Thermodynamics And Kinetics of Materials

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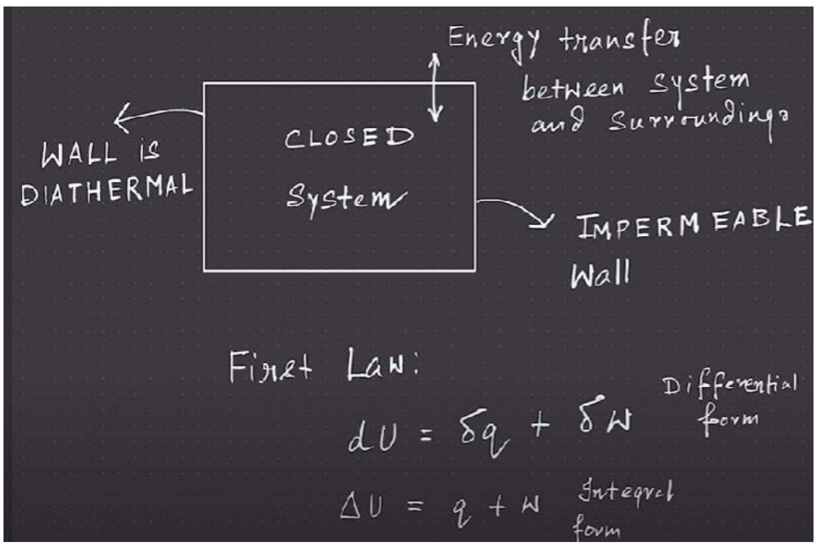
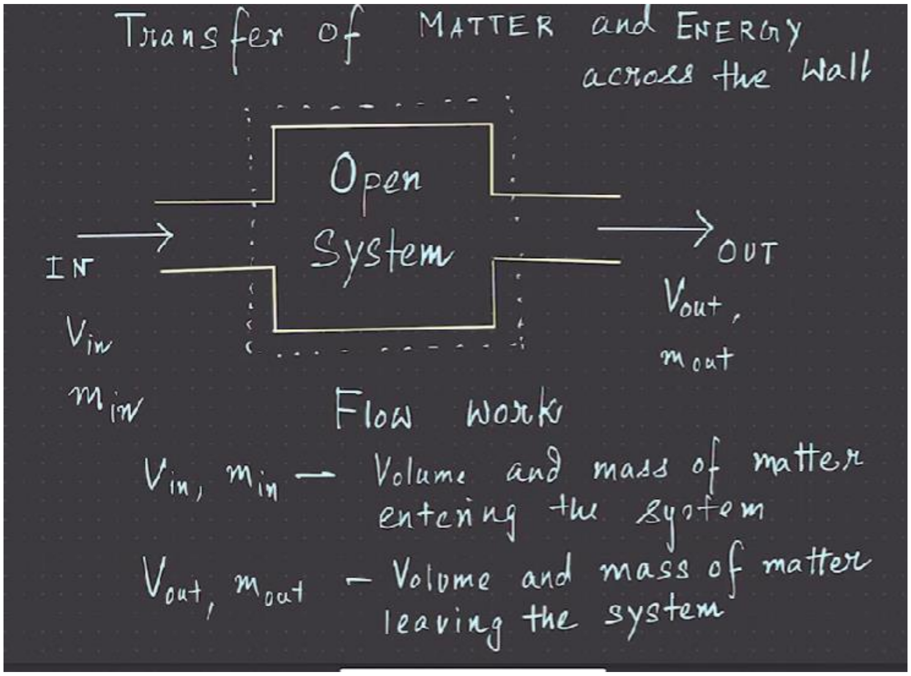
Lecture 4
Heat capacity and Enthalpy

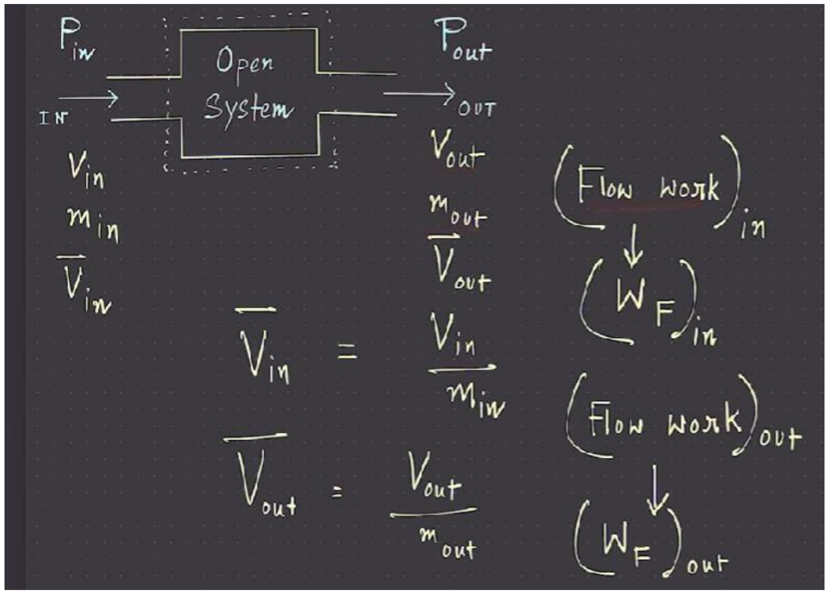
So, today I will be talking about enthalpy, heat capacity and I will be going on talking about the first law means and enthalpy heat capacity and slowly we will go into the second law. So, remember we talked about first law and we have already given a statement of first law in the differential form this is like ΔU du plus δq plus δw and you can write it in the integral form means even more so that becomes like this is the differential form again these are path differentials as you can see here that these are path differentials and if I do this ΔU plus q plus w and this is called the differential form and this is something that you get after integration.



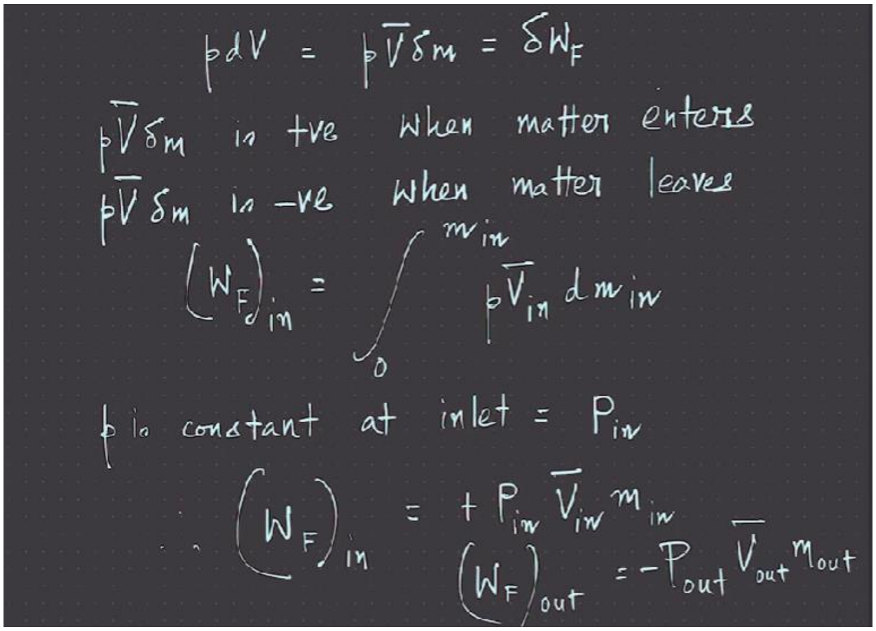
So, when you do integration for example, U is a state function so you are integrating between the initial and final state or between two states so you get ΔU and q and w again depends on the path. So, this is basically you can call it like this is more like a integral form or you can call it like that means where you have done the measurement over say two states this is like that so it is after integration so this is the integral form. Now, as I told you so when you have a closed system then energy transfer is something that is allowed energy transfer between the system and the surroundings is allowed but the wall is impermeable although the wall is diathermal means allows heat transfer at exchange in the surroundings but it is impermeable that is it does not allow exchange of matter. So, in such cases for closed systems this is the first one.



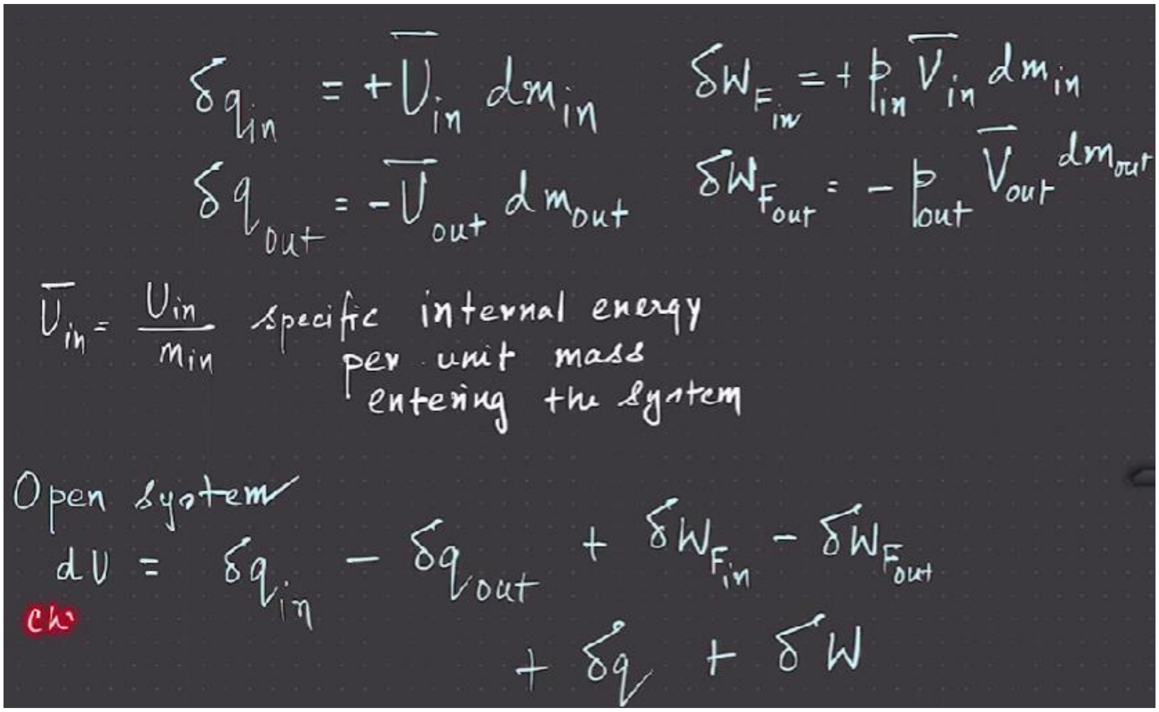
Now, what about open system open system means for example, I have taken this system this is my system boundary please understand this is my system boundary is dotted like this is my system boundary and there is some substance that is pushed in and substance that is pushed out right matter pushed in matter pushed out so basically this open system allows exchange of matter as well as energy so it is allowing some matter as well as it is not energy right across the boundary. Now, in these cases when you have such a system at steady state for example, steady state means we are not talking about any rate of accumulation or stuff so then we have to include something called flow because you are pushing in some matter here you are pushing in some matter you are taking out some matter it can be some fluid some solid whatever it is now when you are pushing in some matter obviously you are putting some means if you are pushing in some matter then you are applying some pressure on it right and you are taking out some matter then basically again it is you are basically when you are forcing then you are putting a force on it or pressure on it and when you are taking it out then you are relieving some pressure so that is how we can think of it so this what that happens is called flow. Now for example, we tell that the amount of substance that the substance that comes in I specify using something like V_{in}, V_{in} is the volume input and our volume at the inlet of that substance that you are pushing in and m in is the mass of the substance that we are pushing in and again V_{out} and m out are the volume of the substance that we are pushing out and volume of matter that you are pushing out and m is the mass of matter



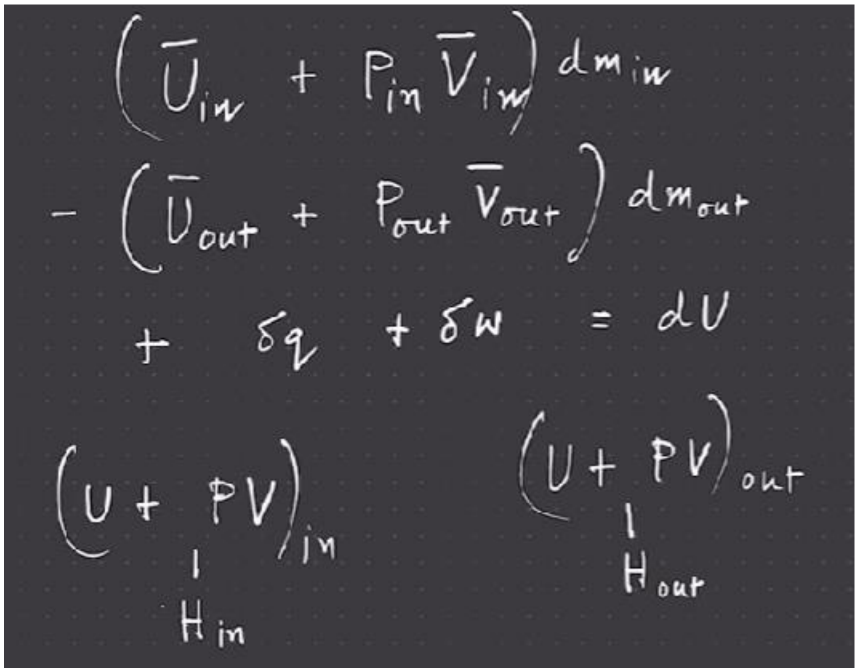
that you are pushing out so basically now as you can see in the open system there is some mass pushed in or some matter pushed in which is some mass and some matter pushed out right so in that open system although it has all these other things that there is an internal energy like you and then there is also you can have some other processes but there is also this process where you are pushing in some matter and taking out some matter right so you are taking out some matter and you are pushing in some matter. Now in such cases if you have such an open system we can think of there is a pressure at the inlet and there is a pressure at the outlet which is again let the flow work and we can call so now we can think of a specific quantity which is basically volume per unit mass inlet so that means you are the m in is the mass at the inlet right mass of matter that is pushed in the open system now $\bar{V}$ in is a specific quantity that is a specific quantity mass or mole and what we are doing $\bar{V}$ in is nothing but V_{in} by m in right and similarly you can have $\bar{V}$ out which is $\bar{V}$out will be V_{out} by m in right so there is a flow work in and there is a flow work out and we call it WF in and WF out now you see when you are pushing in some matter you are applying some pressure P in right so there is a P inlet so we can call it $\bar{V}$ Δ m or dm is a basically a state function so I can replace this with D $\bar{V}$dm which is basically so P $\bar{V}$ dm so P dV so what I am doing is I write P dV right where P is the P in say P in say and then there is D V and dV so what I am doing is I am writing dV equals to $\bar{V}$ dm right $\bar{V}$ dm because $\bar{V}$ is volume per unit mass right so P $\bar{V}$ dm which is ΔWF right that is the V_{in} now P $\bar{V}$ dm is positive when matter is entering when matter enters P $\bar{V}$ dm is positive because it is what you can think of it is like some work done on the system and when P $\bar{V}$ dm is coming out that is matter is coming out then P $\bar{V}$dm is negative right so because what is coming in we are taking as positive that is convention and whatever is coming in is basically giving you a positive contribution coming out is a negative contribution



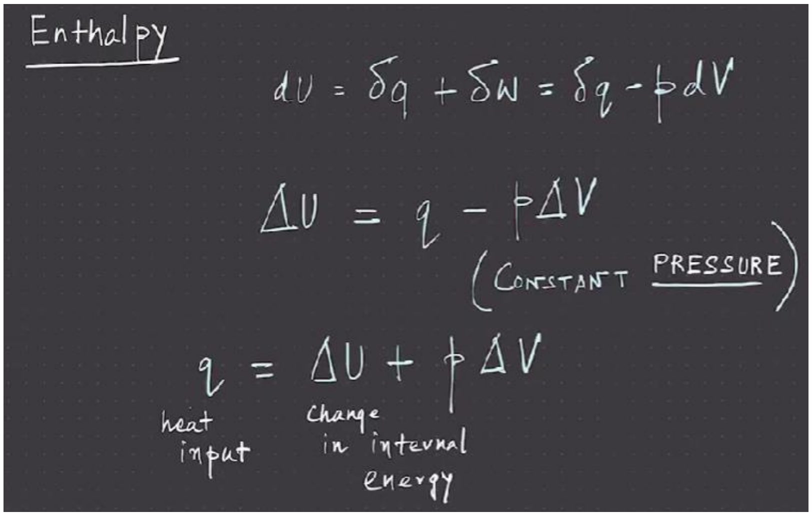
so if I now do this I have WF in which is P $\bar{V}$ in dm and dm in this is and this is and P is constant inlet let us call it P in so basically if you look at this integral so P which is constant at the inlet is P in so I take out P so P in $\bar{V}$ in also I can take out and dm in I am taking from 0 to m in right because it was initially nothing was there and then I have pushed in some matter so 0 to m in and so 0 to m in means basically it will be plus P in $\bar{V}$ in m in that is my WF in right the flow work that is input and the flow work that is output will be minus P out $\bar{V}$ out m so if that is moreover the matter that we are pushing in has some internal energy again I can define something like U in by m in which is nothing but $\bar{U}$in which is specific which is like a specific internal energy per unit mass entering the surface of the system similarly $\bar{U}$ out will be the specific internal energy as set the mass that is leaving the system so this is specific internal energy associated with the mass that is entering this is the specific internal energy as it mass that is leaving and then you have Δ Q which is plus U in dm in and then you have minus U out dm out and you also had W Δ WF in the flow work input and then the flow work output which is P in $\bar{V}$ in dm in P out minus P out V_{out} $\bar{V}$ out dm out so whatever you can see the sign convention that is followed is anything that is coming in corresponding to the same closed system convention that we followed that heat input is positive similarly the flow work that involves matter coming in and along with the matter the flow work coming in flow work that is done to push the matter in and the internal energy associated with that matter that is pushed in all of these we are taking as positive and whatever is leaving the system we are taking as negative now so if I have to now balance the energies what I get is dU, dU is the change in energy is infinitesimal change in energy in the open system it is a change in energy internal energy again it is an infinitesimal change in the open system so this change in internal energy is equal to Δ Q in minus Δ Q out plus Δ W in minus Δ W out plus Δ Q plus Δ W that is the heat input to the open system and definitely the work done on the open system or work done by the open system can be on or by and depending on it we will put negative sign or positive sign.



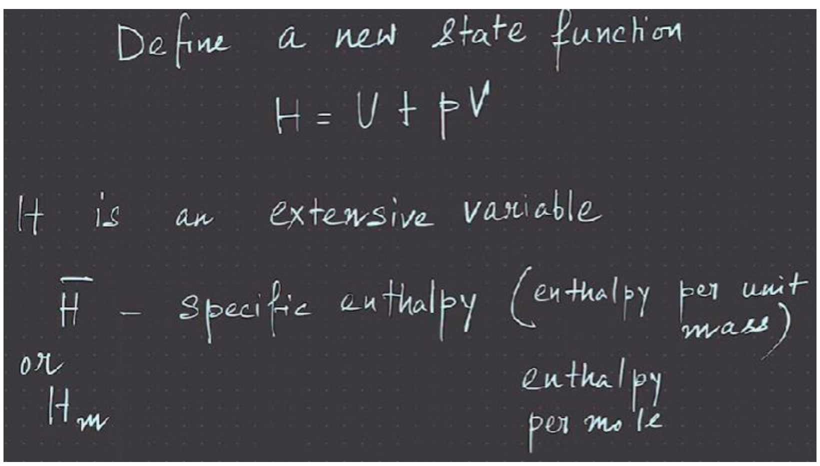
Now so if you have that one interesting part of it is that before I go to enthalpy I want to tell you this in the flow arc that is the energy that is coming in you have $\overline{U}$ in that is the $\overline{U}$ in and you have $\overline{U}$ in plus V_{in} $\overline{V}$in and this is the energy that is coming in and this is the energy that is coming in V_{in} V_{in} right that is how it is and then you have minus $\overline{U}$ in plus V so this is minus so it is going out $\overline{U}$ out plus V_{out} $\overline{V}$out V_{in} out and this is the energy that is coming in and then you have Δ Q and W which is equal to now if you look at this term you have this term which is like U plus PV right and this is the term that you have like U plus PV is coming in and then U plus PV is coming out so it is like U plus PV_{in} and then there is a U plus PV_{out}. Now this I can call as in some way this I can call as this from H in and H out I am just putting some new variable here. Now what is this H so I will define this H as enthalpy so this now if you look at so it is enthalpy which is H now why does this enthalpy why is this enthalpy required because see we know from the first law for a closed system cell that PV is equal to Δ Q plus Δ W and that is basically equal to Δ Q minus PV V now minus PV V because if you are say compressing a gas using a piston so compressing a gas using a piston compressing it with a pressure then there is a change in volume there is a change in volume that dV is negative and you want work done on the system we are not using the pressure because the pressure is positive in our convention so I will put a minus sign here. So you can understand that if TU equals to Δ Q minus PV by the way if you use another convention it will get like the same minus PV because in that case what is done against the external pressure so in such a case where the volume is increasing the volume of a gas will increase for example it is work done against external pressure here we are doing external pressure is being the work on the system but in that



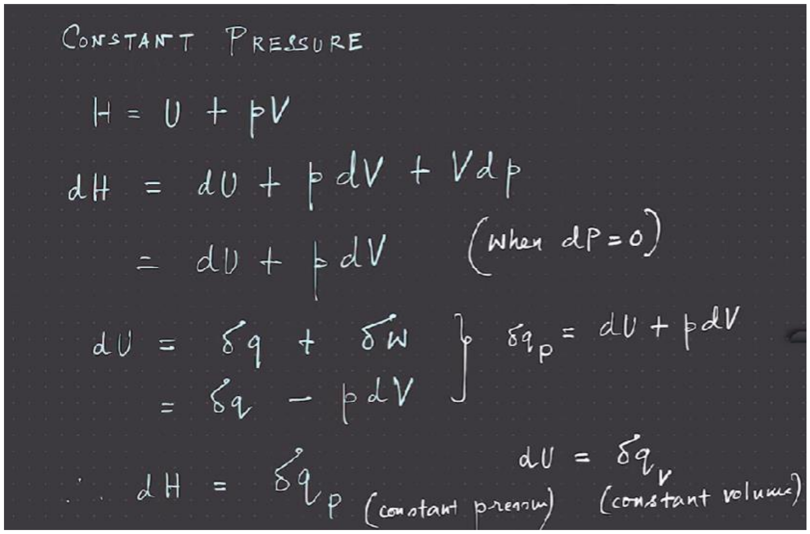
process dV is negative so therefore I have to put a minus sign so in both cases it is consistent now what you get but that is not the matter here the matter is more interesting here that you have a Δ U which is Q, Q is the heat input remember Q is the heat input minus P Δ V so now you will tell is this correct minus P Δ V there should be a V Δ P so I assume so for example that is why I gave a blank here so we are talking about constant pressure and we are looking at energy balance at constant pressure now if you are looking at constant pressure then basically you will see Δ U is nothing but Q minus P Δ V so this is done at constant pressure so Q becomes Δ U plus P Δ V so it is something either more or less than Δ U now can you tell me so this is something that you can think about that Q is the heat input Q is the heat you can think of it as heat input now depending on whether it is negative or positive we can tell whether it is going out to the surroundings or whether it is entering the system and Δ U is the change in internal energy you see unless it is a constant volume process in that case Δ V will be 0 because the volume will not change then only Q equal to Δ U other than that Q is equal to Δ U plus P Δ V now depending on P Δ V Δ U can be more than Q or Δ U can be less than Q or is it that always Q is greater than Δ U by



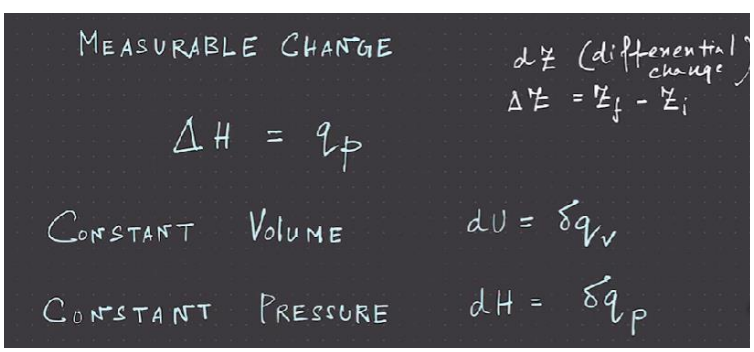
an amount Q differs from Δ U by an amount P Δ V and to absorb this P Δ V we use a new thermodynamic potential called M1P I will later tell you that how this different thermodynamic potentials will come from doing this Legendre transforms how they are related basically these are like conjugate variables you will see different conjugate variables like entropy and temperature volume and pressure chemical potential and concentration and so on and so forth but what I am trying to say is that you can immediately see the need of constant pressure you have Q which is not just Δ U but Q which is Δ U plus P Δ V so now to make our life easy we define a so every time we define a new state function thermodynamics you remember we want to simplify our understanding or simplify the description so we define this new state function called enthalpy which is U plus PV right PV is the mechanical work what did we let the mechanical work and U is the internal energy and H is called enthalpy as U is extensive



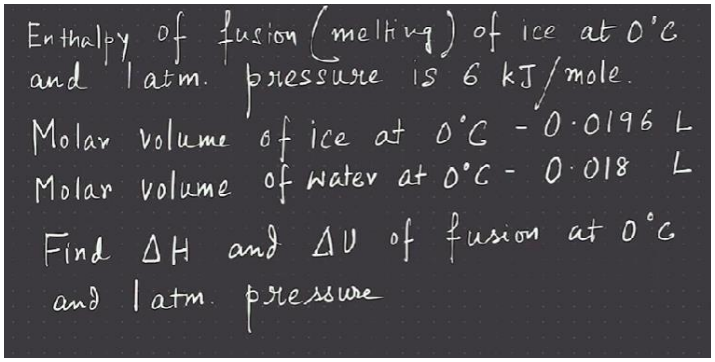
parameter V is extensive parameter H is also an extensive parameter or extensive variable right it is a extensive variable similarly U is a state function U is a state function so H is also a state function right it depends on the states only it does not depend on the path right finding H I do not when I want to integrate I have to know the initial state and the final state of the system I do not have to know in which path these states are arrived at right so an H bar is specific enthalpy specific enthalpy can be enthalpy coordinate mass or enthalpy coordinate mole and we can call it H bar or HN so I will use either H bar or HN in this course right so this is the enthalpy per mole it can be enthalpy per mass ok so every time I will specify which is molar enthalpy or per unit mass now what we told is that is a constant pressure now why do we tell that because you see H goes to U



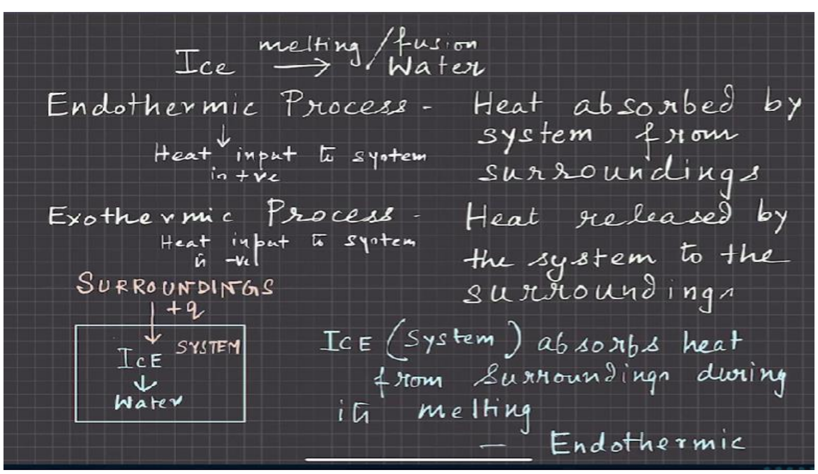
plus PV now if I do differentiate if I differentiate I get dH which is dU plus PdV plus VdP this only becomes dU plus PdV when dV equal to 0 that means constant pressure so you see now dU is equal to Δ Q plus Δ W which is Δ Q minus PdV and as you can see dH is dU plus PdV so from here you can write Δ QP equals to dU plus PV so I gave a suffix P right subscript P I use this subscript P to denote that it is a constant pressure so dH is equal to Δ QP that means heat input at constant pressure so in general as you can see previously dU is equal to Δ QV which is a constant volume this is constant because if it is constant volume process then Δ V is 0 so in the process volume case you have dU equal to Δ QV and in this constant pressure



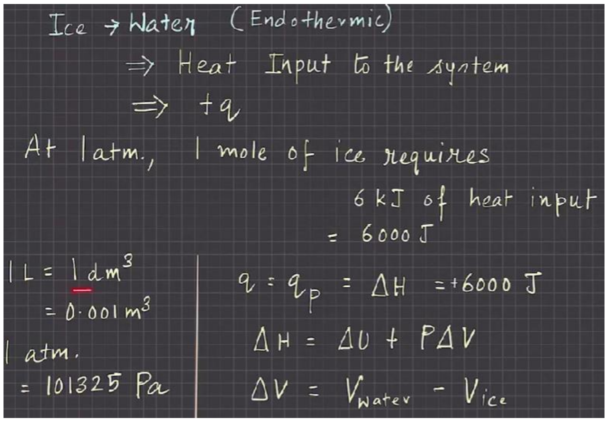
I am now differentiating it you see dH equals to Δ QP so as you can see here this is at constant H is a thermodynamic potential that we will use when we are looking at processes where the pressure is constant right so something like that so we will come to see that more.Now if I look at measurable change again I am integrating between the states so basically and Δ H basically Δ H is equal to QP that is heat input at constant pressure this if this heat input at constant pressure changes my system from initial state I to final state F then the difference Hf minus H I which is basically expressed as Δ H this is a measurable change Δ H is a measurable change.



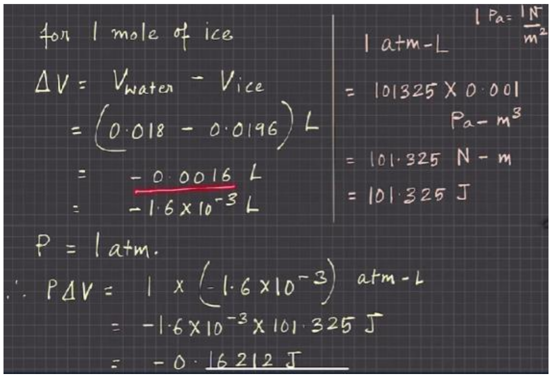
So please notice that d of something say d of z is a infinite symbol change it is a differential but when I tell Δ of z it is a measurable change so which is basically like z F minus z I where F and I denote the two states and dz basically is a differential change and I have also told what is an exact difference so in constant volume as I told again it is dU and at constant pressure it is dH right. So now at constant pressure one can write dH equals to as I told dH equals to dU plus PdP and if you now integrate what you get is Δ H equals to Δ U plus P Δ B plus Δ H is Hf minus H I Δ U is Uf plus I and Δ B is V of mass. Now let us look at a problem we will try to look at a problem and we will see because enthalpy is something very interesting in a constant pressure process many a times we use like heat means when we express like heat of reaction or heat of change of phase say from solid to liquid or liquid to solid or solid to gas or liquid to gas and some such process like evaporation condensation solidification melting

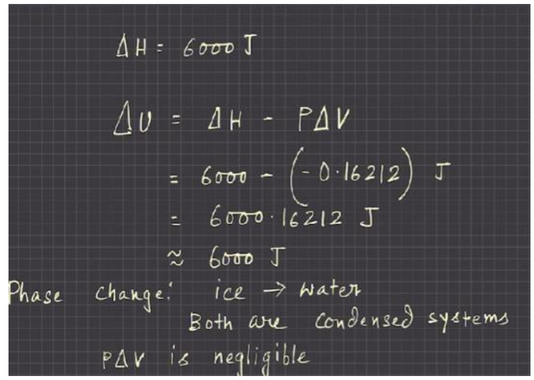


we will use Δ H we also use Δ U if the process are constant volume otherwise at constant pressure we will only use enthalpy we call it like transformation enthalpy or formation and stuff. So here for example I have given a problem here which is enthalpy of fusion now enthalpy of fusion means fusion is nothing but melting so of ice at 0 degree Celsius remember ice and water are two phases or two states of H2O of water so liquid water and ice so at 0 degree Celsius both ice and water can coexist now enthalpy of fusion that is like latent heat often we call it as latent heat also of fusion of ice at 0 degree Celsius and monatose pressure is 6 kilojoules per mole that means you have to supply 6 kilojoules per mole of ice to melt it at 0 degree Celsius now you see another very interesting thing molar volume of ice at 0 degree Celsius is 0.0196 liters and of water is 0.018 liters you see this is liquid water remember ice is the solid form of water this is the liquid water let's call it liquid so water in the liquid form and ice is water in the solid form so if you see the solid form has a higher molar volume 0.0196 and water has a molar volume of 0.018 at 0 degree Celsius again this is measured at 0 degree Celsius now I am telling find Δ H and Δ U of fusion at 0 degree Celsius Δ H of fusion

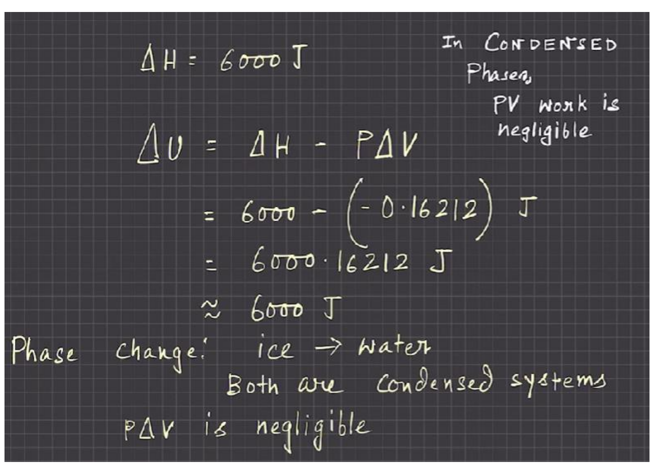


I have already given 6 kilojoules per mole now we have to see whether it is positive or negative so let us look at it so the process is ice melts to ice is melting to water right now there are two types of processes generally you know you might have also read about it in your 12th and the textbook I have read some textbooks that you have this endothermic process and exothermic process endothermic process is where heat is absorbed by the system and the heat is coming from the surroundings so basically heat when heat is absorbed by the system then and from the surroundings it is entering from the surroundings and it is getting absorbed by the system then we have something called as endothermic process and where heat is released or it is evolved by the system and is released to the surroundings basically then it is called as exothermic process



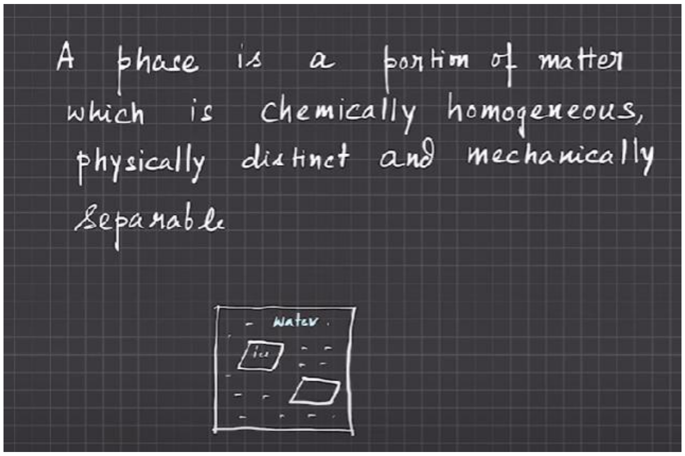


so exothermic process there are two types of processes one case it is absorbed and another case it is given out say for example when I am looking at melting ice melting to water in that case ice requires heat input so it absorbs heat and then it melts to water on the other hand if water freezes to ice when water freezes to ice it gives out heat right it gives out the enthalpy of fusion now when it is giving out as you know in the endothermic process heat is absorbed by the system or heat is input to the system right so here what you can tell is basically heat input to system is positive on the other hand it is an exothermic process system is giving out heat right so it is like heat output from the system so heat input in that way is negative because heat is extracted out of the system right or heat is evolved it is not really extracted it is released from the system to the surroundings so heat input to system in this case is negative right so basically because the system is giving out heat to the surroundings right now when surroundings and ice transfers to water so ice absorbs heat right from the surroundings so it is a melting is an endothermic process freezing is an exothermic process so at one atmosphere as we see one mole of ice requires 6 kilojoules of heat that means it requires 6000 joules now we also know the molar volume right molar volume of water and ice so as you know Q

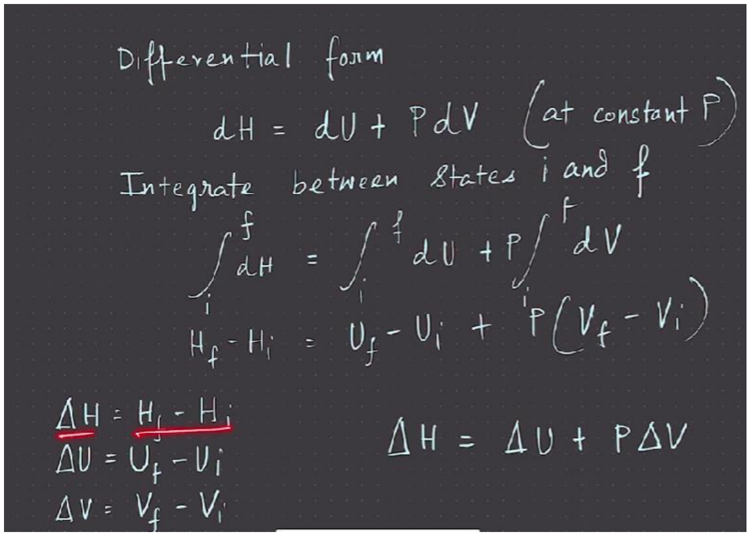


basically is nothing but Δ H here because we are keeping the pressure at one atmosphere right pressure is fixed so you have Δ H Q3 that is the heat input at most pressure which is Δ H or heat of fusion and this is given as plus so it will be plus 6000 joules right so Δ

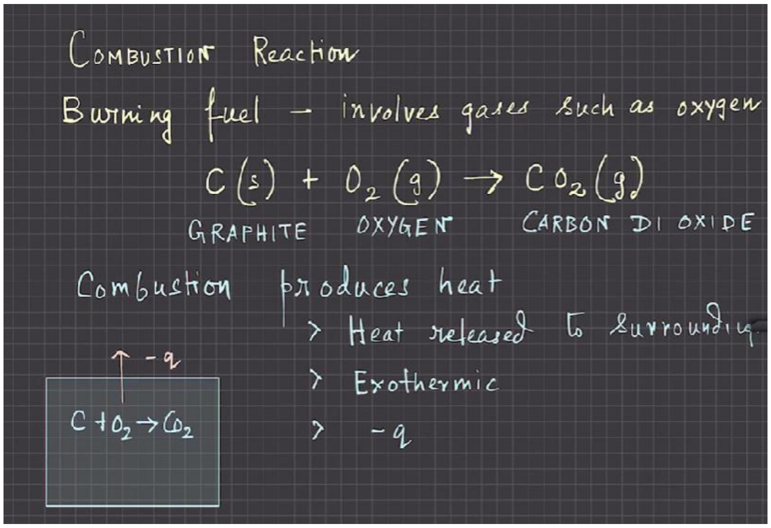
H equals to 6000 joules now I have to find out what is Δ U of the process I have to find out what is Δ U now we know the relation Δ H equals to Δ U plus P Δ V and we know the molar volume of ice which is 0.0196 as it 0.018 so now remember 1 liter is 1 decimeter cube so this is something that you have to know the units 1 decimeter cube is like 0.1 meter right so you have decimeter cube so you have 0.001 meter cube and one atmosphere is 10135 pascal pascal is the pressure right pascal is Newton per meter square and one atmosphere is also under pressure but one atmosphere is 10135 pascal now Δ V is what it will be its final state is water liquid water and the initial state is ice so it will be V water minus V ice right V water minus V ice and we are looking at only one mole of the system so we are taking the molar volume of water here at 0 degrees Celsius and this molar volume of ice and what do we get V water minus V ice is negative right it is negative right and it is like minus 1.67 10 minus 3 V plus and P is one atmosphere so P Δ V if I now convert atmosphere liter to joule you have to multiply with 101.325 this is because 1 liter is 0.001 meter cube and 1 atmosphere is 101325 if you multiply you get 101.325 as the conversion factor so if you use 101.325 you get a value which is as you can see here minus 0.16212 joules which is quite small it is very very small see 6000 joules is the enthalpy of fusion and P Δ V term is only minus 0.16212 joules as you can see here Δ H is 6000 joules Δ U is going to be 6000 minus of minus of 0.16212 or this is 6000.16212 joules so Δ U is slightly more than Δ H but it is not really that much different so we get Δ U to be approximately the same as Δ H remember



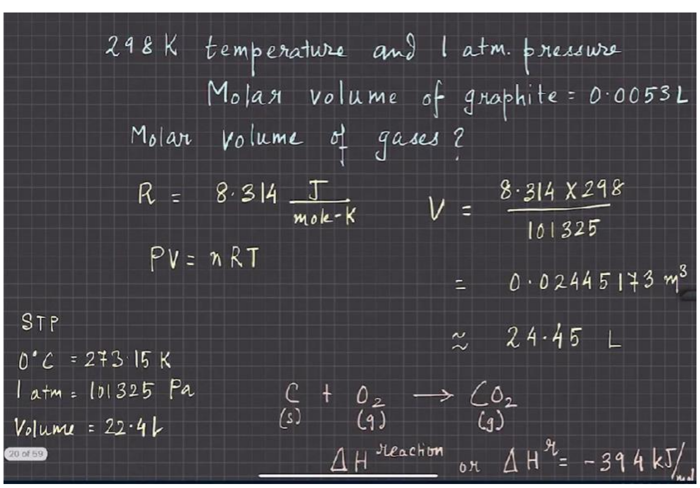
I have given a working definition of phase but I have not given the proper definition that is accepted in textbooks and stuff but phase basically see for example ice and water these are two states of matter and these are like you can call them as two phases because they have their own physical characteristics like this stick physical characteristics and they have also came to the conclusion in both are H2O and H2O is basically one component I can think of water as H2O as one component these are like unary system consider water as a component and these are phases with physical characteristics which are distinct and



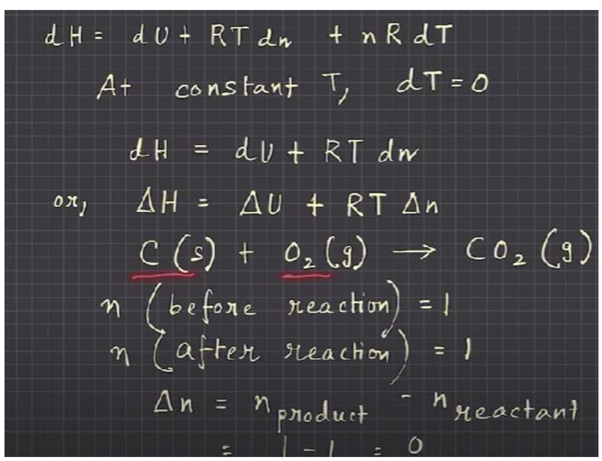
they are also mechanically separable so I come to this mechanically separable stuff in a while so when I give a more when I look at different phase the equilibrium between phases in a short file so these are mechanically separable these are physically distinct and they should have uniform chemical composition that is the idea so the idea of mechanically separable is interesting and I will talk about like mechanically separable means by some such process but there is a little bit of confusion there and I will come to that where it can be sometimes it can be confusing but anyway the point that I want to tell phase ice is a phase the solid phase of water liquid water and water liquid is also another phase the solid phase has different properties like different molar volume different density water has different property like molar volume density refractive index whatever it is and both are condensed phases how? condensed phases means they are I will talk about this they are compressibility like it is not as compressible as gas right so water or ice are not as compressible as gas gas is much much way more compressive right so in case of ice and water both are called condensed phases basically the PV work in condensed phases in condensed phases is that solids and liquids PV work is negligible so again I will just give you give a working definition of phase if you missed it a phase is that portion of matter or phase is that portion of matter or region of matter or region of space can be matter so is that portion of matter which is chemically homogeneous physically distant and mechanically separate for example I have a system where you have this ice and you have water so see there is a clear boundary between ice and water although both are H2O one is in the solid form and another is in the liquid form they have different densities they have different molar volumes they have different refractive indices and so on and so forth they are physically distant and both ice and water are chemically homogeneous so as you can see these are the things so this is remain an ice so ice and water is one example that I can talk about that I have to distinct phase liquid water is a different phase ice is a different phase but you see that ice and water both are condensed phases PV work is negligible because the volume change pressure is very



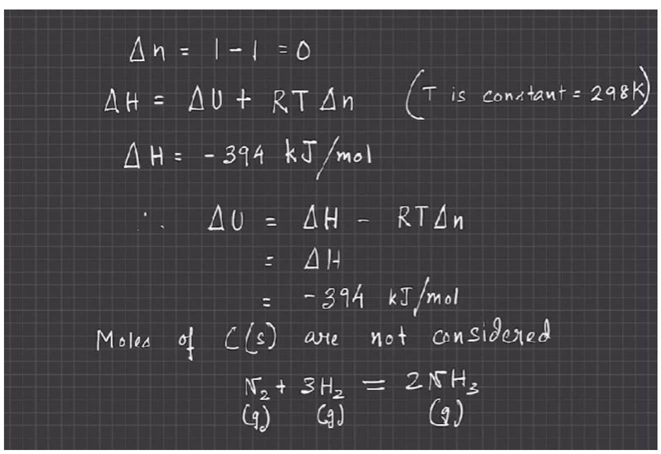
very small you have to give enormous pressure to see appreciable volume change as much volume change as you see in gas you can't get unless if you have really really enormous pressure so PV work is negligible but I will come to this PV work soon now think of another reaction so to understand the concept of enthalpy we think of reaction where you have gas involved so for example we are thinking of combustion reactions now in combustion reactions you think of combustion what do you think you have fuel that is liquid or solid it can be gasoline it can be coal coke it can be some pure form of graphite whatever it is and you are putting oxygen and you are getting oxygen and this graphite is burning graphite and oxygen burn graphite marks in oxygen and gives you carbon dioxide this is the reaction C plus O2 equal to CO2 now when combustion happens in general it will produce heat that is why we do we do use combustors we want to produce heat for example you take wood and you put fire and when you want to have fire then what you do you basically involve oxygen in it without oxygen the fire will die the burning will happen it gets oxygen so carbon plus oxygen goes to carbon dioxide now this reaction or this combustion reactions all combustion reactions produce heat you will produce heat so heat will be released to the surroundings



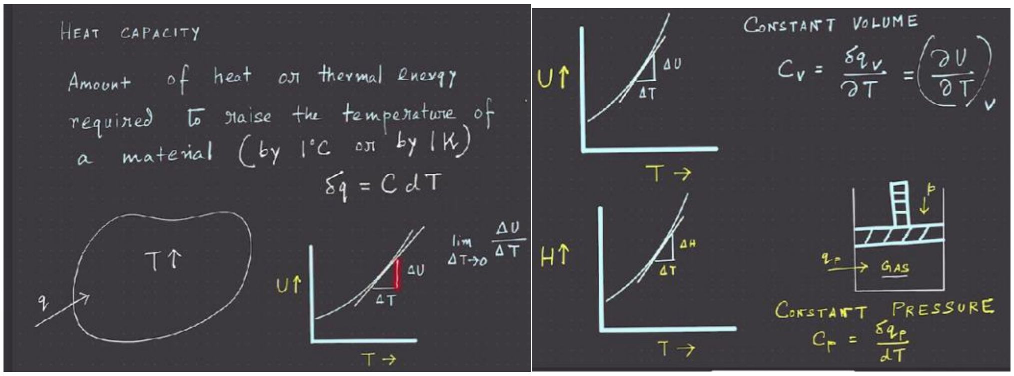
so as a result it will be exothermic and that means heat input is negative because heat is released to the surroundings it is as you can see here it is released to the surroundings so this reaction happens in the forward right carbon solid which can be coke which can be graphite pure form of carbon graphite and that is reacting with oxygen forming carbon dioxide and this is producing heat and because it is producing heat we call this reaction as combustion reaction so all reactions burn well to produce heat are called combustion reactions in presence of air air basically helps in burning now we are thinking of a temperature of so the burning here or combustion is happening at 298 Kelvin the temperature that you have is like room temperature 25 degree Celsius 298 Kelvin and you have one atmosphere pressure and in that temperature and pressure molar volume of graphite is 0.0053 meters which is quite small right look at molar volume of gases remember at STP you might have read which is like 0 degree Celsius molar volume of pressure the volume is 20.4 meters for ideal gases again if you assume oxygen and carbon dioxide to be ideal gases you can basically get the volume of one mole of a gas so R is 8.31 4 joules per minute Kelvin you have P equals to nRT, A equals to 1 because you are taking 1 mole say and then V is this 8.3 or 298 by 101325 because see V is equals to AN RT by P and P is one atmosphere which is 101325 kPa or Newton per meter square so what you get is 0.02445 173 meter cube which is 24.45 liters so as you can see here 24.45 liters is the volume of the gases oxygen or carbon dioxide on the other hand the molar volume of graphite that is for 1 mole of these gases on the other hand the volume of graphite 1 mole of graphite is 0.0053 liters you can see how much the volume differs for 1 mole and now let us look at ok we understand that volume does differ but see ultimately if I am looking at if I give an ideal gas assumption I will use only the gases C plus O2 goes to CO2 so what is the Δ H reaction?



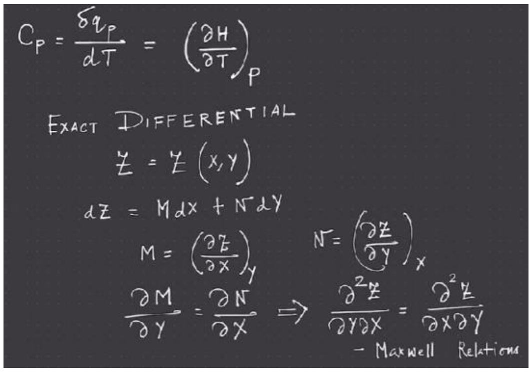
It is given as minus 394 kilojoules per mole so it gives out 394 kilojoules of heat this reaction C plus O2 CO2 at room temperature and pressure now this is minus 394 kilojoules of heat per mole now we are assuming oxygen and carbon dioxide to be ideal gases and that means they follow this equation step p equals to n of T and we know H which is Q plus p$_{Vin}$stead of pV I write U plus n of T now you have dH which is TU plus TART R is gas constant it is constant you can take it out now you have RT dn because it is like R dn T and this will be R dn and there is a T plus nR d so this is what it is so you will have these two terms RT dn and RTT but as you can see here it is constant temperature 298 Kelvin constant temperature TU is 0 so this becomes dU plus RT dn now TH plus TU plus RT dn now I can now integrate in a measurable form it will be Δ H in the finite form it is Δ H plus Δ U plus RT Δ n the reaction is C solid combining with oxygen gas to keep carbon dioxide gas n before reaction now if I am looking at n I am not caring about the n of graphite I don't care about graphite so I will look at the n because I am using pV equals to nRT here so I will look only at the gases participating gases O2 and CO2 see this is like one mole of gas if you look at the balance and this is also one mole of it produces one mole of oxygen reacts with one mole of carbon to give one mole of carbon dioxide so n of gas before reaction is one after reaction is one Δ n which is product minus reactant is zero so Δ H equals to Δ U plus zero and Δ is minus 394 kilo roots per mole so Δ U equals to Δ H minus RT Δ n and therefore which is equal to zero here so Δ U equals to Δ H plus one minus 394 kilo roots per mole so and as you can see most of carbon are not considered so even in this case that gases are involved you see very interestingly that the change in energy and change in helium is the is becoming of the same obviously if you have a reaction like say for example

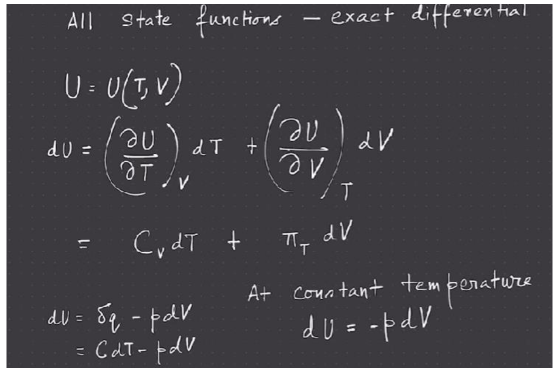


you can do it yourself say I am talking about say n2 plus 3H2 equal to 2nH3 in this case this is gas right this is gas and this is also gas in such a case and you can see here one mole of nitrogen three moles of hydrogen and two moles of ammonia these are some cases where you will see that there will be there may be some difference between Δ U and Δ H basically find out examples you can find out examples but Δ U and Δ H are different right so please think about it think about different reactions I will also give some examples later now I will come to a very important quantity called heat capacity I will come to a very very important quantity called heat capacity and heat

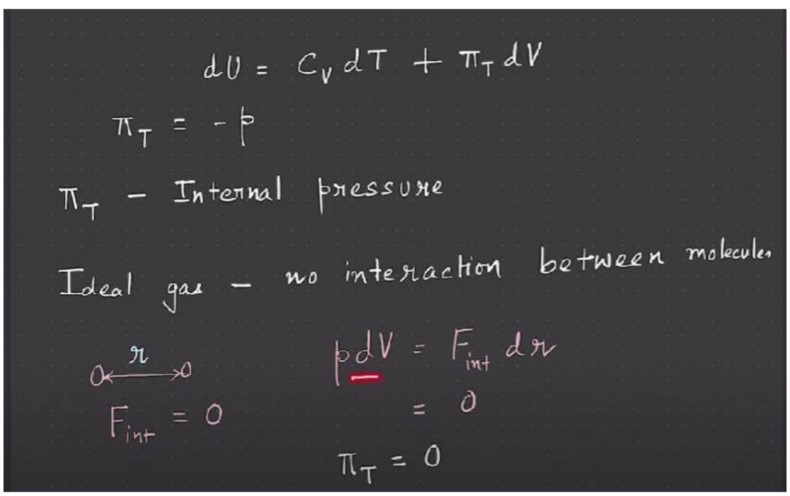


capacity is basically the amount of heat or thermal energy required by a substance right heat capacity of a substance or a material is the amount of heat or thermal energy required by a substance to raise the temperature of this material or substance by some amount right it is not specified right in general but we will by convention use like by 1 dB Celsius or by 1 Kelvin or by 1 dB Fahrenheit say for example I haven't even yet defined the Kelvin scale but I am telling because you already know about Kelvin scale so there are different types of temperature scales that you know you know like there is a centigrade scale there is a Fahrenheit scale and there is also this absolute scale of temperature obviously how does it come? I have to cover but before that what we understand is heat capacity heat capacity is a very very important property of matter now what we can write is so this is the amount of heat or thermal energy so that means you can write some relation like this is something that you have often seen Δ Q is equal to C dP right so basically C is a ratio between Δ Q and dP that means heat input and change in temperature right now if you think of this in general if you have a heat input for a system the temperature increases so you will have typically curves like this this is a curve U versus T so U increases as T increases and if you now draw if you take one point here if you take point here say here you draw a common tangent line this is your common tangent line you can now take the slope at that point so this will be like you have this is Δ U this is Δ T so the slope is limit Δ T tends to 0 Δ U by Δ T or you can also write this is equal to dU by dP right now this basically gives you C now is it always dU by dP? we will come to know so you see know at constant volume it will be C V that means this is heat capacity at constant volume which is Δ T which is Δ Q V by Δ T or dU by dP remember this this is very important dU by dP at constant volume right it is constant volume that is C V now when you look at constant pressure processes again what comes in is enthalpy not U right because you have enthalpy at constant pressure as you know Δ H is Δ U plus P Δ V so there is this P Δ V one right for example think of this gas enclosed here and you are having a twister that is just coming in now you are seeing that there is a heat input and there is a pressure you are giving a pressure and the volume is changing so all of these contribute to the heat capacity of constant pressure right you have pressure volume as well as heat input and that both of them are contributing to the constant pressure process right so at

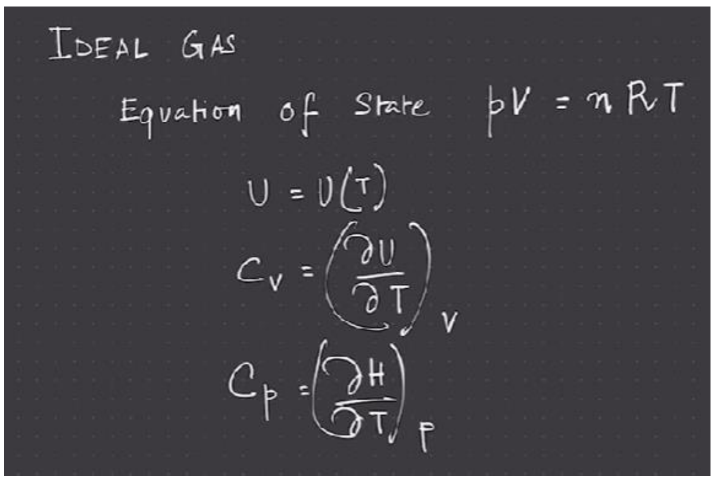




constant pressure we have to look at how H varies with temperature you will get essentially a very similar curve H will increase as a function of temperature right in general H will increase as a function of temperature in that case again whether it is increasing or decreasing it is a slope right it is Δ H by Δ T again with Δ T tends to zero so this basically gives you Δ Q V by Δ T or you can think of this as del H by del T at constant pressure so as you can see here C P is del H by del P right C P is equal to del H by del T so again just recollect that we talked about exact differential we talked about Z Z X Y and Z is exact differential is m dX plus m dY m is del Z by del X constant Y and N is del Z by del Y constant X and you have also this del m by del Y is equal to del m by del X which gives rise to this and this will be used to find some relations called Maxwell's relations or Maxwell relations I will come to that but before that we will come to this second derivative because remember when we write Maxwell relations we are basically relying on this relation del m by del Y and del m by del X which basically gives you second derivative



but see this exact differential gives you m and N now this m and N say for example U if I write as a function of T and V I get del U by del T V T T plus del U by del V T dV right so del U by del T V at constant volume this is del U by del V that is the change in internal energy with change in temperature at constant volume this change in internal energy with change in volume at constant temperature at constant temperature so you get C V dT and you get some coefficient like del U by del V T which is pi T dV so but at constant if you think of constant temperature then dU you know is minus P dV right because dU is Δ Q say for example you can write this as dU is equal to Δ Q minus P dV now Δ Q I can write as C dT minus P dV C is the heat capacity now I can take dT equal to 0 that means at constant temperature then dU is minus P dV now have a look at this now you have del U by del T V which is C V right del U by del T V that is the change in temperature at constant volume which is C V and here you have pi T and if you look at this relation here dU equals to minus P dV and here this pi T is obviously having a unit of pressure and this pi T this coefficient is called internal pressure right pi T is basically nothing but minus P if I compare that so dU is C V dT plus pi T dV and dU equals to C V dT minus P dV so as you can see pi T is minus P which is the internal pressure right so however remember in fact you can show it later



but now please understand if there is no interaction between molecules that is there is no force of interaction between molecules then P dV which is nothing but force of interaction with the so this is an interaction force and this is the I can think of like separation distance between particles then this P dV term or this internal interaction term basically goes to 0 this is not an external pressure remember this is the let us not call it pi T and pi T is the internal pressure which arises due to internal forces of infraction between the molecules I think there is no force of interaction between molecules for example an ideal gas or perfect gas so R is like an interaction distance between these particles or molecules or atoms if F interaction is 0 then pi T comes out to be 0 so this is a very very important contribution so as you know equation of state P d is NRT and you have C V which is dU dT dV right C V dU dT dV and C P which is dU dT dV we will try to find relations between them we will also try to find not only find the relations between them but we will also try to find out more measurable quantities that we can define like temperature, pressure you have already looked at different variables so what variables so far we have learnt that are measurable directly like T or temperature which is measurable by a kilometer then you have P which is measured by barometer and then you have C P and C V these things you can measure basically using calorimetry you can use calorimeters to measure it so I will give you some principle how it is done the principle is based on what I have taught right this is basically the first law is what you can use so you use calorimetry to find out C P C V so these are measurable quantities temperature is a measurable quantity pressure is a measurable quantity volume again if I know the dimensions I can calculate volume measurable quantity so we are getting a bunch of measurable quantities I will also give some more measurable quantities and we will try to find out interrelations between them that is something very very important when you want to organize data and all you require all these thermocliminal data consistently then only you can give an energy description of matter so this is something that I will deal with in the next class thank you thanks for your attention