Indian Institute of Technology Madras

NPTEL

National Programme on Technology Enhanced Learning

COMBUSTION

Lecture 2
Chemical Reactions, Heat of Reactions and Formation
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Today let us start the proceedings with considering the equilibrium thermodynamics as I said the goal for this is going to be.

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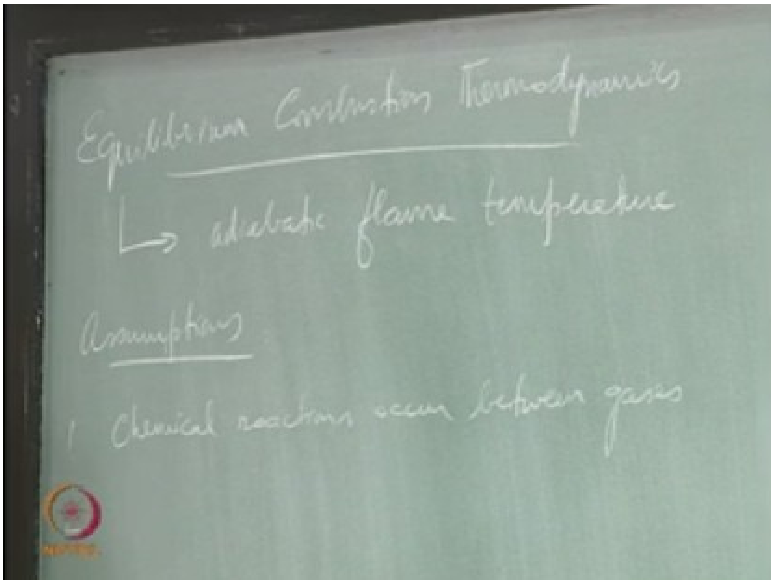

Equilibrium Combustion Thermodynamics
↳ adiabatic flame temperature

Assumptions
1 Chemical reactions occur between gases

To look at the adiabatic flame temperature we will talk about this adiabatic flame temperature in significant detail as we go along, but before we get to that point there is a few more things that we have to learn, so let us start with some assumptions the first assumption that we will make is that chemical reactions we are talking about are happening in the gaseous state, so occurred between gases right this is something that we talked about previously where we are basically looking at fast exothermic reactions and the speed the high speed at which these reactions are happening or the high reaction rates.

That are happening is primarily coming out of the fact that we are looking at gases that are reacting in for most parts, so this is not a bad assumption anytime you make an assumption you have to justify the assumption okay something that you have to look at how broadly valid it is or whether the invalidity is or where the exceptions would be okay, so this assumption here kind of precludes things like surface reactions or heterogeneous what is called what is meant by heterogeneous reaction system.

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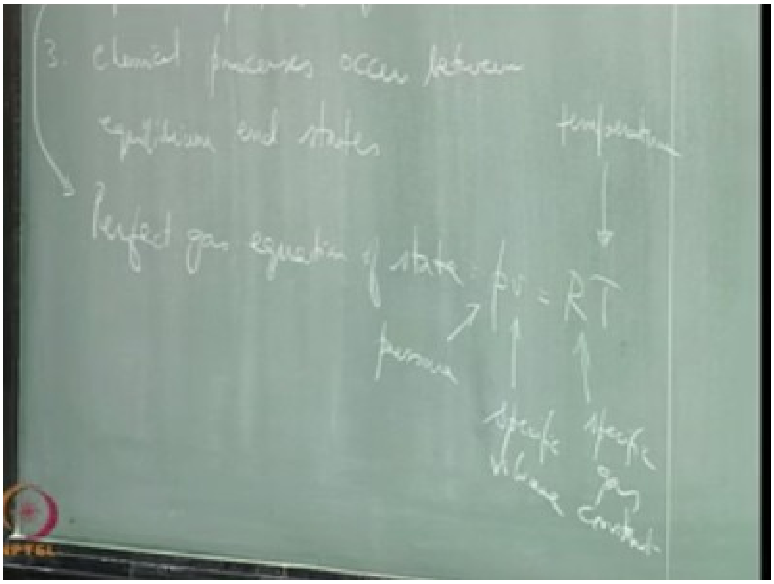

3. chemical processes occur between equilibrium end states

Perfect gas equation of state: $pv = RT$

And the reactions are taking place between molecules which are belonging to two different physical states, okay here we are looking at homogeneous reactions and then we assume that gases obey perfect gas laws this is also a fairly reasonable assumption for most gases which are the which we encounter and our typical temperature and pressure, but then the question that arises is when you and we know that combustion is a high temperature situation, if not a high pressure situation so maybe we are looking at atmospheric pressure or a few tens of bars or at the most a few hundreds of bars but we are not looking at thousands of bars.

Unless you are looking at gun propellant kind of applications okay, so we are not looking at very high pressures but temperatures are high, so the question is it okay at the moment let us say we will just assume this for the sake of simplicity, but it is possible to relax this assumption that is another thing that you have to examine when you are looking at assumptions you have to see is it possible to relax this assumption and make it make the analysis a little bit more complicated right so from that point of view this would now qualify as what is called as a simplifying assumption.

So we are trying to simplify our analysis by making this assumption the third is chemical processes occur between equilibrium in states right, so we are talking about a few things in this in this assumption first of all as I said the other day we are dealing with thermodynamics, so thermodynamics is all about dealing with States and parts not necessarily, how fast you are going from one state to the other state through apart number one number two you are always better off talking in terms of state properties and state variables a supposed to part variables.

So we will always look for those kinds of thermodynamic variables that are state variables rather than pot variables, so that we can essentially look at a starting state and an ending state or state one and state two those kinds of things, the third that you are looking at here is you know making the assumption the assumption about this is that these states are equilibrium states that means you started out with a state let us say in this case of reactants all right, so you know started with a couple of reactants which are in equilibrium that means there they are in thermal and chemical equilibrium.

With themselves and then you let the process happen and let us say the reactions happen and you now get to the final state and when the when you get to the final state you know get products right, so the products are now at the let us say the adiabatic flame temperature or at an elevated temperature when compared to the initial state okay at that state at which the products are they are again at equilibrium that means they can equilibria among themselves, so that they will have interactions like collisions and energy exchange.

And all those things happening but they are all in equilibrium they are not disturbed out of their equilibrium state okay, so that is exactly what we are assuming over here and this is important because we are essentially looking at equilibrium combustion thermodynamics, we are not looking at non equilibrium processes we are not looking at departure from the equilibriums situation where we are looking at the rate at which things are happening and so on.

Okay no rates considered here okay, so here if you now go back to this the perfect gas equation of state that will be applicable for us is the notation that, we will use is $P_V = R_T$ where we small v is the specific volume P it is understood that P is pressure the small V here is specific volume later on we will reserve the symbol for velocity, when you are looking at flows but not now this is the specific gas constant right and this is the temperature all right so the specific this is not the universal gas.

Okay this is the specific gas constant when you are actually using a specific volume over here they go together make sure that you do not make a mistake on this.

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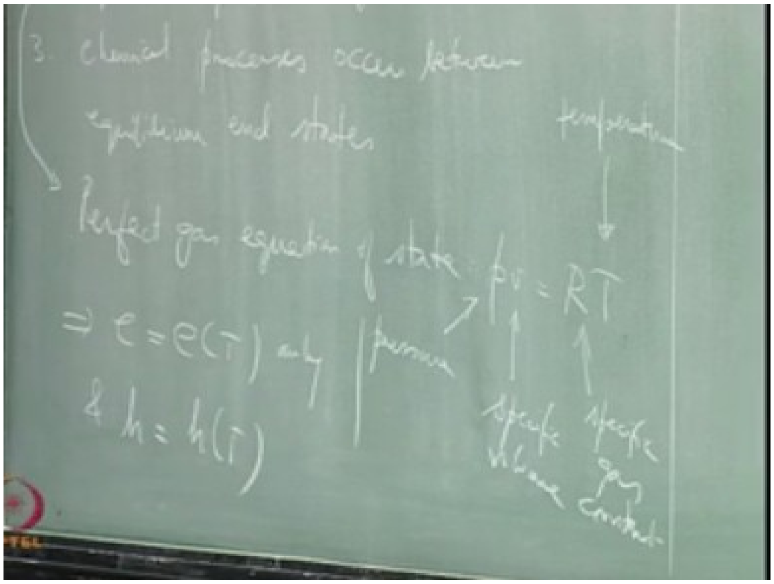

3. chemical processes occur between equilibrium end states

Perfect gas equation of state $pv = RT$

$\Rightarrow e = e(T)$ only

& $h = h(T)$

When you now adopt this equation of state as the perfect gas equation of state then this implies that your internal energy will be only a function of temperature okay, so the notation here is to say a equals e of T only simply means that e is only a function of temperature and the enthalpy is only a function of temperature oops.

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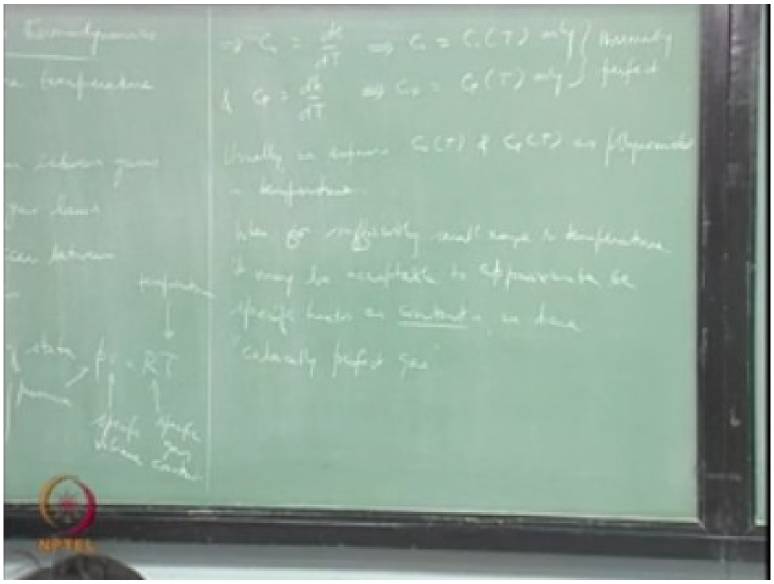

So this further means that you now have a specific heat at constant volume d over dt this means that cv is a function of temperature only okay, so we could go back and write h as h is a function of temperature only and C_P is a function of, so you could write here and C_P = dh over dt which implies C_P is a function of temperature 1 d okay, so long as you have the C_P and C_V as functions of temperature only we call this thermally perfect, so basically what it means is if you now assume the perfect gas equation of state it follows.

That your gases are thermally perfect okay in other words if you ask the question what is so perfect about the gas you can say thermally perfect it is just one on the same alright, so what you do not normally do is usually xb we express C_V of t and C_P of t as polynomials as polynomials in temperature okay, so such polynomials are available for different chemical species in the literature so it is sort of like something that you can for most analysis that you want to do treat it as given okay.

So if you want to take a temperature dependence of the specific heats for specific species you should you should now treat it as given a right, now so what so what happens like first of all the question that you have to ask is so why does the C_P and C_V vary with temperature in the first place right, so there are quite many reasons for that and we would not get into this you have to get into physical gas dynamics for learning these things so essentially you have the molecules can that translate and they get some energy out of heating.

By virtue of having a certain temperature but he has you elevate the temperature they start rotating and then vibrating and so on, okay but there are some processes which will now cause a departure for these molecules for these gases to not just depend on temperature only, but also one other thermodynamic property in which case we are now departing from the ideal gas situation all right or the thermal thermally perfect situation right, now so we can expect that as you increase the temperature you are now exciting some rotations and then the C_P increases and then after some point all the molecules are rotating okay.

So that the C_P does not really change for some time and then after sometime you are beginning to significantly higher vibrations and then the C_P increases and so on, so it is possible for us to think that there could be rain of temperature over which C_P could be treated as a constant there is it does not be vary with temperature right, so when for sufficiently small range of tests small range in temperature small range in temperature it may be acceptable to approximate it may be approximate the specific heats as constants right.

This is what we would call we have we have what is called as calorically perfect calorically prefer gas okay, so a calorically perfect gas is like a subset of the thermally perfect only perfect gas is essentially the one that starts obeying the ideal gas equation of state but it does not really mean thermally calorically perfect gas all the time this is like a further assumptions that we have to make all right.

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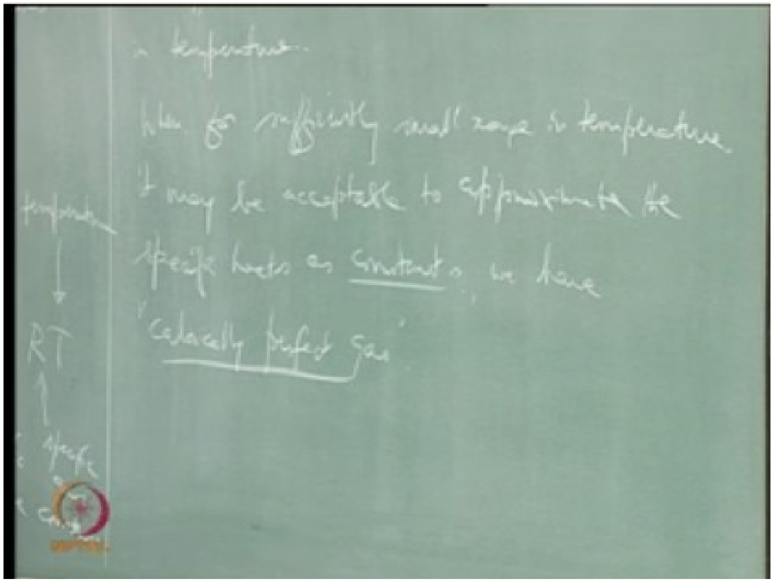

temperature

RT

specific

in temperature.

When, for sufficiently small range in temperature, it may be acceptable to approximate the specific heats as constants, we have 'calorically perfect gas'

What about killer caloric perfection yeah all right.

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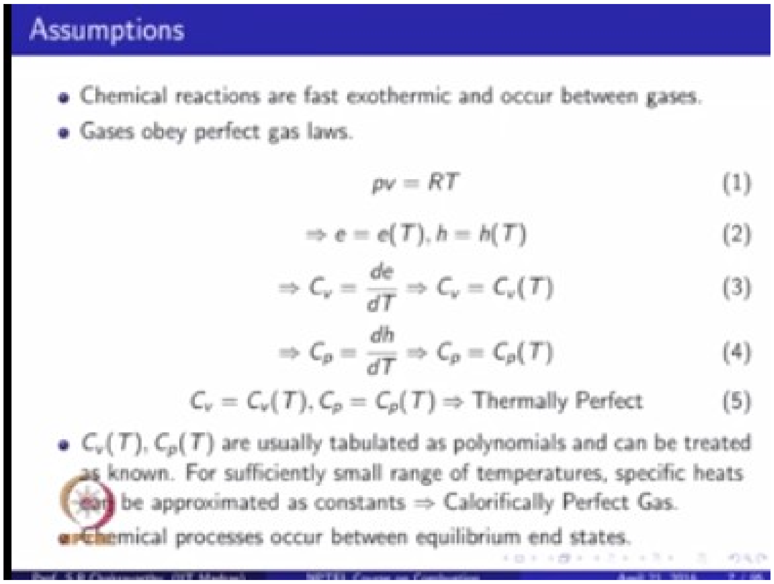

Assumptions

- Chemical reactions are fast exothermic and occur between gases.
- Gases obey perfect gas laws.

$$pv = RT \tag{1}$$

$$\Rightarrow e = e(T), h = h(T) \tag{2}$$

$$\Rightarrow C_v = \frac{de}{dT} \Rightarrow C_v = C_v(T) \tag{3}$$

$$\Rightarrow C_p = \frac{dh}{dT} \Rightarrow C_p = C_p(T) \tag{4}$$

$$C_v = C_v(T), C_p = C_p(T) \Rightarrow \text{Thermally Perfect} \tag{5}$$

- $C_v(T)$, $C_p(T)$ are usually tabulated as polynomials and can be treated as known. For sufficiently small range of temperatures, specific heats can be approximated as constants ⇒ Calorifically Perfect Gas.
- Chemical processes occur between equilibrium end states.

Now this is like a prologue if you will but the prologue is going to continue on with some more thing.

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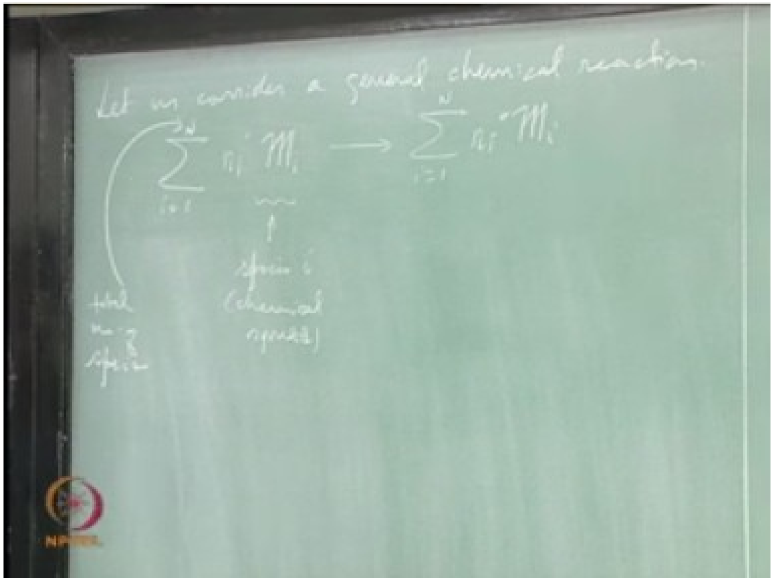

Let us now consider a general chemical reaction right and this chemical Mi gives σ I =1 to n ni double prime small n_i double Prime script Mi okay we are talking about a chemical reaction here now what we are used to looking on high school is like let us CH4 + O2 gives CO2 + H2O or something else like let say I do not know I d in a Na OH + HCl gives Na Cl + H2O those kinds of things right and then we look at the Mendeleev's periodic table look at those symbols for these different elements and then we now form compounds based on those symbols and all that stuff.

This does not look anything like that and this is supposed to be a chemical reaction right, so how do we figure out that this is actually a chemical reaction yeah so the answer is this is these species right, so script M stands for the chemical symbol of the species that you would use yeah and we are now looking at the species out of a capital n number of species keep in mind this capital n or the or the summation running from I from I going from 1 to n appears on both sides yeah.

So that means n being the total number of species okay so there is a species I chemical symbol there is this total number of species right.

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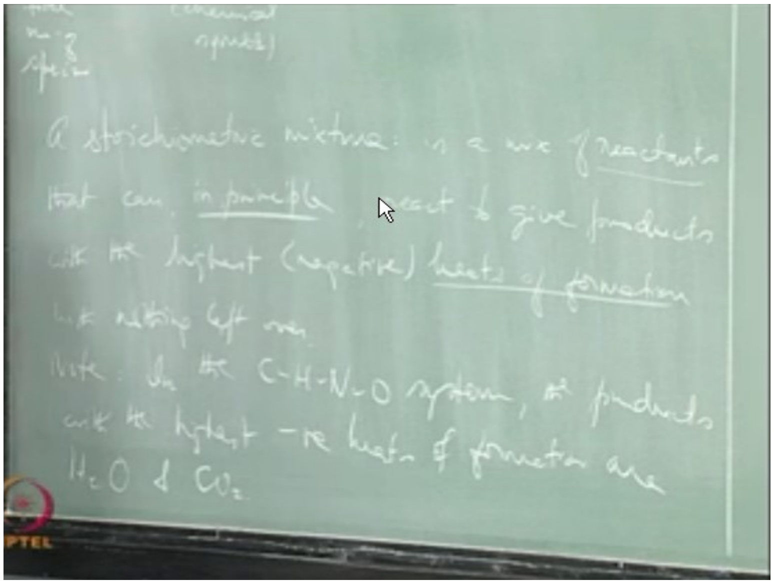

A stoichiometric mixture: is a mix of reactants that can, in principle, react to give products with the highest (negative) heats of formation with nothing left over.

Note: In the C-H-N-O system, the products with the highest -ve heats of formation are H_2O & CO_2

So why would the total number of species up here on both sides why would then all the species appear on either side, so they are sort of like saying Na OH + HCl + NaCl + HO gives NaCO + HCl + NaOH + NaC + H2O right, so you are putting everything on either side but in reality you are having only a couple of them here and a couple of others there sometimes you could have one of them there like, let us say you have an excess reactant okay so let us say you have a what is called as a fuel lean situation okay.

And we will rule out to figure out what that means a little later so you allow you will now have an oxygen excess, so you can you can out throw an oxygen on either side of your reaction but not all of them that does not make sense, but that is going to be taken care of by these so if one of the species is going to be purely a reactant it is coefficient and n_i single prime is going to be non zero and it is coefficient n_i double prime is going to be 0 that means we now written that as a purely a reactant okay.

And vice-versa see if something is a purely a product this survives this becomes zero so you can essentially kind of construct a list of n_i single primes and n_i double Prime's look at which is all zero and then figure out which is reacting to meet this product okay, so this kind of like good for you to plug in into like a computer program yeah, so you do not necessarily have to distinguish between reactants and products so in reality as well you now look at like very complicated combustors right.

So in when you now have the flow coming in is essentially reactants that are coming into the combustor you ignite and then you have a flame you typically have some recirculation zones like you have like a bluff body or like a sudden expansion and so on, and then you have products and the products actually re circulate in this recirculation zone okay and then feedback into the flame in fact the products are hot as we will try to find out the aerobatic flame temperature and these hot products are the ones that are actually re circulating back to the cold reactants and heating them up to actually get them to burn further and further right.

So at any particular point in your combustion zone you will have everything you will have in general you will have the reactants you will have the products all of them together, so it is always good to treat all of them together simultaneously you are always looking at a mixture of reactants and products together all the time yeah, so there is a reason why we are always running this Σ from I equals 1 to n through all species regardless of whether they are reactants or products okay, so this is this is something that you have to kind of get accustomed to you have to get used to.

And essentially what you have done is to sort of Albrecht LJ algebra sighs okay, if I can gin up a word like that chemistry, so instead of actually writing chemical reactions we now write an algebraic equivalent of a chemical reaction, so that it can go along with this okay so with this then we now look at what is a stockmetric mixture right, what is stockmetric mixtures talk here metric is basically then denoting that particular combination of n_i primes like single primes okay that is what is the proportion of the reactants.

That they are going to take such that you will have all of them completely react into products with none of the reactants left over right, but how do I know what is meant by products I can take reactants all right I can get them to react all right and then I get something and how am I supposed to know that they are products, what else can it be you just produce them right so what you produce is products or I will be using something, we are looking for stable products right.

So that means the reaction should be complete as it is in thermodynamics we do not really have a notion of how fast things are supposed to happen, so now you got a couple of reactants to get together and ignited and got the reaction going and then you wait and wait and wait and I got something how am I sure that I am not going to get something more right wait for some more time go for coffee come back and see what happens is that how it is does it how it works, so how do we figure out is that like a metric begin.

We can figure out that the reaction is complete now I got stable products and then I look at the products and if I do not find any of the reactants right then I figured that the combination of the reactants that I took was the stoichiometric mixture this is all I am going to say right, so how do I decide that I got stable products right, so there we go so there is a some someone who is beginning to say we have to look at their energy states we will get into quantum mechanics stand right, so let us do it a little bit simply we do not want to get into the molecular level as much as we can okay we want to stick to a continuum framework in this approach.

So well but there are notions of energy okay so that is what we are we are now beginning to get into so a stoichiometric mixture is a is a is a mix of reactants it does refer to the reactants that is the original set of reactants alone that you took up okay, so if you are now taking methane and oxygen for example that particular proportion of methane and oxygen that will give you let us say carbon dioxide and water alone and no methane and no oxygen left over is what you are looking at okay.

But the question that I asked you is how do I know that I need to expect only carbon dioxide and water and nothing else could I have settled for carbon monoxide that is possible as possible that is possible, so if I now can take like carbon a methane and oxygen and allow for it to react and produce carbon monoxide maybe some carbon monoxide some carbon dioxide okay, so now different combinations are possible yeah, so which proportion is supposed to be struck your metric.

You see what I am saying I get again give you these kinds of exam problems are so it is a consider like carbon monoxide carbon dioxide and water although as a products, now tell me what is should be the proportion of carbon monoxide and, so you maintain an oxygen that will give you a complete set of these products would that work for identifying a stoichiometric mixture so what is the catch is there a catch so what you are looking at is a stoichiometric mixture is a mix of reactants okay.

It is what I was beginning to identify that can in principle in principle this does not have to happen in reality there could be lots of barriers for the reaction to happen you put two things together they do not need to react for example in principle you can you can get aluminum to react with water, but if you now try to put an aluminum kettle on this table okay and then pour some water in that to make a cup of tea you do not see an explosion there right you want to have some tasty tea so that that is a reaction that is physically stopped okay, so it is it is possible in principle but does not happen in practice usually okay so in principle react to give products with the highest negative each of formation highest heat of highest negative heat of formation.

With nothing left over nothing left over is nothing none of the reactants left over right okay so we have, now started throwing in some jargon in there we are now we are trying to say you are looking at products we are looking at products which were sharp specifically the ones with the highest negative heat of formation okay so we can say heats because these are products so, so first we have to understand what is meant by heat of formation right one and then we will be able to understand stoichiometric what would the stoichiometric mixtures so note then in the CH and O system.

When you now write something like CH and O what it means is we are now looking at a system with these as the atoms that are constituting the molecules in that system okay so these refer to the atoms that are that are available so in the CH and that is a carbon hydrogen nitrogen oxygen system the products the products with, with highest negative heats of formation are h2o and co2 so that is the reason why I was expecting that if methane was getting oxidized I was I would look for carbon dioxide and water as the final stable products.

Once I get them then I start looking at whether I have some old methane or oxygen left over if not I look at what is the proportion at which I took my oxygen and maintained and then that proportion is the stoichiometric mixture okay so now we know why we want to look for water and carbon dioxide we still do not know what is meant by heats of formation yeah okay.

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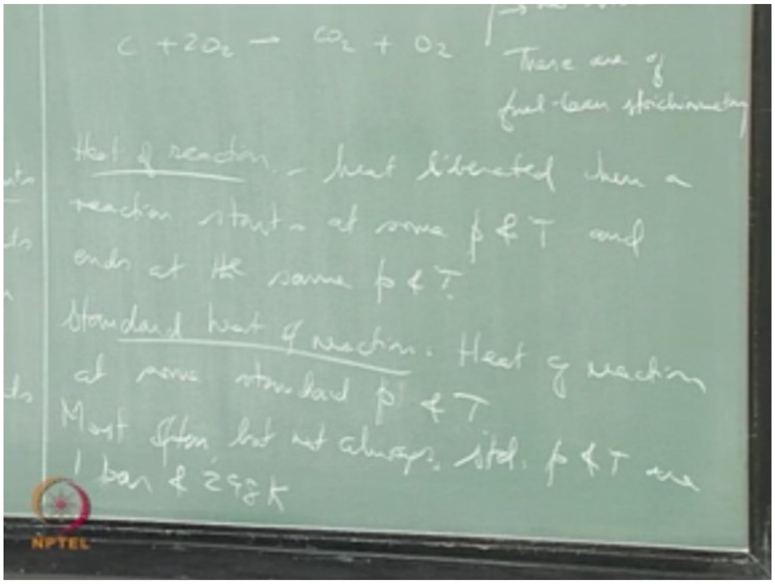

$C + 2O_2 \rightarrow CO_2 + O_2$

There are of
fuel-lean stoichiometry

Heat of reaction – heat liberated when a reaction starts at some p & T and ends at the same p & T.

Standard heat of reaction: Heat of reaction at some standard p & T

Most often but not always std. p & T are 1 bar & 298 K

So example h2+ 1/2 O_2 gives h2o that is reasonable right and C+ O 2 gives co2 or stoichiometric, stoichiometric if you have h 2 +O_2 gives h2o +h1/2 O_2 or c +2 0_2 gives Co_2+ O_2 these are not stoichiometric right.

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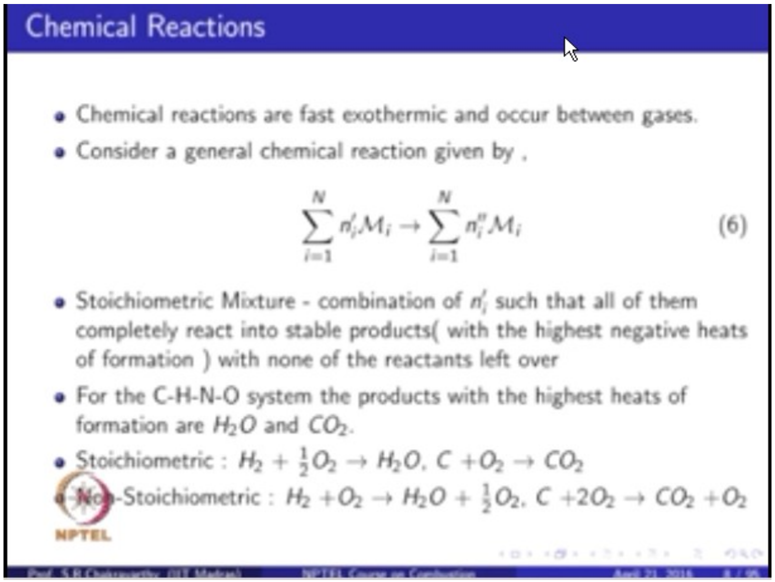

Chemical Reactions

- Chemical reactions are fast exothermic and occur between gases.
- Consider a general chemical reaction given by ,

$$\sum_{i=1}^{N} n_i' \mathcal{M}_i \rightarrow \sum_{i=1}^{N} n_i'' \mathcal{M}_i \qquad (6)$$

- Stoichiometric Mixture - combination of n_i' such that all of them completely react into stable products(with the highest negative heats of formation) with none of the reactants left over
- For the C-H-N-O system the products with the highest heats of formation are H_2O and CO_2.
- Stoichiometric : $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$, $C + O_2 \rightarrow CO_2$
- Non-Stoichiometric : $H_2 + O_2 \rightarrow H_2O + \frac{1}{2}O_2$, $C + 2O_2 \rightarrow CO_2 + O_2$

Because we did not have this condition that nothing is left over we have some, some of the reactants leftover yeah in these cases okay and typically this is what we are looking at and this is what we would call as.

These are or of fuel-lean stoichiometric okay so look at the dogging here stoichiometric is something that refers to any combination of make of any combination of the reactants in a mixture okay so you can have a fuel lean stoichiometry or you can have a fuel rich stoichiometry or you have a structure metric stoichiometry.

So what is stoichiometry is very specific but anything that is having excess oxygen to whatever extent is all fuelling anything that is having excess fuel to whatever extent is all fuel rich okay now I would like you as your talk as we speak of course I am not giving an example of where for example you can say let us suppose that you have a, a fuel rich situation then it is possible that you have excess carbon but you have a deficient oxygen you might actually get only partial oxidation of the carbon.

That is available and get into carbon monoxide alright and with no oxygen leftover or no carbon left over that is stoichiometry either because we are not looking at products with the highest negative heats of formation okay so that is something that I talked about the other thing that that is come out in what we are what we are discussing here is something about notions of what is fuel and what is oxidizer okay.

Now here we are, we are ,we are, we are okay because we are always looking at oxygen being there and whatever is not oxygen in the reactants must be the fuel it is essentially our brain wiring going on but how when you now look at a reaction like A+ B gives C + B how do you figure out which is the fuel huh only then you can tell, tell me whether, whether just fuel lean a fuel rich so how do you know you ever look at electronics change and all those things.

So again you had to get into the molecular level long can we do without that so he is talking about economics okay air is something that is available for free in this planet for you to screw around with and okay, okay and keep contributing to global warming and that is for free you can you can do it with that with no penalty for yourself except for your future generations wrong but fuel is something that you have to pay for now so you want to use it less that is not quite true well.

We will come to that so it is not quite true okay for example in rockets okay we have to provide both the fuel and oxidizer ourselves and we choose usually to go for a fuel rich composition all right so it is not completely true that you always have the deficient species as the fuel okay now we take the answer that we have we have from back there so the answer is you look at the heats of formation right.

So based in the heat of formation without looking at electrons and all those things we should be able to decide what is a fuel okay that is the purpose of this lecture okay so if you have to get there we first of all have to understand what is meant by heat of formation yeah okay So before we get into a heat of formation we first have to look at what is the heat of reaction right so the heat of reaction is heat liberated heat liberated when a reaction starts at some P & T and ends at the same P& T how is that possible it or is it possible is it, is it possible for you to have a reaction that started a certain pressure and then come back to the same pressure and temperature of course it is possible right.

So you can now take a container and typically you know you can you can have a container which is like a cylinder and then put a piston on ah come on the thermodynamics we were missing piston and cylinder all the way along so they are coming back to back, back to haunt us it is a confit do without piston and cylinders in thermodynamics we will do pretty soon huh so but for this photo for the idea of conceiving what is what we are talking about let us say you know how they a piston cylinder arrangement.

And then you now put in some reactants into the cylinder you now throw in a weight on it on top of this piston okay which is acting in a time non varying gravitational field okay and then you, you know and then you have a certain pressure and temperature there and then you ignite and then get the reactions going okay obviously a lot of heat is liberated and the gases that are coming out or expanding and then the it is now pushing the piston up let us say okay it is still acting at the same pressure because the piston has to balance the weight okay.

So the, the piston being allowed to move up a date with a constant weight on top is essentially ensuring that you have a constant pressure situation and any heat that is liberated that is going to heat up okay you now take it out you now put this in a water pot all right and then you take, take it out and then get, get and then you know get it back to the same temperature as before now you look at the heat that you now take out and the work done do we have to worry about the work done.

What worked? but that was to maintain the pressure constant the piston is mass less but it is going to carry a weight on it on top of it okay so the thing is the thing is we are now basically looking for getting the same pressure and temperature we try to maintain the pressure we get the temperature back by removing the heat, that heat is what we are talking about okay so you still have this nagging doubt in your mind we had this expansion work right is that we counted or some supposed to be counted okay.

From this you are like no, no, no, no whatever heat you are actually getting out by bringing the temperature back to its original position is what is the heat is what, what you are talking about that means we are not talking about expansion work okay so keep this in mind you have an expansion work to account for or maybe it is already accounted we all we had to bother about it so let us, let us keep, keep that in mind okay there is something that is going on there okay .

Now is it possible for us to talk about this without piston cylinder okay so let us say for example you are like aerospace engineers and therefore we want to have engines and you want to crank up the engines and run them and all that stuff that is what we are here for what are we talking about piston cylinder sorry so you are basically looking at it in the map of thermodynamics right so we are looking at what is the pressure and temperature of the system when it was when it was the form of reactants.

And what is it now when it is now become products this could be happening for all we care inside a gas turbine engine and as a matter of fact most of these open systems like gas turbines and rockets and so on which have a nozzle or an exit they happen to maintain the pressure pretty much more or less so they are all typically constant pressure systems fortunately for us so we do not have to we do not have to have a piston and a weight on top of it and all those things gravitational feeling right.

So we have a constant pressure situation for most, most of the time okay the one who is to capture the products and bring them back to the same temperature okay if you did that then we would not be flying this engine right so if you want to now figure out the heat you cannot be flying so get back to the piston and cylinder that is good enough good so now we talk about standard, standard heat of reaction right.

Now this is the heat of reaction at some standard oops P and T so previously we did not fix what the pressure and temperature were we just simply said whatever we started out with we wanted to come back but now we fix that to be some standard okay and why would we want to do this is something that we want to keep looking forward to, to understanding as we go along so we want to standardize something is here so we will now take for example most often but not always but not always standard P&T or 1 bar and 298 Kelvin, 298 Kelvin right.

Now 1 bar is like 10 to the 5 Pascal's, Pascal's is actually the SI units for pressure but atmospheric pressure is approximately like one point not one three to five bars therefore we go in terms of bars instead of Pascal's itself and 298 is pretty convenient okay so it says like about 25degrees Celsius which is reasonably warm okay so it is not unrealistic for let us say Indian conditions or something.

So this is a reasonably good standard for us to and this choice for all practical purposes of analysis that we want to do is arbitrary okay. So you do not know you do not have the question can I change this in your own planet yes when you say standard that means everybody accepts something that is, that is what it is but it is an arbitrary choice okay.

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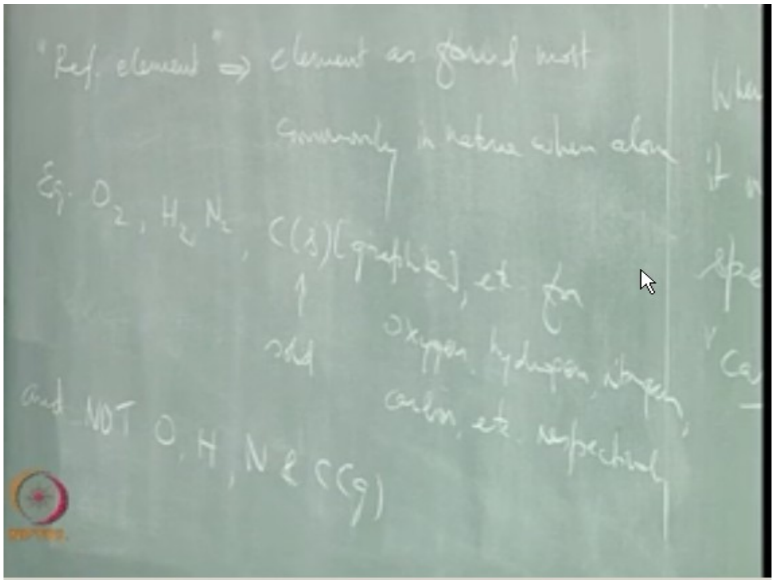
"Ref. element" ⇒ element as found most commonly in nature when alone

Eg. O_2, H_2 N_2, C(s)[graphite], etc. for oxygen, hydrogen, nitrogen, carbon, etc. respectively

↑ std

and NOT O, H, N & C(g)

So now we come to heat of formation now the heat of formation is what we are really interested in okay we have been we have been beginning to talk about heat of formation when we talked about a stoichiometric mix mixture and we also noticed that if you wanted to recognize a particular component as a fuel the heat of formation is going to help us this is pretty important you know like for example let us say you become an astronaut and then you are sent to a new planet.

And then you are now beginning to dig up okay and then you are now getting something, something new you have to know whether it is fuel or not is not it so and you will start making a lot of money if you if you knew how to figure out what a fuel is so, so heat of formation at some P and T some P and T yes the negative heat of reaction negative by convention more than anything else negative heat of reaction at that P and T for a compound for a compound found.

From its I am going to use within quotes reference elements okay you are beginning to get an idea of what the sentence means first of all we are talking about any species which could be a compound, compound is like basically a bunch of molecules put together right and then we are looking at this being formed from its reference elements so elements are like the, the building blocks of the compound okay but we have something called the notion of what's called as a reference element.

So we have to see what that means and I also want to point out so formed so I also want to point out that this reaction as it is does not have to happen in reality okay you do not necessarily need a compound to be formed from its reference elements in reality this is a hypothetical idea of any compound that could be formed from its reference elements okay so now we have to see what that means though so reference element means that element as found most commonly, commonly in nature, in nature when alone okay.

This is for every element so every for every element you have to look at what is the most natural state at which it would be found and that is what is called the reference element okay so still it is a little bit enigmatic so here example, example O_2, h2 n2 carbon within brackets S to denote solid okay solid and when we say solid we are looking at graphite not diamond okay because if it were a diamond that is most commonly found you do not it will be very expensive right so graphite etc for okay now let us use words for, for, for oxygen, oxygen hydrogen nitrogen carbon etc, respectively okay.

And, and not okay so every time you give an example we also give a counter example like what we did here so, so you always know what is good and what is bad so not is O H N and let us say carbon in gaseous form you try to vaporize carbon get it up to very high temperatures or something and then look at the carbon that is not considered a reference element looking at carbon in, in a solid form for graphite.

And since we started out with the assumption that we're looking for reactants react reactions to happen between gases, gases is by default the state for most of the reactants that we are looking at that means we are not going to say within, within brackets G H within brackets G and so on so we are not going to specify gas so it is only if it is a liquid or a solid we will use parentheses likes and L and so on okay.

So when you now have S in parentheses that means it refers to a solid if it is a l it refers to a liquid like for example you are looking at al2o3 that is being formed in rockets it states stays in molten form as it comes out of the nozzle but as it goes through the nozzle it the flow cools and therefore it solidifies so there is like a al2o3 l that gives rise to al2o3s okay.

So in there we grab that we will specify Ellen yes very specifically so this is what is meant by reference, reference elements so the phase is indicated only for liquids and solids and not for gases because gases are the default okay so what is meant by so what we have done here is to explain only the last couple of words in this in this sentence right so what does it meant by looking at a heat of formation.

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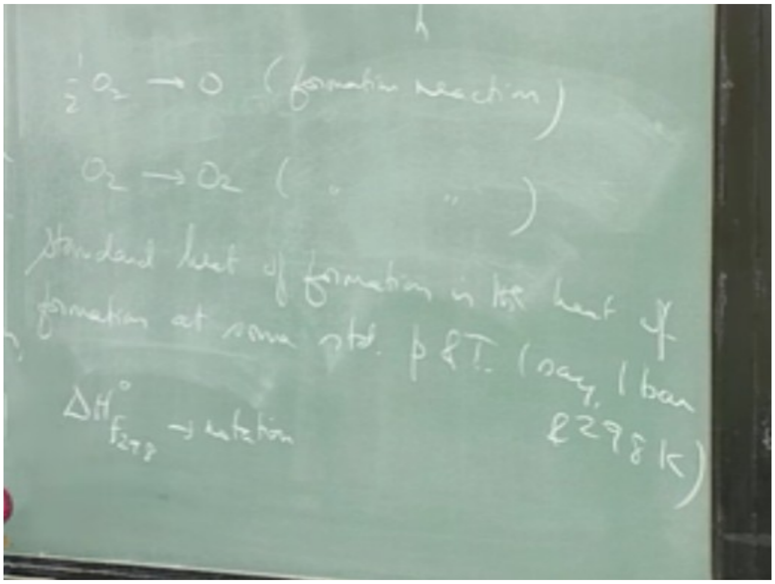

$\frac{1}{2}O_2 \rightarrow O$ (formation reaction)

$O_2 \rightarrow O_2$ (" ")

Standard heat of formation is the heat of formation at some std. p & T. (say, 1 bar & 298 K)

$\Delta H^{\circ}_{f_{298}}$ → notation

That means if you now look at h2 +1/2 O_2 gives h2o okay see solid plus o2 gives Co two these are formation reactions for formation reactions for $h2_o$ co_2 respectively right so what else could not be an example so if you now said H+ O gives so it is 2h+O gives H2O this is wrong there Is not a formation reaction okay not a formation reaction right so what about formation reactions for O self O is not going to be like a reference element okay that could be formed because O2 should be the reference element.

Therefore we can say 1/2O2 gives O is a formation reaction we are always looking for one mole of what is being formed so everything is normalized for the reactants correspondingly okay now if O2 is supposed to be the reference element what would be the reference element for it itself right so O2 gives O2 is also a formation reaction that sounds silly does it no it says it tells it tells us something if O2 has to react with itself to form O2 will it take any energy no right.

So what do you expect for the heat of reaction 0 we will now assign a 0 for the standard heat of reaction we still haven't looked at what is the standard heat of reaction keep in mind we are looking at a heat of heater for standard heat of formation okay so you are looking at a heat of reaction and a standard heat of reaction a formation reaction is a particular reaction so it is real heat is going to be the heat of formation and then we should be looking at a standard heat of formation.

So we now arbitrarily a sign zero for the standard heat of formation for reference elements because at standard state we now suppose that there is no change in the reference elements right

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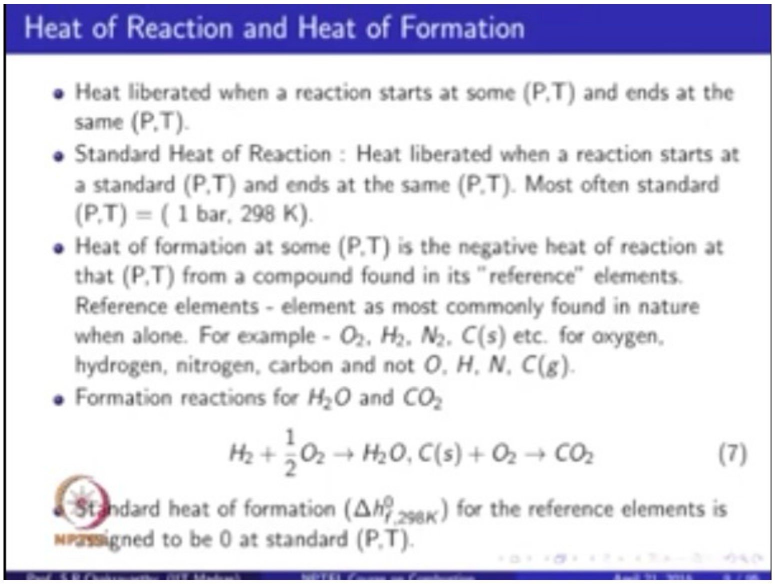

Heat of Reaction and Heat of Formation

- Heat liberated when a reaction starts at some (P,T) and ends at the same (P,T).
- Standard Heat of Reaction : Heat liberated when a reaction starts at a standard (P,T) and ends at the same (P,T). Most often standard (P,T) = (1 bar, 298 K).
- Heat of formation at some (P,T) is the negative heat of reaction at that (P,T) from a compound found in its "reference" elements. Reference elements - element as most commonly found in nature when alone. For example - O_2, H_2, N_2, $C(s)$ etc. for oxygen, hydrogen, nitrogen, carbon and not O, H, N, $C(g)$.
- Formation reactions for H_2O and CO_2

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O, C(s) + O_2 \rightarrow CO_2 \qquad (7)$$

- Standard heat of formation ($\Delta h^0_{f,298K}$) for the reference elements is assigned to be 0 at standard (P,T).

So standard heat of formation, formation is, is the heat of formation, formation at some standard P and T okay so it could be the same as same as what we have noted there one bar say one ball and 298 K and the notation for this is ΔH F^0 298 is he notation ΔH stands for a enthalpy change okay and F stands for formation 298 is the temperature not refers to the standard, standard pressure so this is the notation that we will use I will pick up from here in the next class and then point out to the question that is have in our minds if you now have a constant pressure and temperature what happened to the, the expansion work okay so I will see you next class.

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