Materials and Energy Balance in Metallurgical Process

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Module No. 01

Lecture No. 04

Stoichiometric Concept and Exercise

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So, in the previous lecture on stoichiometry, I have introduced you, the information that can be derive from the balanced chemical equations.

Now, let us see about the gas mixtures. Most of the gases that involve metallurgical processes or metal extraction and refining, at high temperature; they follow ideal gas behavior.

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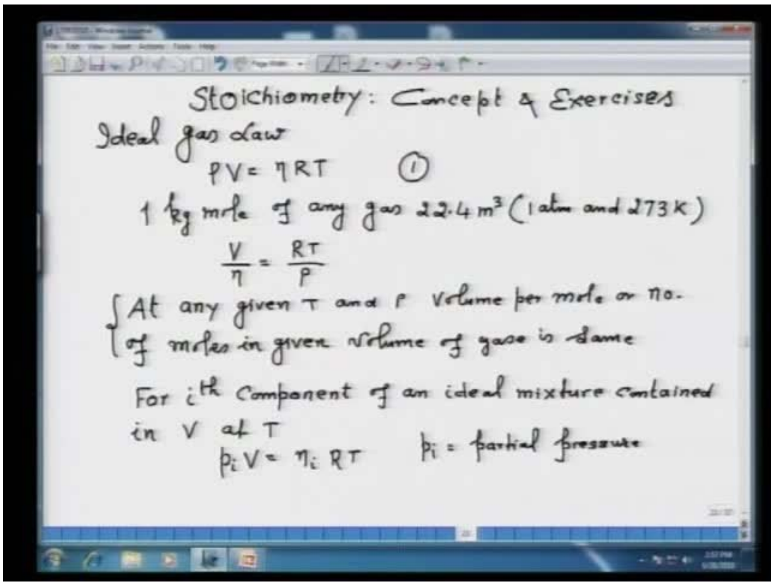

So in fact, what I am going to write is the ideal gas law; and as all of you know; that is pressure into volume; that is n R and T. R is the universal constant; T is temperature; and n is number of moles.

Now, it is also known that 1 kg mole of any gas occupies 22.4 meter cube, at 1 atmosphere and 273 Kelvin.

From equation 1 (Refer Slide Time: 01:42), we get V upon n; that is equal to R T upon P. Now this equation suggests that at any given temperature and pressure, volume per mole, that is V by n; or number of moles in a given volume of gas is the same.

You may be requiring it for some application. Now coming to the mixtures; in gas mixtures, which is made up of ideal gases, each component in the gas mixture follows the ideal gas law. So for I th component of an ideal mixture contained in volume V, at temperature T; that is, p_i into V; that is equal n_i into R T. Note here that this p_i is the partial pressure.

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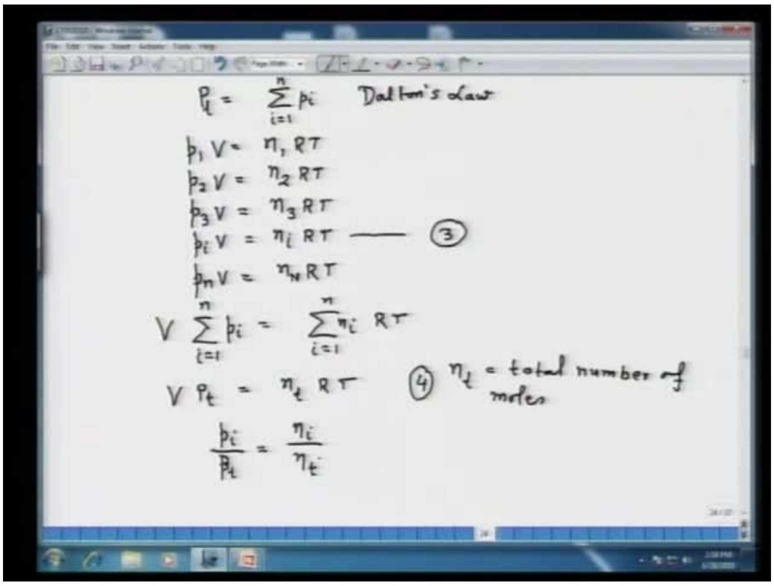

Now, from here, we can derive the Dalton's law; that is, the total pressure in a gas mixture will be equal to summation I equal to 1 to n, p_i, which is the Dalton's law for partial pressure in an ideal gas mixture.

So, if p_1 into V is equal to n_1 into R T; P_2 into V that is equal to n_2 into R T; and similarly, we can write down p_3 V is equal to n_3 into R T; such that p_i, I th component into V, that is equal to n_i into R T; I call this equation number 3. And if I put for n th component; p_n into V is equal to n_N into R T; then I can write down now, V, summation i equal to 1 to n, p_i; that is equal to sigma n_i, I is equal to 1 to n, into R T.

From here we get V into P_t; that is equal to n_t into R T, where n_t is equal to total number of moles of gas in a given mixture.

Now by 3 and 4, we can get p_i upon P_t; that will be equal to n_i upon n_t.

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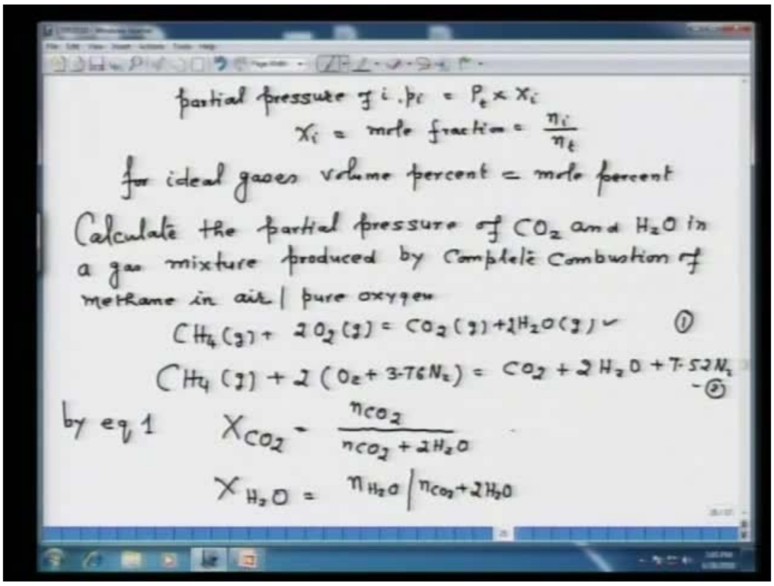

We can further write down, the partial pressure of component I, that is p_i; that is equal to P_t into X_i, where X_i is the mole fraction of component i and is equal to n_i upon n_t which we can obtained by using equations 3 and 4.

This relation is sometimes very important, say, if you want to find out the mole fraction in a gaseous mixture. This is a very simple relation, but still, I thought it might be an important thing.

Also, one thing to remember, for ideal gases volume percent equals to mole percent. Many times, this information will help in solving the material balance problem, where gas is produced, because volume percent is given; volume percent and mole percent are equal and that concept may help in solving the problem.

Now let us take an example, say, calculate the partial pressure of CO_2 and H_2O in a gas mixture produced by complete combustion of methane in air.

Now, we can write down CH_4, gaseous phase; plus let us take now, $2O_2$,in the gaseous phase; that is equal to CO_2, gaseous; plus H_2O, rather $2H_2O$, gaseous phase.

Now, you can calculate both ways; the partial pressure of CO_2 and H_2O, when it is combusted in air; oblique; in pure oxygen. The equation which I have written is for pure oxygen.

If we want to write the equation for air, then it will be CH_4, gaseous; plus 2 O_2 plus $3.76N_2$; because 1 mole of air contains 3.76 moles of nitrogen.

So accordingly, you have CO_2 plus 2 H_2O plus 7.52 nitrogen; that is because air contains nitrogen, so that will also come out. We can calculate the mole fraction.

For example, I take this, equation number 1; this I write as equation 2. So, if I take equation number 1, very easily, I can calculate say X_{CO_2}, that is equal to n_{CO_2} upon $n_{CO_2 \text{ plus } 2\,H_2O}$; this is by equation 1.

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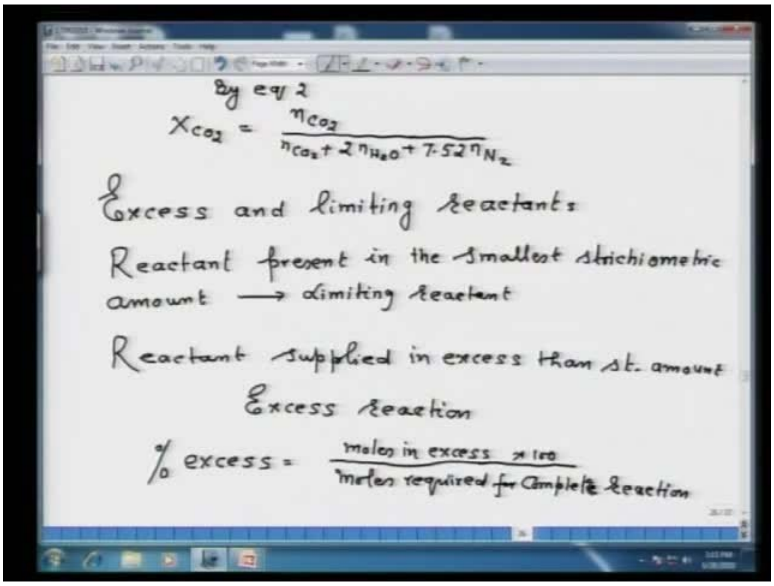

Similarly X_{H_2O}, that will be equal to n_{H_2O} divide by $n_{CO_2 \text{ plus } 2H2O}$.

Now, if I take equation 2, then I can find out by equation 2, X_{CO2} will be equal to n_{CO2} divide by n_{CO2} plus $2n_{H2O}$ plus $7.52n_{N_2}$.

Similarly, X_{H2O} can also be found out; this you can do yourself and one can determine this way, the partial pressure and the mole fractions; there are inter related.

So now, let us go to excess and limiting reactants. Now, the exact amount of reactants in any process can be determined by writing a balanced chemical equation or by writing the stoichiometry of the reaction.

In many cases, one or more reactant in a reaction can be supplied either excess or lower, than that is required by the stoichiometric relationship. The reactants, which are present in the smaller amount than the stoichiometric amount, they are called the limiting reactants.

So I will write for you, reactant present in the smallest stoichiometric amount are called the limiting reactant.

Now, the meaning of the limiting reactant is that it is because of the presence of a smaller amount of the reactant, the reaction will correspond to the amount of reactant that is available. That is, you have taken an amount which is less than the stoichiometric amount; so, this particular reactant will control the reaction. That is what is meant by the limiting reactant. The other reactant is the excess reactant.

So we can also put it as: reactant supplied in excess than stoichiometric amount for complete reaction is called the excess reactant.

So what is important to know here? That from the stoichiometry, you know the amount of reactant 1 and reactant 2. Now, if reactant 1 is less than the stoichiometric amount, you call that as limiting reactant; then, if the reactant 2 is in the excess, then that is called the excess reactant. I will try to make it clear, when I solve a particular problem.

But here, the limiting or excess - that is with reference to stoichiometry of the reaction. We can also find out percent excess; that is equal to moles in excess upon moles required for complete reaction into 100. That is how we can determine the limiting and excess reactant.

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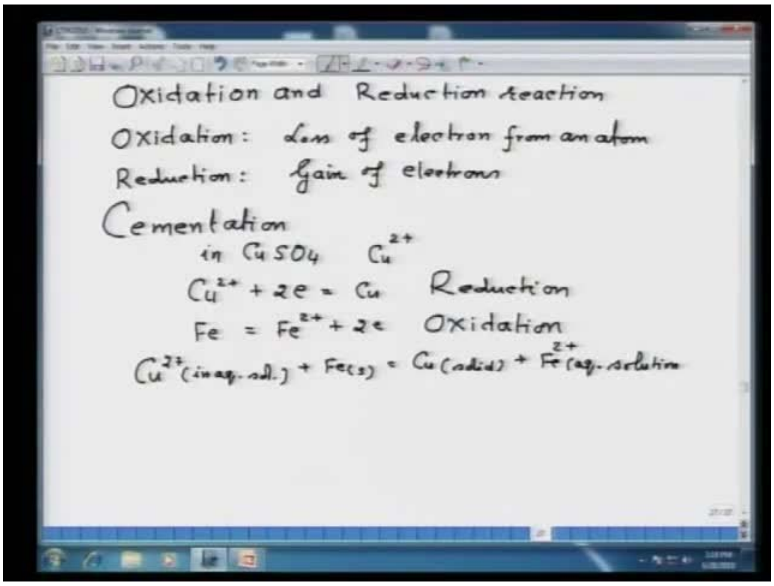

Next important thing is the oxidation and reduction reaction. In fact, oxidation reduction involves loss of electron from an atom whereas, reduction reaction, naturally, gain of electrons by an atom.

Now, oxidation and reduction reactions occur simultaneously, so that electrons are conserved.

Now for example, if we consider the cementation reaction; what is done in a cementation reaction? you deposit copper from a copper sulphate solution by adding iron. Once again I repeat, in the cementation reaction, copper sulphate solution is taken, iron files are added and copper is deposited.

So, this reaction can be written as: In copper sulphate, copper ions are Cu 2 plus; that means the reaction would be, Cu 2 plus will gain 2 electron and will become Cu; and similarly, iron will lose 2 electrons to become Fe 2 plus plus 2 electrons. So total reaction we can write down, Cu 2 plus, in aqueous solution, plus iron which you added as a solid; that will become copper that is as a solid, plus Fe 2 plus in aqueous solution.

So, what is here is an oxidation reaction; besides the number of atoms, electrons are also conserved; that is also important; and both reactions, oxidation and reduction; they occur simultaneously. You see, Cu 2 plus plus 2e is equal to Cu; that is a reduction reaction.

Whereas Fe, Fe 2 plus plus 2e; that is the oxidation reaction. So with writing the electro chemical method of expressing the chemical equation, one has to see that the electrons should also be conserved.

Now with this, I have given you enough the concepts on stoichiometry. You must be knowing already, because it simply involves basic chemistry, where you try to write the balance chemical equation and try to derive as much information as you can get.

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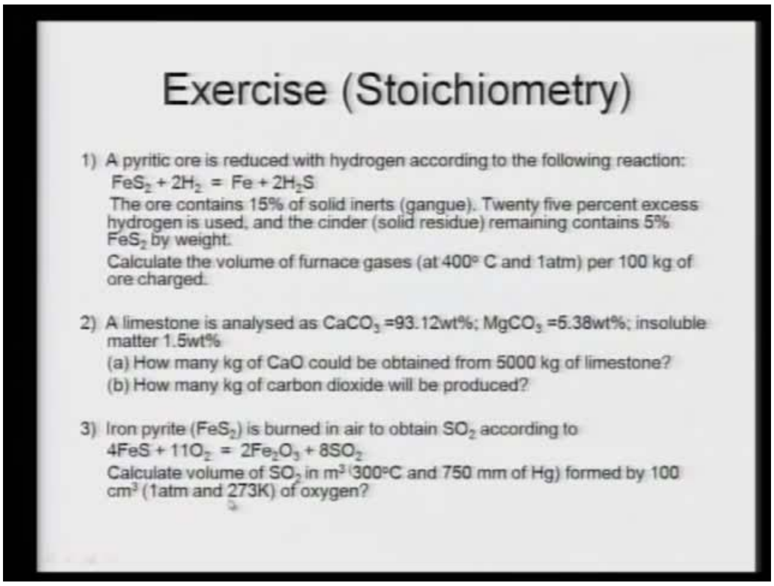

So with these concepts now, what I will do is I will, first of all, give you some problems and then we will proceed to solve some particular problems. So, here, I have formulated some of the problem for you. What will I do is I will read, first of all, all the problem that I am going to give you. Some of them, I will be solving and some of them I will leave for you for solve. I will read the problems now.

Problem 1: A pyritic ore is reduce with hydrogen according to the following reaction FeS_2 plus $2H_2$ that is equal to Fe plus $2H_2S$.

The ore contains 15 percent of solid inerts; in the metallurgical terminology, in an ore, the non-valuable portion are called gangue, that is why it is written in the bracket also, gangue; 25 percent excess hydrogen is used.

Now remember, stoichiometrically you need 1 mole of FeS_2; you require 2 moles of hydrogen; in the reaction 25 percent excess hydrogen is used and the cinder, that is a solid residue remaining, contains 5 percent FeS_2 by weight.

Calculate the volume of furnace gases at 400 degree Celsius and 1 atmosphere per 100 kg of ore charge. Now remember you have to calculate the volume of gas at temperature of 400 degree Celsius; so that point is important to note.

Second problem: A limestone is analyzed a calcium carbonate, 93.12 weight percent; $MgCO_3$, 5.38 weight percent; insoluble matter 1.5 weight percent. (a) how many kg of calcium oxide could be obtained from 5000 kg of limestone; and how many kg of carbon dioxide will be produced.

Problem 3: Here, the iron pyrite, that is a FeS; well, iron pyrite is written in both waysm FeS_2 as well as FeS; 4FeS plus $11O_2$ is equal $2Fe_2O_3$ plus $8SO_2$; that is the reaction occurring between iron sulphite and oxygen. Now calculate volume of SO_2 in meter cube at 300 degree Celsius and remember, 750 millimeter of mercury, formed by 100 centimeter cube of oxygen; this is expressed in 1 atm and 273 Kelvin.

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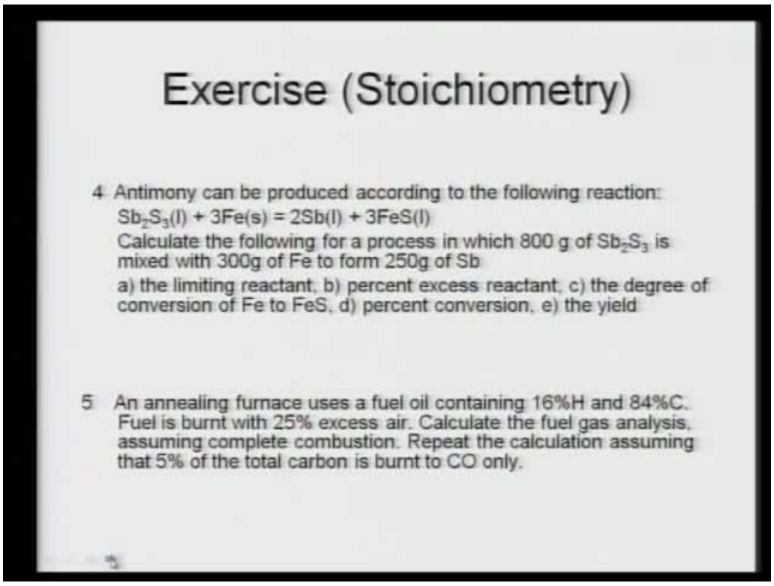

Problem 4: Antimony can be produced accordingly to the following reaction. The reaction is given to you. Now, you have to calculate the limiting reactant, percentage excess reactant, the degree of conversion of Fe to FeS, percent conversion and the yield when the process occurs, in which 800 grams of Sb_2S_3 is mixed with 300 grams Fe to form 250 gram of antimony.

Here, we will note that one of the reactant is lower than the stoichiometric proportion; and that will clear the concept of limiting reaction.

Problem 5: An annealing furnace uses a fuel oil containing; its composition is given to you; fuel is burnt in 25 percent excess air. Calculate the fuel gas analysis, assuming complete combustion. Repeat the calculation assuming that 5 percent of the total carbon is burnt to CO only.

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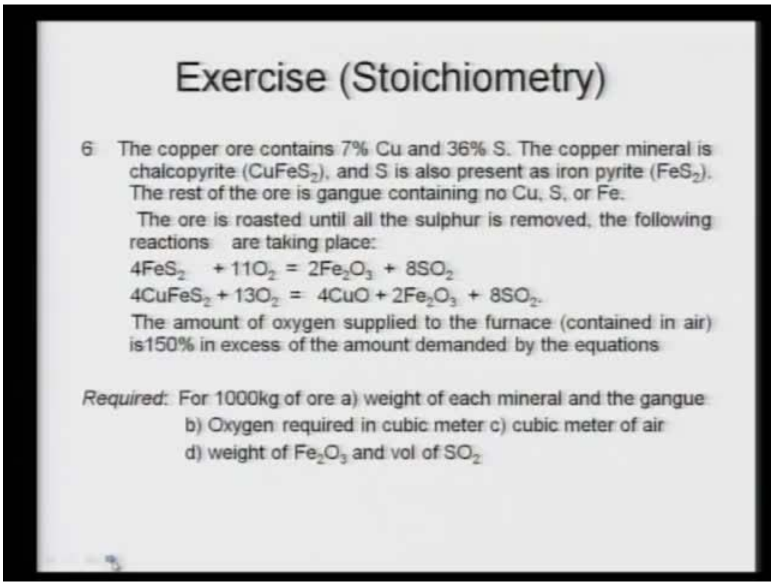

Problem number 6: The copper ore contains; the composition is given to you; copper mineral is $CuFeS_2$ and sulphur is also present as iron pyrite, as FeS_2. The rest of the ore is gangue, containing no copper, sulphur or iron.

That is the clue to solve the problem. The ore is roasted until all the sulphur is removed. The following reactions are taking place; the reactions are given to you. The amount of oxygen is supplied contains 50 percent in excess of that amount demanded by the equation.

So, you have to find out (a), (b) and (c); weight of each minerals; oxygen required; and weight of Fe_2O_3 and volume of SO_2.

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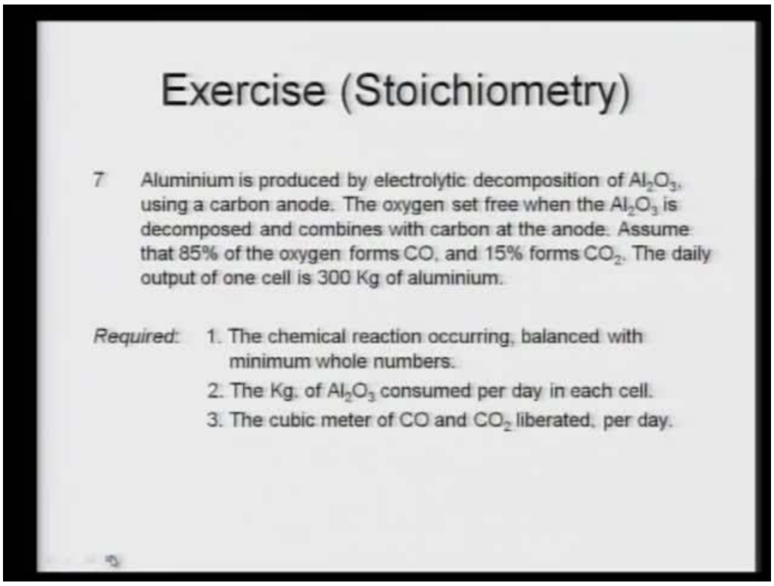

Problem 7: Aluminium is produce by electrolytic decomposition of Al_2O_3; it is a very standard and common method for production of aluminum from bauxite. What is being done? From bauxite, first of all Al_2O_3 is brought into solution by leaching; and then Al_2O_3 is electrolyzed as such, because Al_2O_3 has a very high melting point; so, in order to make an electrolyte, you try to dissolve in cryolite; and in cryolite, Al_2O_3 is soluble.

So, that is what the process is. Aluminum is produce by the electrolytic decomposition of Al_2O_3 using a carbon anode. The oxygen is set free when the Al_2O_3 is decomposed and combines with carbon at the anode; assume that 85 percent of the carbon forms CO and 15 percent forms CO_2.

Then, you have to find out the chemical reaction; kilogram of Al_2O_3; and cubic meter when 300 kilogram of Aluminium is produced by 1 cell; that is problem number 7.

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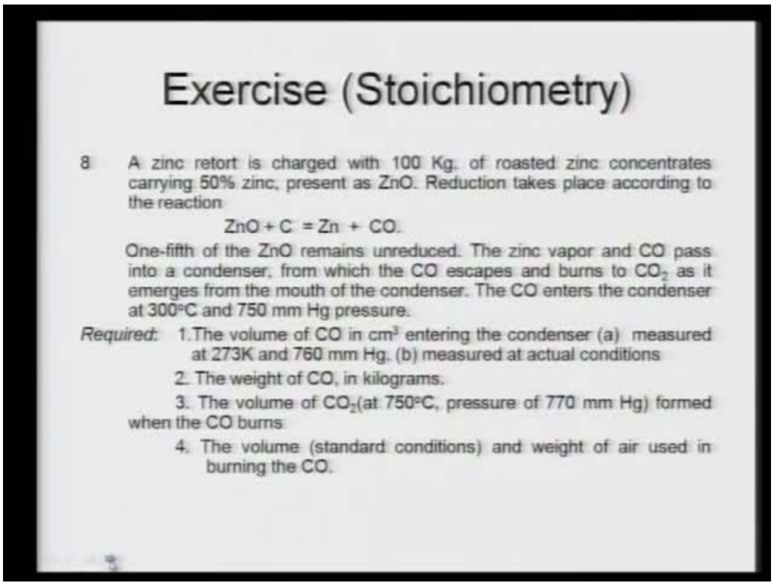

Problem number 8: it is the reduction of zinc oxide by carbon; a zinc retort is charged with 100 kg of roasted zinc concentrate carrying 50 percent zinc, present as ZnO. The reduction equation is given. Now, the problems says that one-fifth of the ZnO is unreduced.

The zinc vapor and CO pass into a condenser from which the CO escapes and burns to CO_2 as it emerges from the mouth of the condenser.

The CO enters the condenser at 300 degree Celcius and 750 millimeter of mercury pressure. So, we have to find out volume of CO; the weight of CO; volume of CO_2; and the volume and weight of air used in burning the carbon monoxide.

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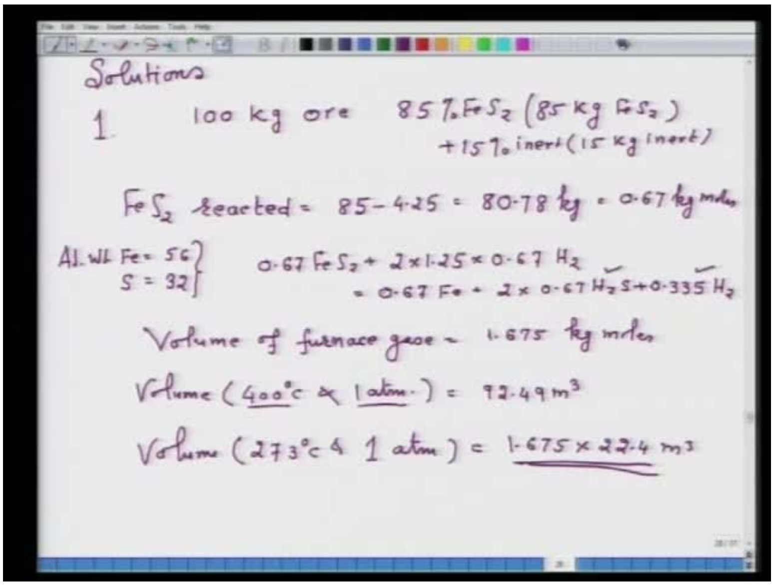

So, these are essentially some of the problems that I am giving to you for solution. Now, let us see the solution 1 by 1.

Let us take problem number 1: It says you have 100 kg ore. Now, in 100 kg ore, we have 85 percent FeS_2; you can also write 85 kg FeS_2; and well problem say 15 percent inert, so, we can also put 15 kg inert.Now, problem says 25 percent excess oxygen and 5 percent FeS_2 remains unreduced. So, FeS_2 reacted will be equal to 85 minus 4.25, that will be equal to 80.78 kg; and that will be equal to 0.67 kg moles.

Now, here I have used the atomic weight of iron and sulphur; iron I have used 56; sulphur I have used 32.

So now, straight away I can write down the equation; that equation would become 0.67 FeS_2, mind you, I am using 25 percent excess; so that will be equal to 2 into 1.25 into 0.67 H_2; that will be equal to 0.67 iron plus 2 into 0.67 H_2S plus 0.335 hydrogen.

So, now you can find out, from here, volume of furnace gasses; that will be H_2S and hydrogen; so volume of furnace gases will be equal to 1.675 kg moles.

Here, remember, in the problem the equation was given, it was given stoichiometrically; that is 1 mole of FeS_2 reacts with 2 moles of hydrogen; and problem says 25 percent excess, so I have directly written in terms of excess hydrogen.

So remember, when there is excess hydrogen than the stoichiometric amount, you get hydrogen also in the furnace gasses. So volume of furnace gases is known. Now you can find out volume, we have to find out, I believe, at 400 degree Celsius and 1 atmospheric pressure.

So, that volume will be equal to; you can find out yourself; will be 92.49 meter cube. This is at 400 degree C and 1 atmosphere pressure.

If you want to find out volume, let us say, at 273 degree Celsius and 1 atmosphere, then it will be 1.675 into 22.4 meter cube; please multiply and get the answer.

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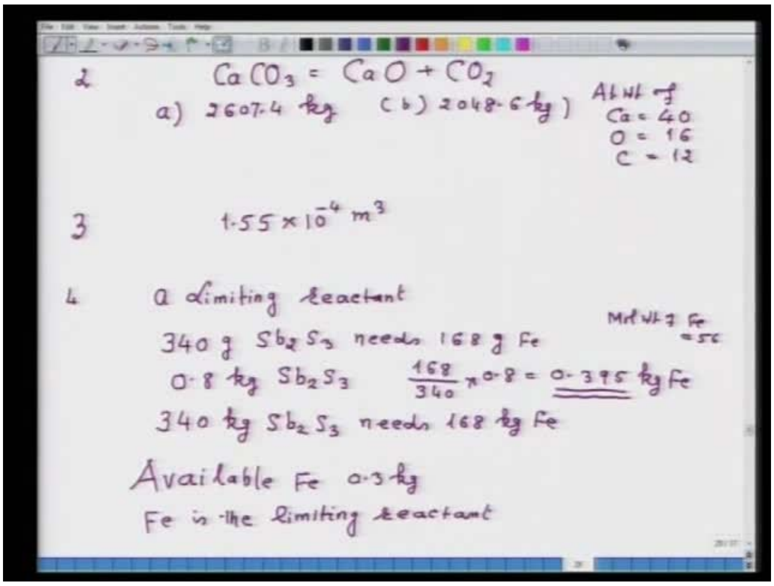

Now, the solution to problem 2: I am just giving the answer; you can solve it yourself. Just write the stoichiometric balanced equation, that is, $CaCO_3$ that is equal to CaO plus CO_2; now, you can write down; I am giving the answer.

a) The answer is 2607.4 kg and b) 2048.6 kg. Here, now I have used atomic weight of calcium – 40; oxygen – 16; carbon – 12.

Similarly, I will give the answer straight away. For question number 3, I hope that you solve yourself. The answer for question number 3 is equal to 1.55 into 10 to the power minus 4 meter cube.

Now, let us go to the problem number 4 and get a feel of the limiting reactant, because the problem says the production of antimony by the equation, which is given; you have to calculate, for a process in which 800 gram of Sb_2S_3 is mixed with 300 gram of iron to form 250 gram of antimony. That is what is given to you in this particular problem.

Now, first we have to find out limiting reactant. Let us address now, how to find out the limiting reactant. That is the first thing we want to find out.

Now limiting reactant is the one which is deficient than the stoichiometric amount. Let us see now.

Now, what we see from the stoichiometric reaction; that is, 340 gram of Sb_2S_3 needs 160 gram of iron, 3 moles of iron. Now, here, I am using molecular weight of iron, that is equal to 56; also we may use 55.85 or 56; that does not matter.

So that is what the stoichiometric says. Now we are having 0.8 kg of Sb_2S_3 that needs 168 upon 340 into 0.8, that is equal to 0.395 kg, iron.

Now, in fact I can also write down 340 gram of Sb_2S_3 needs 168 gram of iron; or I can also say 340 kg Sb_2S_3 needs 168 kg of iron; that is why straight away I have multiplied by 0.8.

So here, 340 kg Sb_2S_3 needs 168 kg of iron; so we get now, for 0.8 kg of a Sb_2S_3, you require 0.395 kg iron, stoichiometrically.

Now see, the available iron is only 0.3 kg. So the answer is: hence, iron is the limiting reactant, because available is only 300 gram or 0.3 kilogram.

You require stoichiometrically, 395 gram or 0.395 kilogram; so naturally, iron has become the limiting reactant. Now second, you have to find out percent excess reactant; the percent excess reactant that is part (b); we can find out.

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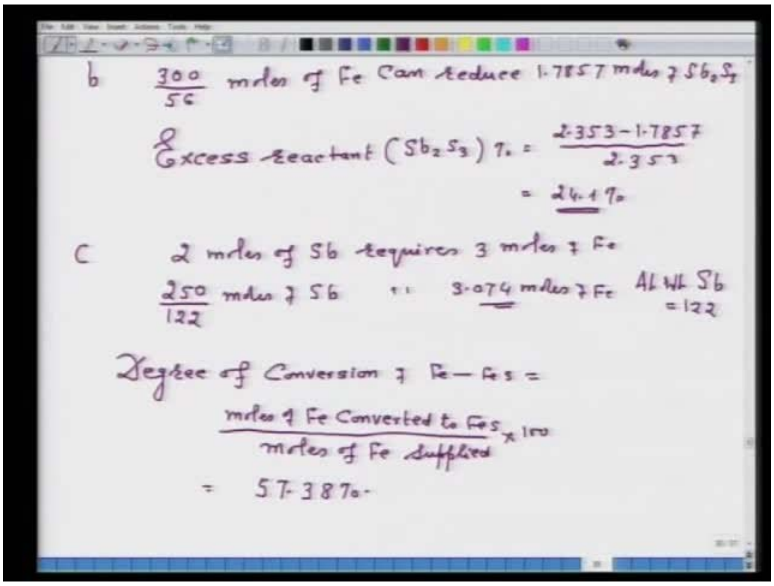

That means 300 upon 56 moles of iron can reduce 1.7857moles of Sb_2S_3. That is what is given; 300 gram of iron can reduce only that many moles of Sb_2S_3.

So, excess reactant: Naturally, when iron is a limiting reactant; its reacting partner Sb_2S_3 has become excess. So the excess reactant, which is Sb_2S_3 here, in percent; that is equal to 2.353 minus 1.7857 divide by 2.53; that is equal to 24.1 percent.

That is what the answer is, because; this 2.353 moles you will get 800 gram of Sb_2S_3, that is given, divide by its molecular weight, you get 2.353.

Now the third thing says that degree of conversion of iron to FeS; so we can now find out (c) part: 2 moles of antimony requires 3 moles of iron from stoichiometric relation. Therefore, 250 gram antimony is being produced; so 250 upon 122; I am using the atomic weight of antimony as 122; moles of antimony, you would require 3.074 moles of iron. So you can do that calculation and you will get moles of iron.

Degree of conversion of iron to FeS; that is equal to moles of iron converted to FeS divide by moles of iron supplied. Of course, you have to multiply by 100 if you want to get in percent; otherwise it will be a fraction; that does not matter.

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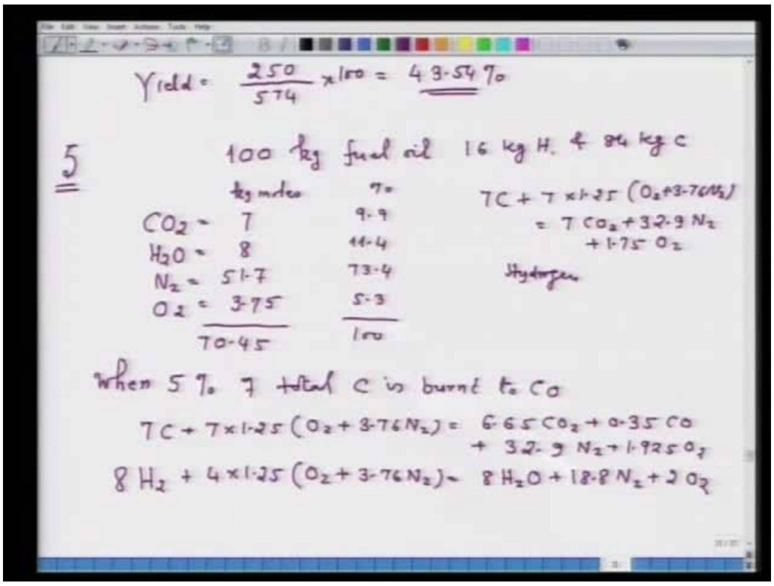

So you can substitute the values and you can find out. I am giving the answer; that is 57.38 percent. The next part it says about the yield; and yield that is equal to 250 which is produced; 574 is available by Sb_2S_3; multiply by 100 that is equal to 43.54 percent.

So, this particular problem, in fact, clears the concept of limiting reactant. You are seen here that, stoichiometrically, the requirement of iron was more than available.

We calculated 395 grams of iron would be required by stoichiometry, but available was only 300; so, that is why, iron has become the limiting reactant. So that should clear the concept of limiting and excess reactant. So that is what the problem number 4 was.

Now, let us see the problem 5 quickly: The statement of the problem is already given. For example, if you consider 100 kg fuel oil and this contains say 16 kg hydrogen and 84 kg carbon. That is what is given to us.

We have to assume now, it is burnt with 25 percent excess air. So again, you will be writing down the reaction, C plus O_2 that is equal to CO_2; H_2 plus half O_2 is equal to H_2O; balance it; use the proper moles; and get those equation. I am, straight away, writing down the analysis of fuel gas that is being produced.

So CO_2; that will be equal to 7, I am writing in kg moles; H_2O, that will be equal to 8; nitrogen that will be equal to 51.7; and oxygen that will be equal to 3.75.

So, total will be 70.45, if you want to write down in percent that will be 9.9, 11.4, 73.4, 5.3; that makes 100. So you can write this down. I am just writing for you; carbon, that is 7 moles of carbon, 84 upon 12, 7 moles of carbon; plus 7 into $1.25O_2$; plus $3.76N_2$; because that is the composition of air; so you get 7 CO_2 plus 32.9 nitrogen plus 1.75 oxygen; similarly, you write down now for hydrogen, I am not writing. Please write down and see that you get this particular thing. Now another part; when 5 percent of the total carbon is burnt to CO. So when 5 percent of the carbon is burnt to CO, we know the amount of carbon; again we can write down the stoichiometric reaction so for (b) part or for the part, when 5 percent of total carbon is burnt to CO, I will write the stoichiometric reaction that is 7C plus 7 into $1.25O_2$ plus $3.76N_2$; that is equal to $6.65CO_2$ plus 0.35CO plus 32.9 nitrogen plus 1.925 oxygen; similarly, you can write down for hydrogen.

Let me write down for you, for hydrogen - $8H_2$ plus 4 into $1.25O_2$ plus $3.76N_2$

That will be equal to $8H_2O$ plus $18.8N_2$ plus $2O_2$. So you develop your own technique of writing the equation; do not barrow the technique, which I am giving; take it as a guideline.

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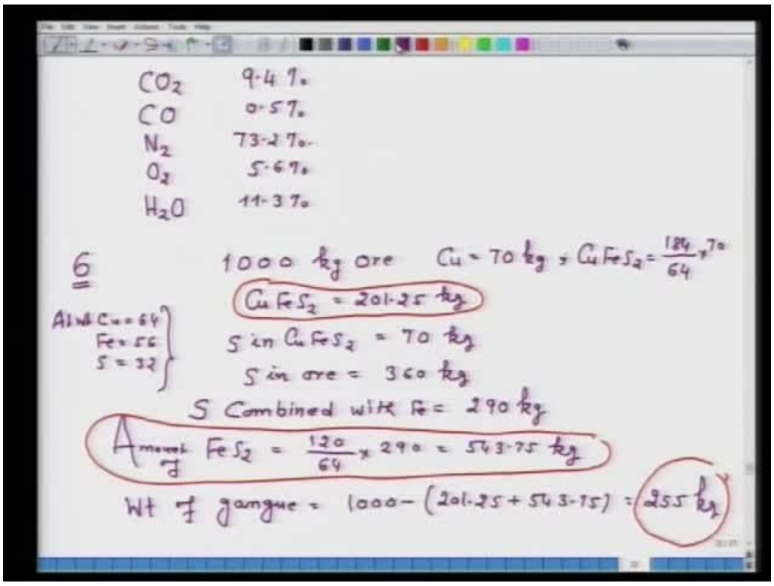

From here, we can find out the composition, so the gases will consists of CO_2, CO, nitrogen; do not forget to include oxygen, because, excess here; and H_2O. So straight away, I will give you the percentage. Here it is 9.4 percent; here it is 0.5 percent;

nitrogen is 73.2 percent; oxygen is 5.6 percent; and H_2O is 11.3 percent. So that is the solution for the problem from 5.

Now, let us see the problem number 6: now problem 6 says a copper ore is there, where the analysis is given; roasting of the ore is done; and you have to find out the weight of each mineral and the gangue and so on.

Let us take part one. That is, we are given 1000 kg ore; copper in this ore is 70 kg and this 70 kg copper, we can find out from here, $CuFeS_2$, that will be equal to 184 upon 64 into 70; so the $CuFeS_2$; that is equal to 201.25 kg.

Now, here I am using atomic weight of copper – 64; iron, I have given already, but well, I may write down – 56; and sulphur - 32

So $CuFeS_2$, I know now. I have to find out amount of Fe; because the copper ore will contain $CuFeS_2$, FeS_2 and the gangue. Now, I have to find out FeS_2. How can I find out? So, first of all, I find out sulphur in $CuFeS_2$. Sulphur in $CuFeS_2$; that will come out to be 70 kg.

But sulphur in ore is given as 36 percent; that is 360 kg. So, the remaining sulphur will combine with iron, because there is no other element, which will combine with the iron. That way you have to find out what is the amount of FeS_2.

So sulphur combined with iron will be equal to 290 kg. So, from here I can find out, the amount of FeS_2; that is equal to 120 upon 64 into 290; that is equal 543.75kg.

Now, weight of gangue, because the problem says gangue does not contain any copper sulphur or iron; the amount of copper sulphur and iron is 0 in the gangue; so, gangue will be equal to 1000 minus 201.25 plus 543.75. That will be equal to 255 kg. The weight of each mineral: $CuFeS_2$ is 201.25; FeS_2 is this one; and gangue is 255 kg. That is the answer for the part (a). Now the answer for the part (b); you have to find out oxygen required in cubic meter and moles of oxygen. I will give you the answer, straight away, because a similar problem, I have solved earlier. I will write down.

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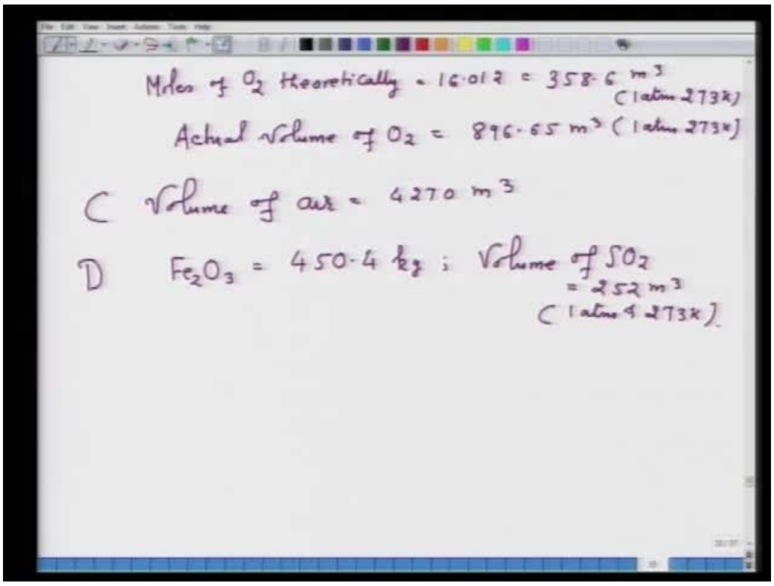

Moles of oxygen theoretically required; that will be equal to 16.012 and that is equal to 358.6 meter cube expressed at 1 atm and 273 Kelvin.

Now, this is theoretical, but it is said there is excess amount; so the actual volume of oxygen actual will be equal to the excess amount is 150 percent.

That is, actual amount of oxygen is 250 percent; so, actual amount of oxygen is equal to 896.65 meter cube, again expressed at 1 atmosphere and 273 Kelvin.

You can find out these, both way; either you can find out 358.6 plus 1.5 into 3.586; or you multiply 358.6 by 2.5, whichever way is convenient to you.

Now (c) part says volume of air; that is 4270 meter cube; (d) part says, what is the weight of a Fe_2O_3? Now you know the reactions, you can find out; I am giving the answer: weight of Fe_2O_3 is equal to 450.4 kg and volume of SO_2 is equal to 252 meter cube, expressed at 1 atm and 273 Kelvin.