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Course
on
Laws of Thermodynamics

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Lecture 20: Introduction to Third Law

Good afternoon and I welcome you all to this lecture session of the course laws of thermodynamics now today I will give you a brief introduction to the third law of thermodynamics.

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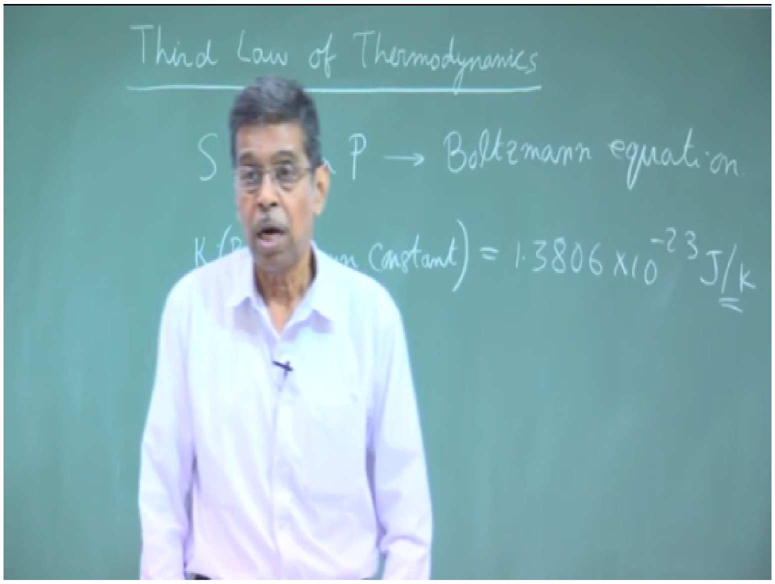

Third law of thermodynamics in fact the people working in the field of engineering science know very little about third law and its concept not much this is because of its limited use in engineering calculations but definitely it has contribution in the calculations of engineering science I will tell you and then I will explain as much as I can the concept of third law.

So far we have defined entropy from the classical thermodynamics point of view through the heat transfer in irreversible process and we have seen that this definition has come out that is very fast rate in terms of the difference of entropy or change of entropy in a process from one state to other state that s is integral of del Q reversible by T that means if a process executes if a system is the process at internally reversible condition then what is the amount of integral del Q by T del s.

So always we define the entropy in terms of its changes okay and in all engineering calculation the changes are required but sometimes we require the absolute entropy but even if we do not require absolute entropy the changes unknown but if you have to ascribe the value of entropy it is not exactly the absolute entropy from an absolute data but you have to fix a common data the third law of thermodynamics is that common bottom where the entropy can be taken as zero or entropy is actually zero of it substance.

So this statement to understand we have to understand little bit of microscopic point of view of thermodynamics or microscopic thermodynamics though this is totally beyond your scope of calculation or usefulness of thermodynamics in your at your level but we can discuss this little bit now we know from the kinetic theory of matter that molecules moves at random indifferent direction and they collide with each other in any matter.

Now this randomness or disorderliness of the molecule is actually the measure of entropy the randomness of this organism are made by the variation of velocities over a higher spectrum large variations and they are change very fast there they are change that means more randomness or more disorder needs means the velocity is a magnitude and the direction changes very fast and over a large spectrum.

If it happens in any matter we tell that this ordinance or randomness is more so more is the disorder less more is the randomness more is the entropy now what happens because of this disorder needs or randomness of the molecular motion it becomes difficult to predict a particular molecular configuration for a given macroscopic state that means with this randomness the predictability of molecular configuration or the molecular position or we can tell the molecular state sometimes it is told as microscopic state.

To define a particular microscopic State for a given macroscopic state it becomes very difficult it becomes much less predictable which means that with this randomness and disorder names of the molecules a given macroscopic state at thermodynamic equilibrium which so far we have discussed we have a number of possible molecular configuration or microscopic and more is the disorder more is the randomness more is this number of microscopic states that means the uncertainty of defining the microscopic state increases becomes less predictable okay.

And that way entropy increases so it is not surprising at this stage at this stage to understand that substance in solid phase will be having less entropy than that in gas phase because of the fact that in solid phase the randomness is much less compared to that in gas phase and the molecules in solid phase usually oscillate continuously about an equilibrium position.

So therefore absolute entropy in solid phase is less than that of gas phase where randomness is much more and they collide frequently the molecules collide frequently and the randomness is much more in statistical thermodynamics this is explained or this is written in a mathematical form through a parameter known as thermodynamic probability it is very simple concept very preliminary and simple concept the thermodynamic probability is the number of probable microscopic states with respect to a given macroscopic state and it depends upon the state variables at that macroscopic state.

For an example I am telling you we have considered an isolated system you know what is isolated system which does not interact with the surrounding the isolated system is at equilibrium it does not interact with the surrounding it properties remain invariant with time and uniform throughout the mass of the system but it may have a very high absolute entropy because the randomness of B or disorderneeds of the molecules so therefore you see microscopic state is different from that of the macroscopic state in which were that here for a given macroscopic equilibrium state of an isolated system we have a large number of probable microscopic States or molecular configure.

So this is expressed in terms of thermodynamic probability in statistical thermodynamics that probability indicates the number of possible microstates for a given microstate of a system and the absolute entropy is in that case is expressed by a very well-known equation K LN P where P is the thermodynamic probability and K is the Boltzmann constant and this equations known as volts man equation this equation is known as Boltzmann equation and K is case Boltzmann constant Boltzmann constant.

Boltzmann constant whose value is one point three eight zero six into 10 to the power minus 23June 30 which is the unit of entropy so this is the absolute entropy in statistical thermodynamics expressed by the well-known Boltzmann equation in terms of thermodynamic probability that means the possible or probable microstates for a given microstate and where this probability is more means we can have more microstates more number of microstates for a given microstate so at the absolute entropy is more.

So therefore absolute entropy depends upon the number of probable microscopic States which in turn depends upon the molecular disorder is randomness more is the disorder Nina's mode is the randomness more is the probability of the microstate okay. Number of microstates now with this equation we can understand that how then absolute entropy is expressed now you consider a solid where the randomness is much less because the molecules continuously oscillate about equilibrium position and this randomness where the less random that means uncertainty is list also decreases or fades out at the temperature increases so this randomness or this uncertainty even for solid which is much less also fades out or decreases with the decrease in the temperature absolute temperature any temperature decrease in the temperature okay.

And when it approaches towards absolute zero it becomes the uncertainty becomes minimum and in this respect I can tell that we assume that when absolute zero is approached all molecular motion ceases out all molecular motions cease out that means are stopped there is no molecular motion and this is sometimes called as ultimate molecular order that means the order of the molecule reaches this maximum value and uncertainty is zero and certainty is 100% that means molecular configuration is fixed.

But if you proceed towards absolute zero for a solid substance the uncertainty is reduced the molecular randomness or disorder needs is reduced and these substance approaches an absolute zero entropy and this is more so for a crystalline solid this is because for other solids non crystalline solid still there are fewer certain uncertainties even if the temperature absolute temperatures approaches zero so it is for a crystalline solid substances where when the absolute temperature approaches zero we can tell the randomness approaches 0 that means uncertainty approaches 0 and molecular order reaches is maximum.

So this concept this concepts were derived from experiments from chemical reactions data from chemical reactions at very low temperature data from heat capacities of substances at very low temperature by collecting the data and through deduction it has been established and this law actually was formulated by two scientist arced and simony and known asnarsimha statement which steps like that the absolute entropy of a crystalline substance approaches zero as the absolute temperature approaches zero this is known unsacred Simon statement.

I will show it afterwards the statement now with this narsimha statement we can have some idea about the absolute entropy how it is useful in engineering calculation that to have a common bases that we can ascribe the entropy values at different states from its changes calculated by our well-known formula in classical thermodynamics through reversible heat transfer we can ascribe if we know this base and that common base.

And that is very important I am telling in chemical reactions which has not been taught in your discourse that if you read the thermodynamics of reactive systems then you will see it is very important to have a common base for calculations of entropy at different states of the substances known as reactants or products in a chemical reaction and that base is at zero absolute temperature base where the entropy absolute entropy is zero.

This is of very practical use for in engineering calculations now this is one approach of defining the third law there is another approach of defining the third law this comes from the attainability ofabsolute zero in fact I have told that absolute zero is approach but exactly we cannot have absolute zero we cannot attain absolute zero in fact is this has-been found you know that there are probably you know this has not been also taught that there are various ways overcooling.

So if you pull a system how much cooling you can do or at what temperature you can go you can never got absolute zero in this respect I will tell you in brief what are the methods there is a method known as joule-Kelvin effect the method which uses the joule-kelvineffect joule-Kelvin effect is like this if a gas is coming at a high pressure and temperature is allowed to pass-through a small restriction or constriction where there is a pressure drop because of the mechanical friction then it is found that temperature of the gas is decreased if we isolate the entire constricted systems decreased provided the initial temperature is below certain temperature known as inversion temperature.

I am not going into that detail that is known as dual Kelvin effect and if you think from the steady flow energy equation that the first law of thermodynamics applied to control volume and if the constricted system is totally insulated then the enthalpy at the inlet will be equal to the enthalpy at the outlet if you consider the kinetic energy and potential energy changes are negligible that means in this case the enthalpy at the inlet and outlet remains same.

But this is highly an irreversible process where the pressure is reduced and the temperature is reduced provided the inversion in the initial temperature is less than the inversion temperature most of the gases are cooled by utilizing this effort this effect where initial temperature is usually lower than the inversion temperature to realize thiscooling effect otherwise the gas has to be pre cooled to a temperature below the inversion point temperature of that gas okay.

Now this process is known as bottling process and by throttling a gas like this we can produce a low temperature and this is utilized for liquefaction of air okay and we can produce liquefaction of any gas and by joule-Kelvin effect wean produce helium at five Kelvin today now again there is another process to go for a further cooling to reduce the temperature which is the adiabatic vaporization that means if you have an helium at five K if you make an adiabatic vaporization that means entire system is insulated there is no heat transfer with the surrounding and because of the vaporization the cooling effect okay.

So this is another way by go to go for further cooling another way overcooling a system is by magnetocaloriceffect this effect is known not much this is that on a paramagnetic substance by decreasing the adiabatically the magnetic field we can go on changing the temperature to a very low value but in all these processes of cooling it is observed and it comes from the commonsense also that as you cool the cooling becomes more tough for example when you compress a gas the compression becomes more tough as the pressure is increased as you compress the next compression becomes tough similarly as the cooling proceeds.

If you cool the next cooling is more tough so this way if you have finite number of processes you can never achieve to Absolute Zero cooling becomes gradually difficult so that you can never achieve zero key and this has been established from several experiments so therefore this statement that the absolute zero can never be achieved in any finite number of processes executed by any system is also another way of defining the third law of thermodynamics.

So therefore we have two ways one by defining the absolute entropy its base where the absolute entropy is zero we use it at a base for entropy to ascribe the entropy a different state for our calculation engineering calculation similarly the third law is also explained in terms of unattainable 'tiphenomena that absolute zero can never be approached .So I now show you and the two statements of thermodynamics.

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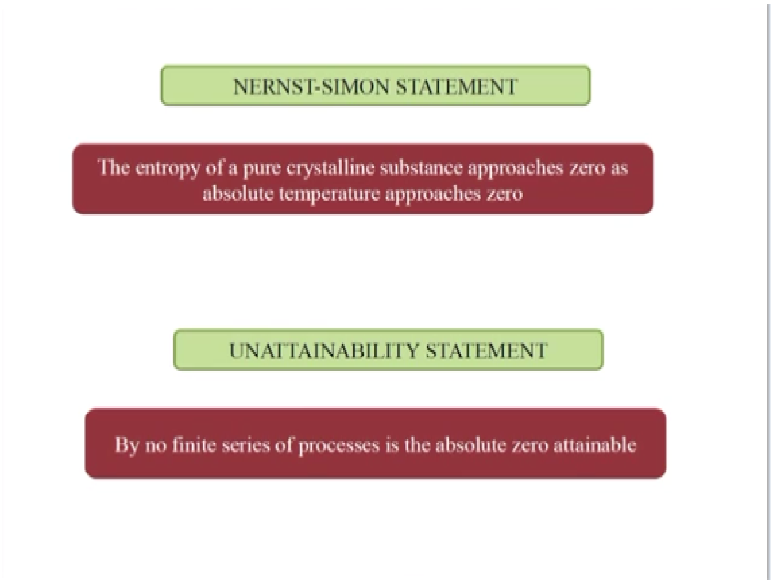

NERNST-SIMON STATEMENT

The entropy of a pure crystalline substance approaches zero as absolute temperature approaches zero

UNATTAINABILITY STATEMENT

By no finite series of processes is the absolute zero attainable

Not statement not shaman statement this statement is the entropy of a pure crystalline substance approaches zero as absolute temperature approaches zero that as I have explained and another is the unattainable it statement which is the statement by no this is the statement of unattainable 'it phenomena what is that that is by no finite series of processes is the absolute zero attainable.

So therefore these are the true statements of thermodynamics third law we do not have to put much you need much effort in it only an overall understanding and a brief introduction of third Locke for the completeness of the course it is required so you must know there're four laws of thermodynamics one is zeros law which defines the concept of temperature which defines the temperature gives the concept of temperature another is the first law which is nothing but typically the law of conservation of energy okay.

The second law which is the law that puts a directional constant which imposes the directional constraint on unidirectional characteristics of process occurring in nature which has-been dealt elaborately how this constraint or you variationalcharacteristics is imposed on any natural process and last one is the thermodynamics third law which defines the absolute entropy at Absolute Zero.

State which is again not attainable through two statements on is not Simon statement which defines that absolute entropy which tells that the absolute entropy of a fist aligned substance approaches zero when the absolute temperature approaches zero an absolute temperature cannot be attained in any finite series of processes which is unattainable ax T statement okay by this I conclude thank you all.