welcome back to this unit on thermodynamics

so in today's lecture 4 we will talk about determination of del u and del h experimentally and then we will talk about change in enthalpy ah in different processes or in reaction in last lecture we talked about enthalpy and heat capacity just to ah recollect ah quickly enthalpy we mathematically define h as u plus pv and as u is a extensive quantity u is h is also extensive quantity and you cannot be determined experimentally absolute value

so h cannot be also determined ah absolute value of h cannot be determined experimentally del h is a state function we also have seen that del u is almost the value of del h is similar to del h for solid and liquid subnet in this case we are ignoring the volume change in a process for solid and liquid but for gas ideal gas we have seen that w is 10 u plus d n g r t which is change in moles number of moles of gas this is for iodine gases you also have seen for any process any processes at constant volume del u is q v and for any process at constant p is del h is q p and we also seen for any process for ideal gas of course closed system is there del e u is given by c v del t c v is the heat capacity as constant volume and we for this course we are considering c v is independent of temperature and del h is c p denty this is for again one more time this is for ideal gas cp is always greater than c v mainly for ideal sorry for gaseous substances for solid and liquid c p is very close to cv for solid and liquid and for ideal gas for ideal gas cp minus cv is nr

so these are the things we learn from last class

so i will continue to ask few question and see whether your understanding about these terms are ah clear or not

so again i will mention a process and you have to tell me the sign of q w del u and del h

so thats question 7 continuing from last class

so in question 7 first is reversible adiabatic expansion of an ideal gas

so you have to tell me what is the sign of q w del h n obviously adiabatic which means q is 0 expansion you know expansion means w is negative

so daily would be also this is q plus w

so it would be also negative now we know for ideal gas del u is c v del t if del u is negative c v cannot be negative is always a positive number as del u is negative del 2 must be negative which means if i write now del u is equal to del h we know del h is del u plus del pv instead of pv we can write n r del t ideal gas now del t is negative delta e u is negative

so del h has to be negative you can get directly also del h is ah c p d t for ideal gas because delta t is negative del h also has to be negative

so i will move to the next example which is ah two it is a adiabatic expansion of an ideal gas into vacuum now quickly adiabatic q is equal to zero expansion into vacuum

so w is zero q zero w zero then delta u zero as delta zero ideal gas delta t zero as delta t zero ideal gas delta h zero this is this was easy three is reversible heating of an ideal gas at constant p we talking about heating

so q must be greater than 0 constant pressure

so q p is del h must be greater than zero ideal gas and c p del t must be greater than zero hence del t must be greater than zero if del t greater than zero del u is cv denty must be greater than zero if del u if del t is greater than zero v del v which is given by n r we talking about constant pressure process

so p skins constant for ideal gas del v is given by n r p del t as del t is greater than zero del v is also greater than zero and as del v is greater than zero w is less than zero

so in this series i will give the last example reversible cooling of an ideal

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gas at constant v again cooling means q less than zero constant v w is equal to zero del uq plus w less than 0 hence delta t less than 0 once delta t is less than 0 means del hcp denty which is also less than zero

so i am just i just gave you few examples how you can basically it will clarify your understanding and the sign of the process different processes will mainly discussed about ideal gas now we will talk about experimental determination of or measurements of del u and del h how it is done in the lab now the instrument which is used to measure daily and del h in the lab is called calorie meter and the process of the reaction is carried out the process or the reaction is carried out in a vessel in a reaction vessel or the process vessel whatever you call which is called calorimeter which is basically the vessel is immersed in in water but mainly whatever it could be other liquid but mainly water bath is used of known quantity and non specific heat of course if you use water known heat capacity in this case heat capacity of the heat capacity and the weight or mass of the or the calorimeter is also known or the vessel is known is known as well as the mass

so from the if post the process suppose the reaction if we can find the delta t we can find out the ah from the value of density we can find out q

so first we will talk about del u daily how to measure del u and the calorimeter we use is the name called bomb calorimeter and i have taken the picture from your textbook and if you look at this picture this is a boom calorimeter here what happen this is a steel vessel

so volume is fixed they are not expandable and sample is kept within the vesicle the vessel the vessel is called bomb and in this case we are showing example of a combustion reaction burning of the sample in presence of oxygen

so sample is kept within the bomb and oxygen is passed and sample reaction happens now this entire bomb is kept in a surrounding water bath which is again sealed by adiabatic wall

so any change in temperature in the surroundings surrounding means in in the bath here water bath here can be measured by the thermometer and there is a star is also used which just to make the mixing or the temperature uniform remember this is the entire system is kept in a adiabatic condition

so no heat is allowed to go out and come in and because in this process the volume is kept constant and you know with the volume process ah constant volume process we can get the delta u if we know cv of the material

so once the reaction is over we can find out from this thermometer what is the del t and if we know the heat capacity for the surrounding water plus the bomb then we can find out w value from c v d t this is we can apply this expression because we are doing this reaction at constant volume if you want to calculate del h del u as you found out that it can be calculated from constant volume process generally del u are obtained when by measuring the heat exchange at constant pressure processes and generally we keep a the pressure is kept at one atmosphere or atmospheric pressure and the heat which ex get exchange or it generates we call that as a heat of ah of the reaction or ah or enthalpy of the heat change which is associated with this reaction enthalpy of reaction and generally we use this symbol delta h r sometimes we can also write del h r also some books also refer these are for exothermic reaction if the reaction is exothermic heat comes out

so cube and if you are doing at constant pressure

so q p is less than zero negative hence den r h also negative value and for endothermic keep is positive

so den h r is zero

so you can that's why if you do reaction chemical reactions constant pressure pressure condition then we can write for the exothermic reaction del h is

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negative and for endothermic reaction del h is positive and it is simple you can get this measurements done in a lab using very simple calorimeter where ah the reaction is done inside this vessel reaction vessel and this is kept in a container in this case it is a foam polystyrene cup which is basically ah thermal insulator

so it basically prevents heat to go out from the surroundings or come in from surroundings and there is a thermometer which measure the temperature before and after

so once the reaction is over from the temperature ah before the reaction and temperature after the reaction you can get del t value and once you know the delta value and if you know the cp of the calorimeter used here then we can get the value from c p del t ok we can get this because we are doing it atmospheric pressure in this constant pressure process constant pressure process

so i will give you a problem again from your book and solve this here i will just write down the problem from your book

so it is question 8 for this course where one gram of graphite is brand in a bomb calorie meter in excess of oxygen at 298 k and one atmospheric pressure as per the following x equation c graphite during the experiment the temperature goes from

so t 1 was 298 k and t 2 is 299 k which means del t is 1 k and heat capacity is given at is a constant pressure heat capacity cp is given as 20.

7 kilo joule per kelvin

so what is the delta h value for this reaction

so is it is given here what is supply del t is supplied cp is supplied

so we can get q as c p delta t twenty point seven kilo joule per mole inverse into you convert into moles

so twenty twelve gram per mole and it is for one gram

so we put one gram now it is a burning reaction in presence of oxygen you know in burning of any substance in presence of oxygen will produce heat

so q must be a its exothermic reaction

so q is lost from the system

so the value of q must be a negative quantity

so we put just to take care of the sign from a system point of view we will put a negative number here which will give us this value as 2.

4 to 10 to the power 2 kilo joule per mole again just to emphasize about the sign because in this case system is losing some energy as this is exothermic reaction any burning is a exothermic reaction as you know hence this negative sign is appearing in this case

so the magnitude would be this but the absolute value would be with a negative sign

so what i will do i will put one more question in front of you which is question 9 in this case

so we talked about all these quantities in last two three classes and then just to revise or recap um the lessons you just tend to tell me this quantities whether they are intensive quantity or extensive quantity they are intensive or extensive and obviously as i said you need is a very important thing in solving physical chemistry problem

so you must you must remember ah the units or the handle units very carefully

so density is a intensive quantity or extensive quantity is a intensive quantity intensive intensive quantity and unit should be kg meter my cube per meter cube internal energy is as we said is extensive quantity extensive its energy

so the unit should be joule this is molar enthalpy

so enthalpy per mole

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so it must be a intensive quantity its energy per mole

so joules per mole c p c p is a heat capacity at constant pressure now its a capital letter as you see you can see its upper case or capital error

so it is a heat capacity not molar heat capacity or specific heat capacity

so it depends on the size of the system the more the higher is the mass higher will be center of c p

so it must be extensive quantity and its energy heat per kelvin

so it per degree rise in temperature

so joules per kelvin this is a smaller letter c and

so is a specific heat capacity constant pressure sorry is constant pressure

so per gram which means its a intensive quantity

so it will be joules per kelvin per kg cpm is a molar heat capacity at constant pressure

so it should be intensive again

so again j k inverse mole inverse pressure pressure you know its say intensive quantity and s i unit is pascal molar mass is again intensive

so most of the molar quantities or specific per gram quantities are are intensive quantities

so its kg per mole and temperature is of course intensive quantity and this i unit is kelvin

so we just to recap we did exercise to find out whether you know ah which is intensive quantity and extensive quantity and as i said the units you must be very careful about the units

so you need to solve numerical problem if you write the units properly you will you are bound to get ah the final answer right next we will move to the enthalpy of enthalpy change of a reaction of or a process and we also call this as reaction enthalpy or on the sign we write del h r or in some cases we write in the nature but in this case your book it is textbook resident this

so we will use this as a representation of reaction enthalpy

so in generally a reaction a chemical reaction can be written as ah react set of reactants to products

so by can by doing the reactions or by transforming reactants to product there should be ah change in enthalpy between the products and reactants that enthalpy change is what we call the enthalpy of reaction or reaction enthalpy

so we can write the reaction enthalpy as sum of sum of enthalpy of products minus sum of enthalpy p is capital net and ps of reactants as you can write a i h products minus b i h reactants where e i and b i a i n b i are the two isometric coefficient of the products and reactants respectively in the careful in the balanced

so you have to when you talking about the stoichiometric coefficient that has to be in the balanced balanced chemical equation unless if you do ah balancing you will not be able to get the stoichiometric coefficient right

so these are a i and b i they are the stoichiometric coefficients for products and reactants in balanced chemical equation

so just to take a specific case for example if we take this reaction c h four gas plus two o2 gas coco gas two h2o liquid then delta h reaction or reaction enthalpy or reaction heat heat of reaction should be given by as wrote in last page products minus summation of v i h reactants which will be given by products means h m c o two g plus twice h m h2o liquid minus hm ch4 gas plus two h two h m go to gas now what is this hms this hm is molar enthalpy of carbon dioxide in gaseous state molar enthalpy of water at liquid state

so h m is called molar enthalpy of the corresponding reaction reactants or products

so for exothermic reaction as we discussed earlier exothermic reaction del r h

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should be negative and for endothermic reaction then h r should be positive and this is very important to know the value of ah these quantities because if you are doing a reaction in a plants or in the lab unless you do not know what is the amount of ah heat comes out it will very difficult for you to control the reaction

so its

so the value for when you are doing a reaction a chemical reaction in the lab or in in a plant especially a large scale then you should you must have idea about what is the amount of del h in this reaction

so that you can accordingly design your machinery or equipment to handle that heat generation in this case or or it ah man basically managing the heat which is coming out it is also important if you want to know the temperature dependence of equilibrium constant

so it is very important now as you can see that del hr depends on the conditions under which a reaction is carrying carried out isn't it reaction is carried out

so we must know ah we must need to know a specific condition or the standard condition by which we can compare

so we must know we must need to specify standard consider

so that we can compare ah between the reactions and we

so in see if the reactants and products in standard conditions reactants to products if all of them are in in standard condition same here standard condition then the corresponding del h would be del h r and we put a super escape degree superscript or not whatever you can call

so this signifies a standard heat of reaction of enthalpy of reaction now you have noticed that we are talking about reactants in standard conditions and product in standard conditions

so obviously we will ask what is a standard conditions

so we must define the standard conditions and at standard considers the molar enthalpy would be standard molar enthalpy

so h m we wrote h m in um few minutes back it is molar in molar enthalpy

so if in standard condition we can write this as standard molar enthalpy

so obviously your question should be what is ah standard conditions

so we must define standard condition

so definition of standard condition

so this we can write the nation of standard conditions and we limit in this course we will talk about mainly pure substance we will not about talk about pure substances we will not talk about the mixtures or in solutions

so in case of pure solid and liquid

so this is what i said you will restrict our discussion on pure substances it does not mean that we cannot describe standard conditions in solutions or in mixtures but for this unit or this course will describe or limit our discussions for pure substances

so for pure solid and liquids we define standard state as pressure equals to one bar and at a part at a specified temperature of value t this t is the temperature we are interested in

so basically say we can want to say that standard state of liquid water

so if you want to turn the standard state of water it will be a state where what water is at one bar pressure and we have to specify the temperature

so if you want to write standard of water at 25 degree centigrade then the standard state of water at 25 degree centigrade would be water at 1 bar pressure and at 25 degree centigrade which means the standard state is not a fixed state it depends on the temperature which you are interested in pressure is fixed for each standard state we are mentioning that pressure is one bar sometimes we call

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this as a standard pressure but one bar but this is this will change as we change our temperature

so if we just talk about molar enthalpy standard enthalpy then we must mention a particular temperature

so in this case it will be molar enthalpy see if you talk about say water of water then more enthalpy of water at one bar pressure and at temperature t if you talk about hundred degree centigrade then it will be hundred degree centigrade or twenty five degree centigrade it will be 25 degree centigrade for gas we talked about pure solids and pure liquids then we will talk about pure gas now pure gas standard state is again p is one bar at temperature temperature is equal to t and there is a third condition we are writing where the gas behaves as an ideal gas now you know that at one bar pressure no real gas no real gas will behave ideally at one bar pressure and at temperature any temperature t hence for a gas for a pure gas this is is something which is imaginative or fixes

so for gas standard state is

so since no real gas with behave ideally at one bar pressure standard state we can write that standard states of gases pure gases are alpha tcs states which is is not a real state because really we cannot get a condition where the gas behaves as ideal gets at one per pressure now this important if we do not write any temperature sometimes your book it is also not mentioned as i said the standard state all the standard cell will have a temperature you have to mention temperature for corresponds to standard case bought in case of gas as well as we talked about in liquid and solids but in case it is not mentioned then you can safely assume that it is 25 degree centigrade but this is incorrect way of representation without mentioning as temperature in standard state but in case in case there is no mention of temperature in standard state then it is usually meant that temperature is twenty five degree celsius

so you can safely assume that its a temperature twenty shape

so we can assume temperature twenty five degree c if no temperature is given or mentioned but as i said this is not correct way to define standard state ideally every time when somebody refers to standard state it should mention about the temperature but in case somebody do not mention you can assume that it to be twenty five degree centigrade

so we can for any reaction any for the following reaction a a plus b b into c c plus d d we can write the standard standard reaction enthalpy now you have to mention a temperature at t would be given by c h m t c plus d h m t d minus a h m t a h m not t b now this h m for example h m t this if i just want to mention this quantity this i can write separately this is standard molar enthalpy of a at temperature is equal to t

so when you talking about this reaction enthalpy you should mention t as i said if temperature is not mentioned then you can truly assume that t is twenty five degree centigrade we can write ah a expression um now we can also imagine that this now this all this number a b c d these are what these are are stoicimetric coefficients in balanced chemical equation which means these are their unit less

so they have no dimension unit less quantities which means this term will have the same dimension of this molar enthalpies this they all have same dimension same units which means del h r 0 t will have same dimension or unit as h m which is what energy per mole

so joule per mole or say calorie per mole

so this is important the unit of reaction standard reaction enthalpy that would be joule per mole or calorie per mole now this is exception where we are writing per mole but you will soon find out that this is not a intensive quantity its actually a extensive quantity i will just give you example now delta standard

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reaction enthalpy will depend on or depends on how you writing the expression how you how the reaction is written and it is a extensive quantity even though its unit is joule per mole quantity for example i write expression equation this this is a obviously first thing you have to check whether this is a balanced equation not

so once you check the balance equation and the delta h value the heat change or heat of reaction of this reaction at 298 k is given by minus 572 kilojoule per mole now if we consider all these hydrogen oxygen and water in standard condition in this reaction which is at one bar and this particular temperature then we can write this standard enthalpy of reaction this now if i write the same reaction i can write this way as well this is also balanced equation here two moles of hydrogen and one mole of oxygen is reactant we can say half mole of oxygen and one mole of h two is reacting in this case the the reaction enthalpy at the same temperature would be half of what we had earlier

so depending upon how i ah we are expressing the how the reaction is written depending upon how the reaction is written

so if the reaction is written like this we have reaction enthalpy standard reaction and then p of some number if we write in different way then it will be a different number though we both cases we have per mole if we write 4 2 4 then the number would be double

so basically its standard enthalpy change per mole of the reaction as we have written

so your cl i i hope this has not this has clarified that even though it is per mole term is written it is not exp invasive quantity its indeed extensive quantity

so if you double the amount each of this reactions amount it will be double if you make half then it will be half as well now in when we are writing this expression for ah reaction enthalpy at particular temperature we are all referring to this molar standard molar enthalpy or molar enthalpy at standard set whatever you call now as you have seen earlier that the absolute value of h or absolute value of u cannot be determined experimentally which means the absolute value of h a 0 m also cannot be determined experimentally only it can be determined relative to something

so we have to get this value relative to in comparison to something or in indirect way and for that we will define something which is called standard heat of formation later on we can show that instead of standard molar enthalpy we can replace this with standard heat of formation we will show that in the next lecture now standard heat of formation is or standard heat of ah standard enthalpy of formation is we write again this has to be a particular temperature we can write this is for a a pure substance at a specified temperature t is equal to the delta h 0 or reaction enthalpy of a reaction or for the process or for the reaction or reaction in which one mole remember we are talking about one mole here of substance in its standard state at t is formed from the corresponding sepa rated elements at t each being being in its reference state or sometime called reference form or something called reference phase

so its a quite long definition delta h formation of a pure substance is at a specified temperature we always have this temperature at which is the is equals to the reaction enthalpy for the process of the reaction when the substance one mole of substance is formed from the elements in their reference state or reference form or reference phase how do you call now what is this reference phase or reference state of the elements of the constitutive elements is is the reference state or phase or form is the most stable state of the element at one bar pressure and at at the specified temperature t now if temperature is not mentioned sometimes like in your text book it is assumed that t is 25 degree

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centigrade

so sometimes unless it is mentioned sometimes if the reaction hm the reaction enthalpy for the formation reaction is not the temperature is not mentioned then you can consider the temperature is at ah is equals twenty five degree centigrade

so the you can reference state would be the most stable state ah at one bar pressure and at twenty five degree centigrade

so what i will do i will stop ah now in this in this lecture and then in next class on i will talk about the enthalpy change associated with other processes like phase change and in chemical reactions and will also continue our discussion about this reaction enthalpy ah little more or basically the the enthalpy of formation little more with some examples you

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