

Main Group Chemistry
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Lecture – 13
Chemistry of Hydrogen

I once again welcome you all to MSB lecture series on main group chemistry in my last several lectures I discussed about structure and bonding concepts. And today let me start about the chemistry of main group elements, before I proceed group wise looking into the chemistry of s and p block elements. Let me begin with the chemistry of hydrogen. Hydrogen the simplest elements in the periodic table and ambiguity is there about its position in the periodic table; that means, where it has to be placed, and before I dig deep into all this aspects. Let us look into the abundance of elements in the earth crust as well as in the universe.

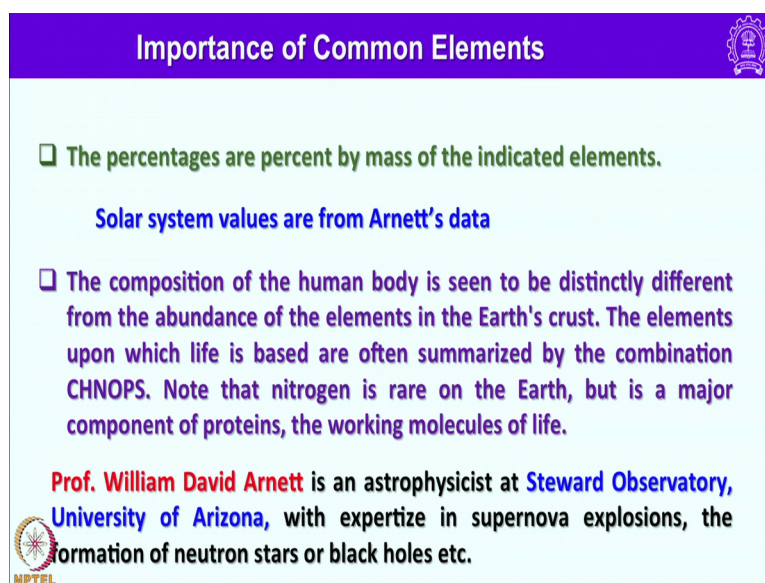
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Abundance of elements				
Abundance of elements in the earth's crust		Abundance of elements in the universe		
Element	Approximate % by weight	Element	Mass fraction in PPM	Atomic No
Oxygen	46.6	Hydrogen	739,000	1
Silicon	27.7	Helium	240,000	2
Aluminum	8.1	Oxygen	10,400	8
Iron	5.0	Carbon	4,600	6
Calcium	3.6	Neon	1,340	10
Sodium	2.8	Iron	1,090	26
Potassium	2.6	Nitrogen	960	7
Magnesium	2.1	Silicon	650	14
All others	1.5	Magnesium	580	12
		Sulfur	440	16

So, I have listed here abundance of elements in the earth crust you can see the most abundant elements is oxygen accounts for 46.6, percent and silicon 27.7 percent the third one is aluminum accounts for 8.1 percent, then iron 5 percent, calcium 3.6 sodium potassium and magnesium accounts for respectively 2.8 2.6 and 2.1 percent. And rest of the elements consisted about 1.5 percent, and you will be surprised to see among these top 7 elements hydrogen is not there.

So, let us look into the abundance of elements in the universe. So, you will be surprised to see a hydrogen occupying the top position, and then next helium comes and next oxygen, and carbon, neon, iron, nitrogen, silicon, magnesium and sulfur. These are the top 10 most abundant elements in the universe. And you will be surprised to see both in the earth crust and in the universe main group elements occupies major position, and except for iron in both the instance most abundant elements are essentially the main group elements.

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Importance of Common Elements

- ☐ The percentages are percent by mass of the indicated elements.

Solar system values are from Arnett's data

- ☐ The composition of the human body is seen to be distinctly different from the abundance of the elements in the Earth's crust. The elements upon which life is based are often summarized by the combination CHNOPS. Note that nitrogen is rare on the Earth, but is a major component of proteins, the working molecules of life.

Prof. William David Arnett is an astrophysicist at **Steward Observatory, University of Arizona**, with expertise in supernova explosions, the formation of neutron stars or black holes etc.



The percentages are percent by mass by the indicated element, and solar system values are from Arnett's data you may be surprised to know you are Arnett professor William David, Arnett is an astrophysicist at Steward Observatory University of Arizona. He is an expert in supernova explosions the formation of neutron stars or black holes etcetera. So, the composition of human body; so, now, after getting some information about the abundance of elements in the earth crust, and the elements in the universe. Let us look into the composition of the human body and what are the elements that are there in the human body in different form.

In fact, it is very interesting if you just look into the elements that constitute or essentially 6 elements, they are carbon, hydrogen, nitrogen, and oxygen, phosphorus and sulfur these 6 elements constitute the human body. The elements that are found in the earth crust, and the universe are essentially different from those that compose the human

body and human body are composed of 6 important elements such as carbon, hydrogen, nitrogen, oxygen, phosphorous and sulfur. And nitrogen is a rare element on the earth, but is a major component of proteins the working molecules of life that is DNA RNA and all those things.

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Common Elements in Living Organisms					
Element	Symbol	Atomic Number	% by Mass in Solar System	Percent in Earth	Percent in Human Body
Hydrogen	H	1	70.6	0.14	9.5
Helium	He	2	27.5	Trace	Trace
Carbon	C	6	0.30	0.03	18.5
Nitrogen	N	7	0.11	Trace	3.3
Oxygen	O	8	0.59	47	65
Sodium	Na	11	0.0033	2.8	0.2
Magnesium	Mg	12	0.0069	2.1	0.1
Phosphorus	P	15	Trace	0.07	1
Sulfur	S	16	0.0396	0.03	0.3
Chlorine	Cl	17	Trace	0.01	0.2
Potassium	K	19	Trace	2.6	0.4
Calcium	Ca	20	0.006	3.6	1.5
Iron	Fe	26	0.12	5	Trace

And let us look into the common elements in living organisms in this most of this elements, whatever I have shown in by mass by solar system. So, you can see here hydrogen is the major 1 accounts for 7.6 percent, and helium 27.5, and iron is 0.12; that means, potassium chlorine and other elements are present in that trace quantities and you can look into the percentage of these elements in human body hydrogen accounts for almost 9.5 percent, and carbon accounts for 18.5 percent, nitrogen accounts for 3.3 percent whereas, oxygen accounts for 65 percent, because 2/3rd of our body weight is made up of water and as a result what happens you can see hydrogen is present in 9.5 percent and oxygen present in 65 percent. And rest of the elements are as per the percentage I have given here ok.

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Table of Elements in the Human Body by Mass						
oxygen	43 kg	(61%, 2700 mol)	aluminum	60 mg	niobium	1.5 mg
carbon	16 kg	(23%, 1300 mol)	cadmium	50 mg	zirconium	1 mg
hydrogen	7 kg	(10%, 6900 mol)	cerium	40 mg	lanthanum	0.8 mg
nitrogen	1.8 kg	(2.5%, 129 mol)	barium	22 mg	gallium	0.7 mg
calcium	1.0 kg	(1.4%, 25 mol)	iodine	20 mg	tellurium	0.7 mg
phosphorus	780 g	(1.1%, 25 mol)	tin	20 mg	yttrium	0.6 mg
potassium	140 g	(0.20%, 3.6 mol)	titanium	20 mg	bismuth	0.5 mg
sulfur	140 g	(0.20%, 4.4 mol)	boron	18 mg	thallium	0.5 mg
sodium	100 g	(0.14%, 4.3 mol)	nickel	15 mg	indium	0.4 mg
chlorine	95 g	(0.14%, 2.7 mol)	selenium	15 mg	gold	0.2 mg
magnesium	19 g	(0.03%, 0.78 mol)	chromium	14 mg	scandium	0.2 mg
iron	4.2 g		manganese	12 mg	tantalum	0.2 mg
fluorine	2.6 g		arsenic	7 mg	vanadium	0.11 mg
zinc	2.3 g		lithium	7 mg	thorium	0.1 mg
silicon	1.0 g		cesium	6 mg	uranium	0.1 mg
rubidium	0.68 g		mercury	6 mg	samarium	50 µg
strontium	0.32 g		germanium	5 mg	beryllium	36 µg
bromine	0.26 g		molybdenum	5 mg	tungsten	20 µg
lead	0.12 g		cobalt	3 mg		
copper	72 mg		antimony	2 mg		
			silver	2 mg		

And of course, I have listed another table here that list the elements that are found in the human body by mass of course, here whatever the I have listed the top 10 are very essential rest of them are not really essential of course, iron is needed fluorine is needed, but whatever I have shown in 2nd row and 3rd row are essential present they were not be essential for human body.

But they are also found in human body for; obviously, two reasons one is because of the food we eat is not pure it is contaminated, the air we breathe is contaminated, and the water we drink is contaminated, as a result some of these elements which are essentially not needed for human to have a good and healthy life still found. And of course, once if they are in the limit there is no harm one if they exceed certain permeable quantity than they can very toxic and they can even kill the living beings.


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Hydrogen

H
Hydrogen

Atomic Weight: 1.00794
Melting point : -252.9 °C
Density : 0.084
First ionization energy: 13.598 eV
Oxidation states: +1 and -1
Reduction potential: 0 eV
Electronegativity: 2.2

- ❖ Simplest element in the Periodic Table
- ❖ But chemistry is vast and diverse
- ❖ It is very difficult to place it in any group of the Periodic Table
- ❖ Electronic configuration is similar to alkali metals ($1s^1$) and for this reason it is placed at the top of Group 1 belongs to alkali metals

 <https://www.youtube.com/watch?v=6rdmpx39PRk&index=1&list=PL7A1F4CF36C085DE1>

With this let me look into the more properties of hydrogen; hydrogen, atomic weight is 1.00794 for all practical purposes we can consider it as 1. And melting point is 252.9 degree centigrade, and density is 0.084, and first ionization energy is quite high that is 13.598 electron volts and also it exist in 2 oxygen states that is plus 1 and minus 1, and its reduction potential is 0 electron volts.


And electronegativity is 2.2 which is slightly less than that of carbon that is about 2.4 or 2.5. And reduction potential of hydrogen is 0 as a result that is considered as a standard in determining the reduction potential of rest of the elements in the periodic table. Whatever we measure as reduction potential of other elements is with reference to hydrogen reduction potential that is considered as 0 electron volts.

And of course, you know the fact that it is a simplest elements in the periodic table; however, the chemistry is vast and diversified. And in fact, it reacts with most of the elements in the periodic table with different structural and bonding properties, because of its unique property it is very difficult to place it in any group of the periodic table. Simply by looking into the electronic configuration that is very similar to alkali metals having 1 electrons in valence shell, we may think that it is appropriate to place it in the group 1 along with alkali metals on the other hand. It is in short of 1 electron to have next inert gas configuration that is helium.


So, as a result it can be considered as an element belongs to group 17 that is halogens because all halogens have 1 electron short that is s^2p^5 electronic configuration, and require just one electron to complete their octate to achieve. The next inert gas configurations; that means, now we have 2 options whether it should be kept in group 1 along with alkali metals by virtue of being $1s^1$ having $1s^1$ electronic configuration or by virtue of having one short of inert gas configuration, it can also be placed along with halogens in the group 17.

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Hydrogen



- ❖ Simplest element in the Periodic Table
- ❖ But chemistry is vast and diverse
- ❖ It is very difficult to place it in any group of the Periodic Table
- ❖ Electronic configuration is similar to alkali metals ($1s^1$) and for this reason it is placed at the top of Group 1 belongs to alkali metals
- ❖ $H \rightarrow H^+ (s^2)$. $Cl \rightarrow Cl^- (s^2p^5 \text{ to } s^2p^6)$
- ❖ Cl readily forms Cl^- compared to H forming H^- owing to the large electron affinity
- ❖ Halide ions are stable in water, whereas hydride ions readily hydrolyze in water.


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But let us look into some aspects here, as I said it is a simplest elements. So, electronic configuration we have a dilemma where it should be placed along with group 1 or group 17. Then H when an electron is added it achieves s^2 electronic configuration that is that of helium. And then same thing happen in case of chlorine; chlorine when, it takes 1 electron it becomes chloride it goes from s^2p^5 to s^2p^6 , but chlorine readily forms Cl^- compared to H forming H^- owing to the large electron affinity. And another difference between halides and hydrogen is halide ions are stable in water whereas, hydride ions readily hydrolyze in water.

So, because of this difference in the properties of hydrogen with respect to the halides, eventually it was thought that it is appropriate to place it along with alkali metals in group 1 as a result we find hydrogen in the group 1 along with alkali metals.

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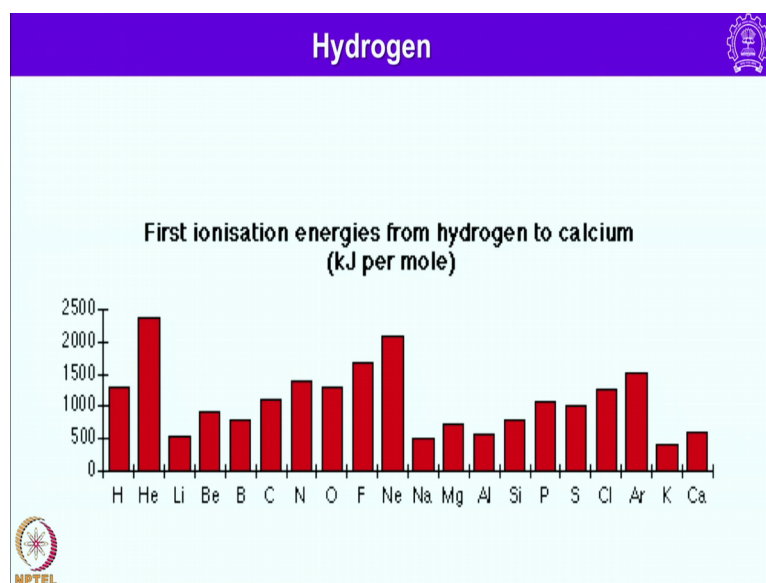
Hydrogen	
First IEs (kJ mol^{-1})	First IEs (kJ mol^{-1})
Lithium +526	Hydrogen +1312
Sodium +502	Fluorine +1681
Potassium +425	Chlorine +1251
Rubidium +409	Bromine +1140
Cesium +382	Iodine +1008
	Astatine +890 ₋₄₀



So, now let us look into some more properties, let us look into the first ionization energy of alkali metals I have listed here for 5 alkali metals starting from lithium, sodium, potassium, rubidium and cesium. And the values are given in kilo joules per mole lithium has plus 526 sodium 502, potassium 425, rubidium 409 and cesium 382 as expected first ionization energy is decreasing down the group, because of the increase in the size of the atoms.

Now, let us look into the first ionization energy of halogens series. I have placed here hydrogen along with halogens for hydrogen first ionization energy is plus 1312 kilo joules per mole, for fluorine it is 1681, chlorine 1251, bromine 1140, iodine it is 1008, and for astatine it is 890 plus or minus 40, we do not have a precise value for astatine, because it is a radioactive element and; that means, here if you look into the ionization energy of halogens is quite comparable to the hydrogen whereas, ionization energy is not all comparable with the alkali metals.

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First ionization energy also I have listed here for first 20 elements here, you can see ionization energy steadily increases in a period whereas, that decreases in the group those things I will more again as and when I go to the respective group.

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Isotopes of Hydrogen

Three isotopes of hydrogen are known

The most abundant one is hydrogen, also known as

Protium	${}^1\text{H}$ (1 p and zero n)	stable isotope
0.02% of Deuterium	${}^2\text{H}$ (symbol D) (1 p + 1 n)	stable isotope
3 rd isotope is Tritium	${}^3\text{H}$ (Symbol T) (1 p + 2 n)	radioactive (half-life is 12.26 years)

It is prepared by cosmic ray bombardment of ${}^{14}\text{N}$ in the upper atmosphere, or in a nuclear reactor, by bombarding lithium with neutrons

$$6\text{Li} + n \rightarrow 3\text{H} + 4\text{He}$$

And let us come to the isotopes of hydrogen 3 isotopes of hydrogen are known the most abundant 1 is hydrogen also known, as protium having 1 proton and 0 neutron. And let say very stable isotope, and next isotopes is having 1 proton and 1 neutrons it is also stable isotopes. And it accounts for 0.02 percent that is deuterium are called 2 H the

symbol is D, and 3rd isotopes is tritium ^3H symbol is t is has 1 proton and 2 neutrons. And it is radioactive and half-life of tritium is 12.32 years.

And essentially this tritium is prepared by cosmic ray bombardment of ^{14}N in the upper atmosphere or in a nuclear reactor by bombarding lithium with neutrons we can see that equation I have given here. For example, it takes 6 lithium atoms and bombard with neutrons; you get 3 hydrogen that is tritium plus helium. So, you get 1 hydrogen and 1 helium.

So, all the 3 isotopes are chemically identical, but they react at different rates and this difference in reaction rates is used in the production of deuterium. As I mentioned 99.98 percentage of water essentially as H_2O . And remaining 0.02 percent is essentially D_2O , and the sea water is essentially the source of deuterium. And here there is anormous difference is there in the rate of the reaction of these 3 isotopes and of course, when we look into the reactivity of other elements having more than one isotopes.

The rate of the reaction may not differ significantly whereas, in case of hydrogen, and deuterium the rate differs significantly because here the increase in the mass is almost 100 percent ^1H atomic weight is 1 whereas, ^2H atomic weight is 2; that means, 100 percent increase is there this kind of increase in the magnitude may not be seen in heavier elements as a result the impact of this one is very minimum whereas, in this case it is significant and this significance in the rate of the reaction is exploited in the isolation of deuterium from normal water.

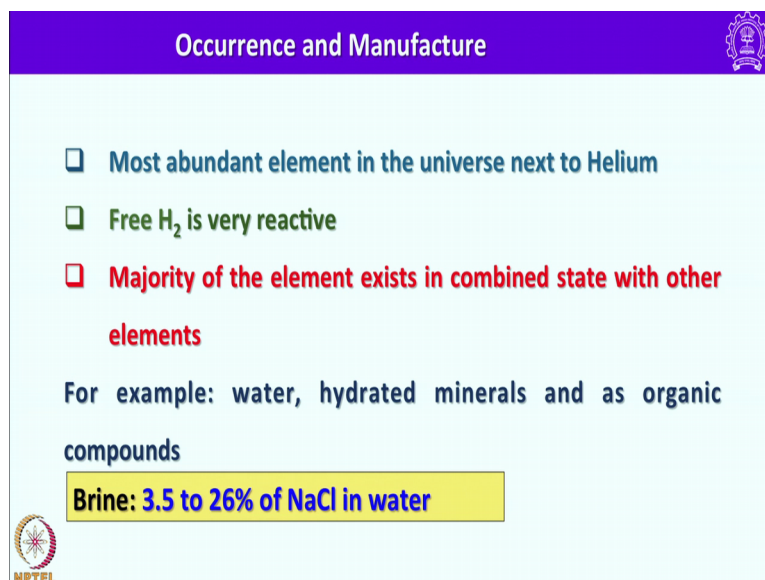
So; that means, in every 6420 atoms of hydrogen, 1 atom is deuterium and this accounts for 99.98 percent of hydrogen and 0.02 percent of deuterium mostly in ocean as D_2O and of course, deuterium was first discovered in 1932 by (Refer Time: 14:52) the deuterium to protium ratio found in comets is very similar to that in earth's oceans. This is one interesting observation, I repeat again the deuterium to protium ratio found in comets is very similar to that in earth oceans that is 156 atoms of deuterium per million hydrogen. This also supports the fact that much of the earth ocean water is originated from comets.

There are some theories that say that some of the comets have hit the earth and through which water has been transferred from comets to earth, and there is some evidence from this aspects that is deuterium to protium ratio in ocean water is essentially similar to that

found in comets. For example, how we isolate deuterium plus how we isolate or separate deuterium from hydrogen is by electrolysis of water. So, in electrolysis of water hydrogen gas produced is enriched in 1H and the residual water is enriched in heavier and more slowly reacting D ; that means, when you perform electrolysis of water as more and more water is decomposed to give hydrogen and oxygen the residual water is left is essentially concentrated with only D_2O .

So, at some point of time this D_2O can be taken out and separated. So, the most abundant element in the universe next to helium is hydrogen I repeat again and free hydrogen is very reactive and majority of the element exist in combine state with other elements.

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Occurrence and Manufacture

- ❑ Most abundant element in the universe next to Helium
- ❑ Free H_2 is very reactive
- ❑ Majority of the element exists in combined state with other elements

For example: water, hydrated minerals and as organic compounds

Brine: 3.5 to 26% of NaCl in water




That means essentially in the free form it is not at all there in the earth crust; however, it is in the combine form it is there, and mostly in the combined form is mostly in the form of water so; that means, water hydrated minerals and also has organic compounds in organic compounds hydro carbons of course, H is always there and in brain we have and brain is nothing, but a sodium chloride in water with percentage of sodium chloride varying between 3.5 to 26, and how one can prepare hydrogen.

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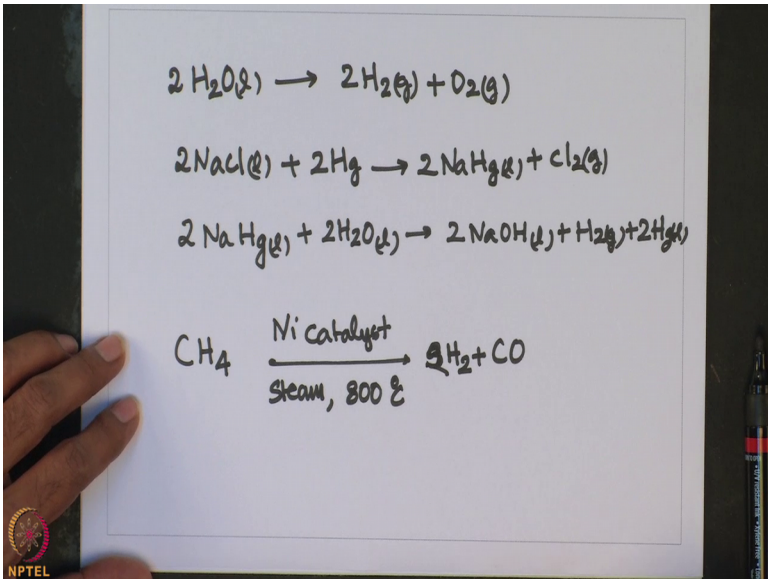
Methods of preparation of H₂

1. Electrolysis of water
2. Electrolysis of brine using mercury as an electrode
3. Reforming of hydrocarbons
4. Thermal cracking of hydrocarbons
5. Hydrolysis of ionic metal hydrides




So, essentially we have several methods at our disposal to prepare hydrogen one is electrolysis of water, the electrolysis of brine using mercury as an electrode reforming of hydrocarbons thermal cracking of hydrocarbons, and hydrolysis of ionic metal hydrides essentially alkali metal and alkaline earth metals which are highly electro positive. And their ionic hydrides and they react violently with water liberating hydrogen.

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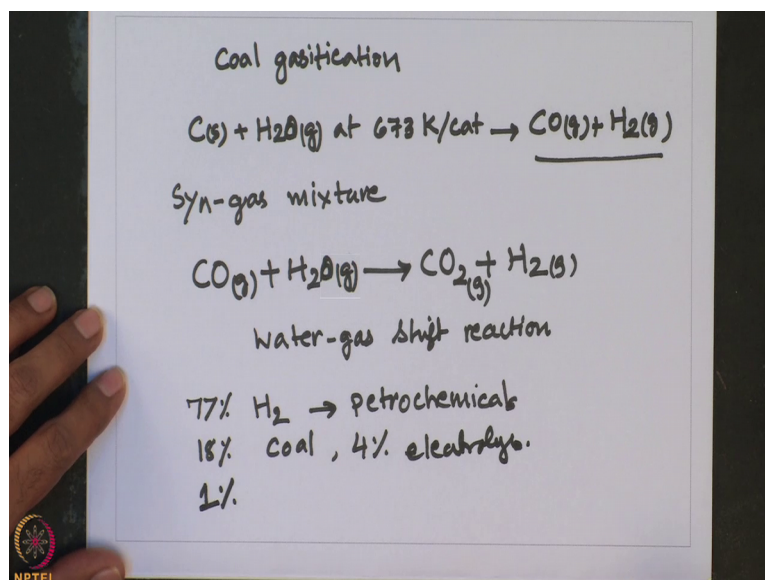
Handwritten chemical equations on a whiteboard:

$$2 \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{H}_2(\text{g}) + \text{O}_2(\text{g})$$
$$2 \text{NaCl}(\text{l}) + 2 \text{Hg} \rightarrow 2 \text{NaHg}(\text{l}) + \text{Cl}_2(\text{g})$$
$$2 \text{NaHg}(\text{l}) + 2 \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{NaOH}(\text{l}) + \text{H}_2(\text{g}) + 2 \text{Hg}(\text{l})$$
$$\text{CH}_4 \xrightarrow[\text{Steam, } 800^\circ\text{C}]{\text{Ni catalyst}} 3 \text{H}_2 + \text{CO}$$


So, let us look into some of these methods, so this is one method it is electrolysis of water you get H₂ and O₂. And then I mentioned electrolysis of brine using mercury as an electrode.

Initially brine as I mentioned it is sodium chloride in water with percentage varying between 3 to 26 initially sodium chloride is reactive with mercury to form sodium amalgam or sodium mercury alloy, through the liberation of chlorine, this reacts with water to form sodium hydroxide plus H₂ plus 2 Hg in solution. So, this is the method used to generate hydrogen from brine solution using mercury as an electrode. And another method is decomposition or oxidation of methane using a nickel catalyst. This gives a mixture of 2H₂ plus CO.

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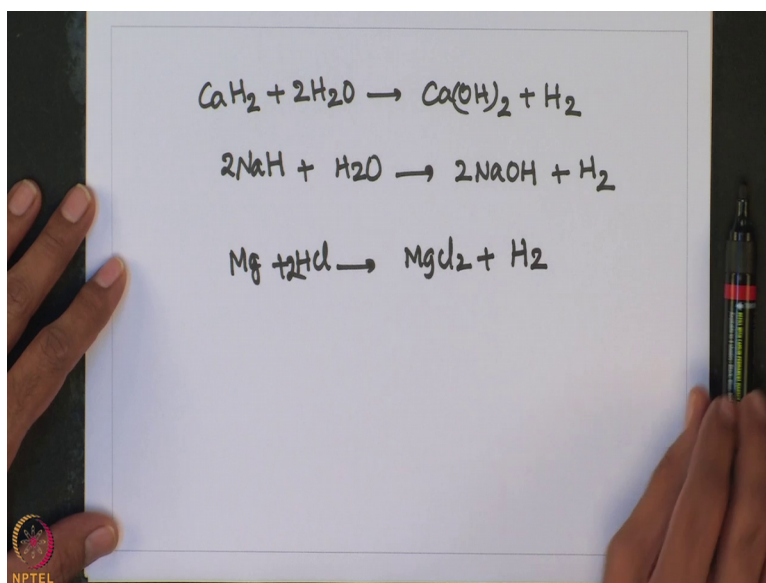


So, another method we have is coal gasification. So, here coal is treated with steam at very high temperature using a catalyst so, this gives essentially a mixture of CO plus H₂ so, this mixture is called syn gas mixture. So, this syn gas mixture with steam using iron chromate at 673 kelvin essentially gives CO₂ and H₂ for example, you consider this CO gas syn gas a mixture of you get CO₂ plus H₂. This reaction is essentially called water gas shift reaction and of course, yeah besides this 77 percent of industrial H₂ is from petrochemicals.

So, 77 percent of industrial H₂ the source is petrochemicals and 18 percent from coal, and 4 percent from electrolysis, I showed you in my previous slide 4 percent from

electrolysis, and 1 percent from some other sources. So, as I mentioned a mixture of carbon monoxide and hydrogen in 1 is to 1 ratio is essentially called as synthesis gas or syn gas, it is used to synthesis other organic compounds such as methanol syn gas is also produced from sewage, saw dust, scrap wood, newspaper etcetera. And as I mentioned by hydrolysis of metal hydrides 1 can generate H₂.

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For example consider alkaline earth metal hydrides such as calcium hydride and treat this 1 with water, it gives calcium hydroxide plus H₂. And similarly takes sodium hydride treat with water gives or 1 can also generate by simply reacting magnesium with hydrochloric acid. So, this are some of the methods that are used to generate or prepare hydrogen 1 is electrolysis another one is from reformation reactions. And another one is by reacting most electropositive metal hydrides with water. So, in my next lecture I will be discussing more about the chemistry of hydrogen.

Thank you and have a very pleasant in (Refer Time: 25:16) and chemistry reading.