Materials and Energy Balance in Metallurgical Processes
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Module No. # 01
Lecture No. # 05
Exercise on Stoichiometry and Introduction to Thermochemistry

In the last lecture on Stoichiometry, I had solved some problems and some two problems we had left. So, I am projecting those problems again and I will solve these problems also.

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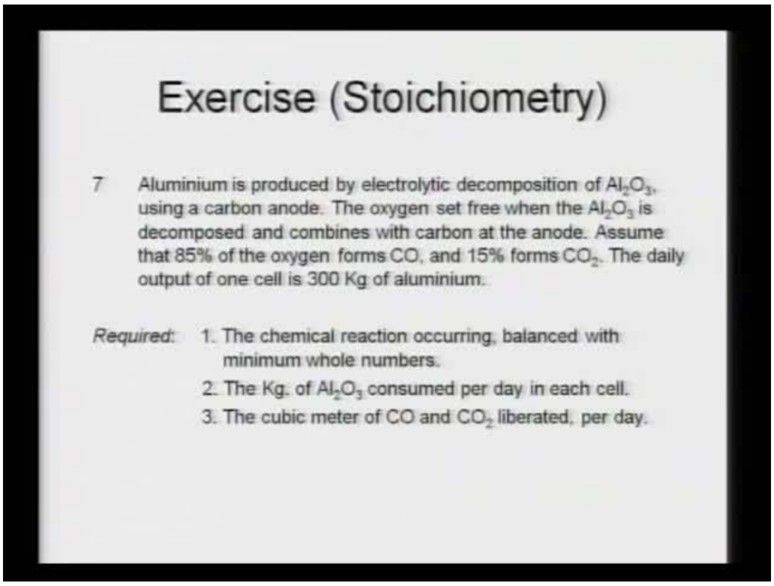

So, although these problems are there in lecture 1, but I thought may be I will repeat. This problem 7 is about the Aluminum, which is produced by electrolytic decomposition of Al 2 O 3 using a Carbon anode. What you have to calculate is the chemical reaction occurring balance with minimum whole numbers. You are not required to round off, but you have to find a chemical reaction with minimum whole numbers and kg of Al 2 O 3 consumed and cubic meter of CO and CO 2.

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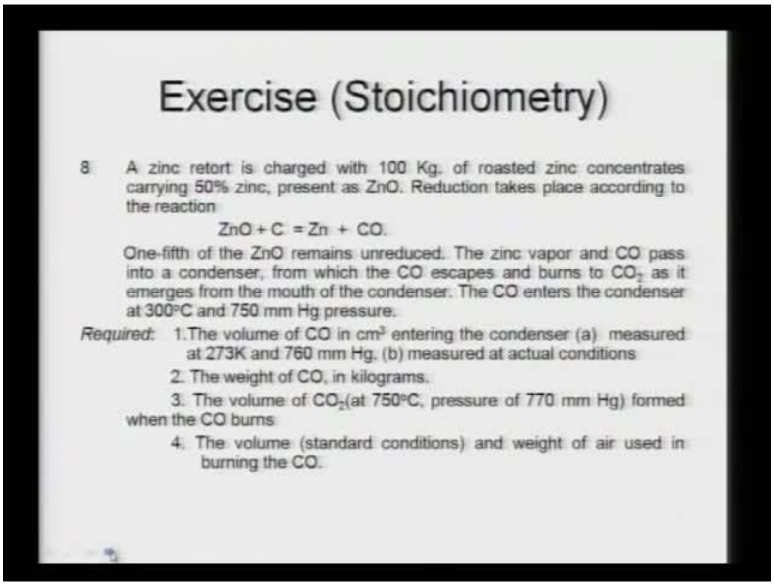

The next problem which we have to do is about the reduction of Zinc oxide by Carbon and some of the conditions are given for the reduction, say one-fifth of the ZnO remains unreduced and so on.

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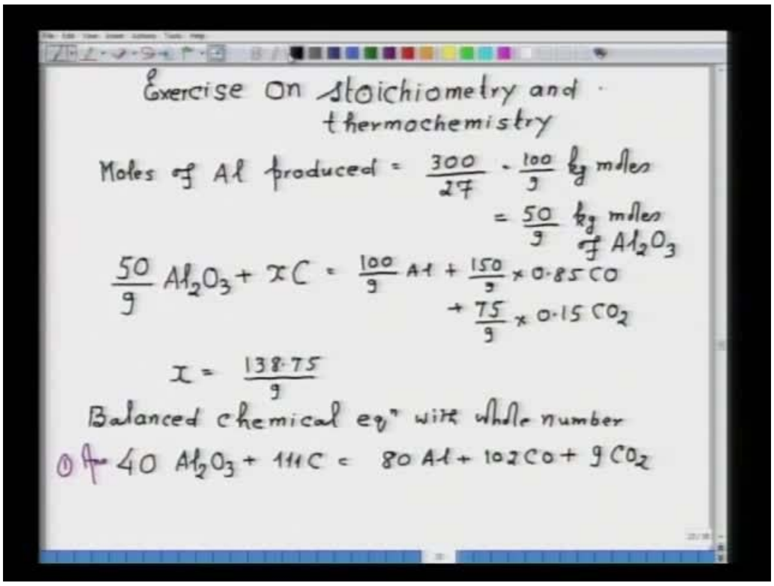

So, you are required to calculate volume of CO, weight of CO, volume of CO 2 and so on. So, I will be solving these problems, so that this lecture on Stoichiometry completes. So, the solution of problem 7, for example, says that I will write moles of Aluminum produced. Moles of aluminum produced will be 300 divided by molecular weight of

Aluminum - I have taken here 27 that are equal to 100 by 9 kg moles which is also equal to 50 by 9 kilogram moles of Aluminum, because the Al 2 O 3 there is 2 moles of Aluminum - that is very simple. So, if I write down now the equation say 50 upon 9, Al 2 O 3 plus x mole of carbon, because x to be determined that is equal to 100 by 9 moles of Aluminum plus 150 upon 9 into 0.850 - as per the statement of the problem plus 75 upon 9 into 0.15 CO 2. Now, this equation I have written as per the statement of the problem that says 85 percent of the Oxygen form CO and 15 percent forms CO 2.

So, from here one can find out x; that will come up to be equal 138.75 9 and rest of the exercise I leave on you to find out the balance chemical equation with whole numbers. I am writing the answer, which is the balanced chemical equation with whole numbers and you are not required to round off. The equation is now 40 Al 2 O 3 plus 111 moles of Carbon that is equal to 80 moles of Aluminum plus 102 moles of Carbon monoxide plus 9 moles of Carbon dioxide.

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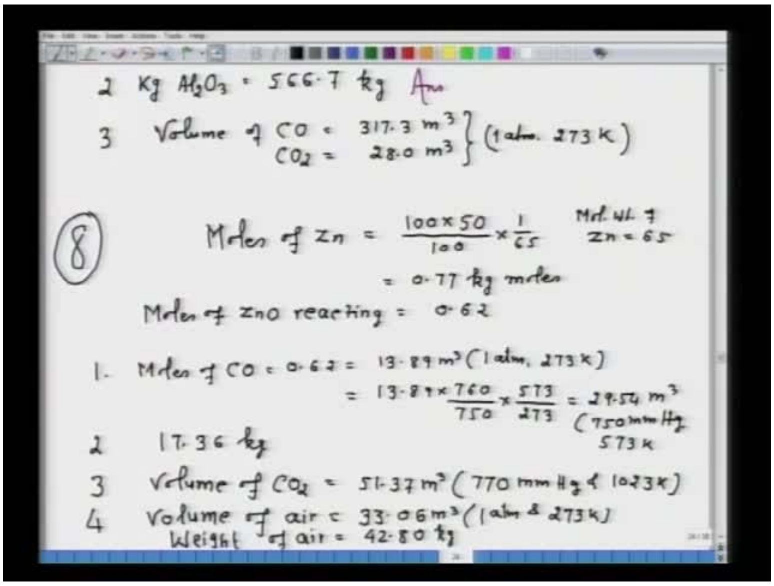

Say, this is the answer for part 1, answer this is for 1, that is a balance chemical equation. Now, for second, straightway we have to find out the kilogram of Al 2 O 3; that is straight forward from the balance equation. So, kilogram Al 2 O 3 used and the answer would be 566.7 kilogram. That is the answer for 2 and for 3 that is the volume of CO. Now, once you have the balance chemical equation, then everything follows on it is own. 317.3 meter cube and volume of CO 2 that is equal to 28.0 meter cube; mind you, these volumes are at 1 atmospheric pressure and 273 Kelvin. You always make a habit that whenever you report the volume of the gasses, please mention pressure and temperature; without mentioning of both, the expression of volume has no meaning at all. So, this is the answer solution for question number 7.

Now, let us take the question number 8. Now question 8; again, if you follow the way the question is there and the conditions under which Zinc is produced. You start, I will you give a brief solution. Say, you start with moles of Zinc that will be equal to 100 into 50 upon 100 into 1 upon 65 and here molecular weight of zinc - I took 65. So, I will be getting here 0.77 kg moles. Now, the problem says one-fifth of the ZnO remains unreduced; so, moles of ZnO reacting. Now, mind you, 1 mole of Zn is also 1 mole of ZnO; so 0.77 kilogram moles of Zn that is equal to 0.77 moles of ZnO also.

So, moles of ZnO reacting will be 80 percent of this; that is 0.62. Now, straightway one can find out the answer. So, I am writing down the answer for you - answer for 1 that is moles of CO that is equal to 0.62, this is equal to 13.89 meter cube at 1 atmosphere and 273 Kelvin. The problem says you have to find out at 273 Kelvin and 760 millimeter of mercury and also problems says that you have to find out at 300 degree Celsius also. That will also be equal to 13.89 into 760 upon 750 into 573 upon 273. So, that is equal to 29.54; this is meter cube at 750 millimeter mercury and 573 Kelvin. This is the answer for question 1.

Weight of CO; this straightaway we can find out - 17.36 kilogram you have to multiply by the molecular weight of CO and third volume of CO 2 - volume of CO 2 straightaway you can find out. You have to find out volume of CO 2 formed at 750 degree Celsius and 770 millimeter pressure due to burning of CO.

So, straightaway I will write down the answer - you find out yourself that is 51.37 meter cube at 770 millimeter mercury and 1023 Kelvin that for 3.

And the answer for question 4 - the volume and weight of air used in burning the CO. So, volume of air, that is equal to 33.06 meter cube expressed at 180 m and 273 Kelvin; whereas, the weight of air - here I am writing down weight of air - you multiply by it is molecular weight 42.80 kg.

So, with the solution of both these problems, the lecture on Stoichiometry

Today, I will again be starting with a fresh topic that is the Thermochemistry and introduction to Thermochemistry.

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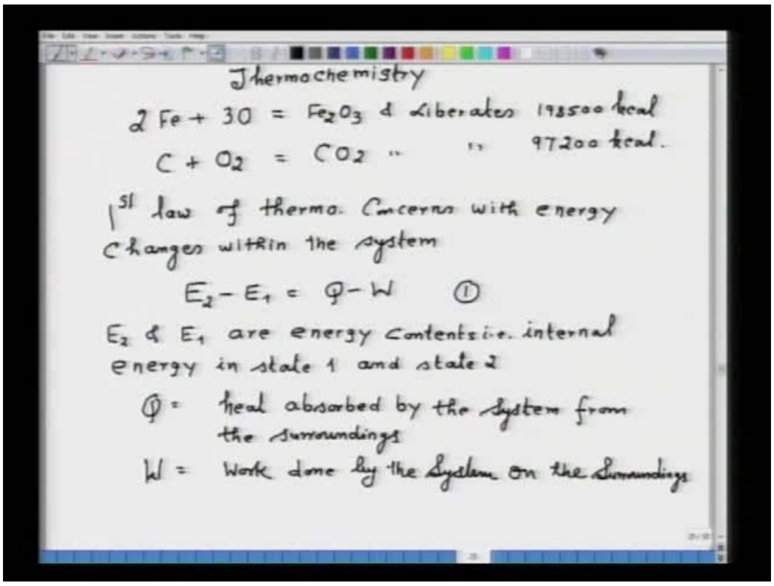

Now, you know whenever you want to perform the heat balance of a process you require to do at a steady state heat input that is equal to heat output. So, you are required to calculate the heat effects produced by the chemical reactions. In fact, the chemical reactions are often accompanied by either liberation of heat or absorption of heat.

Now, for example, 2 Fe plus 3O that gives Fe 2 O 3 and liberates heat of the order of 198000 kilocalorie; similarly, another example C plus O 2 that is equal to CO 2 and liberates heat of the order of 97200 kilocalorie. Now, these heat effects are very important when you want to analyze the energy balance of a process, because you must know what reactions are producing heat; how to calculate the heat of the reaction from a temperature of T 1 to temperature of T 2. For all these purposes the First law of Thermodynamics - it concerns with energy changes within the system.

Now, I am not going into the detail of the first law of Thermodynamics. I will be giving you only that particular portion of first law of Thermodynamics, which is relevant for heat balance calculation. So, the first law of Thermodynamics states that change in internal energy that is E 2 minus E 1 that is equal to Q minus W. I think all of you know where E 2 and E 1 are energy contents that are internal energy of the system in state 1 and state 2. I must mention here, the Thermodynamics deals with the initial and final states only and not in between that point - it should be clear. Q here is heat absorbed by the system from the surrounding, whereas W that is equal to work done by the system on the surrounding.

This is very simple and you must have read very often in your undergraduate course on Thermodynamics. Now, heat content or enthalpy of a system is a thermodynamic property to which we are concerned.

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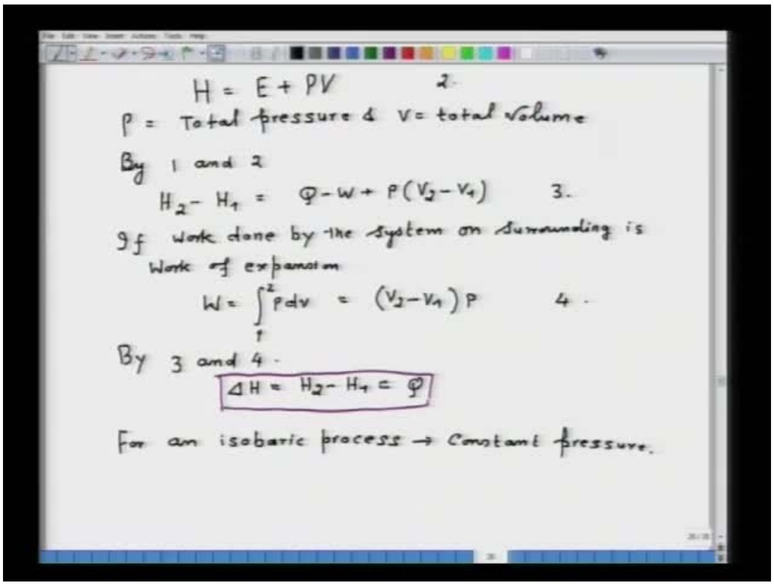

So, this heat content or enthalpy which is thermodynamic property - H that is equal to E plus PV, where P that is equal to total pressure and V that is equal to total volume. Let me call this equation as number 2. Now by the equation 1 and 2, we get H 2 minus H 1 that we are considering system is initially in a state 1 and finally in a state 2. So, H 2 minus H 1 that is equal to Q minus W plus P into V 2 minus V 1. Consider this as equation number 3.

Now, if work done by the system on surrounding is work of expansion that is only expansion work is done. So, in this case W that equals to integral of 1 to 2 P dv and that is equal to V 2 minus V 1 into P; let us call this equation number 4. So, by 3 and 4, we get a very important relationship; by equation 3 and 4 we get delta H that is equal to H 2 minus H 1 that is equal to Q; this is a very important relation, because this suggest that heat absorbed by the system can be determined in terms of it is enthalpy in the initial state as well as in the final state; remember that enthalpy is also a state property. Now, this particular equation is valid when the change from state 1 to state 2 occurs by a path of constant pressure in which only expansion work is done on the surrounding; that means this is valid for an isobaric process.

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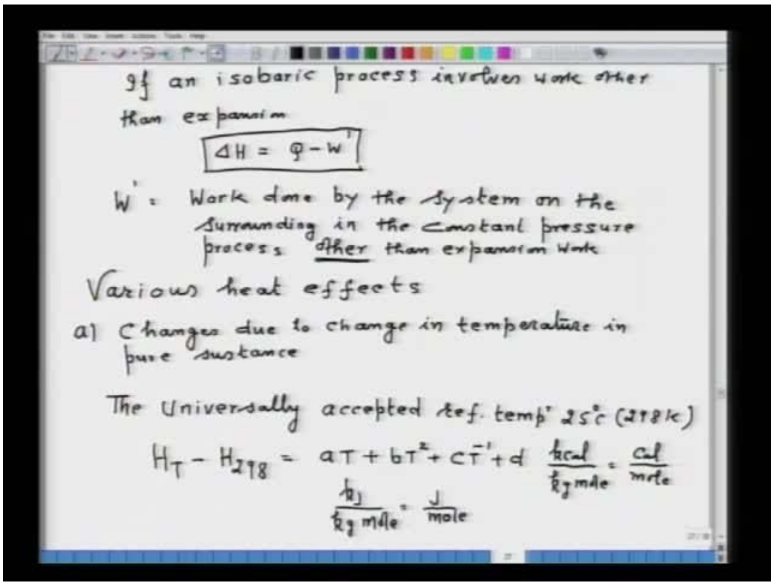

That means taking place at constant pressure, delta H is equal to Q and also the Q is a heat absorbed and heat absorbed by the system can be related to the change in enthalpy or the heat content and enthalpy is also a state property of the system. Now, if an isobaric process involves work other than expansion work, then in that case, delta H that will be equal to Q minus W dash.

Now, that is an important thing here because delta H is equal to Q is only valid for an isobaric process, which involves only work of expansion, but if there is other work of expansion - for example, in electric furnace electricity is supplied. So, in that case, then electric process at constant pressure - this minus W equals to the input of electrical work with this system. So, that is important and I will write for you say W dash that is equal to work done by the system on the surrounding in the constant pressure process other than expansion work.

As I have just now given an example, in an electric furnace which also operates at constant pressure, so, minus W means that much amount of electricity has to be supplied into the system. Now, most metallurgical processes, they follow a path of constant pressure that is in various metal extractions and refining hardly the pressure is other varies.

So, most of the processes, they occur at constant pressure and in that case, the heat effect for a process up can be related or relates very well to the property of the system; that is enthalpy. So, that is an important conclusion. That means, the change in heat content depends only on the initial and final state and not on the path taken by the process.

So, that is an important conclusion on the first law of Thermodynamics, which forms a basis of calculation for various heat effects while performing the heat balance of a particular process. This is a very brief introduction of first law of Thermodynamics and the detail you can go through in any book on Thermodynamics to clear a concepts of enthalpy, but what is important over here is that because most metallurgical processes they occur at constant pressure. Therefore, the enthalpy can be very well used in order to find out the heat content that is where the important thing over here.

Now let us see various heat effects - what are the various heat effects? First, a change due to change in temperature in pure substance. Now, clearly a substance contains heat by virtue of its temperature; when a material has certain temperature it has a certain amount of heat; what is important is the change in heat due to change in temperature - that is what we require.

Now, this is calculated by taking a basis - the universally excepted reference temperature - I hope you must be knowing from your elementary course on Thermodynamics - is 25 degree Celsius or 298 Kelvin, because the enthalpy at 298 Kelvin or 25 degree Celsius is taken equal to 0. Therefore, the change in heat content is defined with reference to the enthalpy content H, 25 degree Celsius.

Now, heat content of most of the inorganic materials, whether elements or compounds, you can find out in any standard Thermodynamic book and various books give the values of heat content due to change in temperature in terms of H T; that is the enthalpy at temperature T minus H 298; that is, the change in heat content when a material is heated from 298 Kelvin to a temperature T Kelvin.

So, the values are listed in the table by using the following formula - that is, H T minus H 298 that is equal to aT plus bT square plus CT to the power minus 1 plus d and the units are kilocalorie per kg mole, which is also equal to calorie per mole or a sometimes you may find this also written in kilo joule per kg mole; that is also equal to joule per mole and in FPS system it is also given in the respective units.

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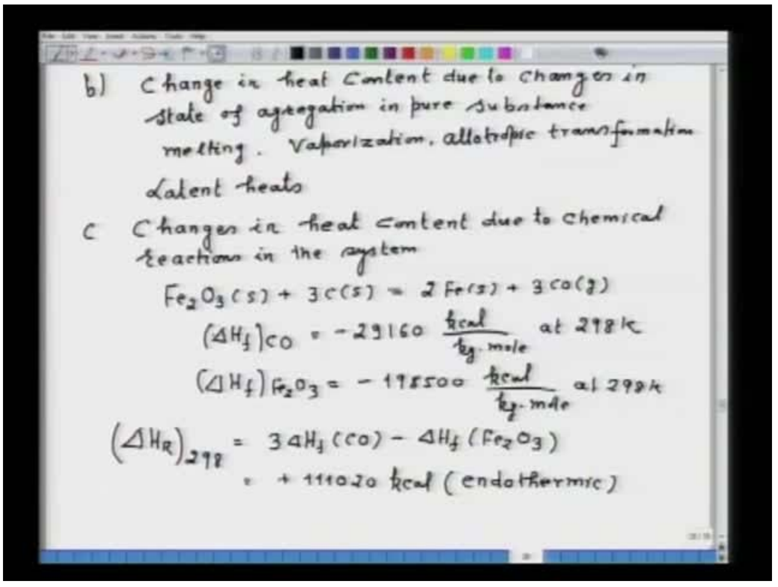

So, that is one important thing - that the change in heat content of any material can be determined from seeing this particular table and another heat effect is that the change in heat content due to changes in state of aggregation in pure substances. Now, for example, melting, vaporization - do you know still another change can you get and it is the allotropic transformation in common system added changes from alpha to gamma to delta. So, accordingly the heat evolved or heat will be absorbed that depends on the system under consideration.

Now, here the changes, which occur at a constant temperature - that point is important - and no change in temperature occur due to change in the state of aggregation. So, that is commonly called the latent heat or sometimes you also call it as heat of fusion. So, latent heat of melting, latent heat of vaporization, and the heat evolved or absorbed during allotropic transformation is also very important, because when you calculate, say if you want to calculate the heat content in, for example, a pure material from 25 degree Kelvin to a temperature T, then you must see what changes occurring during it is variation of temperature from 25 to that particular temperature. If you have to take into account all these changes, which are occurring to calculate the heat content that is an important.

C Part is that say, changes in heat content due to chemical reactions in the system, because if a chemical reaction occurs, then heat may be evolved or heat may be absorbed and that you have to calculate. Now, in order to calculate the heat content due to chemical reaction, one has to proceed with the data on the heat of formation of compounds. Now, this heat of formation of compounds that is also listed in any standard book of Thermodynamics, that is also to be noted while finding out the heat of formation of the compound.

Now, for example, if we take a reaction say Fe 2 O 3 solid plus 3C solid that is equal to 2 Fe solid plus 3 CO gas. You have required finding out the heats of these particular chemical reaction. Now, you can find out the heat of this reaction from the heat of formation of the compounds. So, I am giving you the heat of formation of compound, say delta H f CO that is equal to minus 29160 kilocalorie per kg mole mind you this value is at 298 Kelvin.

Similarly, delta H f Fe 2 O 3 that is equal to minus 1985000 kilocalorie per kg mole this is also at 298 Kelvin. Now, you must note that the tabulated values or all the thermodynamic tabulated values they are listed at 298 Kelvin temperature that is an important thing. Now, a heat of formation of the pure element is 0 that is the thing you have to know.

So, delta H R that is heat of reaction H 298, that will be equal to 3 delta H f CO that is heat of formation of the product minus heat of formation of the reactant minus delta H f Fe 2 O 3. Now, what I have to do is very simple; now, I have to substitute the value of delta H f CO, which is 29160, and Fe 2 O 3 and I have to do multiplication and subtraction or whatever you want you can do it.

So, the answer would be plus 111020 kilocalorie. Now, this reaction is highly endothermic. Now this Fe 2 O 3 reaction will have 111020 kilocalorie and we can say per kg of mole of Fe 2 O 3 or per kg mole of carbon or per kg mole of iron whichever you want to say; so that is what the calculation on the heat of reaction.

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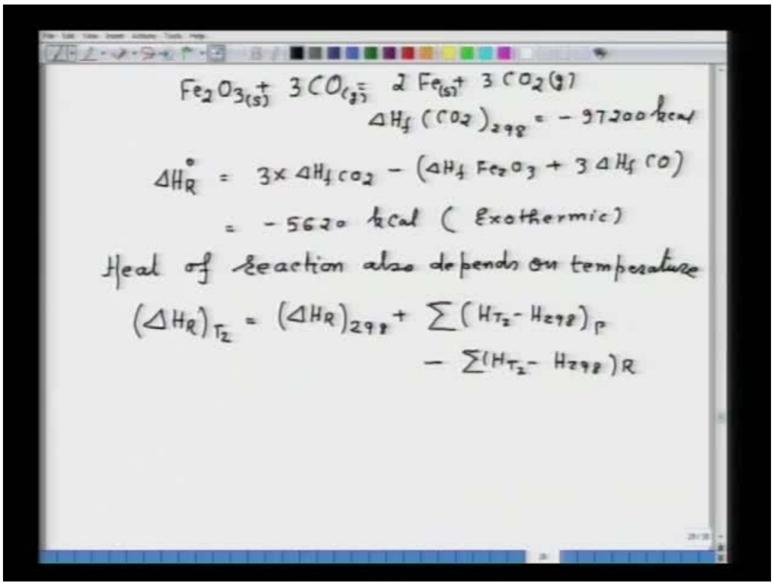

Now, let me take another example - let us take it now say Fe 2 O 3 plus 3 CO that is equal to 2 Fe plus 3 CO 2 all the values are given and now I am giving also here delta H f CO 2 which is not given above 298 that is equal to minus 97200 kilocalorie. Now, if I forget somewhere to write 298, I mean tabulated value there are always at 298 Kelvin, so there should be no confusion.

So, now I can calculate delta H naught R and for this reaction delta is not normally refers at 298 Kelvin; so that will be equal to 3 into delta H f CO 2 minus delta H f Fe 2 O 3 plus 3 into delta H f CO.

However, if in this equation you also write down the state, say this is the solid; this is gas; this is solid and this is gas this will also help you. For example, in some reaction, one of the products is liquid and then you have to take the latent heat of fusion also in calculated heat of content. Therefore, it is advisable in the beginning to calculate the heat of reaction and from the heat of formation of the compound to write down the equation by mentioning the state also in the parenthesis that is I mean important thing here.

So, if we just substitute the values, then you will be getting minus 5620 kilocalorie; now remember this reaction is exothermic. So, that is how you will be calculating the so-called heat of reaction at 298 Kelvin. Now, the heat of reaction also depends on the reaction temperature. So, I will write down heat of reaction also depends on temperature of the reactant as well as temperature of the product.

So, the law - I think you must have read it - is used; so heat of reaction say delta H R at any temperature T 2 that will be equal to say delta H R at 298 Kelvin plus H T 2 minus H 298 products minus H T 2 minus H 298 reactant. That is how you have to find out the heat of reaction at any temperature.

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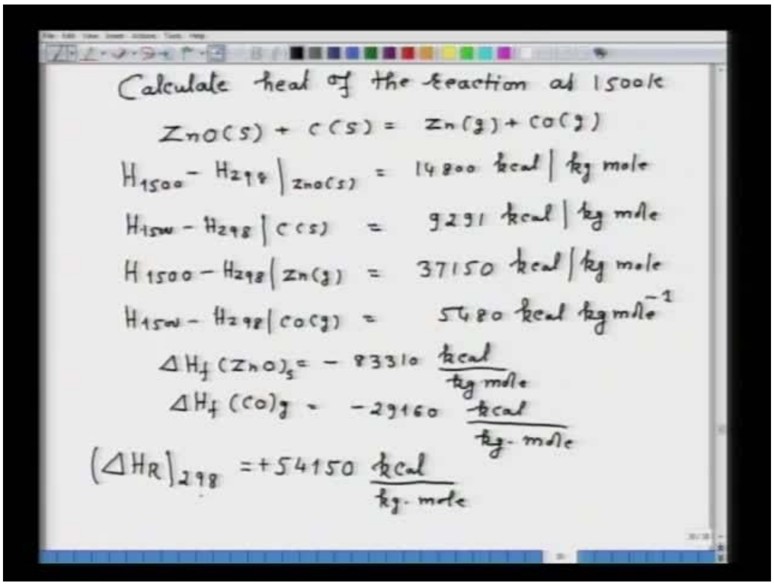

Now, let me illustrate by an example. Now, let us calculate heat of the following reaction mentioned below at 1500 Kelvin. Now, the reaction is ZnO S plus C S that is equal to Zn gaseous plus CO gaseous. Now, mind you in this reaction, it is very important to write down the state of the reactant and product in the parenthesis, because you note that in this reaction the reactants are in the solid, whereas, the products are in the gaseous state; Zinc is also in the gaseous state.

So, while calculating the heat of reaction you have to consider the state of transformation of solid Zinc to gaseous Zinc via liquid; so that thing is important for that purpose in Thermodynamics. It is always advisable to write a chemical reaction by putting the state of substance in the parenthesis.

So, now all that we need is the value of heat contents. I am giving heat contents H 1500 minus H 298 for ZnO solid that is equal to 14800 kilocalorie per kilogram mole. For carbon H 1500 minus H 298 this carbon, which is solid that is equal to 9291 kilocalorie per kg mole. So, H 1500 minus H 298 Zinc gaseous state that is equal to 37150 kilocalorie per kg mole.

Similarly, last one H 1500 minus H 298 for CO gaseous state that is equal to 5480 kilocalorie kg mole to the power minus 1. So, that is what the various values are given and now also you require to calculate the heat of reaction say delta H f ZnO that is equal to minus 83310 kilocalorie per kilogram mole. Delta H f CO gaseous this is the solid that is equal to minus 29160 kilocalorie per kg mole. So, you see in calculating the heat effects, you have to collect large number of values and it is very important that you collect the right values in the right state that is an important.

Now, see, first we have to calculate delta H R 298. So, delta H R 298 that is already illustrated in the previous example product minus reactant that is heat of formation of product minus heat of formation of reactant; I am writing straightway the answer - that is 54150; mind you this is plus kilocalorie per kg mole.

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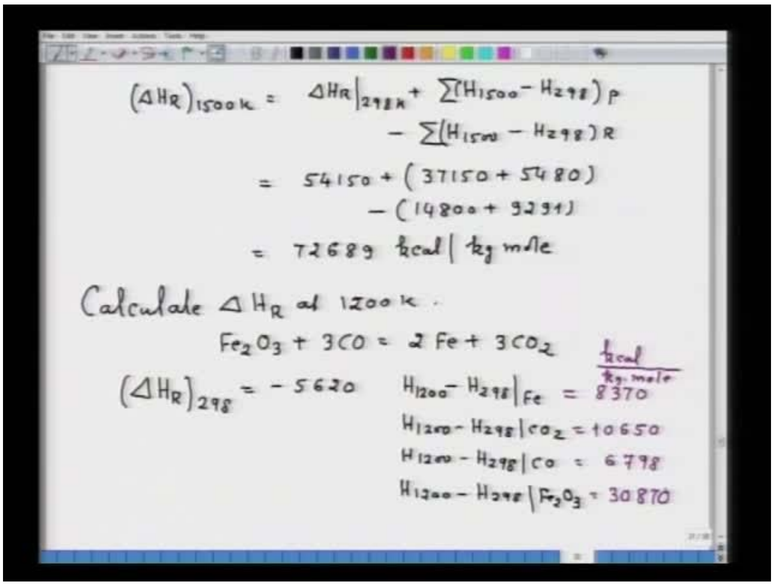

Now, this is heat of chemical reaction at 298 and now a 1500 degree Celsius. So what we have to do now say delta H R 298 Kelvin plus sigma H 1500 minus H 298 product minus H 1500 minus H 298 reactant. Now, the values are already given, I am straightaway substituting the values 54150 plus 37150 plus 5480 minus 14800 plus 9291. So, if I solve you will be getting 72689 kilocalorie per kg mole.

Now, suppose if you want to calculate kilocalorie per kg of Zinc and what you will do? You will divide this value by the molecular weight of Zinc and if you required calculating kilocalorie per kg of ZnO, then you have to divide by the molecular weight of ZnO. So that is what kilocalorie per kg mole it means.

Now, I will give you another example; say, for example, calculate delta H R at H 1200 Kelvin for the reaction Fe 2 O 3 plus 3 CO that is equal to 2 Fe plus 3 CO 2. In earlier problem, we have calculated for this reaction delta H R 298 - it was minus 5620. So, I straightaway put down the value delta H R at 298 that we calculated in earlier problem minus 5620. Now, you need certain value. So I have to give you certain values say H 1200 minus H 298 you need for iron; you need say H 1200 minus H 298 for CO 2; you also need H 1200 minus H 298 for carbon oxide and H 1200 minus H 298 for Fe 2 O 3.

So, let me give you these values that are equal to 8370. The units I am writing at the top - kilocalorie per kilogram mole for CO 2, 10650; this is 6798; this is 30870. Now, once these values are given, then it is simply addition and subtraction.

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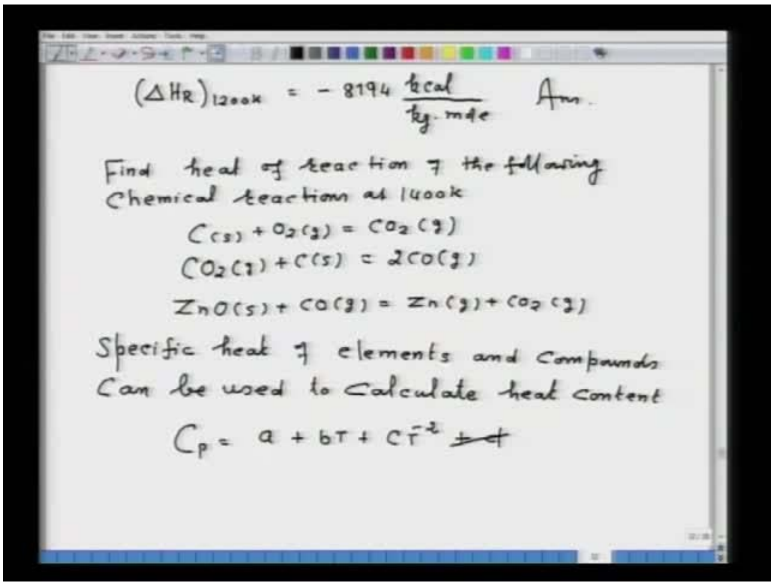

So, delta H R at 1200 Kelvin for this reaction I am straightaway writing down that will be equal to minus 8194 kilocalorie per kg mole and this will be the answer for this. So, that is the way you will be calculating. Now, I give you further more exercises so you do it.

Find heat of reaction of the following chemical reaction at 1400 Kelvin.

Just for your practice C solid plus O 2 gaseous CO 2 gaseous. Find out for this reaction CO 2 gaseous plus C solid 2 CO gaseous and also find out ZnO solid plus CO gas that is equal to Zn gas plus CO 2 gas. Collect the values from thermodynamics and find out this thing.

Now, this is one way of finding out the heat content; very straightaway you are given with the value of H T minus H 298 because - so these values are tabulated and somebody has work for you so that you do not need to do a lot of calculation, but the tabulated values are at the particular temperatures.

Suppose, you want to calculate the heat content in between temperature - suppose tabulated value is at 1400 Kelvin and 1500 Kelvin - you want to calculate the heat content at 1450 Kelvin and what will you do? So, for that, the heat content can also be determined by specific heat values of the elements and compounds.

So, the specific heat of elements and compounds can be used to calculate heat content, because here you are not restricted with the temperature that is given in the table. The table does not give the values of all temperature, it starts 200,400,800,900. You want to calculated in between, for that you can use the value of C p; now, the specific heat of a substance it also varies with the temperature you know.

That is the C p that is equal to a plus bT plus CT to the power minus 2, where a, b, C are constant also in some books written as plus d. Well, the d value is so small if you can neglect it does not matter much. So, normally C p is equal to a plus bT plus CT minus 2 is used for calculation of heat content at any temperature; however, for the sake of convenience one may take C p is equal to a plus bT; also you must note that the calculated values will not be accurate.

If will looking for accurate and correct calculation, then you have to use the C p that is equal to a plus bT plus CT minus 2; a,b,C are constant and these values of C p they are listed for most of the elements and compound of interest in metallurgic in any thermodynamic book.

So, from that value, one can determine the heat content value and in the next lecture I will give you an example how to calculate the heat content from using the C p values. Till then, enjoy.