welcome back to this unit on thermodynamics and we this is lecture five in this unit

so in in the first four lecture we have gone through the introductory part definitions ah essential definitions and heat work and energy internal energy then we talked about first law of thermodynamics we went through in details about calculations of work heat in different processes especially for an ideal gas and we also talked about enthalpy and heat capacity in last lecture and then we also found out or learned how we can experimentally measure delta u and delta h in a process or especially in a chemical reaction then we started about ah finding out del h the enthalpy change in a process mainly in chemical reactions and if we can go back and just recap the enthalpy of reaction what we have found out in last class remember we talked about enthalpy of reaction which is given by delta r h naught and t means that particular temperature which is given by a i h m not t minus b i h m not t a i n bi are the stoicimatic coefficients for products and reactants in their balanced chemical equation and hm knots are standard molar heat capacity for each substances now we do not if we do not mention generally um if sometimes the temperature is not mentioned then we consider ah the conventional ah conventional temperature temperature considered as 25 degree centigrade or point 298.
1 five k

so if we just write ah delta r h naught as i a i a minus bihm naught then you will understand that it means that we are talking about the reactants and products are there in standard state and this change is happening at 25 degree centigrade now we talked about just started discussing about standard heat of formation or we call standard enthanp of formation now you you notice that you know this standard heat of formation and enthalpy these two terms are very frequently used interchangeably

so you can either call standard heat of formation heat enthalpy of formation or standard heat of reaction or enthalpy of reaction

so heat and enthalpy are very you know basically they used synonymously in this in this case

so you even you can tell any of these two quantities and this definition ah required because as we discussed in last lecture that we cannot experimentally determined this molar heat capacity molar enthalpies sorry you know as i said heat capacity its molar enthalpies now we cannot calculate the molar enthalpies because you know as we discussed earlier hence we we require the indirect method to find out the reaction ah heat of standard heat of ah reaction or standard enthalpy of reaction and that is the reason we define this ah this term standard heat of formation or stand of heat of reaction and you represent this as this for a particular temperature and if i just write like this then you will understand this is for 25 degree centigrade now we defined heat of formation in last lecture standard heat of formation was it is for a pure substance at a specified temperature t is the heat of reaction or enthalpy reaction for the process of the reaction in which one mole remember one mole of substance in its standard state at temperature t is formed from the corresponding separated element again at that particular temperature t and each being its in reference state or reference form or reference phase this is what we defined at the end of last lecture and you also ah mention what is a reference state or phrase or whatever form is the most stable state of the element at one bar pressure and that particular specified temperature t and if we do as again if you do not mention t then it would be a at twenty five degree centigrade and as you can see we have defined it for one mole of substance which means that it is a intensive quantity it is always for one mole of substance what are the standard reference state example so we can reference state reference states for some common substances at twenty five degree centigrade

so dihydrogen is hydrogen gas similarly di oxygen is oxygen gas carbon is carbon in graphite form with that 25 degree centigrade one bar pressure graphite is a stable form of carbon similarly sulphur in rhombic phase

so these are the example the where reference state means is the most most stable state for that particular element at one bar pressure and the specified temperature in this case we are talking about temperature as 25 degree centigrade

so you give you example ah some of the ah how to get this enthalpy of formation or heat standard heat of formation

so if we talk about ah for water

so standard heat of formation of water h two liquid then we have to find out the standard enthalpy of reaction or heat of reaction if we want to get it at 298 k then we have to get it at 298 k what is the product product would be h to a one mole at standard state at 298 k standard state means as we have described or defined in last class its a for pure solid and liquid its the state which has one bar if you can you know and that particular temperature for the pure substance and the reactants would be from the elements from which it is formed

so elements are oxygen and hydrogen in this case and at the same standard states 1 bar and 298 k most stable state state is for hydrogen is hydrogen gas and for oxygen this oxygen gas

so it would be in one bar one bar two ninety eight k

so these are the reactants as for our definition of standard heat of formation and this will be your product

so the reaction would be h2o gas plus half o two giving rise to h two l these are all at one bar pressure standard pressure two ninety eight k and the value for heat of reaction for this particular reaction which is equals to our according to our definition of water at 298 k is minus 286 kilojoule per mole

so this is you can find out where we are the state the enthalpy or heat of formation of a substance is the heat of reaction of formation of that particular substance from its constituents elements which are at their reference state and in standard condition and reference state is the most stable state at that particular temperature and pressure we can talk about other example this is we talked about h two o we can talk about methane c h four quickly

so in this case ah the elements are carbon and hydrogen

so most stable is graphite plus two hydrogen gas and ch four gas

so the heat of reaction for this reaction at 298 k would be equal to minus 78
74.
8 kilo joule per mole hence delta f formation of ch4 at 298 k would be same minus 74.
8 kilogram we talk about other examples c two h five o h ethan alcohol again the constituent elements are carbon hydrogen and oxygen

so we can write a balance equation for one mole of ethanol graphite plus three h two gas plus half o two giving us c two h five now this is all all we are talking about one mole

so in this case one mole of methanol one mole of ethyl alcohol

so delta r for this or reaction enthalpy of this particular reaction would be equals to this for c two h five then ah enthalpy of formation of ethanol and the value is kilojoule per mole

so this is how we found we can defined the reaction ah the heat of formation or enthalpy of formation one more example if you want to get h b or gas the enthalpy of formation now the constituent elements are bromine and hydrogen now at twenty five degree centigrade if you consider twenty five degree centigrade ah we want to find heat of formation at twenty five degree centigrade now at twenty five degree centigrade one bar pressure bromines most stable form is bromine liquid

so we have to for heat of formation we can write this reaction

so it will be half of this half of this h br if you just for example which is not a enthalpy of formation for example calcium carbonate we can form from by this equation solid calcium carbonate but in this case the ah delta r reaction enthalpy for this reaction is not equal to the formation of c a c o three solid because in this case calcium carbonate solid is not formed from the constituent elements

so remember the for form heat of formation it has to come from the ah elements now the heat of formation of of an element in its stand reference state is taken as zero because ah know standards it is the same reaction like if i take if i want to take the delta h formation of graphite graphite the graphite is form reference state is c graphite

so so the delta h formation for graphite would be the heat of reaction for this particular reaction at one bar and this particular temperature but this is always delta r for this reaction is zero which means that we can always consider that delta f rho for any elements at ah elements at at their reference state is always zero now we can we defined delta h reaction as summation of h m 0 of products minus h m 0 of the reactants i am not writing the term products and reactant because we have discussed this earlier now to make it simpler we can just write a equation like a plus b b just a simpler reaction now a b c d are stoichiometric coefficients now i can make a cycle like i can consider the reactants in this case a plus b b in their standard state standard states at some temperature t to products obvious we are talking about this reactions which is c c plus d d again in their corresponding standard standard states and at temperature t

so this is our reaction for which we want to get the reaction enthalpy or delta h r we mark this number one equation number one now we can take it back we can divide into two step first step we are taking back to their constituent elements in their reference state at that particular at this particular temperature and from here we go back to the product because the constituent elements for the reactants are and product has to be same

so we can think or imagine that another reaction where constitutive elements are forming the products we we mark them as equation number two and this is three because delta h is a state function or state does not depend on path

so we can consider the delta h r for first reaction reaction number one is equal to delta r h for reaction number two plus delta r h for reaction number three we can consider because del h does not depend on the path now what is reaction we can find out these two for the second reaction and third reaction what is second reaction all the reactants going to the constituent elements which is basically the device reaction of formation reaction and in this case tree from constant element to the products which is basically a formation reaction

so we can write the second reaction minus

so this is delta r h 0 for second reaction 2 and this is delta r h 0 for third reaction now this is reverse of the formation reaction

so we are putting minus sign we can write this is formation of a a moles of because this is for one mole and we are dealing with a moles in this case in this reaction we deal with a moles of a b moles of b c moles of c and d moles of d and delta h or heat of heat of formation is for one mole

so we have to multiply by the number of moles here

so we are writing b and for the third reaction we can similarly write these are all at same temperature ok that is given

so now onwards i probably will not write the temperature thing going forward which means you i can write delay 0 for reaction 1 as del r h 0 2 plus del r h 0 3 which is c del f i am writing this first because it is positive sign which is nothing but as a general we can write the heat of reaction for any reaction would be given by summation of a i h i for the products minus b i at particular temperature at temperature t

so if you compare that with the original definition of heat of reaction

so in this case we are instead of molar enthalpy standard molar enthalpy we can write we can exchange this standard molar enthalpy as the standard heat of formation for that particular reactants or or products we can give example ah like we can talk about this reaction burn combustion or methane in comparison particular temperature and all are in standard state then the heat of reaction or enthalpy of this reaction can be obtained from the enthalpy of formation for this products and reactants

so we can write for the products first delta f h 0 of carbon dioxide gas plus delta f is 0 of h2 l 2 moles

so we have to put 2 here minus delta f h 0 c h 4 gas minus delta f h 0 o 2 gas 2 here because of two moles here now this is the oxygen as the reference state at two ninety eight

so this term then the enthalpy of formation would be zero

so if you know this these values then we will be able to find out the reaction enthalpy of this particular reactions

so from this table these values are obtained from thermodynamic tables

so we can get those number i am omitting the units just to make it faster one mole plus 2 is into 285.

8 minus minus 74.

8 this is 0 which will give us eight ninety point four kilo joule per mole

so this means that we can get the enthalpy of reaction or heat of reaction for any particular reaction if we know the enthalpy of formation of the reactants and products now this equations where we write the balanced equation balanced equation along with the delta r h values we call this as thermo chemical equation and this thermodynamics which deals with the chemical reactions and the heat change along with this we we call this is branch this branch of subject we call often thermo chemistry now for in this balance equation we have to mention the ah physical state of the reactants and products and if it is in a particular allotropics state also we have to mention

so this we have to take care in the balanced equation just for giving one example of thermo chemical equation we have just written in a last example where we are giving ah the physical state of each reactants and each product now in this case we are also giving the value for the nth npm reaction it is better to write what temperature it is eight ninety point four kilo joule per mole

so this entire thing is mentioned as thermo chemical reaction and the few things you should ah remember ah or keep it in mind about this thermo chemical reaction and the property of ah delta h reaction first of this number the stoic symmetric coefficients this few things to remember three things to remember one ah about three things remember about this thermo chemical ah react reactions ah equations one is this twicemetric number or coefficients they represents number of moles not number of not number of molecules

so please be careful it is not the number of moles that is why it is always we can we can write fractions

so hence we we can write fractions if you do as just ah molecules then we could have not written half of o two or fifteen by two o two which means half o two means half moles of o two is reacting not half molecules of oxygen is reacting second we have talked about in the last ah lecture also that this is a extensive quantity extensive property or extensive quantity

so the value of this will be written will be as we write the expression

so if you multiplied the is this reaction like 2 4 2 4 then this value would be double of what it is or if you divide by half then this will be half

so it is extensive quantity and this mole is per mole of the reaction what we ah talking about the third thing you must remember that reverse chemical reaction will have opposite sign

so reverse chemical reaction will have opposite sign but equal magnitude in del hr

so the standard reaction heat of reaction or standard temperature oxygen for the opposite reaction would be plus eight nine point four in this case if we want to just elaborate with the example we know this example in decomposition of calcium carbonate solid plus co2 gas now delta r or heat of reaction for this is one seventy eight point three kilo joule per mole

so if i write multiplied by twice this amount and reverse the reaction gas twice csu3 solid then delta r for this particular reaction would be reverse

so minus and this is twice

so minus 2 into 178.

3 which is minus 356.

6 kilo joule far more

so these are the three things you must remember again one more that these are stoichiometric na coefficient they represents moles of the reactants and the products then delta r h which is the standard enthalpy of reaction of heat of reaction is extensive quantity and reverse chemical reaction will have opposite sign but of equal magnitude we will talk about now about the other process enthalpy change in other process and we will talk about enthalpy change during phase transition we all know ah what is phase transition is between transition between different phases of a particular substance it also sometimes called standard enthalpy of phase transition and the symbol is obviously there we always associate the particular temperature this is often called ah latent heat often it is called as latent heat the festive example of phase change phase change or phase transition like solid to liquid the process is called fusion or melting and we the symbol will write delta h if u s fusion standard at a particular temperature of course liquid to gas this is vaporization and the corresponding symbol would be this similarly solid to gas is called subli mason and corresponding symbol would be this now generally phase transition generally take place in at constant ah phase transition generally takes place generally happened at different temperature and pressure for example water or ice melts at one atmospheric pressure at zero degree centigrade to water or a water at 100 degree centigrade and one atmospheric pressure transition to gas water vapor

so we need to mention the temperature at which we are talking about this transition is happening

so if we write for example one one phase transition example we can write say h2o liquid to h2o gas now what is the condition it has to be obviously pure pure h2o one bar standard state one bar and if we consider hundred degree centigrade three ninety eight k similarly this is also pure water gas pure water liquid here one bar pressure 393 k

so the corresponding reaction enthalpy is found to be forty point six six kilo joule per mole

so this is the delta h vaporization of water liquid water at 393 k

so this example where we are not talking about 25 degree centigrade

so any likewise any heat of reaction or heat of formation also we can define temperature other than 25 degree centigrade so you have to calculate this is 2 373

so 73 not ninety three will define ah

so how we will define this is a standard enthalpy of vaporization of liquid water

so we can define standard enthalpy of vaporization is the is the amount of heat required to vaporize one mole again this is one mole of a liquid at a constant temperature and under standard pressure which is one bar

so something that is why sometimes it is called molar enthalpy of vaporization also and the symbol we have just mentioned here similarly we can define other standard enthalpy related to the other phase transition

so like standard enthalpy of fusion in this case one mole of solid is getting transferred to or transformed to liquid at it the standard state and that particular temperature and we also can talk about standard enthalpy as i said it could be heat of fusion or enthalpy of fusion like that enthalpy of sublimation where a solid is getting transition to a liquid the magnitude of the transition we can you can commonly also we can instead of vaporize and vaporize which you can generalize that ah delta is transition at particular temperature you can just like a general form and the magnitude obviously will depend on ah the intermolecular forces which binds the molecules together

so if the intermolecular attraction forces are higher for example a delta a vibration a standard enthalpy of vibration of water will be ah higher than the standard enthalpy of vaporization for acetone because the interaction attractive interaction force between water molecules are higher because of hydrogen bonding than acetone molecules now we have talked ah earlier also that delta h is a state function

so we it does not depends it only depends on initial and final states

so we can just to hm we can break any ah as i showed earlier also we can break any reactions is there many number of steps we can possible think of

so sublimation sublimation which is a ah solid to gas we can think of as two step process solid to liquid to gas

so in case of water we can like solid to h2o gas is your sublimation which corresponding delta h reaction would be 10 times zero

so we can break into two steps we can write delta s half sublimation is equals to fusion plus dentum vaporization that is that is we can write now this is related to ah what do you many times you are calling that delta h only depends on the initial and final state

so this is what is the principle behind the hesse law which will now discuss hess's law of constant heat summation suppose we want to find out it just it with the example it will be clear

so we want to find out delta f is 0 of at 298 k of ethane gas

so what is the formation reaction constituted elements of ethane is carbon and hydrogen

so we can write carbon in their reference states graphite plus hydrogen in this reference state to ethane gas standard state at 298 k and then we can balance it the reaction as per requirement now this reaction is is not feasible you know graphene graph graphite reaction react with the hydrogen to produce ethanol is its not that common reaction

so this reaction reaction enthalpy for this particular reaction at k is not experimentally determinable

so so the reaction though we can we can imagine this formation reaction but this is not the way ethan is formed at 298 degree centigrade

so this particular for this particular formation reaction the enthalpy of reaction is not possible to obtained ah experimentally

so we have to take indirect plot

so what is the indirect part we can think about we come on think about that measure the heat of combustion of ah graphite hydrogen and ethane and then using those three reactions we can find out the enthalpy of reaction of this reaction formation reaction will give you example ah

so we can write the combustion reaction which is basically burning in oxygen and delta r for this reaction at two ninety eight k is one five six zero i am not liking kilo joule per mole just to make it faster but you always should write unit associated with this i also writing the temperature all the time minus three ninety three point five and h two h2 gas plus half o2 gas gives you h2 liquid and dental h 0 for this reaction is minus 286 kilojoule per mole this is common for all these things now we can rearrange this equation and and and multiply with ah moles with numbers because this is extensive quantity and rearrange to get this equation this equation we just basically combine these equations to get the re our this is what our equation we need ah to get from combining and rearranging this expression

so if this is my first reaction this is second this is third what we can do we can the product is this side

so we have to reverse this reaction and this is one mole

so you can just reverse these things in this case product reactant is three moles of hydrogen

so we can multiply three with this reaction and in this case two moles of graphite

so we have we can multiplied by two this reaction

so what i will do what we will combine reaction one and multiplied by minus one because i want to reverse it which will give us two co2 gas c two h six gas plus seven by two o two gas and we have multiplied by minus one and this is a extensive quantity

so we will multiply the earlier we have this value we should multiply by minus one

so we will get fifteen sixty in this case

so delta h r is 1560 again i am not writing the units just for our convenience

so in the second reaction we will multiply by two to get to carbon graphite gas and it will be again twice of the reaction we had

so it will be twice multiplied by minus 393.

5 which we had earlier and the third reaction we had we can multiply by number three is 2 gas plus 3 by 2 oxygen gas is 2 liquid we have to multiply it by 3 here

so three into minus two eighty six

so if you can add this what will get this ah carbon dioxide and this will cancel out this water three water tree water been cancelled out and two oxygen and three by two oxygen will cancel out with seven by two oxygen both sides

so we will end up as two c graphite plus three h two graph right side c two h six gas

so this is exactly the equation we we wanted to get it our interest

so it is exactly the expression

so we can add this number and we can find out the formation reaction the enthalpy of formulation reaction this will will find out to be minus 85 kilo joule per mole which means delta h formation of ethane gas at 298 k is minus 85 kilo joule

so this is how what is hess's law is all about where you can combines equations to get the reaction gives reaction enthalpy of reactions which is not practically attainable which is cannot be determined experimentally

so as a generic process we can write if this is my reaction a to b

so this is the enthalpy of reaction we can consider intermediate step so this is del h one another intermediate h two another third step then r h three then del h r for this reaction will be del r h one del r h two plus del r h three

so this is the basically this is the general form of ah the hessian's law

so we will just take example numerical problem ah if you can focus this problem here it says given the standard enthalpy of combustion of graphite is ah 373 combustion reaction c graphite

so this is question 10 in our thermodynamics unit

so graphite is plus oxygen co 2 gas the reaction is the delta h zero is minus three ninety three point five i am not writing the unit one more time and that of diamond is ah three ninety five

so c of diamond this is combustion reaction gas is zero is minus three ninety five point four if we can if we add this and reverse this

so our interest from graphite

so we have to calculate the enthalpy change from graphite to diamond transition that is the problem is graphite to diamond

so graphite is a reactance and diamond is a product

so we will reverse this second equation

so c graphite between two c diamond

so it will be again the sum of summing up will be to delta for this particular reaction would be minus three ninety three five ok and reverse which will add the reverse one

so basically three ninety five point which will turn out to be 1.
90 kilo joule per mole

so this is the example how you can the example of ah hesse's law what we are applying and this reaction which we are talking about all the time is a combustion reaction and

so we can also define a ah heat of reaction or ah enthalpy of ah ok we will talk about that in in in the next class where we will talk about enthalpy of various types of processes different types of processes or reactions

so that will be ah from where we will starts and one of the ah example would be the combustion reaction we just talked about

so we this will stop now and we will start about the enthalpy of different types of standard enthalpy of different type of process in next next class you