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CHM 111



Introduction to Inorganic Chemistry Module 2

CHM III Introductory Inorganic Chemistry Module 2

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Module 2

Unit 1 Electron Affinity

1.0 Introduction

You will recall that in the last unit (Unit 5) of Module 1, you studied the process of removal of electron from a neutral atom. You learnt that the energy required to remove an electron from an isolated neutral atom in gaseous state is known as the ionisation energy. In this unit, you will study the process of addition of an electron to the gaseous atom in its ground state. In effect, what you are going to learn about is the reverse of the process of ionisation which we studied earlier on. We shall be talking about electron affinity.

2.0 Objectives

At the end of this unit, you should be able to:

- define electron affinity
- list the three factors affecting electron affinity
- discuss how electron affinity varies across periods and groups.

3.0 Main Content

3.1 Electron Affinity

Electron affinity of an atom is a measure of its ability to accept an electron to form an anion. **It is defined as the energy released or absorbed when an electron is added to the gaseous atom in its ground state.** It can be represented by the following equation in which EA represents electron affinity of X.



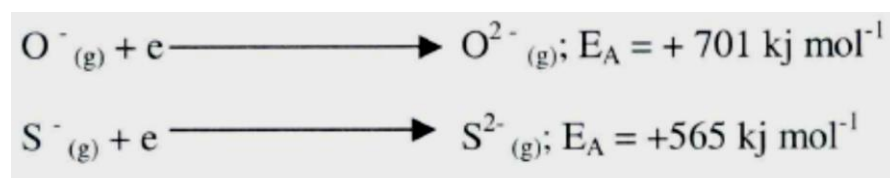
When one mole of chlorine atom accepts one mole of electron, 348 kilojoules of energy is released. So the electron affinity of chlorine is -348 KJmol^{-1} .

In the reverse process of removal of an electron from the chloride ion to form a chloric atom, obviously an equal amount of energy has to be supplied. So, the electron affinity can also be expressed as the ionisation energy of the anion. Thus, the electron affinity of chlorine atom is clearly the ionisation energy of the chloride ion. Electron affinities are difficult to measure because the accurate values for all elements are not available. Values for some elements are given in Table 1.1

You learnt in the preceding unit that energy is required to overcome the attractive force of the nucleus before an electron is removed from an isolated neutral atom in a gaseous state. It follows therefore that the reverse process of the addition of an electron to the neutral atom should release energy. Thus, the electron affinities of most elements are negative.

However, a few elements are known to have positive values for electron affinity which means that the electron must be forced onto the neutral atom to form an anion. For example, nitrogen, alkaline earth metals and noble gases have positive values. All second and higher electron affinities also have large positive values.

This is not surprising, since the second and the subsequent electrons must be forced on against the negative charge of the anion. For example:



Note that as it is conventionally acknowledged, a negative value means an exothermic process. That is the reaction $\text{X}(\text{g}) + \text{e}^- \longrightarrow \text{X}^-(\text{g})$ is exothermic \implies

Also by high electron affinity, it is meant that the electron affinity is large and negative.

Table 1.1: Electron Affinities of some elements in KJmol^{-1}

1	2	13	14	15	16	17	18
H -73							
Li -60	Be +100	B -27	C -122	N +9	O -141	F -328	He +54
Na -53	Mg +30	Al -44	Si -134	P -72	S -200	Cl -348	Ne +99
K -48	Ca -	Ga -30	Ge -120	As -77	Se -195	Br -325	
Rb -47	Sr -	In -30	Sn -121	Sb -101	Te -190	I -295	
Cs -45	Ba -	Tl -30	Pb -110	Bi -110	Po -183	At -270	

3.2 Factors Affecting Electron Affinity

Factors affecting electron affinities are generally the same with those affecting ionisation energies. These factors are:

Atomic Radius: When an electron adds on to any atom, the nucleus of the atom holds it by an electrostatic force of attraction which depends upon the effective nuclear charge and size of the atom. The smaller the size of the atom, the greater will be the force of attraction of the nucleus for the extra action added. Therefore the higher will be the electron affinity of the atom thus; more energy will be released in picking up an electron.

Effective Nuclear Charge: The higher the effective nuclear charge, the greater the force of attraction exerted by the nucleus on the added electron and hence, higher will be the electron affinity of the atom.

Electronic Configuration: Electronic configuration of the atom also plays an important role in determining the magnitude and sign of electron affinity. Halogens can achieve a stable noble gas configuration by accepting just one electron. Therefore, they have large negative

(exothermic) electron affinities. On the other hand the noble gases with closed shell ns^2np^6 configuration, beryllium and magnesium with np^2 (stable due to filled sub shell) and nitrogen having $np^2 np^3$ (stable due to half-filled p sub shell) configurations strongly resist the addition of any electron. Therefore, the electron affinities of these elements are either zero or have small positive values.

3.3 Periodicity in Electron Affinity

We have so far defined electron affinity and considered the factors that affect it. In this sub section, we will discuss how the electron affinity varies in the provided descriptions.

Trends across periods:

On moving from left to right in a period, the size of an atom decreases and effective nuclear charge increases. Both these factors favour an increase in the force of attraction exerted by the nucleus on the extra electron. Consequently, the electron affinity generally increases across a period though irregularly. Thus electron affinities of alkaline metals have small negative values indicating their reluctance to form an anion. On the other hand, electron affinities of halogens in a period have the highest negative values which reflect their ability to form anions most readily. As explained earlier, the electron affinities of noble gases, beryllium, magnesium and nitrogen have small positive values.

Trend across groups:

We know from the previous section that on moving down the group of s- and p- block elements in the periodic table, the effective nuclear charge remains almost steady, but there is a general increase in atomic radius due to increase in the value of the principal quantum number n .

As a result, the electron affinity generally decreases down any group in the periodic table. This is evident from the values given listed in Table 1.1 values of electron affinities of second row non-metals that is B, C, N, O, F are however against the general trend, being smaller than those of corresponding elements that is Al, Si, P, S, Cl of Period 3. This is apparently an indirect result of the small size of the atoms of these elements that is B, C, N, O, F. Thus, the crowding of electrons in the smaller outer shell of an atom of an element of Period 2 makes mutual repulsion of electrons substantially greater than that in the relatively larger outer shell of an atom of an element of Period 3.

Therefore even though an electron added to an atom of an element of Period 2 is closer to the nucleus than one added to an atom of an element of Period 3, the greater inter electronic repulsion in a smaller shell leads to a lower electron affinity.

4.0 Conclusion

In conclusion, we can say the electron affinity of an element determines how easy or difficult it is for that element to participate in a chemical reaction.

5.0 Summary

In this unit, you have studied the following:

- that the electron affinity of an element is the energy released or absorbed when an electron is added to a gaseous atom in its ground state

- that it is affected by three factors viz: atomic radius, effective nuclear charge and electronic configuration
- that the electron affinity varies across periods and groups in the periodic table.

Self-Assessment Exercise

- i. List three factors that affect electron affinity?
- ii. Why does the electrons affinity generally decreased down a group.

6.0 Self-Assessment Exercise

1. Explain why the second electron affinity values are always positive.
2. Explain the difference between electron affinity and electro-negativity.

7.0 References/Further Reading

Cotton & Wilkinson (n. d.). *Basic Inorganic Chemistry*. John Wiley and Sons.

Wilson, J. G. & Newell, A. B. (n. d.). *General and Inorganic Chemistry*. Cambridge: Cambridge University Press.

Unit 2 Electronegativity

1.0 Introduction

Earlier, you studied ionisation energies and electron affinities of isolated gaseous atoms. These quantities are a measure of the tendency of isolated atoms to lose or gain electrons. In this unit, you are going to learn about electronegativity of an element. The electronegativity of an element is a measure of the power of an atom in a molecule to attract shared electrons to itself. Unlike ionisation and electron affinity, it is not a directly measurable physical quantity but rather, a theoretical concept for which several numerical scales have been developed.

In this unit, the three most important scales that have been developed for measuring electro-negativity are going to be discussed.

2.0 Objectives

At the end of this unit, you should be able to:

- define the concept of electronegativity
- calculate, given all the necessary impact, the electronegativity of an element, using Pauling, Mulliken-Taffe and Alfred-Rochow electro negativity scales
- discuss with at least eighty per cent accuracy periodicity in electro negativity.

3.0 Main Content

3.1 Pauling Electronegativity Scale

As you know in homonuclear diatomic molecule like A_2 (A-A) and B_2 , (B-B) the electron pair is equally shared between the atoms bonded together. In a heteronuclear diatomic molecule of the AB type however, the situation is quite different. In the process of formation of a bond between A and B. Atom A slowly start stripping off its electrons thereby becoming a partially cationic species (it becomes partially positively charge). As the positively develops on A, its tendency to attract electron increases.

Meanwhile, a similar process also takes place on atom B, thus both atoms A and B start attracting the electron pair towards themselves. They continue doing so until the tendencies of both the atoms in the bonded state to attract the electron pair towards themselves balance.

If one of the atoms say B, has higher tendency to attract the electron pair toward itself compared to that the other atom say A, the electron pair will spend more time on B than A. Partial charges will thus be generated on A and B. This tendency of attracting the shared electron pair toward itself by an atom a molecule has been termed the electro negativity of the element

The concept of electro negativity was first developed by Pauling. He defined it on the basis of the patterns desirable in the single bond energies of elements which were derived from

the thermo chemical data. He realized that bond energy, E_{A-B} between two unlike ion like atom A and B is greater than $\sqrt{E_{A-A} E_{B-B}}$ where E_{A-A} and E_{B-B} are bond energies of A-A and B-B homonuclear bonds. He assigned the course of this excess bond energy $E_{A-B} - \sqrt{E_{A-A} E_{B-B}}$ to the electrostatic attraction between partially charged atoms are separated due to difference in electron attracting tendencies of A & B that is the difference in the electro negativity of A and B. He was able to derive a relationship which can be stated as:

$$\Delta X_{A-B} = \frac{\sqrt{E_{A-B} - \sqrt{E_{A-A} E_{B-B}}}}{96.49}$$

Where X_A is the electro negativity of element A and X_B is that of element B.

Knowing bond energies, it is possible to calculate the difference between the electro negativities of the two elements. This formula only gives the difference in the electro negativities of the two elements and not the absolute value assigned to a particular element. The largest electro negativity difference is that between fluorine the most electronegative element and calcium, the most electropositive element that came out to be 3.3. Pauling assigned arbitrarily a whole number value 4.0 for fluorine so that values of electro negativity of all elements remain positive. Table 2.1 shows values of electronegativity of different elements (bold faced) as calculated by Pauling using his Formulae.

3.2 Mulliken — Jaffe Electronegativity Scale

Mulliken defined electronegativity as the mean value of first ionisation energy and first electron affinity. Both quantities are given positive values if loss of electron involves absorption of energy and negative values if gain of electron involves release of energy. Thus electronegativity X_A of atom A is given by the following relationship.

$$X_A = \frac{(I)_A + (E_A)_A}{2}$$

According to this relationship, a very electronegative element has very high ionisation energy. So it will be difficult to remove its electrons. It also has a very high electron affinity. Hence, a very stable species results when electrons are added. On the other hand, an element of low electro negativity will have a low ionisation energy and low electron affinity. So it loses an electrons readily and has little tendency to pick up electron.

It is very difficult to measure electron affinity for all elements (as we learned in Unit I). Therefore this method is not universally applicable. The electro negativity values on Mulliken Scale are about 2.8 times those of Pauling's values. The trends in the variation of electronegativity are however the same.

3.3 Alfred—Rochow Electronegativity Scale

According to Alfred Rochow, electronegativity is equated to the force of attraction between an atom and the electron separated by a distance equal to the covalent radius of the atom. The force of attraction is expressed according to coulomb's law as:

$$F = \frac{Z^* e^2}{r^2}$$

Where Z^* is Slater's effective nuclear charge e the electronic charge and r - the covalent radius.

Table 2.1 Electronegativity Values of Element

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IA	IIA	IIIB	IVB	VB	VIB	VII B	VIII B			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
H 2.1 2.1	<div>← Pauling Scale</div> <div>← Allred - Rochow Scale</div>																He
Li 1.0 1.15	Be 1.5 1.50											B 2.0 2.0	C 2.5 2.5	N 3.0 3.05	O 3.5 3.5	F 4.0 4.1	Ne
Na 0.9 1.0	Mg 1.2 1.25											Al 1.5 1.45	Si 1.8 1.74	P 2.1 2.05	S 2.5 2.45	Cl 3.0 2.85	Ar
K 0.8 0.9	Ca 1.0 1.05	Sc 1.3 1.2	Ti 1.5 1.3	V 1.6 1.45	Cr 1.4 1.55	Mn 1.5 1.6	Fe 1.5 1.65	Co 1.8 1.7	Ni 1.8 1.75	Cu 1.9 1.75	Zn 1.6 1.65	Ga 1.6 1.8	Ge 1.8 2.0	As 2.0 2.2	Se 2.4 2.5	Br 2.8 2.75	Kr
Rb 0.8 0.9	Sr 1.0 1.0	Y 1.2 1.1	Zr 1.4 1.2	Nb 1.6 1.25	Mo 1.8 1.3	Tc 1.9 1.35	Ru 2.2 1.4	Rh 2.2 1.45	Pd 2.2 1.35	Ag 1.9 1.4	Cd 1.7 1.46	In 1.7 1.5	Sn 1.8 1.7	Sb 1.9 1.8	Te 2.1 2.0	I 2.5 2.2	Xe
Cs 0.7 0.85	Ba 0.9 0.95	La 1.1 1.1	Hf 1.3 1.25	Ta 1.5 1.35	W 1.7 1.4	Re 1.9 1.45	Os 2.2 1.5	Ir 2.2 1.55	Pt 2.2 1.45	Au 2.4 1.4	Hg 1.9 1.45	Tl 1.8 1.45	Pb 1.8 1.55	Bi 1.9 1.65	Po 2.0 1.75	At 2.2 1.90	Rn
Fr 0.7	Ra 0.9	Ac 1.1	Unq	Unp	Unh	Uns	Uno	Une									
Ce 1.1 1.82	Pr 1.1 1.82	Nd 1.2 1.82	Pm — —	Sm 1.2 —	Eu — 2.04	Gd 1.1 1.79	Tb 1.2 1.77	Dy — 1.77	Ho 1.2 1.76	Er 1.2 1.75	Tm 1.2 1.74	Yb 1.1 1.93	Lu 1.2 1.74				
Th 1.3 1.80	Pa 1.5	U 1.7 1.4	Np 1.3 —	Pu 1.3 —	Am 1.3 —	Cm 1.3 —	Bk 1.3 —	Cf 1.3 —	Es 1.3 —	Fm 1.3 —	Md 1.3 —	No 1.3 —	Lr — —				

Electronegativity is a measure of the attraction that an atom has for electrons in a bond it has formed with another atom. The ability of an atom to attract electrons depends upon the charge on the atom and the hybridisation of the atom. An atom which has acquired a positive charge will tend to attract electrons to it more readily than will a neutral atom. In turn, a negatively charged atom will be less attractive to electron than a neutral atom.

Hybridisation also affects electronegativity because of lower energy and hence, greater electron attracting power of s-orbital. Thus hybrid orbitals having greater s-character possess higher electronegativity. An atom in sp hybridised state will be more electronegative than the same atom in sp^2 hybridised state which will in turn be more electronegative than the same atom in sp^3 hybridised state. Thus the carbon atom in CH_4 , C_2H_4 and C_2H_2 has different values of electronegativity.

So you can say that electronegativity is not a constant quantity. All the electronegativity scales give only average values of electronegativity of element in different bonding environments.

All the electronegativity scales we studied give only relative values of electronegativities. These values are nevertheless useful in making quantitative comparisons between elements. Electronegativities can be used to predict the value of the bonding that a compound will have. The larger the difference between the electronegativities of the two elements, the more polar will be the bond between these elements. An electronegativity difference of about 1.7 corresponds to a partial ionic character of about 50%. So, a bond can be considered predominantly ionic, if the difference in the electronegativities of the bonded is more than 1.7. On the contrary, a difference in the range of 0.4 to 1.7 results in a covalent bond's partial ionic characters or polar covalent bond.

3.4 Periodicity in Electronegativity

Electronegativity values of elements show fairly discernible periodic trend throughout the periodic table. The trend is similar to that of ionisation energies. Thus, as expected, electronegativity of elements increases sharply across a row of S and P-block element. This is as a result of the sharp increase in effective nuclear charge of these elements example from lithium to fluorine. However, across a series of transition elements, the increase in electronegativity is much smaller. This is because the additional electron is being added to an inner shell which provides relatively good shielding for the outer electron from the nucleus. On moving down a group of representative elements, for example in the lithium group, there is a general decrease in electronegativity. The decrease is relatively small except between the first two elements.

The much greater electronegativity of lithium row elements correlates well with their small size. As expected, the elements of Period 4 from gallium onwards that is Ga, Ge, As, Se and Br have greater electronegativities than would be expected by extrapolation from values for the first two elements in the respective groups. This is due to the insertion of transition elements because of which the effective nuclear charge of these elements is greater than that, if the transition elements were not there. Similarly, the presence of the lanthanide elements is responsible for greater electronegativity of the elements of 5d series than would be expected by extrapolation from values of the elements of 3d and 4d series.

4.0 Conclusion

Let us conclude this unit by pointing out that, studies of ionisation energy and electron affinity show us the tendency of elements to loose or gain electron while going into a relationship. In this unit on the other hand, we studied the power of these elements while in a relationship with each other to attract to it the electrons in the bond between them.

5.0 Summary

In summary, you have learnt the following from this unit:

- electronegativity is the tendency of an atom to attract toward itself the shared electron pair of a bond in which it is involved
- electronegativity can be measured by using any of the three scale developed by either, Pauling, Mulliken or Alfred Rochow
- the measurements vary according to the method used in measuring it

- the values of electronegativity vary across periods and groups of the periodic table.

Self-Assessment Exercise

Name the least and most electronegativity elements in the periodic table.

6.0 Self-Assessment Exercise

Explain why the electro negativity values of noble gases are zero while those of halogens are the highest in each period.

7.0 References/Further Reading

Cotton & Wilkinson (n. d.). *Basic Inorganic Chemistry*. John Wiley and Sons.

Wilson, J. G. & Newell, A. B. (n. d.). *General and Inorganic Chemistry*. Cambridge: Cambridge University Press.

Unit 3 Hydrogen

1.0 Introduction

In the Units 1 and 2, you studied the development of the periodic table and periodicity in the properties of elements. I am sure that you noticed the fact that the very first element in the periodic table is hydrogen. The hydrogen atom consists of only one proton and one electron. In spite of that, hydrogen forms more compounds than any other element. In addition, it is the most abundant of all the elements in the universe (73.9% by weight). It is also the principal element in the solar atmosphere. However although hydrogen is very much in abundance (0.14% by weight) on earth, it exists only in the combined state.

Seeing how important hydrogen is and its peculiarity of being the first element in the periodic table, you will like to know more about hydrogen. In this unit, you will be studying some important aspects of the chemistry of hydrogen. You will also be studying its position in the periodic table, its isotopes and other forms.

2.0 Objectives

At the end of this unit, you should be able to:

- justify the position of hydrogen in the periodic table
- describe isotopes of hydrogen
- differentiate between Ortho and Para forms of hydrogen.

3.0 Main Content

3.1 Position of Hydrogen in the Periodic Table

The position of hydrogen in the periodic table is of particular interest. Hydrogen is the first element of the periodic table, with an electronic configuration of $1s^1$. This electronic configuration is similar to the outer electronic configuration of the alkali metals (ns^1). On the other hand, like halogens, it is one electron short of the corresponding inert gas helium ($1s^2$). Hydrogen, therefore show some properties similar to alkali metals, while some others are similar to those of the halogens.

Like alkali metals, hydrogen forms halides, oxides and sulphides. We have seen in Unit 5 of Module 1 that the alkali metals have tight tendency of losing their outer most electron to form m^{+ion} . Hydrogen also forms H^+ ion, but it does not do so, under normal conditions, because the ionisation energy of hydrogen (1312 kJ mol^{-1}) is much higher than that of the alkali metals, e.g. Li-520; Na-495; K kJ mol^{-1} .

With high ionisation energy, hydrogen resembles halogens. (Their first ionisation energies are fluorine (1618 kJ mol^{-1}) chlorine (1255 kJ mol^{-1}) bromine (1142 kJ mol^{-1}) and iodine (1007 kJ mol^{-1})). Due to its high ionisation energy, hydrogen forms large numbers of covalent compounds by sharing a pair of electrons. Hydrogen like halogens, forms a diatomic molecule by sharing a pair of electrons between the two atoms. By picking up an electron, hydrogen forms the hydride ion (H^-), just like the halogens form the halide ion (X^-).

). From the previous discussion, it is clear that hydrogen resembles both the alkali metals as well as the halogens. So hydrogen can be placed with either of them in the periodic table. However conventionally, it is kept along with the alkali metals in Group 1 in the periodic table.

3.2 Isotopes of Hydrogen

Atoms of an element which have the same atomic number but different mass number are called **Isotopes**. Hydrogen has three different isotopes having mass numbers 1, 2, and 3 called ordinary hydrogen or **Protium** ^1H , **deuterium** (D) or ^2H and **Tritium** (T) or ^3H respectively. These isotopes differ from one another in respect of the presence of neutrons. Ordinary hydrogen has no neutrons, deuterium has one and tritium has two neutrons in the nucleus (Figure 3.1)

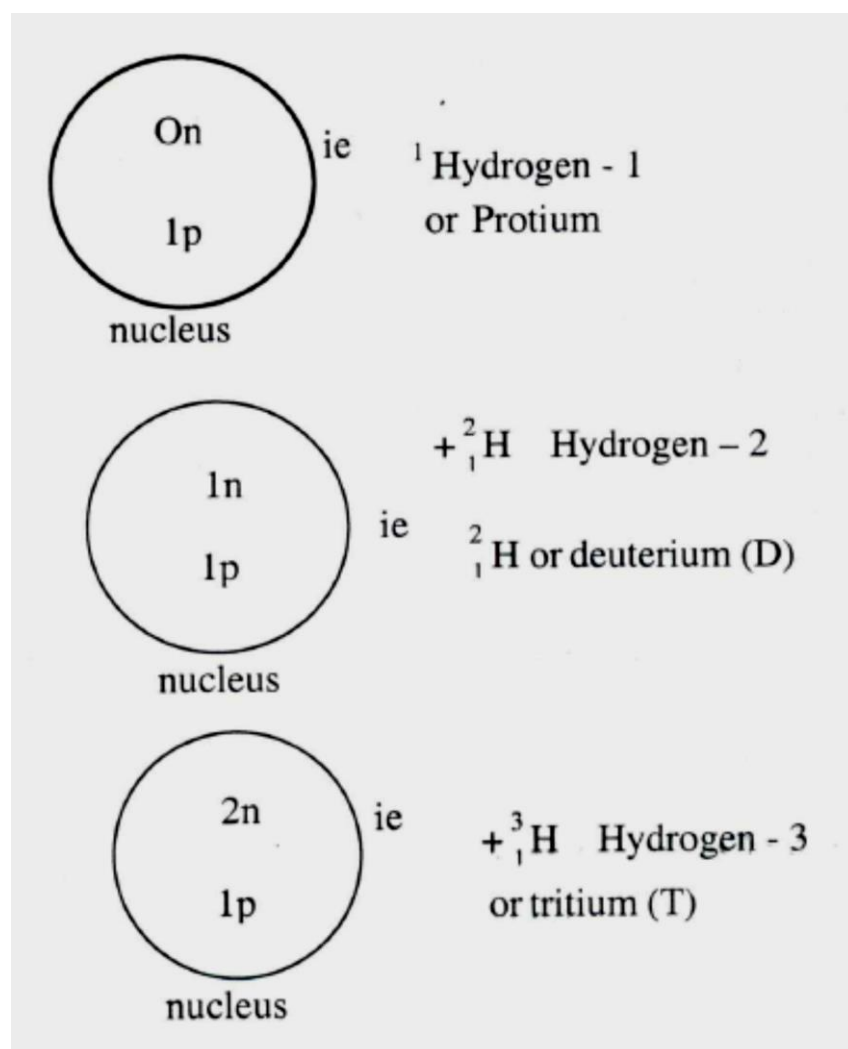


Fig. 3.1: Isotopes of Hydrogen

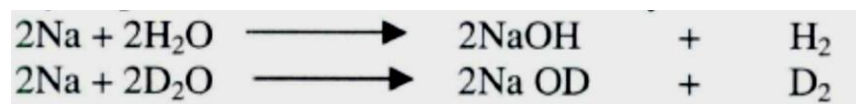
Deuterium is also called heavy hydrogen. These isotopes have the same electronic configuration and therefore their chemical properties are almost the same. The only difference is in the rate of reactions. For example, protium has a lower energy of activation than deuterium in its reaction with halogens and therefore, reacts faster.

The physical properties of hydrogen, deuterium and tritium differ considerably due to their large mass differences. You can study more on the important physical properties of hydrogen, deuterium and tritium.

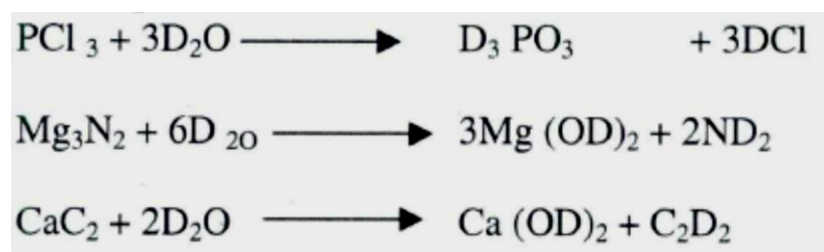
3.3 Deuterium Compounds

Naturally occurring hydrogen contains 0.0156% deuterium. Like water, (H_2O) which is the oxide of hydrogen, deuterium also forms an oxide, D_2O , which is known as **Heavy Water**. It can be obtained from ordinary water which contains 0.016% of deuterium oxide. This can be done either by fractional distillation or by electrolysis. Hydrogen is liberated more quickly than deuterium at the cathode and the residual liquid continuously gets richer in deuterium content on prolonged electrolysis of water. Deuterium oxide is used as a moderator in nuclear reactions since it slows down neutrons quickly. Physical properties of H_2O and D_2O and also differ from each other as in the case of H_2 and D_2 .

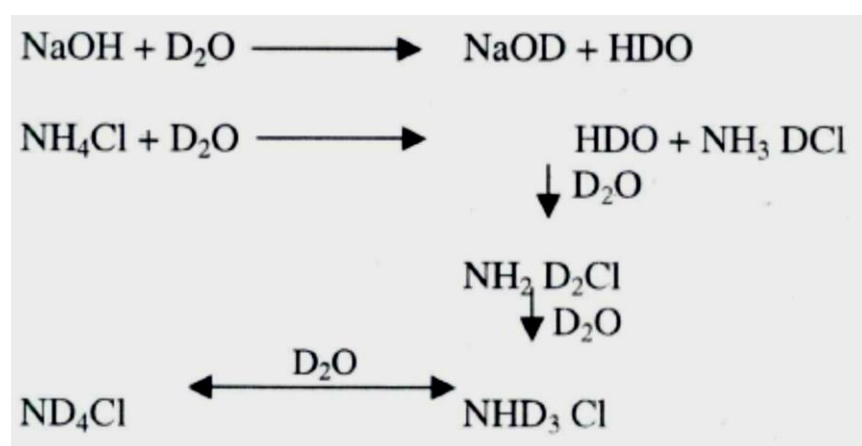
Hydrogen and deuterium are obtained by similar methods.



Many deuterium compounds, similar to those of hydrogen, are obtained from D_2O



We can also employ exchange reactions like those given below for the preparation of deuterium compounds:



3.4 Tritium

Tritium differs from the other two isotopes of hydrogen in being radioactive. Naturally occurring hydrogen contains nearly 10-15% tritium. The concentration of tritium increased

by over a hundred fold when thermonuclear weapon testing began in 1954 but is now subsiding again as a result of the ban on atmospheric weapon testing.

Tritium was first obtained synthetically by the bombardment of deuterium compounds such as $(\text{ND}_4)\text{SO}_4$ with fast deuterons.



It is now prepared on a large scale by irradiation of lithium-6 in the form of Li/Mg alloy of LiF with slow neutrons in a reactor.



The following reaction occurs in nature.



Tritium is radioactive and decays by emission of a beta — particle. Its half life period is 12.3 years



Tritium can be easily incorporated into biological molecules because it behaves chemically, just like ordinary hydrogen. The radiation tritium gives off within an organism as a result of its decay can cause many diseases including cancer.

3.5 Ortho and Para Hydrogen

Ortho and Para are two different forms of hydrogen molecule. These different forms arise as a result of differences in the direction of nuclear spin. When two hydrogen atoms combine to form a molecule, there are two possibilities. The two nuclei will either spin in the same direction (parallel spins) to give the form called **Ortho Hydrogen**, or they would spin in opposite directions to give **Para Hydrogen**. (Figure 3.2). This phenomenon is known as **Spin Isomerism**.

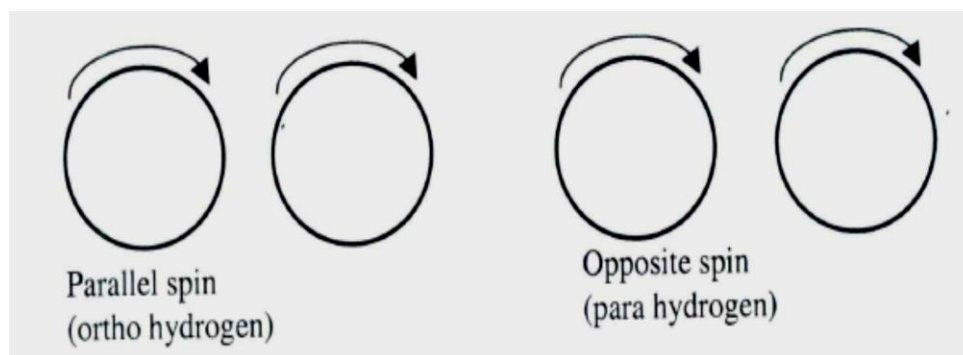


Fig. 3.2: Ortho and Para forms of Hydrogen

Due to spin isomerism, differences in the internal energy of the two forms of hydrogen arise, causing differences in the physical properties like boiling point, specific heat and thermal conductivity. Para hydrogen has a lower internal energy than that of ortho hydrogen. Hydrogen gas is an equilibrium mixture of Ortho and Para hydrogen. The ratio of Ortho to Para hydrogen varies with temperature as shown in Figure 3.3.

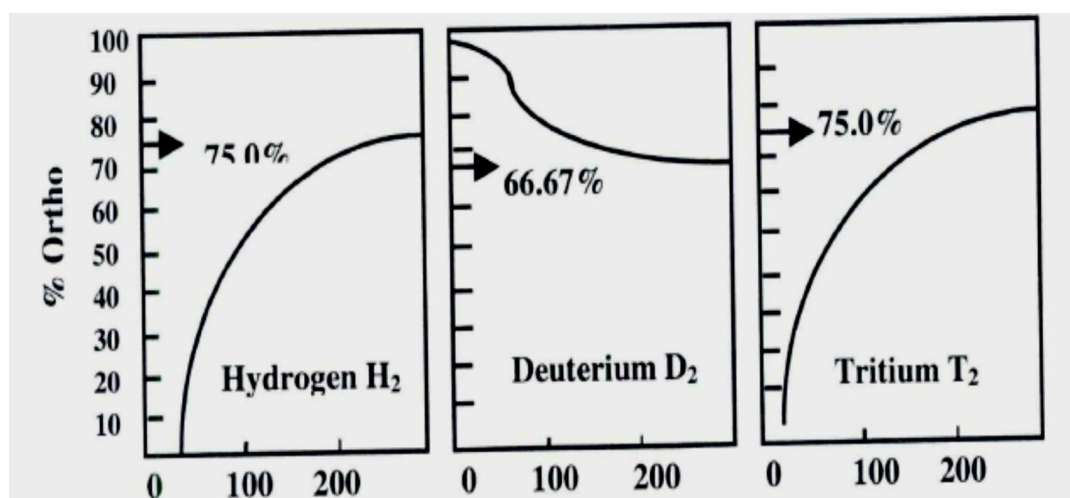


Fig. 3.3: Ortho-Para Equilibria for H₂, D₂ and T₂

Evidently, this ratio increases with the rise in temperature up to a temperature of about 300K (27°C) and remains constant thereafter. The percentage of hydrogen at 300K and above is 75%. This means it is not possible to get 100% ortho hydrogen at any temperature.

The equilibrium mixture of Para and Ortho hydrogen changes to almost 100% Para hydrogen when cooled to nearby absolute zero. Para hydrogen is stable for weeks in the absence of catalysts like activated charcoal, Fe, Ni Pt, O₂, NO₂ etc. these catalyse the conversion of Para to Ortho hydrogen, deuterium and tritium also exhibit spin isomerism and exist in Ortho and Para forms.

However the ratio of Ortho to Para forms in deuterium and tritium is different from that in hydrogen. The variation of Ortho/Para ratio at different temperatures is also different if you look carefully in Figure 3.3, you observe that tritium resembles hydrogen more closely than deuterium in this respect.

4.0 Conclusion

We can conclude this unit by observing that hydrogen holds a unique position in the periodic table. It is the first element in the periodic table and also exhibits properties of the alkali metals as well as that of the hydrogen. Hydrogen also exists in different forms thus explaining some of its properties.

5.0 Summary

In this unit, you studied the following:

- hydrogen with an electronic configuration of $1s^1$ occupies a unique position in the periodic table
- hydrogen has Isotopes known as deuterium tritium and the normal hydrogen we know
- the weights of these Isotopes are H = 1 Deuterium (**D**)2 and Tritium (T) 3
- hydrogen has in addition to H, D and T two other forms, Ortho and Para Hydrogen
- these two forms arise as a result of differences in spins of the two molecules that make up the H_2 molecule.

Self-Assessment Exercise

Write 'T' for true and 'F' for false in the given books for the following statements about Ortho and Para forms of hydrogen:

- Ortho and Para hydrogen are different due difference in their nuclear spins.
- Ortho and Para hydrogen are different due to difference in their electron spins.
- Physical properties Ortho and Para hydrogen are similar.
- Para hydrogen is more stable at lower temperatures.
- At look percentage of Ortho hydrogen in the mixture is 70%.

6.0 Self-Assessment Exercise

1. Why does hydrogen resemble alkali metals?
2. Explain the formation of hydride ion.
3. Why are the chemical properties of Isotopes similar?

7.0 References/Further Reading

Cotton & Wilkinson (n. d.). *Basic Inorganic Chemistry*. John Wiley and Sons.

Wilson, J. G. & Newell, A. B. (n. d.). *General and Inorganic Chemistry*. Cambridge: Cambridge University Press.

Unit 4 Manufacture of Hydrogen

1.0 Introduction

In the last unit (Unit 3), you studied the unique position of hydrogen in the periodic table, you also studied the various isotopes of hydrogen and also the two forms of the hydrogen molecule.

In this unit, you shall be studying the ways hydrogen is manufactured, its properties and uses.

2.0 Objectives

At the end of this unit you should be able to:

- list at least three methods used in the manufacture of hydrogen
- explain using appropriate equations and examples, what takes place during the process of the manufacture of hydrogen
- list and explain at least five properties of hydrogen
- list and explain with eighty percent degree of accuracy at least four uses of hydrogen.

3.0 Main Content

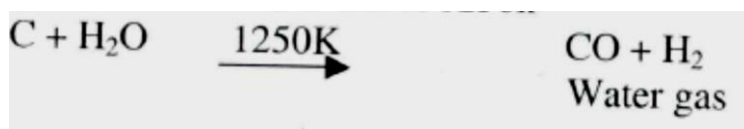
3.1 Manufacture of Hydrogen

Most if not all the methods used to manufacture hydrogen make use of water. Water is a natural abundant source for the manufacture of hydrogen. Water can be reduced to hydrogen either chemically or electrically.

(a) Manufacture by chemical means

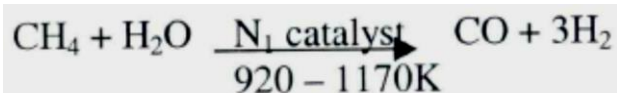
The common reducing agents are Coke, (obtained from the destructive distillation of coal), carbon monoxide or hydrocarbon.

- (i) The hydrogen is manufactured by allowing steam to react with red hot coke at about 1250K

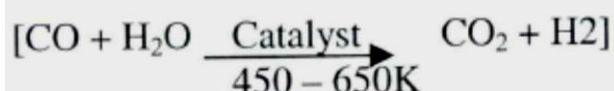


- (ii) The mixture of CO and H₂, known as **water gas**, is also called **synthesis gas** because it is used for the synthesis of methanol and other hydrocarbons.

- (iii) Hydrogen is also produced by the reaction of gas (chiefly methane) with steam in the presence of nickel catalyst.

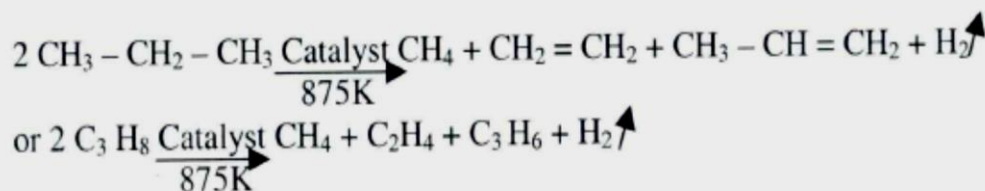


Similar reaction can occur with other hydrocarbons. In both cases above CO is converted to CO₂.



Hydrogen and carbon dioxide can easily be separated from each other by bubbling the gas mixture through water in which CO₂ is fairly soluble and H₂ is virtually insoluble.

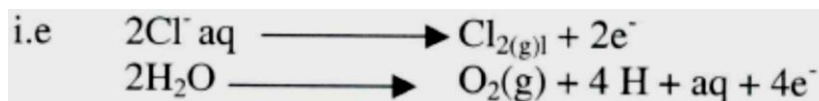
At higher temperatures, in the presence of catalysts (silica, alumina) hydrocarbon break up and rearrange in what are called cracking reactions. These reactions, which are used in refining of petroleum, produce hydrogen as a bi-product. One example of simple cracking reaction is cracking of propane.



(b) Manufacturing by Electrolysis

i. Electrolysis of acidified water using platinum electrodes is a convenient source of hydrogen (and oxygen). On a large scale, very pure hydrogen (>99.95%) can be obtained from the electrolysis of aqueous solution of barium hydroxide between nickel electrodes. Hydrogen obtained by electrolysis of water is relatively expensive because of the cost of electrical energy.

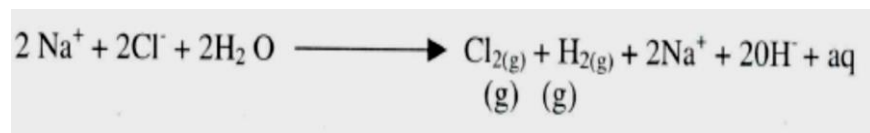
ii. Hydrogen can however be obtained economically as a bi-product in the electrolysis of brine during the manufacture of sodium hydroxide. During electrolysis, there is a competition at the anode between the oxidation of chloride ion and the oxidation of water.



When a concentrated salt solution (brine) is used, the first reaction preferentially takes place at the cathode, the reaction is the reduction of water because it is more easily reduced than Na⁺



The anode and the cathode reactions are combined to give the reactions thus:



In the laboratory hydrogen can be prepared by the reaction of water or dilute acids on electropositive metals such as alkali metals alkaline earth metals, the metals of group 12 (e.g. Zn) and the lanthanides. The reaction can be explosively violent with alkali metals (e.g. Rb) convenient laboratory methods employ sodium amalgam or calcium with water or zinc and tin with hydrochloric acid.

3.2 Properties of Hydrogen

(i) Hydrogen is the lightest element known. It is colourless, odourless and tasteless gas. The hydrogen molecule is

(ii) Thermally stable and has little tendency to dissociate at normal temperatures, the reaction $\text{H}_2(\text{g}) \rightleftharpoons 2\text{H}(\text{g}) = +436\text{kJ mol}^{-1}$ being an endothermic one. However, at high temperature in an electric or under ultraviolet light, H_2 does dissociate. The atomic hydrogen produced, exists for less than half a second after which it recombines to give molecular hydrogen and liberates a large amount of energy (436kJ mol^{-1}), in form of heat. Most of the transition metals catalyse the combination reaction of hydrogen.

(iii) Atomic hydrogen is a powerful reducing agent and reduces copper, silver and mercury salts to the metallic state of. e.g.



(iv) It combines with alkali metals to form hydrides



(v) It reduces sulphur to hydrogen sulphide



(vi) Carbon monoxide is reduced to formaldehyde.



(vii) It also reacts with oxygen at room temperature to form hydrogen peroxide.



(viii) H is used for welding.

Atomic hydrogen is produced by passing ordinary hydrogen through electric arc maintained between two electrodes. The atoms set free are carried away by a stream of incoming hydrogen gas. These free atoms recombine at once on coming in contact with a metallic surface liberating a large amount of heat and thus arising temperature of the metal to say 4000 — 5000K. This principle is utilised in the making of the 'atomic hydrogen welding torch' (Figure 4.1) It provides an opportunity of welding at a very high temperature but in a reducing atmosphere.

- (ix) Despite the fairly high bond dissociation energy of the hydrogen molecules it is moderately reactive and forms strong bonds with many other elements. It reacts with almost all elements except the noble gases.
- (x) Hydrogen reacts with alkali and alkali earth metals by accepting an electron to form ionic hydrides; e. KH, CaH₂
- (xi) With non-metals it forms covalent hydrides, e.g NH₃, H₂O and HF.

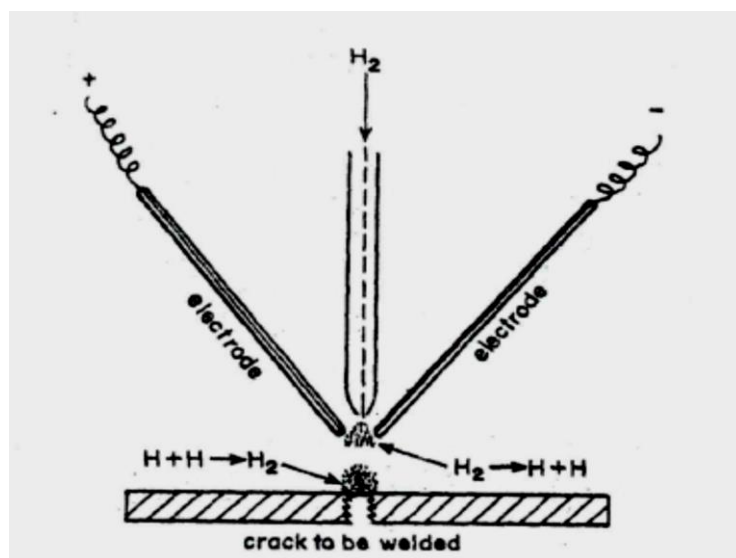
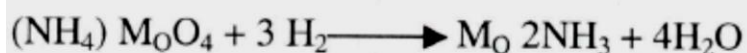
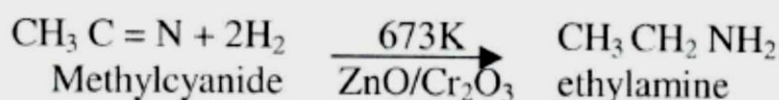
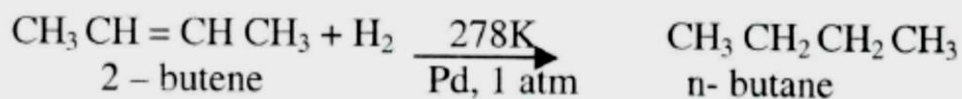


Fig. 4.1: Atomic Hydrogen Welding Torch

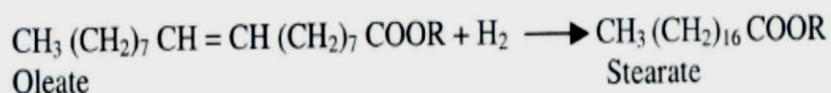
- (xii) Hydrogen is easily oxidised to water and; therefore it acts as a very good reducing agent in a variety of situations
- (xiii) Hydrogen is used in metallurgy to reduce metal oxides to metals in cases where carbon cannot be used because the metal can form carbide. Such metals include Mo and W.



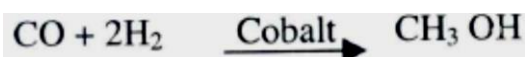
- (xiv) Hydrogen adds on the multiple bonds in organic compounds. In the presence of catalysts such as finely divided nickel, palladium or mixtures of metal oxides, unsaturated organic compounds are thus reduced to saturated compounds. For example:



(xv) Catalytic hydrogenation of unsaturated liquid vegetable oils to solid edible fats illustrates the industrial application of the reduction reactions; for example the reduction of an oleate (ester of oleic acid) to ester of stearic acid.



(xvi) Hydrogen reacts with carbon monoxide in the presence of catalysts to form methanol.



This reaction is known as hydro-formulation reaction and is used in the industrial preparation of methanol.

3.3 Uses of Hydrogen

Some of the uses of hydrogen include the following:

1. The largest single use of hydrogen is in the syntheses of ammonia which is used in the manufacture of nitric acid and nitrogenous fertilizers.
2. Hydrogen is used in the hydrogenation of vegetable oils and the manufacture of methanol.
3. In space crafts, hydrogen gas is used in fuel cells (fig 3.2) for generating electrical energy and for providing clean drinking water to the astronauts. In a fuel cell, electrical energy is generated by the reaction of hydrogen and oxygen. This is sometimes called "**cold combustion**". A hydrogen oxygen fuel cell may be having an alkaline or acidic electrolyte.

The one in Figure 4.2 has porous carbon electrodes and KOH as electrolyte.

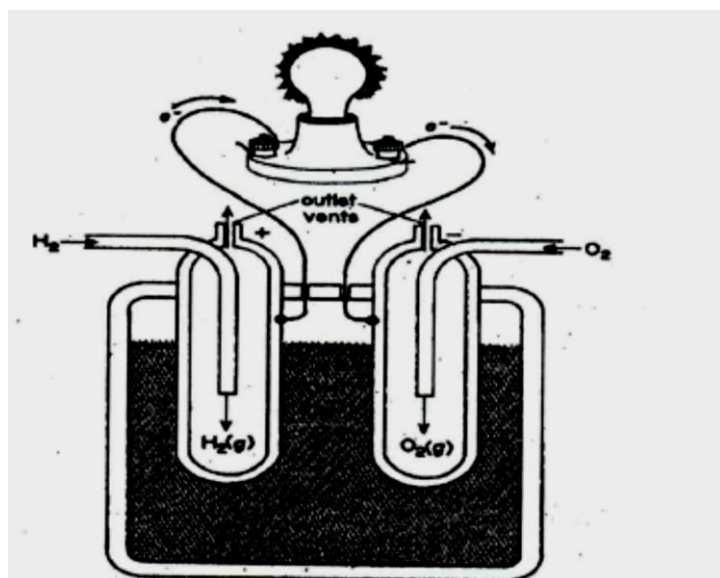
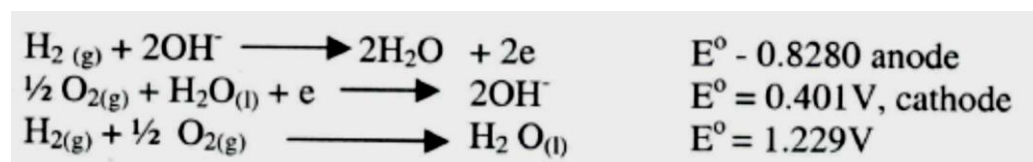
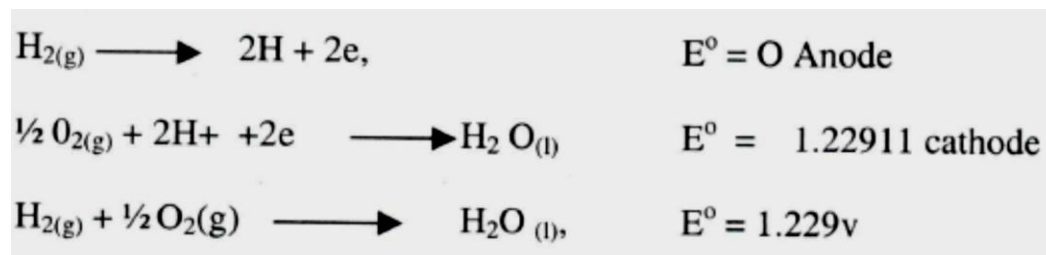


Fig. 4.2: A Hydrogen-Oxygen Fuel Cell with KOH Electrolyte and Porous Carbon Electrodes

The half-cell reactions are given below:



With acidic electrolyte, the half-cell reactions are:



We can see from the equations above that the electromotive force of the cell remains the same whether we use alkaline or acidic electrolyte. This is because we are using the same reactants at the electrodes in both cases.

Fuel cells have several advantages over other sources of energy. Firstly in a fuel cell unlike in the dry cell or storage battery (which requires recharging also), the cathode and anode reactants are continuously supplied so that energy can be indefinitely withdrawn from it. Secondly, in a fuel cell energy is extracted from the reactants under almost ideal conditions. Therefore, the thermodynamic efficiency of the fuel cells are higher than of most of the ordinary combustion processes. Fuel cells have efficiencies approaching 75% whereas power plants that burn fuels have efficiencies of only about 40%.

Combustion of hydrogen is a highly exothermic reaction and produces no pollutants:



Liquid hydrogen is therefore, used as a rocket fuel.

It is now clear that world reserves of fossil fuels like coal, oil and gas are finite, so they cannot last forever. Nuclear and hydroelectric power cannot meet the world's energy needs. Moreover, these resources pose a danger to the world's environment. With these facts in mind there is now an active search for alternative source of energy. In addition to solar power, hydrogen is being considered a potential fuel for the future.

Hydrogen as a fuel has many advantages over the conventional fossil fuels and electric power. It is available in unlimited quantities in sea water. It is pollution free because the major product of its combustion is water with only traces of nitrogen oxides. It releases greater energy per unit weight of fuel in comparison to gasoline and other fuels. Hydrogen can be transported as a gas in high pressure pipelines, as a liquid in tankers and even as a solid in form of metal hydrides. Unlike electricity hydrogen can be stored and used when needed.

Hydrogen however has the following disadvantages viz:

Hydrogen like electricity is a secondary source of energy because it is produced using energy from a primary source such as coal, nuclear fission or sun.

Preparation of hydrogen through electrolysis is not economical at present in fact more energy has to be spent in electrolysis of water than what can be liberated by burning hydrogen as a fuel.

Decomposition of water by solar energy in presence of catalysis is known as photochemical decomposition of water. Using catalysts scientists in France have been able to achieve the efficient decomposition of water under visible and ultra violet light. If this process can be made industrial, a convenient method of converting solar energy directly to a useful form of store chemical energy will be available.

4.0 Conclusion

We can conclude this unit by observing that the major material for the manufacture of hydrogen is water. Since water is abundant, the production of hydrogen should be simple. However, it is not efficient to produce hydrogen by electrolysis. This is non economical because of the cost of electricity. The single most important use of hydrogen is in the manufacture of ammonia which is used in the production of nitric acid and nitrogenous fertilizers. Hydrogen is also used in space crafts as a source of fuel cell.

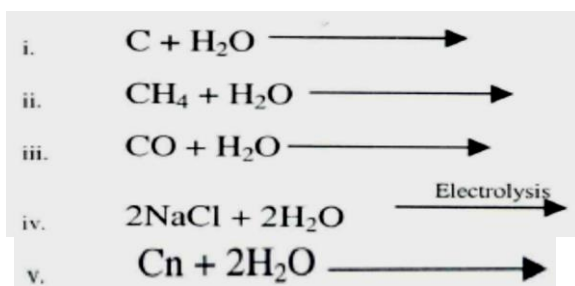
5.0 Summary

In summary, you have studied the following in this unit:

- the major source for the manufacture of hydrogen is water
- there are two primary methods for the manufacture of hydrogen:
 - a. manufacture by chemical means
 - b. manufacture by electrolysis
- even though manufacturing by electrolysis would have been preferred it is too expensive, because of the cost of the energy needed for electrolysis
- the largest use of hydrogen is in the manufacture of ammonia, which is used to manufacture nitric acid and nitrogenous fertilizers
- hydrogen is made use of in the production of fuel cells for space crafts
- hydrogen is also used in extraction of metal and hydrogenation of vegetable oils.

Self-Assessment Exercise

1. Complete the following chemical reactions which take place during the formation of hydrogen.



2. Write five important industrial uses of hydrogen

6.0 Self-Assessment Exercise

Write chemical equation for the following reactions:

- Formation of methanol from coal.
- Reduction of methyl cyanide.
- Conversion of Oleic acid into stearic and
- Reduction of ammonium molybdate to molybdenum.

7.0 References/Further Reading

Cotton & Wilkinson (n. d.). *Basic Inorganic Chemistry*. John Wiley and Sons.

Wilson, J. G. & Newell, A. B. (n. d.). *General and Inorganic Chemistry*. Cambridge: Cambridge University Press.

Unit 5 Ionic or Salt-Like Hydrides

1.0 Introduction

In the previous units, you became aware of the fact that hydrogen forms more compounds than any other element. You also saw that despite the fairly high bond dissociation energy of the hydrogen molecule, it is moderately reactive and forms strong bonds with many other elements. You also learnt that it forms ionic and covalent hydrides with metals and non-metals respectively.

In this unit you will be studying the formation of hydrides, their types and characteristics of the hydrides.

2.0 Objectives

At the end of this unit, you should be able to:

- list the three classes of hydrides
- discuss for each of the different types of hydrides and their properties.

3.0 Main Content

As already pointed out at the beginning of this unit, Hydrogen combines with a number of elements to form hydrides. As electronegativity of the element increases the stability of the hydrides also increases. Three types of hydride compounds are formed depending upon the electronegativity of the element. They are classified into:

- Ionic or salt like or salic hydrides
- Covalent or molecule hydrides
- Metallic or non-stoichiometric hydrides.

3.1 Ionic or Salt — Like Hydrides

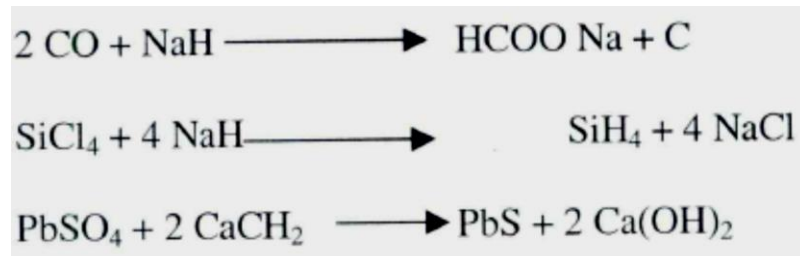
These are formed by metals with low electronegativity values and are more electropositive with respect to hydrogen. These hydrides are formed by transfer of an electron from the metal to the hydrogen atom. Hydride ion is a peculiar chemical species and in contrast to proton which has small size, it is unusually large. It is larger than any of the negative ions except iodide.

The reason for this apparent paradox lies in the lack of control by a single nuclear proton over two naturally repelling electrons.

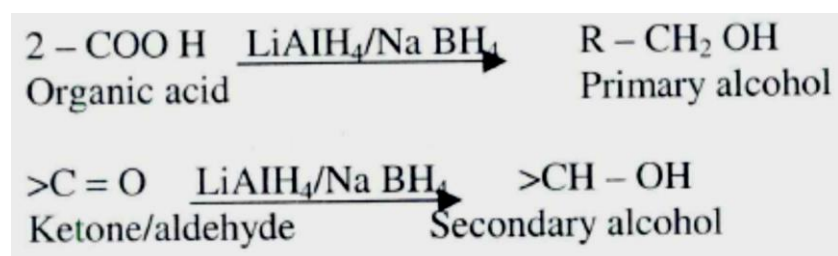
Alkali and Alkaline-earth metal of Groups 1 and 2 are sufficiently electropositive and force the hydrogen atom to accept an electron to form the hydride ion, if eg Lithium hydride LiH - and calcium hydride $\text{Ca}^{2+}(\text{H})_2$.

Ionic hydrides are formed by heating metals in hydrogen at 973K. Ionic hydrides are white crystalline solids. They have high melting points and conduct electricity in liquid state, liberating hydrogen at the anode. Their density is higher than that of the metal.

They are powerful reducing agents especially at high temperatures e.g.



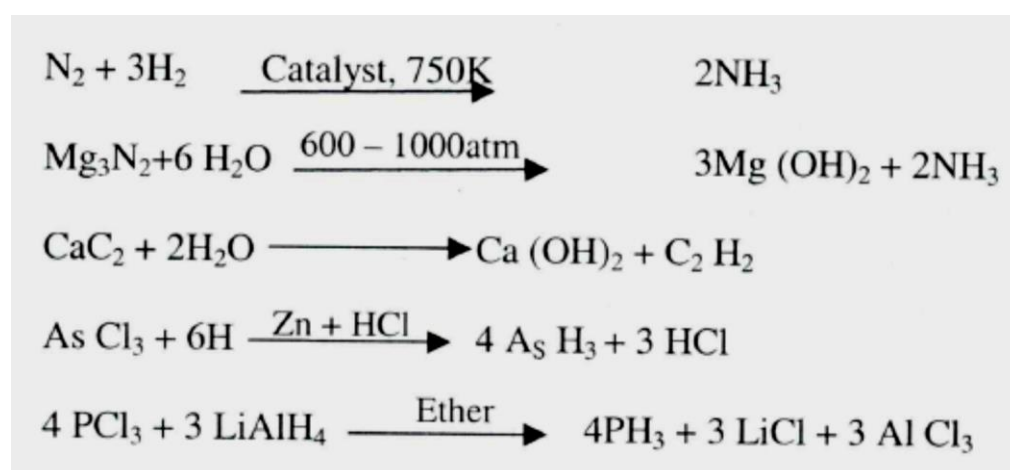
$\text{Li}^+ \text{H}^-$ and $\text{Na}^+ \text{H}^-$ are used in making valuable reducing agents like lithium aluminium hydride (LiAlH_4) and sodium-boro-hydride (NaBH_4). The complex hydrides are frequently used in the reduction of aldehydes, ketones, acids and their derivatives to give alcohols.



3.2 Covalent Hydride

These bonds are formed by elements of comparatively higher electronegativity such as the P- block elements and Be and Mg. The bonds formed in this class of hydrides are mostly covalent in character but in some cases, for example, in HF, the bond may be partially ionic.

The covalent hydrides can be prepared either by direct reaction of non-metals with hydrogen under suitable conditions or by the reaction of H_2O or acids or nitrides, carbides, borides, silicides, stannides of alkali and alkaline earth metals or by the reduction of halides. These are illustrated by the following reactions:



These hydrides have molecular lattice made up of individual saturated covalent molecules, with only weak van der Waals forces and in some cases along with hydrogen bonds. This accounts for their softness, low melting and boiling points, their volatility and lack of conductivity. Some covalent hydrides are unstable in the presence of air, e.g. stannane, SnH_4 .

Some covalent hydrides of Groups 2 and 13 are electron deficient. These have structures between ionic and covalent hydrides. These are either dimeric, e.g. boron hydride (B_2H_6), or polymeric, e.g. beryllium hydride $(\text{BeH}_2)_n$, magnesium hydride $(\text{MgH}_2)_n$ and aluminium hydride $(\text{AlH}_3)_n$.

3.3 Metallic Hydrides

When heated, hydrogen reacts with many transition metals (lanthanides and actinides) to form metallic hydrides. Most of these have metallic appearance and are less dense than the parent metal. They all conduct heat and electricity though not as well as the parent metal.

They are almost always non-stoichiometric, being deficient in hydrogen. For example, $\text{TiH}_{5.8}$, $\text{VH}_{0.56}$, $\text{CrH}_{1.7}$, $\text{NiH}_{0.6-0.7}$, $\text{TaH}_{2.2-2.76}$, $\text{LaH}_{2.8}$, YbH etc.

Most of these hydrides are stable to water up to 375K but are quantitatively decomposed by acids and show some reducing properties.

Formerly, these hydrides were formed as interstitial compounds in which hydrogen was thought to be accommodated in the interstices in the metal lattice producing distortion but no change in its type. But recent studies have shown that except for hydrides of nickel, palladium, cerium and actinium, other hydrides of this class have lattice of a type different from that of the parent metal. For example, the hexagonal close packed lattice of some lanthanides is transformed to a face-centred cubic lattice in their dihydrides.

As pointed out earlier, these interstitial hydrides are poorer conductors of electricity, exhibit less paramagnetism and are more brittle than the parent metal. These characteristics suggest that hydrogen is present in the metal lattice as hydrogen atoms rather than as hydrogen molecules. The single electron of hydrogen is paired with an electron of the metal, thereby reducing the extent of metallic bonding. Breaking of the H-H bond is in agreement with the fact that these metals catalyse reactions of hydrogen.

4.0 Conclusion

You can conclude this unit by putting the fact that despite the fairly high bond dissociation energy of the hydrogen molecule, it reacts with certain elements to form three types of hydrides; ionic, covalent and metallic hydrides.

5.0 Summary

In this unit, you learnt the following:

- hydrogen reacts with certain metals to form hydrides
- these hydrides are classified into three viz ionic or salt-like hydrides, covalent hydrides and metallic hydrides

- ionic hydrides are powerful reducing agents, covalent hydrides are soft have low melting points and are poor conductors of electricity.

Self-Assessment Exercise

i. Silt is an example of which of the following type of hydrides

- (a) Ionic
- (b) Interstitial
- (c) Metallic
- (d) Covalent.

ii. List three properties of ionic hydrides.

6.0 Self-Assessment Exercise

What types of bonding do you expect of?

- Sodium hydride
- Methane
- Ammonia

7.0 References/Further Reading

Cotton & Wilkinson (n. d.). *Basic Inorganic Chemistry*. John Wiley and Sons.

Wilson, J. G. & Newell, A. B. (n. d.). *General and Inorganic Chemistry*. Cambridge: Cambridge University Press.