Materials and Energy Balance in Metallurgical Processes

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Module No. # 01

Lecture No. # 06

Thermochemistry

In an earlier lecture on Thermochemistry, you will recall that I have introduced you to the fundamentals of thermochemistry. Essentially, it is the use of first law of thermodynamics. Based on it, heat balance is made. For heat balance, one requires to calculate heat content, heat of reaction and so on. So, the concepts were introduced in a previous lecture on thermochemistry.

Now, in this lecture, I will be illustrating the concept further, through problems. So, as such, let us now solve the problem together. So, please take out your calculator and begin to solve the problem along with me.

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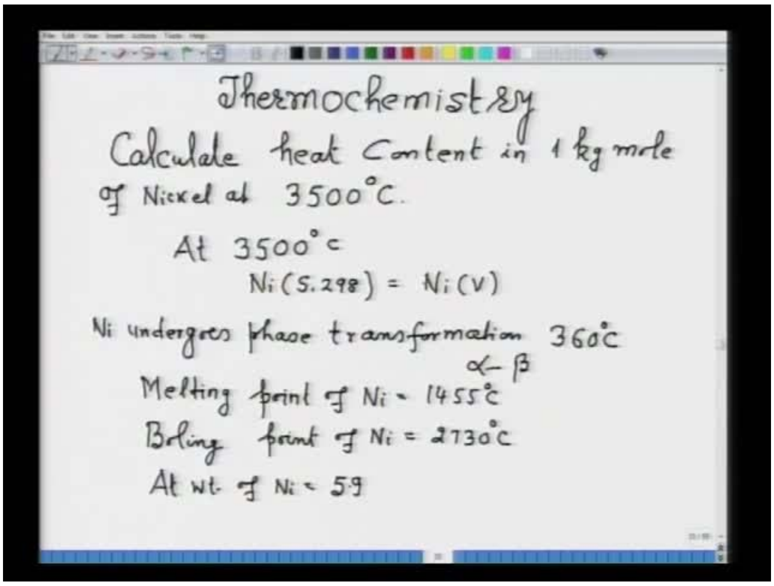

So, first let us calculate heat content in 1 kg mole of nickel at 3500 degree celsius. So, you have to calculate the amount of heat that 1 kg mole of nickel will have, when it is heated from 298 degree kelvin to 3500 degree celsius. So, you have to calculate the heat content. Now, for that one requires several data and you should also know what type of data would be required for that. It is also important to know what types of transformations occur, when you begin to calculate the heat content in an element or in a compound. For example, you must know at what temperature, the phase transformation is occurring, if at all it is occurring. Then, what is its melting point? Is that the heat content above the melting point? You have to see what is the latent heat. If the heat content is above the boiling point, then you have to see, what is the latent heat of vaporization and accordingly you have to search all the values.

So, in this particular problem, what we have to see is that at 3500 degree celsius, nickel solid, which is at 298 degree kelvin and that will be in the form of vapor; that is one thing. Now, let us collect the information about nickel. First of all, nickel undergoes phase transformation and that is from nickel to nickel alpha. This temperature at 360 degree celsius and that is the transformation occurs at 360 degree celsius from alpha to beta phase and from beta it melts. So, accordingly, we need melting point of nickel. We must know it and that is equal to 1455 degree celsius. Similarly, we must know boiling point of nickel, boiling point of nickel is equal to 2730 degree celsius. We should also know, if at all we require to calculate heat content per kg, you should know atomic weight of nickel. I will be using 59, though it is 58 something 59 something but, then I am using 59.

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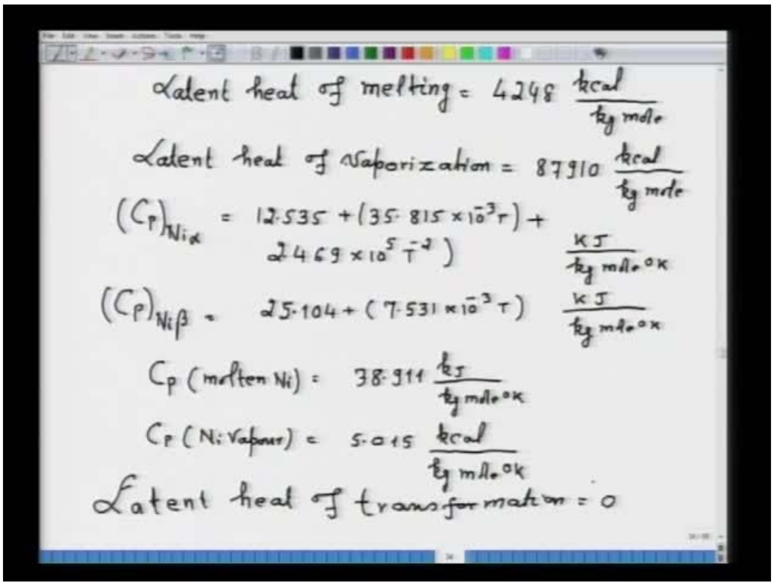

Then, you are also required to know latent heat of melting and this value is 4248 kilocalorie per kg mole, you can also consider calorie per mole. Now, by this time, you must have realized that the nickel at 3500 degree celsius will be in the vapor form. As I had already said the boiling point of nickel is 2730 degree celsius. So, I will also need latent heat of vaporization. Latent heat of vaporization is 87,910.

Now, you will also be needing the C_P value. Say, C_P nickel alpha and that is equal to 12.535 plus 35.185 into 10 to the power minus 3 T plus 2.469 into 10 to the power 5 T raised to the power minus 2. It is given to you in kilo joule per kg mole degree kelvin. C_P beta nickel and that is equal to 25.104 plus 7.531 into 10 to the power minus 3 T, again that is in kilo joule per kg mole degree kelvin and so these are the certain values. Also we need C_P molten nickel. C_P of molten nickel is equal to 38.911 kilo joule per kg mole degree Kelvin and you also need C_P nickel vapor and that is equal to 5.015 kilo calorie per kg mole degree kelvin.

Now, here I have purposely given the variables in mixed units, so that you should be careful, while calculating the heat content in single unit. Later on, you can find out the values in single unit. Just for the matter of practice, I have given the values in different units. This has been done purposely and so that you are careful to use the proper unit to calculate the various values; this is one. Second important thing is that you must know what values you require for that. You must know the calculation of heat content in an element or a compound in question. Number 1 - you should know the phase transformation, which is occurring. If it is occurring, what is the latent heat of phase transformation? Then C_P value, heat at the melting point, the melting point and latent heat.

If it is in the vapor, then you should know latent heat of vaporization. If the heat content required to be calculated is above the boiling point, then you must know C_P of vapor of that particular element. So, these are the important things. Now, since I said alpha to beta phase transformation here. So, you also need latent heat of transformation. We take latent heat of transformation as 0 kilocalorie.

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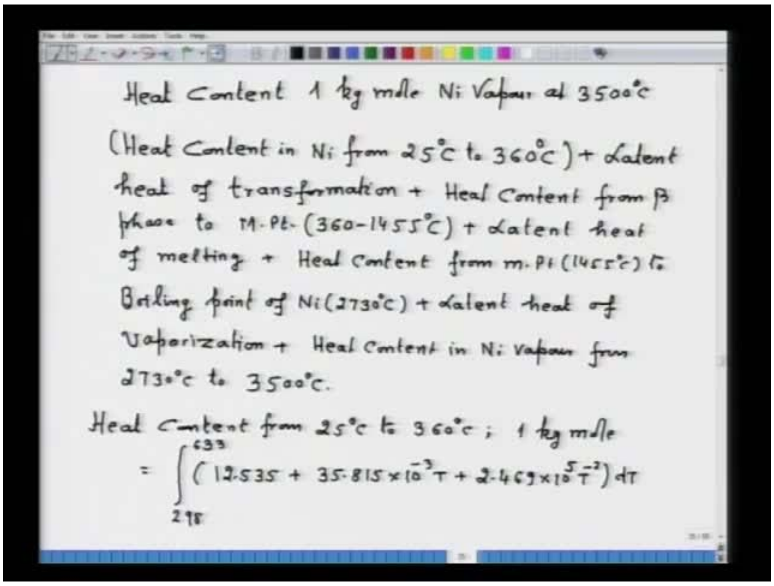

So, now I can write down in words; say, heat content in 1 kg mole nickel vapor at 3500 degree celsius would comprise of: first, heat content in nickel from 25 degree celsius to 360 degree celsius plus latent heat of transformation plus heat content from beta phase to melting point and that is in between temperature; 360 degree to its melting point, which is the melting point of nickel, which is 1455 degree celsius. Between this you know the to calculate the required heat content, plus latent heat of melting plus heat content heat content from melting point of nickel, which is 1455 degree celsius to boiling point of nickel. Boiling point of nickel, which is 2730 degree celsius plus, what will be the next quantity? It will be latent heat of vaporization plus heat content in nickel vapor from 2730 degree celsius to our end temperature, which is 3500 degree celsius. That is how the heat content is calculated. That is the important thing and you should not forget any item. For example, if you forget latent heat of melting, then accordingly your values will be less.

So, now all the values are given. So, all you have to do is substitute the value and integrate. So, here in such calculations, there are two things required, one is the concept and the concept lies in knowing the various transformations. Second thing, to some extent, it also requires the mathematical skill because now onwards, you have to integrate. You have to calculate and so little bit of mathematical skill will be required in this calculation.

Now, let us calculate the quantities one by one. So, if I calculate, for example, I will show you one or two example; say, heat content is from 25 degree celsius to 360 degree celsius. I am considering as my weight. So, it will be equal to integration 298 to 633; 12.535 plus 35.815 into 10 to the power minus 3 T plus 2.469 into 10 to the power 5 T raised to the power minus 2 and this has to be integrated from 298 to 633.

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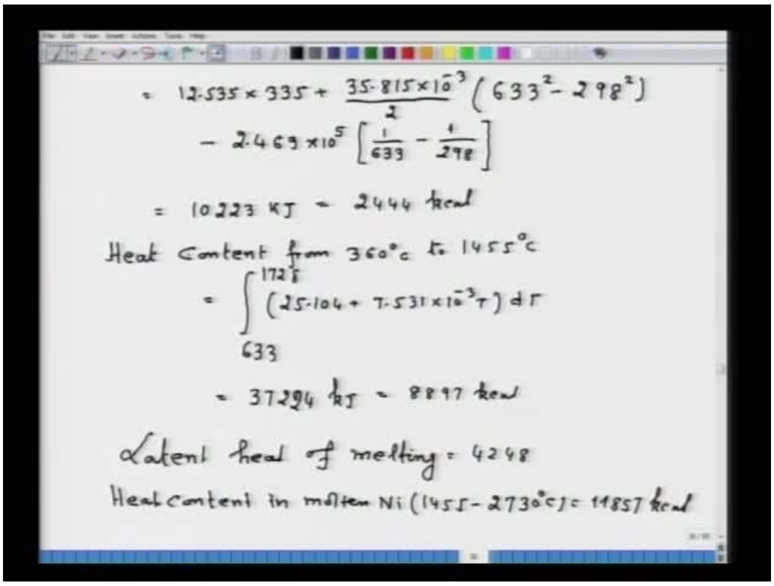

So, I will just do this integration for you. That will be equal to 12.535 into 335 plus 35.815 into 10 to the power minus 3 upon 2 into 633 square minus 298 square minus 2.469 into 10 to the power 5 into 1 upon 633 minus 1 upon 298. So, you do require little bit skill in the integration and also a little bit of patience. You should not forget one or the other values and that is the very important thing in calculation of the heat content values.

So, now it is only simplification. So, I will be putting this straight away. It will be equal to 10223 kilo joule and that will be equal to 2444 kilocalorie in this particular one. Now, latent heat of phase transformation is already 0. Now, again you have to calculate, say heat content from 360 degree celsius to 1455 degree celsius. Again, you have to integrate. So that will be equal to the integration limit 633 to 1728, 25.104 plus 7.531 into 10 to the power minus 3 T dt. So, you are lucky that it does not have further term. So, it becomes little simple and this value will be equal to 37224 kilo joules and it is equal to 8897 kilocalorie.

Now, as we already know latent heat of melting per mole. Latent heat of melting is equal to 4248 and that is per kg mole. So, you do not need to do anything. Then you have to do heat content in molten nickel, when it is heated from 1455 to 2730 degree celsius. So, this heat content will be equal to 11857 kilocalorie.

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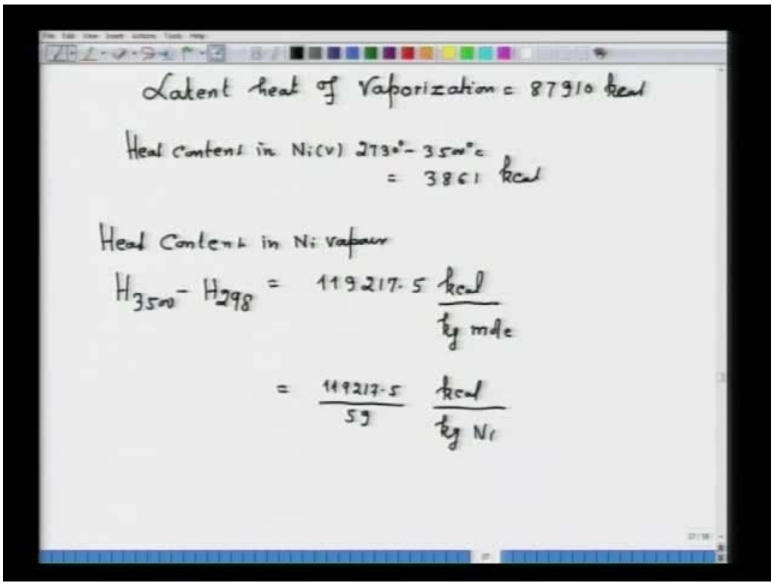

Now, you can calculate latent heat of vaporization. Latent heat of vaporization for per kg mole is also given and so you do not need to calculate. It will be 87910 kilocalorie and then heat content in vapor. Heat content in nickel vapor, when it is heated from 2730 degree celsius to 3500 degree celsius is equal to 3861 kilocalorie. So, I have to add them all. Heat content in nickel vapor is H_{3500} minus H_{298} and that will be equal to 119217. 5 kilocalorie per kg mole or this is also equal to119217; 5 upon 59 - you have to find out its number and that will be kilocalorie per kg nickel.

So, that is how you can calculate the heat content in nickel vapor. Now, let us take another example about the heat of reaction, as these are very important things. You must practice well because these are the things that you will require to calculate, while performing heat balance in various metallurgical processes. A very good practice is required.

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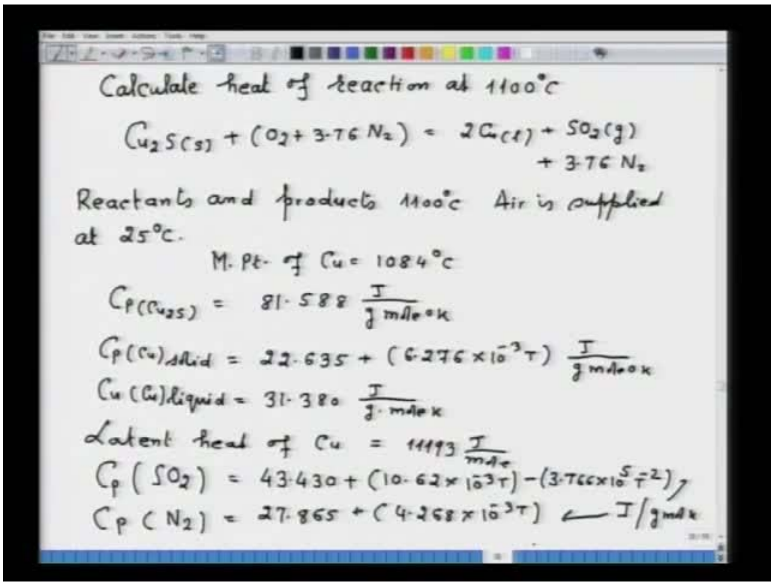

So, another example, I will take heat of reaction. Let us calculate heat of reaction at 1100 degree celsius. The reaction is Cu_2S; solid, plus O_2 plus 3.76 into N_2 and that is equal to 2Cu; liquid, plus SO_2; gas, plus 3.76 N_2.

We have to calculate the heat of reaction. From here, the two things are possible: one, the reactants are at 25 degree celsius, while the products are at 1100 degree celsius and that is one particular case. In another case, reactants and products, both are at 1100 degree celsius. So, in the first case, when the reactants are 25 degree celsius, the heat carried by the reactant will be 0. In another case, when the reactants and products are 1100 celsius, the reactants as well as product will have sensibility in them. So, what we will say? We will say that reactants and products in this particular example are at 1100 celsius, while air is supplied at 25 degree celsius and that means air will not bring any sensible heat to the system.

Now, again we require the various values. So, I will give you the value. First of all, melting point of copper is 1084 degree celsius. Now, C_P of Cu_2S and that is equal to 81.588 joule per gram mole degree kelvin. Then C_P Cu, you remember now, you see that the copper, which is forming as liquid. So, when it is formed, your basis of calculation is always 298 kelvin. In thermodynamics, a 298 kelvin and it is always taken as a basis. So, first of all copper will be heated from 298 to its melting point. So, you require C_P Cu;

solid and that is equal to 22.635 plus 6.276 into 10 to the power minus 3 T and that is joule per gram mole degree kelvin.

Now, C_P Cu liquid and that is equal to 31.380 joule per gram mole kelvin. Latent heat of copper, you must always think about what values you will be needing. If you forget one value, then your whole calculation will be wrong. That is the most important part, while doing any calculation on thermochemistry, where the heat content is very important to know, what reaction you are considering and what is happening.

So, latent heat of copper is equal to 11193 joule per mole. I mean, this is the latent heat of melting of copper. Now, you also need C_P, SO_2 is equal to 43.430 plus 10.62 into 10 to the power minus 3 T minus 3.766 into 10 to the power 5 T raised to the power minus 2. C_P SO_2 , you also need C_P nitrogen and it is equal to 27.865 plus 4.268 into 10 to the power minus 3 T. I mean the units in both the cases are joule per gram mole Kelvin. Here also the unit is same. So, with that you need further more values. I mean in this calculation, you require more values than the space you require for the solution and that is always there.

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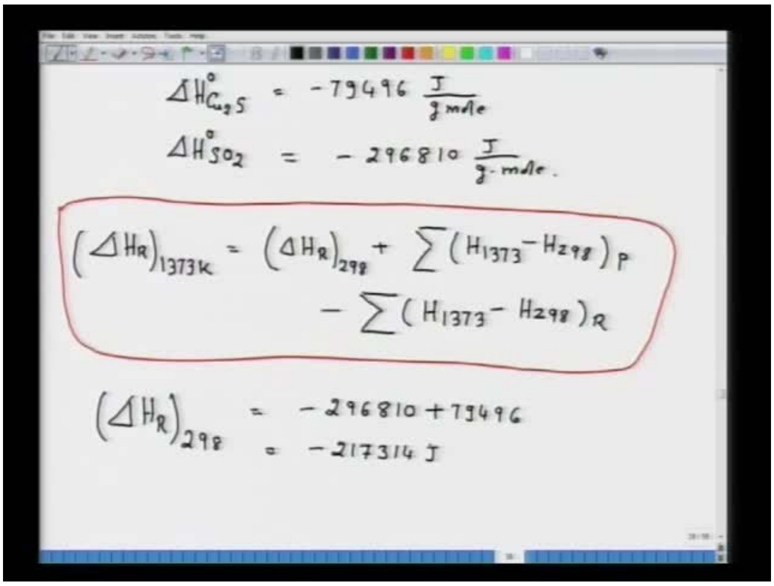

So, you also need the delta H0 Cu_2S and that is heat of formation of Cu_2S and naught means at 290 kelvin. It is equal to minus 79469 joule per gram mole. Similarly, delta is not SO_2 and that is equal to minus 296810 joule per gram mole. Now, you are in a position to start your calculation because you have collected all the required values. I will stress upon the fact that you should know what values you require. Otherwise, your calculation will have an error.

Now, delta H_R at 1373 kelvin will be equal to delta H_R at 298 or you can put delta H0; whichever way you like, plus summation of heat content 3 minus H_{298} product minus summation of H_{1373} minus H_{298} reactant. So, that is the way, you will be calculating the heat of reaction in this case at 1100 celsius. Now, all that we have to substitute the values and I will calculate, first of all, delta H_R at 298 and that will be product minus reactant. On the product, oxygen and nitrogen do not have any (( )) value. So, delta is naught, 298 will simply be equal to minus 296810 minus of minus will be equal to plus 79496. That will be equal to minus 217314 joule and that is delta H_R at 298.

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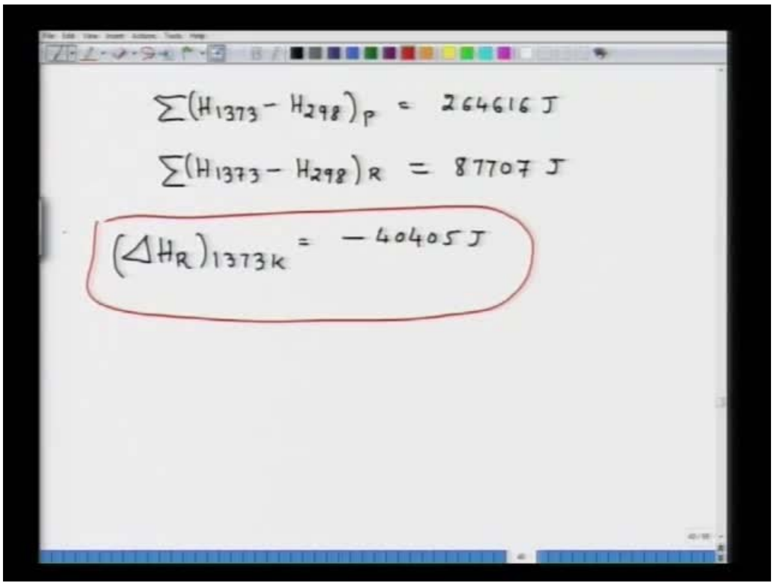

Now, I have calculated for you, the summation of the heat content H_{1373} minus H_{298} of all products and that is equal to 264616 joule. Then summation of H_{1373} minus H_{298} of all reactants will be equal to 87707 joule. So, if you substitute these values into the equation that I wrote, delta H_R at 1373 and the answer will be equal to minus 40405 joule. So, this is how the heat content at a temperature other than 298 is calculated.

Now, here several cases are possible, one of the cases could be- both the reactants are at 25 degree celsius. Here, the Cu_2S was heated to 1100, but air was at 25 degree celsius. It is possible in certain cases that air is also the reactant. Either reactants, three reactant or whatever, the reactant that takes part, all are at 25 degree celsius. So, this is the general the procedure to calculate the heat content.

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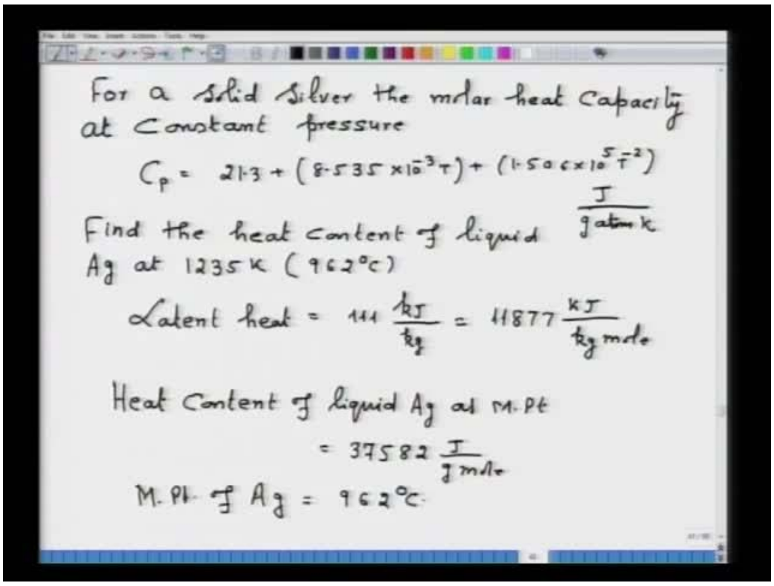

Now, let us take another example, let us calculate for solid silver. The molar heat capacity at constant pressure is given as C_P is equal to 21.3 plus 8.535 into 10 to the power minus 3 T plus 1.506 into 10 to the power 5 T raised to the power minus 2. Units are joule gram or mole kelvin; it does not matter whether it is gram or mole for silver.

So, find the heat content of liquid silver at 1235 Kelvin. This translates to 962 degree celsius. Now, you require various values. So, latent heat is 111 kilo joule per kg and that will also be equal to 11877 kilo joule per kg mole. So, now all that you have to do is substitution. So, this exercise, I leave it to you and I directly give you the answer. So, heat content of liquid sliver at its melting point should be equal to 37582 joule per gram mole or per atom and that does not make any difference. Please note the melting point of sliver is 962 degree celsius. Now, let us take the next problem. Earlier, we have evaluated the enthalpy change from summation of products and reactants and so on.

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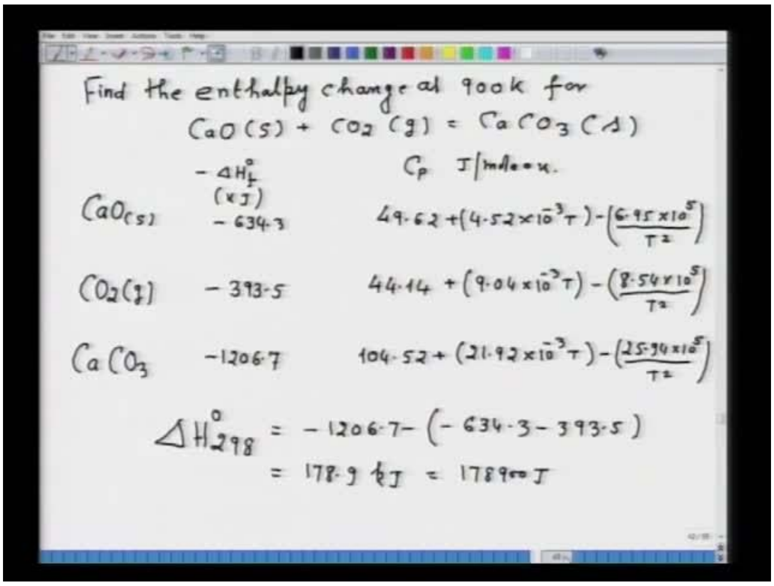

Now, let us evaluate by some other method. So, for example, let us calculate the enthalpy change at 900 Kelvin for the following reaction: The reaction is CaO; solid plus CO_2 gas is equal to $CaCo_3$; solid. Now, various values are given. So, calcium oxide solid minus delta H_f0 is given in kilo joule or delta H_f at 298 and then you require C_P value and C p is given joule per mole degree kelvin. So, calcium oxide is minus 634.3 C_P is 49.62 plus 4.52 into 10 to the power minus 3 T minus 6.95 into 10 to the power 5 upon T square and that is the value of C_P CO. Then CO_2 gaseous minus 393.5 C_P is 44.14 plus 9.04 into 10 to the power minus 3 T minus 8.54 into 10 to the power 5 upon T square. Then calcium carbonate $CaCO_3$ is minus 1206.7, C_P is 104.52 plus 21.92 into 10 to the power minus 3 T minus 25.94 into 10 to the power 5 upon T square.

So, these are all the given values and we have to find out the enthalpy change. So, as usual, first you have to find out delta H0 at 298. For this reaction, easily you can find out that it will be equal to minus 1206. 7 minus of minus 634.3 minus 393.5 - if you solve it, the value will be equal to 178.9 kilo joule. You can also put 178900 joule. Now, another way, you can also find out by determining the value of delta C_P and then integrating this value from 298 to 900.

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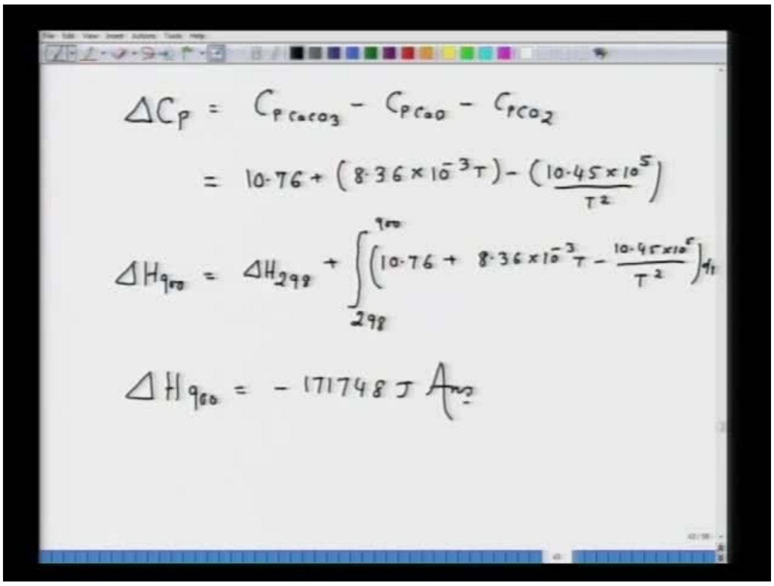

This is another method. So, we will try to find out delta C_P. Delta C_P will be equal to C_P $CaCO_3$ minus C_P CaO minus C_PCO_2. So, from the given values you have to find out. So, if you do this, delta C_P will be equal to 10.76 plus 8.36 into 10 to the power minus 3 T minus 10.45 into 10 to the power 5 upon T square. Now, delta H0 or delta at 900 celsius that will be equal to delta H_{298} plus integration from 298 to 900 kelvin and that is 10.76 plus 8.36 into 10 to the power minus 3 T minus 10.45 into 10 to the power 5 upon T square dt.

So, this is one integration, you have to do this integration. So, I straight away write down the answer, say, delta H_{900} and that will be equal to minus 171748 joule. Only my objective is to illustrate that the enthalpy change can also be calculated by evaluating delta C_P, which is the difference between the C_P of products minus reactant. This is also another method for calculating the heat content.

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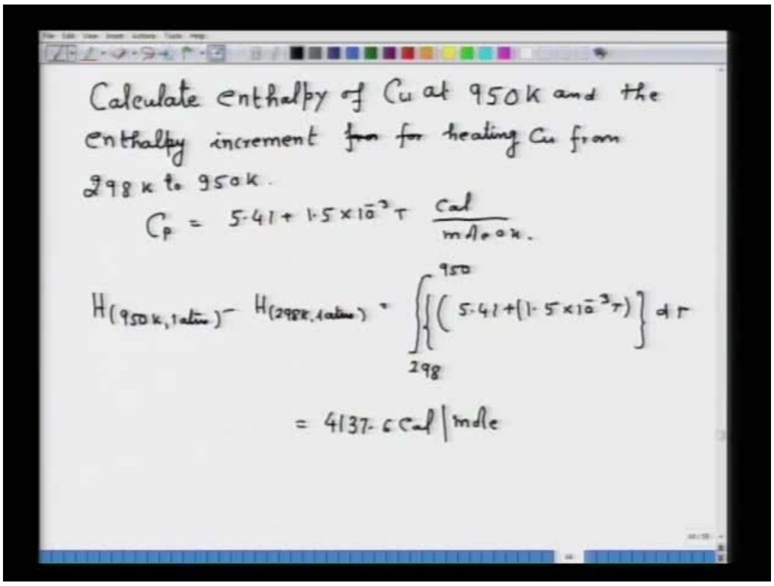

Now, let us see another way of calculation. Let us try to simplify and calculate enthalpy of copper at 950 kelvin. The enthalpy increment for heating copper is from 298 kelvin to 950 kelvin. Now, C_P value is given, C_P is equal to 5.41 plus 1.5 into 10 to the power minus 3 T calorie per mole degree kelvin.

So, enthalpy increment will be H at 950 kelvin. Of course, we are calculating it one atmosphere minus H at 298 kelvin at one atmosphere. It will be equal to integration from 298 to 950, 5.41 plus 1.5 into 10 to the power minus 3 T dt. So, if you integrate this thing, this value will be equal to 4137.6 calorie per mole. This is the usual method of calculating the enthalpy increment. In certain cases, sometimes to simplify the calculation, we have few options available, one option is there to use the value C_P and it is equal to a plus bt. We ignored the value of ct and other variables.

Another option is there, we use the mean specific heat and that is between the temperature region. You evaluate the mean specific heat and you calculate the heat content. So, these are the some of the options available. So, I will try to illustrate that. If you take the mean specific heat, what difference it makes?

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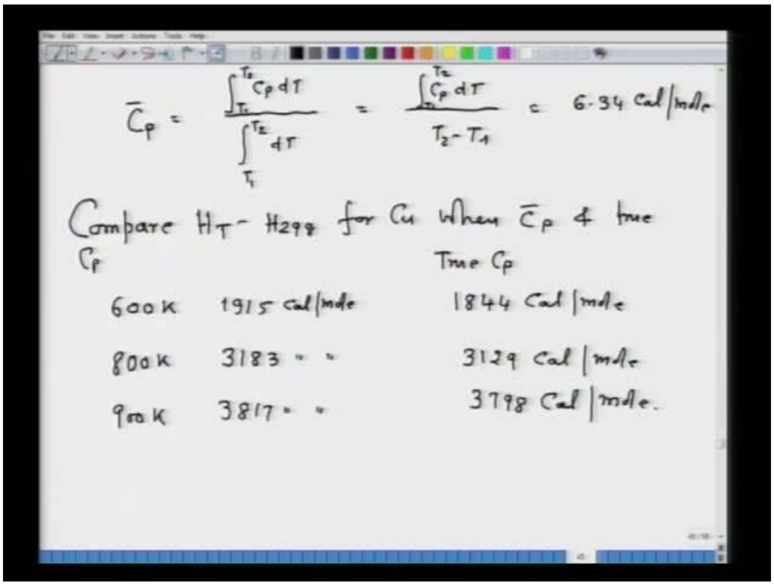

So, let us calculate based on the mean specific heat. Now, mean specific heat C_P bar and that is equal to integration from T_1 to T_2 C_P dt upon T_1 T_2 dt and that will be equal to C_P dt T_1 to T_2 upon T_2 minus T_1. So, if we substitute these values, we will get 6.34 Calorie per mole C_P dt T_1 T_2, which we have already calculated.

Now, this is the mean specific heat. Let us calculate from this, now the question is- compare H_T minus for copper, when mean specific heat is used and when true specific heat; C_P is used. So, now I selected three temperatures and let me take one temperature as 600 kelvin. So, if I take the mean value of C_P then at 600, I will calculate 1915 calorie per mole. If I take 800 degree Kelvin, then I will calculate 3183 calorie per mole. If I take 900 kelvin, then I will calculate 3817 calorie per mole.

Now, if I use true C_P value and the C_P I had already given to you. Integrate it from 298 to the respective temperature. So, in one case, you will be getting… Please do this exercise, I am simply writing the answer as 1844 in same unit, calorie per mole. So, you note down the difference, here it is 3129 and here it is 3798. So, these are the difference, when you calculate the heat content, utilizing mean specific heat. Of course, the exact value of heat content will be…, when you use the actual value of C_P, which is in the form of a plus bt plus ct to the power minus 2 and that is the most accurate. However, all other simplified versions of calculating of heat content either by using a mean specific heat or by using C_P is equal to a plus bt. No doubt, it will simplify your calculation or your effort of calculation, but the value will not be accurate. So, this point is to be noted in calculating the various values.