Fundamentals Of Combustion (Part 1)

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Lecture - 08

Laws of Thermodynamics and Stoichiometry

So, in the last lecture we are basically dealed with how we will be handling the enthalpy and today we will be looking at basically about the laws of thermodynamics and also the other thermochemical laws what will be required to handle the chemical reactions. So, let us start this lecture with thought process you are a big chemical reaction everything you say all that you do, all that you see decide, remember, think or feel is nothing but, the manifestation of the chemical reaction that is you. So, that is of course, told by the Jim Eadon and Sheffield university and which is true to some extent when you get in the biological aspects of it, right?

So, what basically will be doing we will be you know handling the chemical reactions and then a heat released during that in combustion therefore, we need to use the laws of thermodynamics what are the laws, how many laws you are aware any idea total somebody is saying 3 somebody, but actually there are total 4 laws 0 th law of thermodynamics, first law of thermodynamics, second law of thermodynamics and third law of thermodynamics.

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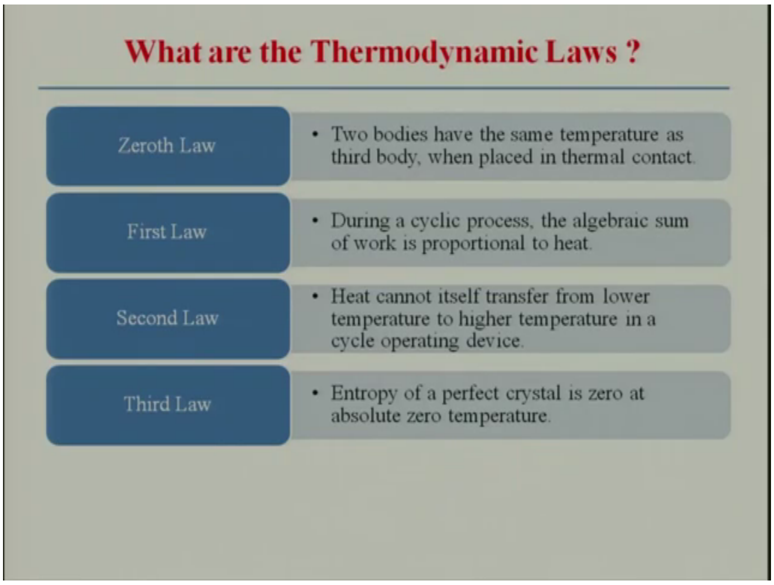

What are the Thermodynamic Laws ?

Zeroth Law	• Two bodies have the same temperature as third body, when placed in thermal contact.
First Law	• During a cyclic process, the algebraic sum of work is proportional to heat.
Second Law	• Heat cannot itself transfer from lower temperature to higher temperature in a cycle operating device.
Third Law	• Entropy of a perfect crystal is zero at absolute zero temperature.

So, what will do will not derive them will not or also discuss it at length, but; however, will try to recall what we are learnt. If we look at 0 th law of thermodynamics is basically talking about the how to you know dealing with temperature. We says that 2 bodies have the same temperature as the third body, when they are placed in thermal contact with each other separately if the object a is thermal equilibrium with let us say, c and the b is also equilibrium with the c therefore, object a will be thermal equilibrium with the b, that is the 0 th law of thermodynamics by which we basically measure the temperature. If you look at day to day experience, that what you do you put the thermometer in your body in armpit or on the tongue you know like, then allow it to attain the thermal equilibrium with the body right allow certain time.

So, that thermal inertia will be taken care and then that, body temperature is same as that of the whatever is shown in your thermometer, that is basically by the 0 th law of thermodynamics and first law of thermodynamics you know very well that, whenever a system undergoes a cyclic process and in a cyclic manner; however, the complex cycle it may be the cycle integral of the heat interaction is proportional to the cyclic integral of the work interaction is not it and that is being talked about during a cyclic process algebraic sum of work is proportional to the algebraic sum of heat, then what will happen it is proportional then where you get the law.

Student: internal energy.

Internal energy, that you will have to look at the system whatever there we use the you know first law delta Q minus delta W is equal to du, right? That is for the system this is for the cyclic process and there terms in the proportionality constant joule constant, that is equal to j equal to 1 in case of Si unit, whenever use Si unit j is equal to 1. So, in the second law we say that, heat cannot itself transfer from low temperature to high temperature in a cyclic operating device, right?

What is this statement this basically it is impossible to have a cyclic operated device, which will take the heat from the low temperature and transfer the same amount to the high temperature source, right? That is basically which statement clasius, right? That is the clasius statement, but the Kelvin plan statement is what? It is impossible to have a cyclo operated device to absorb certain amount of heat from a source and perform the same amount of work it is impossible.

That means, the efficiency will be 100 percent it is not possible, that is the Kelvin plan statement and this is basically constitute the second law of thermodynamics and the third law is basic entropy of perfect crystal is 0 at absolute 0 temperature and this is not being used except to define the entropy. Because, you will have to say entropy at the perfect crystal will be 0 at absolute temperature you know; that means, 0 Kelvin then you define then you do that, but we do not use.

We use basically first law and second law profusely and 0 th law is very obvious. So, what will be doing in our combustion we will be using the first law and second law of thermodynamics.

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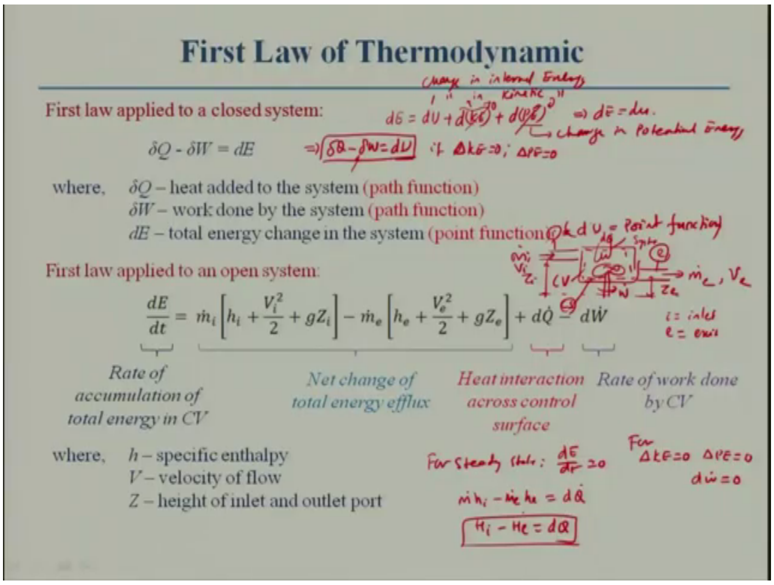

First Law of Thermodynamic

First law applied to a closed system:

$$\delta Q - \delta W = dE$$

$$dE = dU + d(KE) + d(PE) \Rightarrow dE = dU.$$

Change in internal Energy; change in kinetic energy; change in Potential Energy

$$\Rightarrow \boxed{\delta Q - \delta W = dU} \text{ if } \Delta KE = 0;\ \Delta PE = 0$$

where, δQ – heat added to the system (path function)
δW – work done by the system (path function)
dE – total energy change in the system (point function) & dU = Point function

First law applied to an open system:

$$\underbrace{\frac{dE}{dt}}_{\substack{\text{Rate of}\\ \text{accumulation of}\\ \text{total energy in CV}}} = \underbrace{\dot{m}_i\left[h_i + \frac{V_i^2}{2} + gZ_i\right] - \dot{m}_e\left[h_e + \frac{V_e^2}{2} + gZ_e\right]}_{\substack{\text{Net change of}\\ \text{total energy efflux}}} + \underbrace{d\dot{Q}}_{\substack{\text{Heat interaction}\\ \text{across control}\\ \text{surface}}} - \underbrace{d\dot{W}}_{\substack{\text{Rate of work done}\\ \text{by CV}}}$$

i = inlet
e = exit

where, h – specific enthalpy
V – velocity of flow
Z – height of inlet and outlet port

For Steady State: $\frac{dE}{dt} = 0$

For $\Delta KE = 0$ $\Delta PE = 0$ $d\dot{W} = 0$

$$\dot{m}h_i - \dot{m}_e h_e = d\dot{Q}$$

$$\boxed{H_i - H_e = dQ}$$

Now, first law of thermodynamic applied to a closed system we know delta Q minus delta W is equal to dE, what is this dE? Is it internal energy it is change in total energy which is nothing but, change in internal energy plus change in kinetic energy plus change in potential energy this is change in internal energy and this is change in kinetic energy, right? This one and this is basically change in potential. In a closed system if you look at mostly kinetic energy and potential energy is 0, but that is not true for all the time keep in mind. So, therefore, if that is 0 right, then what will get dE is nothing but dU right when it is 0.

So, therefore, you can right down delta Q minus delta W is equal to dU for a closed system provided, if d or delta kE is equal to 0 and delta pE is equal to 0, that is true generally when people say that what is first law of thermodynamics you will say delta Q minus delta W is equal to dU, but that is not true this is derived from the first law of thermodynamics and is it is handy to use in a closed system, right?

And keep in mind that delta Q is basically path function; that means, it will be dependent on the path and the delta W is a also a path function, but the total energy change in the system is a point function or in other words dU is also a point function, right? The first law of thermodynamics for an open system what it would be right some people say that you know like basically delta Q minus delta W is equal to what dh, right? But that is a little limited, but if you look at this equation elaborate one is this dE by dt is equal to M dot i, i means inlet if I say there is a system here, this is your inlet i and this is your exit, right? Then mass flow what is give i this is exit and keep in, right?

Whenever you are talking about open system basically the continuity has to be taken care right; that means, mass conservation has to be taken care, right? In this case like it has to be taken care and then this is your if I take this as my reference this height is Zi and if I take my this reference this is your Ze right and it is moving with a velocity Vi and the fluid is moving with VE.

So, therefore, dE by dt is equal to m dot i hi is your enthalpy at the inlet this not i species, i means inlet, E means exit plus this kinetic energy Vi square plus gZi is basically potential energy, g is your gravity acceleration, right? Minus m dot i into hE plus V square by 2 plus gZe plus delta dQ, dQ means some heat is interaction is taking place you know this is your dQ and some you know like a let us say, some work is going on right this is a fan which is rotating, that is your work done w soft work you can say, right?

So, therefore, this is basically rate of accumulation of total energy in control volume this is your control volume, right? This is your control volume CV control volume, right? And this is your net change of total energy efflux this one this portion is coming in certain amount of energy, certain amount of energy is going out that is a net of flux and this is your net heat interaction across the control surface because, this is your control surface if you look at this is your control surface, right? And the other one is your rate of work done in control volume, right?

So, these you will have to apply in your our open system whenever we are looking at for combustion and whenever we are looking at closed system I have to apply this first law right you can even think of using this one because, change in kinetic and potential energy in a control mass system is very rare and in combustion system hardly it will be there.

So, for a steady state if I want to use this one for steady state what will be dE by dt is 0, and if there is a change in kinetic energy is 0, and change in potential energy is 0, and there is no work done dW is equal to 0 then what will get, I will get m dot hi minus m dot he is equal to dQ is not it and in some cases we will be considering also adiabatic; that means, there would not be any heat interaction we will be doing that, are you getting this is the thing what you can think of you can write down this is hi minus he is equal to dQ, right?

Under this condition for the change in kinetics is 0, change in potential is 0, and work done is 0 in combustion system there is no work done as such right, there will be heat interaction there will be what you call enthalpy change or kind of things. So, therefore, the heat being generated is basically change in enthalpy at the inlet and the exit. Is that clear, and keep in mind that the when the work is done by the system will be positive, work is done on the system is negative and heat is transferred to the system will be what? Positive heat is transferred from the system will be negative, right? So, those sign convention you should keep in mind.

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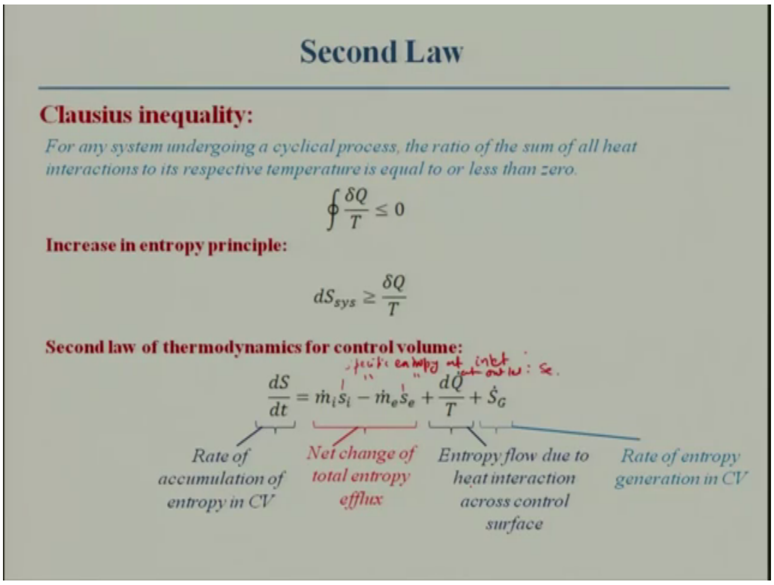

Second Law

Clausius inequality:

For any system undergoing a cyclical process, the ratio of the sum of all heat interactions to its respective temperature is equal to or less than zero.

$$\oint \frac{\delta Q}{T} \leq 0$$

Increase in entropy principle:

$$dS_{sys} \geq \frac{\delta Q}{T}$$

Second law of thermodynamics for control volume:

specific entropy at inlet
at outlet : se.

$$\underbrace{\frac{dS}{dt}}_{\text{Rate of accumulation of entropy in CV}} = \underbrace{\dot{m}_i s_i - \dot{m}_e s_e}_{\text{Net change of total entropy efflux}} + \underbrace{\frac{dQ}{T}}_{\text{Entropy flow due to heat interaction across control surface}} + \underbrace{\dot{S}_G}_{\text{Rate of entropy generation in CV}}$$

So, if you look second law means basically clasius inequality which is nothing but, that for any system whenever undergoing a cyclic process the ratio of sum of all heat interaction to it is respective temperature of the source or the sink if I will say thermal preserver is equal to or less than 0, right? This is your clasius inequality which is being used for basically relating the entropy with the heat interactions, right? And that is nothing but, your cyclic integral delta Q divided by t less than equal to 0, right?

But for a system, if you look at this is equal to change in entropy will be always greater than equal to delta Q by t and this is known as increase in entropy principle like, there will be always entropy of a system will be increasing right, and that is the true right if you look at what you mean by entropy? Physically any idea these are degree of disorderness right; that means, wherever there will be heat interactions there will be molecules will be moving expanding temperature will go up and disorderness entropy basically increases, and that is happening with the mind if you remember that I had related a entropy, right?

With the mind and as today is the bombardment of information lot of noise is coming in your mind coming up in your mind therefore, you should not use this internet, mobile other things you know too much, but sparingly you should use the whole country now, is addicted with the internet a thing, right?

Now, it is something coming up. So, therefore, they are spoiling their mind from baby to old man all are engaged in the what you call internet, mobile, what isapp and all those thing and that is causing a lot of noise and noise leads to your entropy increase, entropy increasing means it is useless is not it and that is happening and we are saying we are developed. So, therefore, you will also have to look at this thing in combustion process there will be always increase in entropy, right? We will always try to minimize it of course, that is a difficult job particularly in combustion.

So, therefore, second law of thermodynamics for control volume and this is can be for this system, right? For control volume will be similar way dS by dt is equal to m dot i S i; that means, this is at the inlet keep in mind this is specific you know entropy at station i or I can say at inlet that in better I will write down at inlet and m dot iSe that is specific entropy basically specific entropy at outlet is nothing but your Se and dQ by t and Sg at the g basically entropy generation, right?

This is rate of change of accumulation of entropy, right? Net change of total entropy efflux this portions and this is of course, the rate of entropy generation in control volume and this is entropy of flow due to heat interaction across the control surface, if there is a some heat interactions heat will be taking place right. So, one has to use it, but will be using basically this entropy in whenever will be looking at chemical equilibrium then will have to use entropy is not it from, that only we will calculate what will be the equilibrium composition of a particular chemical systems. So, we will be using that, but otherwise will be using mostly the first law of thermodynamics.

So, what you mean by stoichiometry because, when you talk about it we will be dealing with some chemical reaction, when you talk about chemical reaction will be dealing with basically stoichiometry.

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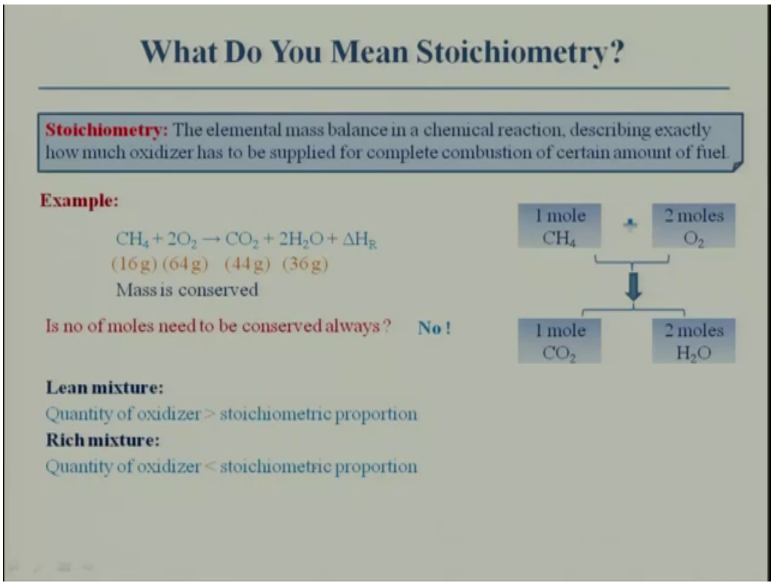

What Do You Mean Stoichiometry?

Stoichiometry: The elemental mass balance in a chemical reaction, describing exactly how much oxidizer has to be supplied for complete combustion of certain amount of fuel.

Example:

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \Delta H_R$

(16 g) (64 g) (44 g) (36 g)

Mass is conserved

Is no of moles need to be conserved always? **No !**

Lean mixture:

Quantity of oxidizer > stoichiometric proportion

Rich mixture:

Quantity of oxidizer < stoichiometric proportion

And stoichiometry is basically the elemental bar mass balance in chemical reactions, right? This can be exactly how much of oxidizer has to be supplied for complete combustion of certain amount of fuel, right? So, that is basically a mass balance what you do for example, if I take this is 1 mole of methane is reacting with you know 2 moles of oxygen leading to the carbon 1 mole of carbon dioxide and 2 moles of water and releasing certain amount of heat, right?

Because, this will be a exothermic reaction overall. So, therefore, some amount of heat will be released and now, by these what you are saying it is basically mole is balanced here in this reaction in this reaction is it mole is balanced or not certainly yes because, in this case one mole left hand side 1 mole of methane 2 mole of oxygen 3 moles and in the right hand side 1 mole of carbon dioxide and 2 moles of; that means, 3 moles of left hand side 3 mole in the right hand side this is balanced, but it need not to be true for all the reaction this is a just a example which I have taken it happens to be true, but it is not true for all reactions, but; however, if you take right mole 1 mole of the methane means basically 16th gram, right? If you look at left hand side 2 moles of oxygen means 64 grams total is how much, something 80 grams right, in the left-hand side in the right-hand side carbon dioxide is 44 gram and water is 36 gram that is 80.

That means mass is conserved right, that it says elemental balance is that which is developing exactly how much oxidizer has to be supplied, right? And by these thing if mass is balanced; that means, everything is fine that is a stoichiometry reaction are you getting, but is it true is it not defined your E is equal to mc square that mean, the energy can be converted into mass will be converted into energy, right? Is it not defined because, you are saying mass is conserved there is some amount of heat released, right? Are you getting my point see if the some heat is there; that means, some mass will be consumed is not it, but here, it is not some heat is released the mass is also conserved. So, is it true or not yes, that is true; that means, the mass the heat released is very, very low here, in this case as compared to nuclear energy.

Therefore, the change in mass is so small, that you cannot measure any instrument therefore, you are calling it as a mass is conserved are you getting. So, you can take some examples you can refer my book in on thermodynamics there is an example you can look at it or you can may be I will give an assignment for that so that you can find out yourself whether true or not fine. So, mass is conserved here, but as I told it is number of moles is not conserved, right?

Whenever you are saying stoichiometry is basically means, if more amount of oxygen is there as compared to stoichiometry we call it as a lean mixture, when it is the quantity of oxidizer less than the stoichiometric proportion then we call it as a rich mixture, right? And so, we will be discussing more about this stoichiometric in the next class and today we will stop over here.

Thank you very much.