Materials and Energy Balance in Metallurgical Processes

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Module No. # 01

Lecture No. # 07

Exercise on Thermochemistry and Frequently Asked Questions

Sir, I have some doubts.

Please.

Can you tell me the significance of delta H naught?

Delta H naught is the heat, which is calculated at reference temperature and it is 298. So, you can either write it as delta H naught or you can also write as delta H 298. It simply says that this heat of reaction is calculated at the reference temperature, which is there in all thermodynamic calculation and it is taken as 25 degree celsius or 298 kelvin.

Sir, is it necessary to include latent heats in calculation of delta H, while calculating at measuring or boiling points of material?

It depends. Now, I will give you an example.

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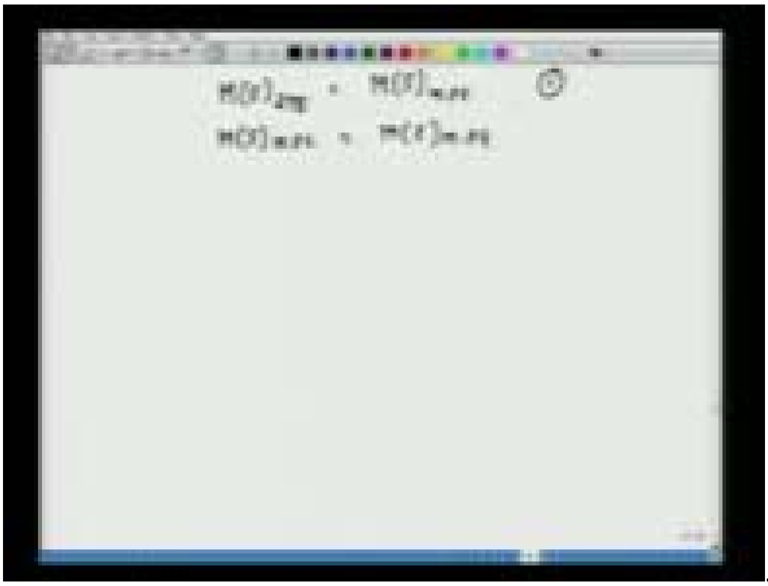

Suppose, you want to calculate the heat content, for example, I take a metal, which is solid at 298 kelvin and I want to calculate heat content. For example, a metal, which is also solid at melting point, this is one situation. In another situation, when I take a metal, which is solid at melting point and that is equal to M liquid at melting point. I hope this is your question.

Now, suppose, if I calculate or If I want to calculate heat content in the first case, then definitely latent heat will not be included because a metal or material or any compound. It is not melting, it is simply solid at the melting point. So, there you do not need to include the latent heat. Similarly, in the case of latent heat of vaporization, whichever the case may be. Whereas is in the second case, where the metal at the melting point is transferring into metal at liquid at the melting point. So, there you have to consider the latent heat of melting or latent heat of vaporization, if M l at melting point is transferring to M l at the vapor point. You should also know or you should also note that when the liquid melts, temperature does not change and that is what in fact, the latent heat means. Say, if you consider the thermal latent heat, it is the heat, which is latent and it is formed. It is because of the disruption of the bonds in the solid and making everything free in the liquid. So, at that transformation the temperature does not change and that is important.

Sir, will heat of formation be different, when calculated from different compounds or from pure element?

Yes, if you just imagine, you are forming a compound using pure elements. Let us take any example, for example, you want to form calcium carbonate. You can form calcium carbonate by using calcium carbon and oxygen. Definitely, you will require very large amount of heat, when you form from calcium oxide and CO2. I can illustrate this again by giving an example.

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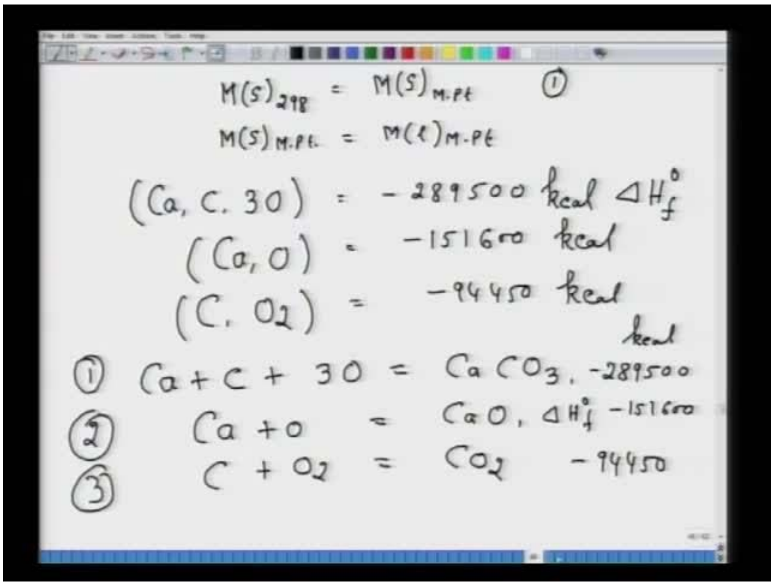

For example, I have taken an example of calcium carbonate. So, let us form calcium carbonate Ca, C, 3O as heat of formation minus 289500 kilo calorie and this is delta H naught f; heat of formation, when calcium carbonate forms from Ca, C, 3O. Now, again I take an element, for example, I now take calcium, oxygen and that has heat of formation minus 151600 kilo calories. C, O2 and that will be equal to minus 94450 kilo calories.

Now, your question is- for example, if I want to form calcium carbonate by using CaO in CO2, will the heat of formation be same or different? So, now let us see, if I form a Ca plus C plus 3O and that is equal to CaCO3, where delta H naught f is minus 289500. Let me write down again minus 289500 kilo calorie. Now, let me form - it is a Ca plus O and that is equal to CaO and delta H naught f. It is equal to minus 151600. Similarly, then C plus O2 is equal to CO2 and here it is minus 94450. (Refer Slide Time: 05:53) Now, if I subtract, say, take this equation as 1, this is a 2 and this is a 3.

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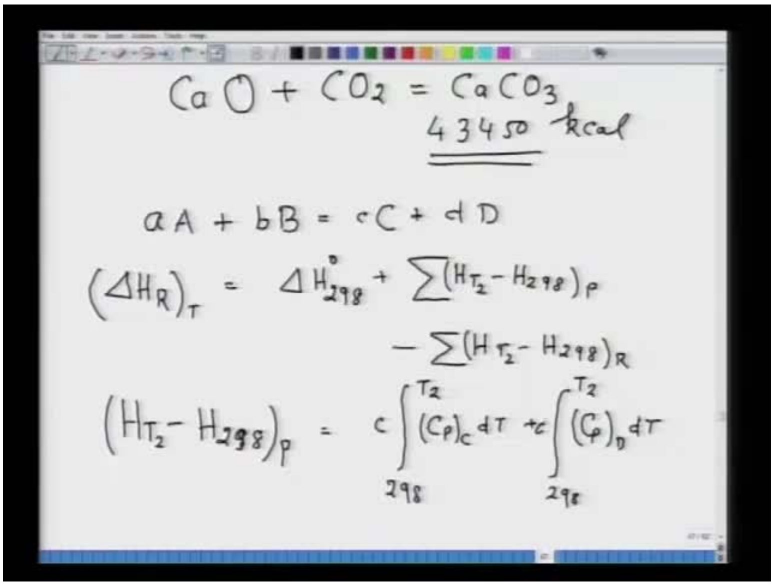

Now, if I use equation 1, 2 and 3 all together and try to form an equation, which is CaO plus CO2, then I calculate by subtracting this heat of formation for the formation of calcium carbonate. It will be equal to 43450 kilo calorie So, note that when calcium carbonate is forming from compounds like CaO and CO2, then heat of formation is much less as compared to its formation from the pure elements. So, for that the case, I will illustrate these things one more time, while taking the example.

Sir, can you derive the formula of heat of reaction at high temperature using delta C p?

Yes, for that let us take an example, a A plus b B is equal to c C plus d D, where small a, small b, small c and small d are the moles of the respective reactants and product. Now, if I want to find out delta H R at temperature T, which is other than 298 kelvin and this will be equal to delta H naught 298 plus summation of H T 2 minus H 298 of all products minus H T 2 minus H 298 of all reactants. Now, we can calculate, for example, I want to calculate H T 2 minus H 298. Now, this H T 2 minus H 298 is calculated for all the products and as well as for all the reactants.

So, if I see on the product side, I have c into C plus d into D. so, H T 2 minus H 298 for each product, I have to calculate. So, for example, if I say for all product, then this will be equal to c moles integration from 298 to T 2, C p c dT plus integration from 298 to T 2 C p D dT. Now, this is the - which is one right sorry sorry, it has to be multiplied by the mole say d into D. So, this becomes the heat content in the product.

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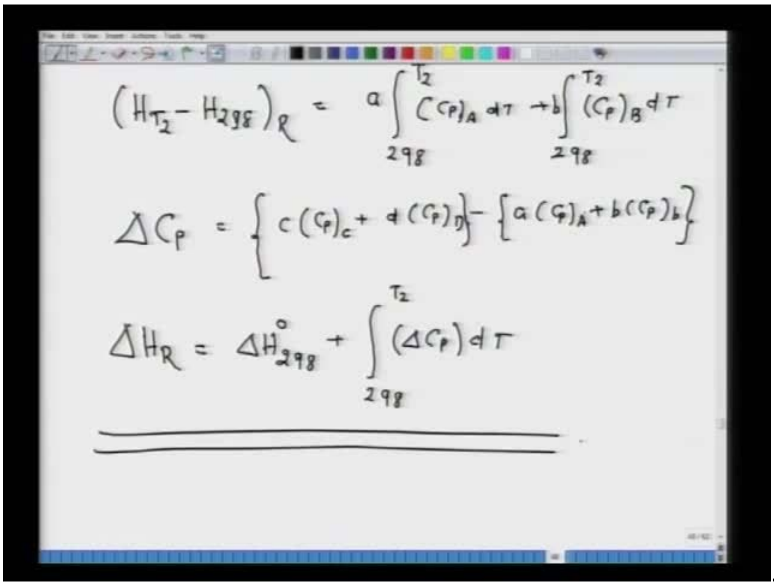

Now, similarly, I can calculate for reactant also. H T 2 minus H 298 for all reactants and that will be equal to a into 298 to T 2, C p A dT plus 298 multiplied by the moles to T 2 C p B to dT. So, I can also calculate delta C p. Now, delta C p will be equal to C into C p c plus d C p D minus a C p A plus b C p b. Delta H R is equal to delta H naught 298. Well, you can write as 298 or naught, but once you put the superscript as naught, it means, it is at the reference temperature delta H naught 298 plus 298 to T 2 delta C p into dT. So that is how you can evaluate the heat content at temperature other then 298 kelvin. You can evaluate in this way or in the way as I said in the lecture that we saw. Any other question?

No Sir.

Thank you.

Now, when there is no question, I will proceed with the solution of the problem. So, first of all, what will I do? I will give you the problems and then I will follow the solution one by one.

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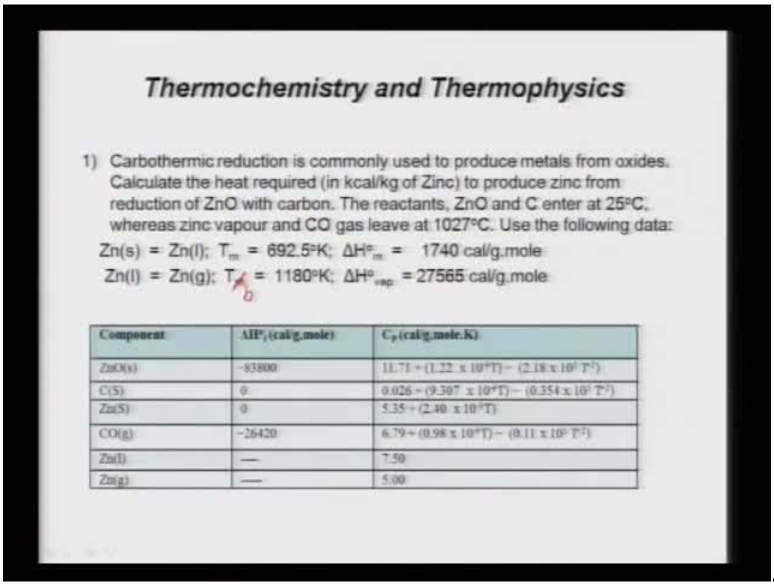

So, here are some of the questions. Question 1 - Carbothermic reduction is commonly used to produce metals from oxides. Now, in the pyrometallurgical extraction, reduction of oxide is commonly done to produce liquid matter. Typical example is that of iron making, where Fe2O3 is reduced by carbon. Another example is production of zinc by using carbon because carbon is abundantly available. It is cheap and it economically works better, while producing metal using carbon as a reductant.

Calculate the heat required in kilo calorie per kg of zinc. Remember, I did not ask kilo calorie per kg mole, but kg of zinc to produce zinc from reduction of ZnO with carbon. The reactant ZnO and carbon enters at 25 degree Celsius; whereas, zinc vapour and CO gas leave at 1027 degree Celsius. Now, remember zinc is produced in the form of vapour and not as a liquid. Use the following data: ZnS, whether the liquid melting point is given or latent heat is given. Similarly, zinc liquid, zinc gas, boiling point; Tb. Tb stands for boiling point, which is 1180 K and latent heat of vaporization even which is that is…

Now, remember to simplify the problem. We have given you the values of heat of formation of the oxides as well as C p value. In fact, while proceeding any thermodynamic calculation, one has to be very careful about the data you need to calculate the problem. Now, for example, if I just stop by not giving the data, then probably you have to think about what data you will need to solve the problem, but for simplification, I have given all the data, which will be required for solution of the problem. Normally, when you perform heat balance in any unknown situation, then you have to think about what data you will need. It is a very important exercise in calculation or in the thermodynamic calculation. So, here ZnO, carbon, zinc CO, ZnS, heat of formation, C p values are given. This is the problem number 1.

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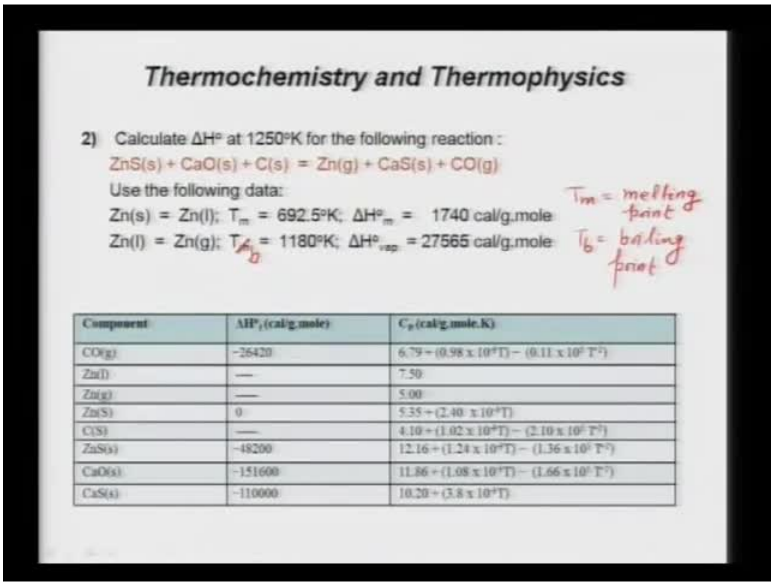

Problem 2 - Calculate heat of formation at 1250 kelvin for the following reaction: zinc sulphide plus CaO plus carbon zinc gas plus calcium sulphide solid plus CO gas.

Here, zinc solid to zinc liquid melting point is given. In zinc liquid to zinc gas, instead of melting point, it is the boiling point and T b is the boiling point. T b is equal to boiling point, where T m is equal to melting point and so all the data is given. Now, you have to find out the heat of formation at 1250 kelvin. I have just now explained, how to calculate and here is a problem to calculate the heat of reaction. Various values of C p are given and the data is with you.

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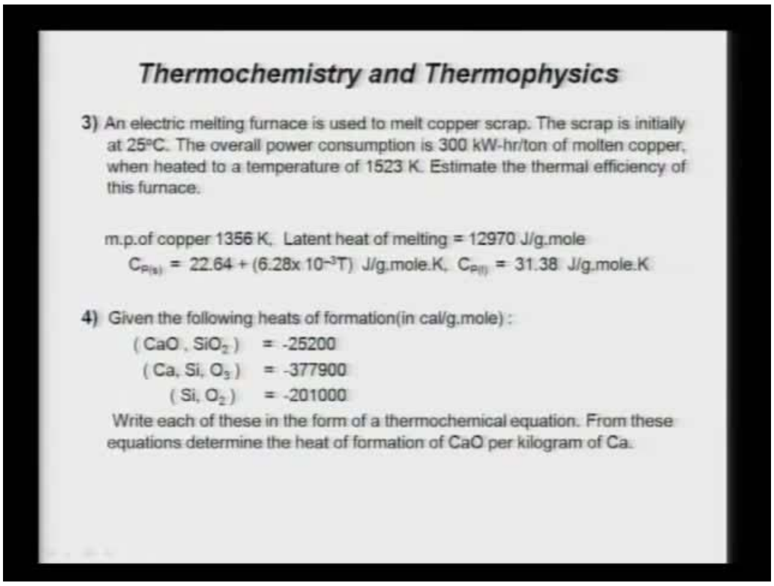

Let us go to problem 3 – It says, an electric furnace is used to melt copper scrap. Now, this particular problem tells you that straight away application of the calculation of the heat of reaction or for production purposes. So, this problem is based on this. Electric furnace is used to melt copper scrap. Scrap is initially at 25 degree Celsius. The overall power consumption is 300 kilo watt hour per ton of molten copper, when heated to a temperature of 1523 kelvin.

Now, copper is heated from 298 kelvin to 1523 kelvin. It is in that process of heating from 298 kelvin to 1523 kelvin, the power consumption is 300 kilo watt hour per ton. Estimate the thermal efficiency of the furnace, the data are again given: melting point of copper is 1356. So, you must be note here that we are heating to a high temperature; 1523 kelvin. So, first of all, you need the melting point of copper, while we naturally need that. In the absence of this data, you should also think that you would require the latent heat of melting and as well as the C p value of liquid copper. This is an important thing and I mean you should know what values you need before you begin to calculate.

Now, here, I have given all the values, but in unknown problem, again I am stressing this as the main issue. In various thermo dynamic calculations, many times, you do not get the data. You have to estimate the data and search the data. So, it is an important thing and C p and everything is given.

Now, problem 4 - The following is given: heat of formation in calorie per gram mole. CaO, SiO2 and this one Ca, Si, O3 and SiO2 is given to you. Write each of these in the form of a thermochemical equation. From this equation, determine the heat of formation of calcium oxide per kilogram of calcium.

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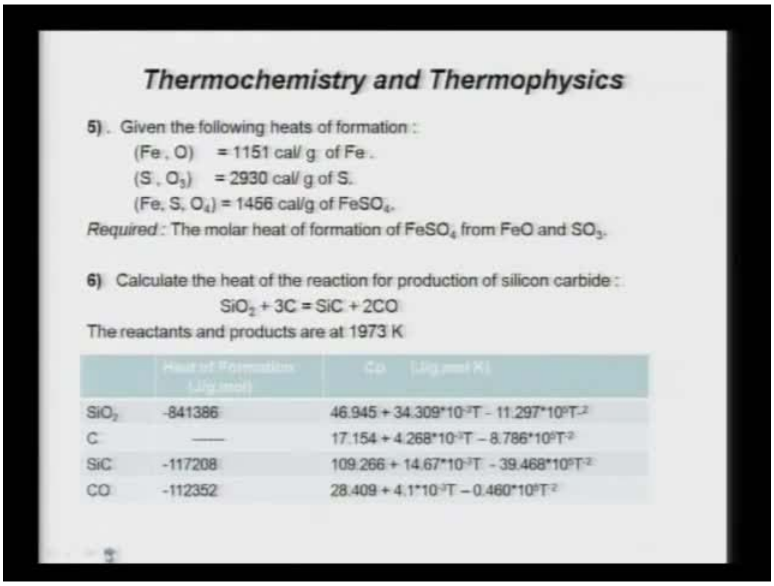

Take the next problem, given the following: heat of formation of (Fe, O), (S, O3), (Fe, S, O4). The required molar heat of formation FeSO4 from FeO and SO3. Now, here you must have noted that this problem is… Just now, I had explained about the calculation of calcium carbonate. So, this is another problem for calculating the molar heat, when FeSO4 from two different components.

Problem 6 - Calculate heat of reaction for production of silicon carbide. The reactants and products are at 1973 kelvin. Again the values are given and you should calculate.

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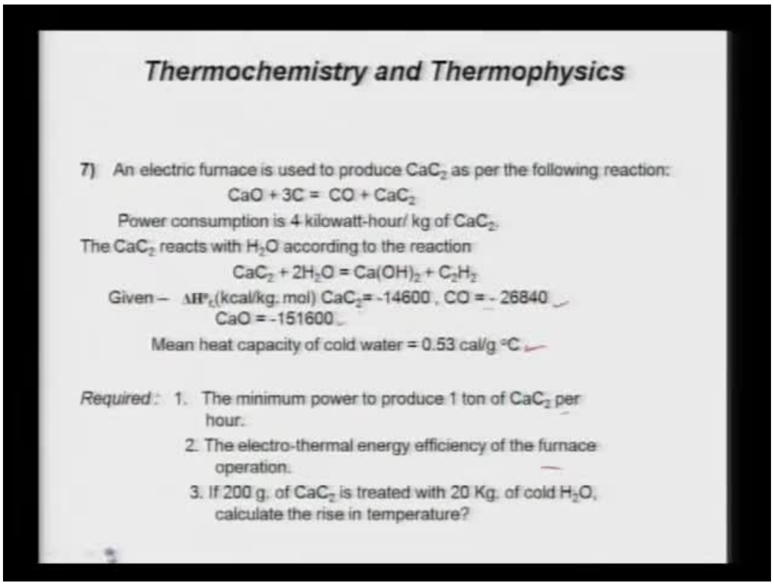

Problem 7 - An electric furnace is used to produce calcium carbide for the following reaction: power consumption is given, the calcium carbide reacts with H2O. According to the reaction here, (Refer Slide Time: 18:58) the thermodynamic values are given. You have heat of formation of calcium carbide, calcium monoxide and calcium oxide. Mean heat capacity of cold water is given and so you have to answer the minimum power to produce 1 ton of calcium carbide, the electro thermal efficiency. If 200 gram of calcium carbide is treated with 20 kg of cold water; note 20 kg and not 20 gram, calculate the rise in temperature.

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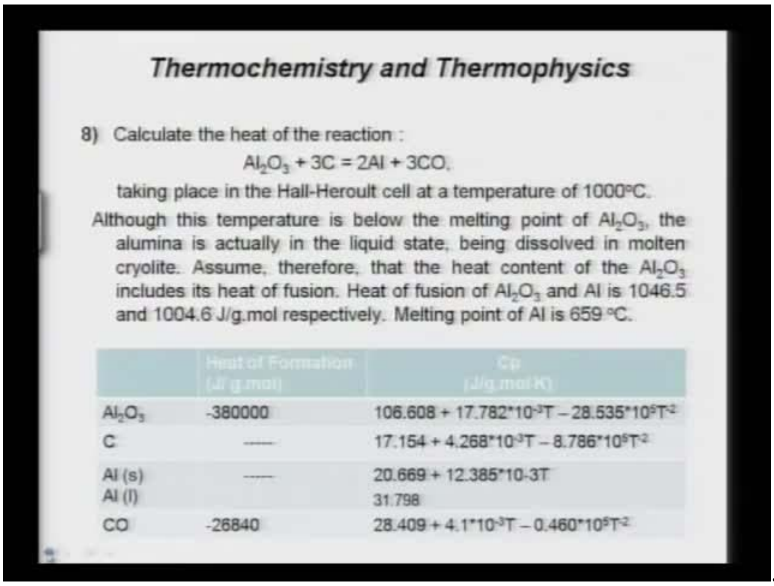

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The last problem - Calculate the heat of reaction Al2O3 plus 3C and it is equal to 2Al plus 3CO. Now, before this, I have to tell little bit about this reaction or what happens in the Hall-Heroult cell; the electrolysis of Al2O3 is done. Al2O3 has a very high melting point and therefore to bring Al2O3 in the liquid form, a cryolite is used and with the presence of cryolite, the Al2O3 dissolves at very low temperature. Otherwise, melting point of Al2O3 is 2500 degree Celsius, when cryolite is used. Then Al2O3 dissolves at around 1000 degree celsius and electrolysis is possible. So, this problem addresses to the electrolysis of aluminum.

Just a short introduction about the electrolysis of aluminum, calculate the heat of reaction taking place in the Hall-Heroult cell in a temperature of 1000 degree celsius. Although, this temperature is below the melting point of Al2O3, I have said the melting point of Al2O3 is 2500 degree Celsius. The alumina is actually in the liquid state, being dissolved in molten cryolite because it forms a compound. So, Al2O3 dissolves into the cryolite bar. Assume, therefore, the heat contained of the Al2O3 includes its heat of fusion. So, heat of fusion of Al2O3 and melting point of aluminum is given and you have to find out the heat of reaction of this reaction.

So, let us proceed now for the solution of the problem. Now, in fact, I wanted to hide this slide before I go for the solution, but we are fortunate enough that the slide contains the answer. I have projected this slide before proceeding to solution. I hope that you will not see the solution. You will do the problem first and then see the solution. So, I proceed with the solution to the problem.

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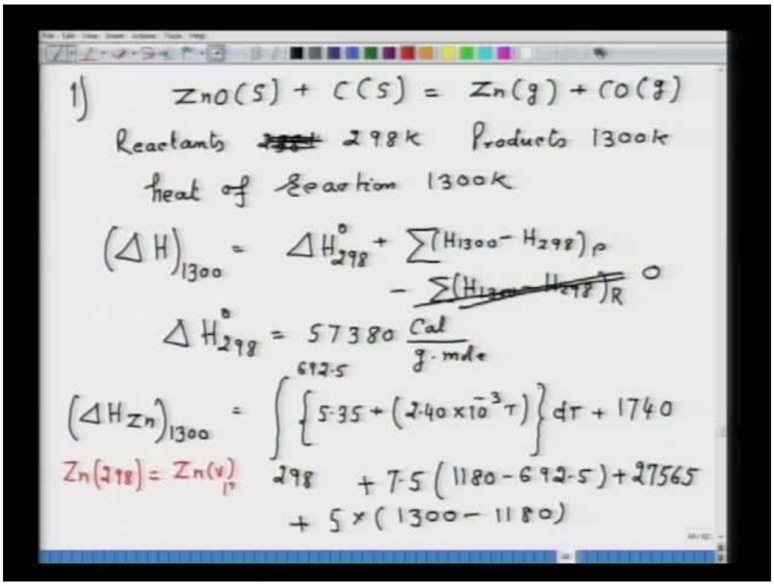

Here, we will go for the solution. The problem 1 says, ZnO solid plus carbon solid is equal to zinc gas plus carbon oxide gas. Now, it is given that reactants are at 298 kelvin and the products at 1300 kelvin; it is given to us. So, now, we have to find out the heat of reaction at 1300 kelvin. As usual, we know that heat of reaction R at 1300 kelvin will be equal to delta H naught 298 kelvin plus H 1300 minus H 298 product minus H 1300 minus H 298 reactant. Now, you mind because the reactants are at 298 kelvin and therefore this term (Refer Slide Time: 23:31) is ruled out and it will be equal to 0 in this present case. So, delta H 1300 will be simply, delta H naught 298 plus you have to valid the heat content in the product and that is all. So, delta H naught 298 and you can evaluate from the data, which is given; it is equal to 57380 calorie per gram mole. You please do this exercise and try to get a practice on how to calculate delta H naught 298.

Now, as I said, since the reactants are at 298, sigma H R is equal to 0. Now, we have to calculate the product. So, delta H Zn at 1300 kelvin and that will be equal to… Now, here you have to be careful to integrate from one temperature to another; say, in the state in which the zinc is. So, 298 for somewhere and you go up to the melting point and that is 692.5. So, you will use the C p of solid zinc and it is 5.35 plus 2.40 into 10 to the power minus 3 T dT. Now, what will be the next step? Next step will is you have to write the latent heat of melting. Do not forget and that is 1740. What will be the next step? The next step is you have to add the heat content from liquid zinc to the boiling point of the zinc and it is plus 7.5; the specific heat of liquid copper into 1180 minus 692.5 plus, what will you do now? You have to add latent heat of vaporization because there is a transformation. So, latent heat of vaporization is given as 27565. Still your heat content is not yet complete at the temperature, which is given in the problem because so far, you have reached up to only the vaporized state. Now, vapours are further heated up to 1300 and so you have to add it; plus 5 into 1300 minus 1180. So that makes the heat content in zinc vapor at 1300. In fact, what I have done? I have done, zinc at 298 .You have to do zinc vapor at 1300 kelvin. You can also subdivide this step and say zinc 298 to zinc melting point is 692.5. Should I do for that?

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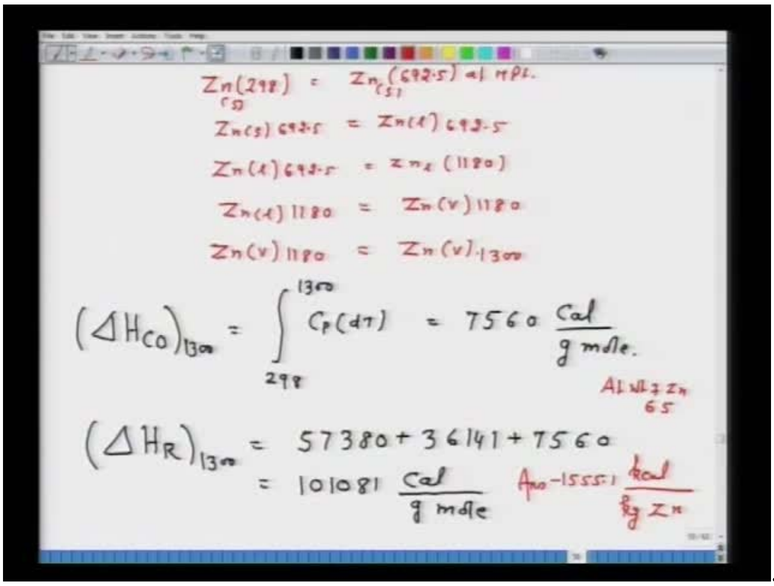

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You can also do this way; say, zinc at 298. It will go to zinc 692.5 at melting point, this is in solid and this is also in liquid. Now, zinc solid at 692.5 will go to zinc liquid at temperature at 692.5. Zinc liquid at temperature at 692.5 will go to zinc liquid at 1180. Then zinc liquid at 1180 will go to zinc vapor at 1180 and then zinc vapor at 1180 will go to zinc vapor at 1300. So, we can also divide the sub step in the beginning. It is good, if you divide this sub step, then you proceed to calculate.

Now, again, we have to calculate the delta H CO. We have calculated only Zn. So, delta H CO at 1300 will be equal to integration 298 to1300 into C p dT. You can use the values, which are given. The value will be coming be equal to 7560 calorie per gram mole. So, delta H R 1300 kelvin will be equal to 57380 plus 36141 plus 7560 will be equal to 101081 calorie per gram mole. Now, since the question says, you have to calculate kilo calorie per kg of zinc. So, all you have to do is use the atomic weight of zinc. I have written down the atomic weight of zinc as 65. So far, the answer will be equal to 1555.1 kilo calorie per kg zinc. So that will be the answer for this particular problem. I hope you must have understood this particular problem.

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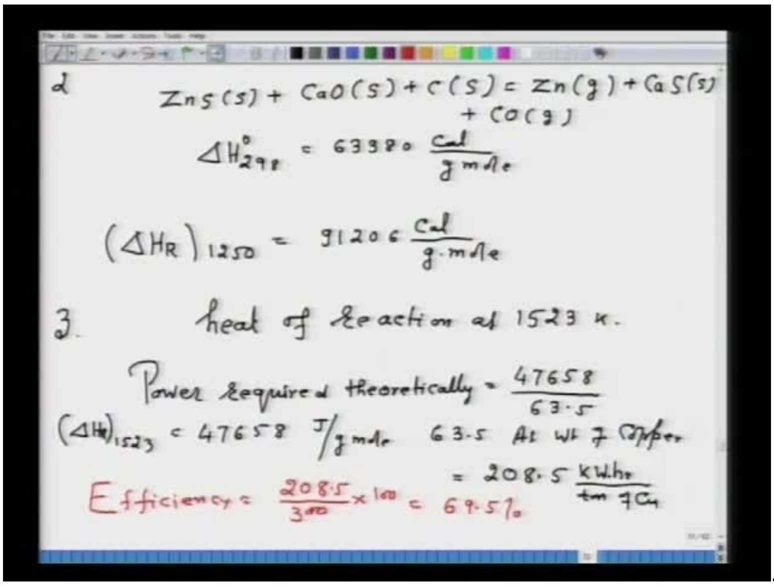

Now, let us do the problem number 2. Problem number 2, says that you have to calculate the heat for the following reaction: that ZnS solid plus calcium oxide solid plus carbon solid is equal to zinc vapor state plus calcium sulphide solid plus carbon oxide gas. So, same thing you can calculate. I am straight away giving you delta H naught 298 and that value will be 63380 calorie per gram mole. So, this problem, I will leave it to you and so that you can do it.

Here, what will I do? I am simply writing down the answer, which is delta H R at 1250 and it is coming out to 91206 calorie per gram mole. I have done the problem once and problem 2 is similar. All that you have to do is calculate the heat of summation of the heat of product and heat of reactant and you can proceed yourself.

In the problem number 3 - In order to calculate the efficiency, what you have to do? You have to find out the heat of reaction at 1523 kelvin. So, if you find out the heat of reaction at 1523, then you can calculate power required theoretically because we have calculated the heat of reaction and only that much power will be required. So, power required theoretically will be equal to 47658 upon 63.5, where 47658 is the delta H R at

1523. Input delta H R 1523 is in joule per gram mole. 63.5 is atomic weight of copper. So, this will be equal to 208.5 kilo watt hour per ton of copper. I have done this conversion in my lecture on Units and Dimensions. So, please follow it. So, the efficiency would be 208.5 upon 300 into 100. So, efficiency will be 69.5 percent and that is the answer for problem number 3.

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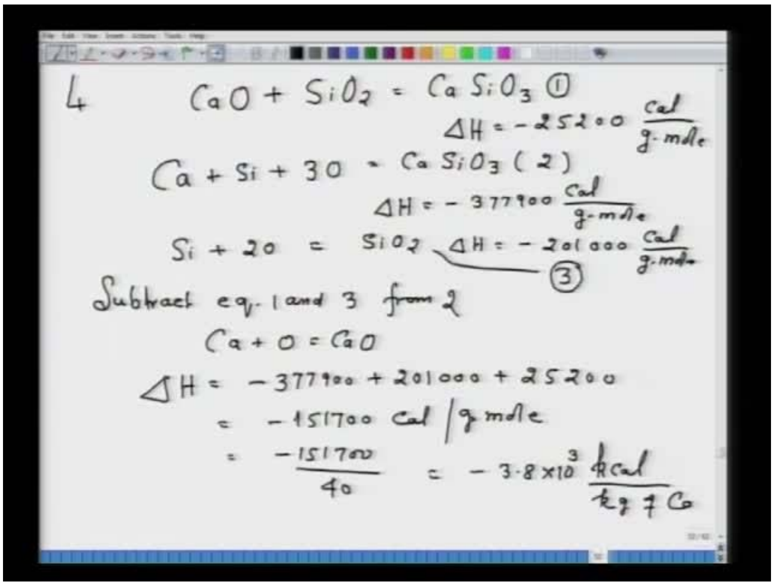

Problem number 4 is very simple problem. You only have to write down the equation. May be I will write down. The equation will be CaO plus SiO2 and it is equal to CaSiO3 and let us take this equation as number 1 (Refer Slide Time: 34:27) and here delta H is equal to minus 25200 calorie per gram mole. Another thermo chemical equation would be calcium plus Si plus 3O will be equal to CaSiO3 and take it equation number 2. So, delta H is equal to minus 377900 calorie per gram mole and the third equation would be Si plus 2O is equal to SiO2 and delta H that is equal to minus 201000 calorie per gram mole. So, this is the part where you have to write down in the form of a thermochemical equation. From this equation, determine the heat of formation of calcium oxide per kilo gram of calcium. Subtract equation 1 and 3 from 2 and let me put this equation as 3 (Refer Slide Time: 36:04).

So, if you do that and from these equation, we have to build an equation, which gives us the formation of calcium oxide and that is what we mean. So, we have build the equation Ca plus O is equal to CaO and delta H for this reaction will be equal to minus 377900 plus 201000 plus 25200 will be equal to minus 151700 calorie per gram mole. So, if I divide it by the molecular weight of calcium, which is 40. So, if I divide this minus 151700 divided by 40, then I will get the answer as minus 3.8 into 10 to the power 3 kilo calorie per kilo gram of calcium and so that is the answer for problem number 4.

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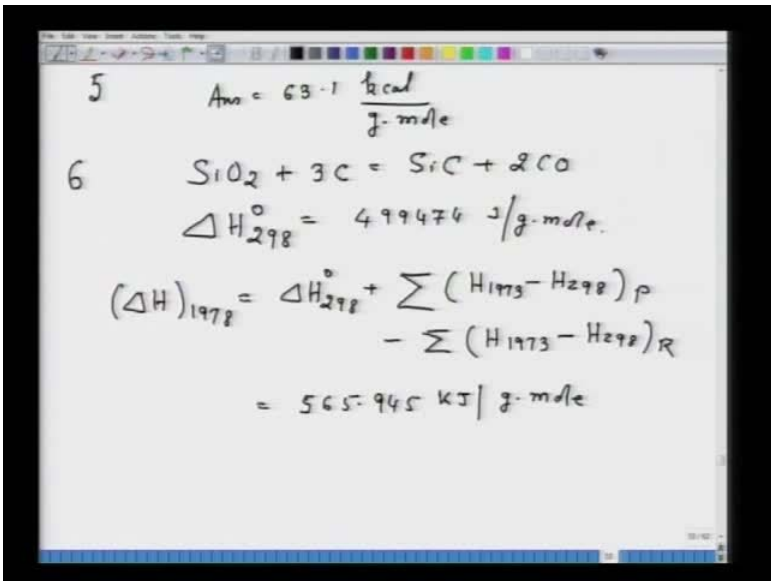

Now, about the problem number 5 - I will straight away give the answer because the problem is simple and I have done the problem 4. So, I am writing down the answer I had already given, but still the answer for this problem is 63.1 kilo calorie per gram mole.

Now, let us go to the solution of problem number 6 - It says that you have to find out the heat of reaction for the production of silicon carbide. So, here the reactants and products are at 1973 kelvin and the various values are given to you. So, just take the reaction SiO_2 plus 3C is equal to SiC plus 2CO. From the data, I can find out delta H naught 298 is equal to 499474 joule per gram mole. I can calculate delta H 1973 and I will write down the reaction for you, that is delta H naught 298 plus H 1973 minus H 298 product minus H 1973 minus H 298 reactant. So, you calculate and I am straight away writing down the value or the answer, which is 565.945 kilo joule per gram mole. So that is the answer for problem 6.

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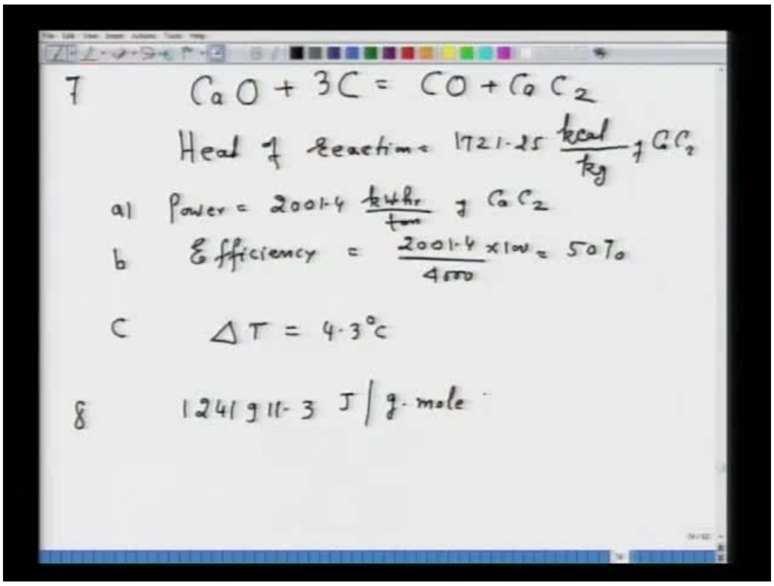

Similarly, for problem 7 - This electric furnace is used to produce calcium carbide and so on. So, you have to calculate minimum power efficiency. You have to calculate, for example, if I take CaO plus 3C is equal to CO plus calcium carbide. So, I have to calculate heat of reaction and I am straight away calculating it for you. The data given are: heat of reaction will be equal to 171.25 kilo calorie per kg of calcium carbide.

So, I will give the answer now. a - power required to convert it now is 2001.4 kilo watt hour per ton of calcium carbide. b - I will give efficiency straight away and you can find it out as 2001.4 upon 4000 into100 is equal to 50 percent. For the C part - you have to calculate and the rise in temperature that I am getting is 4.3 degree Celsius. So, I am leaving you to calculate the rise in temperature. You have to do the heat balance some in that to remember.

Now, problem 8 - It says you to calculate the heat of reaction. As I have done so many problems on heat of reaction, what I will do is that I will straight away give the answer for this problem. So, answer for this problem is 1241911.3 joule per gram mole. So, I have given these exercises and the solutions.

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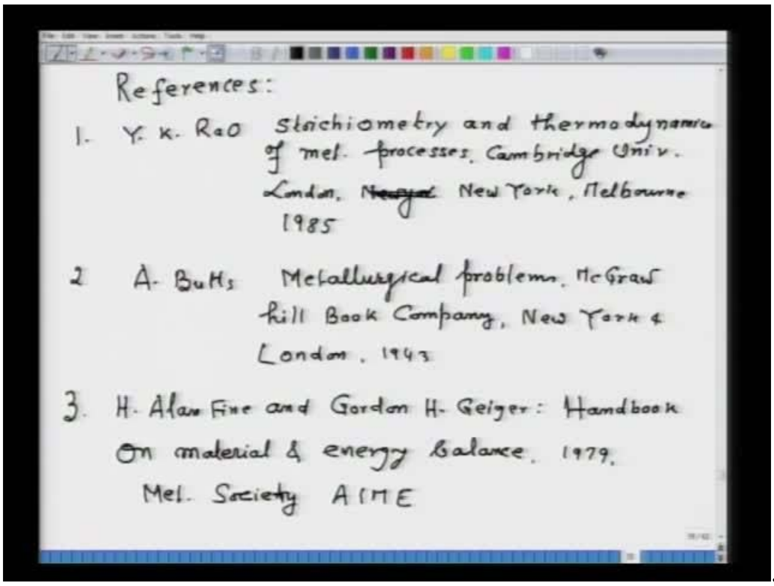

Now, I would like to give you the references, from where you can see for further reading. So, the reference number 1: Y K Rao, Stoichiometry and thermodynamics of metallurgical processes. I will say this as a good book and you should also see this book and read. This is Cambridge University, London, New York, Melbourne, 1985.

Second one: A. Butts, this particular book has lot of problems and you should see, if you want to do more problem metallurgic problems. Metallurgic problems, McGraw hill book company, New York and London, 1943. This book has a very good compilation of problems in various areas of metallurgy.

Third book, which is by H. Alan Fine and Gordon H Geiger, name of the book is Handbook on material and energy balance, 1979 published by Met Society AIME. So, you should also go through these references for further reading.