Materials and Energy Balance in Metallurgical Processes

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Module No. # 01

Lecture No. # 17

Heat balance in Roasting illustration

Today, I will be talking about Heat balance in Roasting. This heat balance is a very important exercise, particularly in extraction of metal by Pyrometallurgical techniques, because Pyrometallurgy by name itself, it is done at very high temperature. Though roasting involves lower temperature, but around 900 to 1100 degree celsius temperature is required during roasting of any sulphide to oxide.

Now, why we should carry out heat balance? It is one of the important information that we would like to have. Before we design a reactor, what is the temperature attainted by the roasting product during roasting of a concentrate?

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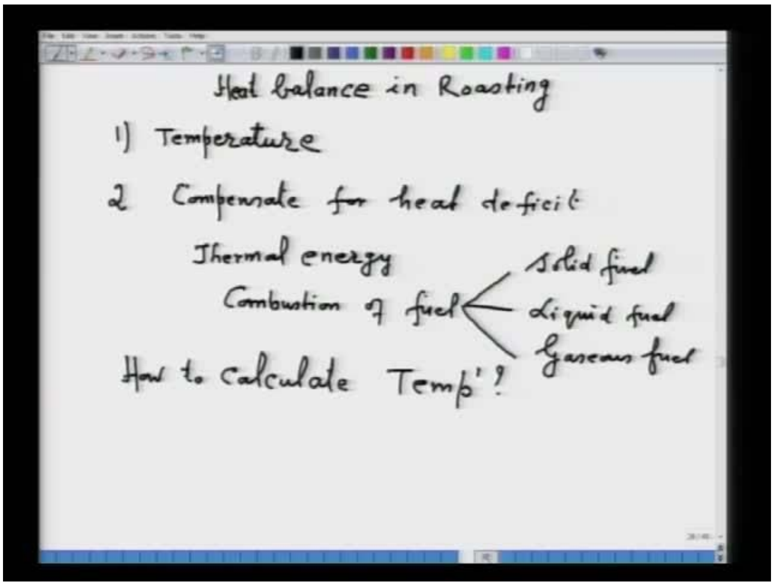

The first information that we would like to have is the temperature attainted by the roast product inside the reactor. Why this temperature is important? This temperature is important because you have to find out the material for the construction of the reactor. Now, material must be able to sustain that particular high temperature. It means that material should not fuse at that temperature.

In order to have this information, heat balance can tell us the temperature, which will be attained during roasting for given amount of input. So, this is one of the very important information that is required while designing a reactor for high temperature. For lower temperature, it may not be much of a problem for 300 or 400 degree celsius because you have enough choices of material. Once you cross 900 or 1000 or 1100 degree celsius, then the choices are very limited. You cannot afford to take only metallic reactor because the heat loss will be very high because of the higher thermal conductive of the metallic material. So, all that you would like to have is reflective material. Now, the question comes, the thermal stability of the material is important. Therefore, knowledge of the information about the temperature prior to design of the reactor for roasting is very important.

Second important information that we can derive from heat balance is compensating for heat deficit, if at all there is heat deficit. I mean the heat input from several sources, the heat output loss. In all these information, you are doing input and output calculation. If you find the difference between the two, it means heat output is more than the heat input and then you are required to supply the extra amount of thermal energy. Now that is again very important to compensate for the deficit. You have to supply thermal energy from outside source.

Now, what are the sources? The sources could be the combustion of fuel or electricity. The combustion of fuel then, one of the sources to meet the deficit of thermal energy is through combustion of fuel. Once you decide for combustion of fuel, then you have to know which type of fuel you want to use. Whether you want to use solid fuel, you want to use liquid fuel or you want to use gases fuel. Now, having decided the type of fuel, then you must make sure that sufficient quantity of this fuel is also available because you are not treating a kg or a ton reactor per day, you may be treating 100 tons or 1000 tons of concentrate per day. So, accordingly you have to have a reserve of the fuel, if extra amount of energy is need during roasting. So, these are some of the important information that can be obtained from heat balance.

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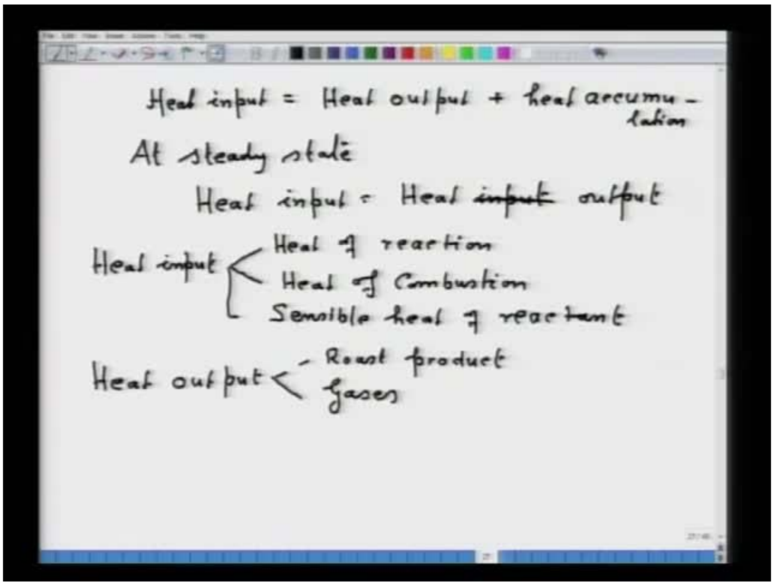

As I have mentioned the calculation of temperature, how to calculate temperature? Now, what this heat balance comprises? Heat balance comprises of heat input and it is equal to heat output plus heat accumulation. Now, you want to work at a particular temperature. That much amount of heat has to be retained in the reactor, so that you can perform your roasting operation. It means at a steady state, when the temperature of the reactor has come to the desired temperature of roasting and at that point; at steady state, heat input is equal to heat output.

Now, heat input is equal to heat output. In doing this balance, what is required? You must know all sources from where heat is entering into the system. For example, the heat input could be from heat of reaction, you must collect the data on the formation of compound or chemical reaction or whatever way you want to calculate. If combustion of fuel is required for deficit of energy, then heat of combustion is another way of heat input.

Suppose, you are heating the reactant to a particular temperature, it means you require sensible heat of reactant. If the reactant is supplied at 298 kelvin, then naturally heat of reactant will be equal to 0, but higher is the temperature, then you have to see what is the amount of rough sensible heat of reactant that is entering into the system. Now, in this heat balance calculation, one of the important things is that you have to declare the basis of all thermodynamic calculation as 298 kelvin. Heats of formation of compounds, heat of reaction are all given at 298 kelvin. So, it is more or less clear in all such calculation that the basis is 298 kelvin.

Now, after knowing the different sources of heat input, you also have to see heat output. For example, if you consider roasting, then heat output here is the roast product of the roasting reactor. You have to consider the heat taken by the roast product. Here, you have to see that you also get all the relevant values to calculate heat content in the roast product and the important value we need is the CP value. In heat output, roast product and gases are the 2 important outputs, while performing the roasting operation.

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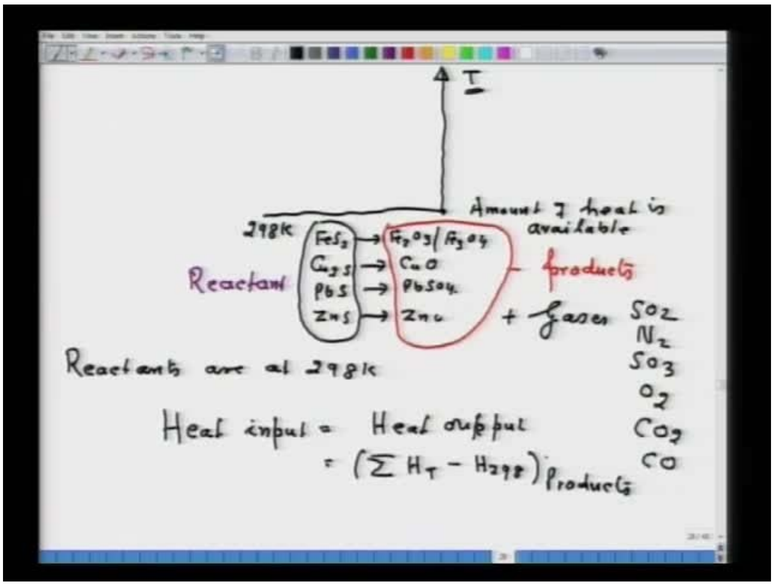

Now, if you want to calculate the temperature, then what we do? For example, we select a reference temperature as 298 kelvin. I supply the reactants at 298 kelvin. What will I do? I will carry out all the possible reactions at 298 kelvin and calculate the heat of reaction. I will write some of the reactions, for example, say FeS2 is converted to Fe2O3 or Fe3O4. Cu2S is converted to CuO. PbS is converted to PbSO4. ZnS is converted to ZnO. So, for all these reactions, you are required to calculate the heat of reaction. This side, I will call as the reactants and this side is the products.

Now, what we are considering here? The reactants are supplied at 298 kelvin. In this, reactants are at 298 kelvin and therefore, sensible heat of reactant is equal to 0 and that is why I have taken this as my reference point. So, at 298 kelvin, I have to carry out the reactions and these are the products that have been formed at this particular point.

Now, when these products are formed at particular point, certain amount of heat is accumulated, certain amount of heat is liberated or heat is available. I am telling it as liberated because these reactions are exothermic in nature, so that much amount of heat is liberated or that much amount of heat is available. When this much amount of heat is available, all the products will take heat from this and they will raised to a temperature, which is the temperature attainted by the products in combustion during roasting.

You should not forget that the roasting gives you roast product plus gases. I have not written and gases could be SO2, N2, SO3, excess oxygen and whatever the gases, which are present in the system. For example, CO2, CO depending upon the reactions that you are calculating. So, all these products will be raised to a temperature from the heat, which is available at 298 kelvin.

So, do you get a feel of how to calculate a temperature? First, from the given amount of reactant, you have to write down the roasting reaction. If nothing is specified, then you can write down the reaction by considering stoichiometry of the chemical reaction. If something is given, then you have to adjust according to what is… For example, problem can say that x percent SO2 and y percent SO3 is formed and so you have to adjust accordingly. After writing down those equations, the first thing you have to find the material balance. You have to know what amount of materials is being produced. Once you calculated the amount of material or amount of product or amount of gases, then you calculate the heat of reaction.

Then you will know the amount of heat liberated and then this whole thing you take it to a temperature T and that T can be calculated by making the balance. Heat input is equal to heat output and this output will have sigma H T minus H 298 of all products. Naturally, it will be equal to C P into dt integrated from 298 to T, so it is the total of all. One can calculate the temperature and this is what the scheme of calculation of temperature attainted during the roasting of sulphide.

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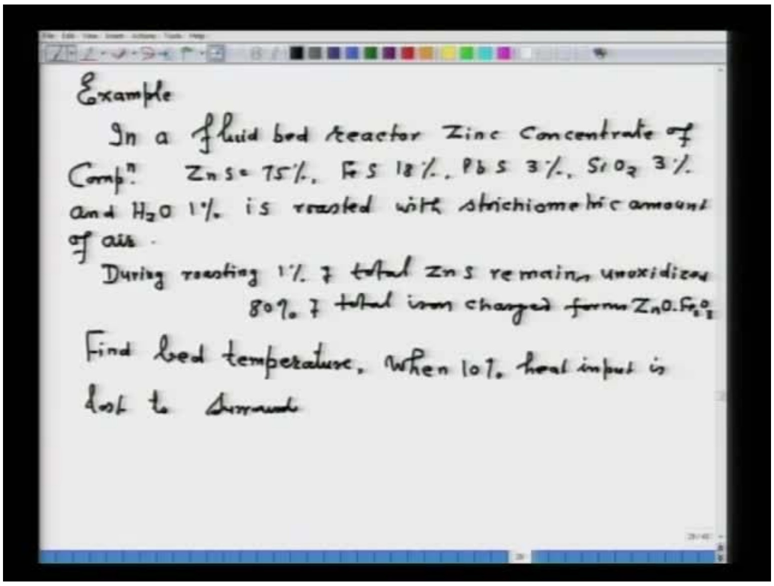

Now, let me give an example to calculate this temperature attainted. So, let me take an example, when I was telling to you about the roasting, I have said at that point of time that there is a fluidized bed roasting. Now, in the fluidized bed roasting, the reaction rate is very fast. Some of the company employs fluidized bed roasting.

The problem in a fluid bed reactor is that zinc concentrate of composition, let us say, ZnS is 75 percent, FeS is 18 percent, PbS is 3 percent, SiO2 is 3 percent and H2O is 1 percent is roasted with stoichiometric amount of air. Here, I am specifying with stoichiometric amount of air. Normally, in the fluidized bed roasting, the roast products are discharged from the other end of the reactor.

Now, some condition - during roasting, 1 percent of total ZnS charge remains unoxidized and this is one particular condition. Second, say, 80 percent of total iron charged forms ZnO into Fe2O3. What you have to do? Find the bed temperature, when 10 percent of the heat is lost to the surrounding. Naturally, when you are carrying out the reactors, some heat loss will be there and accordingly the temperature will be affected.

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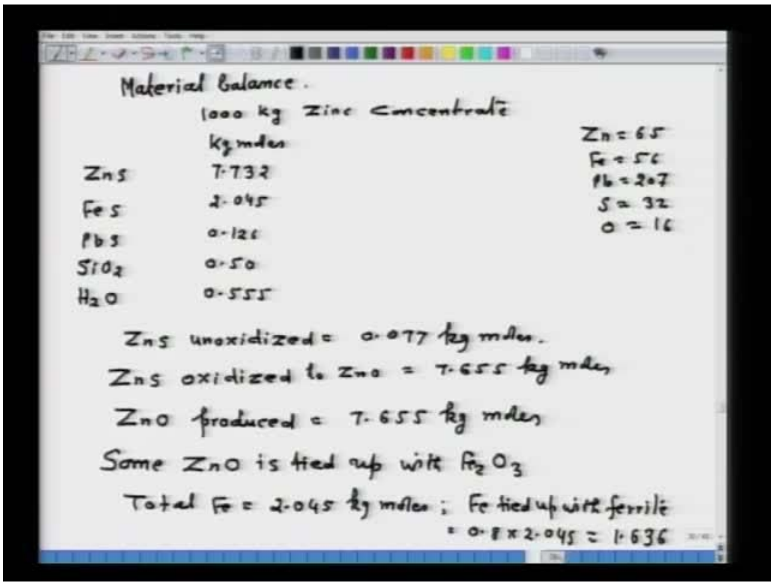

Now, we have to calculate the bed temperature in the fluidized bed. There is a bed, which is in the fluidized state and this is a technology for rapid conversion of sulphide to oxide. As usual, in all heat balance, material balance has to be done first. So, let us take material balance, we have taken 1000 kg zinc concentrate and let me put it kilogram moles. So, I know ZnS, Fes, PbS, SiO2, H2O.

Now, in this calculation, I am using zinc atomic weight as 65, iron has 56 and lead has 207, sulphur as 32 and oxygen as 16. So, I convert it to kg moles 7.732. I do not think it should be difficult. If you have the calculator, you please calculate along with me. PbS is 0.126, SiO2 is 0.50 and H2O is 0.555. Now, I am following the problem and calculating the amount of roast product. You can also follow the problem and calculate in your style and I will calculate in my style.

So, first of all, I say that ZnS unoxidized equals to 0.077 kg moles. ZnS oxidized to ZnO will be equal to 7.655 kg moles and that means 7.732 minus 0.077 is oxidized. So, total ZnO produced will be equal to 7.655 kg moles because 1 mole of ZnS forms 1 mole of ZnO. Now, the problem says ZnO is tied up with Fe2O3 and that you have to find out. Total iron charged is equal to 2.045 kg moles and of course, I am doing all calculations in kg moles. If I forget somewhere, you please see that I am writing 1 kg moles.

It says 80 percent of iron is oxidized and forms ferrite. So, iron tied up with ferrite will be equal to 0.8 into 2.045 and that will be equal to 1.636.

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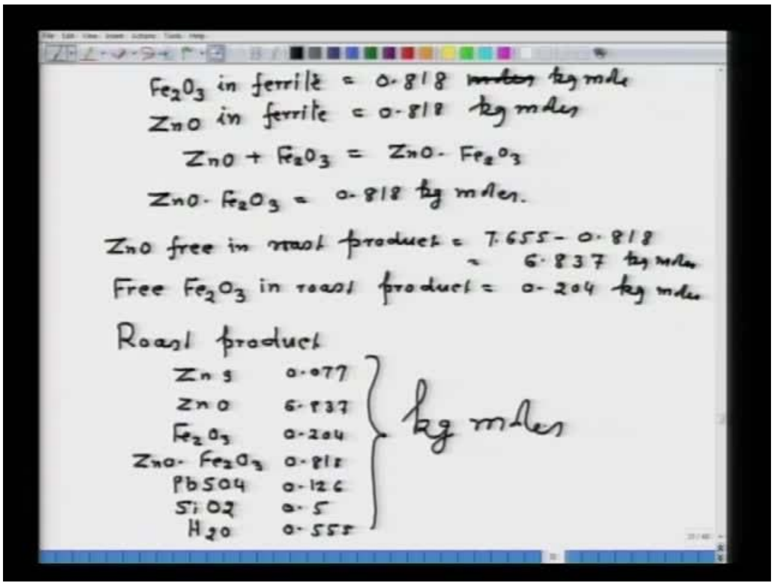

Now, we can find out for Fe2O3 in ferrite and that will be equal to 0.818 moles. ZnO in ferrite is equal to 0.818 kg moles and here also they are kg moles. Now, in these, the reaction, which is to be pursued is ZnO plus Fe2O3 is equal to ZnO into Fe2O3. According to this reaction, material balance has come and therefore, amount of ZnO, Fe2O3 is equal to 0.818 kg moles. ZnO, which is free in roast product will be equal to 7.655 minus 0.818 and that will be equal to 6.837.

Since some Fe2O3 will be free in roast product, it will be equal to 0.204 kg moles. They are all in kg moles, even if I forget somewhere, they are kg moles. Now, with that we know the amount of roast product. The roast product comprises of ZnS, ZnO, Fe2O3, ZnO into Fe2O3, PbSO4, SiO2, H2O. So, all the amounts known to us are 0.077, 6.837, 0.204, 0.818, PbSO4 is 0.126, SiO2 is 0.5, H2O is 0.555 and they are all in kg moles.

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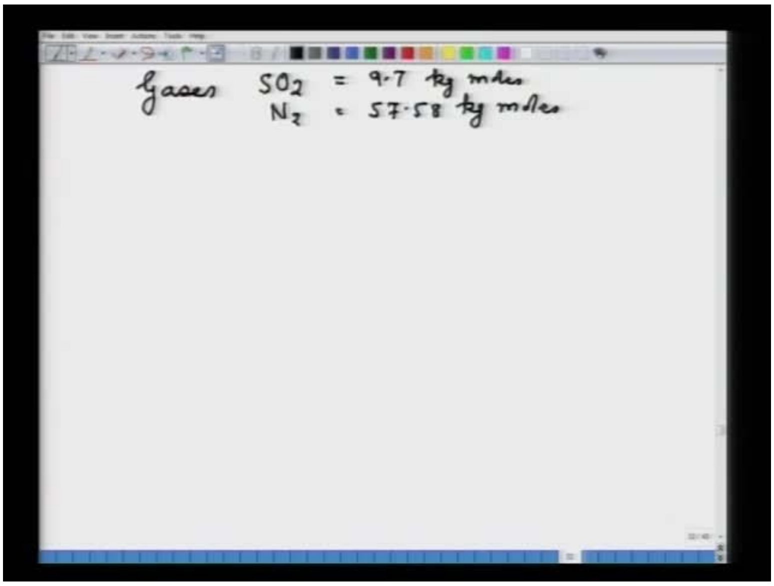

Now, we have to calculate gases also because they are all product. So, Gases will comprise of SO2 and nitrogen, which are unreactive. Now, I have already illustrated this during material balance. I will not go into the detail and so SiO2 will be 9.7 kg moles and nitrogen will be 57.58 kg moles.

Now, with this material balance, we are now in the position to do their heat balance. For the heat balance, we will be needing a large amount of data. The data that you need is the value of CP or the values directly in terms of H T minus H 298 of all the products. So, either you know the C P value of the product or H T minus H 298 in terms of T of all the products. You should also know the heat of reaction of all the chemical reactions, which are occurring. What have I done? I have prepared a slide and the slide shows the values of various heat content of the products as well as heat of reaction.

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Material And Heat Balance In Roasting

$H_T - H_{298}| ZnO = 11.71T + 0.61 \times 10^{-3}T^2 + 2.18 \times 10^5 T^{-1} - 4277$ kcal/kg.mol

$H_T - H_{298}| ZnS = 12.16T + 0.62 \times 10^{-3}T^2 + 1.36 \times 10^5 T^{-1} - 4137$ kcal/kg.mol

$H_T - H_{298}| Fe_2O_3 = 31.71T + 0.88 \times 10^{-3}T^2 - 8446$ kcal/kg.mol

$H_T - H_{298}| ZnO.Fe_2O_3 = 27.71T + 8.86 \times 10^{-3}T^2 - 9044$ kcal/kg.mol

$H_T - H_{298}| PbSO_4 = 10.96T + 15.5 \times 10^{-3}T^2 - 4.20 \times 10^5 T^{-1} - 3327$ kcal/kg.mol

$H_T - H_{298}| SiO_2 = 14.41T + 0.97 \times 10^{-3}T^2 - 4455$ kcal/kg.mol

$H_T - H_{298}| SO_2 = 11.04T + 0.94 \times 10^{-3}T^2 + 1.84 \times 10^5 T^{-1} - 3992$ kcal/kg.mol

$H_T - H_{298}| N_2 = 6.83T + 0.45 \times 10^{-3}T^2 + 0.12 \times 10^5 T^{-1} - 2117$ kcal/kg.mol

$H_T - H_{298}| O_2 = 7.16T + 0.50 \times 10^{-3}T^2 + 0.40 \times 10^5 T^{-1} - 2313$ kcal/kg.mol

$H_T - H_{373}| H_2O_{(g)} = 7.30T + 1.23 \times 10^{-3}T^2 - 2286$ kcal/kg.mol

$H_2O_{(l,298)} = H_2O_{(g,373)}$ $\Delta H = 11170$ kcal/kg.mol

$ZnS + 1.5O_2 = ZnO + SO_2$ $\Delta H_R = -105950$ kcal/kg.mol ZnO

$PbS + 2O_2 = PbSO_4$ $\Delta H_R = -197000$ kcal/kg.mol $PbSO_4$

$ZnO + Fe_2O_3 = ZnO.Fe_2O_3$ $\Delta H_R = -4750$ kcal/kg.mol $ZnO.Fe_2O_3$

$2FeS + 3.5O_2 = Fe_2O_3 + SO_2$ $\Delta H_R = -292600$ kcal/kg.mol Fe_2O_3

Now, for example, if you see the slide, it shows H T minus H 298 for zinc oxide. Similarly, H T minus H 298 for zinc sulphide and mind that is given in terms of temperature. Then H T minus H 298 for Fe2O3, ZnO into Fe2O3, nitrogen, sulphur dioxide, H2O are given. As you can see from the slide, it also gives the value of the heat of reaction.

Now, the various heat of reaction values are given on the slide. You can see ZnS plus 1.5 O2 is equal to ZnO plus SO2. The values of delta H R are given at 298 kelvin. Similarly, PbS plus 2 O2 is the chemical reaction and this value is also on this slide. ZnO into Fe2 O3 value of the heat of formation is also on the slide. 2FeS plus 3.5 O2 is equal to Fe2O3 plus SO2 and that value can also be see on the slide.

The slide very clearly shows all these value. Now, on the slide, I have also given you the values of H T minus H 298, in terms of T square and 1 by T. If you see the slide, you will find, for example, H T minus H 298 for ZnO says 11.71 T plus 0.61 into 10 to the power minus 3 T square plus 2.18 into 10 to the power 5 upon T minus 4277. Now, the calculation, which I am going to do is ignore 1 by T term, in order to illustrate the temperature attainted by the products in combustion. So, I can finish my lecture in time.

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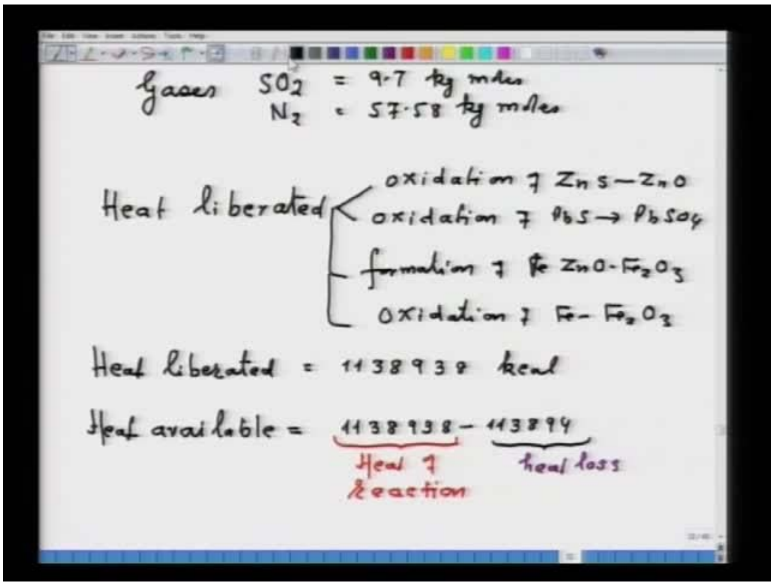

So, with those values, I can calculate heat liberated. Now, heat liberated will be oxidation of ZnS and that is one thing. Oxidation of ZnS to ZnO is the reaction that I have already shown you on this slide. Oxidation of PbS is PbSO4, then formation of ZnO into Fe2O3 is this one and then oxidation of Fe to Fe2O3 has no reaction. So, one can calculate heat liberated because of the chemical reaction. I am not substituting, but you can directly substitute the values.

It is simply the multiplication because the values are given in kilocalorie per kg mole. All of you know the heat liberated that will be equal to 1138938 kilo calorie and that is the heat liberated through oxidation reaction during roasting. Now, the problem also says that 10 percent of the heat is lost. Therefore, the heat available will be equal to 1138938 minus 113894. I am rounding off the last digit and so, this comprises heat loss and this one has the heat of reaction.

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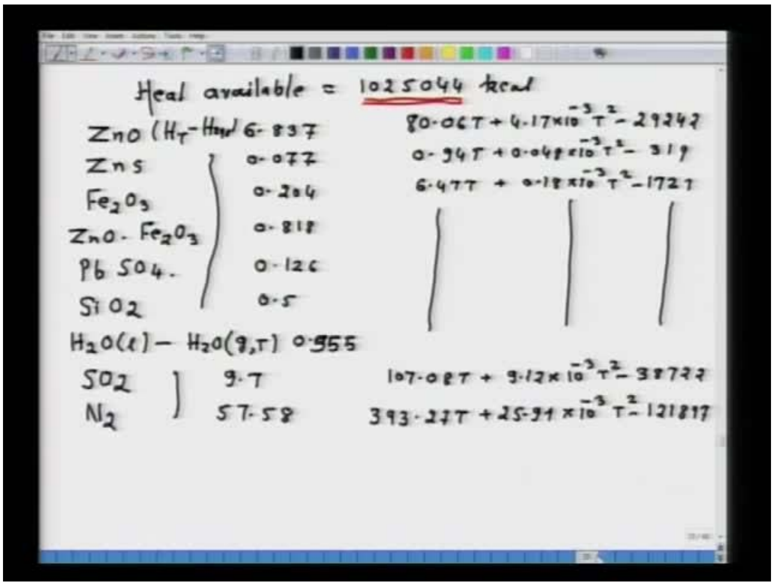

Now, the heat available would be just I subtract it so heat available I have to write again here heat available that will be equal to 1025044 kilo calorie. So, this much amount of heat is available, which will be utilize by the product to raise the temperature from 298 kelvin because our reference temperature was 298 kelvin. The product will be raised from 298 kelvin to a temperature, which we have to calculate. We will now calculate all the values of the heat output. Heat output 1 will be by ZnO, ZnS, Fe2O3, then we have ZnO into Fe2O3, PbSO4, SiO2, H2O liquid. H2O liquid is transferred to H2O gas at a given temperature T, you have SO2 and nitrogen. So, all these values have to be multiplied by the kg moles, which I have already given.

I can write it down once again as ZnO, it is 6.837 and has to be multiplied by value of H T minus H 298 for Zn. From this slide, ZnS is 0.077, Fe2O3 is 0.204, ZnO into Fe2O3 is 0.818, PbSO4 is 0.126. This (Refer Slide Time: 33:19) is 0.5 and the moles are 0.555 SO2 moles are 9.7 and nitrogen moles are 57.58. You have to multiply, for example, I can write for ZnO, the value will be 80.06 T plus 4.17 into 10 to the power minus 3 T square minus 29242. Another example for ZnS is 0.94 T plus 0.048 into 10 to the power minus 3 T square minus 319. Similarly, for Fe2O3 that will be 6.47 T plus 0.18 into 10 to the power minus 3 T square minus 1723. Similarly, one can write down for all.

In the same way, you can write down, for example, the values for SO2 will be 107.08 T plus 9.12 into 10 to the power minus 3 T square minus 38722. For nitrogen, this value is very important and has a very high value 393.27 T plus 25.91 into 10 to the power minus 3 T square minus 121897, all these values are in kilo calories. Now, we have calculated this H T minus H 298 for ZnO, ZnS. All these values, what I calculated here can be just put as H T minus H 298.

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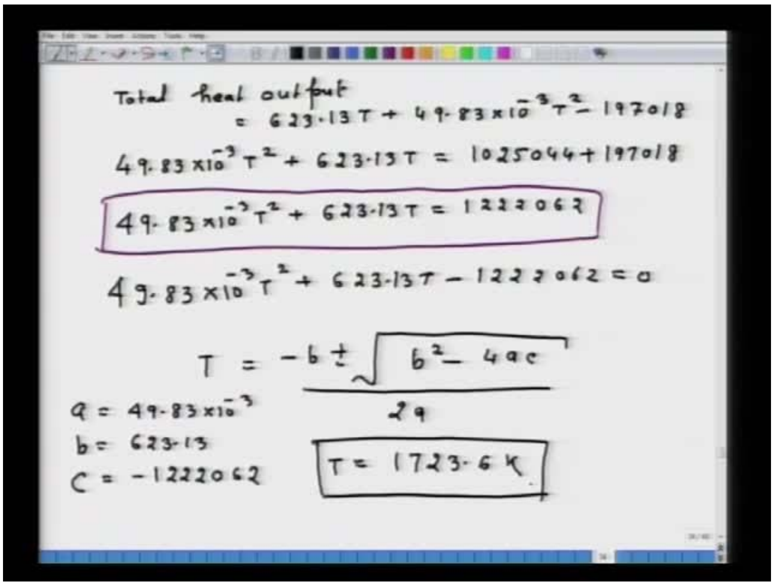

Now, we can total all these values. If you have some total heat output, it will be equal to 623.13 T plus 49.83 into 10 to the power minus 3 T square minus 197018. Now, remember in this illustration, the values I have calculated by ignoring 1 by T terms in H T minus H 298, which you have seen in the slide. Remember, again and again I am repeating this for the illustrating purposes, I have neglected the term 1 by T the values. It may be slightly in accurate, but it may not make much difference. For exact calculation, you have to take all the terms, which are given on the slide for H T minus H 298. For illustration, again I am repeating, I am neglecting the 1 by T term and so please note it.

This heat input must be equal to heat output. So, I will get and rearrange the equation that is 49.83 into 10 to the power minus 3 T square plus 623.13 T equal to the calculated heat input as 1025044 plus 1970108, as you have heat input equal to heat output. So, we will be getting the equation, which we have to solve as 49.83 into 10 to the power minus 3 T square plus 623.13 T and that is equal to 1222062. Now, mind T is in kelvin and now all of you know that this equation is a quadratic equation. This equation is a quadratic equation of the type a x square plus b x plus c. It is equal to 0 and we can also transform into that particular form. It will become 49.83 into 10 to the power minus 3 T square plus 623.13 T minus 1222062. That is equal to 0 and T will be from here, it is minus b plus minus b square minus 4 a c upon 2 a, where a is equal to 49.83 into 10 to the power minus 3, b is equal to 623.13 and c is equal to minus 1222062.

Now, it requires substitution, if I do it, T will be equal to 1723.6 kelvin. This is the answer, when stoichiometric amount of air is used and this temperature is very high. So, this calculation suggest you what should be the material of construction and what should be done. Now, I may tell you here, since I have neglected 1 by T term in H T minus H 298, I hope that if you include that particular term, the temperature could be could be around 30 or 40 degree or more. So that is the illustration for stoichiometric amount. Now, the question comes, what happen if we take excess? Remember, roasting is a solid state reaction, the reactants are in the solid state and products are also in the solid state.

If you happen to know the details of kinetics of solid reaction, then the rate of reaction is relatively slow as compared to liquid liquid reaction, gas liquid reaction and gas solid reaction. So, solid solid reactions are extremely slow. If you want to carry out roasting by the stoichiometric amount, the roasting will not be complete. The reason is simple because 1 mole of oxygen will be carrying 3.76 moles of nitrogen in order to form 4.76 moles of air. So, when a reactant comes into contact with air, then the chances are there. It will always find nitrogen compared to oxygen and the probability of finding nitrogen is more as compared to the probability of finding oxygen. Therefore, the stoichiometric amount of air, which is used for roasting is good to calculate.

It is good to do the calculation, but normally excess amount of air is always used. What happens, if you use excess amount of air on the temperature attaint by the roast product? So, this I am going to illustrate now. Suppose, we take that excess air is 20 percent how was if we take now excess air that is equal to 20 percent. Now, once we have taken the excess air as 20 percent, then our material balance is not valid; particularly in case of gases. It is because the roast product, the material balance will be valid, but in case of Gases, we again have to do material balance. How much amount of Gases is coming?

SO2 amount will be affected because S plus O2 is equal to SO2, it will react in that stoichiometric amount. Now, the gases will include SO2, N2 and O2. So, now we have to recalculate all these values. If you calculate, SO2 will be same, as we have calculated for stoichiometric amount. Now, you have to recalculate nitrogen because now 20 percent excess air. So, the nitrogen will be 69.1 and they are in kg moles. Other change will occur because you are raising 20 percent excess air in the stoichiometric amount and the gases comprises of SO2 and N2.

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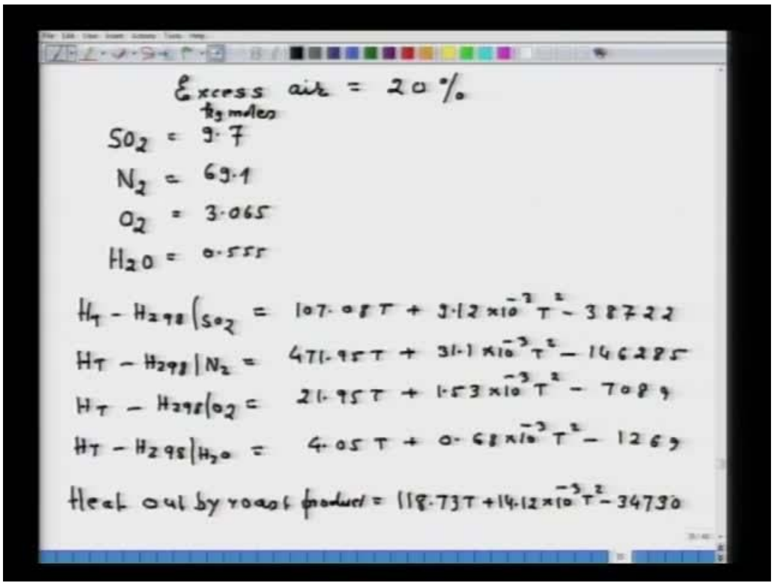

Now here the gases will comprise of SO2, N2 and excess oxygen. The excess oxygen will be equal to 3.065 plus moisture equals to 0.555. The amount is same as it was earlier and there is hardly any change. So, with this modified material balance of the gases, we have to recalculate the H T minus H 298 for nitrogen, oxygen, SO2 and H2O and we can take it from the stoichiometric amount.

So, I am doing it, for example, if I write H T minus H 298 for SO2, I am borrowing from stoichiometric amount and it was 107.08 T plus 9.12 into 10 to the power minus 3 T square minus 38722. Now, I have to calculate for H T minus H 298 for nitrogen and that will be 471.95 T plus 31.1 into 10 to the power minus 3 T square minus 146285. Similarly, I have calculated H T minus H 298 for oxygen, which was not earlier and it has an additional amount. It is equal to 21.95 T plus 1.53 into 10 to the power minus 3 T square minus 7089. Of course, I am borrowing moisture, H T minus H 2 98 for H2O. I can use my earlier value that is 4.05 T plus 0.68 into 10 to the power minus 3 T square minus 1269. So, these are the values here, SO2 and H2O, they are the value from the stoichiometric amount. Nitrogen and oxygen are the modified values. So, we can take the same value for heat out by roast product and that will be equal to the one as we have calculate earlier as 118.73 T plus 14.12 into 10 to the power minus 3 T square minus 34730.

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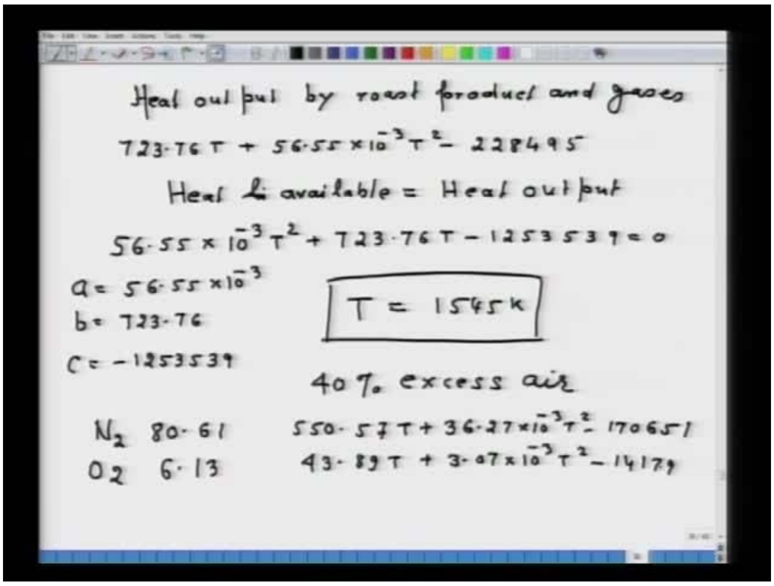

Now, in heat output by roast gases, we will total everything. So, this will be equal to 723.76 T plus 56.55 into 10 to the power minus 3 T square minus 228495. Now, we do that heat input or heat liberated or heat available. We can better write it as heat available because it contains the losses also and that will be equal to heat output. We have already calculated heat available. If I do that balance and I restructure the equation in terms of the quadratic equation, then I will get the final equation, which is 56.55 into 10 to the power minus 3 T square plus 723.76 T minus 1253539. It is equal to 0 and again it is a quadratic equation solution and I have given already.

Here, the value of a will be equal to 56.55 into 10 to the power minus 3, value of b will be equal 723.76, value of c will be equal to minus 1253539. If I use the solution of the quadratic equation, then the value of T will be around 1545 kelvin. So, just by taking a 20 percent excess air, the temperature drops to the order of 200 kelvin. The reason is quite obvious, there is no change in the roast product. The only change is the additional amount of nitrogen and oxygen. They will also take away the heat and as a result of which, the temperature decreases to 1545 kelvin. The temperature is still very high temperature. Suppose, if you take 40 percent excess air, obviously, it is a common sense that if we increase the amount of excess air, the temperature will drop because large amount of nitrogen will be created. Additionally, oxygen will also be created and they will all take away the heat, which is available and naturally the roasting or the product temperature will decrease.

For example, if I take 40 percent excess air, then the roast product's heat output, SO2 heat output, moisture heat output will all be the same. The only thing is that the nitrogen moles will be 80.61 and oxygen moles will be 6.13; mind, these are the additional. They are the modified form of material balance for the gases. If I calculate H T minus H 298 for nitrogen, it will be 550.57 T plus 36.27 into 10 to the power minus 3 T square minus 170651. For oxygen, it will be 43.89 T plus 3.07 into 10 to the power minus 3 T square minus 14179.

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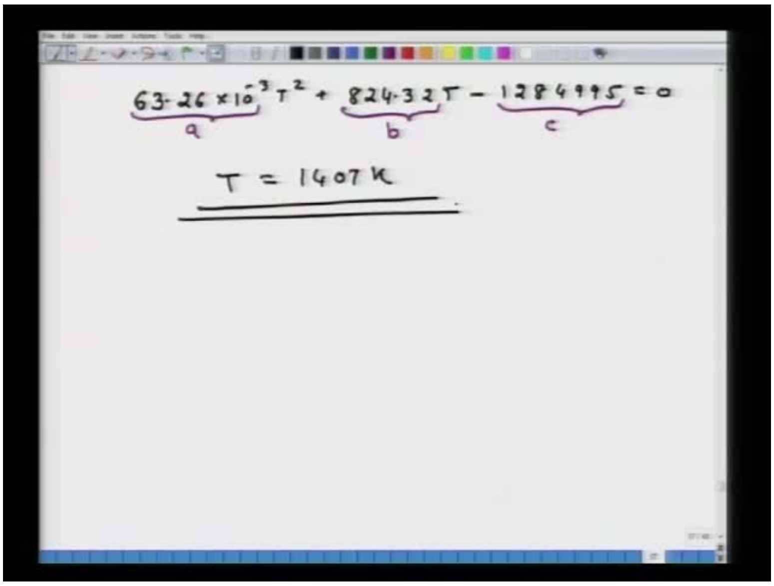

So, I am arranging the equation in a quadratic form. It will be 63.26 into 10 to the power minus 3 T square plus 824.32 T minus 1284995 and that is equal to 0. You know that the value of this is a, this is the value of b and this is the value of c, including its minus sign. If you calculate, then you see the temperature reduces further to 1407 kelvin.

So, what we have learnt today? Heat balance can lead us to a very important parameter for the design of a reactor and that is the temperature. From here onwards, I can find out what should be the material of constructions for the reactor design. In case of roasting, the material should be able to sustain at least a temperature of the order of 1407 kelvin. If we believe on the calculations and assumption that we have made, it helps to design the roasting reactor and that is the importance of heat balance calculation.