produce grams.

Sometimes, division produces a pure, dimensionless number. These situations are rare and occur when the units for numerator and denominator are identical.

One special pair of conversions involves temperature scales. The metric temperature scale is Kelvin, and Kelvin temperatures are given as "______ Kelvin"; room temperature is 298 Kelvin. Strictly speaking, we don't us a degree symbol – we don't write 298 °K and we don't say "two hundred and ninety eight degrees Kelvin". However, if you should include the degree symbol, it's not really that big of a deal for now.

While Kelvin is the metric temperature scale, we almost never measure temperatures directly in Kelvin. Instead, we measure temperature using the Celcius temperature scale (°C) and convert to Kelvin whenever necessary. The conversion is:

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

Frequently, the decimal "0.15" is omitted, and $K = {}^{\circ}C + 273$ is used.

Another temperature conversion frequently encountered is converting from Celcius to Fahrenheit (°F). This conversion is:

$$\left({}^{\circ}C \times 1.8\right) + 32 = {}^{\circ}F$$

Water boils at 100 °C. The equivalent Fahrenheit temperature is:

$$(100\ {}^{\circ}C \text{ x } 1.8) + 32 = (180) + 32 = 212\ {}^{\circ}F$$

Other conversions will be introduced when necessary. For now, worry about metric conversion factors and temperature conversions.

Practice all of the homework problems over and over again, until you can perform the calculations rapidly and accurately.

Vocabulary. The following terms are defined and explained in the text. Make sure that you are familiar with the meanings of the terms as used in chemistry. Understand that you may have been given incomplete or mistaken meanings for these terms in earlier courses. The meanings given in the text are correct and proper.

Chemistry

Conversion factor

Liquid

Plasma

Nucleus

Molecule

Heterogeneous

Theory

Atom

Gas

Element

Compound

Mixture

Law of conservation of mass

Scientific law

Solid

Vapor

Atomic number

Chemical formula

Homogeneous

Law of definite proportions (Law of constant composition)

Homework: Use the dimensional analysis procedure to make the indicated calculations. Practice these problems over and over, until solving them is fast and correct.

1. How many grams of iron are in 3.75 kg of iron?
2. What is the distance between Nashville and Murfreesboro centimeters? The distance between Nashville and Murfreesboro is 48 km. Equivalent quantities: 1 meter = 100 centimeters; 1 kilometer = 1000 meters.
3. The density of mercury is 13.5 g/mL. What is the density of mercury in grams/cm^3? 1 cm^3 = 1 mL.
4. The wavelength of green light is 600 nm (nanometers). What is the wavelength of green light in meters? 1 meter = 1,000,000,000 nm.
5. How many milliliters of water are in 15 liters of water? Equivalent quantities: 1 liter = 1000 milliliters.
6. The density of gold is 19.3 g/cm^3. What volume does 500 grams of gold occupy?

7. Complete the following table by filling in appropriate values.

17.5 g	mg	kg
cm	0.339 m	mm
86,400 s	ks	Ms
fg	µg	37mg
570 mL	L(liters)	cL
57 K	mK	kK
mol	mmol	0.58 kmol
nm	55.9 cm	m
ks	ms	245 s
mg	5.99 kg	g

8. Density is the ratio of mass to volume, and is calculated from $density = \frac{mass}{volume}$. Complete the following table.

15.01 g	37.9 mL	g/mL
kg	19.0 cm^3	2.95 g/cm^3
21.5 g	mL	8.34 g/mL
0.995kg	1510 cm^3	g/cm^3
g	15.03 mL	1.95 g/mL
2100 g	m^3	133 kg/m^3
g	27.6 µL	15.3 mg/L
1175 mg	15 dL	g/L
g	1 m^3	1.225 kg/m^3
1.00 g	mL	1.116 g/mL

9. Make the indicated conversions between temperature scales.

158 K	^{o}C	^{o}F
K	77 ^{o}C	^{o}F
K	^{o}C	350 ^{o}F
25 K	^{o}C	^{o}F
K	212 ^{o}C	^{o}F
K	^{o}C	98 ^{o}F
610 K	^{o}C	^{o}F
K	55 ^{o}C	^{o}F
K	^{o}C	1100 ^{o}F
1200 K	^{o}C	^{o}F

10. State whether each of the following represents an atom or a molecule.

Au	CCl_4	H_2O	Na	Pb
NH_3	KCl	Xe	NaCl	H_2SO_4
Zn	N	Fl	CH_3OH	$Zn(OH)_2$
O_2	Fe	C_6H_6	NaH_2PO_4	Ca

11. For the following compounds, indicate which elements are present (by symbol, not name) in the compound and indicate how many atoms of each element are present in one molecule. For example: $NaNO_3$ has 1 Na, 1 N, and 3 O.

a. NaH_2PO_4

b. $Zn(OH)_2$

c. $Ni(NO_3)_2$

d. CCl_4

e. NH_3

f. H_2O

g. $NaCl$

h. H_2SO_4

i. CH_3OH

j. KCl

k. C_6H_6

Answers:

1. $3.75 \text{ kg} \times \dfrac{1000 \text{ g}}{1 \text{ kg}} = 3750 \text{ g (or } 3.75 \text{ x } 10^3 \text{ g)}$

2. $48 \text{ km x } \dfrac{1000 \text{ m}}{1 \text{ km}} \text{ x } \dfrac{100 \text{ cm}}{1 \text{ m}} = 4{,}800{,}000 \text{ cm (or } 4.80 \text{ x } 10^6 \text{m)}$

3. $13.5 \dfrac{\text{g}}{\text{mL}} \text{ x } 1 \dfrac{\text{mL}}{\text{cm}^3} = 13.5 \dfrac{\text{g}}{\text{cm}^3}$

4. $600 \text{ nm x } \dfrac{1 \text{ meter}}{1{,}000{,}000{,}000 \text{ nm}} = 6.00 \text{ x } 10^{-7} \text{m}$

5. $15 \text{ L x } \dfrac{1000 \text{ mL}}{\text{L}} = 15{,}000 \text{ mL (or } 1.5 \text{ x } 10^4 \text{ mL)}$

6. $\dfrac{500 \text{ g}}{19.3 \text{ g/cm}^3} = 25.9 \text{ cm}^3$

7.

17.5 g	**17,500 mg**	**0.0175 kg**
33.9 cm	0.339 m	**339 mm**
86,400 s	**86.4 ks**	**0.0864 Ms**
3.7 x 10^{13} fg	**37,000 µg**	37 mg
570 mL	**0.570 L**	**57.0 cL**
57 K	**57,000 mK**	**0.057 kK**
580 mol	**580,000 mmol**	0.58 kmol
5.59 x 10^{8} nm	55.9 cm	**0.559 m**
0.245 ks	**245,000 ms**	245 s
5,990,000 mg	5.99 kg	**5,990 g**

8.

15.01 g	37.9 mL	**0.396 g/mL**
0.05605 kg	19.0 cm^3	2.95 g/cm^3
21.5 g	**2.58 mL**	8.34 g/mL
0.995kg	1510 cm^3	**0.659 g/cm^3**
29.3 g	15.03 mL	1.95 g/mL
2100 g	**0.0158 m^3**	133 kg/m^3
4.22 x 10^{-7} g	27.6 µL	15.3 mg/L
1175 mg	15 dL	**0.783 g/L**
1225 g	1 m^3	1.225 kg/m^3
1.00 g	**0.896 mL**	1.116 g/mL

9.

158 K	-115 °C	-175 °F
350 K	77 °C	171 °F
450 K	177 °C	350 °F
25 K	-248 °C	-414 °F
485 K	212 °C	414 °F
310 K	37 °C	98 °F
610 K	337 °C	639 °F
328 K	55 °C	131 °F
866 K	593 °C	1100 °F
1200 K	927 °C	1701 °F

10.

Au **Atom**	CCl_4 **Molecule**	H_2O **Molecule**	Na **Atom**	Pb **Atom**
NH_3 **Molecule**	KCl **Molecule**	Xe **Atom**	NaCl **Molecule**	H_2SO_4 **Molecule**
Zn **Atom**	N **Atom**	Fl **Atom**	CH_3OH **Molecule**	$Zn(OH)_2$ **Molecule**
O_2 **Molecule**	Fe **Atom**	C_6H_6 **Molecule**	NaH_2PO_4 **Molecule**	Ca **Atom**

11.

a.	NaH_2PO_4	**1 Na, 2 H, 1 P, 4 O**
b.	$Zn(OH)_2$	**1 Zn, 2 O, 2 H**
c.	$Ni(NO_3)_2$	**1 Ni, 2 N, 6 O**
d.	CCl_4	**1 C, 4 Cl**
e.	NH_3	**1 N, 3 H**
f.	H_2O	**2 H, 1 O**
g.	NaCl	**1 Na, 1 Cl**
h.	H_2SO_4	**2 H, 1 S, 4 O**
i.	CH_3OH	**1 C, 4 H, 1 O**
j.	KCl	**1 K, 1 Cl**
k.	C_6H_6	**6 C, 6 H**

CHAPTER 2 Chemical Reactions

SECTION 2

Chemical Formulas and Equations

BEFORE YOU READ

After you read this section, you should be able to answer these questions:

- What are chemical formulas?
- What are chemical equations?
- How do you balance a chemical equation?

National Science Education Standards

PS 1b

What Is a Chemical Formula?

We use letters to form words. We put words together to form sentences. In the same way, scientists use symbols to form chemical formulas that describe different substances. They put chemical formulas together to show how chemical reactions happen.

Remember that substances are formed from different elements. Each element has its own chemical symbol. You can find the symbol for an element in the periodic table. Scientists combine the symbols for different elements when they write chemical formulas. A **chemical formula** shows which elements are found in a substance. It also shows how many atoms of each element are found in a molecule of the substance. ☑

In order to learn how chemical formulas work, let's look at an example. The chemical formula for water is H_2O. This formula means that a molecule of water is made of two hydrogen (H) atoms and one oxygen (O) atom.

The small 2 in the formula is a subscript. A *subscript* is a number that tells you how many atoms of an element are in a molecule. Subscripts are always written below and to the right of the symbol for an element. No subscript with an element's chemical symbol means the substance has only one atom of the element.

STUDY TIP

Ask Questions As you read this section, make a list of questions that you have. Talk about your questions with a small group. When you figure out the answers to your questions, write them in your notebook.

READING CHECK

1. Identify What are two things that are shown by a chemical formula?

____

____

____

____

Water

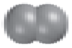
H_2O

Water A molecule of water contains 2 hydrogen (H) atoms and 1 oxygen (O) atom.

Oxygen

O_2

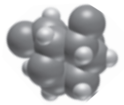
Oxygen A molecule of oxygen is made of 2 oxygen (O) atoms.



Glucose

$C_6H_{12}O_6$

Glucose A molecule of glucose cotains 6 carbon (C) atoms, 12 hydrogen (H) atoms and 6 oxygen (O) atoms.



Math Focus

2. Calculate How many oxygen atoms are in three molecules of water?

____

FORMULAS FOR COVALENT COMPOUNDS

In many cases, the name of a covalent compound tells you how to write its chemical formula. This is because the names of many covalent compounds use prefixes. Prefixes represent numbers. For example, the prefix di- means "two." The prefixes tell you how many atoms of an element are found in a substance. The table below shows the meanings of different prefixes.

Critical Thinking

3. Apply Concepts Write the formula for the covalent compound whose name is phosphorus trichloride.

____

Prefix	Number
mono-	1
di-	2
tri-	3
tetra-	4
penta-	5

Prefix	Number
hexa-	6
hepta-	7
octa-	8
nona-	9
deca-	10

Carbon dioxide

CO_2

The ***absence of a prefix*** indicates one carbon atom.

The prefix ***di-*** indicates two oxygen atoms.

Dinitrogen monoxide

N_2O

The prefix ***di-*** indicates two nitrogen atoms.

The prefix ***mono-*** indicates one oxygen atom.

FORMULAS FOR IONIC COMPOUNDS

If the name of a compound contains the name of a metal and a nonmetal, the compound is ionic. To write the name of an ionic compound, make sure the compound's charge is 0. Therefore, the formula must have subscripts that cause the charges of the ions to cancel. The figure below shows some examples of how to name ionic compounds.

Math Focus

4. Identify What is the charge on the Fe ion in the ionic compound $FeCl_3$? Hint: find the charge of a chloride ion.

____

Sodium chloride

$NaCl$

A sodium ion has a **1+ charge.**

A chloride ion has a **1– charge.**

One sodium ion and one chloride ion have an **overall charge of (1+) + (1–) = 0.**

Magnesium chloride

$MgCl_2$

A magnesium ion has a **2+ charge.**

A chloride ion has a **1– charge.**

One magnesium ion and two chloride ions have an **overall charge of (2+) + 2(1–) = 0.**

How Are Chemical Formulas Used to Write Chemical Equations?

Scientists use chemical equations to describe reactions. A **chemical equation** uses chemical symbols and formulas as a short way to show what happens in a chemical reaction. A chemical equation shows that atoms are only rearranged in a chemical reaction. No atoms are gained or lost in a chemical reaction. ☑

The starting materials in a chemical reaction are the **reactants**. The substances that form during the reaction are the **products**. In a chemical equation, the reactants and products are written using chemical formulas. Scientists use a plus sign to separate the formulas of two or more reactants or products. An arrow points from the formulas of the reactants to the formulas of the products.

READING CHECK

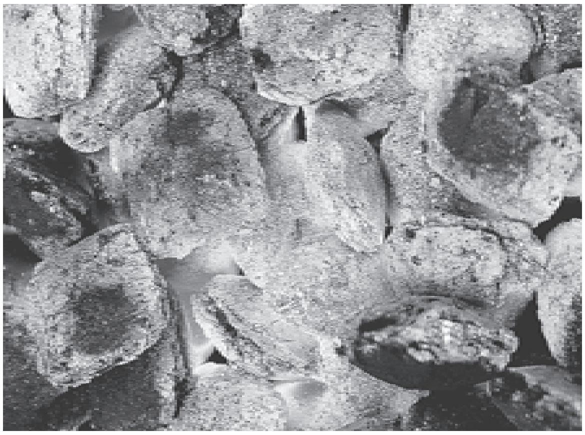
5. Define What is a chemical equation?

____

____

____

____



The formulas of the reactants are written before the arrow.

The formulas of the products are written after the arrow.

Carbon is the main element in charcoal. When charcoal burns, it reacts with oxygen in the air. The reaction produces heat, light, and carbon dioxide.

$$C + O_2 \rightarrow CO_2$$

A **plus sign** separates the formulas of two or more reactants or the formulas of two or more products.

The **arrow,** also called the *yields sign,* separates the formulas of the reactants from the formulas of the products.

TAKE A LOOK

6. Identify List the reactants and the products of the reaction in the figure. Use chemical symbols and chemical formulas in your answer.

reactants: ____________

products: ____________

CHECKING SYMBOLS

When you write a chemical formula, it is important that you check to make sure that it is correct. If you use the wrong formula or symbol in an equation, the equation will not describe the correct reaction. Even a small mistake can make a big difference. ☑

As an example, consider the three formulas Co, CO, and CO_2. These formulas look very similar. However, the substances they represent are very different. Co is the symbol for the element cobalt, a hard, bluish-grey metal. CO is the formula for carbon monoxide, a colorless, poisonous gas. CO_2 is the formula for carbon dioxide, a colorless gas that living things give off when they breathe.

READING CHECK

7. Explain Why is it important to check to make sure that your chemical formulas are correct?

____

____

____

____

____

Examples of Similar Symbols and Formulas

CO_2
The chemical formula for the compound **carbon dioxide** is CO_2. Carbon dioxide is a colorless, odorless gas that you exhale.

CO
The chemical formula for the compound **carbon monoxide** is CO. Carbon monoxide is a colorless, odorless, and poisonous gas.

Co
The chemical symbol for the element **cobalt** is Co. Cobalt is a hard, bluish gray metal.

CONSERVING MASS

The **law of conservation of mass** states that mass cannot be lost or gained during a chemical reaction. The total mass of the reactants in a chemical reaction is the same as the total mass of the products. You can use this law to help you figure out how to write a chemical equation.

During a chemical reaction, atoms are not lost or gained. Every atom in the reactants becomes part of the products. Therefore, in a chemical equation, the numbers and kinds of atoms in the reactants and products must be equal. In other words, the chemical equation must be balanced.

STANDARDS CHECK

PS 1b Substances react chemically in characteristic ways with other substances to form new substances (compounds) with different characteristic properties. In chemical reactions, the total mass is conserved. Substances often are placed in categories or groups if they react in similar ways; metals is an example of such a group.

Word Help: chemical
of or having to do with the properties or actions of substances

8. Explain How does a balanced chemical equation show the law of conservation of mass?

____

____

____

____

____

HOW TO BALANCE A CHEMICAL EQUATION

To balance an equation, you must use coefficients. A *coefficient* is a number that is placed in front of a chemical formula. For example, 2CO represents two carbon monoxide molecules. The number 2 is the coefficient. ☑

For an equation to be balanced, all atoms must be counted. So you must multiply the subscript for each element in a formula by the formula's coefficient. For example, $2H_2O$ contains a total of four hydrogen atoms and two oxygen atoms. Only coefficients, not subscripts, may be changed when balancing equations. The figure below shows you how to use coefficients to balance an equation. ☑

READING CHECK

9. Describe What is a coefficient?

____

____

____

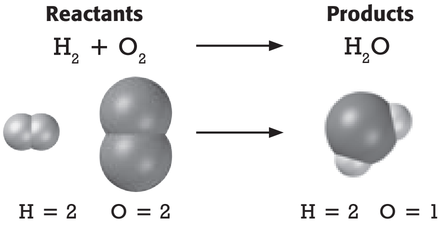
READING CHECK

10. Identify What can't be changed when balancing a chemical equation?

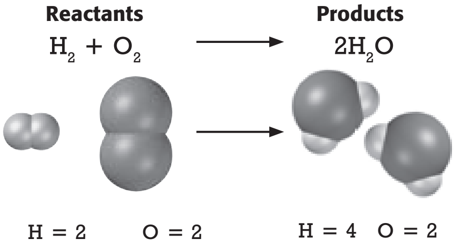
____

Follow these steps to write a balanced equation for $H_2 + O_2 \longrightarrow H_2O$.

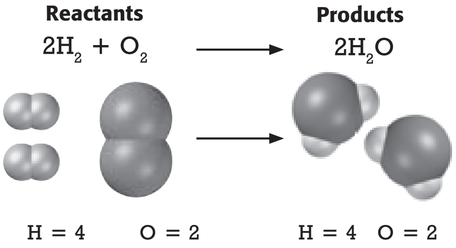
❶ **Count the atoms** of each element in the reactants and the products. Here, you can see that there are more oxygen atoms in the reactants than in the products. Therefore, the chemical equation is not balanced.



❷ **Add coefficients to balance the atoms** of oxygen. There are two atoms of oxygen in the reactants. Place the coefficient 2 in front of the products to give two atoms of oxygen in the products. Then, count the atoms again. Now, the hydrogen atoms are not balanced.



❸ **Add coefficients to balance the atoms** of hydrogen. Add the coefficient 2 to the H_2 reactant to give four atoms of hydrogen in the reactants. Then, count the atoms again to double-check your work.



Math Focus

11. Applying Concepts Balance the equation:

___Na + ___$Cl_2 \longrightarrow$ ___NaCl by putting coefficients where needed.

Name ______________________ Class ____________ Date ____________

Section 2 Review

NSES PS 1b

SECTION VOCABULARY

chemical equation a representation of a chemical reaction that uses symbols to show the relationship between the reactants and the products

chemical formula a combination of chemical symbols and numbers to represent a substance

law of conservation of mass the law that states the mass cannot be created or destroyed in ordinary chemical and physical changes

product a substance that forms in a chemical reaction

reactant a substance or molecule that participates in a chemical reaction

1. Compare How is a chemical equation different from a chemical formula?

____

____

2. Identify Fill in the blank spaces in the table.

Chemical equation	**Number of atoms in the reactants**	**Number of atoms in the products**	**Is the equation balanced?**
$Na + Cl_2 \rightarrow NaCl$	Na = Cl =	Na = Cl =	
$HCl + NaOH \rightarrow NaCl + H_2O$	H = Cl = Na = O =	H = Cl = Na = O =	
$2Sb + 3I_2 \rightarrow 2SbI_3$	Sb = I =	Sb = I =	

3. Describe Give the names of the covalent compounds listed below.

SiO_2 ____

SbF_3 ____

4. Explain Why can't you change the subscripts in a formula in order to balance a chemical equation?

____

____

5. Applying Concepts Balance the equation:

____Mg + ____$N_2 \rightarrow$ ____Mg_3N_2 by putting coefficients where needed.

4. The properties of oxygen change; water does not have the same properties as oxygen.
5. Metals can conduct electricity, can be stretched into wires, and can be hammered into thin sheets.

Chapter 2 Chemical Reactions

SECTION 1 FORMING NEW SUBSTANCES

1. One or more substances break apart or combine to form one or more new substances.
2. A solid forms in a solution.
3. No, some physical changes, like boiling, may produce a gas.
4. The chemical properties of the new substances are different from those of the original substances.
5. Some bonds are broken and new bonds form.
6. The bonds in the hydrogen and chlorine molecules are broken. The bonds in the hydrogen chloride molecule form.

Review

1. New substances are formed during a chemical reaction. Formation of a precipitate is one sign that a new substance has been formed.
2.

Observed during a chemical reaction	Sign of a chemical reaction
precipitate in a solution	solid formation
heat given off	energy change
green gas	gas formation
colorless solution turned blue	color change

3. chemical bond
4. When water boils, a new substance is not formed. The water vapor that forms during boiling can condense into liquid water.
5. The chemical properties of the material in the beaker are different from those of the original substances. This shows that a chemical reaction must have occurred.

SECTION 2 CHEMICAL FORMULAS AND EQUATIONS

1. the elements found in a substance and how many atoms of each element are in a molecule
2. three
3. PCl_3
4. 3+
5. a short way to show what happens in a chemical reaction using symbols and formulas
6. Reactants: C, O_2

   Products: CO_2
7. If you use the wrong chemical formula, a chemical equation will not describe the reaction you are trying to describe.
8. A chemical equation shows that no atoms are lost or gained during a chemical reaction.
9. a number that is placed in front of a chemical formula
10. subscripts
11. $2Na + Cl_2 \longrightarrow 2NaCl$

Review

1. A chemical formula represents a substance. A chemical equation represents a chemical reaction.
2.

Chemical equation	Number of atoms in the reactants	Number of atoms in the products	Is the equation balanced?
$Na + Cl_2 \longrightarrow NaCl$	Na = 1 Cl = 2	Na = 1 Cl = 1	no
$HCl + NaOH \longrightarrow NaCl + H_2O$	H = 2 Cl = 1 Na = 1 O = 1	H = 2 Cl = 1 Na = 1 O = 1	yes
$2Sb + 3I_2 \longrightarrow 2SbI_3$	Sb = 2 I = 6	Sb = 2 I = 6	yes

3. SiO_2: silicon dioxide

   SbF_3: antimony trifluoride
4. Changing the subscripts changes the substance in the chemical reaction. Therefore, if you change subscripts, you change the chemical reaction that you are describing.
5. $3Mg + N_2 \longrightarrow Mg_3N_2$

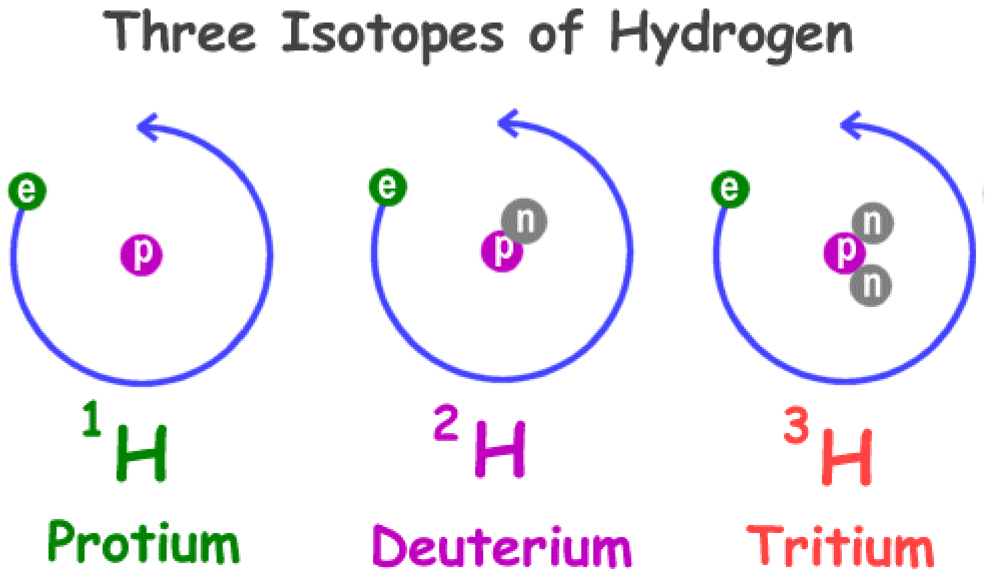
Isotopes

About Atoms and Elements

We learned in the atoms and elements sections that each element has its own unique atom which is made up of a specific number of protons. The number of protons determines the atomic number of the element. Each atom also has the same number of electrons as protons.

What is an isotope?

Isotopes are atoms that have the same number of protons and electrons, but a different number of neutrons. Changing the number of neutrons in an atom does not change the element. Atoms of elements with different numbers of neutrons are called "isotopes" of that element.



Naming Isotopes

Since neutrons have no electrical charge, changing the number of neutrons does not affect the chemistry of the element. It does, however, change the mass of the element. Isotopes are identified by their mass, which is the total number of protons and neutrons.

There are two ways that isotopes are generally written. They both use the mass of the atom where **mass = (number of protons) + (number of neutrons)**. The first way is to put the mass as a superscript before the symbol of the element:

- ^{4}He
- ^{14}C
- ^{235}U

The other way is to write out the element and write the mass after a dash next to the element's name:

- helium-4
- carbon-14
- uranium-238

Hydrogen

Hydrogen is the only element where the isotopes are given specific names. Common hydrogen, which has zero neutrons, is called protium. Hydrogen with one neutron is called deuterium and hydrogen with two neutrons is called tritium. See the picture at the top of the page.

How many isotopes can an element have?

All elements have a number of isotopes. Hydrogen has the fewest number of isotopes with only three. The elements with the most isotopes are cesium and xenon with 36 known isotopes.

Stable and Unstable Isotopes

Some isotopes are stable and some are unstable. When an isotope is unstable it will decay over time and eventually it will turn into another isotope or element. Unstable isotopes are considered radioactive. Most elements that are found in nature are made up of stable isotopes. The element with the most stable isotopes is tin which has ten different stable isotopes.

Interesting Facts about Isotopes

- Many elements only exist in an unstable or radioactive form.
- All non-natural or man-made elements are radioactive isotopes.
- Heavier isotopes tend to react more slowly than lighter isotopes of the same element.
- Deuterium (the hydrogen isotope with one neutron) can form water with oxygen. This is called "heavy water" as deuterium has twice the mass of normal hydrogen (protium).
- There are 254 known stable isotopes and 80 elements which have at least one stable isotope.
- Twenty-six elements only have one stable isotope. These elements are called monoisotopic.

Methods of Expressing Concentration

Solutions may be described as **single phase** systems composed of two or more chemical substances representing **homogeneous molecular dispersion.** In general, the components of a solution retain their individual identities. Thus, a solution is properly termed a homogeneous mixture on the basis of the variability of composition.

The properties of a solution are uniform throughout the mixture because the dispersion of the solute molecules in the solvent is on a molecular scale, making the molecules indistinguishable by usual observation procedures.

Colloidal Solutions in Contrast **true solutions** contain very small particles, but these are not of molecular dimensions and may be observed by various techniques.

I. Concentration Expressions

The concentration of solute in a solution may be expressed in many ways, depending upon the convenience to those concerned with its use. Chemists more frequently prefer to work with the number of moles or equivalents of a particular solute. These quantities are also of importance to pharmacists as will be seen in the use of milliequivalents per litre (mEq/Ltr) for electrolyte solutions.

Pharmacists will also use percentage concentrations or some ther expression of the constituents by parts. The commonly employed concentration expression are reviewed in the following on a **physical basis** (weight or volume).

Expression of Strengths

Percent Concentration : The term "Per cent" or more usually the symbol "%" is used with one of four different meanings in the expression of concentrations according to circumstances. In order that the meaning to be attached to the expression in each instance is clear, the following notation is used...

a) Percent w/w (%w/w) - (Percentage weight in weight) expresses the number of grams of solute in 100 gm of product. The concentrations of strong acids, as available commercially, are expressed in this way.

e.g. H_2SO_4 98.0% w/w; CH_3COOH 33% w/w etc.

Also expressing the percentage purity of the solid dosage forms such as tablets, capsules etc. as percent weight/weight (%w/w).

b) Percent w/v (%w/v) - (Percentage weight in volume) It expresses the number of grams of solute in 100 ml of product. (i.e. 100 ml of solution). This is a common way of specifying solution composition of mixtures of miscible liquids, or solids in liquids.

e.g. H_2O_2 solution 5-7% w/v; $BaCl_2$ solution 10% w/v etc.

c) Percent v/v (%v/v) - (Percentage volume in volume) It expresses the number of millilitres of solute in 100 ml of product.

e.g. Alcohol 95% v/v.

d) Percent v/w (%v/w) - (Percentage volume in weight) It expresses the number of millilitres of solute in 100 gm of product.

Usually the strength of solutions of solids in liquids are expressed as percentage weight in volume, of liquids as percentage volume in volume and of gases in liquids as percentage weight in weight.

e) Parts per million (ppm) - When the concentration of a solution is expressed as **parts per million (ppm),** it means **weight in weight ,** unless otherwise specified. **ppm-** the number of grams of solute contained in 10^6 gm of solution.
e.g. In the limit test of chloride 25 ppm of cl.

II. The Chemical methods of expressing concentration

The Chemical methods of expressing concentration are based upon chemical formula or combining power, **The word "Concentration" is frequently used as a general term referring to a quantity of substance in a defined volume of solution .** But for quantitative titrimetric analysis use is made of standard solutions in which the base unit of quantity employed is the **"mole".** This follows the definition given by the International Union of Pure and Applied Chemistry (IUPAC) .

Solution containing very small amounts of solute may be expressed is millimolar (mM) concentration, defined as the number of millimole/ml of solution.

$$(1 \text{ mM} = 1 \times 10^{-3} \text{ M})$$

1. Molarity (M) : The molarity of a solution expresses the number of moles (gram-molecular weights) of solute contained in1000 ml (1 Litre) of solution.

A solution containing 1 mole of solute in each litre of total solution is said to be a one molar (M) solution.

2. Molality (m) : The molality of a solution expresses as the number of moles of a solute contained in 1000 gm of a solvent.

This method of denoting concentration is used in many equations to express **thermodynamic properties** of solutions.

3. Normality (N) : The normality of a solution expresses the number of equivalents (gram-equivalent weight) of the solute in one litre of solution.

This is generally a much more useful expression since it is directly related to reactive concentrations of various species in solution.

4. Equivalent weight of Acid

Equivalent weight of the substance is that weight which contains 1 gm of replaceable hydrogen ion (1.008 gm).

5. Equivalent weight of Base

Equivalent weight of base is that weight which contains one gram of replaceable hydroxyl groups i.e., 17.008 gm of hydroxyl ion.

6. Saturated solution : A saturated solution is one which has dissolved all the solute it is capable of holding at a given temperature. The temperature is a very crucial aspect of saturated solutions, and unless otherwise specified, the temperature is assumed to be 25°C.
An example of a saturated solution is Boric acid solution used as an Eye wash. The concentration of this solution is near enough to saturation (4.5 – 5 %) that a drop to below usual temperature will cause the boric acid to crystallize from the solution. This represents a caution to its use in the eye. If crystals are present, the solution should be warmed to dissolve them.

7*. Formality (F) :* Formality may be defined as the number of gram formula weight (GFW) of the solute dissolved per litre of solution.

Formality (F) = GFW/Litres of solution

III. Solubilty Expressions

The solubility of a compound may be expressed in many ways. The official compendia have adopted a system of stating the amount of a particular solvent necessary to dissolve 1 gm of the substance in question at 25˚ C.

When special quantitative solubility tests are given in the compendia these solubilities can be used as a criterion for assessing the purity of the compound. Whenever the exact solubility of a pharmaceuticall important compound is not known or designated, the following descriptive terms can be used.

S.No.	**Descriptive Term**	**Approximate volume of solvent in millilitres per gram of solute.**
1	**Very Soluble**	**Less than 1**
2	**Freely Soluble**	**From 1 to 10**
3	**Soluble**	**From 10 to 30**
4	**Sparingly Soluble**	**From 30 to 100**
5	**Slightly Soluble**	**From 100 to 1000**
6	**Very Slightly Soluble**	**From 1000 to 10,000**
7	**Practically Insoluble, or Insoluble**	**More than 10,000**

1.1 Introduction to Stoichiometry

Lesson Objectives

The student will:

- explain the meaning of the term "stoichiometry."
- interpret chemical equations in terms of molecules, atoma, formula units, and moles.

Vocabulary

formula unit
one unit of the empirical formula of an ionic compound

stoichiometry
the calculation of quantitative relationships of the reactants and products in a balanced chemical equation

Introduction

You have learned that chemical equations provide us with information about the types and phases of particles that react to form products. Chemical equations also provide us with the relative number of particles and moles that react to form products. In this chapter, you will explore the quantitative relationships that exist between the reactants and products in a balanced equation. This is known as stoichiometry.

Stoichiometry involves calculating the quantities of reactants or products in a chemical reaction using the relationships found in the balanced chemical equation. The word stoichiometry actually comes from two Greek words: *stoikheion*, which means element, and *metron*, which means measure.

Molecules and Formula Units

Before proceeding, recall the major difference between molecules and formula units. The term "formula unit" is used specifically with ionic compounds and refers to the smallest unit of the ionic compound. For example, the formula for potassium chloride, KCl. One formula unit of potassium chloride contains one ion of potassium and one chloride ion. Recall from the chapter "Ionic Bonds and Formulas" that ionic compounds are made up of positive and negative ions held together by electrostatic attraction, or ionic bonds. When we write KCl, we are describing the simplest ratio of K^+ ions to Cl^- ions involved in a crystal of potassium chloride, not an actual molecule that exists by itself, but rather KCl exists as a repeating unit in a crystal lattice network.

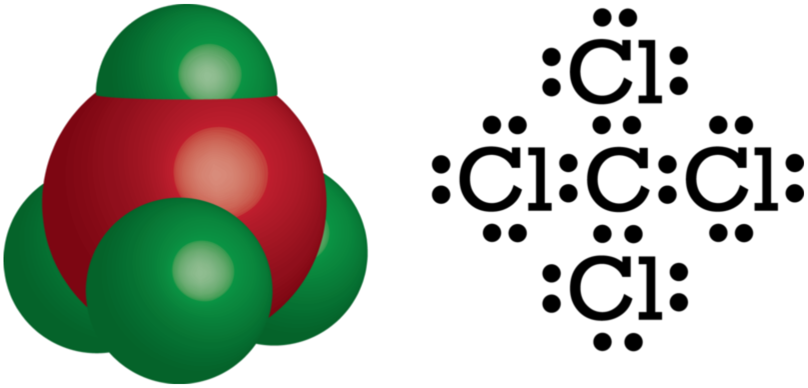
$$\mathrm{KCl} \rightarrow \mathrm{K}^+ + \mathrm{Cl}^-$$

Another example of an ionic compound is copper(II) chloride, $CuCl_2$. A formula unit of copper(II) chloride is composed of one ion of copper and two chloride ions. Again, one unit of $CuCl_2$ does not exist by itself. Instead, $CuCl_2$ is a crystalline structure that has a ratio of one copper ion to two chloride ions.

$$\mathrm{CuCl_2} \rightarrow \mathrm{Cu}^{2+} + 2\mathrm{Cl}^-$$

In other words, ionic compounds are not composed of molecules. Therefore, we use the term **formula unit** to represent one unit of an ionic compound.

Covalent compounds exist as discrete molecules where the atoms join together by sharing electrons. For example, one molecule of carbon tetrachloride, CCl_4, contains one carbon and four chlorine atoms, not ions, joined together by sharing of electrons. In the figure below, a space-filling model for CCl_4 is shown on the left, and the Lewis structure is shown on the right.



We call this a molecule since there is a separate entity consisting of one carbon atom and four chlorine atoms that acts independently from other units or molecules of CCl_4. Water, H_2O, is another example of a covalently bonded compound that exists as discrete molecules.

Interpreting Chemical Equations

Recall from the chapter "The Mole Concept" that a mole is a **count** equivalent to Avogadro's number of particles. How does the mole relate to the chemical equation? Consider the following reaction:

$$N_2O_3 + H_2O \rightarrow 2\ HNO_3$$

We have learned that the coefficients in a chemical equation tell us the relative amounts of each substance involved in the reaction. One way to describe the ratios involved in the reaction above would be, "One *molecule* of dinitrogen trioxide, N_2O_3, reacts with one *molecule* of water to yield two *molecules* of nitrous acid, HNO_3." However, because these are only ratios, this statement would be equally valid using units other than molecules such as a mole or a dozen. As a result, we could also say, "One *mole* of dinitrogen trioxide plus one *mole* of water yields two *moles* of nitrous acid."

We can use moles instead of molecules, because a mole is simply a count equal to Avogadro's number, just like a dozen is an amount equal to 12. It would ***not*** be correct to say that one gram of dinitrogen trioxide plus one gram of water yields two grams of nitrous acid.

Now consider this reaction:

$$2\ CuSO_4 + 4\ KI \rightarrow 2\ CuI + 4\ K_2SO_4 + I_2$$

Here, we can say, "Two moles of copper(II) sulfate react with four moles of potassium iodide, producing two moles of copper(I) iodide, four moles of potassium sulfate, and one mole of molecular iodine." Although we can refer to molecules of iodine, I_2, it is generally not correct to refer to molecules of something like KI. Because KI is an ionic substance that exists as crystal lattices instead of discrete molecules, formula unit is used instead. Often the distinction is not referred to in stoichiometry problems.

Example:

Indicate the ratio of compounds involved in the following balanced chemical equations. Describe the ratios in two ways: a) using the number of formula units or molecules and b) using the number of moles present.

a. $2\ C_2H_6 + 7\ O_2 \rightarrow 4\ CO_2 + 6\ H_2O$
b. $KBrO_3 + 6\ KI + 6\ HBr \rightarrow 7\ KBr + 3\ I_2 + 3\ H_2O$

Solution:

a. Two molecules of C_2H_6 plus seven molecules of O_2 yields four molecules of CO_2 plus six molecules of H_2O.
b. Two moles of C_2H_6 plus seven moles of O_2 yields four moles of CO_2 plus six moles of H_2O.

a. One formula unit of $KBrO_3$ plus six formula units of KI plus six molecules of HBr yields seven formula units of KBr plus three molecules of I_2 and three molecules of H_2O.
b. One mole of $KBrO_3$ plus six moles of KI plus six moles of HBr yields seven moles of KBr plus three moles of I_2 and three moles of H_2O.

Lesson Summary

- Stoichiometry is the calculation of the quantities of reactants or products in a chemical reaction using the relationships found in the balanced chemical equation.

Further Reading / Supplemental Links

This website contains various resources, including PowerPoint lectures, on many topics in chemistry, including one on stoichiometry.

- http://www.chalkbored.com/lessons/chemistry-11.htm

Review Questions

1. Distinguish between formula unit, molecule, and mole. Give examples in your answer.

1.2 Stoichiometric Calculations

Lesson Objectives

The student will:

- explain the necessity of balancing equations in order to determine the mole ratios.
- determine mole ratios in chemical equations.
- calculate the number of moles of any reactant or product from a balanced equation given the number of moles of one reactant or product.
- calculate the mass of any reactant or product from a balanced equation given the mass of one reactant or product.

Vocabulary

mole ratio
a quantitative relationship between two components of a chemical reaction, determined by the coefficients of the balanced equation

Introduction

Earlier, we explored mole relationships in balanced chemical equations. In this lesson, we will use the mole relationship as a conversion factor to calculate moles of product from a given number of moles of reactant, or the of moles of reactant from a given number of moles of product. This is called a "mole-mole" calculation. We will also perform "mass-mass" calculations, which allow you to determine the mass of reactant required to produce a given amount of product, or the mass of product you can obtain from a given mass of reactant.

Mole Ratios

A **mole ratio** is the relationship between two components of a chemical reaction. For instance, one way we could read the following reaction is that 2 moles of $H_{2(g)}$ react with 1 mole of $O_{2(g)}$ to produce 2 moles of $H_2O_{(l)}$.

$$2\ H_{2(g)} + O_{2(g)} \rightarrow 2\ H_2O_{(l)}$$

The mole ratio of $H_{2(g)}$ to $O_{2(g)}$ would be:

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

What is the ratio of hydrogen molecules to water molecules? By looking at the balanced chemical equation, we can see that the coefficient in front of the hydrogen is 2, while the coefficient in front of water is also 2. Therefore, the mole ratio can be written as:

$$\frac{2\text{ mol }H_2}{2\text{ mol }H_2O} \quad \text{or} \quad \frac{2\text{ mol }H_2O}{2\text{ mol }H_2}$$

Similarly, the ratio of oxygen molecules to water molecules would be:

$$\frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol O}_2} \quad \text{or} \quad \frac{1 \text{ mol O}_2}{2 \text{ mol H}_2\text{O}}$$

In the following example, let's find the mole ratios by first writing a balanced chemical equation from a "chemical sentence."

Example:

Four moles of solid aluminum are mixed with three moles of gaseous oxygen to produce two moles of solid aluminum oxide. What is the mole ratio of (1) aluminum to oxygen, (2) aluminum to aluminum oxide, and (3) oxygen to aluminum oxide?

Solution:

Balanced chemical equation: $4 \text{ Al}_{(s)} + 3 \text{ O}_{2(g)} \rightarrow 2 \text{ Al}_2\text{O}_{3(s)}$

a. mole ratio of aluminum to oxygen = $\frac{4 \text{ mol Al}}{3 \text{ mol O}_2}$ or $\frac{3 \text{ mol O}_2}{4 \text{ mol Al}}$
b. mole ratio of aluminum to aluminum oxide = $\frac{4 \text{ mol Al}}{2 \text{ mol Al}_2\text{O}_3}$ or $\frac{2 \text{ mol Al}_2\text{O}_3}{4 \text{ mol Al}}$
c. mole ratio of oxygen to aluminum oxide = $\frac{3 \text{ mol O}_2}{2 \text{ mol Al}_2\text{O}_3}$ or $\frac{2 \text{ mol Al}_2\text{O}_3}{3 \text{ mol O}_2}$

Example:

Write the balanced chemical equation for the reaction of solid calcium carbide (CaC_2) with water to form aqueous calcium hydroxide and acetylene (C_2H_2) gas. From the equation, find the mole ratios for (1) calcium carbide to water and (2) calcium carbide to calcium hydroxide.

Solution:

Balanced chemical equation: $\text{CaC}_{2(s)} + 2 \text{ H}_2\text{O}_{(l)} \rightarrow \text{Ca(OH)}_{2(aq)} + \text{C}_2\text{H}_{2(g)}$

a. mole ratio of calcium carbide to water = $\frac{1 \text{ mol CaC}_2}{2 \text{ mol H}_2\text{O}}$ or $\frac{2 \text{ mol H}_2O}{1 \text{ mol CaC}_2}$
b. mole ratio of calcium carbide to calcium hydroxide = $\frac{1 \text{ mol CaC}_2}{1 \text{ mol Ca(OH)}_2}$

The correct mole ratios of the reactants and products in a chemical equation are determined by the balanced equation. Therefore, the chemical equation must always be balanced before stoichiometric calculations are done. Looking at the unbalanced equation for the reaction of phosphorus trihydride with oxygen, it is difficult to guess the correct mole ratio of phosphorus trihydride to oxygen gas.

$$\text{PH}_{3(g)} + \text{O}_{2(g)} \rightarrow \text{P}_4\text{O}_{10(s)} + \text{H}_2\text{O}_{(g)}$$

Once the equation is balanced, however, the mole ratio of phophorus trihydride to oxygen gas is apparent.

Balanced chemical equation: $4 \text{ PH}_{3(g)} + 8 \text{ O}_{2(g)} \rightarrow \text{P}_4\text{O}_{10(s)} + 6 \text{ H}_2\text{O}_{(g)}$

The mole ratio of phophorus trihydride to oxygen gas, then, is: $\frac{4 \text{ mol PH}_3}{8 \text{ mol O}_2}$

Keep in mind that before any mathematical calculations are made relating to a chemical equation, the equation ***must*** be balanced.

Mole-Mole Calculations

In the chemistry lab, we rarely work with exactly one mole of a chemical. In order to determine the amount of reagent (reacting chemical) necessary or the amount of product expected for a given reaction, we need to do calculations using mole ratios.

Look at the following equation. If only 0.50 moles of magnesium hydroxide, $Mg(OH)_2$, are present, how many moles of phosphoric acid, H_3PO_4, would be required for the reaction?

$$2\ H_3PO_4 + 3\ Mg(OH)_2 \rightarrow Mg_3(PO_4)_2 + 6\ H_2O$$

Step 1: To determine the conversion factor, we want to convert from moles of $Mg(OH)_2$ to moles of H_3PO_4. Therefore, the conversion factor is:

$$\text{mole ratio} = \frac{2\ \text{mol}\ H_3PO_4}{3\ \text{mol}\ Mg(OH)_2}$$

Note that what we want to calculate is in the numerator, while what we know is in the denominator.

Step 2: Use the conversion factor to answer the question.

$$(0.50\ \text{mol}\ Mg(OH)_2) \cdot (\frac{2\ \text{mol}\ H_3PO_4}{3\ \text{mol}\ Mg(OH)_2}) = 0.33\ \text{mol}\ H_3PO_4$$

Therefore, if we have 0.50 mol of $Mg(OH)_2$, we would need 0.33 mol of H_3PO_4 to react with all of the magnesium hydroxide.

Example:

How many moles of sodium oxide (Na_2O) can be formed from 2.36 mol of sodium nitrate $(NaNO_3)$ using the balanced chemical equation below?

$$10\ Na + 2\ NaNO_3 \rightarrow 6\ Na_2O + N_2O$$

Solution:

$$(2.36\ \text{mol}\ NaNO_3) \cdot (\frac{6\ \text{mol}\ Na_2O}{2\ \text{mol}\ NaNO_3}) = 7.08\ \text{mol}\ Na_2O$$

Example:

How many moles of sulfur are required to produce 5.42 mol of carbon disulfide, CS_2, using the balanced chemical equation below?

$$C + 2\ S \rightarrow CS_2$$

Solution:

$$(5.42\ \text{mol}\ CS_2) \cdot (\frac{2\ \text{mol}\ S}{1\ \text{mol}\ CS_2}) = 10.84\ \text{mol}\ S$$

Mass-Mass Calculations

A mass-mass calculation would allow you to solve one of the following types of problems:

- Determine the mass of reactant necessary to product a given amount of product
- Determine the mass of product that would be produced from a given amount of reactant
- Determine the mass of reactant necessary to react completely with a second reactant

As was the case for mole ratios, it is essential that you are using a ***balanced*** chemical equation before carrying out any stoichiometric calculations.

Using Proportion to Solve Stoichiometry Problems

All methods for solving stoichiometry problems contain the same four steps.

Step 1: Write and balance the chemical equation.

Step 2: Identify what is the known value and what is the unknown that you want to calculate.

Step 3: Convert the mass of known to moles of known if necessary. Convert the moles of known to moles of unknown.

Step 4: Convert the moles of unknown to the requested units as necessary (grams, mL of M solution, L of a gas at STP) using relevant information(molar mass, molarity, gaseous molar volume.)

Step 1 has been covered in a previous chapter. We also just saw how to use mole ratios to complete Step 3 in the previous section. In order to complete the remaining two steps, we simply need to know how to convert between moles and the given or requested units.

In this section, we will be solving "mass-mass problems," which means that both the given value and the requested answer will both be in units of mass, usually grams. Note that if some other unit of mass is used, you we usually convert to grams first because molar masses are reported in grams. The conversion factor between grams and moles is the molar mass (g/mol). To find the number of moles in x grams of a substance, and to go from y moles to grams, we use a conversion factor based on the molar mass. This process is best illustrated through examples, so let's look at some sample problems.

The balanced equation below shows the reaction between hydrogen gas and oxygen gas to produce water. Since the equation is already balanced, Step 1 is already completed. Remember that the coefficients in the balanced equation are true for moles or molecules, but not for grams.

$$2\ H_{2(g)} + \ O_{2(g)} \rightarrow 2\ H_2O_{(l)}$$

The mole ratio in this equation is two moles of hydrogen react with one mole of oxygen to produce two moles of water. If you were told that you were going to use 2.00 moles of hydrogen in this reaction, you would also know the moles of oxygen required for the reaction and the moles of water that would be produced. It is only slightly more difficult to determine the moles of oxygen required and the moles of water produced if you were told that you will be using 0.50 mole of hydrogen. Since you are using a quarter as much hydrogen, you would need a quarter as much oxygen and produce a quarter as much water. This is because the molar ratios keep the same proportion. If you were to write out a mathematical equation to describe this problem, you would set up the following proportion:

$$\frac{x \text{ mol } O_2}{0.50 \text{ mol } H_2} = \frac{1 \text{ mol } O_2}{2 \text{ mol } H_2}$$

The given quantity, 0.50 mole of hydrogen, is already in moles. The value we are looking for is moles of oxygen. From the balanced equation, we know that 1 mole of oxygen reacts with 2 moles of hydrogen. Similarly, we want to determine the x moles of oxygen needed to react with 0.50 moles of hydrogen. First write the quantity that you know, 0.50 moles of hydrogen, write the conversion factor with moles of hydrogen in the denominator and moles of oxygen in the numerator. Get the correct mole ratio from looking at the coefficients of the balanced balanced equation- in this case 1 mol oxygen gas : 2 mol hydrogen gas. Cancel like units, calculate, and you will find that $x = 0.25$ moles of O_2.

Example:

Pentane, C_5H_{12}, reacts with oxygen gas to produce carbon dioxide and water. How many grams of carbon dioxide will be produced by the reaction of 108.0 grams of pentane?

Write and balance the equation. Identify known and unknown values.

$$C_5H_{12} + 8\ O_2 \rightarrow 5\ CO_2 + 6\ H_2O$$

Convert the known mass of pentane to moles using calculated molar mass.

$$\frac{108.0\text{ g}}{72.0\text{ g/mol}} = 1.50\text{ mol } C_5H_{12}$$

Apply the correct mole ratio from the equation to find moles of unknown.

Therefore, x mol $CO_2 = 7.50$.

Convert the moles of carbon diooxide to requested units (grams).

$$\text{grams } CO_2 = (7.50\text{ mol}) \cdot (44.0\text{ g/mol}) = 330.\text{ grams}$$

Example:

Aluminum hydroxide reacts with sulfuric acid to produce aluminum sulfate and water. How many grams of aluminum hydroxide are necessary to produce 108 grams of water?

Write and balance the equation. Identify the known and unknown quantities.

$$2\text{ Al(OH)}_3 + 3\text{ H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 6\text{ H}_2\text{O}$$

Convert the given quantity of water to moles.

$$\frac{108.0\text{ g}}{18.0\text{ g/mol}} = 6.00\text{ mol } H_2O$$

Apply the mole ratio to moles of known to find moles of unknown.

Therefore, x mol $\text{Al(OH)}_3 = 2.00$.

Convert the moles of unknown, aluminum hydroxide, to grams using calculated molar mass.

$$\text{grams Al(OH)}_3 = (2.00\text{ mol}) \cdot (78.0\text{ g/mol}) = 156\text{ grams}$$

Example:

15.0 grams of chlorine gas is bubbled through liquid sulfur to produce liquid disulfur dichloride. How much product is produced in grams?

Write and balance the chemical equation. Identify know and unknown.

$$\text{Cl}_{2(g)} + 2\text{ S}_{(l)} \rightarrow \text{S}_2\text{Cl}_{2(l)}$$

Convert the known mass to its mole equivalent.

$$\frac{15.0\text{ g}}{70.9\text{ g/mol}} = 0.212\text{ mol}$$

Use the mole ratio determined from the balanced equation and calculate the moles of unknown.

$$\frac{x\text{ mol S}_2\text{Cl}_2}{0.212\text{ mol Cl}_2} = \frac{1\text{ mol S}_2\text{Cl}_2}{1\text{ mol Cl}_2}$$

Therefore, x mol $S_2Cl_2 = 0.212$.

Convert the moles of unknown to grams using appropriate molar mass.

$$\text{grams } S_2Cl_2 = (0.212\text{ mol}) \cdot (135\text{ g/mol}) = 28.6\text{ grams}$$

Example:

A thermite reaction occurs between elemental aluminum and iron(III) oxide to produce aluminum oxide and elemental iron. The reaction releases enough heat to melt the iron that is produced. If 500. g of iron is produced in the reaction, how much iron(III) oxide was used as reactant?

Write and balance the chemical equation. Identify the known and unknown quantities.

$$Fe_2O_{3(s)} + 2\ Al_{(s)} \rightarrow 2\ Fe_{(l)} +\ Al_2O_{3(s)}$$

Convert the given mass to moles using its molar mass.

$$\frac{500.\ \text{g}}{55.9\ \text{g/mol}} = 8.95\ \text{mol}$$

Use the mole ratio determined by the balanced equation to find the unknown moles of iron (III) oxide.

Therefore, x mol $Fe_2O_3 = 4.48$.

Convert the moles of iron (III) oxide to grams using its calculated molar mass.

$$\text{grams } Fe_2O_3 = (4.48\ \text{mol}) \cdot (160.\ \text{g/mol}) = 717\ \text{grams}$$

Example:

Ibuprofen is a common painkiller used by many people around the globe. It has the formula $C_{13}H_{18}O_2$. If 200. g of ibuprofen is combusted, how much carbon dioxide is produced?

Write and balance the chemical equation. Identify your known and unknown quantities.

$$2\ C_{13}H_{18}O_{2(s)} + 33\ O_{2(s)} \rightarrow 26\ CO_{2(g)} + 18\ H_2O_{(l)}$$

Convert the given mass quantity to moles using its molar mass. (0.967 moles ibuprofen)

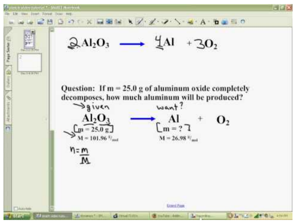
Use the mole ratio derived from the balanced equation to find moles of carbon dioxide from moles of ibuprofen.

Therefore, x mol $CO_2 = 12.6$.

Convert the moles of carbon dioxide to grams using its molar mass.

$$\text{grams } CO_2 = (12.6\ \text{mol}) \cdot (44.0\ \text{g/mol}) = 554\ \text{grams}$$

A blackboard type discussion of stoichiometry **(3e)** is available at http://www.youtube.com/watch?v=EdZtSSJecJc (9:21).



$2Al_2O_3 \rightarrow 4Al + 3O_2$

Question: If m = 25.0 g of aluminum oxide completely decomposes, how much aluminum will be produced?

$Al_2O_3 \rightarrow Al + O_2$

$[m = 25.0\ g]$ $[m = ?]$

M = 101.96 g/mol M = 26.98 g/mol

$n = \frac{m}{M}$

MEDIA

Click image to the left for more content.

Using Dimensional Analysis to Solve Stoichiometry Problems

Many chemists prefer to solve stoichiometry problems with a single line of math instead of writing out the multiple steps. This can be done by using dimensional analysis, also called the factor-label method. Recall that this is simply a method that uses conversion factors to convert from one unit to another. For a review, refer to the section on dimensional analysis in the chapter "Measurement in Chemistry." In this method, we can follow the cancellation of units to obtain the correct answer.

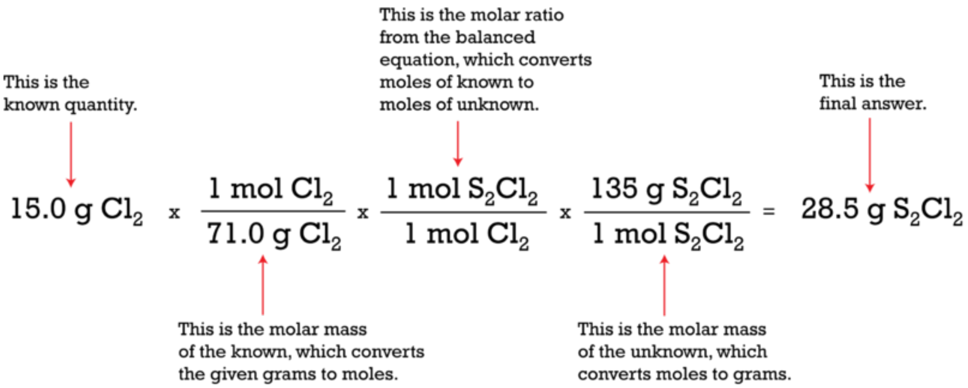
Let's return to some of the problems from the previous section and use dimensional analysis to solve them. For instance: 15.0 g of chlorine gas is bubbled through liquid sulfur to produce disulfur dichloride. How much product is produced in grams?

Step 1: As always, the first step is to correctly write and balance the equation:

$$Cl_{2(g)} + 2\ S_{(l)} \rightarrow S_2Cl_{2(l)}$$

Step 2: Identify what is being given (for this question, 15.0 g of Cl_2 is the given) and what is asked for (grams of S_2Cl_2).

Step 3: Next, use the correct factors that allow you to cancel the units you don't want and get the unit you do want. Make sure all factors represent a valid relationship.



Example:

Consider the thermite reaction again. This reaction occurs between elemental aluminum and iron(III) oxide, releasing enough heat to melt the iron that is produced. If 500.0 g of iron is produced in the reaction, how much iron(III) oxide was placed in the original container?

Step 1: Write and balance the equation:

$$Fe_2O_{3(s)} + 2\ Al_{(s)} \rightarrow 2\ Fe_{(l)} +\ Al_2O_{3(s)}$$

Step 2: Determine what is given and what needs to be calculated:

given = 500. g of Fe calculate = grams of Fe_2O_3

Step 3: Set-up the dimensional analysis system. Cancel units, and solve.

$$500.\text{g Fe} \cdot \frac{1\ \text{mol Fe}}{55.85\ \text{g Fe}} \cdot \frac{1\ \text{mol } Fe_2O_3}{2\ \text{mol Fe}} \cdot \frac{159.7\ \text{g } Fe_2O_3}{1\ \text{mol } Fe_2O_3} = 717\ \text{g } Fe_2O_3$$

Example:

Ibuprofen is a common painkiller used by many people around the globe. It has the formula $C_{13}H_{18}O_2$. If 200. g of Ibuprofen is combusted, how much carbon dioxide is produced?

Step 1: Write and balance the equation:

$$2\ C_{13}H_{18}O_{2(s)} + 33\ O_{2(g)} \rightarrow 26\ CO_{2(g)} + 9\ H_2O_{(l)}$$

Step 2: Determine what is given and what needs to be calculated:

given = 200.g of ibuprofen calculate = grams of CO_2

Step 3: Set-up the dimensional analysis system:

$$200.\text{ g } C_{13}H_{18}O_2 \cdot \frac{1\text{ mol } C_{13}H_{18}O_2}{206.3\text{ g } C_{13}H_{18}O_2} \cdot \frac{26\text{ mol } CO_2}{2\text{ mol } C_{13}H_{18}O_2} \cdot \frac{44.1\text{ g } CO_2}{1\text{ mol } CO_2} = 555\text{ g } CO_2$$

Example:

If sulfuric acid is mixed with sodium cyanide, the deadly gas hydrogen cyanide is produced. How much sulfuric acid must be placed in the container to produce 12.5 g of hydrogen cyanide?

Step 1: Write and balance the equation:

$$2\ NaCN_{(s)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(s)} + 2\ HCN_{(g)}$$

Step 2: Determine what is given and what needs to be calculated:

given = 12.5 g HCN calculate = grams of H_2SO_4

Step 3: Set-up the dimensional analysis system:

$$12.5\text{ g HCN} \cdot \frac{1\text{ mol HCN}}{27.0\text{ g HCN}} \cdot \frac{1\text{ mol } H_2SO_4}{2\text{ mol HCN}} \cdot \frac{98.06\text{ g } H_2SO_4}{1\text{ mol } H_2SO_4} = 22.7\text{ g } H_2SO_4$$

Lesson Summary

- The coefficients in a balanced chemical equation represent the relative amounts of each substance in the reaction.
- When the moles of one substance in a reaction is known, the coefficients of the balanced equation can be used to determine the moles of all the other substances.
- Mass-mass calculations can be done using dimensional analysis.

Further Reading / Supplemental Links

This website has lessons, worksheets, and quizzes on various high school chemistry topics. Lesson 9-3 is on solving mass-mass problems.

- http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson93.htm

Review Questions

1. How many moles of water vapor can be produced from 2 moles of ammonia for the following reaction between ammonia and oxygen: $4\ NH_{3(g)} + 5\ O_{2(g)} \rightarrow 4\ NO_{(g)} + 6\ H_2O_{(g)}$?
   a. 3 mol
   b. 6 mol
   c. 12 mol
   d. 24 mol
2. How many moles of bismuth(III) oxide can be produced from 0.625 mol of bismuth in the following reaction: $Bi_{(s)} + O_{2(g)} \rightarrow Bi_2O_{3(s)}$? (Note: equation may not be balanced.)

   a. 0.313 mol
   b. 0.625 mol
   c. 1 mol
   d. 1.25 mol
   e. 2 mol

3. For the following reaction, balance the equation and then determine the mole ratio of moles of $B(OH)_3$ to moles of water: $B_2O_{3(s)} + H_2O_{(l)} \rightarrow B(OH)_{3(s)}$.
4. Write the balanced chemical equation for the reactions below and find the indicated mole ratio.
   a. Gaseous propane (C_3H_8) combusts to form gaseous carbon dioxide and water. Find the molar ratio of O_2 to CO_2.
   b. Solid lithium reacts with an aqueous solution of aluminum chloride to produce aqueous lithium chloride and solid aluminum. Find the molar ratio of $AlCl_{3(aq)}$ to $LiCl_{(aq)}$.
   c. Gaseous ethane (C_2H_6) combusts to form gaseous carbon dioxide and water. Find the molar ratio of $CO_{2(g)}$ to $O_{2(g)}$.
   d. An aqueous solution of ammonium hydroxide reacts with an aqueous solution of phosphoric acid to produce aqueous ammonium phosphate and water. Find the molar ratio of $H_3PO_{4(aq)}$ to $H_2O_{(l)}$.
   e. Solid rubidium reacts with solid phosphorous to produce solid rubidium phosphide. Find the molar ratio of Rb(s) to P(s).
5. For the given reaction (unbalanced): $Ca_3(PO_4)_2 + SiO_2 + C \rightarrow CaSiO_3 + CO + P$
   a. how many moles of silicon dioxide are required to react with 0.35 mol of carbon?
   b. how many moles of calcium phosphate are required to produce 0.45 mol of calcium silicate?
6. For the given reaction (unbalanced): $FeS + O_2 \rightarrow Fe_2O_3 + SO_2$
   a. how many moles of iron(III) oxide are produced from 1.27 mol of oxygen?
   b. how many moles of iron(II) sulfide are required to produce 3.18 mol of sulfur dioxide?
7. Write the following balanced chemical equation. Ammonia and oxygen are allowed to react in a closed container to form nitrogen and water. All species present in the reaction vessel are in the gas state.
   a. How many moles of ammonia are required to react with 4.12 mol of oxygen?
   b. How many moles of nitrogen are produced when 0.98 mol of oxygen are reacted with excess ammonia?
8. How many grams of nitric acid will react with 2.00 g of copper(II) sulfide given the following reaction between copper(II) sulfide and nitric acid: $3\ CuS_{(s)} + 8\ HNO_{3(aq)} \rightarrow 3Cu(NO_3)_{2(aq)} + 2\ NO_{(g)} + 4\ H_2O_{(l)} + 3\ S_{(s)}$?
   a. <img src="ck12_math.31%20%5C%20%5Cmathrm%7Bg%7D" alt="1.31

1.3 Limiting Reactant

Lesson Objectives

The student will:

- explain what is meant by the terms "limiting reactant" and "excess reactant."
- determine the limiting reactant when given the mass or the number of moles of the reactants.
- calculate the quantities of products by using the quantity of limiting reactant and mole-mole ratios.

Vocabulary

excess reactant
any reactant present in an amount that is more than enough to react with the limiting reactant

limiting reactant
the reactant that determines the maximum amount of product that can be formed in a chemical reaction

Introduction

Suppose you were in the business of building tricycles from the components of frames, handlebars, seats, and wheels. After you completed constructing the tricycle, you boxed it up and shipped it. Suppose further that your supply of components consisted of:

100 frames, 120 sets of handlebars, 80 seats, and 300 wheels.

What is the maximum number of tricycles you could build and ship? You could build a maximum of 80 tricycles because when you run out of seats, you can no longer complete any more tricycles. The number of tricycles you could build will be limited by the number of seats you have available. In other words, the seats are the limiting component in your tricycle construction. The other components, the ones you have more than enough of, are said to be in excess. If you received a shipment of 100 more seats, could you build 100 more tricycles? No, because now one of the other components would become the limiting component.

In the chemical reactions that you have been working with, when you were given the amount of one substance involved in the reaction, it was assumed that you had exactly the required amount of all the other reagents. In this next section, you will be given the amounts of all the reagents, but not in the exact reacting amounts. You will need to determine which of the reactants limits the amount of product that can be formed, as well as how much product can be produced.

Limiting and Excess Reactants

The **limiting reactant** is the one that is used up first in the reaction. Consequently, limiting reactants determine the maximum amount of product that can be formed. An **excess reactant** is any reactant present in an amount that is more than enough to react with the limiting reactant. Some excess reactant remains after the limiting reactant has been used up. Chemists often add one reactant in excess in order to make sure that the limiting reactant is completely consumed. For example, if we wanted to find out how much $CO_{2(g)}$ we would obtain if we combusted an aspirin tablet, we would use excess oxygen to make sure that the entire aspirin tablet reacted.

$$C_9H_8O_{4(s)} + 9\ O_{2(g)} \rightarrow 9\ CO_{2(g)} + 4\ H_2O_{(l)}$$

The limiting reagent is the aspirin tablet because it is used up in the experiment. Oxygen is the excess reactant.

Let's look at another example. When you take a piece of aluminum foil and place it into a solution of copper(II) chloride, heat and gas are given off. When the reaction is completed, the blue color of the copper(II) chloride solution fades and a brownish solid (copper) is produced. What is the maximum number of grams of copper that can be produced when 53.96 grams of aluminum are reacted with 134.4 grams of copper(II) chloride?

The reaction is:

$$2\ Al_{(s)} + 3\ CuCl_{2(aq)} \rightarrow 3\ Cu_{(s)} + 2\ AlCl_{3(aq)}$$

Since 53.96 grams of Al is equivalent to 2 moles of Al and 134.44 grams of $CuCl_2$ is equivalent to 3 moles, we know that both reactants will be completely used up. As a result, 3 moles of Cu, or 187.3 grams, will be produced.

If we only had 10.0 grams of Al instead, what is the maximum number of grams of copper that can be produced? Assuming we still have 134.44 grams of $CuCl_2$, then it is obvious that the Al is the limiting reactant. By doing a mass-mass calculation based on the amount of the limiting reagent, we can determine that 35.5 grams of Cu will be produced.

Consider another example. Assume that we have 72.0 g of water reacting with 190. g of $TiCl_4$.

The balanced equation is:

$$TiCl_{4(s)} + 2\ H_2O_{(l)} \rightarrow TiO_{2(s)} + 4\ HCl_{(aq)}$$

We can see from the balanced equation that one mole of $TiCl_4$ reacts with two moles of water. The 190. g of $TiCl_4$ is exactly one mole. Therefore, $TiCl_4$ will react with two moles, or 36.0 g of water. In this reaction, however, we are given 72.0 g of water. Therefore, the water is in excess and 36.0 g of water will be left over when the reaction is complete.

Example:

You are given 34.0 g of NH_3 and 36.5 g of HCl, which react according to the following balanced equation. Determine the limiting reactant and the reactant in excess.

$$NH_{3(g)} +\ HCl_{(aq)} \rightarrow NH_4Cl_{(s)}$$

According to the balanced equation, one mole of NH_3 reacts with one mole of HCl. The 34.0 g of NH_3 is equivalent to two moles, and the 36.5 g of HCl is equivalent to one. Since they react with a ratio of 1 : 1, one mole of HCl will react with one mole of NH_3. One mole of NH_3 will be left over. As a result, HCl is the limiting reactant, and NH_3 is in excess.

A straightforward way to find the limiting reactant is as follows:

Step 1: Write out the balanced equation.

Step 2: Convert the given amounts of all reactants into moles.

Step 3:

Let us look at some examples using real chemical reactions.

Example:

Andrew was working in the lab and mixed a solution containing 25.0 g of HCl with a solution containing 25.0 g of iron(II) sulfide. What is the limiting reagent, and what reagent was in excess?

Example:

A student mixed 5.0 g of carbon with 23.0 g iron(III) oxide. What is the limiting reactant, and what reactant was the excess reactant?

Step 1: Write the balanced equation:

$$2\ \text{Fe}_2\text{O}_3 + 3\ \text{C} \rightarrow 4\ \text{Fe} + 3\ \text{CO}_2$$

Step 2: Convert given amounts to moles:

$$\text{mol C: } \frac{5.0\ \text{g}}{12.0\ \text{g/mol}} = 0.417\ \text{mol C}$$
$$\text{mol Fe}_2\text{O}_3\text{: } \frac{23.0\ \text{g}}{159.7\ \text{g/mol}} = 0.144\ \text{mol Fe}_2\text{O}_3$$

Step 3:

Example:

While working in the lab, Brenda added 5.0 g of aluminum chloride to 7.0 g of silver nitrate in order to work on her double replacement reactions. Her first goal was to determine the limiting reagent. Can you help her determine which reactant is limiting, and which is in excess given the balanced equation?

Step 1: Write the balanced equation:

$$\text{AlCl}_3 + 3\ \text{AgNO}_3 \rightarrow 3\ \text{AgCl} + \text{Al(NO}_3)_3$$

Step 2: Convert given amounts to moles:

$$\text{mol AlCl}_3\text{: } \frac{5.0\ \text{g}}{133\ \text{g/mol}} = 0.037\ \text{mol AlCl}_3$$
$$\text{mol AgNO}_3\text{: } \frac{7.0\ \text{g}}{170.\ \text{g/mol}} = 0.041\ \text{mol AgNO}_3$$

Step 3:

$AgNO_3$ is the limiting reagent. Note that this is the case even though there are fewer moles of $AlCl_3$. However, since three units of $AgNO_3$ are used up for each unit of $AlCl_3$, it is the $AgNO_3$ that will run out first.

Limiting Reactant and Mass-Mass Calculations

Once we have determined the limiting reactant, we still need to determine the amount of product the limiting reactant will produce. We might also want to know how much of the other reactant we are using and how much is left over. Consider again the example where the student mixed 5.0 g carbon and 23.0 g iron(III) oxide. The reaction is:

$$2\ \text{Fe}_2\text{O}_3 + 3\ \text{C} \rightarrow 4\ \text{Fe} + 3\ \text{CO}_2$$

We found that Fe_2O_3 is the limiting reagent and that 23.0 g of Fe_2O_3 is equivalent to 0.144 mol). In order to determine the mass of iron produced, we simply have to perform two additional steps: convert moles of limiting reactant to moles of product (using a mole ratio), and convert moles of product to mass (using its molar mass value).

The mass of iron produced is then:

$$\text{mol Fe} = (0.144\ \text{mol Fe}_2\text{O}_3) \cdot \left(\frac{4\ \text{mol Fe}}{2\ \text{mol Fe}_2\text{O}_3}\right) = 0.288\ \text{mol Fe}$$
$$\text{mass Fe} = 0.288\ \text{mol Fe} \cdot 55.85\ \text{g/mol} = 16.1\ \text{g Fe}$$

Therefore, the mass of Fe formed from this reaction would be 16.1 g.

Now, let's consider two more example.

Example:

Magnesium chloride is used as a fireproofing agent, but it is also a coagulant in tofu – imagine that! Jack was working in the lab one day and mixed 1.93 g of magnesium oxide with 3.56 g of HCl. The equation is given below. What mass of magnesium chloride was formed? (Remember to balance the equation first!)

$$\text{MgO} + \ \text{HCl} \rightarrow \text{MgCl}_2 + \ \text{H}_2\text{O}$$

Step 1: Write the balanced equation.

$$\text{MgO} + 2\ \text{HCl} \rightarrow \text{MgCl}_2 + \ \text{H}_2\text{O}$$

Step 2: Convert given amounts to moles.

$$\text{mol MgO: } \frac{1.93\ \text{g}}{40.3\ \text{g/mol}} = 0.0479\ \text{mol MgCl}_2$$
$$\text{mol HCl: } \frac{3.56\ \text{g}}{36.5\ \text{g/mol}} = 0.0975\ \text{mol HCl}$$

Step 3:

MgO is the limiting reagent. Thus, we use the values for MgO in our stoichiometric calculations.

Step 4: Convert moles of the limiting reagent to mass of the desired product.

$$\text{mol MgCl}_2\text{: } (0.0479\ \text{mol MgO}) \cdot (\frac{1\ \text{mol MgCl}_2}{1\ \text{mol MgO}} = 0.0479\ \text{mol MgCl}_2$$
$$\text{mass MgCl}_2\text{: } (0.0479\ \text{mol MgCl}_2) \cdot (95.2\ \text{g/mol}) = 4.56\ \text{g MgCl}_2$$

Example:

In the following reaction, 12.8 g of ammonia and 14.5 g of oxygen are allowed to react. How many grams of nitrogen monoxide are formed?

Step 1: Write the balanced equation.

$$4\ \text{NH}_3 + 5\ \text{O}_2 \rightarrow 4\ \text{NO} + 6\ \text{H}_2\text{O}$$

Step 2: Convert given amounts to moles.

$$\text{mol NH}_3\text{: } \frac{12.8\ \text{g}}{17.0\ \text{g/mol}} = 0.752\ \text{mol NH}_3$$
$$\text{mol O}_2\text{: } \frac{14.5\ \text{g}}{32.0\ \text{g/mol}} = 0.453\ \text{mol O}_2$$

Step 3:

O_2 is the limiting reagent. Thus, we use the values for O_2 in our stoichiometric calculations.

Step 4: Convert moles of the limiting reagent to mass of the desired product.

$$\text{mol NO: } (0.453\ \text{mol O}_2) \cdot (\frac{4\ \text{mol NO}}{5\ \text{mol O}_2} = 0.362\ \text{mol NO}$$
$$\text{mass NO: } (0.362\ \text{mol NO}) \cdot (30.01\ \text{g/mol}) = 10.9\ \text{g NO}$$

Lesson Summary

- The limiting reactant is the one that is used up first in the reaction.
- The limiting reactant limits the amount of product that can form from a chemical reaction.
- An excess reactant is any reactant present in an amount that is more than enough to react with the limiting reactant.
- The excess reactant remains after the limiting reactant has been used up.

Further Reading / Supplemental Links

This website has several video lessons on performing stoichiometry calculations, including problems with a limiting reactant.

- http://www.kentchemistry.com/moviesfiles/chemguy/advanced/ChemguyStoich.htm

Review Questions

1. Consider the balanced reaction: $2\ \text{Al} + 6\ \text{HBr} \rightarrow 2\ \text{AlBr}_3 + 3\ \text{H}_2$.
    a. When 3.22 mol of Al reacts with 4.96 mol of HBr, how many moles of H_2 are formed?
    b. What is the limiting reactant?
    c. For the reactant in excess, how many moles are left over at the end of the reaction?
2. Write the balanced equation for this reaction: copper(II) chloride reacts with sodium nitrate to form copper(II) nitrate and sodium chloride.
    a. If 15.0 g of copper(II) chloride react with 20.0 g of sodium nitrate, how much sodium chloride can be formed?
    b. What is the limiting reactant for this reaction?
    c. How many grams of the excess reactant will be left over in this reaction?

1.4 Percent Yield

Lesson Objectives

The student will:

- explain what is meant by the terms “actual yield” and “theoretical yield.”
- calculate the theoretical yield for a chemical reaction when given the amount(s) of reactant(s) available.
- determine the percent yield for a chemical reaction.

Vocabulary

actual yield
the actual amount of product that is formed in the laboratory experiment

percent yield
the ratio of the actual yield to the theoretical yield expressed as a percentage

theoretical yield
the amount of product that could be formed from a chemical reaction based on the balanced chemical equation

Introduction

The amount of product that should be formed when the limiting reactant is completely consumed is called the **theoretical yield**. This is the maximum amount of the product that could form from the quantities of reactants used. In actual practice, however, this theoretical yield is seldom obtained due to side reactions, failure of the reaction to go to completion, and other complications. The actual amount of product produced in a laboratory or industrial reaction is called the **actual yield**. The actual yield is almost always less than the theoretical yield and is often expressed as a percentage of the theoretical yield. This is also referred to as the **percent yield**.

Calculating the Theoretical Yield

When we calculate the amount of product that can be produced from limiting reactants, we are determining the maximum theoretical amount of product we could obtain from the reaction. In other words, the theoretical yield is the maximum amount obtained when all of the limiting reactant has reacted in the balanced chemical equation. You have already been calculating the theoretical yields in the previous section, but let us consider one more example.

Example:

Cindy Lou Who is studying the reaction between silver nitrate and potassium sulfide. The unbalanced equation for the reaction is:

$$\text{AgNO}_{3(aq)} + \text{K}_2\text{S}_{(aq)} \rightarrow \text{Ag}_2\text{S}_{(s)} + \text{KNO}_{3(aq)}$$

When Cindy Lou Who added 5.00 g of the silver nitrate with 2.50 g of potassium sulfide, what was her theoretical yield for silver sulfide?

Notice that this is a limiting reagent problem because we are given two reactant amounts, and we have to determine which of these reactants will run out first.

Step 1: Write the balanced equation.

$$2\ \mathrm{AgNO}_{3(aq)} + \mathrm{K_2S}_{(aq)} \rightarrow \mathrm{Ag_2S}_{(s)} + 2\ \mathrm{KNO}_{3(aq)}$$

Step 2: Convert given amounts to moles.

$$\text{mol AgNO}_3\text{: } \frac{5.00\ \text{g}}{170.\ \text{g/mol}} = 0.0294\ \text{mol AgNO}_3$$
$$\text{mol K}_2\text{S: } \frac{2.50\ \text{g}}{110.\ \text{g/mol}} = 0.0227\ \text{mol K}_2\text{S}$$

Step 3: Divide each amount by the coefficients from the balanced equation.

$$\text{AgNO}_3\text{: } \frac{0.0294\ \text{mol}}{2} = 0.0147\ \text{mol}$$
$$\text{K}_2\text{S: } \frac{0.0227\ \text{mol}}{1} = 0.0227\ \text{mol}$$

$AgNO_3$ has the lowest final value, so it is the limiting reagent. This means K_2S is in excess. We use the values for $AgNO_3$ for the rest of our theoretical yield calculations.

Step 4: Convert moles of the limiting reagent to mass of the desired product.

$$\text{mol Ag}_2\text{S: } (0.0294\ \text{mol AgNO}_3) \cdot \frac{1\ \text{mol Ag}_2\text{S}}{2\ \text{mol AgNO}_3} = 0.0147\ \text{Ag}_2\text{S}$$
$$\text{mass Ag}_2\text{S: } (0.0147\ \text{Ag}_2\text{S}) \cdot (248\ \text{g/mol}) = 3.64\ \text{g Ag}_2\text{S}$$

Therefore, when Cindy Lou Who did her experiment in the lab, her theoretical yield would have been 3.64 g of $Ag_2S_{(s)}$. Yay, Cindy!

Alternatively, if we use dimensional analysis the calculation would be:

$$5.00\ \text{g AgNO}_3 \cdot \frac{1\ \text{mol AgNO}_3}{170.\ \text{g AgNO}_3} \cdot \frac{1\ \text{mol Ag}_2\text{S}}{2\ \text{mol AgNO}_3} \cdot \frac{248\ \text{g Ag}_2\text{S}}{1\ \text{mol Ag}_2\text{S}} = 3.64\ \text{g Ag}_2\text{S}$$

Calculating Percent Yield

Theoretical yields are the optimum yields if conditions allow all 100% of the reactant to react. If, on the other hand, anything were to happen to jeopardize this, the actual yield will differ from the theoretical yield. Remember that the actual yield is measured, while the theoretical yield is calculated.

The actual yield is almost always less than the theoretical yield, and we often calculate how close this actual yield is to the theoretical yield. The percentage of the theoretical yield that is actually produced (actual yield) is known as the percent yield. The efficiency of a chemical reaction is determined by the percent yield. The percent yield is found using the following formula.

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

Example:

A student was able to produce an actual yield of 5.12 g of calcium sulfate from 4.95 g of sulfuric acid and excess calcium hydroxide in the reaction shown below. What was her percent yield?

$$\mathrm{H_2SO_4} + \mathrm{Ca(OH)_2} \rightarrow \mathrm{CaSO_4} + 2\ \mathrm{H_2O}$$

We can calculate the theoretical yield using dimensional analysis.

$$4.95 \text{ g } H_2SO_4 \cdot \frac{1 \text{ mol } H_2SO_4}{98.1 \text{ g } H_2SO_4} \cdot \frac{1 \text{ mol } CaSO_4}{1 \text{ mol } H_2SO_4} \cdot \frac{136.2 \text{ g } CaSO_4}{1 \text{ mol } CaSO_4} = 6.88 \text{ g } CaSO_4$$

Once we have found the theoretical yield, we can use the actual yield given in the problem to find the percent yield.

$$\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{5.12 \text{ g}}{6.88 \text{ g}} \times 100\% = 74.4\%$$

Example:

Potassium hydrogen phthalate, $KHC_8H_4O_4$, is a compound used quite frequently in acid-base chemistry for a procedure known as standardization. Standardization has to do with the process of determining the concentration of a standard solution. In a certain experiment, 12.50 g of potassium hydroxide is mixed with 1.385 g of KHP. If 5.26 g of the product, $K_2C_8H_4O_4$, is produced, what is the percent yield?

$$KOH + KHC_8H_4O_4 \rightarrow K_2C_8H_4O_4 + H_2O$$

Step 1: Write the balanced equation.

The equation is already balanced, so this step is done.

Step 2: Convert given amounts to moles.

$$\text{mol KOH: } \frac{1.385 \text{ g}}{56.1 \text{ g/mol}} = 0.0247 \text{ mol KOH}$$
$$\text{mol } KHC_8H_4O_4\text{: } \frac{12.5 \text{ g}}{204 \text{ g/mol}} = 0.0612 \text{ mol } KHC_8H_4O_4$$

Step 3: Divide each amount by the coefficients from the balanced equation.

$$\text{mol KOH: } \frac{0.0247 \text{ mol}}{1} = 0.0247 \text{ mol}$$
$$\text{mol } KHC_8H_4O_4\text{: } \frac{0.0612 \text{ mol}}{1} = 0.0612 \text{ mol}$$

KOH has the lowest final value, so it is the limiting reagent. We use the values for KOH for the rest of our theoretical yield calculations.

Step 4: Convert moles of the limiting reagent to mass of the desired product.

$$\text{mol } K_2C_8H_4O_4\text{: } (0.0247 \text{ mol KOH}) \cdot \frac{1 \text{ mol } K_2C_8H_4O_4}{1 \text{ mol KOH}} = 0.0247 \text{ mol } K_2C_8H_4O_4$$
$$\text{mass } K_2C_8H_4O_4\text{: } (0.0247 \text{ mol } K_2C_8H_4O_4) \cdot (242.3 \text{ g/mol}) = 5.98 \text{ g } K_2C_8H_4O_4$$

Therefore, the theoretical yield of $K_2C_8H_4O_4$ is 5.98 g. Remember the actual yield given in the question was 5.26 g. Now let's calculate the percent yield.

$$\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \cdot 100\% = \frac{5.26 \text{ g}}{5.98 \text{ g}} \cdot 100\% = 88.0\%$$

Example:

Zeanxanthin is a compound responsible for causing the colors of the maple leaf to change in the fall. It has the formula $C_{38}H_{56}O_2$. In a combustion reaction of 0.95 g of zeanxanthin with excess oxygen, 2.2 g of carbon dioxide was produced. The other product was water. What is the percent yield of CO_2?

Step 1: Write the balanced equation.

$$C_{38}H_{56}O_2 + 51\ O_2 \rightarrow 38\ CO_2 + \ 28\ H_2O$$

Step 2: Convert given amounts to moles.

$$\text{mol } C_{38}H_{56}O_2\text{: } \frac{0.95 \text{ g}}{544 \text{ g/mol}} = 0.00174 \text{ mol } C_{38}H_{56}O_2$$

Step 3: Divide each amount by the coefficients from the balanced equation.

Since $C_{38}H_{56}O_2$ is reacted with excess oxygen, we already know that $C_{38}H_{56}O_2$ is the limiting reagent. We use the values for $C_{38}H_{56}O_2$ for the rest of our theoretical yield calculations.

Step 4: Convert moles of the limiting reagent to mass of the desired product.

$$\text{mol } CO_2\text{: } (0.00174 \text{ mol } C_{38}H_{56}O_2) \cdot \frac{38 \text{ mol } CO_2}{1 \text{ mol } C_{38}H_{56}O_2} = 0.066 \text{ mol } CO_2$$
$$\text{mass } CO_2\text{: } (0.066 \text{ mol } CO_2) \cdot (44 \text{ g/mol}) = 2.9 \text{ g } CO_2$$

Therefore, the theoretical yield of CO_2 is 2.9 g. Remember the actual yield given in the question was 2.2 g. Now let's calculate the percent yield.

$$\%\text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \cdot 100\% = \frac{2.2 \text{ g}}{2.9 \text{ g}} \cdot 100\% = 76\%$$

This video is an electronic blackboard presentation of the calculation of a percent yield **(3f; 1b IE)**: http://www.youtube.com/watch?v=1L12_TRSql8 (9:22).

MEDIA

Click image to the left for more content.

Lesson Summary

- The actual yield of a reaction is the actual amount of product that is produced in the laboratory.
- The theoretical yield is the amount of product that is produced under ideal conditions.
- The percentage of the theoretical yield that is actually produced (actual yield) is known as the percent yield.

Further Reading / Supplemental Links

This website has lessons, worksheets, and quizzes on various high school chemistry topics. Lesson 16-6 is on calculating percent yield.

- http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson166.htm

Review Questions

1. Is it possible for the actual yield to be greater than the theoretical yield?
2. What happens when competing reactions occur while performing an experiment in the lab?
3. If the actual yield is 4.5 g, but the theoretical yield is 5.5 g, what is the percent yield for this data?

4. Solid aluminum and sulfur come together in a reaction to produce 7.5 g of aluminum sulfide: $\mathrm{Al} + \mathrm{S} \rightarrow \mathrm{Al_2S_3}$. If 5.00 gof each solid react together, what is the percent yield? Remember to balance the reaction first.
    a. 32.0%
    b. 53.4%
    c. 96.2%
    d. 100.0%
5. In her experiment, Gerry finds she has obtained 3.65 g of lead(II) iodide. She knows that in her reaction, lead(II) nitrate reacted completely with potassium iodide to produce lead(II) iodide and potassium nitrate: $\mathrm{Pb(NO_3)_{2(aq)}} + \mathrm{KI_{(aq)}} \rightarrow \mathrm{PbI_{2(s)}} + \mathrm{KNO_{3(aq)}}$. The potassium iodide produced is a brilliant yellow colored precipitate. Gerry began with 5.00 gof potassium iodide. What was her percent yield? Remember to balance your equation first.
    a. 26.3%
    b. 36.0%
    c. 52.6%
    d. 72.0%
6. If the percentage yield in the reaction $2\ \mathrm{S} + 3\ \mathrm{O_2} \rightarrow 2\ \mathrm{SO_3}$ was found to be 78.3% and the actual yield was 1.01 g, what was the original mass of the limiting reagent, oxygen?
    a. 0.515 g
    b. 0.773 g
    c. 1.01 g
    d. 1.29 g
7. Bromine pentafluoride can be produced from a reaction between liquid bromine and fluorine gas. If 3.25 g of fluorine reacts with 2.74 g of bromine to produce 4.83 g of bromine pentafluoride, what is the percent yield of the product?
8. Ammonia can react with oxygen in a reaction that is similar to a combustion reaction. The products, however, are nitrogen monoxide and water, rather than carbon dioxide and water. In the reaction between ammonia and oxygen, 15 g of each reactant are placed in a container, and 10.5 g of nitrogen monoxide was produced. What is the percent yield of the nitrogen monoxide?

Chemical Equilibrium

Introduction

Chemical reaction is a process in which one or more reactants react to produce one or more products.

Type of Chemical reaction

(a) Irreversible Reactions
(b) Reversible reactions

Concept Ladder

Physical changes can also be categorised into Reversible and Irreversible changes.

(a) Irreversible Reaction

Unidirectional reactions are known as irreversible reactions. i.e. reactants convert to produce products and where products cannot convert back to the reactants.

Ex.

(1) $BaCl_2(aq) + H_2SO_4(aq) \longrightarrow BaSO_4(ppt) + 2HCl(aq)$

(2) $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$

(b) Reversible Reaction

Reversible reactions occur in both forward and backward directions and therefore never go on to completion.

Ex.

(1) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(2) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

Rack your Brain

Does a physical change accompain a chemical change?

Note :

For any reversible reaction, container should be closed.

Equilibrium

It is defined as the state when measurable properties such as position speed, temperature, concentration and pressure do not change with time.

Equilibirum can be of a no. of types. For example: physical equilibrium, thermal equilibrium, mechanical equilibrium, chemical equilibrium etc.

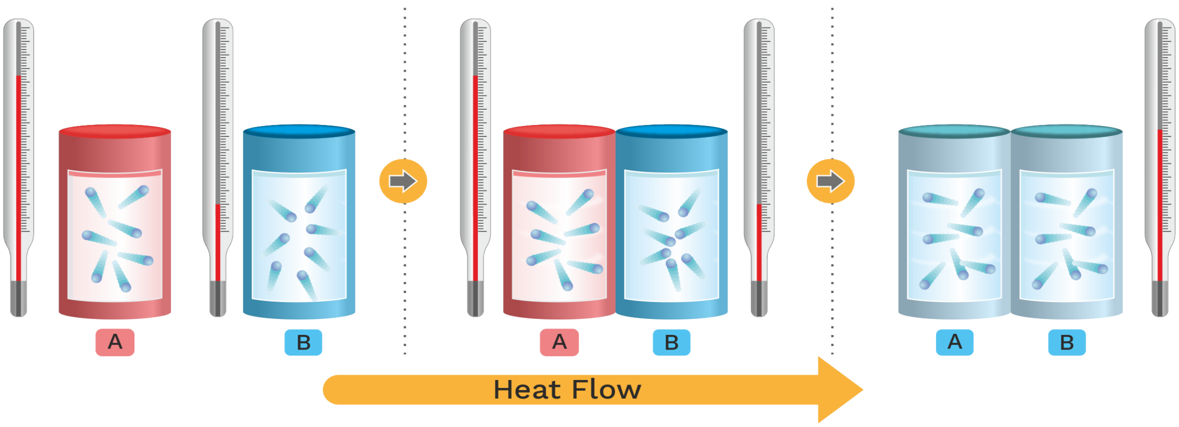
Concept Ladder

In mechanical equilibrium, the net forces on an object is zero.

Thermal Equilibrium

It is that type of equilibrium where the thermal energy between two or more substances are equal in nature.

Thermal Equilibrium



The above figure shows two objects A and B which are far from each other and when the come in contact then their thermal energies become equal. So, they are in thermal equilibrium with each other.

Concept Ladder

Solid-Liquid-Gaseous equilibrium can be seen in it's three states. The point at which these three exist for H_2O is known as triple point of water. Triple point of water is 273.15K

Physical Equilibrium

The type of equilibrium which develops between different phases and there is no change in chemical composition. In physical equilibrium, there is the existence of same substance in different physical states.

(1) Solid-liquid equilibrium

$H_2O\text{ (solid)} \rightleftharpoons H_2O\text{ (liquid)}$

Rate of transfer of ice is equal to the rate of freezing of water

(2) Liquid-vapour equilibrium

Rate of vaporization = Rate of condensation,

$H_2O\text{(liquid)} \rightleftharpoons H_2O\text{(vapour)}$

Conditions necessary for a Liquid-Vapour Equilibrium

(i) The system must be a closed system.

(ii) The system must be at a constant temperature.

(iii) The visible properties of the system should not change with time.

(3) Solid-vapour equilibrium

Certain solid substances on heating get converted directly into vapour without passing through the liquid phase. This process is called sublimation. The vapour when cooled, gives back the solid, it is called deposition or desublimation or sublimation.

$$NH_4Cl\,(solid) \xrightleftharpoons{\text{Heat}} NH_4Cl\,(vapour)$$

For example, Ammonium chloride when. heated sublimes.

(4) Equilibrium between a solid and its solution

If a solid solute is in contact with the saturated solution, there exits a dynamic equilibrium between the solid and the solution phase.

Solid substance $\rightleftharpoons$ Solution of the substance

Example : Sugar and sugar solution. In a saturated solution, a dynamic is equilibrium is established between dissolved sugar and solid sugar.

Sugar (solid) $\rightleftharpoons$ Sugar (aqueous)

Rate of dissolution on of solid sugar =Rate of precipitation of sugar from the solution.

At the equilibrium state, the no. of sugar molecules going into the soln from the solid sugar is equal to the no. of molecules precipitating out from the soln, i.e., at equilibrium.

(5) Equilibrium between a gas & its solution in a liquid.

Gases mixed in liquids. The dependent factors for solubility of a gas in any liquid are :

Concept Ladder

For any pure liquid at 1 atm pressure, the temperature at which the liquid and vapor are at equilibrium is called normal boiling point of liquid.

Rack your Brain

When a solution becomes supersaturated will you be able to observe equilibrium?

Concept Ladder

The number of precipitating molecules at equilibrium state is equal to the number of molecules dissolving in the solution.

(a) Nature of the gas and liquid.
(b) Temp. of the liquid.
(c) Pressure (P) of the gas over the surface of the solution.

This equilibrium is defined by Henry's law, which explains that the mass of a gas mixed in a known mass of solvent at a temp. is proportional to the solvent's pressure of the given gas. It decreases with increases of temperature.

Chemical Equilibrium

In chemical equilibrium, concentration of the reactants and products do not change with time and the system does not show any further change in properties.

In case of chemical equilibrium, rate of forward reaction becomes equal to the rate of backward reaction. i.e. Rate (forward reaction) = Rate (backward reaction)

Forward reaction (In an open glass container)

$$3\,Fe(s) + 4\,H_2O(g) \xrightarrow{\Delta} 3\,Fe(s) + 4\,H_2O(g)$$

If the container tube is closed, both the reactions take place simultaneously and hence reaction become reversible.

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

Other example may include

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

Characteristics of Equilibrium State

- A reaction (or a process) is said to be in equilibrium when the rate of forward reaction (process) becomes equal to the rate of backward reaction (process).
- An equilibrium is dynamic in nature and not static i.e., even after equilibrium is attained, the forward as well as the backward reaction take place but at equal speeds.
- A chemical equilibrium can be established only if none of the products is allowed to escape out.

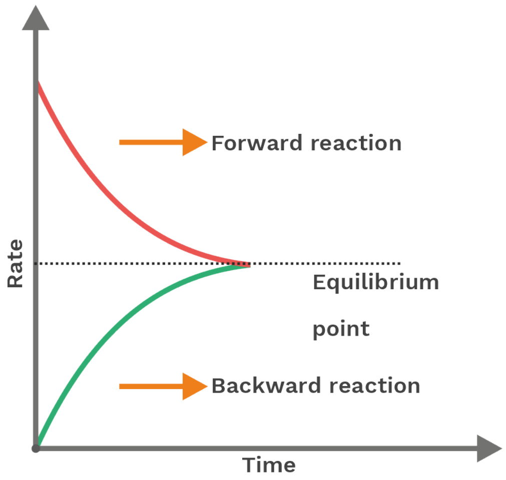
Concept Ladder

When the condition is changed at equilibrium state, the equilibrium changes.

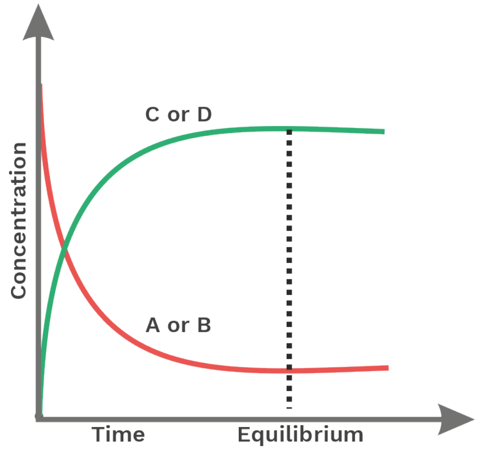
When temperature of a solution of gas is increased, the rate of dissolution of gas decreases.

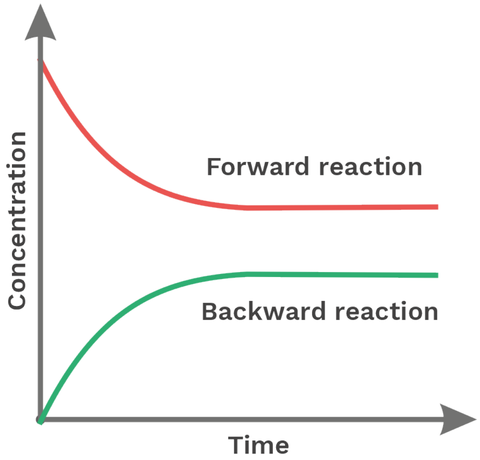
Rack your Brain

Equilibrium state is dynamic in nature. Why it is not static?



- At equilibrium, the concentration of each of the reactants and products become constant.





- When reaction attains equilibrium at certain temperature and pressure, $\Delta G = 0$
- Chemical equilibrium can be achieved from either direction.
-

Law of Mass Action

The rate of a reaction is proportional to the product of the active masses of the reactants, in which each term is raised to the power equal to its stoichiometric coefficient as represented by the balanced chemical equation.

$$aA + bB + cC + ...$$

Rate of reaction is directly proportional to

$[A]^a\,[B]^b\,[C]^c$

Law of Chemical Equilibrium is a result obtained by applying the Law of Mass Action to a reversible reaction in equilibrium.

$$A + B \rightleftharpoons C + D$$

Rate of the forward reaction $\propto [A]\,[B]$

$= k_f\,[A]\,[B]$

Rate of the backward reaction $\propto [C]\,[D]$

$= k_b\,[C]\,[D]$

At equilibrium,

Rate of forward rxn = Rate of backward rxn

Rack your Brain

Does spontaneity play any role in equilibrium being attained?

Concept Ladder

In chemical kinetics for a reaction of the type

$aA + bB \longrightarrow cC + dD$

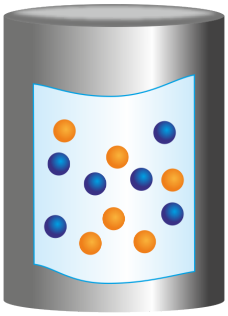
Rate of reaction = $K[A]^a[B]^b$

where K depends upon temperature.

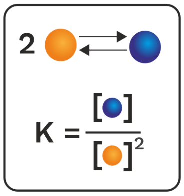
$$k_f[A][B] = k_b[C][D] \text{ or } \frac{[C][D]}{[A][B]} = \frac{k_f}{k_b} = K$$

At constant temperature, k_f and k_b are constant, therefore, $\frac{k_f}{k_b} = K$ is also constant at constant temperature and is called 'Equilibrium constant'.

The product of the molar concentrations of the products, each raised to the power equal to its stoichiometric coefficient divided by the product of the molar concentrations of the reactants, each raised to the power equal to its stoichiometric coefficient is constant at constant temperature and is called Equilibrium constant.



EQUILIBRIUM CONSTANT



EQUILIBRIUM CONSTANT 'K'

For a General Reaction of the type

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

The equilibrium constant expression is

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

where K_c is Equilibrium constant

Q.1 The rate constant for a forward reaction in a reversible reaction ($K_{eq} = 10^8$) is 10^4. Calculate the rate constant for the backward reaction.

A.1 $$K_{eq} = \frac{K_f}{K_b}$$

Where; K_f = Rate constant for forward reaction.
K_b = Rate constant for backward reaction.
K_{eq} = Equilibrium constant.
Now. $K_{eq} = 10^8$; $K_f = 10^4$.
Therefore, from equation (1)

$$K_b = \frac{K_f}{K_{eq}} = \frac{10^4}{10^8} = 10^{-4}$$

Importants Point about Equilibrium Constant

- If the reaction is reversed, the value of equilibrium constant is inversed e.g.,

  $$CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(l)\ K_c = K,$$

  then for

  $$CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq),\ K_c = 1/K$$

Equilibrium Constant on Inversion of Reaction

$$aA + bB \underset{K'_c}{\overset{K_c}{\rightleftharpoons}} cC + dD$$

Then at constant temperature,

The equilibrium constant K_c for forward reaction

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$ ← Forward Product

$$K'_c = \frac{[A]^a\,[B]^b}{[C]^c\,[D]^d} = \frac{1}{K_c}$$ ← Backward Product

- If the reaction is divided by 2, equilibrium constant is the square root of the original e.g.,

  For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $K_c = K$

  then for;

  $$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g),\ K_c = \sqrt{K}$$

  If then reaction is multiplied by 2, equilibrium constant is the square of the original. Equilibrium constatns of the step reactions e.g., if for

  $$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g),$$

  equilibrium constant = K

Previous Year's Question

If the equilibrium constant for $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is K, the equilibrium constant for $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$ will be **[NEET]**

(1) $\frac{1}{2}K$
(2) K
(3) K^2
(4) K^{X_2}

(1) $NO_2(g) + O_2(g) \rightleftharpoons 2NO_2(g)$, $K_c = K_1$

(2) $NO_2(g) + O_2(g) \rightleftharpoons 2NO_2(g)$, $K_c = K_2$

then, $K = K_1 \times K_2$

- Effect of temperature:

  According to Van't Hoff equation

$$\log\frac{K_2}{K_1} = \frac{\Delta H}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

Where K_1 and K_2 are the equilibrium constants at temperature T_1 and T_2 respectively and ΔH is the molar enthalpy change in the temperature range T_1 to T_2.

Note:

- For exothermic reaction, as temperature increases K decreases.
- For endothermic reaction, as temperature increases K increases.

Previous Year's Question

The equilibrium constants of the following are

$N_2 + 3H_2 \rightleftharpoons 2NH_3;$ K_1

$N_2 + O_2 \rightleftharpoons 2NO;$ K_2

$N_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O;$ K_3

The equilibrium constant (K) of the reaction will be:

$$2NH_3 + \frac{5}{2}O_2 \overset{K}{\rightleftharpoons} 2NO + 3H_2O$$

[NEET]

(1) $K_2K_3^3 / K_1$ (2) K_2K_3 / K_1

(3) $K_2^3K_3 / K_1$ (4) $K_1K_3^3 / K_2$

Q.2 For the reactions,

$A \rightleftharpoons B$ $K_C = 1$

$B \rightleftharpoons C$ $K_c = 3$

$C \rightleftharpoons D$ $K_c = 5$

Find K_C for the reaction $A \rightleftharpoons D$ is

(1) 15 (2) 5 (3) 3 (4) 1

A.2 For $A \rightleftharpoons D$

$$\frac{[B]}{[A]} = K_1 = 1;$$

$$\frac{[C]}{[B]} = K_2 = 3;$$

$$\frac{[D]}{[C]} = K_3 = 5$$

$$K = K_1 \times K_2 \times K_3$$

$$\frac{[D]}{[A]} = 1 \times 3 \times 5 = 15$$

[Multiplying all the three]

Q.3 The equilibrium constants of the reactions

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

and $$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

are K_1 and K_2, respectively. The relationship between K_1 and K_2 is

(1) $K_1 = K_2$ (2) $K_2^2 = K_1$

(3) $K_1^2 = K_2$ (3) $K_2 = \sqrt{K_1}$

A.3 $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$; $\therefore K_1 = \frac{[SO_3]}{[SO_2][O_2]^{1/2}}$

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$: $\therefore K_2 = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

$\therefore K_2 = K_1^2$

Q.4 The rate at which a substance reacts, depends on its

(1) Active mass (2) Molecular mass

(3) Equivalent mass (4) Total volume

A.4 Active mass

Q.5 For the reaction:

$$2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$$

Two moles each of A and B were taken into a flask. The following must always be true when the system attained equilibrium

(1) [A] = [B] (2) [A] < [B]

(3) [B] = [C] (4) [A] > [B]

A.5 For the reaction $2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$ 2 mol of A reacts with 1 mol of B to give products. Hence, the concentration of A will be lesser than that of B at equilibrium.

Q.6 The equilibrium constant for the reaction

$$N_2 + 2O_2 \rightleftharpoons 2NO_2$$

At a particular temperature is 100. Determine the values of equilibrium constants for the following reactions.

$2NO_2 \rightleftharpoons N_2 + 2O_2$ ....(1)

$NO_2 \rightleftharpoons 1/2\,N_2 + O_2$ ....(2)

A.6 The equilibrium constant for the reaction

$$N_2 + 2O_2 \rightleftharpoons 2NO_2$$

$$K_c = \frac{[NO_2]^2}{[N_2][O_2]^2} = 100 \qquad \text{........(a)}$$

The equilibrium constant equation for reaction (1)

$$K_1 = \frac{[N_2][O_2]^2}{[NO_2]^2} \qquad \text{........(b)}$$

This equation is reciprocal of equation (a)

So $K_1 = \frac{1}{K_c} = \frac{1}{100} = 1 \times 10^{-2}$

The equilibrium constant equation for reaction (2)

$$K_2 = \frac{[N_2]^{1/2}[O_2]}{[NO_2]} \qquad \text{........(c)}$$

Comparing equation (a) and (c),

$$K_2 = \sqrt{K_1} = \sqrt{10^{-2}} = 10^{-1} = 0.1$$

Q.7 Given:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); K_1$$

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g); K_2$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g); K_3$$

The equilibrium constant for $2NH_3(g) + \frac{5}{2}O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g)$

will be

(1) $K_1K_2K_3$ (2) $\frac{K_1K_2}{K_3}$ (3) $\frac{K_1K_3^2}{K_2}$ (4) $\frac{K_2K_3^3}{K_1}$

A.7 $K_1 = \frac{[NH_3]^2}{[N_2][H_2]^3}; K_2 = \frac{[NO]^2}{[N_2][O_2]}; K_3 = \frac{[H_2O]}{[H_2][O_2]^{1/2}}$

The equilibrium constant for

$$2NH_3(g) + \frac{5}{2}O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g)$$

Will be

$$K = \frac{[NO]^2[H_2O]^3}{[NH_3]^2[O_2]^{5/2}} = \frac{K_2 \times K_3^3}{K_1}$$

Q.8 For a system, A + 2B $\rightleftharpoons$ C, the equilibrium concentration are [A] = 0.06, [B] = 0.12, and [C] = 0.216. The K_c for the reaction is

(1) 120 (2) 400

(3) 4×10^{-3} (4) 250

A.8 A + 2B $\rightleftharpoons$ C

$$K = \frac{[C]}{[A][B]^2} \Rightarrow \frac{(0.216)}{(0.06)(0.012)^2} = 250$$

Homogeneous Equilibrium

When all the reactant and the products are in the same phase for a homogeneous system. This phenomenon is termed as homogenous equilibrium. For example, in the gaseous reaction, $CaCO_3(\text{solid}) \xrightarrow{\Delta} CaO(\text{solid}) + CO_2(\text{gas})$, reactants and products are in the homogeneous phase.

Similarly, for the reactions,

$$CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$$

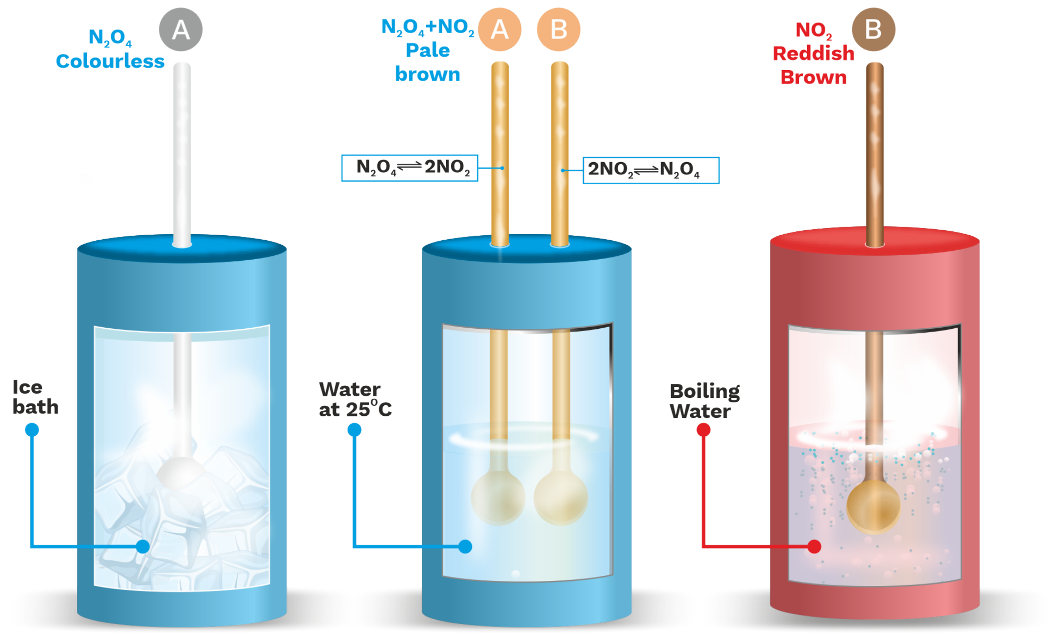
$$Fe^{3+}(aq) + SCBN^-(aq) \rightleftharpoons Fe(SCN^{2+})(aq)$$

Equilibrium constant in gaseous reaction

For gaseous reactions, equilibrium constant is expressed in terms of partial pressure. For example the decomposition of N_2O_4 into NO_2 in close container is gaseous reaction at equilibrium.

Concept Ladder

Is case of Homogeneous equilibrium of gases both the pressure and concentration of gases can be used to represent liquid and equilibrium states.



Ideal gas equation; $PV = nRT$

$$P = \frac{n}{V}RT \qquad \text{......(1)}$$

Where, P = Pressure of gas in “Bar”
n = number of moles of gas in mol
V = volume of gas in liter
T = absolute temperature in Kelvin “K”
R = 0.0831 bar L mol^{-} K^{-1}

Now form equation (1)

$$P = C.R.T. \text{ or } P = [gas]\,RT; \qquad \text{where } C = \frac{n}{V}$$

At constant temperature, pressure of gas is proportional to its concentration i.e.,

$$P \propto [gas]$$

for general reaction in equilibrium

$$aA\,(g) + bB\,(g) \rightleftharpoons cC\,(g) + dD\,(g)$$

or $$K_p = \frac{(P_C)^c\,(P_D)^d}{(P_A)^a\,(P_B)^b}$$

Concept Ladder

R can have different units also.

$R = 0.0821$ atm. L $mol^{-1}K^{-1}$

$$= \frac{8.314\,J}{mol\ K}$$

$$= \frac{2\ cal}{mol\ K}$$

Equilibrium constant in terms of mole fraction

Consider a general reaction in equilibrium

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

Amount of $A = X_A$ (mole fraction of A)

Amount of $B = X_B$ (mole fraction of B)

Amount of $C = X_C$ (mole fraction of C)

Amount of $D = X_D$ (mole fraction of D)

Now equilibrium constant in term of mole fraction

$$K_X = \frac{(X_C)^c (X_D)^d}{(X_A)^a (X_B)^b}$$

Relationship between K_c, K_p and K_X

(a) Relation between K_p and K_X

Consider a general reaction in equilibrium

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

according to Raoult's Law

$$p_A = X_A.P$$

Where, p_A = partial pressure of gas A

X_A = mole fraction of gas A

P = Total pressure.

similarity; $p_B = X_B\,P$

$p_C = X_C\,P$

$p_D = X_D\,P$

Now; $$K_p = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b}$$

$$K_p = \frac{(X_C)(X_D)\,P^{(c+d)-(a+b)}}{(X_A)(X_B)}$$

$$K_p = K_X.P^{\Delta n}$$

where, $\Delta n_g = (c+d)-(a+b)$

(b) Relation between K_p and K_c

Consider a general reaction in equilibrium

$$aA + bB \rightleftharpoons cC + dD \quad \text{.........} \ (1)$$

$$p = \frac{n}{V}RT = CRT \text{ where } C = \frac{n}{V}$$

Concept Ladder

Active mass of a solid substance is taken as unity during calculations.

Previous Year's Question

Equilibrium constant K_p for the following reaction

$$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$$

[NEET]

(1) $K_p = P_{CO_2}$

(2) $K_p = P_{CO_2}\left(\frac{P_{CO_2}P_{MgO}}{P_{MgCO_3}}\right)$

(3) $K_p = \left(\frac{P_{CO_2}P_{MgO}}{P_{MgCO_3}}\right)$

(4) $K_p = \frac{P_{MgCO_3}}{P_{CO_2} \times P_{MgO}}$

for an ideal ‘A’, $p_A = C_A.RT$ .... (2)

where; p_A = Partial pressure of gas ‘A’

C_A = concentration of gas ‘A’

R = gas constant

T = absolute temperature

Similarly for gas ‘B’

$p_B = C_B.RT$ ....(3)

$p_C = C_C.RT$ ....(4)

$p_D = C_D.RT$ ....(5)

Now K_p for the reaction (1) is

$$K_p = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b} \quad .....(6)$$

Now put the values of (2), (3), (4) and (5) in the given equation (6), will get

$$K_p = \frac{[C]^c [D]^d (RT)^{(c+d)}}{[A]^a [B]^b (RT)^{(a+b)}}$$

Here R and T are constants

$$\text{Now,} \quad K_p = \frac{[C]^c [D]^d (RT)^{(c+d)-(a+b)}}{[A]^a [B]^b} \quad ....(7)$$

$$\text{where;} \quad K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Now above equation (7) becomes

Concept Ladder

$$K_P = K_C (RT)^{\Delta n_g}$$

where Δn_g = no. of moles of gaseous product no. of moles of gaseous reactant.

If $\Delta n_g > 0$, then $K_P > K_C$

If $\Delta n_g < 0$, then $K_P < K_C$

If $\Delta n_g = 0$, then $K_P = K_C$

Previous Year’s Question

In which of the following equilibrium K_C and K_P are not equal? **[NEET]**

(1) $2NO(g) \rightleftharpoons N_2(g) + O_2 g$

(2) $SO(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

(3) $H_2(g) + I_2(g) \rightleftharpoons 2H(g)$

(4) $2C(s) + O_2(g) \rightleftharpoons 2CO_2(g)$

Relation Between K_p and K_c

$$K_P = \frac{[P_C]^C [P_D]^C}{[P_A]^a [P_B]^b} = \frac{[C]^c [P]^d}{[A]^a [B]^b} \frac{(RT)^{c+d}}{(RT)^{a+b}}$$

Where $\Delta n_g = (c+d) - (a+b)$

$K_p = K_c (RT)^{\Delta n_g}$

if $\Delta n_g = 0$, then $K_P = K_C$

Δn_g = no. of moles of gaseous products-no. of moles of gaseous reactants

Units of equilibrium constant

Unit of $K_p = (\text{atm})^{\Delta n_g}$

Unit of K_c = $(\text{mol L}^{-1})^{\Delta n}$

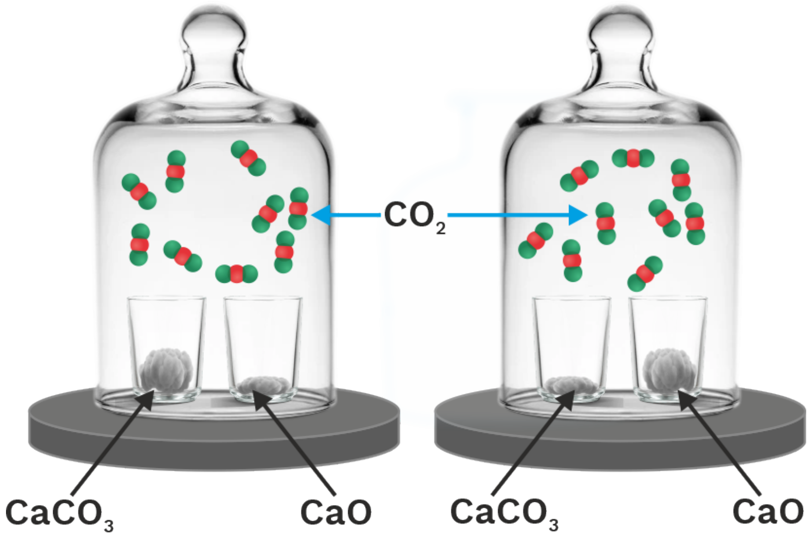
Unit of K_{X_c} = unit less

Heterogeneous Equilibrium

In a heterogeneous system, all the reactants and products are in different phases. For example, in the given reaction, $CaCO_3(\text{solid}) \xrightleftharpoons{\Delta} CaO(\text{solid}) + CO_2(\text{gas})$, reactants and products are in the heterogeneous phase.

Rack your Brain

A reaction which is unimolecular w.r.t to forward reaction and bimolecular w.r.t backward reaction has 2 and 4 moles respectively what would be the relationship between K_p & K_C?



Aa long as some $CaCO_3$ or CaO remain in the system, the amount of CO_2 above the solid will remain the same.

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

$$K_c=[CO_2] \text{ and } K_p = P_{CO_2}$$

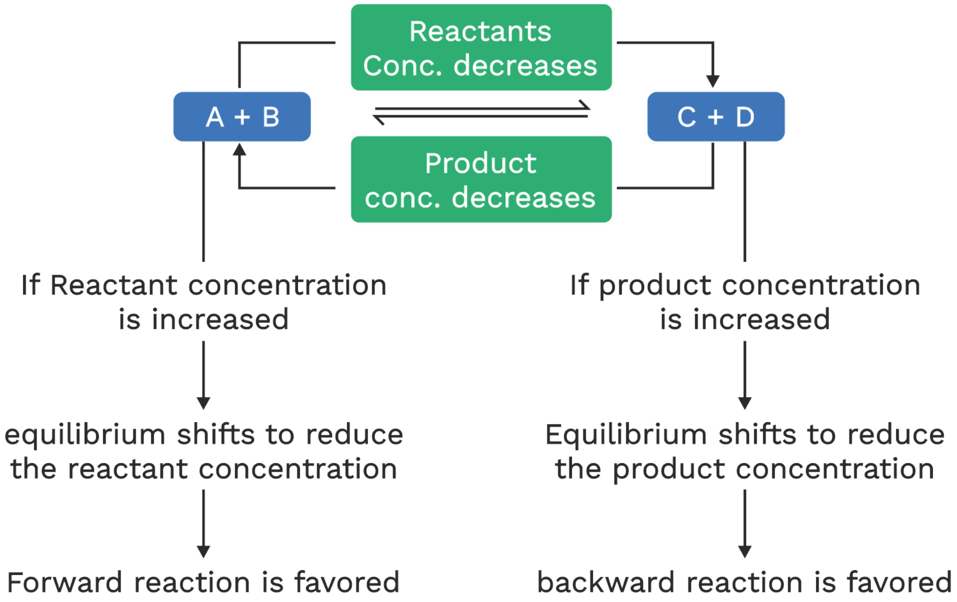
Similarly, for the reactions,

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_3(g)$$

Factors influencing equilibrium

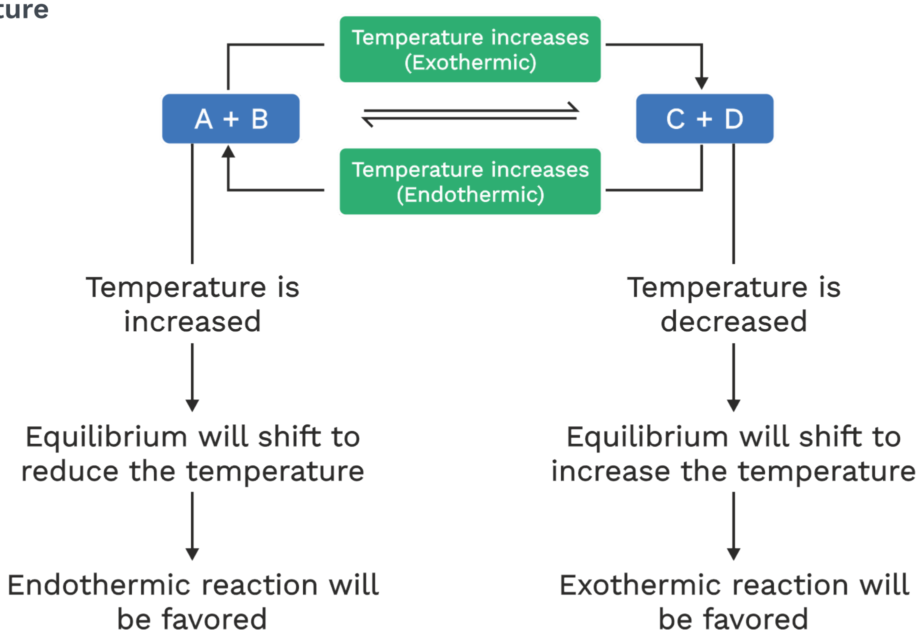
(a) Concentration



Note:

Increasing concentration of one side favours the other side.

(b) Temperature



Note :

- If the forward reaction exothermic then backward reaction will be endothermic and vice-versa.

- For exothermic reaction as temperature increases K decreases; for endothermic reaction as temperature increases K increases.
  According to van't Hoff equation

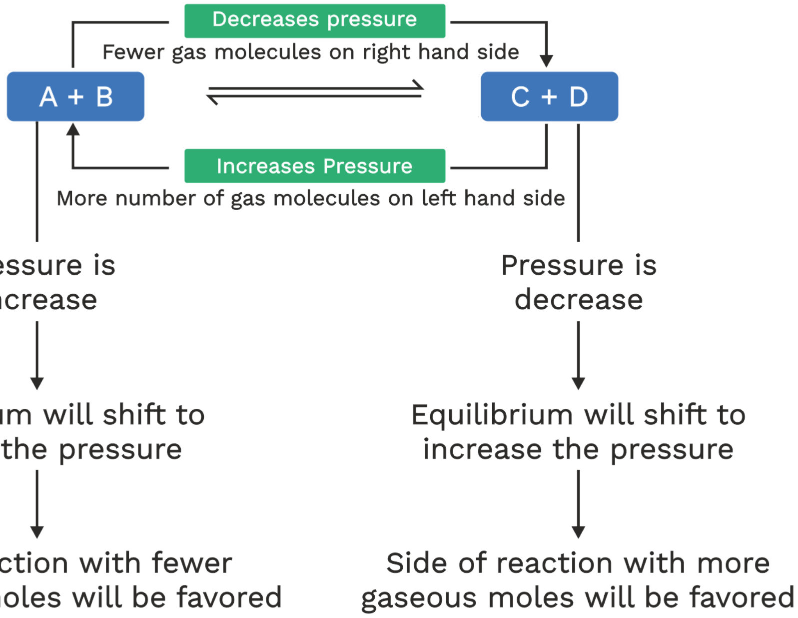
  $$\log\frac{K_2}{K_1} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

  Where K_1 and K_2 are the equilibrium constants at temperature T_1 and T_2 respectively and ΔH is the molar enthalpy change in the temperature T_1 to T_2.

Concept Ladder

When the value of ethalpy change for the reaction would be zero than the value of K is independent of temperature.

(c) Pressure



Note:

If the number of gas molecules is the same on either side, then changing of pressure will have no effect.

Q.9 The following concentrations were obtained for the formation of NH_3 from N_2 and H_2 at equilibrium at 500K. $[N_2] = 1.5 \times 10^{-2}$M, $[H_2] = 3.0 \times 10^{-2}$M, and $[NH_3] = 1.2 \times 10^{-2}$M. calculate the equilibrium constant.

A.9 The equil. const. for the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ can be written as

$$K_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3} = \frac{\left(1.2\times10^{-2}\right)^2}{\left(1.5\times10^{-2}\right)\left(3.0\times10^{-2}\right)^3} = 3.55\times10^2$$

Q.10 For the equilibrium,

$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g) K_c$ is 3.75×10^{-6} at 1069K. Calculate the K_p for this reaction at this temperature.

A.10 $K_p = K_c[RT]^{\Delta n}$

$\Delta n = (2+1) - 2 = 1$

$K_p = 3.75\times10^{-6}(0.0831\times1069)^1 = 0.033$

Q.11 The equation constants of the dissociation of various oxides of an elements A are given at constant temperature:

(1) $2A_2O(g) \rightleftharpoons 2A_2(g) + O_2(g); K_C = 4.0\times10^{30}$

(2) $2AO(g) \rightleftharpoons A_2(g) + O_2(g); K_C = 2.0\times10^{27}$

(3) $2AO_2(g) \rightleftharpoons A_2(g) + 2O_2(g); K_C = 7.0\times10^{13}$

(4) $2A_2O_5(g) \rightleftharpoons 2A_2(g) + 5O_2(g); K_C = 1.0\times10^{31}$

Write the stability of these oxides in increasing order.

A.11 $A_2O_5 < A_2O < AO < AO_2$

At higher rate constant, the reaction will have more tendency to go on completion.

In this case, metal oxide dissociates in forward direction. Therefore, the metal oxide with lesser value of equilibrium constant will be stable.

Q.12 At a certain temperature, the equilibrium constant (K_c) is 16 for the reaction:

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

If we take one mole of each of the four gases in one litre container, what would be the equilibrium concentration of NO and NO_2?

A.12

$$SO_2(g) + \quad NO_2(g) \quad \rightleftharpoons \quad SO_3(g) + NO(g)$$

Initial conc.	1	1	1	1
Equilibrium conc.	1-x	1-x	1+x	1+x

Applying the law of mass action,

$$K_C = \frac{[SO_3][NO]}{[SO_2][NO_2]} = \frac{(1+x)(1+x)}{(1-x)(1-x)} = 16$$

$$\frac{1+x}{1-x} = 4 \qquad \text{or } 1+x = 4-4x$$

Concentration of NO_2 at equilibrium = (1 – 0.6) = 0.4 mol.

Concentration of NO at equilibrium = (1 + 0.6) = 1.6 mol.

Q.13 For an ideal gas reaction

$$2A + B \rightleftharpoons C + D$$

the value of Kp will be

(1) $K_p = \frac{n_C n_D}{n_A^2 n_B} \cdot \frac{V}{RT^2}$

(2) $K_p = \frac{n_C n_D}{n_A^2 n_B} \cdot \frac{V}{RT}$

(3) $K_p = \frac{n_C n_D}{n_A^2 n_B} \cdot \frac{RT}{V}$

(4) $K_p = \frac{n_C n_D}{4n_A^2 n_B} \cdot \frac{V}{RT}$

A.13 $2A + B \rightleftharpoons C + D$

$$K_p = \frac{p_C \cdot p_D}{p_A^2 \cdot p_B} = \frac{\frac{n_C RT}{V} \cdot \frac{n_D RT}{V}}{\left(\frac{n_A RT}{V}\right)^2 \left(\frac{n_B RT}{V}\right)} = \frac{n_C n_D}{n_A^2 n_B} \cdot \frac{V}{RT}$$

Q.14 Prove that the pressure necessary to obtain 50% dissociation of PCl_5 at 250°C is numerically three times of K_p.

A.14

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
(Inital mole)	1		0		0
(Mole at equilibrium)	(1 – 0.5)		0.5		0.5

Total mole of equilibrium = (1-0.5) + 0.5 + 0.5 = 1.5

$$K_p = \frac{p_{PCl_3} \cdot p_{Cl_2}}{p_{PCl_5}} = \frac{\left(\frac{0.5}{1.5}P\right)\left(\frac{0.5}{1.5}P\right)}{\left(\frac{0.5}{1.5}P\right)} \qquad \text{(where; P = inital pressure)}$$

$$\text{or } K_p = \frac{1}{3}P$$

$$\text{or } P = 3K_p$$

Q.15 At 700K, the equilibrium constant K_p for the reaction

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

is 1.80×10^{-3} kPa. What is the numerical value of K_c in moles per litre for this reaction at the same temperature?

A.15 Given

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

1 atm = 10^5 Pa; $\Delta n = 1$

$$K_p = 1.8 \times 10^{-3} \text{K Pa} = 1.8 \text{Pa} = 1.8 \times 10^{-5} \text{atm}$$

$$T = 700 K$$

$$R = 0.082 \text{lit.atm}$$

$$K_p = K_c (RT)^{\Delta n_g}$$

$$K_c = \frac{K_p}{RT}$$

$$K_c = \frac{1.8 \times 10^{-5}}{700 \times 0.0821} = 0.031 \times 10^{-5} = 3.1 \times 10^{-7} \text{mol L}^{-1}$$

Q.16 Write the expressions for equilibrium constant for the following reactions. If the concentrations are expressed in mol L⁻¹, give the units in each case.

(1) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(2) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

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

(4) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

(5) $2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$

A.16 (1) $K_c = \dfrac{[NO_2]^2}{[N_2O_4]}$, units = mol L

(2) $K_c = \dfrac{[NO]^4 [H_2O]^6}{[NH_3]^4 [O_3]}$, units = mol L^{-1}

(3) $K_c = \dfrac{[NO]^4 [H_2O]^6}{[NH_3]^4 [O_3]}$, units = $mol^{-2}L^2$

(4) $K_c = \dfrac{[H_2][I_2]}{[HI]^2}$, no units

(5) $K_c = \dfrac{[NO_2]^4 [O_2]}{[N_2O_4]^2}$; units = mol^3L^{-3}

Applications of Equilibrium constant

(1) It can predict the extent of reaction on the basis of its magnitude.

(2) Predicting the extent of a reaction
High value of equilibrium constant indicates that products concentration is high and its low value indicates that concentration of the products in equilibrium mixture is low

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

$$K_p = \frac{(p_{HBr})^2}{(p_{H_2})(p_{Br_2})} = 5.4 \times 10^{18}$$

The large volume of equilibrium constant indicates that concentration of the product,

Previous Year's Question

If the value of equilibrium constant for a particular reaction is 1.6×10^{12}, then at equilibrium the system will contain **[NEET]**

(1) Mostly products

(2) Similar amount of reactants and products

(3) All reactants

(4) Mostly reactants.

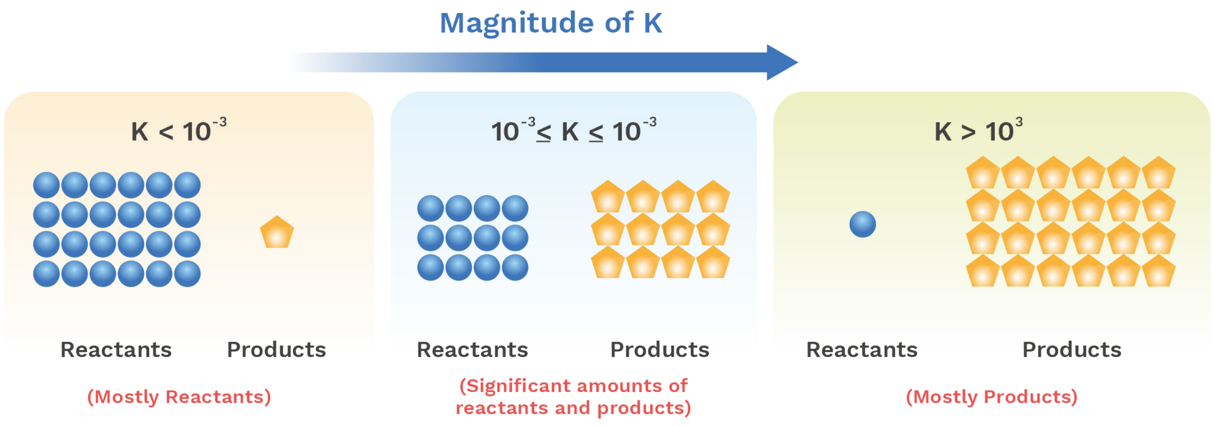
HBr is very high and reaction goes nearly to completion.

Similarly, equilibrium constant for [$H_2(g) + Cl_4(g) \rightleftharpoons 2\,HCl\,(g)$] is very high and reaction goes virtually to completion.

$$K_C = \frac{[HCl]^2}{[H_2][Cl_2]} = 4.0 \times 10^{31}$$

Rack your Brain

An equilibrium reaction has the value of rate constant as 3.8 × 10^{21}. What will happen to the reaction.



- The reaction of hydrogen with oxygen at 500 K temperature has a very large equilibrium constant, $K_c = 2.4 \times 10^{47}$
- When H_2O is decomposed into H_2 and O_2 at 500K, it has a very small equilibrium constant, $K_c = 4.1 \times 10^{-48}$

Note:

large value of K_P, or K_C (larger than about 10^3), favour the products strongly. For intermediated values of K (approximately in the range of 10^{-3} to 10^3), the concentrations of reactants and products are comparable. Small values of equilibrium constant (smaller than 10^{-3})., favour the reactants strongly.

At 298 K for reaction,

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

$$K_C = \frac{[NO]^2}{[N_2][O_2]} = 4.8 \times 10^{-31}$$

Previous Year's Question

In Haber process, 30 litres of dihydrogen and 30 litres of dinitrogen were taken for reaction which yielded only 50% of the expected product. What will be the composition of gaseous mixture under the aforesaid condition in the end? **[AIIMS]**

(1) 20 litres ammonia, 20 litres nitrogen, 20 litres hydrogen
(2) 10 litres ammonia, 25 litres nitrogen, 15 litres hydrogen
(3) 20 litres ammonia, 10 litres nitrogen, 30 litres hydrogen
(4) 20 litres ammonia, 25 litres nitrogen, 15 litres hydrogen

The very small value of. implies that reactants N_2, and 0_2, will be the predominant species in the reaction mixture at equilibrium

(ii) Predicting the direction of the reaction.

The equilibrium constant is also used to find in which direction the reaction will proceed fora given concentration of reactants and products. For this purpose, we calculate the Reaction Quotient (Q). The reaction quotient is defined in the same way as the equilibrium constant (with molar concentrations to give Q_c, or with partial pressure to give Q_P) at any stage of reaction. Fora general reaction:

$$n_1A + n_2B \rightleftharpoons m_1C + m_2D$$

$$Q_C = \frac{[C]^{m_1}[D]^{m_2}}{[A]^{n_1}[B]^{n_2}}$$

Note:

If $Q_C > K_C$ the reaction will proceed in the backward direction

If $Q_c < K_c$, the reaction will move in the forward direction

If $Q_c = K_C$ then reaction will be in equilibrium.

(a) K>>1	If **K>>1,** the reaction is product-favoured; product predominates at **Equilibrium.**
(b) K>>1	If **K>>1,** the reaction is product-favoured; product predominates at **Equilibrium.**
(c) K=1	The reaction lies in the middle (mix of reactants and products)

Previous Year's Question

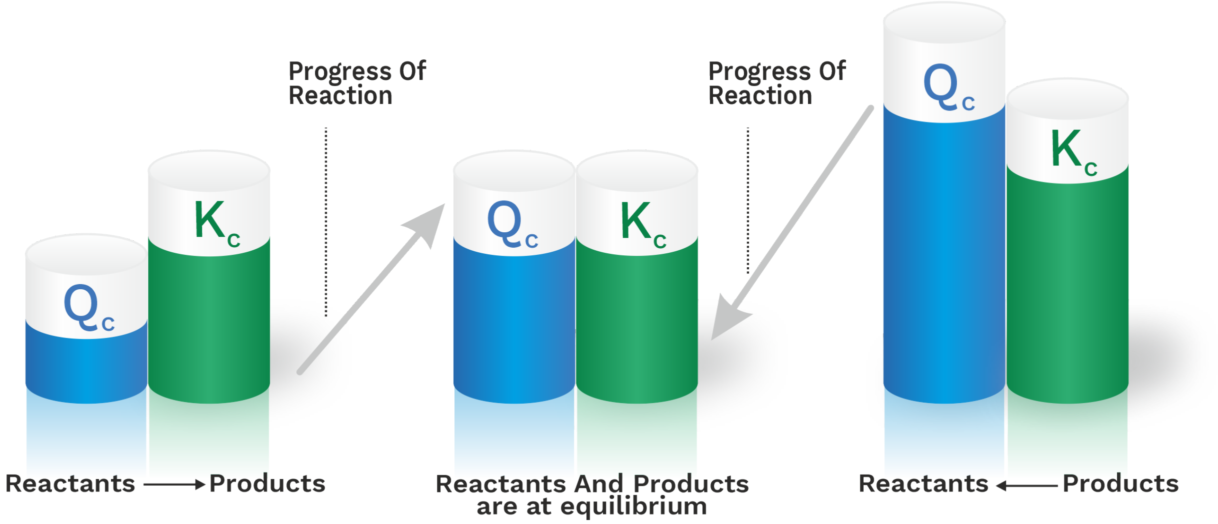
The reaction quotient (Q) for the reaction

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

is given by $Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$. The reaction will proceed from right to left if. **[AIPMT]**

(1) $Q = K_C$ (2) $Q < K_C$

(3) $Q > K_C$ (4) $Q = 0$



For example,

In the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, if the molar concentration of H_2, I_2 and HI are 0.1 mol L^{-1} respectively at 783K, then reaction quotient at this stage of the reaction is

$$Q_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.4)^2}{(0.1)(0.2)} = 8$$

K_C for this reaction at 783 K at 46 and we find that $Q_C < K_C$. The reaction, therefore, will move to right i.e. more H_2 and I_2 will react to form more HI and their concentration will decrease till $Q_C = K_c$.

Degree of Dissociation

Degree of dissociation is the ratio of a mole of the reactant dissociated to the reactant present initially. It is represented by ‘α’

$$\alpha = \frac{\text{no. of moles of reactant dissociated}}{\text{no. of moles of reactant present initially}}$$

For example,

For reversible reaction

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

Moles initially	a	0	0
At equilibrium;	$a(1-\alpha)$	$\frac{a\alpha}{2}$	$\frac{3a\alpha}{2}$

Here, α represented the degree of dissociation.

The process of formation of ammonia takes place by combination of nitrogen and hydrogen gases in the presence of molybdenum as promoter and iron as catalyst.

This process is known as Haber’s process. The reactants and products are in equilibrium phase with each other.

This process takes place at a temperature range 400 - 450 °C and pressure range of 150 - 200 atm.

Rack your Brain

The value of Q_C for a reaction is determined on the basis of active mass. Why not some other term is considered to calculate it?

Previous Year’s Question

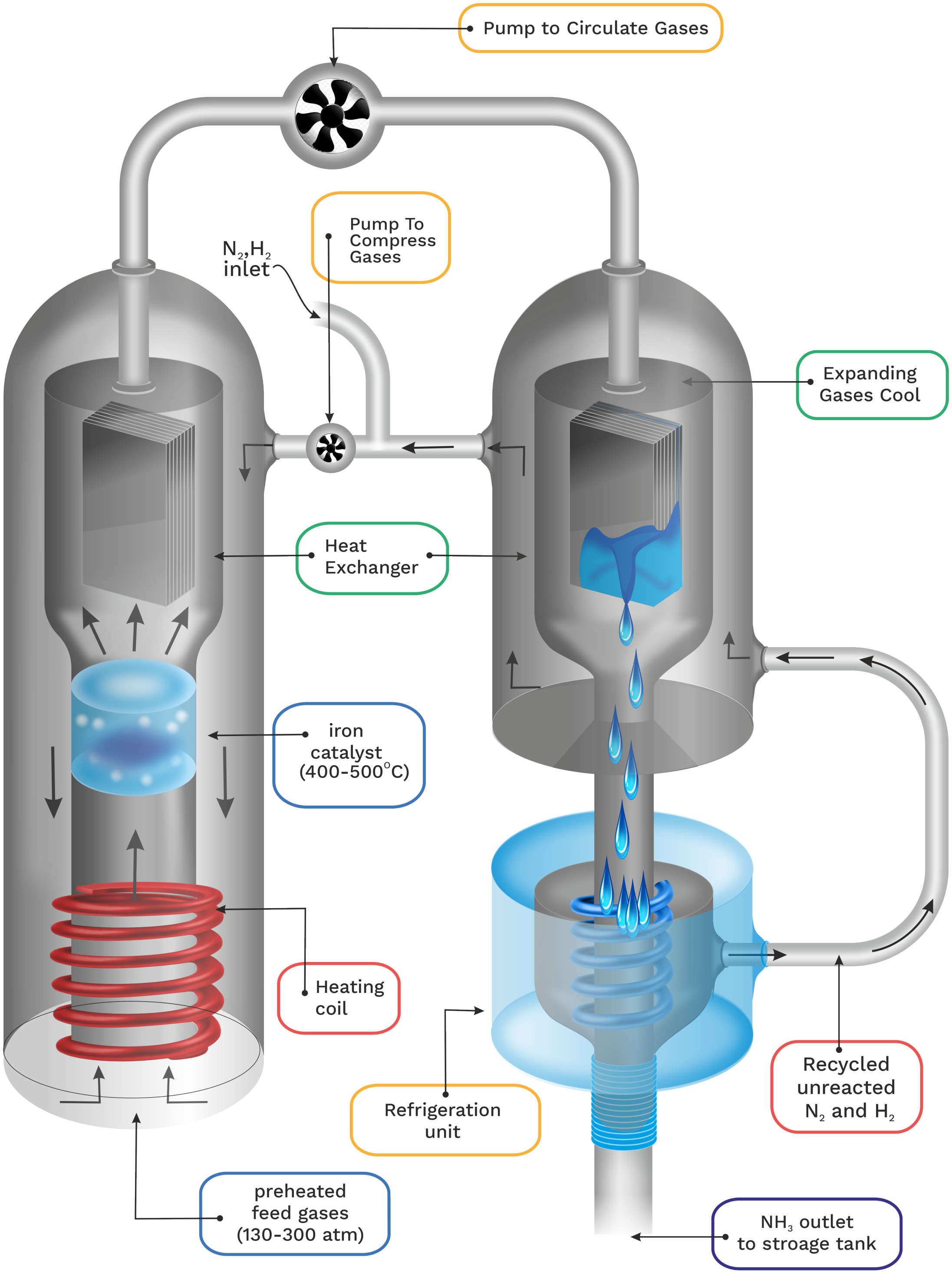
If α is dissociation constant, then the total number of moles for the reaction, $2HI \longrightarrow H_2 + I_2$ will be

[AIPMT]

(1) 1
(2) 1-α
(3) 2
(4) 2-α

Definitions

Degree of dissociation is the fraction of molecules dissociated at any given time.



Pump to Circulate Gases
Pump To Compress Gases
N_2,H_2 inlet
Expanding Gases Cool
Heat Exchanger
iron catalyst (400-500°C)
Heating coil
Refrigeration unit
Recycled unreacted N_2 and H_2
preheated feed gases (130-300 atm)
NH_3 outlet to stroage tank

Q.17 2.56 gm of sulphur S_8(s) is taken which is in equilibrium with its vapour according to reaction, If vapour occupies 960 mL at 1 atm and 273 K then the degree of dissociation of S_8(s) will be

(1) 0.5 (2) 0.55

(3) 0.4 (4) 0.44

A.17 $$n_{S_8} = \frac{2.56}{8 \times 32} = 0.01$$

$$S_8(s) \rightleftharpoons 8S(g)$$

$$0.01(1-\alpha) \qquad 8 \times 0.1 \times \alpha$$

$$1 \times \frac{960}{1000} = (0.01 \times 8 \times \alpha) \times 0.08 \times 273$$

$$\alpha = 0.55$$

Q.18 For the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

The degree of dissociation (α) of HI(g) is related to equilibrium constant K_p by the expression.

(1) $\frac{1+2\sqrt{K_p}}{2}$ (2) $\sqrt{\frac{1+2K_p}{2}}$ (3) $\sqrt{\frac{2K_p}{1+2K_p}}$ (4) $\frac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$

A.18

	$2HI(g)$	$\rightleftharpoons$ $H_2(g)$ +	$I_2(g)$
Initial	1	0	0
At equilibrium	1− α	$\alpha/2$	$\alpha/2$

$$K_p = \frac{\left(\frac{\alpha}{2} P_T\right)^2}{(1-\alpha)^2 P_T^2} \qquad \left(\because K_p = \frac{P_{I_2} \times P_{H_2}}{(P_{HI})^2}\right)$$

$$\frac{\alpha}{1-\alpha} = 2\sqrt{K_p} \qquad \alpha = \frac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$$

Q.19 For the dissociation reaction $N_2O \rightleftharpoons 2NO_2(g)$, the equilibrium constant K_P is 0.120 atm at 298K and total pressure of system is 2 atm. Calculate the degree of dissociation of N_2O_4.

A.19 For the reaction $N_2O \rightleftharpoons 2NO_2(g)$

Initial 1 0

At equilibrium $(1-\alpha)$ 2α

Let α be the degree of dissociation and P is the total pressure, then

Total number of moles $= 2\alpha + 1 - \alpha = 1 + \alpha$

$\therefore P_{N_2O} = \text{moles of } N_2O \times P_{total}$

$$= \left(\frac{1-\alpha}{1+\alpha}\right)P$$

and $P_{NO_2} = \left(\frac{2\alpha}{1+\alpha}\right)P$

$$\therefore K_P = \frac{\left(P_{NO_2}\right)^2}{P_{N_2O}} = \frac{\left[\left(\frac{2\alpha}{1+\alpha}\right)P\right]^2}{\left(\frac{1-\alpha}{1+\alpha}\right)P}$$

$$= \frac{4\alpha^2P^2}{1+\alpha} \times \frac{1+\alpha}{(1-\alpha)P} = \frac{4\alpha^2P}{1-\alpha^2} \qquad \text{....... (i)}$$

Given atm; K_P = 0.120 atm; P = 2 atm

Substituting all the values in equation (i), we get

$$0.120 = \frac{4\alpha^2(2)}{\left(1-\alpha^2\right)} = \frac{8\alpha^2}{\left(1-\alpha^2\right)}$$

$$\Rightarrow 0.120\left(1-\alpha^2\right) = 8\alpha^2$$

Degree of dissociation, $\alpha = \left(\frac{0.120}{8.12}\right)^{1/2} = 0.121$

Calculation of K_P and K_C

(a) Homogeneous equilibrium in gaseous phase
(b) Homogeneous equilibrium in solution phase
(c) Equilibrium constant for various heterogeneous equilibrium

(a) Homogeneous equilibrium in gaseous phase

Formation of Nitric Oxide : ($\Delta n = 0$)

1. Calculation of K_C :–

Suppose the initial concentration of N_2 and O_2 is a and b respectively. x is the degree of dissociation.

	N_2 +	$O_2 \rightleftharpoons$	$2NO$
Initial moles	a	b	0
Moles at equilibrium	(a – x)	(b – x)	2x
Active mass (mol l^{-1})	$\frac{(a-x)}{V}$	$\frac{(b-x)}{V}$	$\frac{2x}{V}$

Here, V is the vol. of container in litre.

According to the law of mass action

$$K_C = \frac{[NO]^2}{[N_2][O_2]}$$

Substitution the values in the above equation

$$K_C = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)}$$

$$\boxed{K_C = \frac{4x^2}{(a-x)(b-x)}}$$

K_C for this reaction is independent of V of the reaction container.

Concept Ladder

The numerical value of equilibrium constant K_C is not influenced by catalyst. Presence of a catalyst simply helps in attaining the equilibrium earlier

Previous Year's Question

The reaction,

$$2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$$

is begun with the concentrations of A and B both at an initial value of 1.00 M. When equilibrium is reached, the concentration of D is measured and found to be 0.25M. The value for the equilibrium constant for this reaction is given by the expression **[AIPMT]**

(1) $\left[(0.75)^3(0.25)\right] \div \left[(1.00)^2(1.00)\right]$
(2) $\left[(0.75)^3(0.25)\right] \div \left[(0.50)^2(0.75)\right]$
(3) $\left[(0.75)^3(0.25)\right] \div \left[(0.50)^2(0.25)\right]$
(4) $\left[(0.75)^3(0.25)\right] \div \left[(0.75)^2(0.25)\right]$

2. Calculation of K_P

All the thing being same as above, except pressure. Let P atmosphere is the pressure at equilibrium

	N_2	+	$O_2 \rightleftharpoons$	$2NO$
Initial moles	a		b	0
At equilibrium	(a – x)		(b–x)	2x

Total no. of moles = (a – x) + (b – x) + 2x = (a + b)

$$P_{N_2} = \frac{(a-x)P}{(a+b)}$$

$$P_{O_2} = \frac{(b-x)P}{(a+b)}$$

$$P_{NO} = \frac{(2x)P}{(a+b)}$$

Rack your Brain

The value of K_P depends upon partial pressure of gases at equilibrium. Would it depend upon degree of dissociation?

According to the law of mass action

$$K_P = \frac{[P_{NO}]^2}{[P_{N_2}][P_{O_2}]}$$

Substituting the value of P_{NO}, P_{N_2}, P_{O_2} in the above equation of K_P.

$$K_P = \frac{\left[\frac{(2x)P}{(a+b)}\right]^2}{\left[\frac{(a-x)P}{(a+b)}\right]\left[\frac{(b-x)P}{(a+b)}\right]}$$

$$K_P = \frac{4x^2}{(a-x)(b-x)}$$

Thermal Dissociation of Phosphorus pentachloride ($\Delta n > 0$)

Concept Ladder

K_P and K_C are equilibrium constant of ideal gas mixture considered under reversible reaction K_P is an equilibrium constant wrt. to atmospheric pressure and the K_C is the equilibrium constant wrt. concentration expressed in molarity.

Dissociation of PCl_5

1. **Calculation of K_C :** Suppose one mole of PCl_5 is take in a closed container of V litre. Further at equilibrium x mol of PCl_5 dissociated

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

	PCl_5	PCl_3	Cl_2
Initial moles	1	0	0
Moles at equilibrium	(1 – x)	x	x
Concentration (mol l^{-1})	$\frac{1-x}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

According to law of mass action

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

Substituting the values in the above equation.

$$K_C = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{1-x}{V}\right)}$$

$$\boxed{K_C = \frac{x^2}{(1-x)V}}$$

The formula of K_C has V in the denominator, hence the equilibrium will be affected by V of the reaction container for the given reaction.

If x << 1, then, $1 - x \approx 1$

So, $$K_C = \frac{x^2}{V}$$

$$x^2 = K_C.V$$

$$x^2 \propto V$$

$$\boxed{x \propto \sqrt{V}}$$

If we increase the volume, the dissociation x is also increased.

Previous Year's Question

The dissociation equilibrium of a gas AB_2 can be represented as:

$$2AB_{2(g)} \rightleftharpoons 2AB_{(g)} + B_{2(g)}$$

the degree of dissociation is x and is small compared to 1. the expression relating the degree of dissociation (x) with equilibrium constant K_P and total pressure P is **[AIPMT]**

(1) $(2K_P/P)^{1/2}$

(2) (K_P/P)

(3) $(2K_P/P)$

(4) $(2K_P/P)^{1/3}$

Concept Ladder

The numerical value of K_C is independent of initial concentration of reactants and product.

2. Calculation of K_p

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Initial moles 1 0
0

Moles at equilibrium (1 – x) x
x

total no. of moles at equilibrium,

$$(1-x)+x+x=(1+x)\text{ moles}$$

According to law of mass action

$$K_P = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}}$$

At equilibrium $P_{PCl_3} = \dfrac{x \times P}{(1+x)}$

$$P_{Cl_2} = \frac{x \times P}{(1+x)}$$

$$P_{PCl_5} = \frac{(1-x)P}{(1+x)}$$

Substituting the values in the above equation of K_P –

$$K_P = \frac{\left(\dfrac{x \times P}{1+x}\right)\left(\dfrac{x \times P}{1+x}\right)}{\dfrac{(1-x) \times P}{(1+x)}}$$

The equation of K_P is not independent of pressure.

Suppose, x<<1, then, $1 - x^2 \approx 1$

$$K_P = x^2P$$

$$x^2 = \frac{K_P}{P}$$

$$\boxed{x \propto \frac{1}{\sqrt{P}}}$$

The degree of dissociation of PCl_5 is inversely proportional to the square root of pressure so, decrease of pressure increases dissociation of PCl_5.

Rack your Brain

Why the concentration of pure solid and liquid should be ignored while writing the equilibrium constant expression?

Previous Year's Question

In which of the following equilibrium K_C and K_P are not equal? **[AIPMT]**

(1) $2NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$

(2) $SO_{2(g)} + NO_{2(g)} \rightleftharpoons 2HI_{(g)}$

(3) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

(4) $2C_{(s)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$

Formation of Ammonia – (Δn < 0)

1. Calculation of K_C :

	N_2 +	$3H_2 \rightleftharpoons$	$2NH_3$
Initial moles	1	3	0
moles at equilibrium	(1 – x)	(3 – 3x)	2x
Active mass (mol l^{-1})	$\left(\frac{1-x}{V}\right)$	$\left(\frac{3-3x}{V}\right)$	$\left(\frac{2x}{V}\right)$

According to law of mass action

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Substituting the values in the above equation

$$K_C = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)\left(\frac{3-3x}{V}\right)^3}$$

$$K_C = \frac{4x^2V^2}{(1-x)(3-3x)^3}$$

$$K_C = \frac{4x^2V^2}{27(1-x)^4}$$

The formula of K_C has V in the numerator; hence the equilibrium will be affected by V of the reaction container.

Dependence If, x<<1 then, $(1-x)^4 = 1$

$$K_C = \frac{4x^2V^2}{27}$$

$$x^2 = \frac{27K_C}{4V^2}$$

$$x^2 \propto \frac{1}{V^2} \qquad \boxed{x \propto \frac{1}{V}}$$

If we increase the volume of container the degree of dissociation x is decreased.

Previous Year's Question

Equilibrium constant K_P for following reaction

$$MgCO_{3(s)} \rightleftharpoons MgO_{(s)} + CO_{2(g)}$$

[AIPMT]

(1) $K_P = P_{CO_2}$

(2) $K_P = K_{CO_2} \times \frac{P_{CO_2} \times P_{MgO}}{P_{MgCO_3}}$

(3) $K_P = \frac{P_{CO_2} \times P_{MgO}}{P_{MgCO_3}}$

(4) $K_P = \frac{P_{MgCO_3}}{P_{CO_2} \times P_{MGo}}$

2. Calculation of K_P:

	N_2	$+ 3 H_2 \rightleftharpoons$	$2NH_3$
Initial concentration	1	3	0
moles at equilibrium	(1-x)	(3-3x)	2x

Total number of moles at equilibrium $= (1-x)+(3-3x)+2x = (4-2x)$

According to the law of mass action

$$K_P = \frac{\left(P_{NH_3}\right)^2}{\left(P_{N_2}\right)\times\left(P_{H_2}\right)^3}$$

At equilibrium; $p_{NH_3} = \dfrac{(2x).P}{(4-2x)}$

$$p_{N_2} = \frac{(1-x).P}{(4-2x)}$$

$$p_{H_2} = \frac{(3-3x).P}{(4-2x)}$$

Substituting the values in the above equation of K_P.

$$K_P = \frac{\left(\frac{2x}{4-2x}.P\right)^2}{\left(\frac{1-x}{4-2x}.P\right)\left(\frac{3-3x}{4-2x}.P\right)}$$

$$K_P = \frac{4x^2(4-2x)^2}{(1-x)(3-3x)^3P^2}$$

$$\boxed{K_P = \frac{16x^2(2-x)^2}{27(1-x)^4P^2}}$$

The equation of K_P is not independent of pressure

Suppose, x << 1 then,

$$(1-x)^4 = 1$$

And $(2-x)^2 = 4$

$$K_P = \frac{64x^2}{27P^2}$$

$$x^2 \propto P^2 \qquad \boxed{x \propto P}$$

If we increase the pressure the degree of dissociation x is also increased.

Previous Year's Question

A 20 litre container at 400K contains $CO_{2(g)}$ at pressure 0.4 atm and an excees of SrO (neglect the volume of solid SrO). the volume of the container is now decreased by moving the movable piston fitted in the container. The maximum volume of the container, when pressure of CO_2 attains its maximum value, will be

(Given by: $SrCO_{3(s)} \rightleftharpoons SrO_{(s)} + CO_{2(g)}$

K_P = 1.6 atm) **[NEET]**

(1) 10 litre (2) 4 litre

(3) 2 litre (4) 5 litre

(b) Homogeneous equilibrium is solution phase

Formation of ethyl acetate

Equilibrium is represented as

$$C_2H_5(OH)(\ell) + CH_3COOH(\ell) \rightleftharpoons CH_3COOC_2H_5(\ell) + H_2O(\ell)$$

Initial moles	1	1	0	0
Moles at equilibrium	1-x	1-x	x	x

$$K_C = \frac{[CH_3COOC_2H_5][H_2O]}{[C_2H_5OH][CH_3COOH]}$$

$$K_C = \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{(1-x)}{v} \times \frac{(1-x)}{v}} = \frac{x^2}{(1-x)(1-x)}$$

Previous Year's Question

If the concentration of HO^- ions in the reaction $Fe(OH)_{3(s)} \rightleftharpoons Fe^{3+}_{(aq)} + 3OH^-_{(aq)}$ is decreased by 1/4 times, then equilibrium concentration of Fe^{3+} will increase by **[AIPMT]**

(1) 64 times (2) 4 times

(3) 8 times (4) 16 times

(c) Equilibrium constant for various heterogeneous equilibrium

Heterogenous equilibrium results from a reversible reaction involving reactants and product that are in different phases. The law of mass action is applicable to a homogeneous equilibrium and is also applicable to a heterogeneous system.

1. Decomposition of solid $CaCO_3$ into solid CaO and gaseous CO_2

Let 'a' moles of $CaCO_3$ are taken in a vessel of volume 'V' litre at temperature 'T' K.

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

Moles initially	a	0	0
Moles at equilibrium	a – x	x	x

$$K_{eq} = \frac{[CaO][CO_2]}{[CaCO_3]}$$

As $CaCO_3$ and CaO(s) are pure solids, so their concentration is unity

$$\therefore K_C = \frac{P_{CO_2}}{RT}$$

$$K_C(RT) = P_{CO_2}$$

Since K_C R and T are constant, their product will also be a constant referred as K_P.

$$\therefore K_P = P_{CO_2} = \frac{xRT}{V}$$

Simultaneous Equilibrium

In simultaneous equilibrium more than one equilibrium are established in a vessel at the same time and any one of the reactant or product is common in more than one equilibrium, then the equilibrium concentration of the common species in all the equilibrium would be same.

For example, if we take $CaCO_3$(s) and C(s) together in a vessel of capacity 'V' litre and heat it at temperature 'T' K, then CaCO3 decomposes to CaO(s) and CO_2(g). further, evolved CO_2 combines with the C(s) to give carbon monoxide. Let the moles of $CaCO_3$ and carbon taken initially be 'a' and 'b' respectively.

Concept Ladder

Equilibrium concentration of common species at equilibrium are always same in case of simultaneous equilibrium.

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

Moles at equilibrium $\quad a - x \qquad x \qquad (x - y)$

$$CO_2(s) + C(s) \rightleftharpoons 2\,CO(g)$$

Moles at equilibrium $\quad (x - y) \quad (b - y) \qquad 2y$

Thus, as CO_2 is common in both the equilibrium so its concentration is same in both the equilibrium constant expression.

Equiliibrium constant for first equilibrium,

$$K_{C_1} = [CO_2] = \frac{x - y}{V}$$

Equilibrium constant for second equilibrium,

$$K_{C_2} = \frac{[CO]^2}{[CO_2]} = \frac{(2y)^2\,V}{V^2(x-y)} = \frac{4y^2}{V(x-y)}$$

Calculation of Degree of dissociation by vapour density measurement

Reactions in which there is a change in the number of moles after dissociation, the extent of dissociation can be determined by vapour density measurement.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

	PCl_5	PCl_3	Cl_2	
Initially	1	0	0	
Moles at equilibrium	(1 – a)	a	a	(‘α’ is the degree of dissociation)

Total number of moles at equilibrium; $(1-\alpha)+\alpha+\alpha=(1+\alpha)$

V is the vol. occupied by 1 mol of PCl_5(s) which have vapour density is ‘D’ before dissociation and after dissociation is ‘d’. For the same conditions, the volume occupied by (1 + a) moles at equilibrium would be (1 + a)V litre.

$$\text{Density} \propto \frac{1}{\text{Volume}}$$

$$D \propto \frac{1}{V} \quad d \propto \frac{1}{(1-\alpha)V}$$

or $$\frac{D}{d} = \frac{\frac{1}{V}}{\frac{1}{(1+\alpha)V}} = (1+\alpha)$$

or $$\alpha = \frac{D}{d} - 1 = \frac{D-d}{d}$$

Molecular mass = 2 × Vapour density

So $$\alpha = \frac{M_t - M_0}{M_0}$$

Where, M_t = calculated molecular mass

M_0 = observed molecular mass

Concept Ladder

For polymerization reaction

$nA(g) \rightleftharpoons A_n(g)$, where $n \geq 2$

$$\alpha = \frac{D-d}{d\left(\frac{1}{n}-1\right)} = \frac{M_t - M_0}{M_0\left(\frac{1}{n}-1\right)}$$

Rack your Brain

In which case the degree of dissociation constant be determined by measuring vapour density?

Q.20 At 627°C and 1 atm SO_3 is partially dissociated into SO_2 and O_2 by the reaction

$$SO_3(g) \rightleftharpoons SO_2(g) + 1/2\,O_2(g)$$

The density of the equilibrium mixture is 0.925g L^{-1}. What is the degree of dissociation.

A.20 Let the molecular mass of the mixture at equilibrium be .
Applying the reaction

$$M_{mix} = \frac{dRT}{P} = \frac{0.925 \times 0.0821 \times 900}{1} = 63.348$$

Molecular mass of $SO_3 = 80$

Vapour density of $SO_3, D = \frac{80}{2} = 40$

Vapour density of mixture, $d = \frac{68.348}{2} = 34.174$

Let the degree of dissociation be x.

$$x = \frac{D-d}{(n-1)d} = \frac{40 - 34.174}{\left(\frac{3}{2} - 1\right) \times 34.174} = \frac{5.826 \times 2}{34.174} = 0.34$$

or x = 34% dissociated
i.e. SO_3 is 34% dissociated.

Q.21 The vapour density of N_2O_4 at a certain temperature is 30. Calculate the percentage dissociation of N_2O_4 at this temperature.

A.21 $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Molecular mass of $N_2O_4 = (28 + 64) = 92$

Vapour density, $D = \frac{92}{2} = 46$

Let the degree of dissociation be x.
Given, d = 30
Applying the relationship,

$$x = \frac{D-d}{d} = \frac{(46-30)}{30} = \frac{16}{30} = 0.533$$

Degree of dissociation = 53.3%

LE-CHAPTELIER'S PRINCIPLE

How an equilibrium state relieves the external stress?

How a state in equilibrium (a stable state) adjusts to the external stress (change in Temperature, pressure or concentration of reactants/products) is generalised in Le-Chatelier's principle.

Le-Chatelier's Principal states that :

If a stress is applied on a system in equilibrium, the equilibrium condition is upset; A net reaction occurs in that direction which tends to relieve the external stress and finally a new equilibrium is attained.

To understand its application to a system, let us consider following example :

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

ΔH = -92 kJ for Forward Reaction

ΔH = +92 kJ for Backward Reaction

Note :

ΔH : Enthalpy Change is a measure of heat evolved or heat absorbed in a chemical reaction. It is negative when heat is evolved and positive when heat is absorbed during a chemical change. You will learn details of it later in the Chapter on Chemical Energetics.

Note that in the above reaction :

(a) Forward reaction is exothermic (favours formation of NH_3) and backward reaction is endothermic (favours decomposition of NH_3)

(b) Formation of NH_3 results in decrease in number of moles (from 4 total moles of N_2 and H_2 to 2 total moles of NH_3) is a decrease in volume to right (in forward reaction)

(c) Both reactants and products are gases and they will be influenced by changes in P, T and changing concentrations.

Concept Ladder

According to Le-Chatelier, to get better yield of NH_3-

(a) High pressure

(b) Low Pressure

(c) High concentration of reactants

(d) Low concentration of product

Previous Year's Question

For the reversible reaction,

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + \text{heat}$$

The equilibrium shifts in forward direction **[NEET]**

(1) by increasing the concentration of $NH_{3(g)}$

(2) by decreasing the pressure

(3) by decreasing the concentrations of $N_{2(g)}$ and $H_{2(g)}$

(4) by increasing pressure and decreasing temperature.

Effect of Temperature

Temperature can be increased by adding heat and can be decreased by taking out heat from the system.

- Increase the temperature by supplying heat: According to Le-Chatelier's principle the disturbed equilibrium state will move in that direction where heat is being absorbed (where stress is relieved) i.e., in endothermic direction. In case of given situation, reverse direction will be favoured (that being endothermic) till whole of extra heat in consumed. so NH3 will decompose on increasing temperature.
- Decrease the temperature by extracting heat: According to Le Chatelier's principle, the system will go in the direction where heat is evolved i.e. in exothermic direction. In given situation, forward reaction will be favoured (i.e. formation of NH_3) till the new equilibrium is again established.

Note:

The new equilibrium state has a new value of equilibrium constant K on changing the temperature.

Effect of Pressure

- Increase in pressure would result in decrease in volume thereby increasing the concentration (mol/L). The system will shift in a direction where number of moles decreases (decreasing concentration). In given situation, there is decrease in number of moles in forward direction, so increasing pressure favours forward reaction (i.e, formation of NH_3)
- Decreasing the pressure would mean lower number of moles/L. The system will shift in a direction which will produce more moles. In given situation, there is increase is number

Previous Year's Question

Which of the following information can be obtained on the basis of Le-Chatelier's principle. **[AIIMS]**

(1) entropy change in a reaction
(2) Dissociation constant of a weak acid
(3) Equilibrium constant of a chemical reaction
(4) Shift in equilibrium position on changing value of a constant

Rack your Brain

Why formation of NO requires high temperature whereas formation of NH_3 is preferred at low temperature?

Previous Year's Question

According to Le-Chatelier's principle, adding heat to a solid and liquid in equilibrium will cause the **[NEET]**

(1) temperature to increase
(2) temperature to decrease
(3) amount of liquid to decrease
(4) amount of solid to decrease

of moles in reverse direction, so decreasing pressure favours backward reaction (i.e., decomposition of NH_3)

Effect of Concentration:

The Concentration can be changed in two ways :

(a) By removing some of a component or

(b) By adding some more of a component.

According to Le-Chatelier's principle :

- The addition of any component to any side (reactants and products) to a reaction in equilibrium, tends the equilibrium in the direction away from that side or one can say that it tends in that direction which consumes increase in concentration.
- In given situation ; increasing amount of pure N_2 and H_2 would favour formation of NH_3 . increasing amount of NH_3 would favour decomposition of NH_3
- The removal of any component from any side (reactants and products) of a reaction in equilibrium tends the equilibrium in the direction towards that side, or one can say the equilibrium tends in that direction which causes decrease in concentration.
- In given situation : Decreasing the amount of NH_3 from right side drives the equilibrium to forward direction i.e. favours formation of NH_3 . Decreasing amount of N_2 or H_2 from left drives the equilibrium to reverse direction i.e. favours decomposition of NH_3

Effect of Catalyst:

- Catalyst will increase the rate for both forward & backward reactions simultaneously and to the same extent in a reversible reaction. By increase in both rates, it reduces the time to reach equilibrium state.

Rack your Brain

What is the effect of a catalyst in a system at equilibrim?

Concept Ladder

Solubility of NaOH increases with temperature although dissolution is exothermic (an exception).

Previous Year's Question

Which one of the following inforation can be obtained on the basis of Le-Chatelier principle? **[AIPMT]**

(1) dissociation constant of a weak acid

(2) Entropy change in a reaction

(3) Equilibrium constant of a chemical reaction

(4) Shift in equilibrium position on changing value of a constraint

- Catalyst doesn't change the relative amounts of either reactants or products, therefore it has no effect on equilibrium constant

Evaluation of K_{eq} at different temperatures:

If K_1 be the equilibrium constant at T_1 (in Kelvin) and K_2 be the equilibrium constant at T_2 (in Kelvin) ($T_2 > T_1$), the two constants (K_1 & K_2) are related by Van't Hoff equation as follows:

$$\log_{10}\frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

Where ΔH° is the standard heat of reaction and R is gas constant.

Le-Chatelier's principle and Physical equilibrium:

Consider the physical equilibrium of change of state:

$$\text{solid} \rightleftharpoons \text{liquid}$$

Effect of pressure on melting:

When a solid melt, there is a decrease in volume for some solids (ice, quartz, carborundum, magnesium nitride, diamond etc.) and there is an increase in volume for some solids (gold, silver, sulphur, copper, iron etc.).

Melting of ice cause decrease in volume. For this type of system where there is a decrease in volume due to melting, increase in pressure will reduce the M.P. of the system. Thus, increasing the pressure will favour the melting of ice.

Similarly, increase in volume is cause due to melting of sulphur. For this type of system where there is an increase in volume due to melting, decreasing pressure will reduce the M.P. of the system. Thus, decrease in the pressure will favor the melting of sulphur.

Rack your Brain

Water boil at high temperature in pressure cooker why?

Concept Ladder

Liquid phase of H_2O, ie., water cannot exist above 647.15K and 218 atm. these values are called critical temperature and critical pressure for water.

Previous Year's Question

For a given exothermic reaction, K_P and K'_P are the equilibrium constants at temperature T_1 and T_2, respectively. Assuming that heat of reaction is constant in temperature range between T_1 and T_2 it is readily observed that **[NEET]**

(1) $K_P > K'_P$
(2) $K_P < K'_P$
(3) $K_P = K'_P$
(4) $K_P = \dfrac{1}{K'_P}$

Vapour pressure of liquids:

Considering liquid vapour equilibrium, it is an endothermic reaction towards forward direction. Therefore rise in temperature will support evaporation. This means, increasing temperature results in increase in vapour pressure of the system.

Effect of pressure on boiling point:

With increase in pressure on the system : Liquid vapour; vapours condense lowering the vapour pressure of system. This means B.P. rises with increase in pressure as to reach the pressure required for the liquid to start boiling, needs to be increased.

Effect of temperature on solubility:

Generally, formation of solution (solute in solvent) is an endothermic process. For such cases, increase in temperature, increases the solubility of solutes. In such cases, where dissolution of solute is followed by evolution of heat; increase in temperature lowers the solubility of solutes.

Solubility of gases in liquid :

With increase in temperature, the solubility of a gas decreases. This implies that with lower temperature, more gas is present in a solution as compared to a solution with higher temperature.

Effect of pressure on solubility :

There is a decrease in volume of the gas (X(g) $\rightleftharpoons$ X(aq.)) when a gas is dissolved in liquid. Therefore, increase in pressure will favour the dissolution of gas in liquid.

Rack your Brain

Why sealed soda water bottle on opening shows the evolution of gas with effervescences?

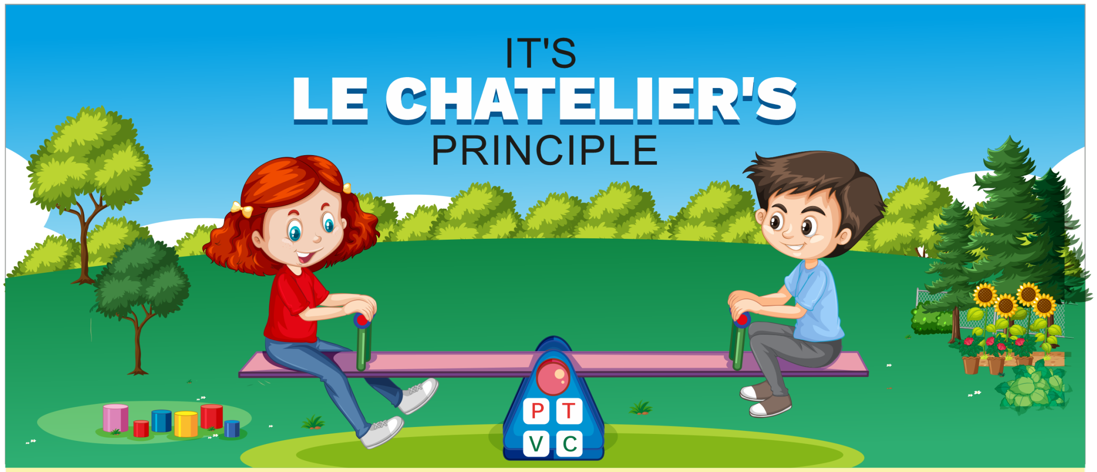
Concept Ladder

The solubility of NH_3 in water also involves H-bonding and thus, solubiliy of NH_3 in water depends on pressure as well as tendency to show H-bonding.

Rack your Brain

Ice melts slowly at higher altitude, Why?

IT'S LE CHATELIER'S PRINCIPLE



I WILL DESTROY YOUR EQUILIBRIUM

I WILL RE- ESTABLISH IT

Reactants	Products
Change a A + b B	c C + d D Counteract
I Will Increase Reactant Concentration	Then I Will Shift The Reaction Forward
I Will Steal Products	I Will Shift The Reaction Forward
I Will Increase Pressure	I Will Reduce Number Of Moles
I Will Decrease Pressure	Then I'll Increase Number Of Moles
I Will Heat Up Your Exothermic Reaction	I'll Shift The Reaction Backward
I Will Put Your Endothermic Reaction In Ice	I'll Warm It Up By Forward Reaction
I Will Catalyze Your Reaction	Hahaha.. It Won't Disturb My Equilibrium
I Will Add Noble Gases To Your Reaction	Hahaha.. It Won't Disturb My Equilibrium

How Did You Bypass My Tricks?

It's Le Chatelier's Principle Dear!

Q.22 What should be the respective active masses of methyl alcohol and carbon tetrachloride, if their densities are 0.5 and 1.2 g/mL?

(1) 15.62 and 7.79
(2) 16.65 and 7.40
(3) 15.46 and 7.80
(4) 15.40 and 6.50

A.22 (1)

$$\text{Active mass} = \frac{\text{Density} \times 1000}{\text{Molecular weight}} \quad \text{(when density in g/mL)}$$

(a) $$[\text{CH3OH}] = \frac{0.5 \times 1000}{32} = 15.62 \text{ g mol L}^{-1}$$

[Molecular weight of CH_3OH = 12 + 3 + 16 + 1 = 32]

(b) $$[\text{CCl4}] = \frac{1.2 \times 1000}{154} = 7.79 \text{ g mol L}^{-1}$$

[Molecular weight of CCl_4 = 12 + 35.5 × 4 = 12 + 142 = 154]

Q.23 Write down the equilibrium constant for the following reactions:

(a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$
(b) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
(c) $3A + 2B \rightleftharpoons C + 4D$
(d) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
(e) $2KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$
(f) $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons \text{CH¬3COOC}_2\text{H}_5(l) + H_2O(l)$
(g) $NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
(h) $H_2O(l) \rightleftharpoons H_2O(g)$

A.23 (a) $$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

(b) $$K = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

(c) $$K = \frac{[C][D]^4}{[A]^3\,[B]^2}$$

(d) $K = [CO_2]$ (Active mass of solid is 1)

(e) $K = [O_2]^3$

(f) $$K = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$ (here H_2O is not in excess)

(g) $$K = \frac{[NH_4^+][OH^+]}{[NH_3]}$$ (here H_2O is in excess (solvent) so its concentration doesn't change.)

(h) $K = [H_2O](g)$

Q.24 If 0.5 mol of H_2 is reacted with 0.5 mol of I_2 in a 10 L container at 444°C and at same temperature value of equilibrium constant KC is 49, the ratio of [HI] and $[I_2]$ will be

(1) 7 (2) $\frac{1}{7}$ (3) $\sqrt{\frac{1}{7}}$ (4) 49

A.24 (1)

$$H_2 + I_2 \rightleftharpoons 2HI$$

$$K_C = \frac{[HI]}{[H_2][I_2]} \text{ if } [H_2] = [I_2]$$

$$K_C = \frac{[HI]^2}{[I_2]^2}$$

$$\text{or} \quad \frac{[HI]}{[I_2]} = \sqrt{K_C} = \sqrt{49} = 7$$

Q.25 One mole of ammonium carbamate dissociate as shown below at 500 K.

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

If the pressure exerted by the released gases is 3.0 atm, the value of K_P is

(1) 7 atm (2) 3 atm (3) 4 atm (4) 8 atm

A.25 (3)

On applying the law of chemical equilibrium,

$$K_P = (P_{NH_3})^2(P_{CO_2})$$

Since total pressure is 3 atm, the partial pressure of $NH_3(g)$ and $CO_2(g)$ are

$$\left[P_{NH_3}\right] = 3 \times \frac{2}{3} = 2 \text{ atm}$$

$$\left[P_{CO_2}\right] = 3 \times \frac{1}{3} = 1 \text{ atm}$$

$$K_P = [2.0]^2\,[1.0] = 4.0 \text{ atm}$$

Q.26 K_p for the reaction $A(g) + 2B(g) \rightleftharpoons 3C(g) + D(g)$; is 0.05 atm. What will be its K_C at 1000 K in terms of R:

(1) $\frac{5 \times 10^{-5}}{R}$ (2) $\frac{R}{5 \times 10^{-5}}$ (3) $5 \times 10^{-5}R$ (4) None of these

A.26 (1)

We know that

$K_P = K_C (RT)^{\Delta n}$

or, $K_C = \frac{K_P}{(RT)^{\Delta n}}$

Here, $\Delta n = 4 - 3 = 1$

$T = 1000$ K, $K_P = 0.05$

$$K_C = \frac{0.05}{(R \times 1000)^1} = \frac{5 \times 10^{-5}}{R}$$

Q.27 For $N_2O_3 \rightleftharpoons NO + NO_2$, if total pressure is P atm and amount of dissociation is 50%, the value of K_p will be:

(1) 3 P (2) 2 P (3) $\frac{P}{3}$ (4) $\frac{P}{2}$

A.27 (3)

	N_2O_3	$\rightleftharpoons$	NO	+	NO_2
Initial mol	1		0		0
at equilibrium	1 – 0.5		0.5		0.5

$$K_P = \frac{x^2P}{(1+x)(1-x)} = \frac{x^2P}{1-x^2}$$

$$K_P = \frac{0.5 \times 0.5 \times P}{1.5 \times 0.5} = \frac{P}{3}$$

Q.28 The equilibrium constant for the reaction $H_2(g) + S(s) \rightleftharpoons H_2S(g)$; is 18.5 at 925 K and 9.25 at 1000 K respectively. The enthalpy of the reaction will be:

(1) −68000.05 J mol^{-1}(2) −71080.57 J mol^{-1}

(3) −80071.75 J mol^{-1} (4) 57080.75 J mol^{-1}

A.28 (2)

Using the relation,

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log \frac{9.25}{18.5} = \frac{\Delta H}{2.303 \times 8.314} \times \frac{75}{925 \times 1000}$$

$$-0.301 = \frac{\Delta H}{2.303 \times 8.314 \times 925 \times 1000} \Rightarrow \quad \Delta H = -71080.57 \text{ J mol}^{-1}$$

Q.29 In reaction,

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ $\Delta H° = -92$ kJ/mol^{-1}

concentrations of hydrogen, carbon monoxide and methanol become constant at equilibrium. What will happen if:

(1) Volume of the reaction vessel containing reactant and product is suddenly reduced to half?

(2) Partial pressure of hydrogen is suddenly doubled?

(3) An noble gas is added to the system at constant pressure?

(4) The temperature is increased?

A.29 For the equilibrium

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

$$K_C = \frac{[CH_3OH]}{[CO][H_2]^2} \Rightarrow K_P = \frac{P_{CH_3OH}}{P_{CO} \times P_{H_2}^2}$$

(1) When the volume of the vessel is suddenly reduced to half, the partial pressure of various species gets doubled. Therefore,

$$Q_P = \frac{2P_{CH_3OH}}{2P_{CO} \times (2P_{H_2})^2} = \frac{1}{4}K_P$$

Since QP is less than KP, the equilibrium shift in the forward direction producing more CH_3COH.

(2) When partial pressure of hydrogen is suddenly, Q_P changes and is no longer equal to K_P.

$$Q_P = \frac{2P_{CH_3OH}}{P_{CO} \times (2P_{H_2})^2} = \frac{1}{4}K_P$$

Equilibrium will shift from left to right.

(3) When an noble gas is added to the system at constant pressure, equilibrium shifts from lower number of moles to higher number of moles (in backward direction).

(4) By increasing the temperature, K_P will decrease the equilibrium will shift from right to left.

Q.30 A mixture of 4.2 moles of N_2, 2.0 moles of H_2 and 10.0 moles of NH_3 is introduced into a 10.0 L reaction vessel at 500 K. At this temperature, equilibrium constant K_C is

1.7 × 102, for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(i) is the reaction mixture at equilibrium?

(ii) if not, what is the direction of the reaction?

A.30 $[N_2] = \frac{4.2}{10} = 0.42$ M

$[H_2] = \frac{2.0}{10} = 0.2$ M

$[NH_3] = \frac{10}{10} = 0.1$ M

For the concentration, reaction quotient (Q) for the reaction

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

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.1)^2}{(0.42) \times (0.2)^3} = 2.976$$

But KC = 1.7 × 102

(i) Since $Q \neq K_C$, hence reaction is not at equilibrium.

(ii) Also $Q < K_C$, the reaction will proceed from left to right.

Chapter Summary

1. Equilibrium is termed as the point at which the rate of forward reaction is equal to the rate of backward reaction.

2. Chemical equilibrium is dynamic in nature and equilibrium state can be approached from both sides.

3. Active mass is molar concentration of the substance. Active mass of solid and pure liquid is taken as unity.

4. Equilibrium constant has definite value for every chemical reaction at a given temperature. It is independent of concentration and catalyst.

5. Overall K_C is equal to the product of equilibrium constant of individual reaction when a reaction is presented as the sum of two or more reactions.

6. Non-affecting factors of the equilibrium constant : The value of equilibrium constant is independent of the following factors :
   (a) Concentration of reactants and products.
   (b) Pressure
   (c) Volume
   (d) The presence of a catalyst.
   (e) Presence of inert materials

7. Degree of Dissociation

   $$\alpha = \frac{x}{a} \Rightarrow \% \ \alpha = \frac{x}{a} \times 100$$

   Where α = Degree of dissociation in percentage
   x = Number of dissociates moles
   a = Initial no. of moles

8. It is not necessary that all the types of equilibrium constants are defined for every reaction for eg. for a reaction involving only solutions K_p is not defined.

9. If inert gas mixed at constant temperature and constant volume in an equilibrium chemical reaction then total number of moles of gases are present in a container, increases i.e. total pressure of gases increases but concentration in terms of moles/litre and partial pressure of reacting substances are unchanged so dissociation (x) unchanged.

10. $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g) \rightarrow K_1$

$NO_2(g) \rightleftharpoons NO(g) + \frac{1}{2}O_2(g) \rightarrow K_2$

then $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g) \rightarrow K$

So $K = K_1 \times K_2$

11. Change in temperature, pressure or concentration favours one of the reactions and thus shift the equilibrium point in one direction.

12. A catalyst allows the system to reach a state of equilibrium more quickly.

13. Pressure and volume has no effect on the reaction in which there is no change in the number of moles.

14. If the concentration of reactants is increased and product is removed, the reaction will take place in forward direction.

15. Free energy change
$\Delta G = \Delta G° + 2.303\ RT \log Q$ At equilibrium $\Delta G = 0$, (T is in Kelvin), $Q = K$ so
$\Delta G° = -\ 2.303\ RT \log K$, where K is equilibrium constant.

Dissociation equilibria for weak acids and bases:

Weak acids are acids that dissociate partially in water. When a weak acids or bases are dissolved in water, partial dissociation occurs.

Weak acids, for example acetic acid, cannot completely donate their acidic protons to the solvent. Instead, most of the acid remains undissociated, with only a small fraction present as the **conjugate base** (CH_3COO^-).

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$

Weak acids are acids that dissociate partially in water. The extent of dissociation is given by the equilibrium constant.

The equilibrium constant for this reaction is called an acid dissociation constant, k_a, and is written as:

$$k_a = \frac{[H_3O^+][CH_3COO^-]}{[CH3COOH]} = 1.76 * 10^{-5}$$

The magnitude of k_a provides information about the relative strength of a weak acid, **The smaller k_a corresponding to a weaker acid.**

On the opposite, small pk_a values characterize stronger acids.

Table I.2: The k_a and pk_a values for a number of commonly-encountered weak acids

Compound	**k_a**	**pk_a**
Hydrocyanic acid (HCN)	4.93×10^{-10}	9.31
Hypochlorous acid (HClO)	2.95×10^{-8}	7.53
Acetic acid (CH_3COOH)	1.76×10^{-5}	4.75
Benzoic acid (C_6H_5COOH)	6.46×10^{-5}	4.19

Formic acid (HCOOH)	1.77×10^{-4}	3.75
Hydrofluoric acid (HF)	3.53×10^{-4}	3.45
Nitrous acid (HNO_2)	4.26×10^{-4}	3.37
Chloroacetic acid ($ClCH_2CO_2H$)	1.4×10^{-3}	2.85

$Ka = 10^{-pKa}$ e.g: K_a for HNO_2 = $\mathbf{10^{-3.37}}$ = 4.26×10^{-4}

For nitrous acid (weak acid) : $HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$

$$K = \frac{[H3O+][NO2-]}{[HNO2][H2O]}$$

$$K\,[H_2O] = \frac{[H3O+][NO_2-]}{[HNO2]} = Ka$$

Where Ka is the acid dissociation constant .

The ranges of k_a values characterize the strengthof acids with the corresponding degree of dissociation α values? (للاطلاع)

Type of acid	**k_a**	**pk_a**	**Degree of dissociation (α) of acid (%)**
Very strong acid	> 0.1	< 1	90-100%
Moderately strong acid	10^{-3} – 0.1	1-3	30-90%
Weak acid	10^{-5} – 10^{-3}	3-5	5-30%
Very weak acid	10^{-15} – 10^{-5}	5-15	1-5%
Extremely weak acid	< 10^{-15}	> 15	< 1%

C

Calculation of *[H_3O^+] concentration for weak acid* [HA]:

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$

$Ka = \frac{[H3O+][A-]}{[HA]}$

As $[H_3O^+] = [A^-]$ from above equation(stiochiometry)

$Ka = \frac{[H3O+]^2}{[HA]}$ (by substitution)

When dissociation is very weak , Then:

$[HA]_{eq} = [HA]_{original} - [H_3O^+] \approx C$ where $C=[HA]_{original}$

Since $[H_3O^+] = [A^-]$

Therefore, $K_a = \frac{[H3O+]^2}{C}$

$[H_3O^+] = \sqrt{Ka\ C}$

Example :

Calculate $[H_3O^+]$ concentration of 0.12 M aqueous solution of nitrous acid?

($Ka= 5.1x10^{-4}$) .

$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$

0.12 – x x x (at equilibrium)

$Ka = 5.1x10^{-4} = \frac{[H3O+][NO2-]}{[HNO2]}$

For a very weak acid $[H_3O^+] = [NO_2^-] = x$

$[HNO_2] = 0.12 - [H_3O^+] \approx 0.12$

$5.1x10^{-4} = \frac{[H3O+]^2}{0.12}$

$[H_3O^+]^2 = (5.1 \times 10^{-4} \times 0.12) = 0.612 \times 10^{-4} = 6.12 \times 10^{-5}$

$[H_3O^+] = \sqrt{6.12 \; x \; 10^{-5}} = 7.82 \times 10^{-3}$

$pH = -\log(7.82 \times 10^{-3}) = 2.11$

relative error% = $\frac{7.82x\ 10^{-3}}{0.12}$ x 100 = 6.5 % (less than 10%)

Then approximation is valid

Weak bases are bases that partially dissociate in water – only partially accept protons from the solvent – and are characterized by base dissociation constant ($\mathbf{k_b}$). For example the base dissociation constant (k_b) for the conjugate base acetate ion is given by:

$$CH_3COO^- + H_2O \rightleftharpoons OH^- + CH_3COOH$$

$$K_b = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]} = 5.71 \times 10^{-10}$$

The magnitude of (k_b) provides information about the relative strength of a weak base, with a smaller k_b corresponding to a weaker base.

Table below gives the k_b and pk_b values for a number of commonly-encountered weak bases.

The k_b and pk_b values for a number of commonly-encountered weak bases

Compound	**k_b**	**pk_b**
Acetanilide ($CH_3CONHPh$)	4.1×10^{-14}	13.39
Acetamide (CH_3CONH_2)	2.5×10^{-13}	12.60
Glycine	2.24×10^{-12}	11.65
n-Diethylamine	3.65×10^{-8}	7.44
Ammonium hydroxide (NH_4OH)	1.79×10^{-5}	4.75

Methylamine	4.38×10^{-4}	3.36
Diethylamine ($C_2H_5NHC_2H_5$)	9.6×10^{-4}	3.02

$\mathbf{K_b=10^{-pK_b}}$ e.g: K_b for Glycine = $\mathbf{10^{-11.65}}$ = 2.24×10^{-12}

For weak base :

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

C_b 0 0

$C_b - x$ x x (at equilibrium)

$K_b = \frac{[NH4+][OH-]}{[NH3]}$

When dissociation is very weak(x is very small) : $[NH_3] = C_b - x \approx C_b$

Since $[OH^-] = [NH_4^+]$ (from stiochiometry)

Therefore , $K_b = \frac{[OH-]^2}{[NH3]} = \frac{[OH-]^2}{Cb}$

$Kb = \frac{[OH-]^2}{Cb}$

$[OH^-] = \sqrt{K_b C_b}$

Example :

Calculate $[H_3O^+]$ concentration of 0.2M aqueous NH_3 solution? $K_b = 1.8 \times 10^{-5}$?

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$0.2 - x$ x x (at equilibrium)

$K_b = \frac{[NH4+][OH-]}{[NH3]}$

For very weak base $[OH^-] = [NH_4^+]$

$[NH_3] = 0.2 - [OH^-] = 0.2 \approx C_b$

$[NH_3] = C_b$

$\text{Kb} = 1.8 \times 10^{-5} = \frac{[OH-]^2}{0.2}$

$[OH^-]^2 = \sqrt{1.8x10^{-5}x0.2} \quad = \sqrt{3.6\ x\ 10^{-6}}$

$[OH^-] = 1.89 \times 10^{-3}$

Relative error % = $\frac{1.89x\ 10^{-3}}{0.2}$ x 100% = 0.95 % (approximation is valid)

$[H_3O^+] = \frac{Kw}{[OH-]} \quad = \frac{10^{-14}}{1.89\ x10\ ^{-3}}$

$[H_3O^+] = 5.29 \times 10^{-12}$

Example : **A**

Determine the pH of a 0.1 M weak acid HA solution ($k_a = 1.8x10^{-5}$). Suppose that 1 mL of this solution is added to a beaker that contains 99 mL of H_2O to produce a new solution with100 mL total volume. What is the pH value of the new solution?

Answer:

HA is a **weak acid** as the k_a value shows. It dissociates partially in water according to equation:

1. pH of the original weak acid

	HA	+ H_2O	⇌	H_3O^+	+	A^-
Initial	0.1 M			0		0
Change	-x			+x		+x
Equil.	(0.1–x)			x		x

$k_a = \frac{[H3O+][A-]}{[HA]} \quad = 1.8x10^{-5}$

$k_a = \frac{[x][x]}{[0.1-x]} \quad = 1.8x10^{-5}$

assume (0.1-x) ≈ 0.1 since HA is a weak acid and dissociates slightly in water (as the $\mathbf{k_a}$ shows). Then:

$k_a = \frac{x^2}{0.1} = 1.8x10^{-5}$

$x = \sqrt{1.8x10^{-5}x0.1} = 1.34 \text{ x } 10^{-3}$

$[H_3O^+] = 1.34 \text{ x } 10^{-3}$

relative error $= \frac{1.34x10^{-3}}{0.1}$ x100 = 1.34 %

assumption is valid since $\frac{[HA_{dissociated}]}{[HA_{initial}]}$ x 100 < 10%

pH = - log (1.34 x 10^{-3}) = 2.87

2. After dilution :

M_1V_1 (concentrated) = M_2V_2 (dilute)

0.1 x 1mL = M_2 x100 mL

$M_2 = \frac{0.1x1}{100}$ = 0.001 M

[HA] = $1x10^{-3}$ M initial conc. of the diluted solution

$k_a = \frac{[x][x]}{[0.001-x]} = 1.8x10^{-5}$

assume (0.001-x) ≈ 0.001 since HA is a weak acid and dissociates slightly in water (as the $\mathbf{k_a}$ shows).

$\frac{x^2}{0.001} = 1.8x10^{-5}$

$x = \sqrt{1.8x10^{-5}x0.001} = 1.34 \text{ x } 10^{-4}$

$[H_3O^+] = 1.34 \text{ x } 10^{-4}$

relative error $= \frac{1.34x10^{-4}}{0.001}$ x100 = 13.4 %

assumption is not valid since $\frac{[HA_{dissociated}]}{[HA_{initial}]}$ x 100 > 10%

the quadratic equation is to be used for solution

pH = 3.87 for the diluted solution

Chem 116 POGIL Worksheet - Week 10
Weak Bases, Acid Strength and Structure, Common Ion Effect, and Buffers

Why?

We have seen that the calculation of $[H_3O^+]$ and pH for a solution of a pure weak acid in water requires solving the K_a equilibrium expression for the acid. In similar fashion, calculating the concentrations of all species in a solution of a weak base in water requires solving the equilibrium expression for the bases's hydrolysis, called K_b. In basic solutions we concentrate on finding $[OH^-]$ and pOH, instead. Some weak bases are the conjugate bases of weak acids. These are generally the anions produced by the acid's hydrolysis. Like molecular bases, these conjugate bases have base hydrolysis equilibria with associated K_b values. The relationship between K_a and K_b for a conjugate acid-base pair allows us to calculate the pH of a solution of either species.

The strengths of acids and their conjugate bases are related to their molecular structure. Knowing the trends allows us to predict whether an acid is strong or weak, and if weak how it compares in strength to other similar weak acids.

Beyond solutions of pure acid or base in water, we need to look at the effect of adding extra amounts of the conjugate base or acid to the solution. The shift in the position of the equilibrium, called the *common ion effect*, changes the pH and imbues the solution with certain properties that are the basis for formulating a *buffer*. Buffer solutions are important for regulating pH in many chemical and biological systems.

Learning Objectives

- Understand the weak base hydrolysis constant, K_b, and its application to calculating the concentrations of all species in the solution.
- Know the relationship between K_a and K_b for a conjugate acid-base pair
- Know the relationships between structure types and acid strength
- Understand the effect of adding the conjugate to a solution of a weak acid or weak base
- Understand the principles of buffer solutions

Success Criteria

- Be able to calculate the concentrations of all species and pOH or pH of a solution of a pure weak base
- Be able to determine and use K_b for a conjugate base, given K_a of its conjugate acid, and vice versa.
- Be able to predict relative strengths of acids or their conjugate bases from structure considerations
- Be able to predict the effect of adding additional amounts of conjugate base or acid to a solution
- Be able to calculate the pH of a solution subject to the common ion effect
- Be able to calculate the pH of a buffer solution and to calculate the ratio of conjugate pair concentrations needed to achieve a certain pH

Prerequisite
Have read all of Chapter 16 and Sections 17.1-17.2

Information (Weak Base Hydrolysis)

When a weak base like ammonia is added to water it hydrolyzes to give small amounts of hydroxide ion and its conjugate acid in water. If we symbolize weak bases as B, then the general hydrolysis equilibrium is

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

for which we can write the equilibrium constant expression

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

We can use K_b to calculate the concentrations of all species in the solution in a manner analogous to the way we used K_a for weak acid solutions. However, with base solutions we focus on determining $[OH^-]$ first, rather than $[H_3O^+]$. Once we have determined $[OH^-]$, we can use $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ to calculate $[H_3O^+]$ and pH.

For a solution of a pure weak base in water with a moderate analytical concentration, C_B, we would have the following concentrations initially and at equilibrium:

	B	+	H_2O	$\rightleftharpoons$	BH^+	+	OH^-
Initial	C_B				0		~0
At equilibrium	$C_B - x$				x		x

Substituting into the K_b expression, we obtain

$$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{x^2}{C_B - x}$$

This is a quadratic equation of the form $x^2 + K_b x - K_b C_B = 0$. Notice that this is virtually the same equation we obtained in the weak acid case, except here $x = [BH^+] = [OH^-]$. As with the acid case, if the analytical concentration of the base is relatively large ($C_B >> K_b$), hydrolysis may be minimal and we can ignore x in the expression for [B]. Then, the equation above simplifies to $K_b = x^2/C_B$ or

$$x = \sqrt{C_B K_b} = [OH^-] = [BH^+]$$

Analogous to the acid case, if $C_B >> K_b$ by two or more powers of 10, then this simplified equation probably can be used. If $C_B \approx K_b$, within two powers of 10, then the quadratic equation will probably need to be solved. If the simplified equation is used, check its validity by calculating the percent hydrolysis of the base:

$$\% \text{ hydrolysis} = \frac{[\mathrm{OH}^-]}{C_\mathrm{B}} \times 100\%$$

If this calculation gives 5% or greater, use the more exact expression $[\mathrm{B}] = C_\mathrm{B} - x$ and solve the quadratic equation. By either method, once $[\mathrm{OH}^-]$ has been calculated, use $K_w = [\mathrm{H_3O^+}][\mathrm{OH}^-] = 1.0 \times 10^{-14}$ to calculate $[\mathrm{H_3O^+}]$, and pH + pOH = 14.00 to calculate pH.

Key Questions

1. What is the pH of a 0.120 M solution of $\mathrm{NH_3}(aq)$? For ammonia, $K_b = 1.77 \times 10^{-5}$. Is it necessary to solve the quadratic equation? Justify the approach you took, either way.

Information (K_b of Conjugate Bases and K_a of Conjugate Acids)

The conjugate base of a strong acid has little tendency to acquire $\mathrm{H^+}$ and reform the acid. Thus, $\mathrm{Cl^-}$, the conjugate base of HCl, has virtually no real base strength. But the conjugate bases of weak acids do have a tendency to acquire $\mathrm{H^+}$, and so they are real weak bases. Like any other weak base, they have a base hydrolysis equilibrium and a related K_b. For example, consider a weak acid HA and its conjugate base $\mathrm{A^-}$. The two are related to each other by the acid's hydrolysis equilibrium:

$$\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{A^-} \qquad K_a = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

But they are also related to each other by the conjugate base's hydrolysis equilibrium:

$$\mathrm{A^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{HA} + \mathrm{OH^-} \qquad K_b = \frac{[\mathrm{HA}][\mathrm{OH^-}]}{[\mathrm{A^-}]}$$

How is the value of K_a of HA related to the value of K_b of $\mathrm{A^-}$? The larger the value of K_a for an acid, the smaller the value of K_b will be for its conjugate base, and vice versa. Recall that when two equilibria are added together the equilibrium constant for the sum is the product of the individual equilibrium constants. If we add the acid hydrolysis equilibrium of HA and the base hydrolysis equilibrium of $\mathrm{A^-}$, the sum is $2\,\mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{OH^-}$, which is water's autoprotolysis equilibrium, governed by K_w:

$$\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{A^-} \qquad K_a = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

$$\mathrm{A^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{HA} + \mathrm{OH^-} \qquad K_b = \frac{[\mathrm{HA}][\mathrm{OH^-}]}{[\mathrm{A^-}]}$$

$$2\,\mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{OH^-} \qquad K_a \times K_b = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \frac{[\mathrm{HA}][\mathrm{OH^-}]}{[\mathrm{A^-}]}$$

$$= [\mathrm{H_3O^+}][\mathrm{OH^-}] = K_w$$

Therefore, in general we can write

$$K_a^{\mathrm{HA}} K_b^{\mathrm{A}^-} = K_w$$

Similarly, if we have a molecular base B with known K_b, its conjugate acid BH^+ would have a K_a given by

$$K_b^{\mathrm{B}} K_a^{\mathrm{BH}^+} = K_w$$

Conjugate bases of weak acids are true bases. For example, the acetate ion (often abbreviated OAc^-), which is the conjugate base of acetic acid (often abbreviated HOAc), can make a basic solution as a result of its base hydrolysis. The K_b value for the acetate ion can be calculated from acetic acid's $K_a = 1.78 \times 10^{-5}$, using $K_a^{\mathrm{HA}} K_b^{\mathrm{A}^-} = K_w$:

$$\mathrm{OAc^- + H_2O \rightleftharpoons HOAc + OH^-} \qquad K_b^{\mathrm{OAc}^-} = \frac{K_w}{K_a^{\mathrm{HOAc}}} = \frac{1.00 \times 10^{-14}}{1.78 \times 10^{-5}} = 5.62 \times 10^{-10}$$

But we cannot simply add acetate ions to a solution. They must be supplied in the form of an ionic salt, such as sodium acetate, which dissociates completely in water to give an equivalent amount of acetate ion and sodium ion in solution. Sodium ion has no acid-base character, so the pH of the solution is the result of the acetate ion's base hydrolysis:

$$\mathrm{NaOAc \rightarrow Na^+ + OAc^-}$$
$$\mathrm{OAc^- + H_2O \rightleftharpoons HOAc + OH^-} \qquad \mathrm{pH} > 7$$

In similar manner, we can create a solution of the conjugate acid of a molecular weak base by adding one of its soluble salts, such as a chloride. For example, ammonium chloride, NH_4Cl, when dissolved in water supplies an equivalent amount of ammonium ion, NH_4^+, the conjugate acid of ammonia, and chloride ion. The chloride ion, being the conjugate base of a strong acid (HCl) has no real acid-base character, so the pH of the solution is the result of the ammonium ion's acid hydrolysis:

$$\mathrm{NH_4Cl \rightarrow Cl^- + NH_4^+}$$
$$\mathrm{NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+} \qquad \mathrm{pH} < 7$$

The K_a for the ammonium ion can be calculated from $K_b = 1.77 \times 10^{-5}$ for ammonia.

$$\mathrm{NH_4^+ + H_2O \rightleftharpoons NH_3 + OH^-} \qquad K_a^{\mathrm{NH_4^+}} = \frac{K_w}{K_b^{\mathrm{NH_3}}} = \frac{1.00 \times 10^{-14}}{1.77 \times 10^{-5}} = 5.65 \times 10^{-10}$$

Key Questions

2. Sodium hypochlorite, NaOCl, is the active ingredient in chlorine bleach (e.g., Chlorox©). For hypochlorous acid, HOCl, $K_a = 3.0 \times 10^{-8}$.

   a. Write the equation for the base hydrolysis equilibrium of the hypochlorite ion.

   b. What is the value of K_b for the hypochlorite ion?

   c. What is the pH of a 0.10 M solution of sodium hypochlorite?

3. Trimethylamine, $(CH_3)_3N$, is a weak base ($K_b = 6.4 \times 10^{-5}$) that hydrolyzes by the following equilibrium:

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

   a. Write the equation for the acid hydrolysis equilibrium of trimethylammonium ion, $(CH_3)_3NH^+$.

   b. What is the value of K_a for the trimethylammonium ion, $(CH_3)_3NH^+$?

   c. What is the pH of a 0.12 M solution of trimethylammonium chloride, $((CH_3)_3NH)Cl$?

Information (Acid Strength and Structure)

The tendency of an acid to lose a proton to solvent water, as indicated by its K_a value, depends upon two principal factors:

- The strength of the H–A bond. The weaker the bond, the greater is the tendency to lose protons, and the larger K_a will be.

- The stability of the conjugate base in solution. The more stable the conjugate base A^-, the greater is the tendency of HA to lose protons, and the larger K_a will be.

For simple inorganic acids, the first factor is more important. The second factor is often important in comparisons among organic acids.

Acid strengths of ***binary acids***, with the general formula H_nX, increase as the H–X bond weakens. This results in the following trends:

- The larger the X atom, the weaker the H–X bond is and the stronger the acid is.

$$HF < HCl < HBr < HI$$

$$H_2O < H_2S < H_2Se < H_2Te$$

- Among acids with similar H–X bond strengths, the more electronegative the X atom, the more polar the H–X bond will be. This makes the H atom more positive, facilitating its removal by solvent water. Thus, across a period,

$$NH_3 < H_2O < HF$$

One of the most studied groups of acids is the family of ***oxyacids***, with the general formula $HOXO_n$, where X is a central atom. In these acids, the acidic hydrogen is always bonded to an oxygen atom, with a linkage of the type X–O–H. Any hydrogen atoms bonded directly to the central X atom (i.e., X–H) are *not* acidic. These acids may also have one or more terminal oxygen atoms, bonded directly to X but not bearing a hydrogen atom (i.e. X–O). In most oxyacids (with some exceptions) there are no X–H bonds, so the number of terminal oxygen atoms is just the total number of oxygen atoms minus the number of hydrogen atoms in the formula. Thus, $HClO_3$ has two terminal oxygen atoms, with the third oxygen atom bonded to the acidic hydrogen atom. The number of these terminal oxygen atoms affects the acid's strength. In general, two factors are important in judging the strengths of oxyacids:

- Among acids of the same structure type, acid strength increases with the electronegativity of the central X atom. For example,

$$HOI < HOBr < HOCl$$

$$H_2SeO_4 < H_2SO_4$$

  As electronegativity of X increases, the polarity of the –O–H bond increases, making removal of H^+ by solvent water more favorable.

- Acidity increases as the number of terminal oxygen atoms (those without H attached to them) increases. For example,

$$HOCl < HOClO < HOClO_2 < HOClO_3$$

  The electron withdrawing ability of the terminal –O atoms increases the formal charge on the central X atom, decreasing electron density in the –O–H bond, thereby weakening it. This is an example of an ***inductive effect***.

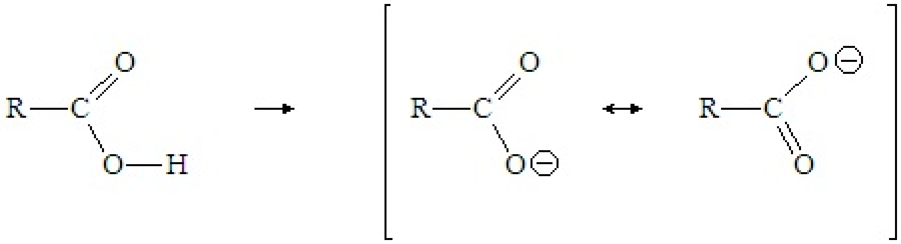
The number of terminal oxygen atoms in the oxyacids bears a strong correlation to K_a.

–O atoms	K_a range	Strength
0	$10^{-7} - 10^{-10}$	very weak
1	$10^{-1} - 10^{-4}$	weak
2	$>10^{-1}$	strong
3	$>>1$	very strong

An important group of organic acids contains the ***carboxyl group***, -CO_2H. Accordingly, such acids are called ***carboxylic acids***.

HCO_2H	CH_3CO_2H	$CH_3CH_2CO_2H$	$CH_3CH_2CH_2CO_2H$	HO_2CCO_2H
formic	acetic	propionic	butyric	oxolic (diprotic)

The acidity of the carboxyl group is partly due to the electronegativity of the double-bonded oxygen, which withdraws electron density from the –O–H bond, thereby facilitating the loss of H^+ to solvent water. Furthermore, when a carboxyl group loses H^+, it forms a resonance stabilized anion, called a ***carboxylate ion***:



(The symbol R represents the rest of the organic molecule.) The acidity of a carboxylic acid can be enhanced by adding electronegative atoms to the rest of the molecule. The electron-withdrawing ability of such atoms weakens the –O–H bond (inductive effect), thereby enhancing the ability of solvent water to remove H^+. For example, Cl_3CCO_2H is a much stronger acid than CH_3CO_2H.

Key Questions

4. Explain the following observations:

    a. H_2Se is a stronger acid than H_2S

    b. HNO_2 is a weak acid, but HNO_3 is a strong acid

    c. H_3PO_4 is a stronger acid than H_3AsO_4

    d. FCH_2CO_2H is a stronger acid than CH_3CO_2H

Information (Common Ion Effect)

Thus far we have only considered the equilibrium of a pure acid or base in water, with no other source for its conjugate but the dissociation itself. What would happen if we were to add a significant amount of the conjugate? Suppose we consider the dissociation of a 0.100 M solution of acetic acid, HOAc, for which $K_a = 1.76 \times 10^{-5}$. What are the concentrations of H_3O^+ and OAc^- in this solution, and what is the pH. We would have the following algebraic expressions for the principal species at equilibrium:

$$\begin{array}{lllll} \text{HOAc} + & \text{H}_2\text{O} & \Rightarrow & \text{H}_3\text{O}^+ & + \ \ \text{OAc}^- \\ 0.100 - x & & & x & \quad\ \ x \end{array}$$

But $C_{\text{HOAc}} >> K_a$, so we can assume [HOAc] = 0.100 M, and $[H_3O^+] = [OAc^-] = x$. As we have seen, this leads to the simple solution

$$x = \sqrt{C_{\text{HOAc}} K_a^{\text{HOAc}}} = \sqrt{(0.100)(1.76\times10^{-5}} = 1.33\times10^{-3}\text{M} = [\text{H}_3\text{O}^+] = [\text{OAc}^-]$$

From this it follows

$$\text{pH} = 2.877$$

Suppose we added sodium acetate, NaOAc, equivalent to 0.200 mole per liter of this solution. Being a strong electrolyte, the sodium acetate will dissociate completely to give 0.200 mole per liter of OAc^-, in addition to any acetate ion provided by acetic acid's hydrolysis. Now we have the following algebraic expressions for the principal species at equilibrium:

$$\begin{array}{lllll} \text{HOAc} + & \text{H}_2\text{O} & \Rightarrow & \text{H}_3\text{O}^+ & + \ \ \text{OAc}^- \\ 0.100 - x & & & x & \quad\ \ 0.200 + x \end{array}$$

Notice that in this solution, unlike the pure acid case, the concentration of hydronium ion *does not equal* the concentration of conjugate base. By LeChatelier's Principle, the added OAc^- will drive the equilibrium to the left, removing some of the H_3O^+ ion and OAc^- ion to reform molecular HOAc and H_2O. Put another way, adding conjugate base to the solution will make the pH go up. From our previous calculation for 0.100 M HOAc, we saw that $x = 1.33 \times 10^{-3}$ M, but now this number will be even smaller, due to the left shift in the equilibrium position. Compared to the analytical concentration of HOAc ($C_{\text{HOAc}} = 0.100$ M) and the analytical concentration of NaOAc ($C_{\text{NaOAc}} = 0.200$ M), this small value of x is now insignificant, actually falling beyond the significant digits of those concentrations. Therefore, we can simplify the calculation of $[H_3O^+]$ by assuming that [HOAc] = C_{HOAc} = 0.100 M and $[OAc^-] = C_{\text{NaOAc}}$ = 0.200 M.

$$\begin{array}{lllll} \text{HOAc} + & \text{H}_2\text{O} & \Rightarrow & \text{H}_3\text{O}^+ & + \ \ \text{OAc}^- \\ \sim 0.100 & & & x & \quad\ \ \sim 0.200 \end{array}$$

All we have to do is plug these values into the K_a expression and solve for $[H_3O^+]$. (No quadratic equation and not even a square root!)

$$K_a = \frac{[H_3O^+][[OAc^-]}{[HOAc]} = \frac{x(0.200)}{0.100} = 1.76 \times 10^{-5}$$

$$x = [H_3O^+] = 8.80 \times 10^{-6}\ \text{M}$$

$$\text{pH} = 5.056$$

As expected, the pH has gone up, compared to the pure acid solution. Also, note that the value of $x = [H_3O^+]$ that we obtain is, indeed, beyond the significant digits of the analytical concentration values of HOAc and OAc^-. In other words, we were justified in ignoring x in our algebraic expressions for the concentrations of those species.

In general, for a solution of an acid with added amounts of conjugate base, except at extreme dilution, we can assume

$$[HA] \approx C_{HA} \qquad [A^-] \approx C_{A^-}$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \approx \frac{[H_3O^+]C_{A^-}}{C_{HA}}$$

$$[H_3O^+] \approx K_a \times \left(\frac{C_{HA}}{C_{A^-}}\right)$$

By a similar reasoning, for a solution of a base B with added amounts of its conjugate acid, BH^+, except at extreme dilution, we can assume

$$[B] \approx C_B \qquad [BH^+] \approx C_{BH^+}$$

$$K_b = \frac{[OH^-][BH^+]}{[B]} \approx \frac{[OH^-]C_{BH^+}}{C_B}$$

$$[OH^-] \approx K_b \times \left(\frac{C_B}{C_{BH^+}}\right)$$

If we take base-10 logarithms of both of these equations, we can obtain equations for the pH and pOH for these kinds of solutions in terms of K_a and K_b. These are called the **Henderson-Hasselbalch equations**. For the HA/A^- case:

$$\log[H_3O^+] = \log K_a + \log\left(\frac{C_{HA}}{C_{A^-}}\right)$$

$$\text{pH} = \text{p}K_a - \log\left(\frac{C_{HA}}{C_{A^-}}\right)$$

$$\boxed{\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{C_{\mathrm{A}^-}}{C_{\mathrm{HA}}}\right)}$$

For the B/BH$^+$ case:

$$\log[\mathrm{OH}^-] = \log K_b + \log\left(\frac{C_{\mathrm{B}}}{C_{\mathrm{BH}^+}}\right)$$

$$\mathrm{pOH} = \mathrm{p}K_b - \log\left(\frac{C_{\mathrm{B}}}{C_{\mathrm{BH}^+}}\right)$$

$$\boxed{\mathrm{pOH} = \mathrm{p}K_b + \log\left(\frac{C_{\mathrm{BH}^+}}{C_{\mathrm{B}}}\right)}$$

These equations are useful if caring out a series of calculations for the same conjugate pair (e.g., using Excel), but for a single calculation it is just as quick to plug the numbers into the appropriate K_a or K_b expression and take the base-10 logarithm of the result, as shown in the example above.

Key Questions

5. What is the pH of a solution prepared by adding 0.20 mole of formic acid, HCO_2H, and 0.25 mole of sodium formate, $NaHCO_2$? The K_a of formic acid is 1.8×10^{-4}.

6. What is the pH of a solution prepared by adding 0.60 mole of formic acid and 0.75 mole of sodium formate in enough water to make a liter of solution? How does your answer compare to the answer you obtained in Key Question 5? Explain.

7. The solution prepared in Key Question 6 was diluted with enough water to make ten liters of solution. What is the pH of the dilute solution? How does it compare to the previous two solutions? Explain.

Information (Buffers)

The solutions we have just examined, in which significant amounts of both weak acid and its conjugate base or weak base and its conjugate acid have been mixed together, are buffer solutions. Buffer solutions have two key properties that make them useful in a wide variety of applications, including biological systems:

- The pH of a buffer does not change with moderate dilution.
- The pH of a buffer changes only slightly with addition of small amounts of acid or base.

We can understand the first property from having worked Key Questions 5 through 7. As those problems show, it is not really the actual concentrations of the acid-base conjugate pair that fix the hydronium ion concentration, but rather the ratio between those concentrations. Diluting a buffer solution does not alter the ratio of the numbers of moles of each component, and so the concentration ratio remains constant. (This breaks down, however, at extreme dilution.)

If we want to make a buffer with a certain pH from a given acid-base conjugate pair, we simply add the ingredients in the proper ratio, as required by the acid's K_a or bases's K_b, to achieve the hydronium ion that corresponds to the desired pH. The ability of a buffer to resist changing pH with small amounts of acid or base depends on how little this concentration ratio is altered by the additions. Adding small amounts of a strong acid (e.g., HCl) will neutralize an equivalent amount of the conjugate base and form an equivalent amount of the weak acid. Conversely, adding small amounts of a strong base (e.g., NaOH) will neutralize an equivalent amount of the weak acid and form an equivalent amount of the conjugate base. In both scenarios the ratio between the conjugate pair will be altered, but if the change is small the pH will be virtually unaffected. The **buffer capacity** is the amount of added acid or base the buffer can tolerate before the pH changes significantly. This depends on minimizing the change in the conjugate pair ratio. For this reason, it is a good idea to make the concentrations of the two components fairly strong, so that numerically small changes in either component from added acid or base will cause relatively insignificant changes in the ratio.

To illustrate, suppose we wish to make up a buffer that has a pH of 5.00, using acetic acid and sodium acetate. A pH of 5.00 means $[H_3O^+] = 1.0 \times 10^{-5}$. We can plug this value into the K_a expression and solve for the ratio $[OAc^-]/[HOAc]$.

$$K_a = \frac{[H_3O^+][OAc^-]}{[HOAc]} = \frac{(1.0\times10^{-5})[OAc^-]}{[HOAc]} = 1.76\times10^{-5}$$

$$\frac{[OAc^-]}{[HOAc]} = = \frac{1.76\times10^{-5}}{1.0\times10^{-5}} = 1.76$$

Any moderate concentrations that have the ratio $[OAc^-]/[HOAc] = 1.76$ will achieve a pH of 5.00. Furthermore, notice that this is really a ratio of moles of sodium acetate to acetic acid, because the volume is the same for both. Any specific concentrations in this ratio will achieve the desired pH, but in order to achieve a good buffer capacity we should use relative high concentrations. Suppose we chose to make a buffer solution that has $[OAc^-] = 1.76$ M and $[HOAc] = 1.00$ M. At equilibrium we would have the following concentrations.

$$\begin{array}{llllll} \text{HOAc} + & H_2O & \rightleftharpoons & H_3O^+ & + & OAc^- \\ 1.00\ \text{M} & & & 10^{-5}\ \text{M} & & 1.76\ \text{M} \end{array}$$

Now suppose we add a small amount of strong acid (e.g., HCl) to supply an additional 0.01 mol/L of H_3O^+. This additional hydronium ion, which is much greater than that provided from the acetic acid's hydrolysis, will shift the HOAc/OAc$^-$ equilibrium to the left to consume the extra H_3O^+, thereby forming an equivalent amount of HOAc. This is essentially the same as neutralizing an equivalent amount of the base OAc$^-$. The changes and new equilibrium are summarized below:

	HOAc +	H_2O	$\rightleftharpoons$	H_3O^+ +	OAc$^-$
Original equilibrium	1.00 M			10^{-5} M	1.76 M
Add				0.01 M	
Change	+0.01 M			-0.01 M	–0.01 M
New equilibrium	1.01 M			?	1.75 M

To find the new $[H_3O^+]$, substitute into the K_a expression:

$$K_a = \frac{[H_3O^+][OAc^-]}{[HOAc]} = 1.76 \times 10^{-5} = \frac{[H_3O^+](1.75)}{1.01}$$

$$[H_3O^+] = \frac{(1.76 \times 10^{-5})(1.01)}{1.75} = 1.02 \times 10^{-5}\ \mathrm{M}$$

$$\mathrm{pH} = 4.99_3 = 4.99$$

As this shows, the small addition of H_3O^+ has negligible effect on the pH because the shift in the equilibrium makes only a minor change in the ratio [OAc$^-$]/[HOAc]. This would not be the case if the concentrations of HOAc and OAc$^-$ were small numbers. Therefore, the buffer's ability to resist a pH change from small addition of acid depends upon having high concentrations of the acid-base pair. In other words, high concentrations of acid and conjugate base result in a high buffer capacity.

Suppose, instead, that we add a small amount of a strong base (e.g., NaOH) to our pH 5.00 buffer to supply an additional 0.01 mol/L of OH$^-$. The addition of hydroxide ion will neutralize an equivalent amount of HOAc, driving the acid hydrolysis equilibrium to the right. In this case, [OAc$^-$] will increase by 0.01 mol/L and [HOAc] will decrease by 0.01 mol/L. Substituting into the K_a expression, we can obtain the new pH as follows:

$$K_a = \frac{[H_3O^+][OAc^-]}{[HOAc]} = 1.76 \times 10^{-5} = \frac{[H_3O^+](1.77)}{0.99}$$

$$[H_3O^+] = \frac{(1.76 \times 10^{-5})(0.99)}{1.77} = 9.8_4 \times 10^{-6}\ \mathrm{M}$$

$$\mathrm{pH} = 5.00_7 \approx 5.01$$

In both cases, the small shift in pH occurs because the amounts of added acid or base are insignificant relative to the large amounts of the conjugate acid-base pair.

If the concentration of the conjugate base is small, a buffer will not have good resistance to pH change with added H_3O^+. Likewise, if the concentration of the acid of the conjugate pair is small, a buffer will not have good resistance to pH change with added OH^-. If we want to make an ideal buffer, with equal resistance to pH changes from added H_3O^+ or OH^-, we should have the concentrations of both the acid and conjugate base be high and equal. By substitution into either K_a or the Henderson-Hasselbalch equation, we can see that a buffer for which $C_{\mathrm{HA}} = C_{\mathrm{A^-}}$ would have $[H_3O^+] = K_a$ and $\mathrm{pH} = \mathrm{p}K_a$.

It is not always necessary to have equal buffering capacity against both acid or base challenges. For example, the goal may be simply to make a solution with a particular pH to use as a standard for instrument calibration. If a particular pH is desired for a buffer from a given acid-base pair, the concentrations of the two components may need to be unequal. But not all ratios are possible for a given pair. The possible limits are set by the ratio achieved when the pure acid or the pure base hydrolyzes to give the amount of conjugate dictated by its K_a or K_b. When trying to make a buffer with a certain pH, the following guidelines should be followed in selecting the acid-base pair and choosing the concentration ratios:

① Try to choose a conjugate pair whose $\mathrm{p}K_a \approx \mathrm{pH}$.

② Adjust the ratio $[A^-]/[HA]$ or $[BH^+]/[B]$ to achieve the desired pH.

③ The practical limit on the choice of conjugate acid-base pair is

$$\mathrm{pH} \approx \mathrm{p}K_a \pm 1$$

Otherwise, one member of the pair is present in too small an amount to make an effective buffer.

Key Questions

8. A student wishes to prepare a buffer with a pH of 4.52. She starts by preparing one liter of 0.10 M formic acid, HCO_2H. How many grams of sodium formate, $NaHCO_2$, must she add to the solution to achieve the desired pH? $K_a = 1.8 \times 10^{-4}$ for formic acid. The formula weight of sodium formate is 68.00 u.

9. A buffer solution is made by adding an equal number of moles of the base pyradine, C_5H_5N, and the chloride salt of it conjugate base, C_5H_5NHCl. What is the pH of the buffer solution? The K_b of C_5H_5N is 1.7×10^{-9}.

DATA and ERROR ANALYSIS

Performing the experiment and collecting data is only the beginning of the process of completing an experiment in science. Understanding the results of any given experiment is always the central goal of the experiment. Presenting those results in a clear concise manner completes the experiment. This overview of the complete process is as valid in an instructional laboratory course as in a research environment. You will not have learned any physics if you did not understand the experiment. Presenting the results of your experimental work is fundamentally saying, **"This is what I did and this is what I learned."** Putting together your presentation of the results should help you clarify the results to yourself. (If your instructor can clearly see what you did and what you learned, you might get a better grade.)

Data analysis should NOT be delayed until all of the data is recorded. Take a low point, a high point and maybe a middle point, and do a quick analysis and plot. This will help one avoid the problem of spending an entire class collecting bad data because of a mistake in experimental procedure or an equipment failure.

First and foremost, data analysis means understanding what your results mean. When analyzing your data, try to think through the physical processes which are occurring. Write your train of thought down. Ultimately, the goal is for you to understand physics and the world a bit better. Your understanding of your results probably occurs in stages, with each stage being a refinement and possibly more mathematical than the previous stage.

For example, one might first note that as time increases so does distance. Next a quick graph of distance vs time might verify this understanding but the relationship is NOT linear, i.e. the data does not form a straight line. By further work, one might discover that distance increase linearly with the square of the time. Or sometimes the mathematical relationship may remain hidden.

Relate each successive stage of your understanding and interpretation of your results to the physical principles that are involved. In the above example, one might note that the change in position with time is caused by velocity that is in turn caused by an acceleration from the gravitational force. Finally, develop the related mathematics. Equations are nearly meaningly unless they are related to the physical laws. (Remember to identify all the variables and constants in you equations.)

Sometimes, your results will not support and may even contradict the physical explanation suggested by the manual or your instructor. Say so! But of course then a few suggestions as to the reason for this apparent failure of the physical laws, would be in order. Do NOT just say " The equipment was a piece of sh_t!" Try to explain what went wrong or what competing effects have come into play.

One of the reasons that you are encouraged to record everything that is going on as it is going on, is that this information may help explain bad results. For example, partly for fun, you note each time your lab partner sneezes. Later while looking at the data, you discover that each data point that was being collected during a sneeze deviates from the pattern of the rest of the data. This may give you good reason for dropping "bad" data.

The quality of the data, determines to a great extent, what conclusions can be reached from them. If you are looking for a small effect, say a total change of 1 mm, and the uncertainties in your data is 2 mm then you really can not make any solid conclusions. (See the section on error analysis below.)

When one considers the **quality of a measurement** there are two aspects to consider. The first is if one were to repeat the measurement, how close would new results be to the old, i.e., how reproducible is the measurement? Scientists refer to this as the ***precision*** of the measurement.

Secondly, a measurement is considered “good” if it agrees with the true value. This is known as the ***accuracy*** of the measurement. But there is a potential problem in that one needs to know the “true value” to determine the accuracy.

A good measurement must be close to the “true value” and be reproducible. In this experiment, if someone made one measurement of ***g*** and got 9.79 m/s_2, it would be an accurate measurement. But if next time they tried they got 4.1 m/s_2, no one would believe that they were anything but lucky in the first measurement. Similarly, if one group got values of 7.31, 7.30, 7.33, and 7.29 m/s_2 their results are reproducible but not really very good.

Accuracy vs. Precision: These two words do not mean the same thing.

"**Accuracy**" deals with how close is a measured value to an accepted or "true" value.

"**Precision**" deals with how reproducible is a given measurement.

Because, *precision* is a measure of how reproducible a measurement is, one can gain some knowledge of the precision simply by taking a number of measurements and comparing them.

If the true value is not known, the *accuracy* of a measurement is more difficult to know. Here are a few things to consider when trying to estimate (or explain) the quality of a measurement:

1.☞ How well does your equipment make the needed measurements? Two examples of problems: a meter stick with 2 mm worn off one end and trying to measure 0.01 mm with a meter stick.

2.☞ How does the lack of precision, or *uncertainty* in any one measured variable effect the final calculated value? For example, if the data is expected to fall on a straight line, some uncertainties may only shift the intercept and leave the slope unchanged.

3.☞ Making a plot that shows each of your measurements, can help you "see" your uncertainty. Also certain uncertainties are sidestepped by extracting a slope from a plot and calculating the final value from this slope.

4.☞ One can estimate the uncertainty after making multiple measurements. First, note that when plotted, about ⅓ of the data points will be outside of the *error bars* as they are normally drawn at one *standard deviation*. For example if there are six measurements, one expects that 2 of the points (probably one too high and one too low) will be outside the normal error bars. One can draw a reasonable set of error bars based on this assumption, by drawing the upper part of the error bar between the highest two points and the lower part of the error bar between the lowest two points.

Data analysis is seldom a straight forward process because of the presence of uncertainties.
Data can not be fully understood until the associated uncertainties are understood.

✦ ERROR ANALYSIS

The words "error" and "uncertainty" are used to describe the same concept in measurement. It is unfortunate that the term, "error' is the standard scientific word because usually there is no mistake or error in making a measurement. Frequently, the uncertainties are dominated by natural irregularities or differences in what is being measured.

Types of Error: All measurements have errors. Errors may arise from three sources:

a) **Careless errors**: These are due to mistakes in reading scales or careless setting of markers, etc. They can be eliminated by repetition of readings by one or two observers.

b) **Systematic errors:** These are due to built-in errors in the instrument either in design or calibration. Repetition of observation with the same instrument will not show a spread in the measurements. They are the hardest source of errors to detect.

c) **Random errors:** These always lead to a spread or distribution of results on repetition of the particular measurement. They may arise from fluctuations in either the physical parameters due to the statistical nature of the particular phenomenon or the judgement of the experimenter, such as variation in response time or estimation in scale reading.

Taking multiple measurements helps reduce uncertainties.

✦ DETERMINING ERRORS:

Although it is interesting and reassuring to compare your results against "accepted values," it is suggested that error analysis be done, before this comparison. One reason is that the accuracy of a set of measurements depends on how well the experiment was done, not how close the measurement was to the accepted value. One could get close to the accepted value, by sloppiness and luck.

Do not base your experimental uncertainties on the accepted values.

Determining the source of uncertainty and the magnitude of this uncertainty is often difficult. Some errors or uncertainties are caused by natural fluctuations or irregularities These can not be eliminated. To estimate these uncertainties one frequently uses mathematical methods similar to those discussed in the section below titled, Averages and Deviation.

Another method of estimating uncertainties is to assign an uncertainty to the measurement equal to the finest scale reading on the measuring instrument. For example, if a ruler may be marked in millimeters. then the uncertainty in any measurement with this ruler can be given as 1 mm. But with practice, one might be able to interpolate the scale and reduce the error to 0.25 mm.

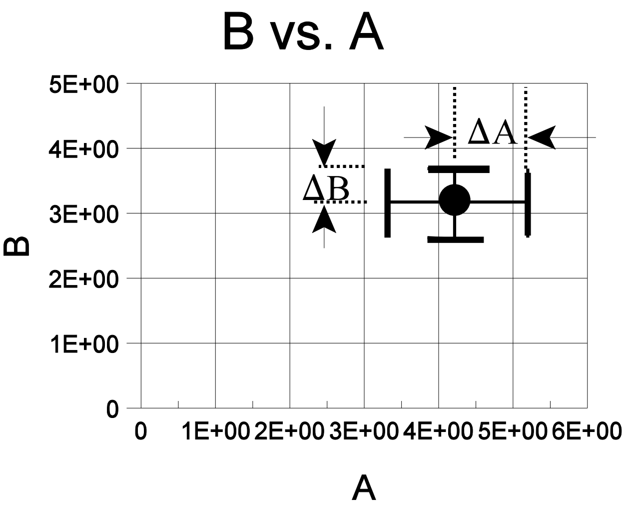
✦ EXPRESSING ERRORS:

For each measured value, **A**, there is an **estimated error,** ΔA. The complete result is given by **A** ± **ΔA**. This means that the "true value" probably lies between a maximum value of **A** + **ΔA** and a minimum value of **A** - **ΔA.** Sometimes the terms **relative error** and **percent error** are used, where:

$$\text{Relative Error} = \frac{\text{Estimated Error}}{\text{Estimated Value}} = \frac{\Delta \mathrm{A}}{\mathrm{A}}$$

$$\text{Percent Error} = \text{Relative Error} \times 100\% = \frac{\Delta \mathrm{A}}{\mathrm{A}} \times 100\%$$

Errors are expressed in graphs by using error bars. Consider a data point (**A,B**) and the associated uncertainties are **ΔA** and **ΔB** respectively. The vertical error bar is drawn from **B-ΔB** to **B+ΔB.** Similarly, the horizontal error bar is drawn from **A-ΔA** to A+**ΔA**. For example if **A** = 4.2±0.8 and **B** = 3.2±0.5 then this point would be plotted like:



✦ PROPAGATION OF ERRORS

When measured values are used to calculate other values, the uncertainties in these measured values causes uncertainties in the calculated values.

Calculating the uncertainties in the calculated values is called ***error propagation.*** For the few simple cases that are discussed below, let **C** be a function of **A** and **B** and the associated uncertainties are **ΔC**, **ΔA**, and **ΔB**, respectively.

1) Product with a Constant

Here **C = k A** where **k** is a constant. Then

$$\Delta C = \mathrm{k}\,\Delta A.$$

This rule can be applied if **k** is a measured quantity with a relatively negligible uncertainty, for example, if **k** were the gravitational constant, **g**.

2) Addition and Subtraction

Here **C = A + B** or **C = A - B.** In either case:

$$\Delta C = \sqrt{(\Delta A)^2 + (\Delta B)^2}$$

Note that **ΔC** is less than **ΔA** + **ΔB**. This is an expression of the fact that the uncertainties in A and B are independent of each other. (In math lingo, one could say that **ΔA**, and **ΔB** are orthogonal or perpendicular to each other. Note how the calculation of **ΔC** is identical to the Pythagorean theorem for the sides of a right triangle.)

Why should the same formula work for additon and subtraction? Notice that the original uncertainties are squared.

3) Multiplication or Division

If C = A B or C = A/B then:

$$\frac{\Delta C}{C} = \sqrt{\left(\frac{\Delta A}{A}\right)^2 + \left(\frac{\Delta B}{B}\right)^2}$$

$$\Delta C = C \times \sqrt{\left(\frac{\Delta A}{A}\right)^2 + \left(\frac{\Delta B}{B}\right)^2}$$

Again the assumption is that the uncertainties in **B** and **B** are independant. An example of when this is not true is **C = A A.** This brings up another rule.

4) Raised to a Power

This is the case were **C = A**^{n}, where **n** is a constant. In this case:

$$\frac{\Delta C}{C} = |n| \frac{\Delta A}{A}$$

5) Graphical Analysis of Uncertainties in , Slopes and Intercepts.

If the slope or intercept of a line on a plot is the required calculated value (or the required value is calculated from these values) then the uncertainty of the slope and intercept will also be required. Graphically one can estimate these uncertainties. First draw the best line possible, and then draw the two lines that just barely pass through the data. The differences of these slopes and intercepts from those of the best fit line provide an estimate of the uncertainties in these quantities.

In the graph below the **solid line** is a good fit to the data and the while the **dotted line** and the **dashed line** represent the extremes for lines that just fit the data.. The dashed line has the steepest slope and will be referred to as the max. line, while the dotted line will be referred to as the min. line. The slopes and y- intercepts for these three lines are:

	Slope	(dif.)	y-inter.	(dif.)
Best fit	1.0		2.0	
Max. line	1.16	(0.16)	-1.5	(-3.5)
Min. Line	0.81	(-0.19)	5.2	(3.2)

Thus if the data was expected to fit the equation:

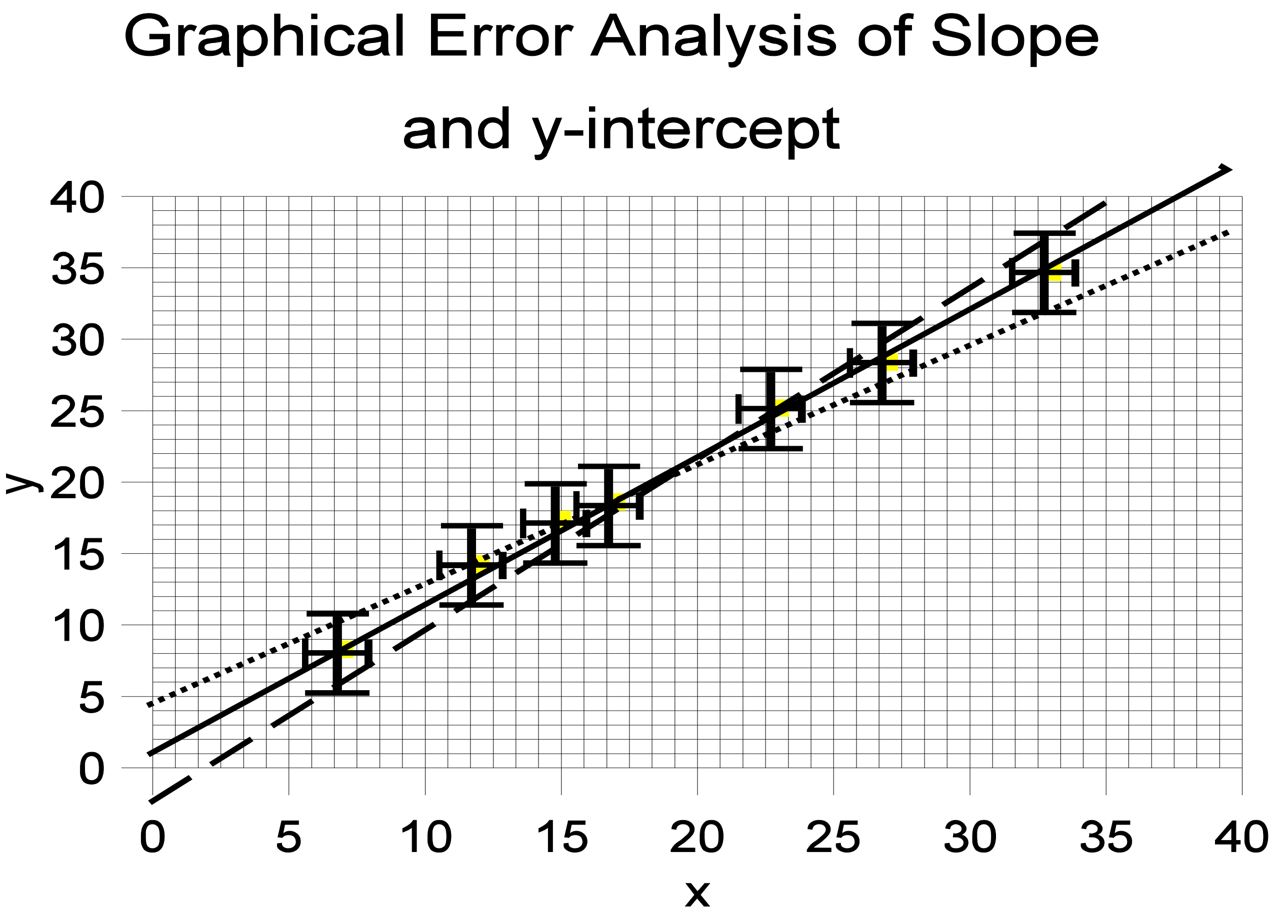
$$y = a + bx,$$

then one would estimate the constants as:

a = 2.0 ± 3.4

b = 1.0 ± 0.2.

The uncertainties are based on averaging the absolute value of the differences (labeled (dif.)).



6) General Formula (*Advanced*)

All of the above examples of propagation of errors are special cases of the a general formula. Consider a calculated variable **z** that is a function of two measured variables **x** and **y,** then one writes:

$$z = z(x, y) . \qquad \textbf{(7)}$$

If the uncertainties associated with **x** and **y** are **Δx** and **Δy**, respectively. The uncertainty, **Δz** in **z** is:

$$\Delta z = \sqrt{\left(\frac{\partial z}{\partial x}\right)^2 (\Delta x)^2 + \left(\frac{\partial z}{\partial y}\right)^2 (\Delta y)^2} \ .\textbf{(8)}$$

Here a symbol $\frac{\partial z}{\partial x}$ that may be somewhat unfamiliar. It is the partial derivative of **z** with respect to **x**. Partial derivatives are used when a variable is a function of more than one variable. To evaluate a partial derivative $\frac{\partial z}{\partial x}$, one just takes the normal derivative $\frac{dz}{dx}$ but treats the variable y as a constant. That is one does not do any chain rule, $\frac{dz}{dy}\frac{dy}{dx}$, kind of stuff. Note that the uncertainties are assumed to be independent of each other and add as if they are vectors at right angles to each other.

AVERAGES and DEVIATIONS

The ***average*** of a series of measurements is one of the most common methods of analyzing data. The average, $\bar{x}$, or ***arithmetic mean*** for a series of **n** numbers: x_1, x_2, x_3, ...,x_n is defined as:

$$\bar{x} = \frac{x_1 + x_2 + x_3 + \ldots + x_n}{n} = \sum_{i=1}^{n} \frac{x_i}{n}$$

Example: The length of a table was measured three times with the following results in meters:

$x_1 = 1.42$, $x_2 = 1.45$, and $x_3 = 1.41$.

Then the average is:

$$\bar{x} = \frac{1.42 + 1.45 + 1.41}{3} = 1.43 \text{ meters}$$

Often one wants to compare individual measurements to the average. The ***deviation*** is a simple quantity that is frequently used for this kind of comparison. The deviation δx_i of the measurement labeled **I**, from the average is:

$$\delta x_i = x_i - \bar{x} .$$

Continued Example: The deviations for the above example are:

$$\begin{aligned} \delta x_1 &= 1.42 - 1.43 = -0.01 \text{ meters} , \\ \delta x_2 &= 1.45 - 1.43 = 0.02 \text{ meters} , \\ \delta x_3 &= 1.41 - 1.43 = -0.02 \text{ meters} . \end{aligned}$$

STANDARD DEVIATION: If the deviations of a measurement were averaged, the result would be zero because of high and low values would cancel each other. Generally one expresses the fluctuation about the average measurement with by calculating and quoting the **standard deviation,** σ of the ***n*** measurements.

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n}}$$

Continued Example: σ = 0.0212 meter

$$\sigma = \sqrt{\frac{(-0.01)^2 + (+0.02)^2 + (-0.02)^2}{3 - 1}} \textbf{(20)}$$

Finally, the term, standard deviation of the mean defined as:

$$\sigma_m = \frac{\sigma}{\sqrt{n}} . \qquad \textbf{(21)}$$

The standard deviation of the mean, σ_m**, is the standard measure for describing of the precision of a measurement,** i.e. how well a number of measurements agree with themselves. Thus:

$$\Delta x = \sigma_m$$

$$\Delta x = \frac{\sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2}}{n} \qquad \textbf{(23)}$$

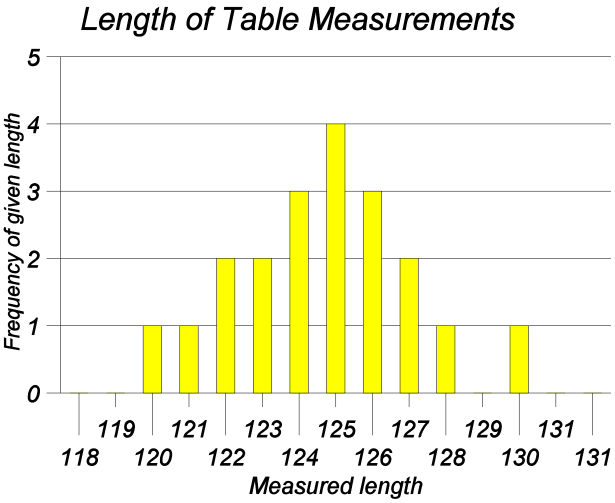
Continued Example: **Δx** = σ_m = 0.012 meter

✦ GAUSSIAN or NORMAL DISTRIBUTION *(Advanced)*

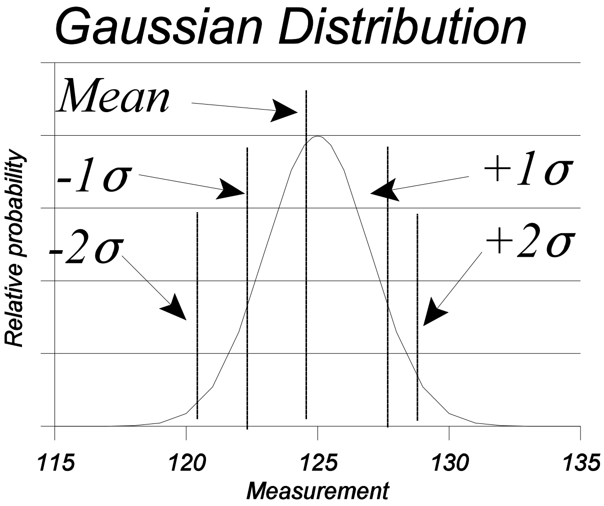
When analyzing data a hidden or implicit assumption is usually made about how results of a number of measurements of the same the quantity will fluctuate about the "true" value of this quantity. One assumes that the distribution of a large number of measurements is a "Nor-mal" or "Gaussian distribution." Here the term distributed refers to a plot of the number of times the measurement results in a given value (or range of values) vs. the measured result. For example, the result (sort in increasing order) of a table twenty times is (in meters)

1.20,
1.21,
1.22, 1.22,
1.23, 1.23,
1.24, 1.24, 1.24,
1.25, 1.25, 1.25, 1.25,
1.26, 1.26, 1.26,
1.27, 1.27,
1.28,
1.30.

then the results could be displayed in a plot



A plot of a Gaussian distribution is a bell curve:



If the measurements are distributed as a Gaussian distribution then for a large number of measurements:

1. The most frequently occurring value is also the average or arithmetic mean of the all of the measurements.
2. The curve is symmetric about the mean.
3. If an additional measurement is made, there is a 68% chance that the measured value would be within 1 ***standard deviation***, **1**σ, of the mean and a 95% chance that the measured value would be within 2 standard deviations, **2**σ of the mean.

The assumption that measurements are distributed in a Gaussian is sometimes based on solid theoretical grounds, e.g cosmic ray counting. Other times it is based on empirical evidence that a large number of measurements have been made and the distribution matches a Gaussian quite well. But frequently it is just assumed because most random measurements are distributed this way. The reason that scientist make this assumption is that it allows a relatively straightforward theoretical analysis of the uncertainties.

✦ LEAST SQUARES ANALYSIS
(Advanced)

Although extracting a slope or a y-intercept from a graph is relatively straightforward, the method has several limitations. The result is effected by the users skill and bias. Also precision may be lost in the process of graphing and extracting the slope and intercept. Evaluating the uncertainties using graphical methods is usually even more difficult. If data is only evaluated graphically, two different people evaluating the same data would get different slopes.

Part of the scientific method is that the techniques must be reproducible. Usually when a curve (e.g. a straight line) is fitted to some data, the method used is **least squares analysis.** Although this method is quite general, only the limited case of fitting a straight line to data is presented here. For this discussion the following assumptions are made:

1) The uncertainties are the same for all of the data points.
2) The uncertainties are only in the dependant variable, **y**.
3) The uncertainties are all random and the multiple measurements for a given value of the independent variable, x, would be distributed according to a Gaussian.

The data in this case would be pairs of measurements ($\mathbf{x}_i$ and $\mathbf{y}_i$) and the goal is to determine the straight line (**y = a + bx**) that best models this data. One wants to make the minimize the difference between the measured value $\mathbf{y}_i$, and a + b$\mathbf{x}_i$ which the associated value calculated from the straight line. Explicitly one is looking for values of **a** and **b** the minimize

$$\chi^2 = \sum_{i=1}^{n} \left(y_i - (a + b x_i) \right)^2 \qquad \textbf{(22)}$$

χ^2 is pronounced chi-squared and is an indicator of the goodness of fit.

With out any prove the following results of the linear least squares analysis of data yields a straight line, **y = a + bx**, are given:

$$a = \frac{1}{\Delta'} \left[\left(\sum (x_i^2) \right) \left(\sum y_i \right) - \left(\sum x_i \right) \left(\sum (x_i y_i) \right) \right]$$

$$b = \frac{1}{\Delta'} \left[n \times \sum (x_i y_i) - \left(\sum x_i \right) \left(\sum y_i \right) \right]$$

$$\Delta' = n \times \sum (x_i^2) - \left(\sum x_i \right)^2$$

Here all of the sums are from i = 1 to n.

Note that all of the individual sums can be built up a point at a time, which make calculation relatively simple. This is especially easy if**, one uses a spreadsheet.** With x and y in the two columns labeled **A** and **B**, one can have column **C** be x^2, column **D** be y^2, and column **E** be the product xy. Then sum each column and calculate the values

Many calculators and spreadsheet programs provide access to least squares analysis routines. You are encouraged to learn to use these programs

If one needs to include uncertainties σ_i associated with the y_i in this calculation the above formula becomes:

$$a = \frac{1}{\Delta'} \left[\sum \left(\frac{x_i^2}{\sigma_i^2} \right) \sum \left(\frac{y}{\sigma_i^2} \right) - \sum \left(\frac{x_i}{\sigma_i^2} \right) \sum \left(\frac{x_i y_i}{\sigma_i^2} \right) \right]$$

$$b = \frac{1}{\Delta'} \left[\sum \left(\frac{1}{\sigma_i^2} \right) \sum \left(\frac{x_i y_i}{\sigma_i^2} \right) - \sum \left(\frac{x_i}{\sigma_i^2} \right) \sum \left(\frac{y_i}{\sigma_i^2} \right) \right]$$

$$\Delta' = \sum \left(\frac{1}{\sigma_i^2} \right) \sum \left(\frac{x_i^2}{\sigma_i^2} \right) - \left(\sum \left(\frac{x_i}{\sigma_i^2} \right) \right)^2$$

REFERENCE: Although there are many good books on data and error analysis, the following two books are the authors standard references. The first book is considerd to be a standard reference in physics.

Data Reduction and Error Analysis for the Physical Sciences, Second Edition, by Philip R. Bevington and D.Keith Robinson, McGraw-Hill Inc., 1992

Statistical Treatment of Data, by Hugh D. Young, McGraw-Hill Book Company Inc., New York, 1962.

OXIDATION AND REDUCTION

1. CLASSICAL CONCEPT OF OXIDATION REDUCTION

A. Oxidation : According to this concept, oxidation is considered as the addition of oxygen or removal of hydrogen in an ion, in a compound or in a species. Or the addition of an electronegative element or removal of electropositive element in a group, in a ion, in a species or in a compound is called oxidation.

For example :

(a) $2Mg + O_2 \rightarrow 2MgO$ Addition of Oxygen.

(b) $C + O_2 \rightarrow CO_2$

(c) $\underline{H_2S} + Cl_2 \rightarrow 2HCl + S$ Removal of Hydrogen

(d) $MnO_2 + 4\underline{HCl} \rightarrow MnCl_2 + Cl_2 + 2H_2O$

B. Reduction : According to this concept, reduction is considered as addition of hydrogen or removal of oxygen in an atom, in a group, in an ion, in a species or in a compound. Or addition of an electropositive element or removal of an electronegative element in a group, in an ion, in a species or in a compound is called reduction.

For example :

(a) $H_2S + \underline{Cl_2} \rightarrow 2HCl + S$ Addition of Hydrogen

(b) $H_2 + \underline{Cl_2} \rightarrow 2HCl$

(C) $\underline{ZnO} + C \rightarrow Zn + CO$ Removal of Oxygen

(d) $\underline{Fe_2O_3} + 3CO \rightarrow 2Fe + 3CO_2$

2. VALENCY CONCEPT OF OXIDATION REDUCTION

A. Oxidation: According to this concept, increase in (+)ve valency or decrease in (–)ve valency in a reaction is called oxidation.

For example :

$$\underset{(0)}{2Mg} + O_2 \rightarrow \underset{(+2)}{2MgO}$$

B. Reduction : According to this concept, It is the process in which (+) ve valency decreases whereas (–)ve valency increases in a reaction is called reduction.

For example :

$$\underset{(+2)}{2HgCl_2} + SnCl_2 \rightarrow \underset{(+1)}{Hg_2Cl_2} + SnCl_4$$

3. OXIDATION NUMBER CONCEPT OF OXIDATION-REDUCTION

A. Oxidation : According to this concept, increase in oxidation no. in an element in a reaction is called oxidation.

B. Reduction : According to this concept, decrease in oxidation no. in an element in a reaction is called reduction.

For example :

$$\underset{+7}{KMnO_4} + \underset{+2}{FeSO_4} \rightarrow \underset{+2}{MnO} + \underset{+3}{Fe_2(SO_4)_3}$$

4. MODERN OR ELECTRONIC CONCEPT OF OXIDATION REDUCTION

A. Oxidation : According to this concept, the process in which involves the loss of e^- in an element or species is called oxidation. It is also called deelectronation.

For example **:**

$Fe \rightarrow Fe^{2+} + 2e^-$ (O.N. of Fe, $0 \rightarrow 2$)

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (O.N. of Fe, $2 \rightarrow 3$)

$2Cl^- \rightarrow Cl_2 + 2e^-$ (O.N. of Cl, $-1 \rightarrow 0$)

B. Reduction : According to this concept, the process which involves the gain of electrons by an element or an atom or an ion is called reduction. It is also called electronation.

For example :

$I_2 + 2e^- \rightarrow 2I^-$ (O.N. of I,0 → –1)

$Fe^{3+} + e^- \rightarrow Fe^{+2}$ (O.N. of Fe, + 3 → + 2)

$Sn^{+4} + 2e^- \rightarrow Sn^{+2}$ (O.N. of Sn, + 4 → + 2)

5. OXIDANT OR OXIDISING AGENT

Species, which oxidise other species, which is present in a reaction and reduce it self. This type of species is called oxidant or oxidising agent. Or species, which accepts electron in a reaction by another species and show decreases in its oxidation no. in the reaction is called oxidant or oxidising agent.

5.1 Some Important oxidising agent or oxidant

1. All elements with high electronegative character like N, O, F, Cl, etc.
2. All metallic oxides like Li_2O, Na_2O, Na_2O_2, CO_2, CaO, MgO, BaO_2 etc.
3. Some nonmetallic oxides like CO_2, SO_2, H_2O_2, O_3.
4. All neutral compound or ion in which element shows their higher oxidation no. or state are act as oxidant or oxidising agent like $KMnO_4$, H_2SO_4, $SnCl_4$, H_3PO_4, $K_2Cr_2O_7$, $HClO_4$, $CuCl_2$, HNO_3, H_2SO_5, $FeCl_3$, $HgCl_2$, etc.

6. REDUCTANT OR REDUCTION AGENT

Species which reduce other element in a reaction and oxidise itself to donate electrons and show increase in its oxidation no. is called reductant or reducing agent.

6.1 Some Important reducing agent or reductant

1. All metals like, K, Mg, Ca, etc.
2. All metallic hydrides like NaH, CaH_2, $LiAlH_4$, $NaBH_4$, AlH_3, etc.
3. All hydroacids like HF, HCl, HBr, H_2S etc.
4. Some organic compounds like Aldehyde, formic acid, oxalic acid, tartaric acid.
5. All neutral compounds or ions, which show their lower oxidation state.

   MnO, HClO, $HClO_2$, H_3PO_2, HNO_2, H_2SO_3, $FeCl_2$, $SnCl_2$, Hg_2Cl_2, CH_2Cl_2 etc.

   Some Important compound which can act as oxidant and reductant both

   HNO_2, SO_2, H_2O_2, O_3, Al_2O_3, CrO_2, MnO_2, ZnO, CuO,

   NOTE : Al_2O_3, CrO_2, MnO_2, ZnO, CuO are called as amphoteric oxide.

7. OXIDATION NUMBER

A. Definition : It represents the number of electron gained or lost by atom when it changes in compound from a free state.

(a) If electron are lose by an atom in the formation of compound, oxidation number is given (+)ve sign.

(b) If electrons are gain by an atom in the formation of compound oxidation number given is (–)ve sign.

(c) It represents the real charge in case of ionic compounds and represents the imaginary charge in case of covalent compounds.

(d) Maximum oxidation no. of an element is equal to group no. in the periodic table

(e) Minimum oxidation no. of an element is equal to group no. – 8.

I group elements always shows +1 oxidation no.

II group elements always shows +2 oxidation no.

III group elements show +3 oxidation no. but +1 becomes more stable going down the group (due to inert pair effect)

IV group shows –4 to +4 oxidation no.

V group shows –3 to +5 oxidation no.

VI group shows –2 to +6 oxidation no.

VII group shows –1 to +7 oxidation no.

Inert gases show zero oxidation no.

7.1 Oxidation no. for Coordinate bond

(a) When coordinate bond is formed from low electronegative element to high electronegative element then the e^- donor element shows +2 oxidation number whereas e^- acceptor element shows –2, oxidation no. in this type of bonded compounds. For example in H_2SO_4.

Here 'S' is low electronegative element than O. therefore, number of S = +2 and O. N. of O = –2

(b) When coordinate bond is formed between the two same electronegative elements then the e^- donor element shows +2 oxidation number where e^- acceptor element shows –2 oxidation number in this type of bonded compound.

For example :– In $Na_2S_2O_3$

Here O.N. of 'S' is +2, Because it is e^- donor and the other 'S' is –2, Because it is e^- acceptor.

(c) When coordinate bond is formed from high electronegative element to low electronegative element then no change will be shown by both the elements, which is bonded by coordinate bond. eg. CH_3NC

8. OXIDATION STATE

Oxidation state of an atom is defined as oxidation number per atom for all practical purposes. Oxidation state is often expressed as oxidation number.

8.1 The rules to derive oxidation number or oxidation state

(a) The O.S. of an element in its free state is zero. Example O.S.' s of Na, Cu, I_2, Cl_2, O_2 etc. are zero

(b) Sum of O.S.' s of all the atoms in neutral molecule is zero.

(c) Sum of O.S.' s of all the atoms in a complex ion is equal number of charge present on it.

(d) In complex compounds, O.S. of some neutral molecules (ligands) is zero. Example CO, NO, NH_3, H_2O.

(e) Generally O.S. of oxygen is –2 but in H_2O_2 it is –1 and in OF_2 it is +2.

(f) Generally O.S. of Hydrogen is +1 but in metallic hydrides it is –1.

(g) Generally O.S. of halogen atoms is –1 but in interhalogen compounds it changes.

NOTE : Some times same atom in a compound has different O.S. For example, structure of $Na_2S_2O_3$ is

Here S_1 and S_2 both are sulphur atoms but they have different O.S.

O.S. of S_1 = 6

O.S. of S_2 = –2 (it is accepting two electrons from S_1)

$$\text{Average O.S. of S} = \frac{6-2}{2} = 2$$

(h) Generally, O.S. of alkali metals is +1 and that of alkaline earth metals is +2.

(i) O.S. of transition elements very high from compound to compound. Mn has O.S. from +1 to +7. $Mn_2O \rightarrow +1$, $MnO \rightarrow +2$, $Mn_3O_4 \rightarrow 8/3$, $MnO_2 \rightarrow +4$, $Mn_2O_5 \rightarrow +5$, $MnO_4^{2-} \rightarrow +6$, $MnO_4^{-} \rightarrow +7$

(j) O.S. of an atom may be fractional, negative, zero as well as Positive.

8.2 Oxidation State As A periodic Property

Oxidation state of an atom depends upon the electronic configuration of atom it is periodic properties.

(a) I A group or alkali metals shows +1 oxidation state.

(b) II A group or alkaline earth metals show +2 O.S.

(c) The maximum normal oxidation state, show by III A group elements is +3. These elements also show +2 to +1 oxidation states also.

(d) Elements of IVA group show their max & min. oxidation states +4 & - 4 respectively.

(e) Non metals shows number of oxidation states, the relation between max & min. oxidation states for non metals is equal to maximum O.S. –minimum O.S. = 8

For example sulphur has maximum oxidation number +6 as being in VI A group element.

8.3 Fractional Oxidation States

Lot of elements shows fractional oxidation states. For example oxidation state of oxygen in superoxides of alkali metals (KO_2, SO_2, RbO_2) is -1/2.

eg. In Fe_3O_4, Fe shows its oxidation state as 8/3 as it is a mixed oxide and can be written as $Fe^{II}\ Fe_2^{III}O_4$.

Example Based on Oxidation number and oxidation state

Ex.1 What is the oxidation state of nitrogen in NaN_3 ?

(A) – 3/1 (B) 3

(C) – 3 (D) – 1/3 **Ans. [D]**

Sol. In NaN_3

Na N_3

$1 + 3x = 0, \quad x = -1/3$

So, oxidation number of nitrogen in NaN_3 is **– 1/3**.

Ex.2 What is the oxidation number of oxygen in OF_2 ?

(A) +2 (B) +4 (D) +3 (D) None **Ans. [A]**

Sol. In OF_2

$x + 2(-1) = 0, \quad x = \mathbf{+2}$

Hence oxidation number of oxygen in OF_2 **= + 2**.

9. REDOX REACTIONS

(a) The reactions in which oxidation and reduction both occur simultaneously are called redox reactions.

(b) Most of the chemical reactions are redox because if one element is there to lose electrons, other element has to be there to accept them.

S.No.	**Reaction**	**Oxidant** (Getting Reduced)	**Reductant** (Getting Oxidised)
1.	$C + O_2 \rightarrow CO_2$	O [0 → – 2]	C [0 → + 4]
2.	$PbS + 4O_3 \rightarrow PbSO_4 + 4O_2$	O [+ 2 → 0]	S [– 2 → + 6]
3.	$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$	O [–1 → –2]	S [– 2 → + 6]
4.	$Sn + 2F_2 \rightarrow SnF_4$	F [0 → –1]	Sn [0 →+ 4]
5.	$SO_2 + 2H_2O + Cl_2 \rightarrow 2HCl + H_2SO_4$	Cl [0 → –1]	S [+ 4 → + 6]
6.	$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$	N [+ 5 → + 4]	I [0 → + 5]
7.	$CuO + H_2 \rightarrow Cu + H_2O$	Cu [+ 2 → 0]	H [0 → + 1]
8.	$2KMnO_4 + 3H_2SO_4 + 5H_2S \rightarrow$ $K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$	Mn [+ 7 → + 2]	S [–2 → 0]
9.	$H_2O_2 + Ag_2O \rightarrow 2Ag + H_2O + O_2$ (Oxygen of H_2O_2)	Ag [+ 1 → 0]	O [–1 → 0]
10.	$H_2SO_4 + 2HI \rightarrow SO_2 + I_2 + 2H_2O$	S [+6 → +4]	I [–1 → 0]

NOTE : In reaction 2 oxygens of ozone have different OS.

Structure of ozone is

$O_3 \leftarrow O_1{=}O_2$

OS of O_1 = + 2

OS of O_2 = 0

Here O_1 is getting reduced in reaction 2

OS of O_3 = – 2

(d) Redox reactions may be intramolecular or disproportionation reactions. It depends upon whether the migration of electron takes place in the atoms of the same compound or different compounds .

(i) Intermolecular redox reaction

$$2H_2\overset{+6}{S}O_4(\text{conc.}) + Cu \rightarrow \overset{+2}{Cu}SO_4 + \overset{+4}{S}O_2 + 2H_2O$$

(ii) Intramolecular redox reaction

$$2K\overset{+5}{Cl}\overset{-2}{O}_3 \rightarrow 2K\overset{-1}{Cl} + 3\overset{0}{O}_2$$

(iii) Disproportions Redox Reaction : In this type of redox reactions same element acts as both oxidsing & reducing agent.

$$\overset{0}{Cl}_2 + H_2O \rightarrow H\overset{+1}{Cl}O + H\overset{-}{Cl}$$

10. BALANCING OF REDOX EQUATIONS BY ION ELECTRON METHOD

10.1 Acidic Medium

(a) consider the example,

$$Cr_2O_7^{2-} + C_2O_4^{2-} \xrightarrow{H^+} Cr^{3+} + CO_2$$

(b) Write both the half reactions.

$Cr_2O_7^{2-} \rightarrow Cr^{3+}$ (Reduction half reaction)

$C_2O_4^{2-} \rightarrow CO_2$ (Oxidation half reaction)

(c) Atoms other than H and O are balanced

$Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$

$C_2O_4^{2-} \rightarrow 2CO_2$

(d) Balance O–atoms by the addition of H_2O to another side

$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$

$C_2O_4^{2-} \rightarrow 2CO_2$

(e) Balance H–atoms by the addition of H^+ ions to another side

$Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

$C_2O_4^{2-} \rightarrow 2CO_2$

(f) Now, balance the charge by the addition of electrons (e^-).

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$

(g) Multiply equations by a constant to get number of electrons same in both side. In the above case second equation is multiplied by 3 and then added to first equation.

$$\begin{array}{l} Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \\ 3C_2O_4^{2-} \rightarrow 6CO_2 + 6e^- \\ \hline Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14\,H^+ \rightarrow 2Cr^{3+} + 6CO_2 + 7H_2O \end{array}$$

10.2 Alkaline Medium

(a) Consider the reaction

$Cr(OH)_3 + IO_3^- \xrightarrow{OH^-} I^- + CrO_4^{2-}$

(b) Separate the two half reactions.

$Cr(OH)_3 \rightarrow CrO_4^{2-}$ (Oxidation half reaction)

$IO_3^- \rightarrow I^-$ (Reduction half reaction)

(c) Balance O– atoms by adding H_2O.

$H_2O + Cr(OH)_3 \rightarrow CrO_4^{2-}$

$IO_3^- \rightarrow I^- + 3H_2O$

(d) Balance H–atoms by adding H_2O to side having deficiency and OH^- to side having deficiency of H–atoms.

$5OH^- + H_2O + Cr(OH)_3 \rightarrow CrO_4^{2-} + 5H_2O$ or $5OH^- + Cr(OH)_3 \rightarrow CrO_4^{2-} + 4H_2O$

$IO_3^- + 6H_2O \rightarrow I^- + 3H_2O + 6OH^-$

or $IO_3^- + 3H_2O \rightarrow I^- + 6OH^-$

(e) Balance the charges by electrons

$5OH^- + Cr(OH)_3 \rightarrow CrO_4^{2-} + 4H_2O + 3e^-$

$IO_3^- + 6H_2O + 6e^- \rightarrow I^- + 3H_2O + 6OH^-$

(f) Multiply first equation by 2 and add to second to give

$10OH^- + 2Cr(OH)_3 \rightarrow 2CrO_4^{2-} + 8H_2O + 6e^-$

$IO_3^- + 6H_2O + 6e^- \rightarrow I^- + 3H_2O + 6OH^-$

$4OH^- + 2Cr(OH)_3 + IO_3^- \rightarrow 5H_2O + 2CrO_4^{2-} + I^-$

Example Based on Balancing of equations

Ex.3 What will be the value of x, y and z in the following equation –

$H_2C_2O_4 + xH_2O_2 \rightarrow yCO_2 + zH_2O$

(A) 2, 1, 2 (B) 1, 2, 2 (C) 2, 2, 1 (D) None

Ans. [B]

Sol. (i) The half reaction for oxidation is,

$H_2C_2O_4 \rightarrow CO_2$

Balancing carbon atoms on both sides,

$H_2C_2O_4 \rightarrow 2CO_2$

Balancing hydrogen atoms on both sides,

$H_2C_2O_4 \rightarrow 2CO_2 + 2H^+$

Balancing the charge on both sides,

$H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^-$ (balanced)

(ii) The half reaction for reduction is –

$H_2O_2 \rightarrow H_2O$

Balancing oxygen atoms on both sides,

$H_2O_2 \rightarrow 2H_2O$

Balancing hydrogen atoms,

$H_2O_2 + 2H^+ \rightarrow 2H_2O$

Balancing the charge,

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

Now, adding both equation,

$H_2C_2O_4 + H_2O_2 \rightarrow 2CO_2 + 2H_2O$

This is balanced equation.

Ex.4 What will be the value of x, y and z in the following equation –

$xI_2 + yOH^- \rightarrow IO_3^- + zI^- + 3H_2O$

(A) 3, 5, 6 (B) 5, 6, 3 (C) 3, 6, 5 (D) 6, 3, 5 **Ans. [C]**

Sol.

$\overset{0}{I_2} \rightarrow \overset{+5}{IO_3}$ ..... (i) Oxidation

$\overset{0}{I} \rightarrow \overset{-1}{I^-}$ ..... (ii) Reduction

Balancing atoms of Iodine on two sides,
we get,

$I_2 \rightarrow 2IO_3^-$

or, $I_2 + 12OH \rightarrow 2IO_3^- + 6H_2O$

Balancing change,

$I_2 + 12OH^- \rightarrow 2IO_3^- + 6H_2O + 10e^-$

$I_2 \rightarrow 2I^-$

and $(I_2 + 2e^- \rightarrow 2I^-) \times 5$

Adding, $6I_2 + 12OH^- \rightarrow 2IO_3 + 10I^- + 6H_2O$

or, $\mathbf{3I_2 + 6OH^- \rightarrow IO_3^- + 5I^- + 3H_2O}$

It is balanced equation.

Ex.5 What will be the value of a, b, c, d, e and f in the following equation –

$aMnO_4^- + bC_2O_4^{--} + cH^+ \rightarrow$
$dMn^{++} + eCO_2 + f\,H_2O$

(A) 2, 2, 10, 8, 5, 16 (B) 2, 5, 16, 2, 10, 8

(C) 2, 5, 10, 2, 8, 16 (D) 2, 8, 16, 2, 5, 10 **Ans. [B]**

Sol. (i) The half reaction for reduction is,

$MnO_4^- \rightarrow Mn^{++}$

Balancing with respect to oxygen by adding $4H_2O$ on R.H.S.,

$MnO_4^- \rightarrow Mn^{++} + 4H_2O$

Balancing with respect to hydrogen by adding $8H^+$ on L.H.S.,

$MnO_4^- + 8H^+ \rightarrow Mn^{++} + 4H_2O$

Balancing charge by adding electrons,

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{++} + 4H_2O$

(ii) The half reaction for oxidation is,

$C_2O_4^{--} \rightarrow 2CO_2$

Balancing with respect to electrical charge by adding electrons on R.H.S.

$C_2O_4^{--} \rightarrow 2CO_2 + 2e^-$

Now, to equalise the number of electrons, the reduction half reaction is multiplied by 2 and oxidation half reaction by 5, so on adding, we get

$(C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-) \times 5$

$(MnO_4^- + 8H^+ + 5e^- \rightarrow$
$Mn^{++} + 4H_2O) \times 2$

$\mathbf{2MnO_4^- + 5C_2O_4^{--} + 16H^+ \rightarrow 2Mn^{++} + 10CO_2 + 8H_2O}$

This is the balanced equation.

11. EQUIVALENT WEIGHT

(a) Equivalent wt. of an oxidant (get reduced)

$$= \frac{\text{Mol. wt.}}{\text{No. of electrons gained by one mole}}$$

$$= \frac{\text{Mol. wt.}}{\text{Decrease in O.S.} \times \text{No. of atom undergoing reduction}}$$

Example :

In acidic medium

$$6e^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$

Here atoms undergoing reduction is Cr its O.S. is decreasing from 6 to 3

$$\text{Eq. wt. of } K_2Cr_2O_7 = \frac{\text{Mol. wt. of } K_2Cr_2O_7}{3 \times 2} = \frac{\text{Mol. wt.}}{6}$$

NOTE : [6 in denominator indicates that 6 electrons were gained by $Cr_2O_7^{2-}$ as it is clear from the given balanced equation]

(b) Similarly equivalent wt. of a reductant (gets oxidised)

$$= \frac{\text{Mol. wt.}}{\text{No. of electrons lost by one mole}}$$

$$= \frac{\text{Mol. wt.}}{\text{increase in O.S.} \times \text{No. of atom undergoing oxidation}}$$

Example :

In acidic medium, $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$

Here, O.S. of carbon is changing from +1 to +2 i.e. each carbon atom is losing one electron and there are 2 atoms of carbon so total electrons lost = 2 so, eq. wt = $\frac{\text{Mol.wt}}{2}$

(c) In different condition a compound may have different equivalent wts. Because, it depends upon the number of electrons gained or lost by that compound in that reaction.

Example :

(i) $\underset{(+7)}{MnO_4^-} \rightarrow \underset{(+2)}{Mn^{2+}}$ (acidic medium)

So, Here 5 electrons are taken so eq. wt

$$= \frac{\text{Mol. wt. of } KMnO_4}{5} = \frac{158}{5} = 31.6$$

(ii) $\underset{(+7)}{MnO_4^-} \rightarrow \underset{(+4)}{MnO_2}$ (neutral medium)

Here, only 3 electrons are gained

$$\text{so, eq. wt} = \frac{\text{Mol. wt. of } KMnO_4}{3}$$

$$= \frac{158}{3} = 52.7$$

(iii) $\underset{(+7)}{MnO_4^-} \rightarrow \underset{(+6)}{MnO_4^{-2}}$ (alkaline medium)

Here, only one electron is gained

$$\text{so, eq. wt} = \frac{\text{Mol. wt. of } KMnO_4}{1} = 158$$

NOTE : It is important to note that $KMnO_4$ acts as an oxidant in every medium although with different strength which follows the order –

acidic medium > neutral med. > Alkaline medium

while, $K_2Cr_2O_7$ acts as an oxidant only in acidic medium as follows

$Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+}$

$(2 \times 6) \rightarrow (2 \times 3)$

Here, 6 electrons are gained

so eq. wt $= \dfrac{\text{Mol. wt. of } K_2Cr_2O_7}{6} = \dfrac{294.21}{6} = 49.03$

(d) It is clear that $KMnO_4$ is better oxidant than $K_2Cr_2O_7$.

(e) Try to balance reaction (a) (b) (c) of reduction of $KMnO_4$ by ion electron method as you should get following –

(i) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (acidic medium)

(ii) $MnO_4^- + e^- \rightarrow MnO_4^{2-}$ (alkaline medium)

Example based on equivalent weight

Ex.6 What will be the equivalent weight of permanganate ion in the following redox reaction –

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{++} + 4H_2O$

(A) M/5 (B) M/6 (C) M/8 (D) 5M

Ans.[A]

Sol. Equivalent weight of MnO_4^-

$= \dfrac{\text{Molecular weight of } MnO_4^-}{5} = \dfrac{M}{5}$

Ex.7 What will be the equivalent weight of a reducing agent is that weight which donates one electron in a chemical reaction–

$2S_2O_3^{--} \rightarrow S_4O_6^{--} + 2e^-$

(A) 2M (B) 3M (C) M /2 (D) M

Ans. [D]

Sol. Equivalent weight of $S_2O_3^{--} = \dfrac{2M}{2}$ **= M.**

Ex.8 In the following reaction, what is the molecular weight of oxidant and reductant respectively –

$5Zn + V_2O_5 \rightarrow 5ZnO + 2V$ [V = 50.94, Zn = 65.38 and O = 16]

(A) 18.2, 32.69 (B) 30, 20 (C) 34.10, 20.2 (D) 40, 10

Ans.[A]

Sol. Change in the O.N. of Zn : Zn → ZnO

Zn = 0, Zn in ZnO = + 2

Change = 2

$V_2O_5 \rightarrow 2V$, [for V_2] + 10 → 0

Change = 10

eqvt. wt. of reductant $= \dfrac{65.38}{2}$ **= 32.69 gm** eqvt. wt. of oxidant $= \dfrac{50.94 \times 2 + 80}{10}$

= 18.18 or 18.2

12. EQUIVALENT WEIGHT IN DISPROPORTION REACTION

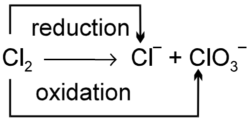
The equivalent weight of the substance undergoing disproportion can be determined by the following method.

Consider the substance 'X' is undergoing disproportionation reaction.

(i) Find out the equivalent weight of 'X' for oxidation reaction, say it is E_1.

(ii) Also find out the equivalent weight of 'X' for reduction reaction, say it is E_2.

(iii) The equivalent weight of 'X' = $E_1 + E_2$ for example, Cl_2 disproportionate in Cl^- & ClO_3^-



$$Cl_2 \longrightarrow Cl^- + ClO_3^-$$

The X factor for oxidation = 2

The X factor for reduction = 10

The equivalent wt of Cl_2 $= \frac{71}{2} + \frac{71}{10} = 35.5 + 7.1 = 42.6$ **Ans.**

Solved Example

Ex.1 Which of the following acts as both oxidant and reductant –

(A) HNO_3 (B) HNO_2

(C) Both HNO_3 & HNO_2 (D) Neither HNO_3 nor HNO_2

(Ans. B)

Sol. O.N. of N in HNO_2 is +3

Max. O.N. of N is +5

Min. O.N. of N is –3

Thus O.N. of N in HNO_2 can show an increase or decrease as the case may be. That is why HNO_2 acts as oxidant and reductant both.

O.N. of N in HNO_3 is +5, Hence it can act only as an oxidant.

Ex.2 State which of the following reactions is neither oxidation nor reduction –

(A) Na → NaOH (B) $Cl_2 \rightarrow Cl^- + ClO^-_3$

(C) $P_2O_5 \rightarrow H_4P_2O_7$ (D) $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

(Ans. C)

Sol. In the reaction $P_2O_5 \rightarrow H_4P_2O_7$

The O.N. of P in P_2O_5 is

$2x + 5(-2) = 0$ or $x = +5$

The O.N. of P in $H_4P_2O_7$ is

$4(+1) + 2(x) + 7(-2) = 0$

$2x = 10$ or $x = +5$

Since there is no change in O.N. of P, hence the above reaction is neither oxidation nor reduction.

Ex.3 In the reaction

$C_2O_4^{-2} + MnO^-_4 + H^+ \rightarrow Mn^{+2} + CO_2$

the reductants is –

(A) $C_2O_4^{-2}$ (B) H^+

(C) MnO^-_4 (D) None of the above

Ex.3 In the reaction

$C_2O_4^{-2} + MnO^{-}_4 + H^+ \rightarrow Mn^{+2} + CO_2$

the reductants is –

(A) $C_2O_4^{-2}$ (B) H^+

(C) MnO^{-}_4 (D) None of the above **(Ans. A)**

Sol. In the above reaction $C_2O_4^{-2}$ acts as a reductant because it is oxidised to CO_2 as

$C_2O_4^{-2} \rightarrow 2CO_2 + 2e$(oxidation)

$C_2O_4^{-2}$ reduces MnO_4^{-} to Mn^{+2} ion in solution.

Ex.4 Oxidation number of cobalt in $[Co(NH_3)_6]Cl_2Br$ is –

(A) + 6 (B) Zero (C) + 3 (D) + 2 **(Ans. C)**

Sol. Let the O.N.of Co be x

O.N. of NH_3 is zero

O.N. of Cl is –1

O.N. of Br is –1

Hence, x + 6 (0) – 1 x 2 –1 = 0

$\therefore$ x = + 3

so, the oxidation number of cobalt in the given complex compound is +3.

Ex.5 The order of increasing O.N. of S in S_8, $S_2O_8^{-2}$, $S_2O_3^{-2}$, $S_4O_6^{-2}$ is given below –

(A) $S_8 < S_2O_8^{-2} < S_2O_3^{-2} < S_4O_6^{-2}$

(B) $S_2O_8^{-2} < S_2O_3^{-2} < S_4O_6^{-2} < S_8$

(C) $S_2O_8^{-2} < S_8 < S_4O_6^{-2} < S_2O_3^{-2}$

(D) $S_8 < S_2O_3^{-2} < S_4O_6^{-2} < S_2O_8^{-2}$ **(Ans. D)**

Sol. The O.Ns. of S are shown below along with the compounds

S_8,	$S_2O_8^{-2}$,	$S_2O_3^{-2}$,	$S_4O_6^{-2}$
0	+ 6	+2	+2.5

Hence the order of increasing O.N. of S is

$S_8 < S_2O_3^{-2} < S_4O_6^{-2} < S_2O_8^{-2}$

Ex.6 The composition of a sample of wustite is $Fe_{0.93}O_{1.00}$. What percentage of iron is present in the form of Fe (III)

(A) 13.05 (B) 14.05

(C) 15.05 (D) 16.05 **(Ans. C)**

Sol. O.N. of. Fe in wustite is = $\frac{200}{93}$ = 2.15

It is an intermediate value in between Fe (II) & Fe (III)

Let % of Fe (III) be a, then

2 x (100 – a) + 3 x a = 2.15 x100

a = 15.05

$\therefore$ % of Fe (III) = 15.05%

Ex.7 The oxid.no. of Cl in $NOClO_4$ is –

(A) + 11 (B) + 9

(C) + 7 (D) + 5 **(Ans. C)**

Sol. The compound may be written as $NO^+ \, ClO_4^-$

For ClO_4^-, Let Ox. No.of Cl = a

$a + 4 \times (-2) = -1$

$a = +7$

Hence, the oxidation no. of Cl in $NOClO_4$ is +7.

Ex.8 The two possible oxidation numbers of N atoms in NH_4NO_3 are respectively –

(A) +3, +5 (B) +3, –5

(C) –3, +5 (D) –3, –5 **(Ans. C)**

Sol. There are two N atoms in NH_4NO_3, but one N atom has negative oxidation number (attached to H) and the other has positive oxid.no. (attached to O). Therefore evaluation should be made separately as –

O.N. of N is NH_4^+ O.N. of N in NO_3^-

$a + 4 \times (+1) = +1$ and $a + 3\,(-2) = -1$

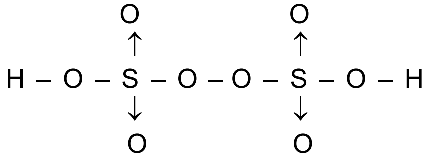
$\therefore\ a = -3$ $\therefore\ a = +5$

Here the two O.N. are –3 and +5 respectivley.

Ex.9 The oxidation number of S in $H_2S_2O_8$ is –

(A) +8 (B) –8 (C) +6 (D) +4 **(Ans. C)**

Sol. In $H_2S_2O_8$, two O atoms form peroxide linkage i.e



$$H-O-\underset{\substack{\downarrow\\ O}}{\overset{\substack{O\\ \uparrow}}{S}}-O-O-\underset{\substack{\downarrow\\ O}}{\overset{\substack{O\\ \uparrow}}{S}}-O-H$$

$2 \times 1 + 2a + 6(-2) + 2\,(-1) = 0$

$\therefore\ a = +6$

Thus the O.N. of S in $H_2S_2O_8$ is + 6.

Ex.10 When $K_2Cr_2O_7$ is converted into K_2CrO_4 the change in oxidation number of Cr is –

(A) 0 (B) 3 (C) 4 (D) 6 **(Ans. A)**

Sol. When $Cr_2O_7^{-2}$ is converted into CrO_4^{-2} the change in oxidation number of Cr is zero

$$\underset{+6}{Cr_2O_7^{-2}} \rightarrow \underset{+6}{CrO_4^{-2}}$$

There is no change in oxidation state of Cr, hence it is neither oxidised nor reduced and remains in the same oxidation state.

Ex.11 The oxidation number of S in $(CH_3)_2\,SO$ is –

(A) 1 (B) 2 (B) 0 (D) 3 **(Ans. C)**

Sol. Let the oxidation no. of S is 'a'

O.N. of CH_3 = +1

O.N. of O = –2

$2(+1) + a + (-2) = 0$

$a = 0$

Hence the oxidation no. of S in Dimethyl sulphoxide is zero.

Ex.12 What will be the oxidation number of I in the KI_3 –

(A) $-\frac{1}{3}$ (B) $-\frac{1}{4}$ (C) + 4 (D) + 3 **(Ans. A)**

Sol. In KI_3 $1 + 3 \times (a) = 0$ $a = -\frac{1}{3}$

or KI_3 is $KI + I_2$

$\therefore$ I has two oxidation no. –1 and 0 respectively. However factually speaking oxidation number of I in KI_3 is on average of two values – 1 and 0.

Average O.N. **=** $\frac{-1+2\times(0)}{3} = -\frac{1}{3}$.

Ex.13 Oxidation number of Fe in $[Fe(CN)_6]^{-3}$, $[Fe(CN)_6]^{-4}$, $[Fe(SCN)]^{+2}$ and $[Fe(H_2O)_6]^{+3}$ respectively would be–

(A) +3, +2, +3 and +3 (B) +3, +3, +3 and +3

(C) +3, +2, +2 and +2 (D) +2, +2, +2 and +2 **(Ans. A)**

Sol. Oxidation number of Fe in–

First	Second	Third	Fourth
$x-6 = -3$	$x-6 = -4$	$x-1 = +2$	$x + 6\times0 = +3$
$x = +3$	$x = +2$	$x = +3$	$x = +3$

Ex.14 Which of the following is not a redox reaction–

(A) $\frac{1}{2}H_2 + \frac{1}{2}I_2 \Leftrightarrow HI$ (B) $PCl_5 \Leftrightarrow PCl_3 + Cl_2$

(C) $2CuSO_4 + 4KI \Leftrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$ (D) $CaOCl_2 \Leftrightarrow Ca^{+2} + OCl^- + Cl^-$ **(Ans. D)**

Sol. In all the above reaction except (D) there is change in oxidation states of reactant and product atoms, hence they are all redox reactions. In reaction (D) the oxidation states of the atoms of the reactants and products remain unchanged hence, it is not a redox reaction.

Ex.15 In the reaction $Al + Fe_3O_4 \rightarrow Al_2O_3 + Fe$ –

what is the total no. of electrons transferred during the change –

(A) 16 (B) 24 (C) 8 (D) 12 **(Ans. B)**

Sol. $2Al^o \rightarrow Al_2^{+3} + 6e^-$ .... (A)

$8e + Fe_3^{+8/3} \rightarrow 3Fe^o$ .... (B)

Multiplying Eq. (A) by 4 and Eq. (B) by 3, then on addition

$$\begin{array}{l} 8Al^o \rightarrow 4Al_2^{+3} + 24e \\ 24e + 3Fe_3^{+8/3} \rightarrow 9Fe^o \\ \hline 8Al^o + 3Fe_3^{+8/3} \rightarrow 9Fe^o + 4Al_2^{+3} \\ \hline \end{array}$$

or $8Al + 3Fe_3O_4 \rightarrow 4Al_2O_3 + 9Fe$

Therefore, it is clear that total no. of electrons transferred during change = 24

Ex.16 In the redox reaction –

$10FeC_2O_4 + x\,KMnO_4 + 24H_2SO_4 \rightarrow$

$5Fe_2(SO_4)_3 + 20CO_2 + y\,MnSO_4 + 3\,K_2SO_4 + 24H_2O$.

The values of x and y are respectively –

(A) 6, 3 (B) 3, 6 (C) 3, 3 (D) 6, 6 **(Ans. D)**

Sol. The balanced redox reaction given above can be written as :

$10FeC_2O_4 + 6KMnO_4 + 24H_2SO_4 \rightarrow$

$5Fe_2(SO_4)_3 + 20CO_2 + 6\,MnSO_4 + 3\,K_2SO_4 + 24H_2O$

so the value of x = 6 and y = 6

Ex.17 A solution containing 2.68×10^{-3} mol of A^{+n} ions requires 1.61×10^{-3} mole of MnO^{-}_4 for the oxidation of A^{+n} to AO^{-}_3 in acidic medium. What is the value of n –

(A) 1 (B) 2 (C) 3 (D) 4 **(Ans. B)**

Sol. The reaction are

$MnO^{-}_4 + 8H^+ + 5e^- \rightarrow Mn^{+2} + 4H_2O$

$A^{+n} + 3H_2O \rightarrow AO_3^- + 6H^+ + (5-n)\ e^-$

Amount of electrons involved in the given amount of MnO_4^- = $5 \times 1.61 \times 10^{-3}$ mol.

Equating these two we get

$5 \times 1.61 \times 10^{-3} = (5-n)\ 2.68 \times 10^{-3}$

$\therefore$ n = 2 (approx.)

Ex.18 Which of the following is correctly balanced half reaction –

(A) $AsO_3^{-3} + H_2O \rightarrow AsO_4^{-3} + 2H^+ - 2e^-$ (B) $H_2O_2 + 2e \rightarrow O_2 + 2H^+$

(C) $Cr_2O_7^{-2} + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O - 6e^-$ (D) $IO^{-}_3 + 6H^+ \rightarrow I_2 + 3H_2O + 5e^-$

(Ans. C)

Sol. The correctly balanced half reaction is –

$Cr_2O_7^{-2} + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O - 6e^-$ It is a reduction half reaction in balancing the equation by ion–electron method.

Electro chemistry

2- ELECTROCHEMICAL CELLS

Let us consider the reaction

$2\ Na + Cl_2 \longrightarrow 2Na^+ + 2Cl^-$

It occurs by the transfer of electrons from Na to Cl. Na loses an electron and is said to be oxidized to Na+ ion. At the same time, Cl gains an electron and is reduced to Cl^- ion. Such a reaction which is brought about by loss of electrons (oxidation) and gain of electrons (reduction) simultaneously, is called an **Oxidation-Reduction reaction or Redox reaction** in brief.

2-1 Types of electrodes

1- Metal-Metal ion electrodes

A metal rode that dipped in an electrolyte solution containing metal ions. Ther is a potential difference between these two phases and this electrode can act as a cathode or anode

Anode: $M \longrightarrow M^{n+} + ne^-$

The potential of a single electrode in a half-cell is called the **Single electrode potential.** So the Nernst eq. takes the form:

$$E = E^{\ominus} - \frac{RT}{zF}\ln a_{M^{+n}}$$

2--Gas electrode (Standard Hydrogen Electrode (SHE)

Electrode gases like H_2, Cl_2….etc. are used with their respective ions , for example: H_2 gas is used with a dilute solution of HCl (H^+ ions). The metal should be inert so that it does not react with the acid.

Anode: $H_2 \longrightarrow 2H^+ + 2e^-$

Cathode: $2H^+ + 2e^- \longrightarrow H_2$

This electrode is also used to measure other potentials **(emf)**. Its own potential is est to 0v as a reference , the Con. Of HCl is 1M and the electrode is called ***Standard Hydrogen Electrode (SHE)*** ,(fig.6)

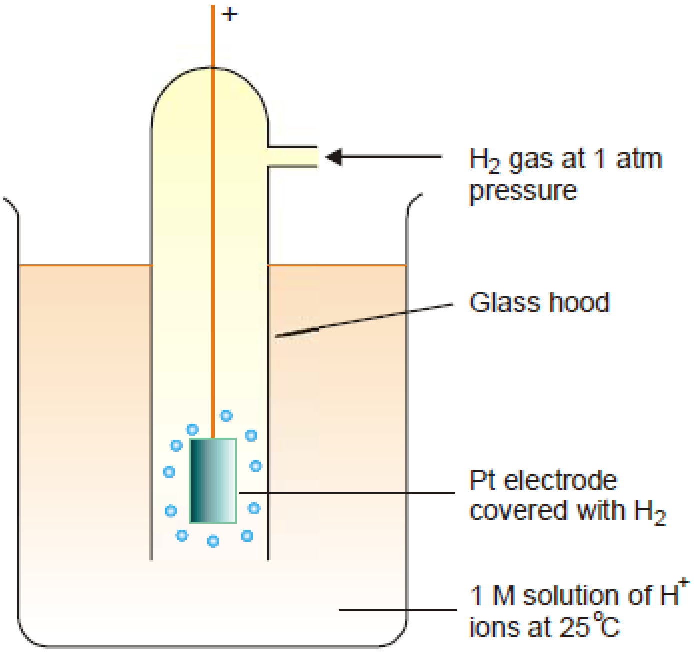


Fig.6: ***Standard Hydrogen Electrode (SHE)***

The emf of the unknown half-cell, E°, can then be calculated from the expression

$$\mathbf{E_{measured} = E_R - E_L}$$

where ER and EL are the **reduction potentials** of the right-hand and left-hand electrodes respectively, The standard hydrogen half-cell or **Standard Hydrogen Electrode (SHE),** is selected for coupling with the unknown half-cell.

The emf of the standard hydrogen electrode is arbitrarily assigned the value of zero volts. So,SHE can be used as a standard for other electrodes.

Example/ it is desired to determine the emf of the zinc electrode, Zn | Zn^{2+}. It is connected with the hydrogen electrode and the emf ofthe complete cell determined with a voltmeter. The emf of the cell is the emf of the half-cell.

$$\mathbf{Ecell = E_R - E_L}$$

$$= -0.76 - 0 = -0.76 \text{ V}$$

– 0.76 V is the emf for Zn

3- Metal- insoluble salt electrode

The standard hydrogen electrode (SHE) is not the most convenient standard electrode to use in the laboratory. The gas has to be carefully controlled.Metal- insoluble salt electrode system whose potential has been determined relative to the SHE can also be used as Secondary standard electrode.

a-The Standard Silver-Silver chloride Electrode:

In this electrode system, silver wire is covered with silver chloride (a highly insoluble substance). It is dipped in potassium chloride solution in which the concentration of Cl^- ion is 1 M This electrode can be represented as

The corresponding half-reactions can be presented as follows:

$$\mathrm{Ag^+ + e^- \rightleftharpoons Ag(s)}$$
$$\mathrm{AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-}$$

or can be written together:

$$\mathrm{AgCl(s) + Ag(s) + e^- \rightleftharpoons Ag(s) + e^- + Cl^- + Ag^+}$$

which can be simplified:

$$\mathrm{AgCl(s) \rightleftharpoons Ag^+ + Cl^-}$$

The Nernst equation below shows the dependence of the potential of the silver-silver(I) chloride electrode on the activity or effective concentration of chloride-ions:

$$E = E^0 - \frac{RT}{F} \ln a_{\mathrm{Cl^-}}$$

The standard electrode potential E^0 against standard hydrogen electrode (SHE) is 0.230 V

b- The Calomel Electrode

It is the most commonly used secondary standard reference electrode. The standard calomel electrode, **SCE,**

The calomel electrode is represented as

Cl^- (1M) | Hg_2Cl_2, Hg

and the half-cell reaction is:

$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$

4- *Glass Electrode*

A commonly used secondary standard electrode is the so-called glass electrode. Its emf is determined by coupling with a standard calomel electrode (SCE). The glass electrode provides one of the easiest methods for measuring the pH of a given solution.

A simple type of glass electrode (Fig. 7) consists of a glass tube having a thin-walled bulb at the lower end. The bulb contains a 1M HCl solution. Sealed into the glass-tube is a silver wire coated with silver chloride at its lower end. The lower end of this silver wire dips into the hydrochloric acid, forming silver-silver chloride electrode.

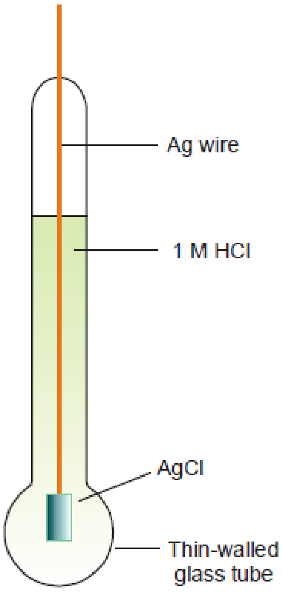


Fig. 7:glass electrode

The glass electrode represented as

$$\text{Ag, AgCl} \mid \text{1 M HCl} \vdots \text{H}^+ \text{ (Test Solution)}$$

When placed in a solution, the potential of the glass electrode depends on the H^+ ion concentration of the solution. The potential develops across the glass membrane as a result of a concentration difference of H^+ ions on the two sides of the membrane. This happens much in the same way as the emf of a concentration cell develops.

The potential Equation of a glass electrode can be determined :

$$E = E^\circ + \frac{2.303RT}{nF} \ PH$$

2-2ELECTROCHEMICAL CELLS

A device for producing an electrical current from a chemical reaction (redox reaction) is called an electrochemical cell.

1- Galvanic Cells

A **galvanic cell,** also known as a is **Voltaic cell** one in which electrical current is generated by a spontaneous redox reaction. A simple voltaic cell is shown in Fig. 5. Here the spontaneous reaction of zinc metal with an aqueous solution of copper sulphate is used.

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

A bar of zinc metal (anode) is placed in zinc sulphate solution in the left container. A bar of copper (cathode) is immersed in copper sulphate solution in the right container. The zinc and copper electrodes are joined by a copper wire. A salt bridge containing potassium sulphate solution interconnects the solutions in the anode compartment and the cathode compartment.

The oxidation half-reaction occurs in the ***anode*** compartment.

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

The reduction half-reaction takes place in the ***cathode*** compartment.

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

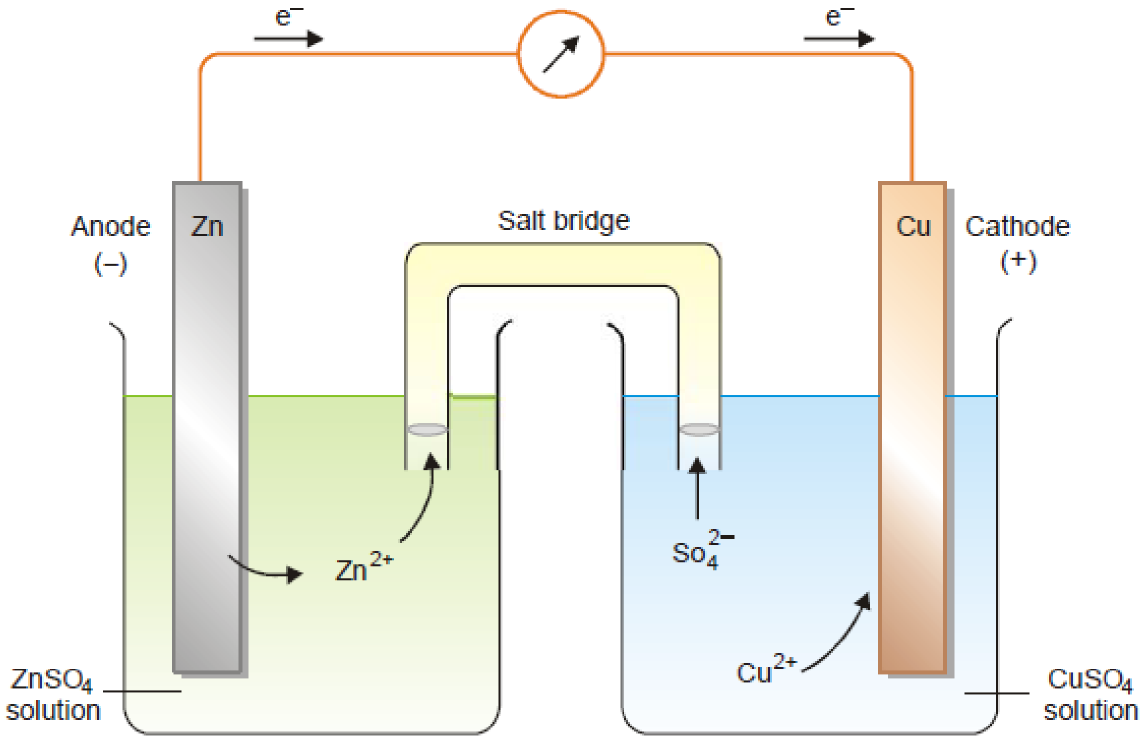


Fig. 5: A **simple galvanic cell**

When the cell is set up, electrons flow from zinc electrode through the wire to the copper cathode. As a result, zinc dissolves in the anode solution to form Zn2+ ions. The Cu2+ ions in the cathode half-cell pick up electrons and are converted to Cu atoms on the cathode. At the same time, $SO4^{2-}$ions from the cathode half-cell migrate to the anode half-cell through the salt bridge. Likewise, Zn^{2+} ions from the anode half-cell move into the cathode half-cell. This flow of ions from one half-cell to the other completes the electrical circuit which ensure continuous supply of current. The cell will operate till either the zinc metal or copper ion is completely used up

Cell reaction:

The flow of electrons from one electrode to the other in an electrochemical cell is caused by the half-reactions taking place in the anode and cathode compartments. The net chemical change obtained by adding the two half-reactions is called the **cell reaction.** Thus, for a simple voltaic cell described above, we have

(*a*) Half-reactions :

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e$ *Anode*

$Cu^{2+}(aq) + 2e- \longrightarrow Cu(s)$ Cathode

(*b*) Cell reaction(cell over all reaction) by adding up the half-reactions

Zn(*s*) + Cu2+ (*aq*) ⟶ Zn2+ (*aq*) + Cu(*s*)

Cell diagram or Representation of a Cell

In 1953 IUPAC recommended the following conventions for writing cell diagrams. We will illustrate these with reference to Zinc-Copper cell.

(1) a **single vertical line** (**|**) represents a phase boundary between metal electrode and ion solution (electrolyte).

(2) A **double vertical line** (**||**) represents the salt bridge, porous partition or any other **means** of permitting ion flow while preventing the electrolyte from mixing.

(3) **Anode half-cell is written on the left** and **cathode half-cell on the right.**

(4) In the **complete cell diagram, the two half-cells are separated by a double vertical line (salt bridge) in between.** The zinc-copper cell can now be written as

$$\underset{\substack{\text{Anode}\\\text{Half-Cell}}}{Zn \mid Zn^{2+}} \;\|\; \underset{\substack{\text{Cathode}\\\text{Half-Cell}}}{Cu^{2+} \mid Cu}$$

Calculating the emf (electromotive force) of a cell

The emf of a cell can be calculated from the half-cell potentials of the two cells (anode and cathode) by using the following formula

$$\mathbf{E_{cell} = E_{cathode} - E_{anode}}$$

$$\mathbf{= E_R - E_L}$$

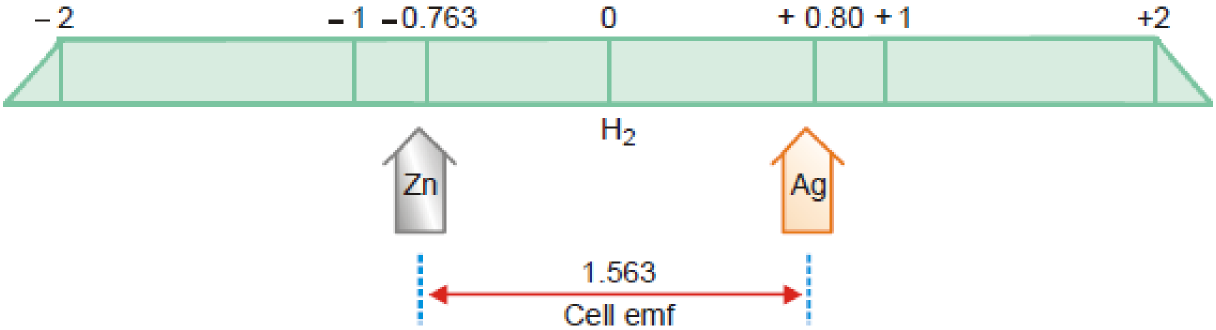
Let us predict the emf of the cell

$$Zn(s) \,|\, Zn^{2+}(aq) \,\|\, Ag^{+}(aq) \,|\, Ag$$

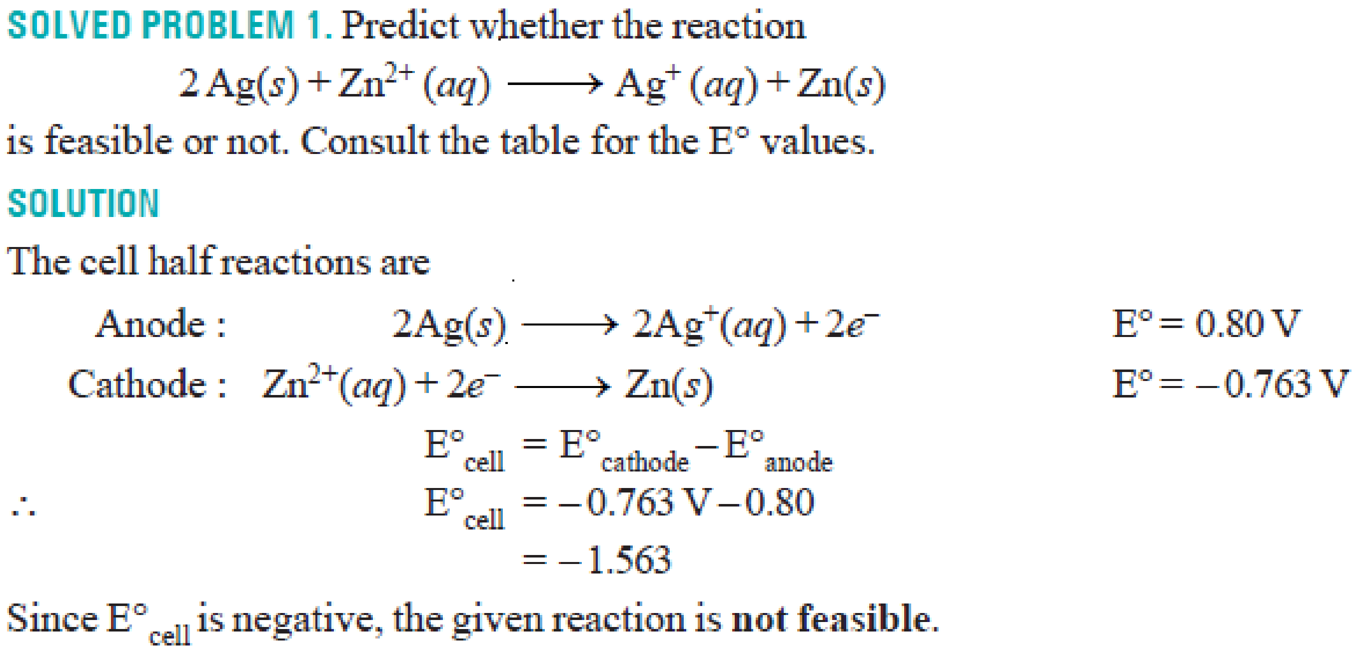
by using the E° values from the Table

$$\begin{aligned} E^\circ_{cell} &= E^\circ_R - E^\circ_L \\ &= 0.80 - (-0.763) \\ &= 0.80 + 0.763 \\ &= 1.563\,V \end{aligned}$$

The answer is so clear from Fig. 29.12.



■ **Figure 29.12**
Diagrammatic representation of Cell emf.



SOLVED PROBLEM 1. Predict whether the reaction

$$2\,Ag(s) + Zn^{2+}\,(aq) \longrightarrow Ag^{+}\,(aq) + Zn(s)$$

is feasible or not. Consult the table for the E° values.

SOLUTION

The cell half reactions are

Anode : $2Ag(s) \longrightarrow 2Ag^{+}(aq) + 2e^{-}$ $E° = 0.80\ V$

Cathode : $Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s)$ $E° = -0.763\ V$

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

$$\therefore \quad E°_{cell} = -0.763\ V - 0.80$$

$$= -1.563$$

Since $E°_{cell}$ is negative, the given reaction is **not feasible.**

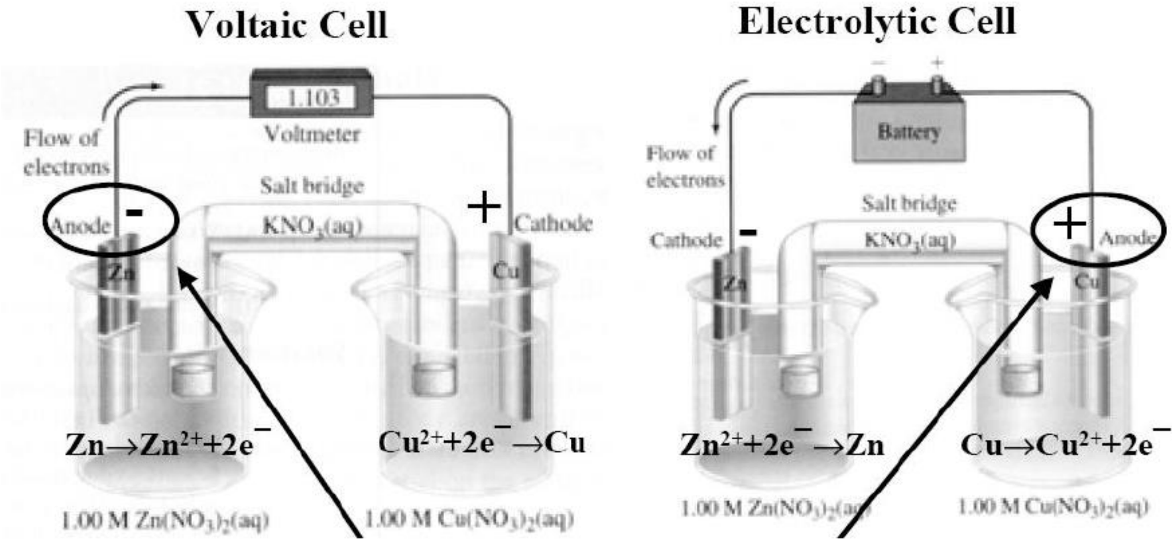
2-1 Electrolytic Cell

Electrolysis: The decomposition of some substance by means of an electric current.

Electrolytic Cell: A cell that requires electrical energy to cause nonspontaneous oxidation-reduction reactions to occur.

1- It utilizes an external source of electrical energy.
2- It forces electrons to flow in the opposite direction by applying a voltage greater than the cell potential.
3- It converts electrical energy into chemical energy
4- A salt bridge can be used in the Electrolytic Cell or not used

Voltaic Cell	Electrolytic Cell
Spontaneous redox reaction releases energy	**Nonspontaneous redox reaction absorbs energy to drive it**



Anode = oxidation = negative
(negative charge supplied by *reaction*)
Cathode = reduction = positive
$E_{cell} > 0$

Anode = oxidation = positive
Cathode = reduction = negative
(negative charge supplied *externally*)
$E_{cell} < 0$

Another Example of electrolytic cells :

<u>Electrolysis of water</u>: is the decomposition of water into oxygen and hydrogen gas due to the passage of an electric current(fig. 6).. This technique can be used to make hydrogen gas, a main component of hydrogen fuel, and breathable oxygen gas,

the base-balanced reactions predominate in basic (high pH) solutions.

Cathode (reduction): $2\ H_2O(l) + 2e^- \rightarrow H_2(g) + 2\ OH^-(aq)$

Anode (oxidation): $2\ OH^-(aq) \rightarrow 1/2\ O_2(g) + H_2O(l) + 2\ e^-$

Combining either half reaction pair yields the overall decomposition of water into oxygen and hydrogen:

Overall reaction: $2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g)$

The number of hydrogen molecules produced is thus twice the number of oxygen molecules.

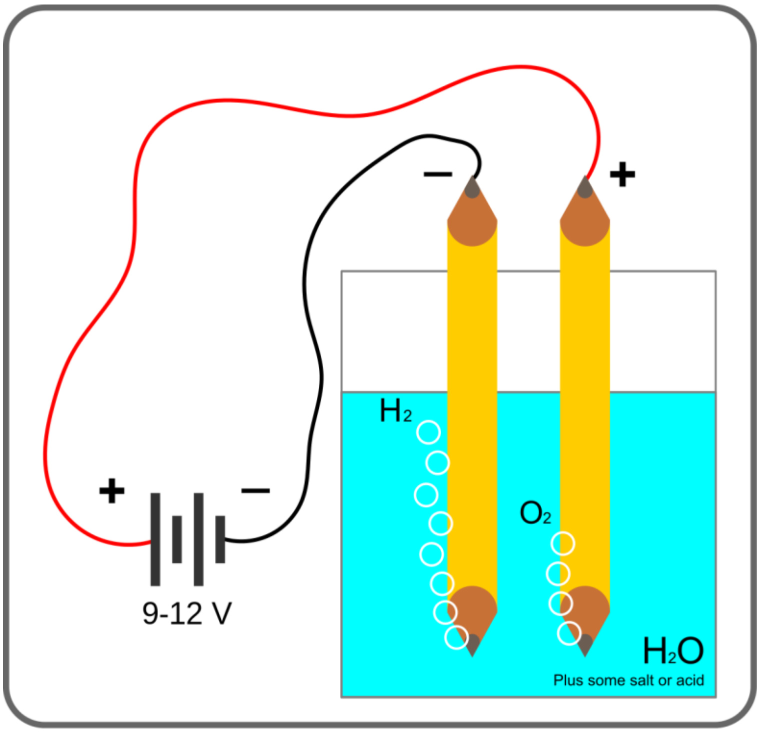


fig. 6: Electrolysis of water

Basic Concepts of Thermodynamics

Every science has its own unique vocabulary associated with it. Precise definition of basic concepts forms a sound foundation for development of a science and prevents possible misunderstandings. Careful study of these concepts is essential for a good understanding of topics in thermodynamics.

Thermodynamics and Energy

Thermodynamics can be defined as the study of energy, energy transformations and its relation to matter. The analysis of thermal systems is achieved through the application of the governing conservation equations, namely *Conservation of Mass*, *Conservation of Energy* (1st law of thermodynamics), the 2nd law of thermodynamics and the property relations. Energy can be viewed as the ability to cause changes.

First law of thermodynamics: one of the most fundamental laws of nature is the conservation of energy principle. It simply states that during an interaction, energy can change from one form to another but the total amount of energy remains constant.

Second law of thermodynamics: energy has quality as well as quantity, and actual processes occur in the direction of decreasing quality of energy.

Whenever there is an interaction between energy and matter, thermodynamics is involved. Some examples include heating and air-conditioning systems, refrigerators, water heaters, etc.

Dimensions and Units

Any physical quantity can be characterized by dimensions. The arbitrary magnitudes assigned to the dimensions are called units. There are two types of dimensions, *primary* or *fundamental* and *secondary* or *derived* dimensions.

Primary dimensions are: mass, ***m;*** length, ***L;*** time, ***t;*** temperature, ***T***

Secondary dimensions are the ones that can be derived from primary dimensions such as: velocity (m/s^2), pressure ($Pa = kg/m.s^2$).

There are two unit systems currently available SI (International System) and USCS (United States Customary System) or English system. We, however, will use SI units exclusively in this course. The SI units are based on decimal relationship between units. The prefixes used to express the multiples of the various units are listed in Table 1-1.

Table 1: Standard prefixes in SI units.

MULTIPLE	10^{12}	10^{9}	10^{6}	10^{3}	10^{-2}	10^{-3}	10^{-6}	10^{-9}	10^{-12}
PREFIX	tetra, T	giga, G	mega, M	kilo, k	centi, c	mili, m	micro, µ	nano, n	pico, p

Important note: in engineering all equations must be dimensionally homogenous. This means that every term in an equation must have the same units. It can be used as a sanity check for your solution.

Example 1: Unit Conversion

The heat dissipation rate density of an electronic device is reported as 10.72 mW/mm^2 by the manufacturer. Convert this to W/m^2.

$$10.72\frac{mW}{mm^2}\times\left(\frac{1000mm}{1m}\right)^2\times\frac{1W}{1000mW}=10720\frac{W}{m^2}$$

Closed and Open Systems

A *system* is defined as a quantity of matter or a region in space chosen for study. The mass or region outside the system is called the *surroundings*.

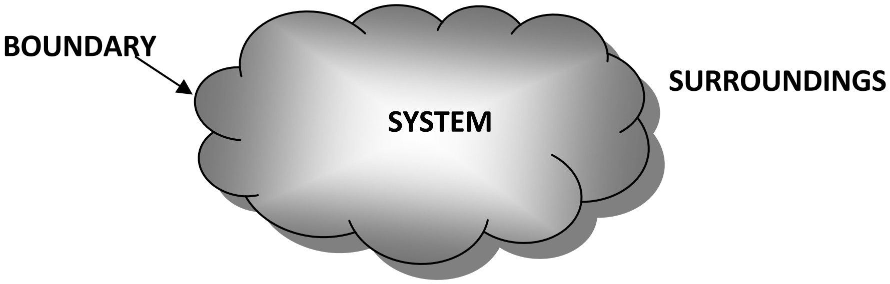


Fig. 1: System, surroundings, and boundary

Boundary: the real or imaginary surface that separates the system from its surroundings. The boundaries of a system can be fixed or movable. Mathematically, the boundary has zero thickness, no mass, and no volume.

Closed system or control mass: consists of a fixed amount of mass, and no mass can cross its boundary. But, energy in the form of heat or work, can cross the boundary, and the volume of a closed system does not have to be fixed.

Open system or control volume: is a properly selected region in space. It usually encloses a device that involves mass flow such as a compressor. Both mass and energy can cross the boundary of a control volume.

Important note: some thermodynamics relations that are applicable to closed and open systems are different. Thus, it is extremely important to recognize the type of system we have before start analyzing it.

Isolated system: A closed system that does not communicate with the surroundings by any means.

Rigid system: A closed system that communicates with the surroundings by heat only.

Adiabatic system: A closed or open system that does not exchange energy with the surroundings by heat.

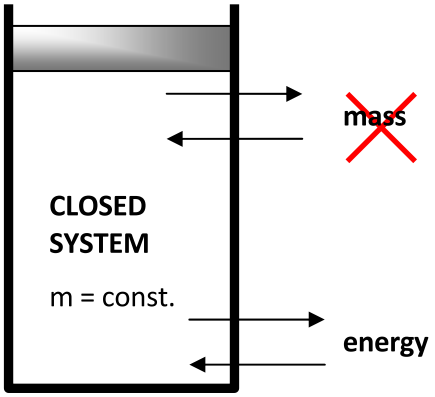


Fig. 2: Closed system, mass cannot cross the boundaries, but energy can.

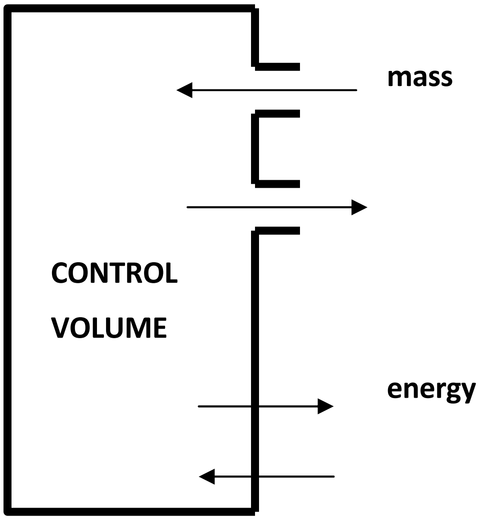


Fig. 3: Control volume, both mass and energy can cross the boundaries.

Energy

In thermodynamics, we deal with change of the total energy only. Thus, the total energy of a system can be assigned a value of zero at some reference point. Total energy of a system has two groups: *macroscopic* and *microscopic*.

Macroscopic forms of energy: forms of energy that a system posses as a whole with respect to some outside reference frame, such as kinetic and potential energy. The macroscopic energy of a system is related to motion and the influence of some external effects such as gravity, magnetism, electricity, and surface tension.

- Kinetic energy: energy that a system posses as a result of its relative motion relative to some reference frame, KE

$$KE = \frac{mV^2}{2} \qquad (kJ)$$

where V is the velocity of the system in (m/s).

- Potential energy: is the energy that a system posses as a result of its elevation in a gravitational field, PE

$$PE = mgz \qquad (kJ)$$

where g is the gravitational acceleration and z is the elevation of the center of gravity of the system relative to some arbitrary reference plane.

<u>Microscopic forms of energy</u>: are those related to molecular structure of a system. They are independent of outside reference frames. The sum of microscopic energy is called the *internal energy, U*.

The total energy of a system consists of the kinetic, potential, and internal energies:

$$E = U + KE + PE = U + \frac{mV^2}{2} + mgz \qquad (kJ)$$

where the contributions of magnetic, electric, nuclear energy are neglected. Internal energy is related to the molecular structure and the degree of molecular activity and it may be viewed as the sum of the kinetic and potential energies of molecules.

- The sum of translational, vibrational, and rotational energies of molecules is the kinetic energy of molecules, and it is also called the *sensible energy.* At higher temperatures, system will have higher sensible energy.
- Internal energy associated with the phase of a system is called *latent heat*. The intermolecular forces are strongest in solids and weakest in gases.
- The internal energy associated with the atomic bonds in a molecule is called *chemical* or *bond energy*. The tremendous amount of energy associated with the bonds within the nucleolus of atom itself is called *atomic energy*.

Energy interactions with a closed system can occur via *heat transfer* and *work*.

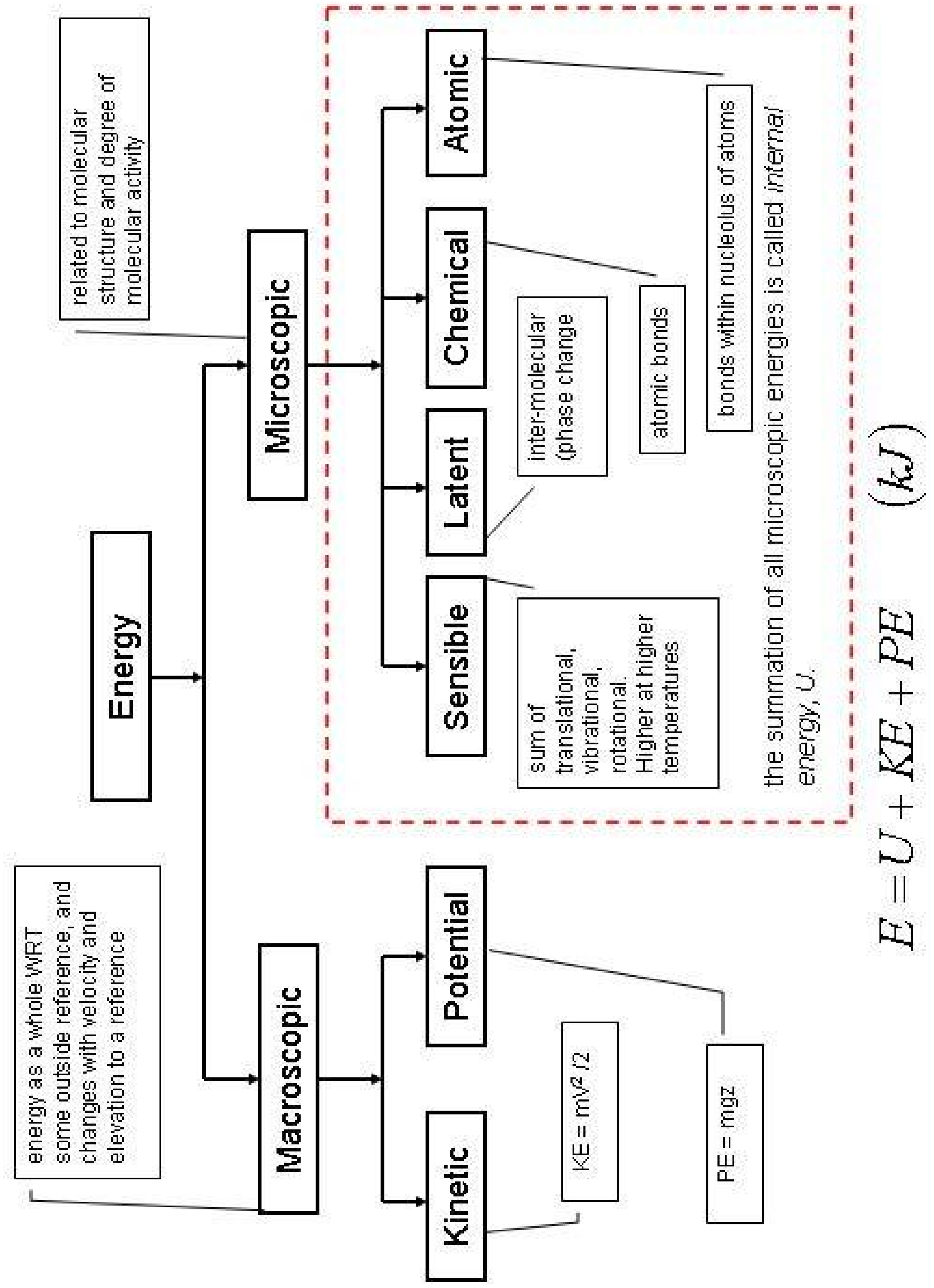


Fig. 1-4: Forms of energy.

Properties of a System

Any characteristic of a system is called a *property*. In classical thermodynamics, the substance is assumed to be a *continuum*, homogenous matter with no microscopic holes. This assumption holds as long as the volumes, and length scales are large with respect to the intermolecular spacing.

Intensive properties: are those that are independent of the size (mass) of a system, such as temperature, pressure, and density. They are not additive.

Extensive properties: values that are dependant on size of the system such as mass, volume, and total energy U. They are additive.

- Generally, uppercase letters are used to denote extensive properties (except mass m), and lower case letters are used for intensive properties (except pressure P, temperature T).
- Extensive properties per unit mass are called specific properties, e.g. specific volume (v=V/m).

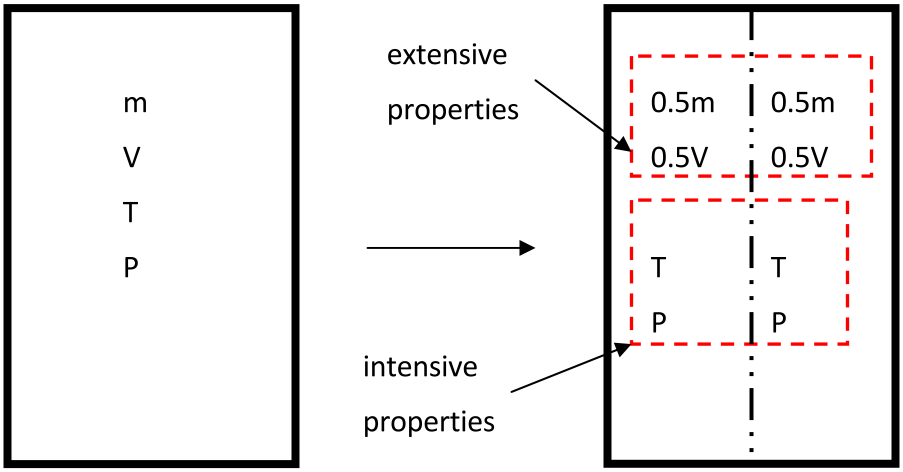


Fig. 1-5: Intensive and extensive properties of a system.

State and Equilibrium

At a given *state*, all the properties of a system have fixed values. Thus, if the value of even one property changes, the state will change to different one.

In an equilibrium state, there are no unbalanced potentials (or driving forces) within the system. A system in equilibrium experiences no changes when it is isolated from its surroundings.

- Thermal equilibrium: when the temperature is the same throughout the entire system.

- Mechanical equilibrium: when there is no change in pressure at any point of the system. However, the pressure may vary within the system due to gravitational effects.
- Phase equilibrium: in a two phase system, when the mass of each phase reaches an equilibrium level.
- Chemical equilibrium: when the chemical composition of a system does not change with time, i.e., no chemical reactions occur.

Processes and Cycles

Any change a system undergoes from one equilibrium state to another is called a *process,* and the series of states through which a system passes during a process is called a *path*.

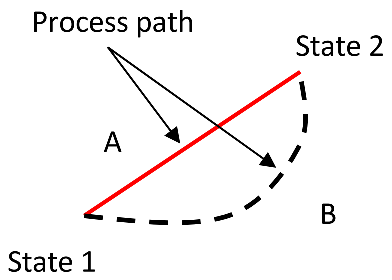


Fig. 6: To specify a process, initial and final states and path must be specified.

Quasi-equilibrium process: can be viewed as a sufficiently slow process that allows the system to adjust itself internally and remains infinitesimally close to an equilibrium state at all times. Quasi-equilibrium process is an idealized process and is not a true representation of the actual process. We model actual processes with quasi-equilibrium ones. Moreover, they serve as standards to which actual processes can be compared.

Process diagrams are used to visualize processes. Note that the process path indicates a series of equilibrium states, and we are not able to specify the states for a non-quasi-equilibrium process.

Prefix *iso-* is used to designate a process for which a particular property is constant.

- Isothermal: is a process during which the temperature remains constant
- Isobaric*:* is a process during which the pressure remains constant
- Isometric: is process during which the specific volume remains constant.

A system is said to have undergone a *cycle* if it returns to its initial state at the end of the process.

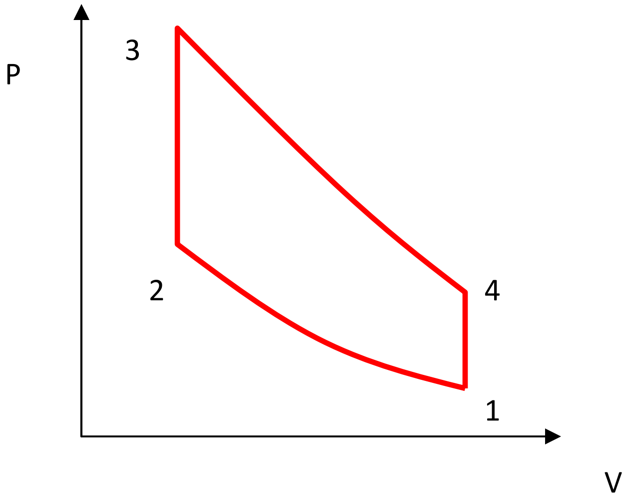


Fig. 1-7: A four-process cycle in a P-V diagram.

The state of a system is described by its properties. The state of a *simple compressible system* is completely specified by two *independent*, intensive properties.

A system is called simple compressible system in the absence of electrical, magnetic, gravitational, motion, and surface tension effects (external force fields).

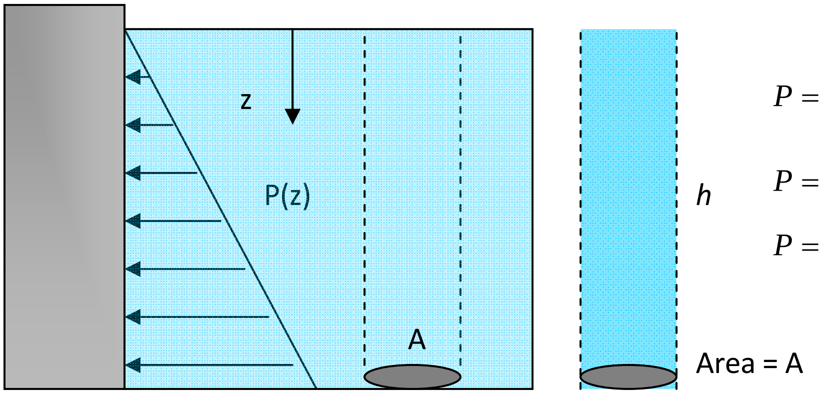
Independent properties: two properties are independent if one property can be varied while the other one is held constant.

Pressure

Pressure is the force exerted by a fluid per unit area.

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} \qquad \frac{N}{m^2} \equiv Pa$$

In fluids, gases and liquids, we speak of *pressure*; in solids this is *stress*. For a fluid at rest, the pressure at a given point is the same in all directions.



$$P = \frac{\text{Weight of liquid}}{\text{Area}}$$

$$P = \frac{mg}{A} = \frac{\rho A h g}{A}$$

$$P = \rho g h$$

Fig. 8: Pressure of a fluid at rest increases with depth (due to added weight), but constant in horizontal planes.

The actual pressure at a given position is called the *absolute pressure*, and it is measured relative to absolute vacuum.

gauge pressure = absolute pressure - atmospheric pressure

$$P_{gauge} = P_{abs} - P_{atm} \qquad P > P_{atm}$$
$$P_{vac} = P_{atm} - P_{abs} \qquad P < P_{atm}$$

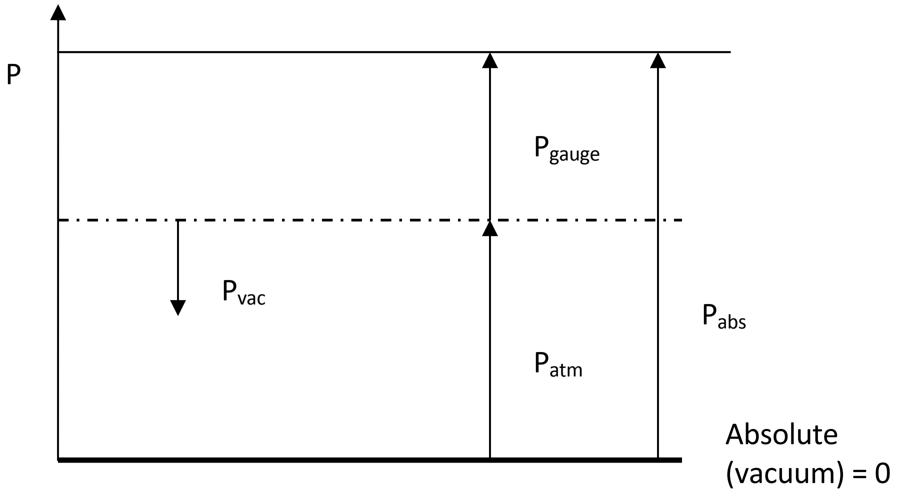


Fig. 9: Absolute, gauge, and vacuum pressures.

In thermodynamics calculations, always use absolute pressure. Most pressure measuring devices are calibrated to read zero in the atmosphere (they measure P_{gauge} or P_{vac}). Be aware of what you are reading!

A device that measures pressure using a column of liquid is called a *Manometer.* The cross sectional area of the tube is not important. The manometer measures the gauge pressure.

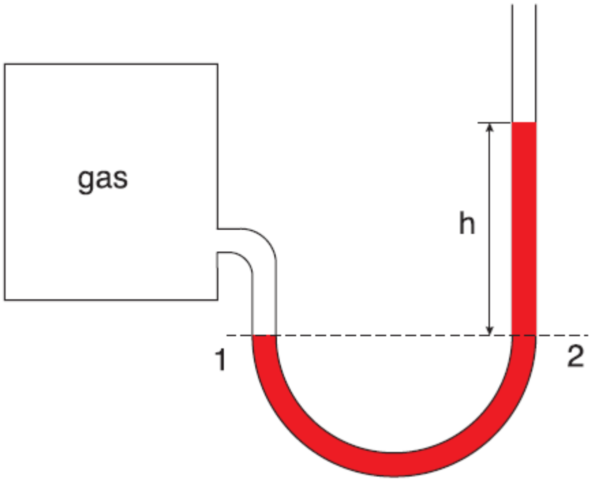


Fig. 10: Basic manometer, $P_2=P_1$.

$$P_1 = P_{atm} + \rho g h \qquad (kPa)$$

Bourdon Tube is a device that measures pressure using mechanical deformation. *Pressure Transducers* are devices that use piezoelectrics to measure pressure.

- very accurate and robust
- can measure from 10^{-6} to 10^{5} atm
- can measure P_{gauge} or P_{abs}

Barometer is a device that measures atmospheric pressure. It is a manometer with a near vacuum on one end

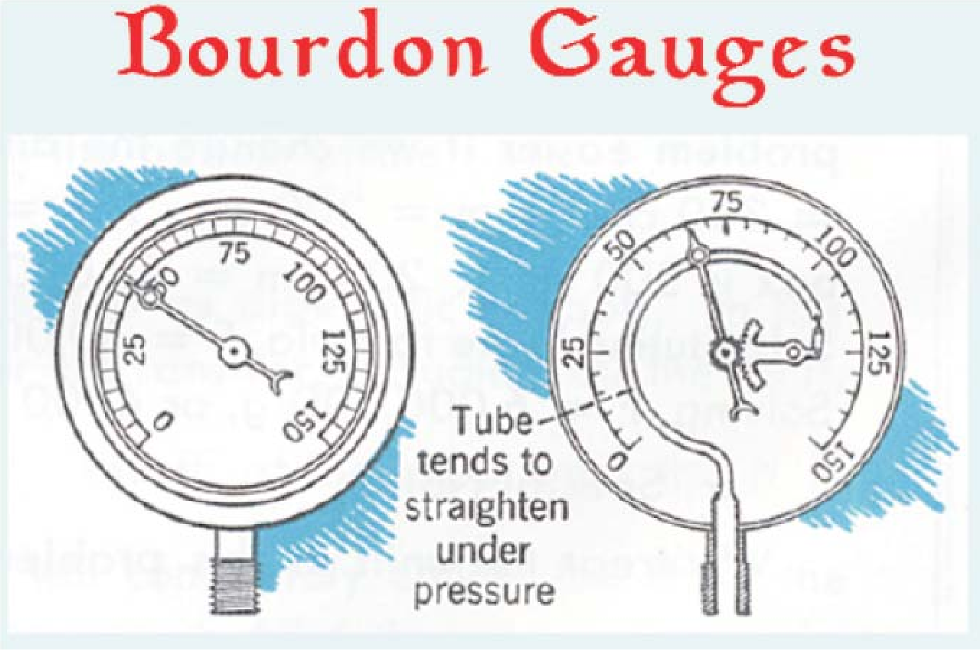


Fig. 11: Burdon gauge.

Example 2: Pressure

The piston of a cylinder-piston device has a mass of 60 kg and a cross-sectional area of 0.04 m^2, as shown in Fig. 12. The depth of the liquid in the cylinder is 1.8 m and has a density of 1558 kg/m^3. The local atmospheric pressure is 0.97 bar, and the gravitational acceleration is 9.8 m/s^2. Determine the pressure at the bottom of the cylinder.

Solution: the pressure at the bottom of the cylinder can be found from the summation of the forces due to atmospheric pressure, piston weight, and the weight of the liquid in the cylinder.

$$W_{bottom} = P_{atm} A + W_{liquid} + W_{Piston}$$

$$P_{bottom} = P_{atm} + \frac{mg}{A} + \rho g h$$

$$P_{bottom} = 0.97(bar) + \left\{ \frac{(60kg)(9.8\ m/s^2)}{0.04\ m^2} + (1558\ kg/m^3)(9.8\ m/s^2)(1.8\ m) \right\}$$
$$\left[\left(\frac{1N/m^2}{1kg/m.s^2} \right) \left(\frac{1bar}{10^5\ N/m^2} \right) \right] = 1.3918 \quad bars$$

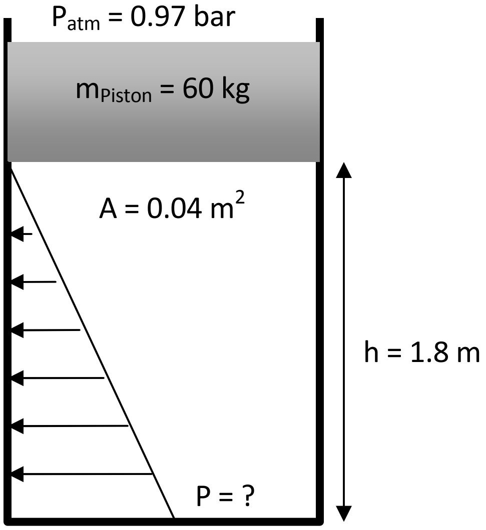


Fig. 12: Sketch for example 2.

Temperature

Temperature is a pointer for the direction of energy transfer as heat.

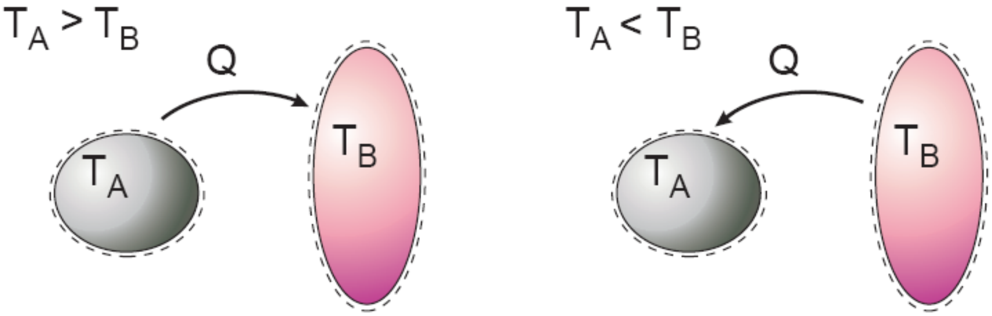


Fig. 13: Heat transfer occurs in the direction of higher-to-lower-temperature.

When the temperatures of two bodies are the same, *thermal equilibrium* is reached. The equality of temperature is the only requirement for thermal equilibrium.

The 0th law of thermodynamics: states that if two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other.

The 0th law makes a thermometer possible.

In accordance with the 0th law, any system that possesses an equation of state that relates temperature T to other accurately measurable properties can be used as a thermometer e.g. an ideal gas obeys the equation of state:

$$T = \frac{PV}{mR}$$

Experimentally obtained Temperature Scales: the *Celsius* and *Fahrenheit* scales, are based on the melting and boiling points of water. They are also called two-point scales.

Conventional thermometry depends on material properties e.g. mercury expands with temperature in a repeatable and predictable way

Thermodynamic Temperature Scales (independent of the material), the Kelvin and Rankine scales, are determined using a constant volume gas thermometer.

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1. **Learning Outcomes**
2. **Limitations of First law of Thermodynamics**
3. **Second law of Thermodynamics**
4. **Carnot Cycle & its Efficiency**
5. **Carnot Theorem**
6. **Summary**

1. Learning Outcomes

After studying this module you shall be able to:

- Limitations of the first law of thermodynamics
- Various statements of the Second law of thermodynamics
- Know about Carnot Cycle and its efficiency
- Brief knowledge about Carnot Theorem

2. Limitations of the first law of thermodynamics / Why SLOT was needed:

1. **No restriction on the direction of the flow of heat**: the first law establishes definite relationship between the heat absorbed and the work performed by a system. The first law does not indicate whether heat can flow from a cold end to a hot end or not. For example: we cannot extract heat from the ice by cooling it to a low temperature. Some external work has to be done.

2. **Does not specify the feasibility of the reaction**: first law does not specify that process is feasible or not for example: when a rod is heated at one end then equilibrium has to be obtained which is possible only by some expenditure of energy.

3. Practically it is **not possible to convert the heat energy into an equivalent amount of work**. First law does not contradict the existence of heat engine of 100% efficiency or self acting machine. But We can say that such heat engine or machines are not attainable in actual practice

To overcome this limitations, another law is needed which is known as second law of thermodynamics. The second law of thermodynamics helps us to predict whether the reaction is feasible or not and also tell the direction of the flow of heat. It also tells that energy cannot be completely converted into equivalent work.

3. The Second Law of thermodynamics

- Nicolas Léonard Sadi Carnot was a French physicist, who is considered to be the "**father of thermodynamics**," for he is responsible for the origins of the Second Law of Thermodynamics, as well as various other concepts. The current form of the second law uses entropy rather than caloric, which is what Sadi Carnot used to describe the law. Caloric relates to heat and Sadi Carnot came to realize that some caloric is always lost in the motion cycle. Thus, the thermodynamic reversibility concept was proven wrong, proving that irreversibility is the result of every system involving work.
- William Thompson, also known as Lord Kelvin, formulated the Kelvin statement, which states "It is **impossible** to convert heat completely in a cyclic process." This means that there is no way for one to convert all the energy of a system into work, without losing energy. Another statement by Kelvin was formulated: "**No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work**."

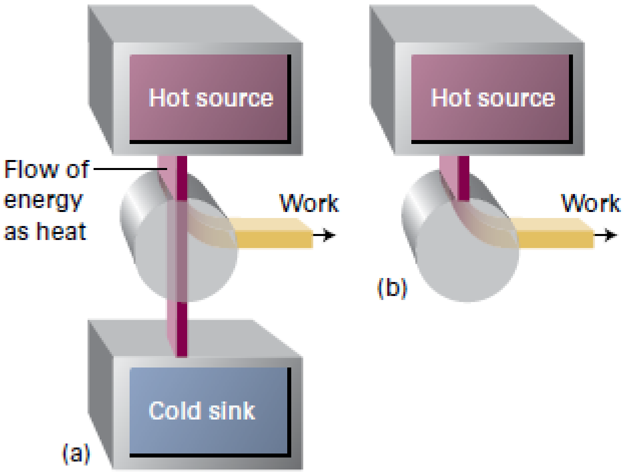


Figure (a) A heat engine is a device in which energy is extracted from a hot reservoir (the hot source) as heat and then some of that energy is converted into work and the rest discarded into a cold reservoir (the cold sink) as heat. (b) The Kelvin statement of the Second Law denies the possibility of the process illustrated here, in which heat is changed completely into work, there being no other change.

- Rudolf Clausius was a German physicist, and he developed another statement of the Second Law which says "**Heat does not flow spontaneously from a cool body to a hotter body**." Or "Heat generally **cannot flow spontaneously** from a material at a lower temperature to a material at a higher temperature."

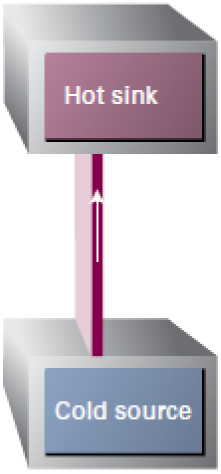


Figure According to the Clausius statement of the Second Law, the process shown here, in which energy as heat migrates from a cool source to a hot sink, does not take place spontaneously. The process is not in conflict with the First Law because energy is conserved.

The Second Law of Thermodynamics also states that entropy of the entire universe, as an isolated system, will always increase over time. The second law also states that the changes in the entropy in the universe can never be negative. It is vitally important when considering applications of the Second Law to remember that it is a statement about the total entropy of the overall isolated system (the 'universe'), not just about the entropy of the system of interest.

The entropy of an isolated system increases in the course of a spontaneous change: $\Delta S_{tot} > 0$.

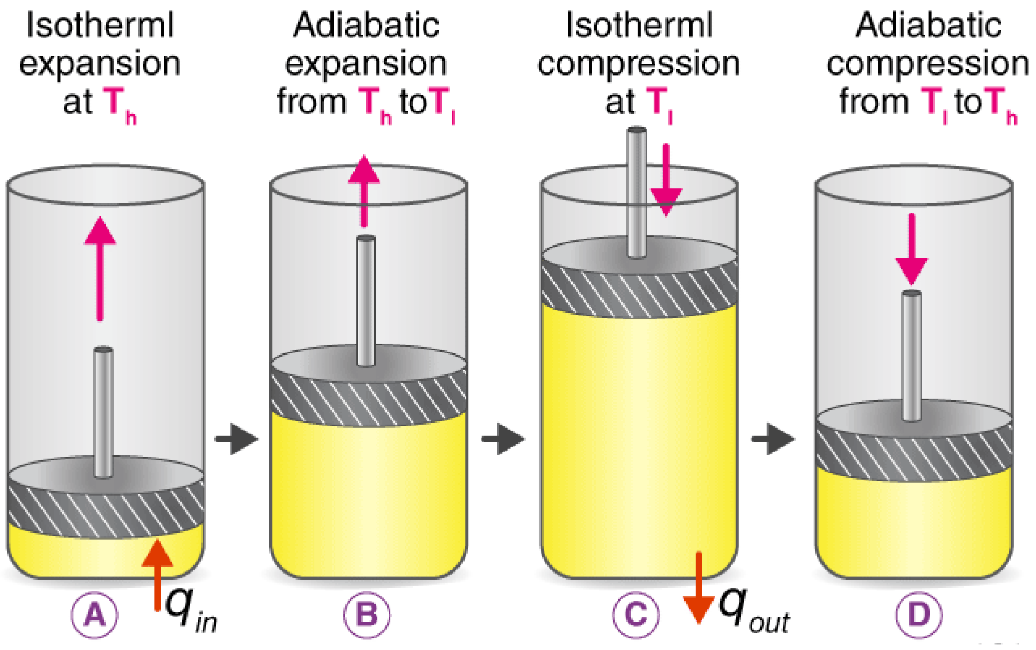
where S_{tot} is the total entropy of the overall isolated system. That is, if S is the entropy of the system of interest, and S_{sur} the entropy of the surroundings, then

$$S_{tot} = S + S_{sur}$$

In summary, the First Law uses the internal energy to identify *permissible* changes; the Second Law uses the entropy to identify which of these permissible changes are *spontaneous*.

4. Carnot Cycle & its Efficiency:

A Carnot cycle is defined as an ideal reversible closed thermodynamic cycle in which there are four successive operations involved, which are isothermal expansion, adiabatic expansion, isothermal compression and adiabatic compression. During these operations, the expansion and compression of substance can be done up to the desired point and back to the initial state.



Following are the four processes of the Carnot cycle:

- In (a), the process is reversible isothermal gas expansion. In this process, the amount of heat absorbed by the ideal gas is q_{in} from the heat source, which is at a temperature of T_h. The gas expands and does work on the surroundings.
- In (b), the process is reversible adiabatic gas expansion. Here, the system is thermally insulated, and the gas continues to expand and work is done on the surroundings. Now the temperature is lower, T_l.
- In (c), the process is reversible isothermal gas compression process. Here, the heat loss q_{out} occurs when the surroundings do the work at temperature T_l.

- In (d), the process is reversible adiabatic gas compression. Again the system is thermally insulated. The temperature again rises back to T_h as the surrounding continue to do their work on the gas.

Steps involved in a Carnot Cycle

For an ideal gas operating inside a Carnot cycle, the following are the steps involved:

Step 1:

Isothermal expansion: The gas is taken from P_1, V_1, T_1 to P_2, V_2, T_2. Heat Q_1 is absorbed from the reservoir at temperature T_1. Since the expansion is isothermal, the total change in internal energy is zero, and the heat absorbed by the gas is equal to the work done by the gas on the environment, which is given as:

$$W_{1\to2} = Q1 = \mu \times R \times T_1 \times ln\frac{v2}{v1} \qquad ...(1)$$

Step 2:

Adiabatic expansion: The gas expands adiabatically from P_2, V_2, T_1 to P_3, V_3, T_2.

Here, work done by the gas is given by:

$$W_{2\to3} = \frac{\mu R}{\gamma - 1}(T1 - T2) \qquad ...(2)$$

Step 3:

Isothermal compression: The gas is compressed isothermally from the state (P_3, V_3, T_2) to (P_4, V_4, T_2).

Here, the work done on the gas by the environment is given by:

$$W_{3\to4} = \mu R T_2 \, ln\frac{v3}{v4} \qquad ...(3)$$

Step 4:

Adiabatic compression: The gas is compressed adiabatically from the state (P_4, V_4, T_2) to (P_1, V_1, T_1).

Here, the work done on the gas by the environment is given by:

$$W_{4\to1} = \frac{\mu R}{\gamma - 1}(T1 - T2) \qquad ...(4)$$

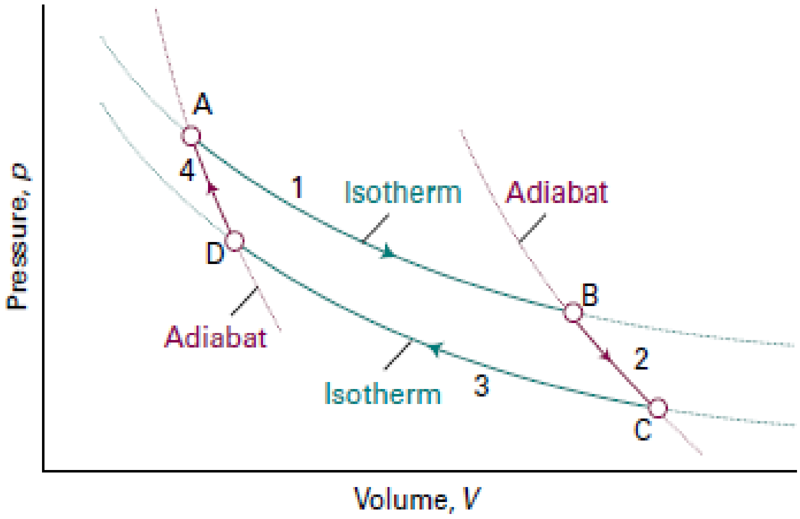


Figure The basic structure of a Carnot cycle. Step 1 is the isothermal reversible expansion at the temperature T_h. Step 2 is a reversible adiabatic expansion in which the temperature falls from T_h to T_c. Step 3 is an isothermal reversible compression at T_c. Step 4 is an adiabatic reversible compression, which restores the system to its initial state.

Hence, the total work done by the gas on the environment in one complete cycle is given by:

$$W = W_{1\to2} + W_{2\to3} + W_{3\to4} + W_{4\to1}$$

Putting the values of works from above work equations 1 to 4

$$W = \mu RT_1 ln\frac{v2}{v1} \quad - \mu RT_2 \ln\frac{v3}{v4}$$

$$Net\ efficiency = \frac{Net\ work\ done\ by\ the\ gas}{Heat\ absorbed\ by\ the\ gas}$$

$$Net\ efficiency \quad = \frac{W}{Q1} = \frac{Q1-Q2}{Q1} = 1-\frac{Q2}{Q1} = 1-\frac{T2}{T1}\frac{\ln\frac{v3}{v4}}{\ln\frac{v2}{v1}}$$

Since the step 2→3 is an adiabatic process, we can write $T_1V_2^{\gamma\ -1} = T_2V_3^{\gamma\ -1}$

Or, $V_2 / V_3 = (T_2 / T_1)^{1/\gamma-1}$

Similarly, for the process 4→1, we can write

$$V_1 / V_4 = (T_2 / T_1)^{1/\gamma-1}$$

This implies, $V_2 / V_3 = V_1 / V_4$

$$V_2 / V_1 = V_3 / V_4$$

So, the expression for net efficiency of carnot engine reduces to:

$$Net\ efficiency\ of\ Carnot\ heat\ engine = 1-\frac{T2}{T1}$$

5. Carnot theorem

Carnot's theorem (1824) is a principle that limits the maximum efficiency for any possible engine. The efficiency solely depends on the temperature difference between the hot and cold thermal reservoirs.

Carnot's theorem states: All irreversible heat engines between two heat reservoirs are less efficient than a Carnot engine operating between the same reservoirs.

All reversible heat engines between two heat reservoirs are equally efficient with a Carnot engine operating between the same reservoirs.

Maximum efficiency is given as:

$$\eta_{max} = \eta_{Carnot} = 1 - T_c / T_H$$

Where,

T_C: absolute temperature of the cold reservoir

T_H: absolute temperature of the hot reservoir

η: the ratio of work done by the engine to heat drawn out of the hot reservoir

In his ideal model, the heat of caloric converted into work could be reinstated by reversing the motion of the cycle, a concept subsequently known as thermodynamic reversibility. Carnot, however, further postulated that some caloric is lost, not being converted to mechanical work. Hence, no real heat engine could realise the Carnot cycle's reversibility and was condemned to be less efficient.

References:

1. **epg Pathshala, (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface chemistry, Fast kinetics)**
2. **Atkins' Physical Chemistry book**

UNIT –III Photochemistry

Photochemistry is the study of the interaction of electromagnetic radiation with matter resulting into a physical change or into a chemical reaction.

Primary Processes

- **One molecule is excited into an electronically excited state by absorption of a photon, it can undergo a number of different primary processes.**
- **Photochemical processes are those in which the excited species dissociates, isomerizes, rearranges, or react with another molecule.**
- **Photo physical processes include radiative transitions in which the excited molecule emits light in the form of fluorescence or phosphorescence and returns to the ground state, and intramolecular non-radiative transitions in which some or all of the energy of the absorbed photon is ultimately converted to heat.**

Laws Governing Absorption Of Light

Lambert's Law: **This law states that decrease in the intensity of monochromatic light with the thickness of the absorbing medium is proportional to the intensity of incident light.**

$$-dI/dx \propto I$$

$$-dI/dx = KI,$$

on integration changes to

$$I=I_0 e^{-Kx}$$

Where , I_0 = intensity of incident light.

I=intensity of transmitted light.

K= absorption coefficient.

Beer's Law :

It states that decrease in the intensity of monochromatic light with the thickness of the solution is not only proportional to the intensity of the incident light but also to the concentration 'c' of the solution.

Mathematically, $-dI/dx \propto Ic$

$$-dI/dx = \epsilon Ic$$

on integration $I=I_0 e^{-\epsilon cx}$

Where,

ϵ = molar absorption coefficient or molar extinction coefficient

Numerical value of Einstein

- **In CGS Units**

  $E=2.86/\lambda(cm)$ **cal per mole**

  or

  $=2.86X10^5 / \lambda(A^0)$ **K cal per mole**

- **In SI units**

  $E=0.1197/\lambda(m) J\ mol^{-1}$

Grotthuss-Draper Law(First Law of Photochemistry):

Only the light which is absorbed by a molecule can be effective in producing photochemical changes in the molecule.

Stark-Einstein's Law (Second Law of Photochemistry):

It states that for each photon of light absorbed by a chemical system, only one molecule is activated for a photochemical reaction.

The energy absorbed by one mole of the reacting molecules is

$$E=Nh\nu.$$

This energy is called one einstein.

Or

$$=11.97X10^{-5}/\lambda(m)KJ\ mol^{-1}$$

Processes of photochemical reactions

1. **Primary Process: Atoms or molecules activated by actual absorption of radiation.**

   Or, the excitation of the species from the ground electronic state to excited state.

2. **Secondary process: Activated species undergoes chemical reaction.**

   ---Does not involve the absorption of light.

Eg., Photochemical combination of Cl_2 and H_2 *(It is chain mechanism)*

a. *Primary Process*

$Cl_2 + h\nu \rightarrow 2Cl^{\cdot}$ Chain Initiation step

Photochemical equivalence is applicable to this step

b. Secondary process

Propagation reaction and Chain terminating step

Utility of the Laws

1. **Calculation of the rates of formation of reactive intermediates in photochemical reactions**
2. **The study of the mechanisms of photochemical reactions .**

Interpretation of Einstein's Law

In terms of Quantum efficiency:

Quantum Efficieny

$$\phi = \frac{\text{No. of molecules reacting in a given time}}{\text{No.of quantas of light absorbed in the same time}}$$

Experimentally,

$$\Phi = \frac{\text{rate of chemical reaction}}{\text{quanta absorbed per second.}}$$

Quantum efficiency :

It expresses the efficiency of a photochemical reaction.
A photochemical reaction strictly obey the laws of photochemical equivalence Φ should be unity.

Because the ratio between the reacting molecules & no. of quanta absorbed =1:1
Only few reactions, $\Phi = 1$ eg. $SO_2 + Cl_2 \rightarrow SO_2Cl_2$
But in major cases, $\Phi \neq 1$

Because, all the primary process (photo activation) does not lead to the secondary process (thermal reaction).

Quantum Yield

- **In the photolysis of Cl_2 and H_2, Φ_{HCl} can be as high as 1 million.**

$$Cl_2 + h\nu \rightarrow 2Cl^{\cdot}$$

$$Cl^{\cdot} + H_2 \rightarrow HCl + H \text{ (exothermic)}$$

$$H + Cl_2 \rightarrow HCl + Cl^{\cdot}$$

- **In the photolysis of Br_2 and H_2, Φ_{HBr} is very low i.e about 0.01**

$$Br_2 + h\nu \rightarrow 2Br$$

$$Br + H_2 \rightarrow HBr + H \text{ (endothermic)}$$

$$H + Br_2 \rightarrow HBr + Br$$

The hydrogen- chlorine reaction

We are considering the photolysis of Cl_2 and H_2

$$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)} (\text{radiation}, \lambda = 4800A^0)$$

Its quantum yield $=10^4$ to 10^6 ,because it is a chain reaction

Chain reaction : A chain reaction is one in which a single photoactivated molecule sets off a sequence of reactions so that a very large number of reactant molecule react through a chain reaction.

***Primary process*, involve the decomposition of chlorine molecule into chlorine radicals.**

$$Cl_2 + h\nu \rightarrow 2Cl^{\cdot} \qquad (1) \text{ Chain Initiation step}$$

In secondary process **- propagate the chain by their continued reaction gives a large no. of HCl molecules.**

$$Cl^{\cdot} + H_2 \rightarrow HCl + H^{\cdot}$$

$$H^{\cdot} + Cl_2 \rightarrow HCl + Cl^{\cdot} \quad \text{Propagation reaction}$$

Exothermic and low activation energy hence large no. of HCl molecule is formed before terminating the reaction.

Hence the no of Cl_2 molecules that undergoes reaction per each quantum of radiation absorbed is very large, ie, 104 to 106 .

So the reaction has very high quantum yield.

The chain is finally terminated by the combination of chlorine radicals on the walls of the vessels or in gas phase.

$$Cl. + Cl. \rightarrow Cl_2 \quad \text{(Chain terminating step)}$$

Photosensitization

Photosensitized reactions:An electronically excited molecule can transfer its energy to a second species which then undergoes a photochemical process even though it was not itself directly excited.

eg, 1. Mercury acting as a photosensitizer:

$$Hg+hv \rightarrow Hg^* \qquad Hg^*+H_2 \rightarrow H_2^* + Hg$$

$$H_2^* \rightarrow 2H^{\cdot}$$

2. Chlorophyll acting as a photosensitizer

$$\text{Chlorophyll} + hv \rightarrow \text{Chlorophyll}^*$$

$$6CO_2+6H_2O+ \text{Chlorophyll}^* \rightarrow C_6H_{12}O_6 + 6O_2 + \text{Chlorophyll}$$

3 Chlorine photosenstizes the reaction of ozone to oxygen.

$$Cl_2 + h\nu \rightarrow Cl_2^*$$

$$Cl_2^* + O_3 \rightarrow Cl_2 + O_2 + O$$

$$O + O_3 \rightarrow 2O_2$$

Luminescence

The glow produced in the body by methods other than action of heat i.e. the production of cold light is called Luminescence.

It is of three types,

1. Chemiluminescence: The emission of light in chemical reaction at ordinary temperature is called Chemiluminescence

e.g. The light emitted by glow-worms

2. Fluorescence: Certain substances when exposed to light or certain other radiations absorb the energy and then immediately start re-emitting the energy.

Such substances are called fluorescent substances and the phenomenon is called fluorescence .

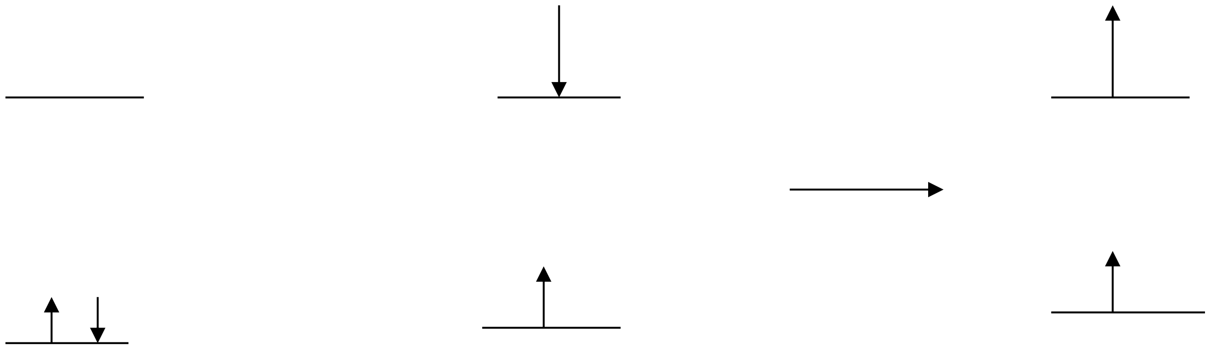
e.g Organic dyes such as eosin,fluorescein etc.

vapour of sodium,mercury,iodine etc.

3. Phosphorescence: There are certain substances which continue to glow for some time even after the external light is cut off.

Thus, phosphorescence is a slow fluorescence.

Fluorescence and phosphorescence in terms of excitation of electrons



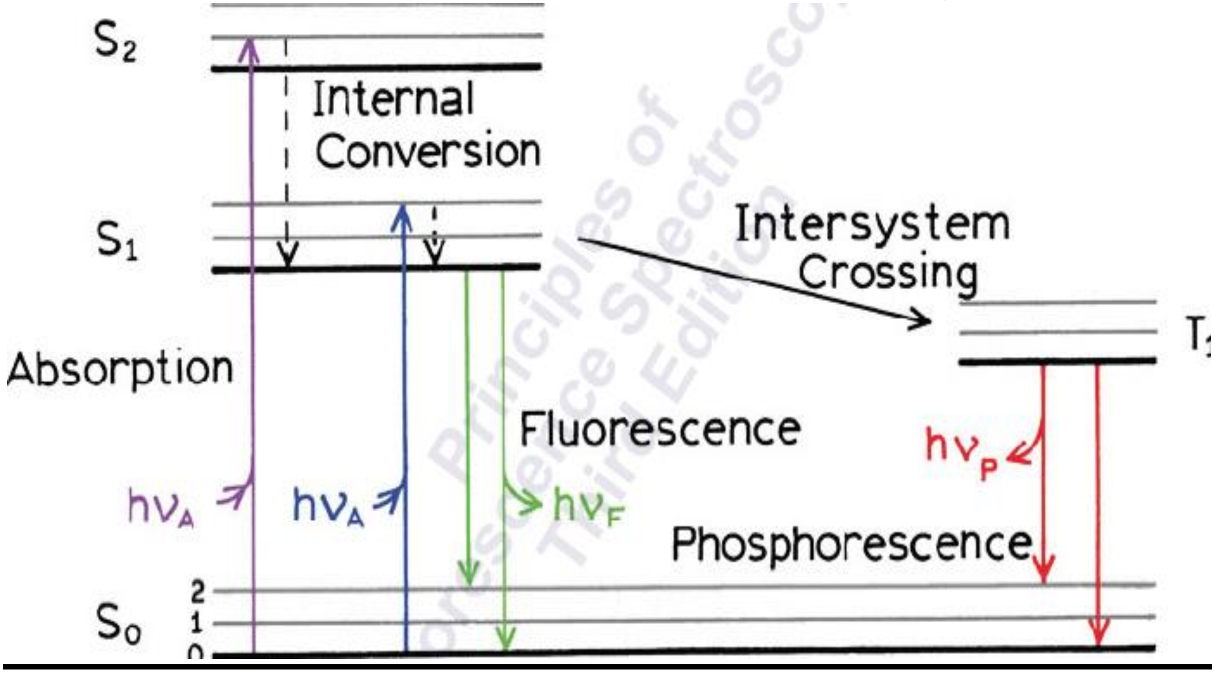
Singlet ground state S_o

Singlet excited state S_1
(pair of electrons with Opposite spins but each in different orbital)

Triplet excited state T_1
(pair of electrons with parallel spins in different Orbital's)

The excited species can return to the ground state by losing all of its excess energy by any one of the paths shown in Jablonski diagram.

Jablonski Diagram for various photophysical processes



Allowed singlet states:

Forbidden triplet states due to spin conversion

Explanation of Jablonski Diagram

First step: is the transition from higher excited singlet states (S_2, S_3, …) to the lowest excited singlet state S_1.This is called internal conversion (IC).

It is a non-radiative process and occurs in less than 10-11 second.

Now from S_1 the molecule returns to ground state by any of the following paths.

Path I : The molecule may lose rest of the energy also in the form of heat so that the complete path is non-radiative or radiation less transitions.

Path II: Molecule releases energy in the form of light or uv radiation. This is called Fluorescence

Path III : Some energy may be lost in transfer from S_1 to T_1 in the form of heat. It is called intersystem crossing (ISC).

This process involves transition between states of different spins (parallel to antiparallel), ie, different multiplicity.

This path is non-radiative.

Path IV : After ISC, the molecule may lose energy in the form of light in going from the excited triplet state to the ground state. This is called phosphorescence.

<u>Chemical reaction</u>

The activated molecule loses energy by undergoing chemical reaction.

Since the molecules in singlet excited sates returns quickly to the G.S, it gets no chance to react chemically.

However the molecules in the triplet state returns to the G.S. slowly, has a opportunity to the activated molecule undergoes chemical reaction.

i.e., the molecule which undergoes chemical reaction is one which is previously present in a triplet state.

Distinction between Fluorescence and Phosphorescence

Fluorescence	**Phosphorescence**
(a)If a system absorbs radiant energy and then emits it partially or completely almost instantaneously(within 10^{-8} S) in the form of radiation.	(a)If a system absorbs radiant energy and then emits partially or completely after a time lag in the form of radiation.
(b)Its emission ceases as soon as the source of exciting radiation is removed.	(b)It continues for some time even after the source of exciting radiation is removed.
©It can be stimulated in gases, liquids and solids.	©It mainly exhibited by solids.
(d)It is caused by $S_1 \rightarrow S_0$ transitions which is a quantum mechanically allowed transition	(d)It is caused by $T_1 \rightarrow T_0$ transitions which is a quantum mechanically forbidden transition

Chemiluminescence

- **Chemiluminescence: The emission of light in chemical reaction at ordinary temperature is called Chemiluminescence**

  e.g. The light emitted by glow-worms.

It is the reverse of a chemical reaction.

- **Chemical reaction—results from the absorption of light**
- **Chemiluminescence— emission of light from a chemical reaction.**

Quantum Efficieny (ϕ)=

$$\frac{\text{No. of photons emitted in a given time}}{\text{No. of molecules of the reactant consumed in the same time}}$$

ϕ is less than 1.

Explanation

- **Excited products undergoes deactivation and the excess energy is emitted as radiation**
- **If the wavelength of the emitted light falls in the visible region, Chemiluminscence is observed.**

$$A \rightarrow B^* \rightarrow B + hv$$

- **The exothermic reaction can produce one of the product to the electronically excited state, it shows chemilumincescence.**

Examples:

1. **Phosphorus glows in air with faint greenish colour due to its oxidation.**

P oxidizes to phosphorus trioxide (P_2O_3 exists as dimer P_4O_6) oxidises to phosphorus pentoxide(P_2O_5 exists as dimer P_4O_{10})

$$4P+3O_2 \rightarrow P_4O_6^* \rightarrow P_4O_6 + hv$$

$$P_4O_6^* + 2O_2 \rightarrow P_4O_{10}^* \rightarrow P_4O_{10} + hv$$

Natural Example:

Photosensitization is that by chlorophyll in the Photosynthesis of carbohydrates in plants.

$$\text{Chlorophyll} + hv \rightarrow \text{Chlorophyll}^*$$

$6CO_2+6H_2O+Chlorophyll^* \rightarrow C6H12O6+O_2 + Chlorophyll$

Bioluminescence

Emission of visible light accompanies a chemical reaction that occurs in the living organism.

Or it is the chemiluminescence from a biological system.

egs: Glow of fire files

Emission of light results from the oxidation of a protein called luciferin in their body by atmospheric oxygen in the presence of enzyme luciferase.

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Phosphorescence

If a system absorbs radiant energy and then emits partially or completely after a time lag in the form of radiation

It continues for some time even after the source of exciting radiation is removed.

It mainly exhibited by solids.

It is caused by $T_1 \rightarrow T_0$ transitions which is a quantum mechanically forbidden transition

Chapter 13
Spectroscopy
NMR, IR, MS, UV-Vis

Main points of the chapter

1. Hydrogen Nuclear Magnetic Resonance
    a. Splitting or coupling (what's next to what)
    b. Chemical shifts (what type is it)
    c. Integration (how many are there)
2. 13C NMR
3. InfraRed spectroscopy (identifying functional groups)
4. Mass spectroscopy (determining molecular weight, structural elements, molecular formula)

The various spectroscopies are the primary method for determining the structure of compounds. If the molecule is not too large or complex, the determination should be very accurate. These are simply done and rapid. They can be combined to give overlapping information.

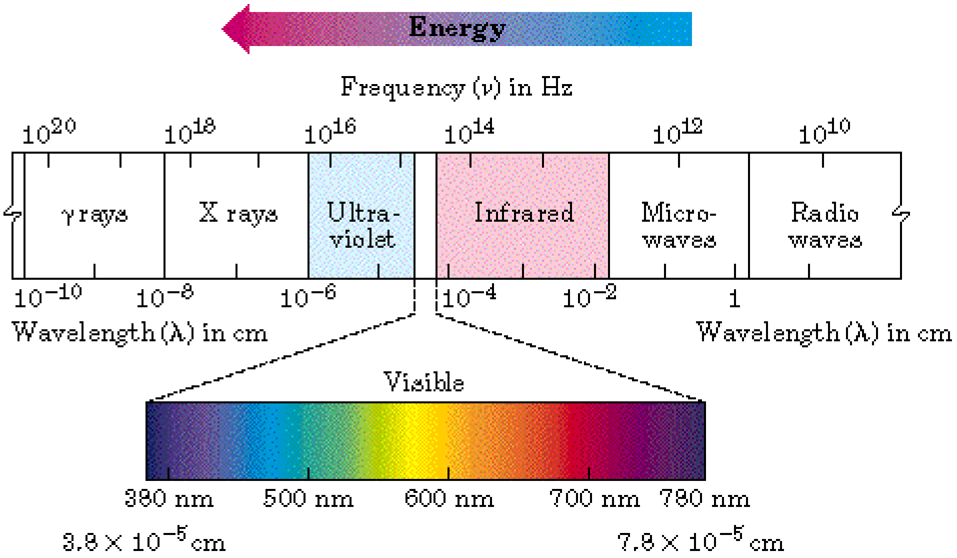
This is not chemistry in the sense of reactions but it is very interesting puzzle solving. Once you understand the rules, you will like it (except of course in exams).

The chapter begins with background information on how these techniques work which is interesting but not essential to using them to determine structures. In the NMR, the information sequence is the logical progression from the simple to the more complex. But do not think that the first item, chemical shift, or the second, integration, is the important component. The splitting or multiplicity is the key element in H-NMR. IR is much more straightforward; memorize a few absorption numbers to identify functional groups. MS is also straightforward. We will not do UV-Vis becauase it is not very useful for structure identification. It is an extremely important tool for quantitating substances and is used widely.

1. Molecular interaction with electromagnetic radiation. (13.1-2)

Molecules have electromagnetic fields derived from their electrons and nuclei. We saw earlier that plane-polarized light interacts by being rotated by an enantiomer. As seen below, energy varies across the spectrum and matches that required for various interactions.

The Electromagnetic Spectrum



Energy increases going to the left. The electromagnetic radiation interacts with the electromagnetic fields of the electrons to raise their energy levels from one state to the next. The nature of that interaction depends on the energy available. Ultraviolet and visible have sufficient energy to effect electronic transitions. Infrared has sufficient energy only to effect transitions between vibrational energy states. Microwave has only enough energy to effect transitions between rotationaly energy states. Thus the radiation absorbed tells us different information. Radio waves have insufficient energy to effect molecules but affect nuclear spin energy states found in magnetic fields. This latter interaction is most important because it is used in Nuclear Magnetic Resonance spectroscopy.

2. NMR theory (13.3-13.5)

A. All nuclei with unpaired protons or neutrons are magnetically active- they have a magnetic field arising from the unpaired nuclear particle. Of greatest interest to an organic chemist is hydrogen (including deuterium) and carbon (the ^{13}C isotope not the ^{12}C isotope which has paired neutrons and protons).

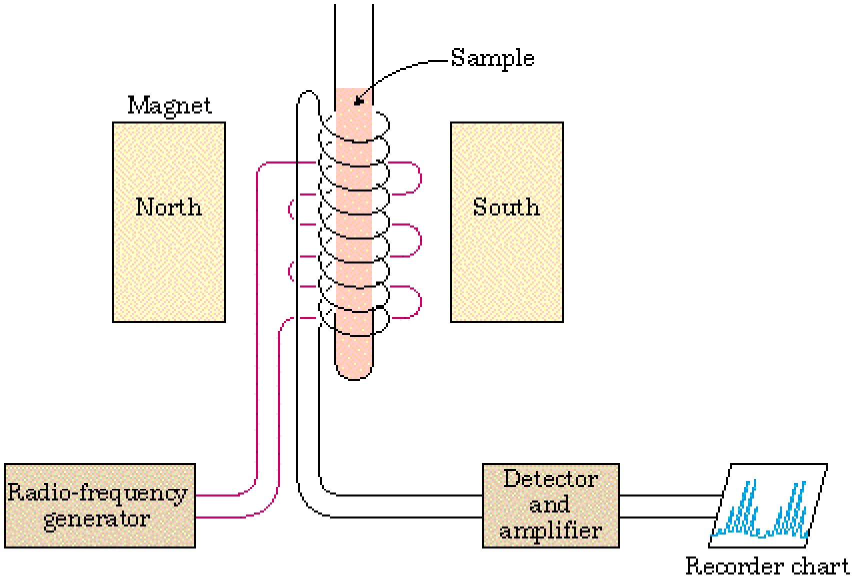
B. Placed in an external magnetic field this magnetic field of the nucleus has two stable states,

alignment with or against the applied field, which are of slightly different energies (aligned against is higher). The greater the applied field the greater this difference (this is a crucial fact).

a. Internal (in the molecule) factors which affect (add to or subtract from) the applied magnetic field so as to put the individual nucleus in a different magnetic environment from that felt by another nucleus create differences in the nuclei.

b. Higher applied magnetic fields will create larger absolute numerical values of the differences between energy states and allow easier distinction between two different nuclei (better resolution).

A schematic of an NMR spectrometer



C. Electromagnetic radiation of radio frequency wavelengths is of the right energy range to cause the nucleus to move (resonate) between these two energy states. This absorption allows detection of the hydrogen or carbon-13 nucleus. Different nuclei experiencing different magnetic fields and thus different energy differences between states will absorb different radio frequencies or at a particular constant frequency will absorb at different applied magnetic fields and allow us to distinguish between them.

This selectivity of energy required to match the energy differences between states is fundamental for all spectroscopies. The energy states are termed quantized. Transitions can occur only when the precise energy corresponding to the energy difference between the states is delivered to the system to excite it to the higher state. So the frequency (or wavelength) of radiation absorbed is specific to that energy transition. When the energy difference between

the states changes or is different, the frequency of light absorbed will change.

D. What internal magnetic factors modify the applied magnetic field to create the effective field experienced by the individual nuclei, thus changing the energy (frequency) needed for the transition (resonance)?

Two:
a. The electrons in the bonds around those nuclei.
b. The magnetic fields of neighboring nuclei.

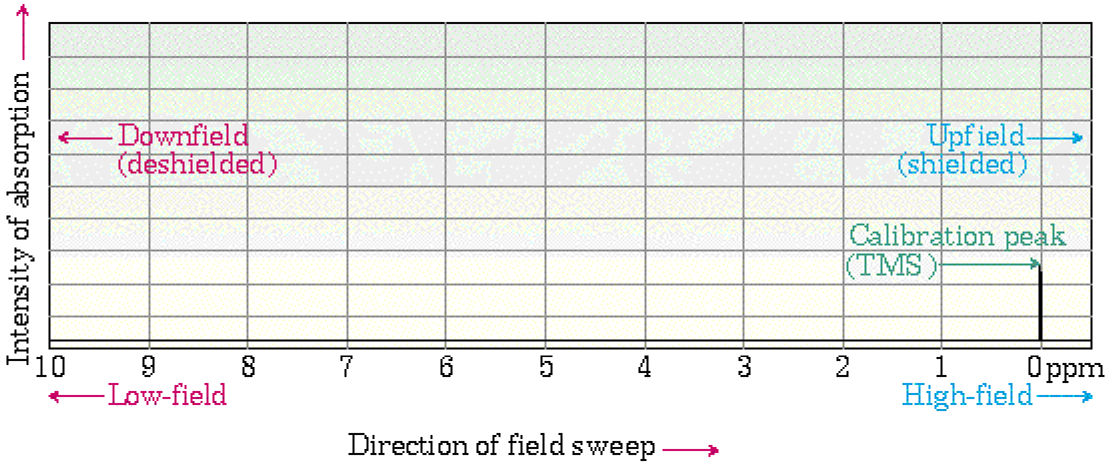
Consider a. first.

The electrons act to oppose the applied field shielding the nuclei form it. Since every different type of hydrogen is an a different electronic environment, each type will experience a different effective magnetic field and thus a different resonance frequency. We can tell one type of nucleus from another type. We term this value the chemical shift. Chemical shift is expressed as a delta value.

delta = chemical shift (number of Hz away from standard TMS)/MHz of instrument

For example, delta = 60 Hz/ 60,000,000 Hz = 1 ppm

The spectrum is presented as follows:



Some simple spectra:

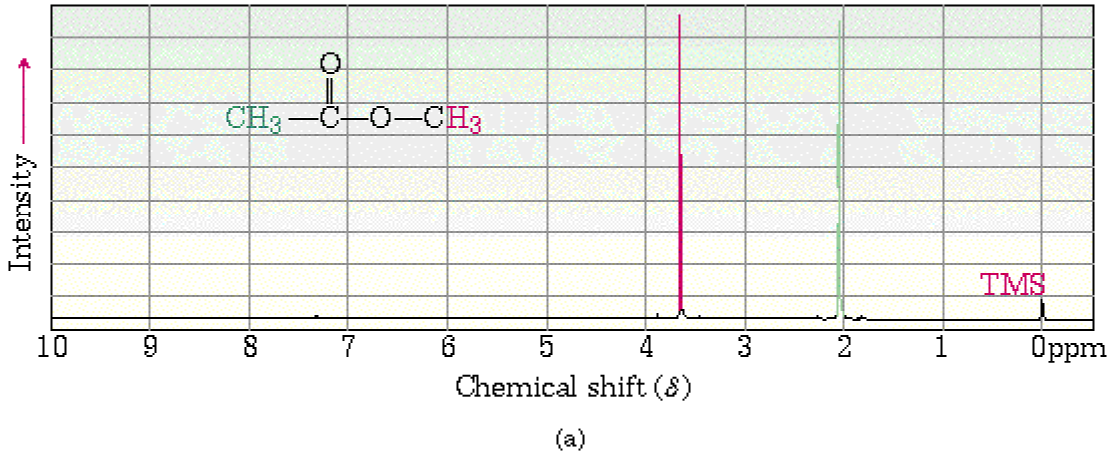
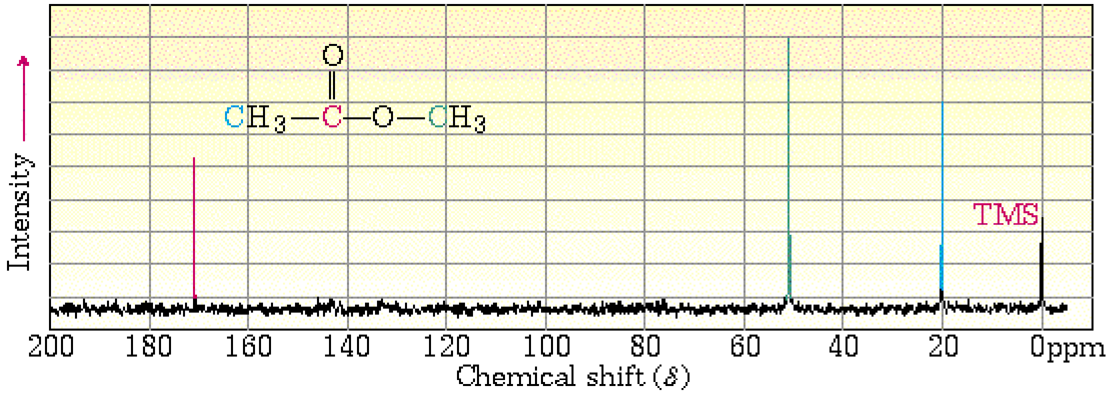


Figure 13.3 (a) The ^{1}H NMR spectrum and (b) the ^{13}C NMR spectrum of methyl acetate, $CH_3CO_2CH_3$.



(b)

Note :

Two types of hydrogens, the hydrogens of a methyl are the same- they spin and experience the same average environment. The oxygen pulls electrons away from the right methyl and it is deshielded from the applied field, shifted downfield, a smaller field is needed to bring it into resonance. Three kinds of carbon. Note how deshielded the carbonyl carbon is.

Look at the chemical shift ranges. Very different for the different nuclei. TMS is tetramethylsilane and is chosen because all resonances are to the left of this peak so it's handy to use as a standard set to zero.

Identical nuclei have the same chemical shift. If you have a hard time deciding if they are identical, imagine subsituting each with a halogen and ask if it would have the same name.

So chemical shifts are somewhat typical of particular types of hydrogen, predictable and useful for knowing what kind of group based on the chemical shift. See the table below. But beware. Due to deshielding substitutions, these values shift down quite a bit.

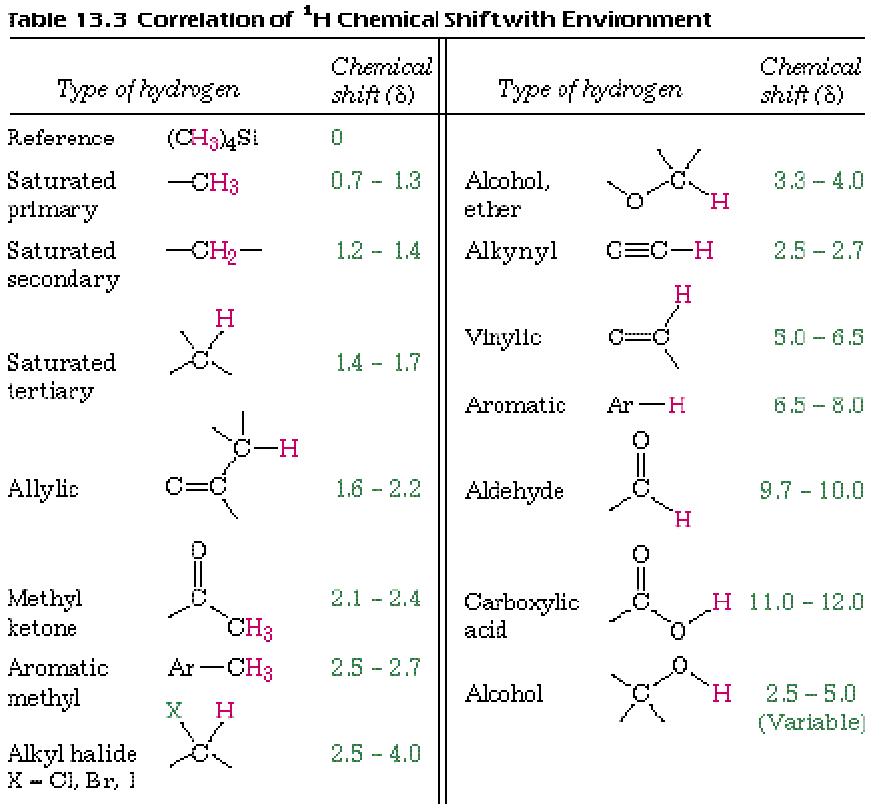


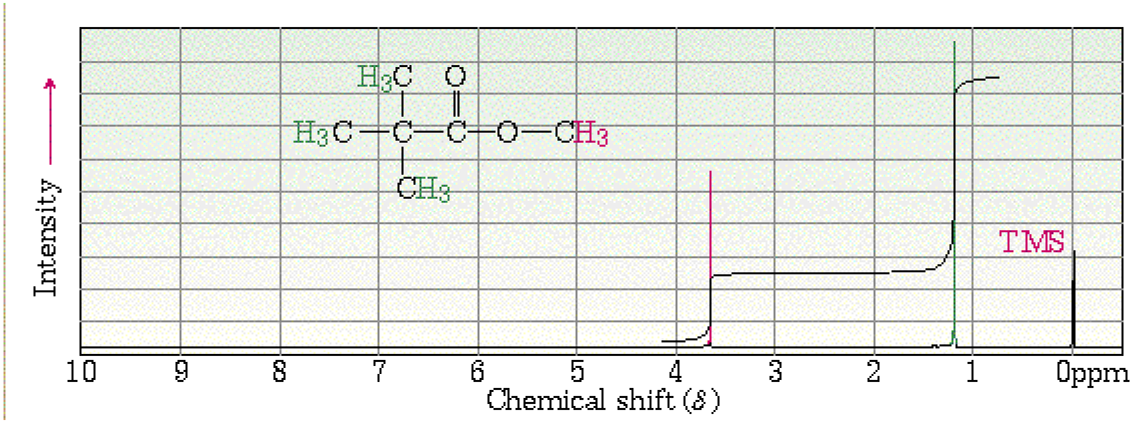
Table 13.3 Correlation of ^1H Chemical Shift with Environment

Type of hydrogen		Chemical shift (δ)	Type of hydrogen		Chemical shift (δ)
Reference	$(CH_3)_4Si$	0			
Saturated primary	$-CH_3$	0.7 - 1.3	Alcohol, ether		3.3 – 4.0
Saturated secondary	$-CH_2-$	1.2 - 1.4	Alkynyl	$C\equiv C-H$	2.5 – 2.7
Saturated tertiary		1.4 - 1.7	Vinylic		5.0 – 6.5
			Aromatic	$Ar-H$	6.5 – 8.0
Allylic		1.6 – 2.2	Aldehyde		9.7 – 10.0
Methyl ketone		2.1 – 2.4	Carboxylic acid		11.0 – 12.0
Aromatic methyl	$Ar-CH_3$	2.5 – 2.7	Alcohol		2.5 – 5.0 (Variable)
Alkyl halide X = Cl, Br, I		2.5 – 4.0			

E. Integration Section 13.6- How many protons are producing this signal (integration does not work for carbon)

The area under the curve (correlates well with peak height) is proportional to the number of

protons producing the signal. So the area is integrated in the calculus sense and compared for the different resonances. The ratio of the areas equals the ratio of the protons producing the signal. This area is presented graphically by an integrating line in which the rise in the line as it passes through the peak is proportional to the area under the peak. Note that it is proportional. The absolute values mean nothing, only the relative areas under the peak. If the number of hydrogens in the molecule are known then the total rise divided by the number of hydrogens gives a rise/hydrogen and dividing that value into the rise in a peak will give the number of hydrogens in the peak. If the total is not known, then some peak must be guessed and the other peaks surmised from the relative areas.



E. Spin - spin splitting: **What's next door - the best information from NMR (sections 13.7-13.11)**

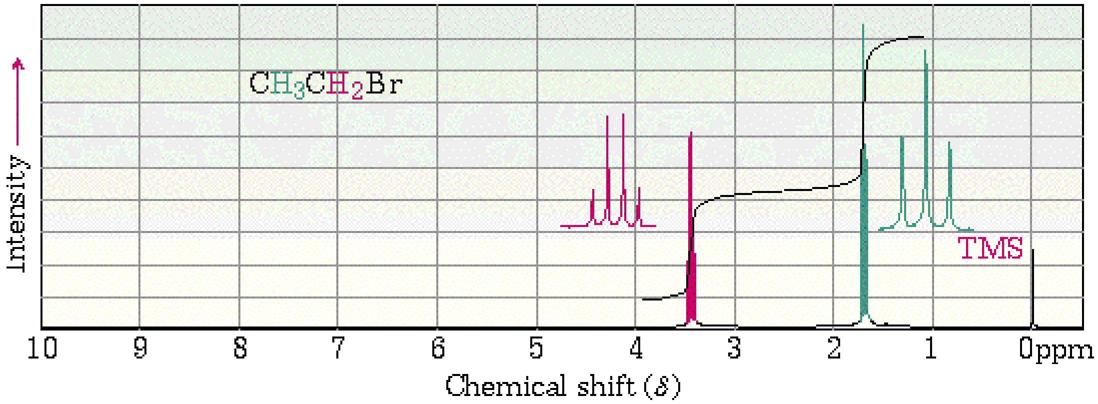
Since nuclei produce magnetic fields (the ones we've been talking about aligning with and against the field), those fields would affect the effective field felt by the hydrogen being measured. In the high energy state they would oppose (reduce) the field and in the low energy state reinforce (increase) the field.

Thus a neighboring hydrogen would cause another hydrogen to feel two fields

effective field = applied field - electron shielding + or - neighboring nuclei field

So instead of seeing one signal, if a single neighboring hydrogen splits the signal you would see two, called a doublet. At first this seems a painful complication but it tells you that if you see a doublet that nucleus has a single hydrogen adjacent. With such information you can put the pieces in order to make a structure.

Similarly, two neighboring nuclei yield three peaks, three yield four, etc. This is termed the n+1 rule stating that a signal will be split into n+1 peaks when n equivalent nuclei (hydrogens) are adjacent. The peak areas are also predictable based on an analysis of the possible states and can be readily remembered by Paschal's triangle.



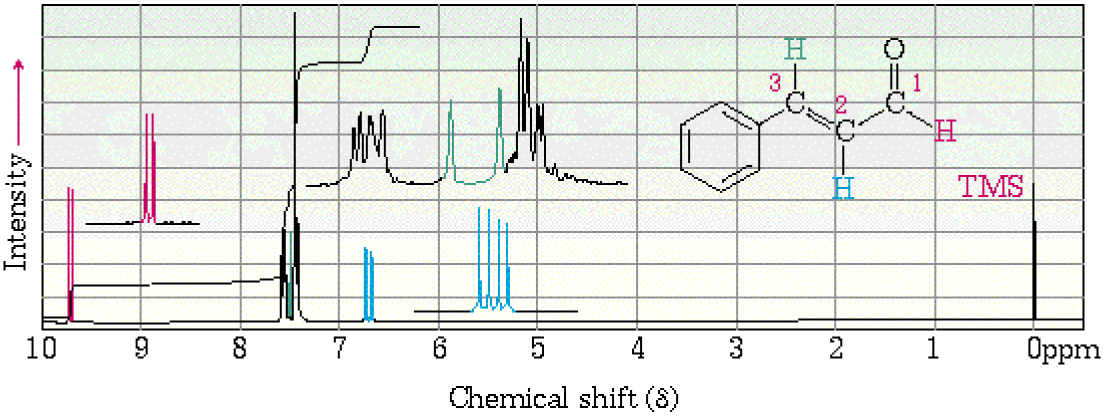
Note that the CH_3 group is a triplet being split by the two neighboring hydrogens of the CH_2. The CH_2 group is a quartet being split by the three hydrogens of the CH_3.

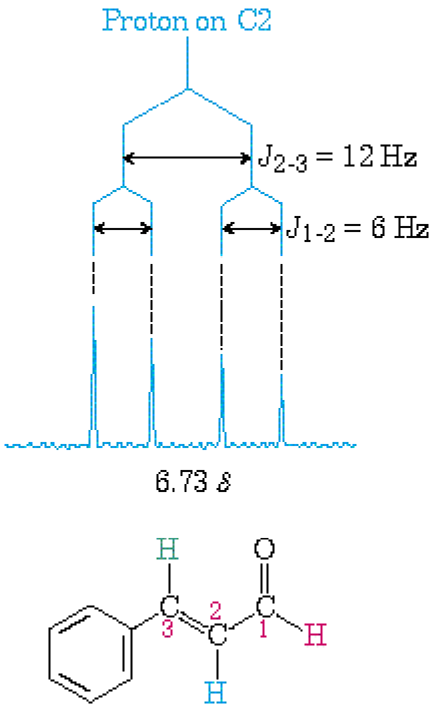
Now let's see if you can predict the chemical shift and splitting pattern of isopropyl bromide.

So , the rules for splitting are:
1. Equivalent hydrogens do not split one another.

2. a.The signal of a type of hydrogen is split into n+1 peaks, where n=the number of equivalent neighboring hydrogens.
b. When two different types of hydrogen are adjacent, they split the signal independently to produce $(n_a+1)(n_b+1)$ peaks.

Consider this more complicated example.





The amount by which the signal is split (the distance apart) is called J , the coupling constant but is not critical for our level of understanding. Hydrogens splitting each other have the same J value.

Aromatic regions are more complex because of the often very similar chemical shifts and small coupling constants and extensive overlaps of signals.

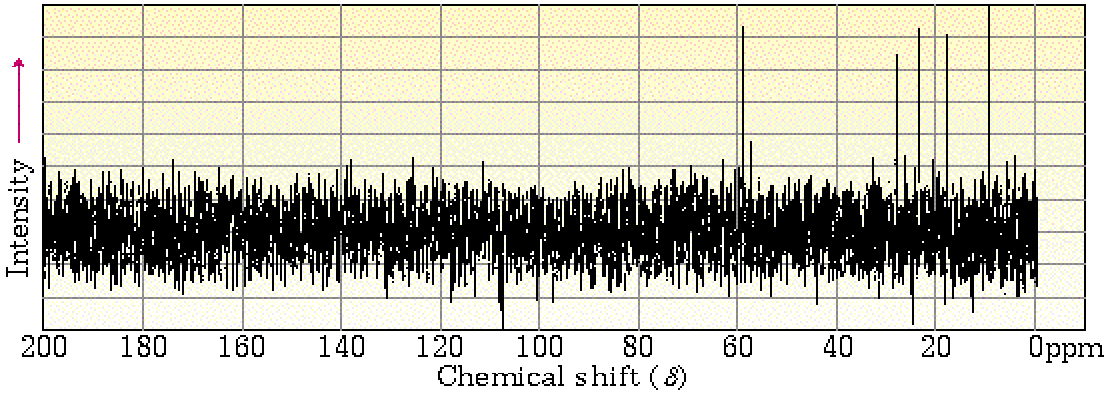
Two principal parameters - the electronic effects of the substituent and the substitution pattern.

3. ^{13}C NMR.

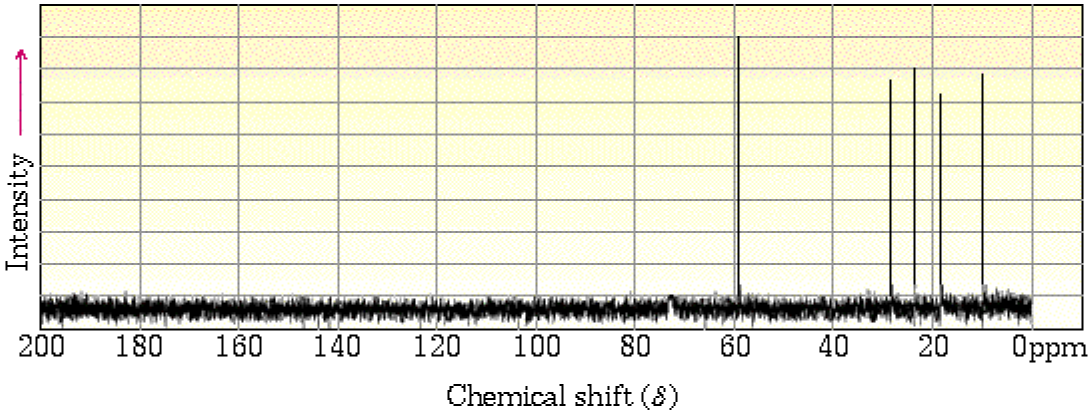
Similarities with H-NMR:
Chemical shift relative values. See earlier figures

Differences:
a. ^{13}C does not split adjacent carbon or hydrogen because it is present in only 1% abundance. Thus the splitting that would occur is not seen because it is only a small contribution to the whole which is dominated by the ^{12}C effect (which is no splitting)

b. Because ^{13}C is in such low abundance it is very hard to see its signal. This requires signal averaging over long times. Many spectra are taken and averaged. Since noise is random it does not increase with time, but the signal is additive over many spectra.

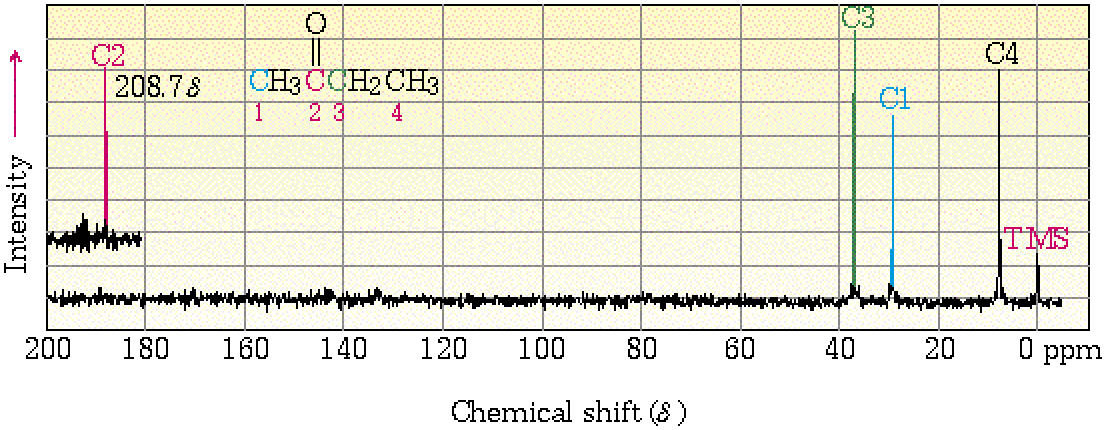


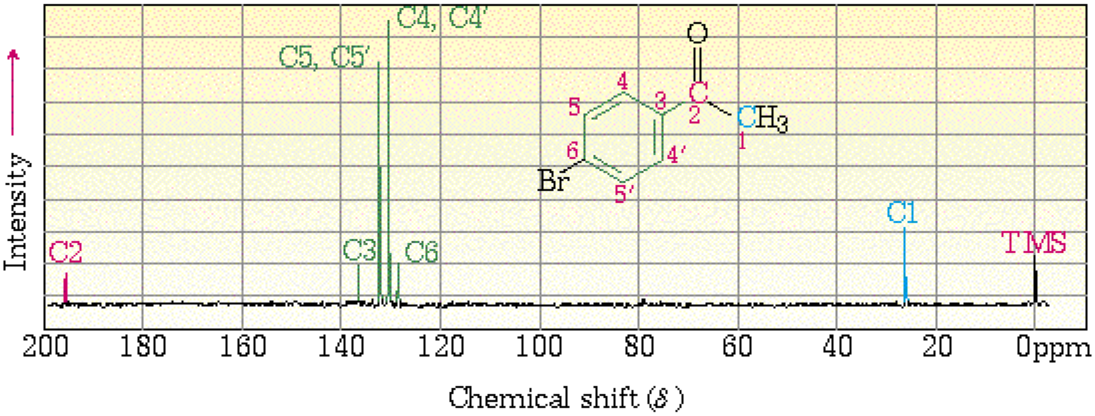
(a)



The above spectra is 1-pentanol, $CH_3CH_2CH_2CH_2CH_2OH$. Notice the five different signals for each carbon because each is different. With the much wider chemical shift range and single peaks there is little chance of overlap. Which resonance is associated with which carbon?

Another Example

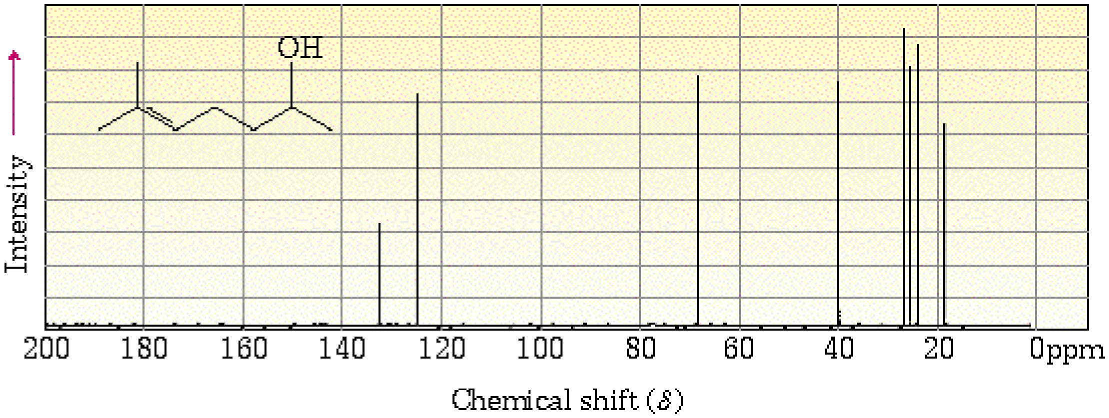




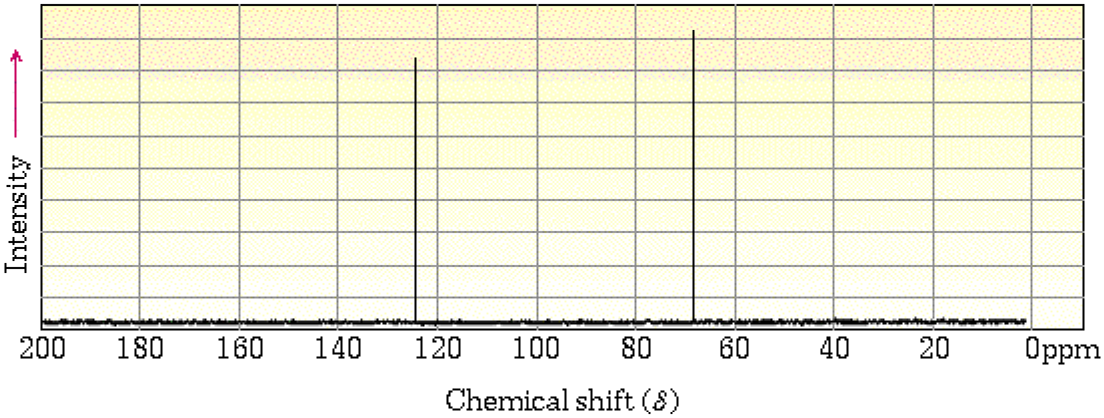
Notice that in these spectra that the peak heights for single carbons are not the same. And no attempt has been made to integrate them. This is because integration does not work for time averaged spectra.

Notice also that the hydrogens are not splitting the carbon signals as would be expected. This

is purposely done to simplify the spectrum by a broad band rf irradiation of the hydrogen region, which removes the splitting, the hydrogens no longer exist in one or the other energy state. Allowing such splitting causes CH_3 carbon to appear as a quartet, CH_2 as a triplet, and CH as a doublet thus allowing determination of what kind of carbon it is. Another technique for the same information is the Distortionless Enhancement by Polarization Transfer (DEPT).



(a)



(b)

In a) all carbons are seen, in b) only CH carbons show, in c) positive signals are seen for CH and CH_3 and negative peaks are seen for CH_2

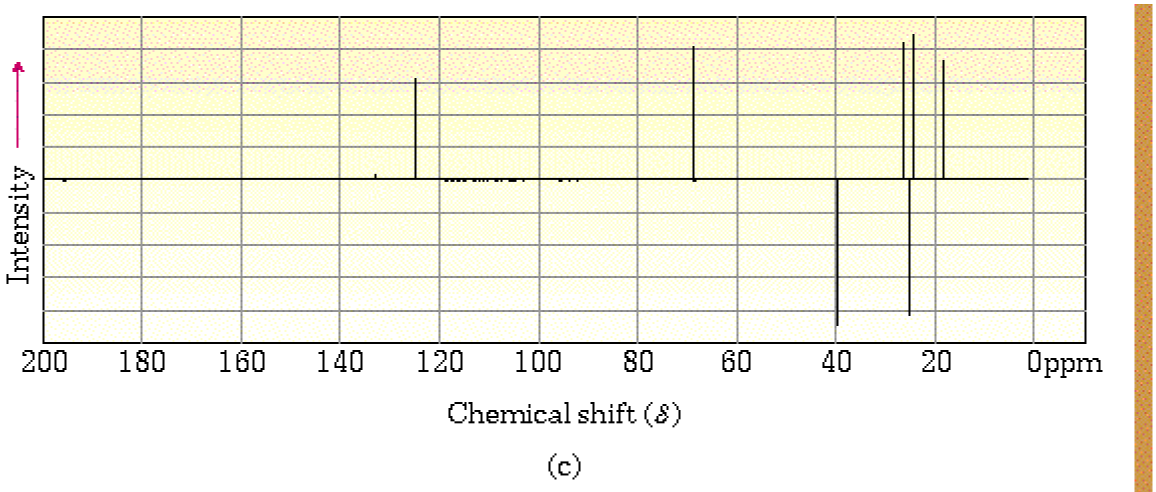
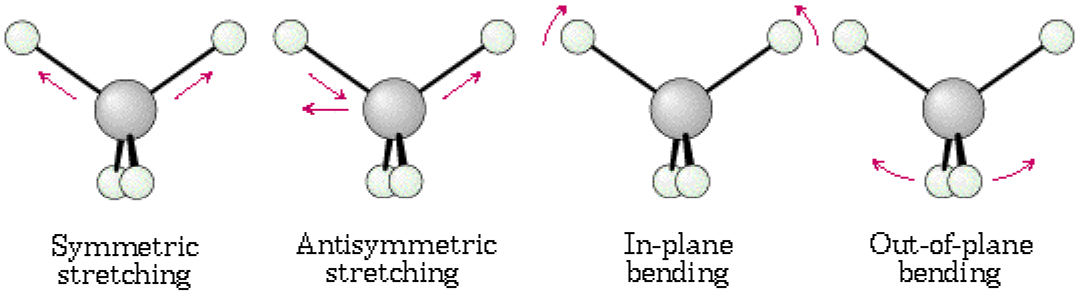


Figure 13.19 DEPT-NMR spectra for 6-methyl-5-hepten-2-ol.

4. Infrared Spectroscopy (section 13.19)

We mentioned in the chapter's beginning that infrared radiation was of the right energy level to cause increases in the vibrational energy states of organic molecules. The energy needed to change vibrational states depends on bond strength and the mass of the atoms bonded. Thus different bonds absorb different IR wavelengths and these are indicative of what functionality (bonds) are in the molecule. Each functionality can vibrate in several different ways and thus absorb several wavelengths but usually we use only one as diagnostic.

For example



In Table 12.1 (or 13.4 of our text) are collected more data than you need

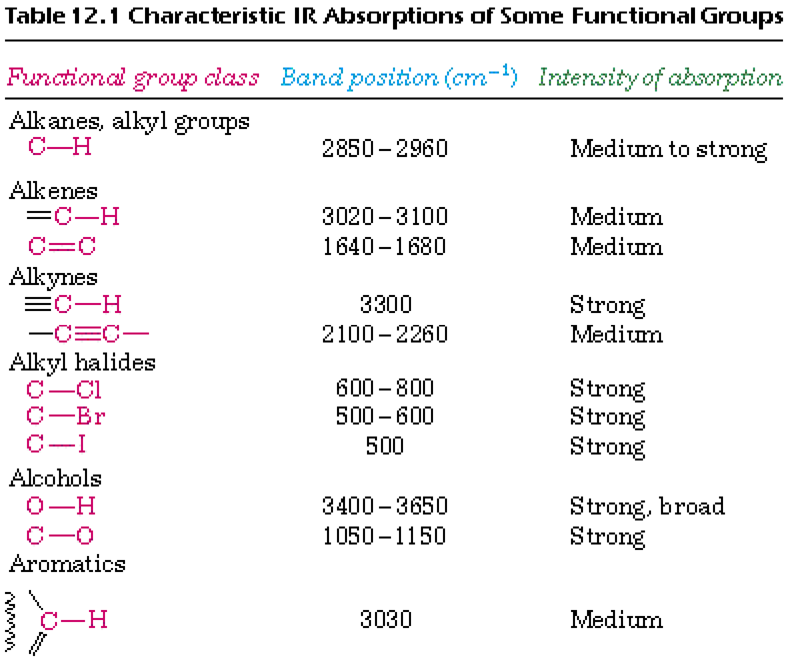
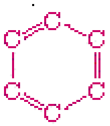


Table 12.1 Characteristic IR Absorptions of Some Functional Groups

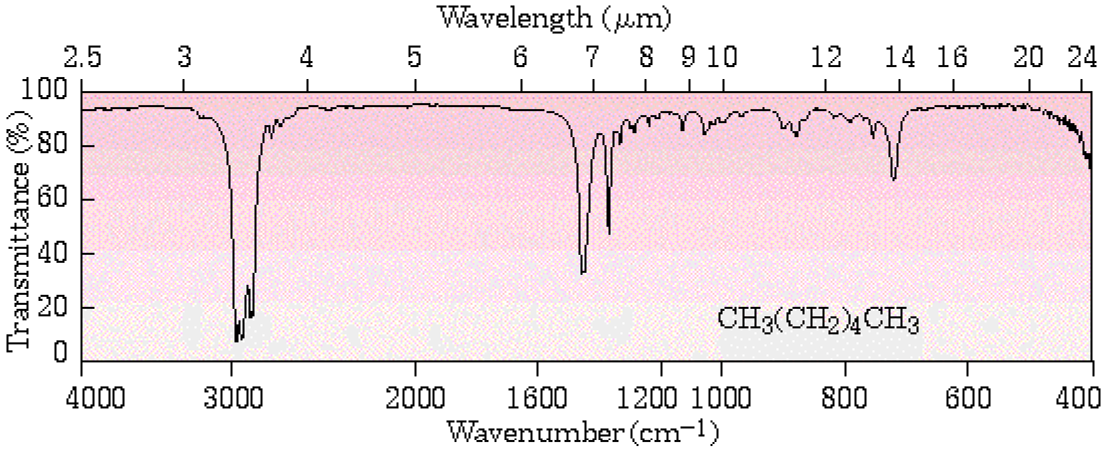
Functional group class	*Band position* (cm^{-1})	*Intensity of absorption*
Alkanes, alkyl groups		
C—H	2850–2960	Medium to strong
Alkenes		
=C—H	3020–3100	Medium
C=C	1640–1680	Medium
Alkynes		
≡C—H	3300	Strong
—C≡C—	2100–2260	Medium
Alkyl halides		
C—Cl	600–800	Strong
C—Br	500–600	Strong
C—I	500	Strong
Alcohols		
O—H	3400–3650	Strong, broad
C—O	1050–1150	Strong
Aromatics		
C—H	3030	Medium

	1600, 1500	Strong
Amines		
N—H	3300–3500	Medium
C—N	1030, 1230	Medium
Carbonyl compounds[a]		
C=O	1680–1750	Strong
Carboxylic acids		
O—H	2500–3100	Strong, very broad
Nitriles		
C≡N	2210–2260	Medium
Nitro compounds		
NO_2	1540	Strong

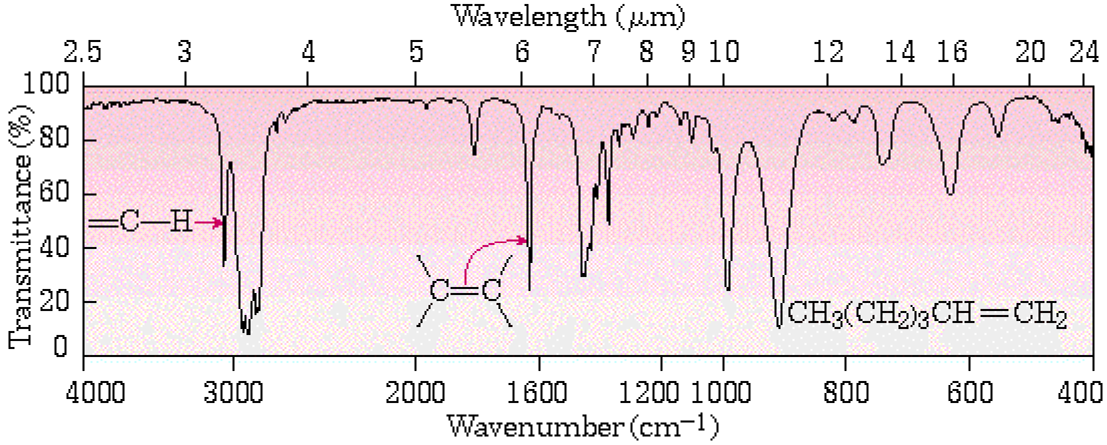
---

[a] Acids, esters, aldehydes, and ketones.

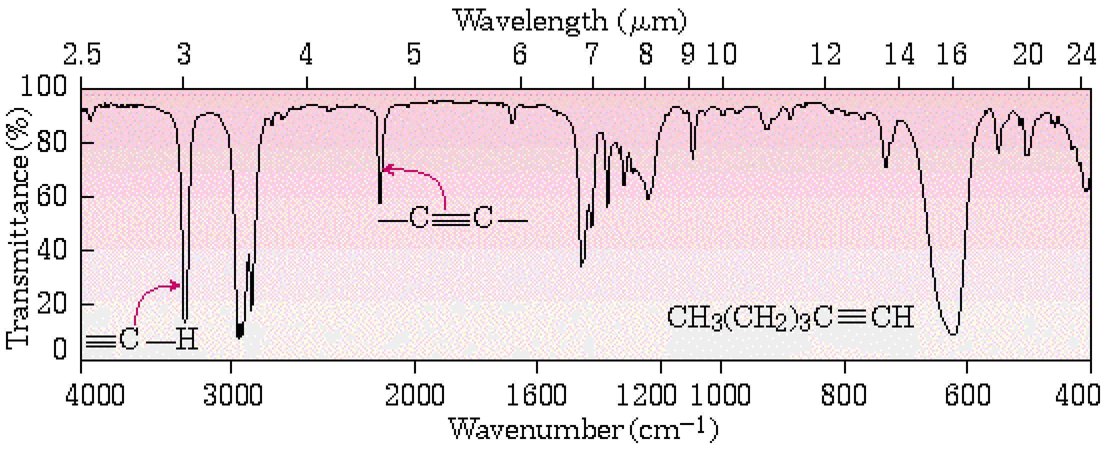
So when we look at an IR spectrum we look for the absorptions that are indicative of particular groups. For example:



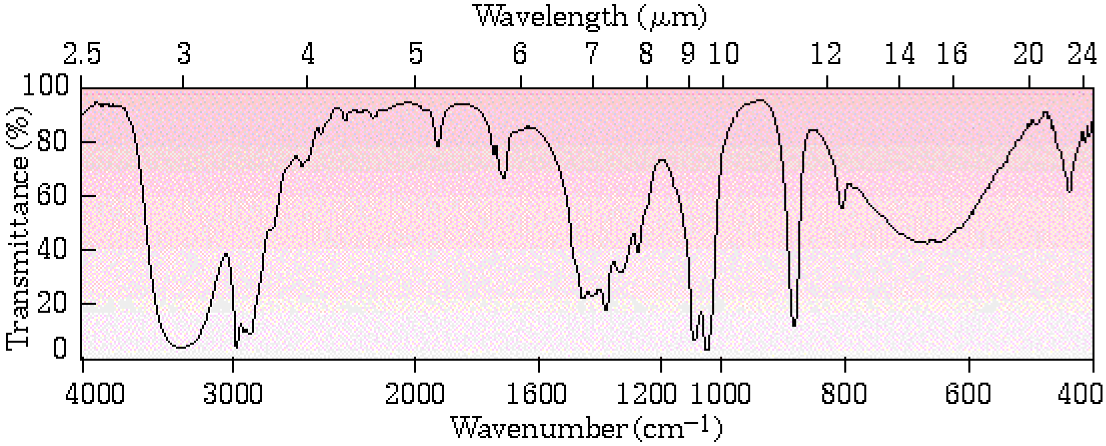
(a)



(b)



(c)



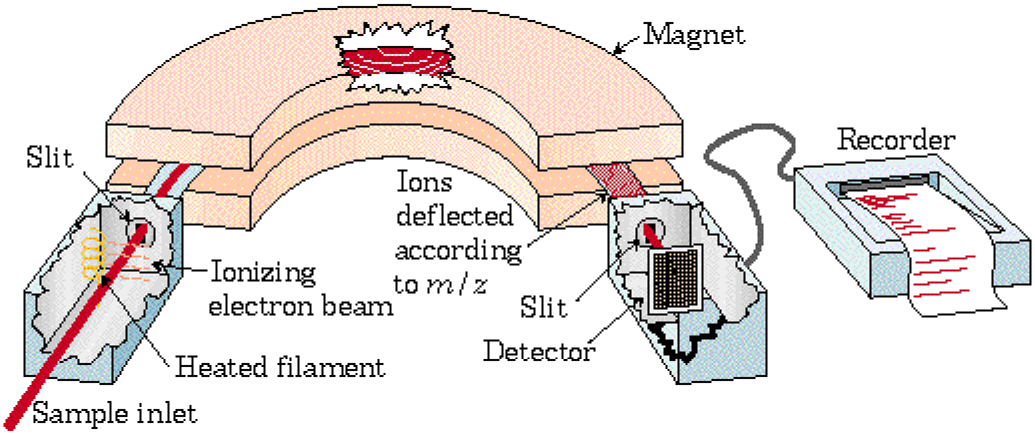
Ethyl alcohol

The fingerprint region is that area below 1600 wavenumbers which is ordinarily too complex to be diagnostically useful. The fingerprint region can be interpreted but is principally used to compare individual compounds to one an another for identification of the compound, hence the name fingerprint.

5. Mass spectrometry

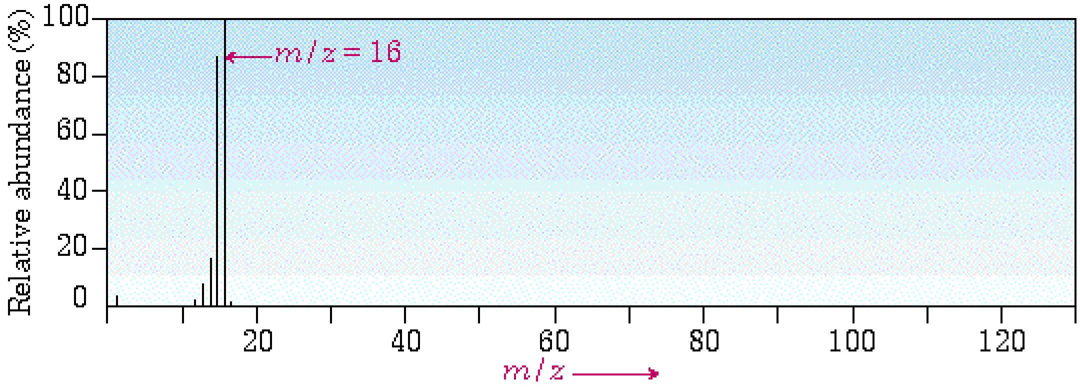
Mass spectra give us information on the molecular weight, the molecular formula (at high resolution), and what substructures are present.

How does it work?



An electron is ejected from the molecules by the ionizing electron beam and passed through an electrical field to accelerate them to a uniform velocity. These ions are then passed through a magnetic field. Moving charges are deflected by a magnetic field, with low mass ions being deflected more than heavy mass ions (the force is constant because they all have a single charge but momentum is greater for the heavier ions). These ion positions are recorded as they strike the detector and a spectrum with mass on the x-axis is recorded.

Two sample spectra:



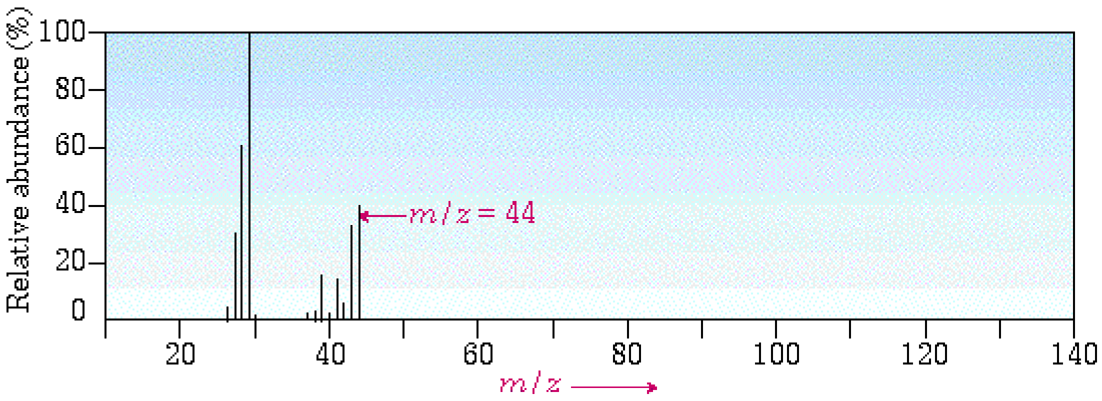
(a)

Figure 12.2 Mass spectra of (a) methane (CH_4; MW=16) and (b) propane (C_3H_8; MW=44).

Parent or molecular ion (M+) = The ion of the compound with only the loss of the electron. Usually the heaviest peak in the spectrum.

M+1, M+2 = Small peaks higher than the molecular ion due the presence of isopes of hydrogen (D,T) and carbon (^{13}C) which give the molecule higher mass. Since the isotopes are low abundance, these mmolecules are not common and the peaks are small. Two exceptions to the low abundance isotope are Chlorine (^{35}Cl : ^{37}Cl, 3:1) and Bromine (^{79}Br : ^{81}Br, 1:1).

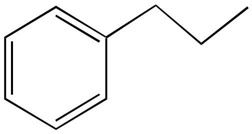
Base peak = a book keeping device to record the intensity of the tallest peak in the spectrum as 100% and measure the other peaks in relation to it in percent. But also the most stable or readily formed cation.



(b)

Propane

Fragment or daughter ion. A molecule with a missing electron is unstable and begins to break down. A typical example would be propyl benzene



Which will yield benxyl cations in good yield.

Other stable cations like t-butyl (57), phenyl (77), isopropyl (43) are common if they can be derived from the structure. Alkyl structures will peel off -CH2- groups to give peaks differing by 14 mass units.

High resolution MS yields exact molecular formulas. If the mass resolution is to the fourth decimal eg. 196.3545 the formula can be determined uniquely, only one combination of elements can produce that value.

The presence of double bonds or rings indicated by molecular formula.

One last item in this chapter is the use of a determination of the number of double bonds or rings from the molecular formula. This can be helpful in problem solving in spectroscopy.

The formula of an alkane is C_nH_{2n+2}, C_4H_{10}. Alkenes or rings have the formula C_nH_{2n}, C_4H_8. Increasing the number of double bonds increases that hydrogen deficiency by two for each double bond or ring. The benzene. C_6H_6, is eight hydrogens short of an alkane (saturated) formula which corresponds to 4 double bonds or ring, in this case one ring and three double bonds.

An oxygen in the formula has no effect on the C,H numbers. A halogen replaces an H so we can count H and X in determining the hydrogen deficiency. Nitrogen adds one hydrogen to the expected alkane formula, so $C_8H_{19}N$ is a saturated alkane. Note the odd number of hydrogens resulting. This has an impact on molecular weight as well because it produces an odd numbered mass while organic molecules are invariably are even-numbered. (This is due to the fact that O,C are even massed, H comes in twos, except when replace by halogen which are odd-numbered). So only compounds with odd numbers of N are odd-number masses.

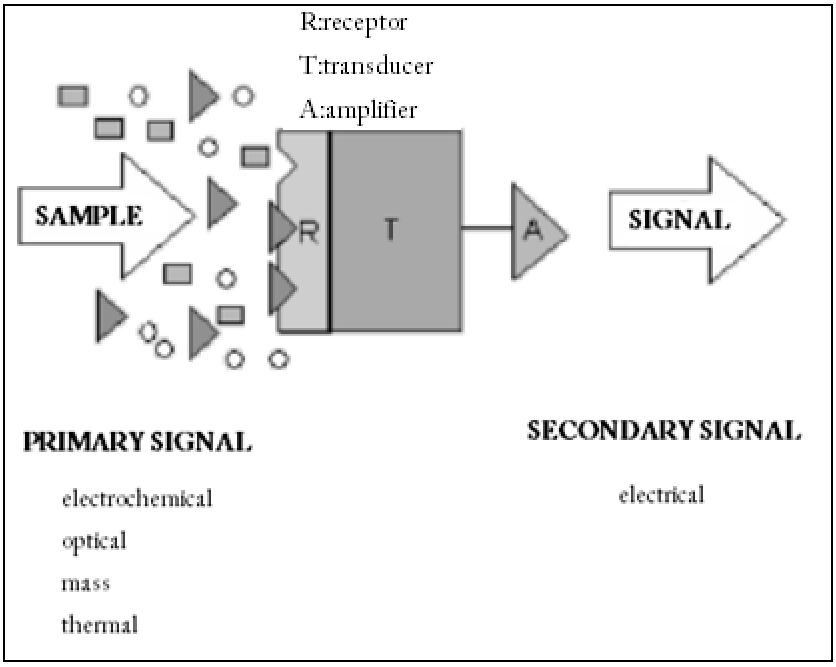
CHEMICAL SENSORS

1. DEFINITION

A chemical sensor is a device that transforms chemical information (composition, presence of a particular element or ion, concentration, chemical activity, partial pressure…) into an analytically useful signal. The chemical information, mentioned above, may originate from a chemical reaction of the analyte or from a physical property of the system investigated. They can have applications in different areas such as medicine, home safety, environmental pollution and many others.

2. COMPOSITION

Chemical sensors usually contain two basic components connected in series: a chemical (molecular) recognition system (receptor) and a physicochemical transducer. In the majority of chemical sensors, the receptor interacts with analyte molecules. As a result, its physical properties are changed in such a way that the appending transducer can gain an electrical signal.



- Receptor: The function of the receptor is fulfilled in many cases by a thin layer which is able to interact with the analyte molecules, catalyze a reaction selectively, or participate in a chemical equilibrium together with the analyte. The receptor layer can respond selectively to particular substances or to a group of substances. The term *molecular recognition* is used to describe this behavior. Among the interaction processes, the most important for chemical sensors are adsorption, ion exchange and liquid-liquid extraction. Primarily these phenomena act at the interface between analyte and receptor surface.

- Transducer: Nowadays, signals are processed almost exclusively by means of electrical instrumentation. Accordingly, every sensor should include a transducing function, i.e. the actual concentration value, a non-electric quantity must be transformed into an electric quantity, voltage, current or resistance. Some of them develop their sensor function only in combination with an additional receptor layer. In other types, receptor operation is an inherent function of the transducer.

3. EXAMPLES

CARBON MONOXIDE DETECTOR

It is a device that detects the presence of the carbon monoxide (CO) gas. CO is a colorless and odorless compound produced by incomplete combustion. It is also known as "silent killer" because it is virtually undetectable without using detection technology. Elevated levels of CO can be dangerous to humans depending on the amount present and period of exposure. Smaller concentrations can be harmful over longer periods of time while increasing concentrations require less exposure times to be harmful.

Carbon monoxide detectors trigger an alarm based on an accumulation of carbon monoxide over time. Detectors may be based on a chemical reaction causing a color change, an electrochemical reaction that produces current to trigger an alarm, or a semiconductor sensor that changes its electrical resistance in the presence of CO.

While CO detectors do not serve as smoke detectors and *vice versa*, dual smoke/CO detectors are also available. Smoke detectors detect the smoke generated by flaming or smoldering fires, whereas CO detectors detect and warn people about dangerous CO buildup caused, for example, by a malfunctioning fuel-burning device. At home, some common sources of CO include open flames, space heaters, water heaters, blocked chimneys or running a car inside a garage.

GLUCOSE DETECTOR

Blood glucose monitors are devices that are used to measure the concentration of glucose within a person's blood. Along with the term blood glucose this reading is also often referred to as blood sugar. Most basic blood glucose monitors have three separate parts that are required for them to work properly: a lancer, a test strip and the meter itself.

Blood glucose monitors measure the amount of sugar in a sample of blood using a complex chemical process. Within the test strip the blood is mixed with glucose oxidase, which reacts with the glucose in the blood sample to create gluconic acid. Another chemical within the test strip, called ferricyanide, then reacts with the gluconic acid to create ferrocyanide. The electrode within the test strip then runs a current through the blood sample and the ferrocyanide influences this current in such a way that the concentration of blood glucose within the sample can be accurately measured within a fair margin o of error.

- **MOSQUITO**

Mosquitoes have a battery of sensors in their antennas and one of them is a chemical sensor. They can sense carbon dioxide and lactic acid up to 36 meters away. Mammals and birds release these gases when they breathe. Certain chemical in sweat also seem to attract mosquitoes. This is the reason that those who sweat more easily will tend to attract more mosquitoes.

- **PREGNANCY TEST**

While there are a number of ways to chemically test for pregnancy, the easiest and most reliable test is one that looks for the presence of the hormone known as human chorionic gonadotropin, or hcG. hcG is produced by the placenta and can be found in a woman's system as soon as implantation of a fertilized egg has occurred.

The most common way to test for hgC, as well as one of the most accurate, is a home pregnancy test, which works through the use of lateral flow technology. A lateral flow test is a type of chemical analysis test which is commonly used to test liquids for the presence of a specific substance, such as drugs, hard water chemicals or hormones.

When urine is collected on the test strip of a home pregnancy test, it then moves across the strip by way of wicking action. Stretched across the test strip is a membrane made of nitrocellulose, a material used because it assists the movement of proteins. As the urine comes into contact with the membrane, it mixes with colored particles present in the nitrocellulose. Then, as the mixture of urine and color moves along the membrane, it comes in contact with a test line. This line contains antibodies for the hcG which, if they come into contact with the mixture, will trap particles in place, creating a colored line. When the liquid moves to the end of the membrane, the color solution is caught at a second test line. This line also contains an antibody, but this antibody will catch the color particles whether or not the solution contains hcG. This means that the second line will appear for both positive and negative results, but if both lines appear, the test is confirmed positive.

4. NANOTECHNOLOGY AND CHEMICAL SENSORS

Nanomaterials and nanotechnology are new fields of science and technology. Nanotechnology is still in its infancy, as it has become a hot area only a few years ago. However, nanotechnology is expected to dramatically change operating characteristics of chemical sensors and will probably gain in importance in all fields of sensor application over the next ten to twenty years. It has been found that with reduction in size, novel electrical, mechanical, chemical, catalytic and optical properties can be introduced. Besides it was established that 1-D structures can be ideal system for studying the nature of chemical sensing effects.

Nanotechnology enables us to create functional materials, devices, and systems by controlling matter at the atomic and molecular scales, and to exploit novel properties and phenomena. Consider that most chemical and biological sensors, as well as many physical sensors, depend on interactions occurring at these levels and you'll get an idea of the effect nanotechnology will have on the sensor world.

Nanotechnology can be used to fabricate sensors that detect very small amounts of chemical vapors. Various types of detecting elements, such as carbon nanotubes, zinc oxide nanowires or palladium nanoparticles have been already used in nanotechnology-based sensors. These detecting elements change their electrical characteristics, such as resistance or capacitance, when they absorb a gas molecule. Due to the small size of such nanotubes, nanowires, or nanoparticles, a few gas molecules are sufficient to change the electrical properties of the sensing elements. This allows the detection of a very low concentration of chemical vapors. The goal is to have small, inexpensive sensors that can sniff out chemicals just as dogs are used in airports to smell the vapors given off by explosives or drugs.

As a conclusion, nanosensors and nano-enabled sensors have applications in many industries, among them transportation, communications, building and facilities, medicine, safety, and national security, including both homeland defense and military operations. Consider nanowire sensors that detect chemicals and biologics, nanosensors placed in blood cells to detect early radiation damage in astronauts, and nanoshells that detect and destroy tumors. Many start-up companies are already at work developing these devices in an effort to get in at the beginning.

Chemical Sensors

We have looked at mechanical and electrical sensors; now we start a new section examining chemical sensors.

What is a chemical sensor?

A sensor sensitive to stimuli produced by chemical compounds


Car exhaust oxygen sensor

In general, the aim of a chemical sensor is t measure the concentration of a specific substance

Substances to be sensed fall into two major classes: liquids and gasses

An example of an important chemical sensor application is the use of oxygen sensors to measure concentration of oxygen in air, blood or car exhaust gases

Chemical Sensors

The most important property of a chemical sensor is *selectivity.*

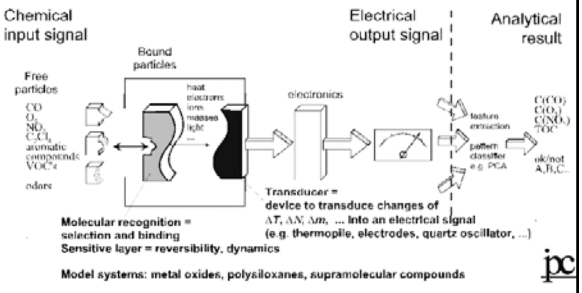
Selectivity is the ability to respond to only one chemical in the presence of other species.

Chemical sensors fall into several important catagories:

- Calorimetric sensors (measuring the heat evolved from a reaction, often using a catalyst)
- Electrochemical sensors (measure voltage, current or conductivity)
- Biological sensors (chemical sensors used for biological applications)

We shall address each of these in turn.

Chemical sensor systems



- www.ipc.uni-tuebingen.de/weimar/pictures/chem_sensor.gif

Calorimetric Chemical Sensors

Heat is liberated by many chemical reactions, called exothermic reactions.

The detection of heightened heat production is often used to sense the existence of a particular chemical.

This accomplished through *calorimetry,* which is the measurement of heat production via a temperature change in a thermally isolated environment.

Calorimetric Chemical Sensors

When the internal energy of the system changes (chemical reaction) it is accompanied by the absorption or evolution of heat.

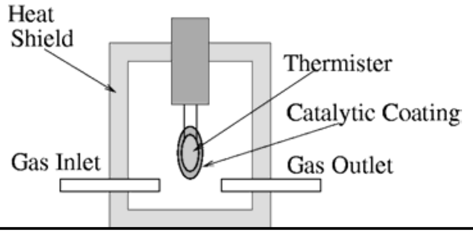
Consequently, a chemical can be detected by sensing the heat evolved from a specific reaction.

Calorimetric Chemical Sensors

A temperature probe is coated with a chemical selective layer.

Upon introduction of a sample, the probe measures the release of heat

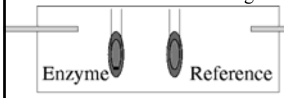
This heat is converted to a temperature change via calorimetry.



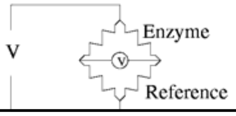
Example: detecting Glucose

Consider an enzyme coated thermistor using an immobilised oxide

The enzymes are in the tip of the thermistor, which is in turn enclosed in a glass jacket to reduce heat loss.



A similar sensor but without the Enzyme loading is placed as reference.



Sensors are placed in a Whetstone bridge (which is a sensitive measure of resistance changes)

The temperature increases by dT as a result of a chemical reaction proportional to the change in enthalpy dH

$$dT = -dH/C_p$$

Where C_p = heat capacity

dH is specific to the chemical reaction, in this case:

$$\beta\text{ - D-glucose} + H_20 + O_2 \rightarrow H_2O_2\text{+d-glucinic acid} \quad \Delta H_1$$

$$H_2O_2 \rightarrow 1/2\ O_2 + H_2O \quad \Delta H2$$

Where ΔH_1 and ΔH_2 are the partial enthalpies ($dH=\Delta H_1+ \Delta H_2$)

The sensor response is linearly dependant on the glucose concentration

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Foil and slug calorimeters

Slug calorimeter measures the temperature rise in a slug of known thermal capacity

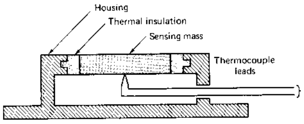


Figure 4-40. Slug calorimeter.

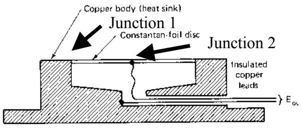


Figure 4-39. Foil calorimeter.

- Foil calorimeter uses two thermocouple junctions to measure heat absorbed by the foil in a differential measurement
- Millivolt output is proportional to heat flux

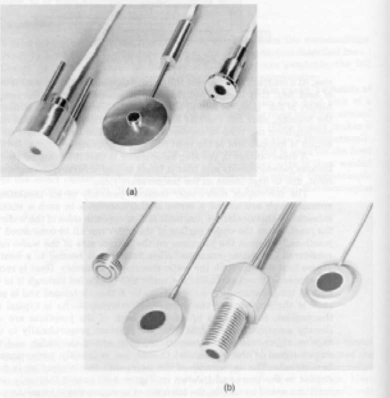
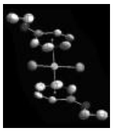


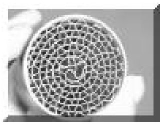
Figure 4-41. Typical calorimeter designs: (a) foil calorimeters; (b) slug calorimeters. (Courtesy of Hy-Cal Engineering, a Subsidiary of Leeds & Northrup.)

Photos of foil and slug calorimeters

Catalytic Sensors



A catalyst can be a molecule



A catalyst is often coated over a large surface area

A catalyst is a chemical or substance that increases the rate of a reaction without being itself consumed.

Heat is liberated as a result of a catalysed reaction

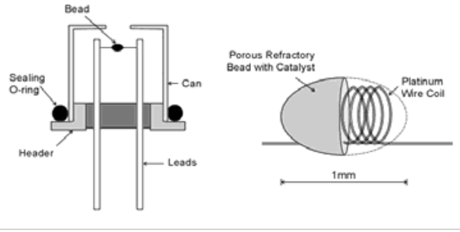
The temperature related to the chemical reaction is measured, using a calorimeter

Catalytic sensors are widely used to detect to detect low concentrations of flammable ages

Catalytic sensors are also called pellistors.

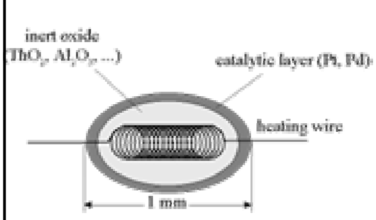
Pellistors

- Pellistors are used to detect the presence of flammable gases
- Any combustible gases present will oxidise on the catalyst bead, raising the temperature of the coil
- The change in resistance is detected by comparing with an uncatalysed reference sensor



- http://www.citytech.com/technology/pellistors.asp

Pellistors



The platinum coil is embedded in a ceramic pellet coated with a porous catalytic metal (palladium or platinum)

This coil acts as both the heater and temperature sensor (like in the Mass Flow Controller)

When the combustible gas reacts at the catalytic surface, the heat evolved increases the temperature inside the thermal shield

This is raises the temperature of the platinum coil and thus its resistance

---

Pellistor operating Modes.

Pellistors have two operating modes:

- Isothermal, where an electronic circuit controls the current in the coil required to maintain constant temperature.
- Non-isothermal, where the sensor is connected as part of a wheatstone bridge whose output voltage is a measure of the gas concentration

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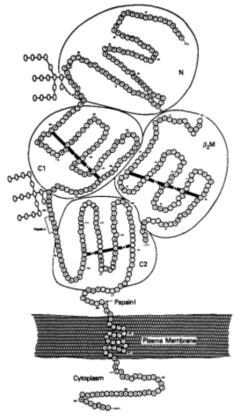


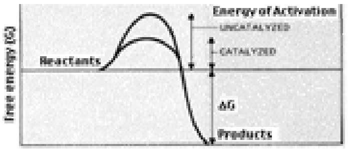
Enzymes

Enzymes are essentially biological catalysts: proteins of high molecular weight found in living organisms

Enzymes operate only in an aqueous environment.

An example of a protein: beta-2 microglobulin

Enzyme Sensors



http://users.rcn.com/jkimball.ma.ultranet/BiologyPages/E/Enzymes.html

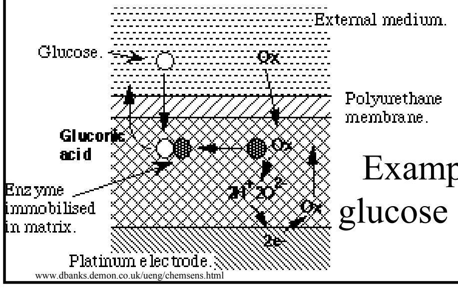
Enzymes are extremely effective at increasing the reaction rate.

Maximum reaction rate is proportional to enzyme concentration.

The best thing about enzyme sensors is that they are *extremely* selective, ensuring that only exactly the desired reaction occurs.

Enzyme sensors can be used in several ways:
- Detect heat liberated by exothermic reactions
- Detect electrons liberated by redox reactions
- Detect light produced by luminescent reactions

- This can be applied to the glucose reaction described earlier: glucose is oxidised to gluonic acid by the enxyme glucose oxidase.
- This and subsequent redox reactions drive a current through an external circuit proportional to the amount of glucose present.

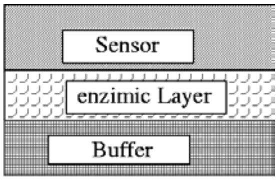


Example: a glucose sensor

www.dbanks.demon.co.uk/ueng/chemsens.html

Mounting enzyme Sensors

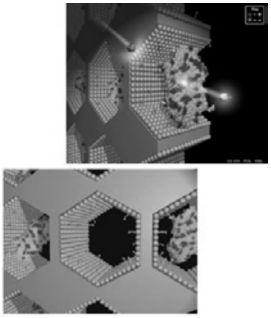
Enzymes can be incorporated into immobilization matrices (for example, gels).



The reagent diffuses into this gel where upon the enzyme catalyzes a reaction.

The products and other species involved must diffuse into and out of the layer.

Mounting enzyme Sensors



In this application, a sensor is made from mounting the enzyme in a porous silica matrix for greater sensitivity

- http://www.technet.pnl.gov/sensors/biological/projects/images/biological288.jpg

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Electrochemical Sensors

Electrochemical sensors are the most versatile and highly developed chemical sensors.

They are divided into several types:

- Potentiometric (measure voltage)
- Amperometric (measure current)
- Conductometric (measure conductivity)

In all these sensors, special electrodes are used.

Electrochemical Sensors

Either a chemical reaction takes place or the charge transport is modulated by the reaction

Electrochemical sensing always requires a closed circuit. Current must flow to make a measurement.

Since we need a closed loop we need at least two electrodes.

These sensors are often called an electrochemical cell.

How the cell is used depends heavily on the sensitivity, selectivity and accuracy.

Potentiometric Sensors

Potentiometric sensors use the effect of the concentration on the equilibrium of redox reactions occurring at the electrode-electrolyte interface of an electrochemical cell

www.chemie.uni-greifswald.de/

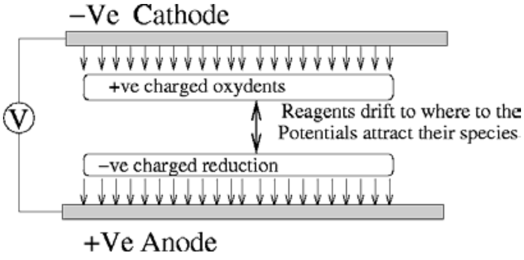
The redox reaction takes on the electrode surface:

Oxidant + Ze$^-$ => *Reduced product*

Z is the number of electrons involved in the redox reaction

Electrochemical Cell

The reaction takes place at the cathode where electrons are "pulled" out of the electrode.



The Nernst Equation

The Nernst equation gives the potential of each half cell:

$$E = E_0 + \frac{RT}{nF}\log_e\left(\frac{C_0}{C_R}\right)$$

In a potentiometric sensor, two half-cell reactions take place at each electrode. Only one of the reactions should involve sensing the species of interest. The other should be a well understood reversible and non-interfering reaction

- Co is the oxidant concentration
- C_R is the Reduced Product Concentration
- n is the number of electrons
- F is the Faraday constant
- T is the temperature
- R is the gas Constant
- E_0 is the electrode potential at a standard state.

CHEMFET Sensors

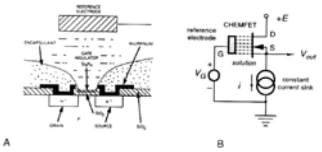
Chemical potentiometric sensors based on the Field-Effect transistors

Very popular where small size and low power consumption is essential. (Biological and Medical monitoring).

CHEMFETs are solid state sensors suitable for batch fabrication.

The surface field effect can provide high selectivity and sensitivity.

These are extended gate field-effect transistor with the electrochemical potential inserted over the gate surface.



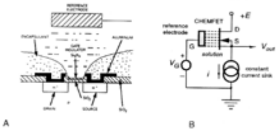
Four types of CHEMFETs

Ion Selective, gas selective, enzyme-selective and immuno-selective sensors.

A lot of the art of CHEMFETs is the nature of the porous layer over the gate.

Ion selective CHEMFET with a silicon nitride gate for measuring PH (H+ ion concentration.)

The sensor is given a PH sensitivity by exposing the bare silicon nitride gate insular to the sample solution.



As the ionic concentration varies, the surface charge density at the CHEMFET gate changes as well.

Ionic selectivity is determined by the surface complexation of the gate insulator. Selectivity of the sensor can be obtained by varying the composition of the gate insulator.

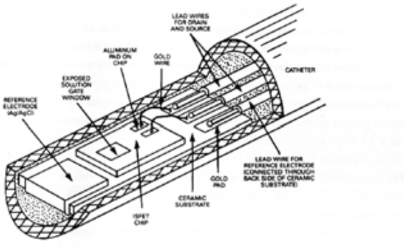
Also add ion-selective membranes can be deposited on the top of of the gate to provide a large selection of different chemical sensors.

A change in the surface charge density affects the CHEMFET channel conductance, which can be measured as a variation in the drain current.

Thus a bias applied to to the drain and source of the FET results in a current I, controlled by the electrochemical potential.

This in turn is proportional to the concentration of the interesting ions in solution.

A biosensor sensitive to a particular protein or virus can be made by coating the electrode with the appropriate antibody.



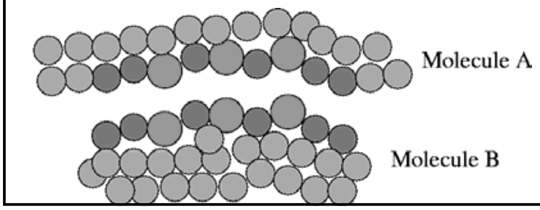
Extreme care must be taken to electrically isolate the signals from the solution!

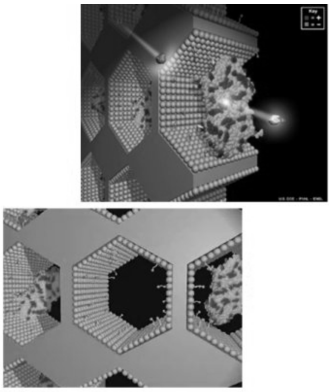
Biosensors

Much better sensitivity and selectivity than traditional chemical sensors

Detect whole organisms, tissues, cells, organelles, membranes, enzymes, receptors, antibodies and nucleic acids.

Selectivity is achieved by shape recognition at the molecular level





Biological sensors- enzymes embedded in a porous silica matrix for increased sensitivity

- http://www.technet.pnl.gov/sensors/biological/projects/images/biological288.jpg

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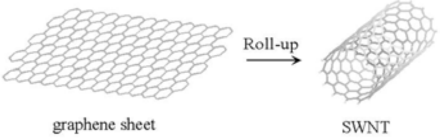
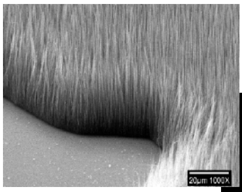
Carbon nanotubes

- Sheets of carbon atoms can be 'rolled' up into tubes of nanometer dimensions
- Layers of nanotubes have a huge surface to volume ratio



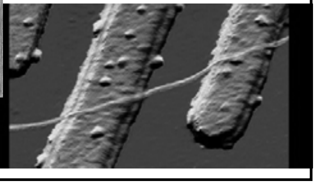
Carbon nanotubes

- Carbon nanotubes can be grown *en masse*, or separated as individuals.



Nanotube forest

Nanotube (blue) lying across electrodes



Carbon Nanotube sensors

The Scanning Electron Micrograph shows a bridge made from a single nanotube.
It is linking two 'cliffs' made of Au and Ti.
N_2 gas is blown up from the bottom

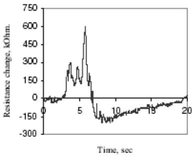
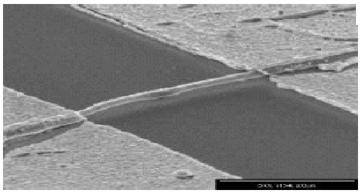


Fig.9 Resistance change(? R) due to N_2 flow



The resistance of the sensor increases upon exposure to N_2 gas

www.bios.el.utwente.nl/internal/Transducers03/Volume_1/2E80.P.pdf

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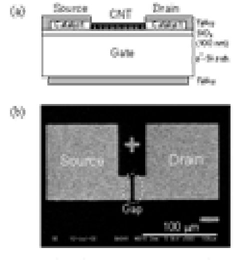
CNT FET sensor



Can also make FET sensors out of carbon nanotubes

A small current in the nanotube causes a much larger current in the FET

This particular sensor responds to light.

Fig. 1 (a) Schematic cross-section of CNT FET and (b) SEM image of patterned catalysts.

www.echo.nuee.nagoya-u.ac.jp/~yohno/research/cnt/qnn03_abstract_submitted.htm

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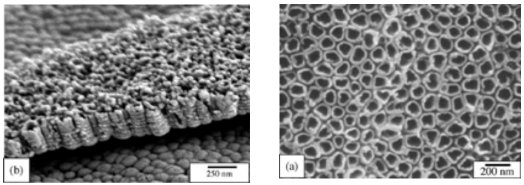
Titanium nanotube sensors

- H_2 gas is ionised when it hits the walls of the titanium nanotubes
- The resulting electron current is a measure of the amount of hydrogen present.



www.eurekalert.org/pub_releases/2003-07/ps-tnm072903.php

Selectivity in Biological sensors

In biological systems selectivity is achieved through shape recognition. (Lock and key metaphor.)

Commonly achieved by increasing the activity of a chemical process

An absolutely sensitive sensor does not exist.

There is always some interference from other species.

Drugs for biological activity exploit this.