Advanced Chemical Thermodynamics & Kinetics
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Lecture - 02
Review of Classical Thermodynamics 02

Hello everyone. So, today we will start our first chapter or first section we in, which we will give you an overview on the thermodynamics that has already been covered in an earlier course. So, this is just to make sure that we are all on the same page, because the concepts which will be developed in these lectures will be subsequently used.

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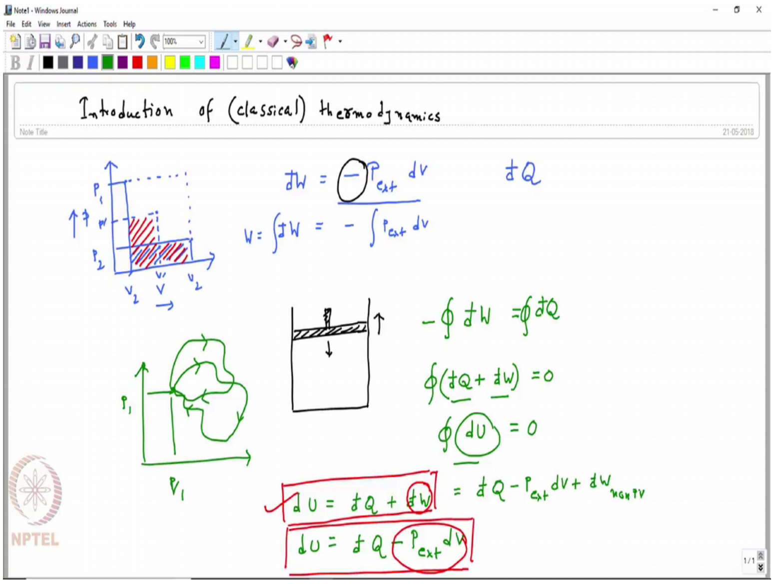

Introduction of (classical) thermodynamics

$\text{đ}W = \boxed{-}P_{ext}\,dV$ $\quad \text{đ}Q$

$W = \int \text{đ}W = -\int P_{ext}\,dV$

$-\oint \text{đ}W = \oint \text{đ}Q$

$\oint(\text{đ}Q + \text{đ}W) = 0$

$\oint \boxed{dU} = 0$

$\boxed{dU = \text{đ}Q + \text{đ}W} = \text{đ}Q - P_{ext}\,dV + \text{đ}W_{non\,PV}$

$\boxed{dU = \text{đ}Q - P_{ext}\,dV}$

So, we will be discussing about an introduction to give you an introduction of classical thermodynamics. Now the word classical means we are not talking about any molecular interpretation or we are not connecting the macroscopic properties to the microscopic properties through the statistical thermodynamics.

So, the only considering the macroscopic properties, and we will be only discussing the existence of matter as it is or like it is a bulk matter, but we will not bother what are the constituent atoms and molecules, what are the individual atoms or molecules properties. So, let us first, I mean give you an overview or give you try to recollect what we usually study in thermodynamics.

Now, whatever I am going to teach in this chapter or in this lecture, is very well known to you, but again this is just to remind you of few basic concepts and some key ideas that we often, I mean encounter problems that conceptual problems. So, the first thing, first we talk about systems and surroundings in a very abstract way. In the sense that the part of the universe which you are, I mean observe, which you are actually working with, is we call as system, basically part of the system and we look at the effects in the surrounding. So, surrounding is basically the part of the universe which excludes the system and system and surrounding together from the universe. And then we talk about many different kinds of systems; like open system, closed system, isolated system and so on and then we talked about the definition of work and heat.

So, work and heat are actually forms of energy, in during a transformation it, there it is, it is meaningless if we have this statement that; suppose a 1 gram of ice has this much amount of heat it does not make sense. However, if I say that the 1 gram of ice when it melts into 1 gram of water, at say 100 degree at 0 degrees centigrade and one atmospheric pressure, then this much amount of heat is released or this much amount of heat when the water phases is withdrawn.

So, that makes sense, because actually heat and work are actually forms of energy during the transformation. There is no such concept that a system has absolute amount of heat or work. Now of course, the system possesses some internal energy and way we define the internal energy is as follows. Before coming to the internal energy let us first discuss what are basically out of the other properties of work and heat.

A work and heat are known as a path functions, meaning it will depend on how you transform the system; like if you remember your introductory thermodynamics lecture which you will get in the, which are all uploaded in the earlier course on YouTube or you can get it this information in any standard physical chemistry textbook, particularly in the textbooks which has been recommended to you.

Now, we usually suppose we are talking about a pressure volume or a mechanical work and suppose you are going from one particular initial pressure, initial pressure and initial volume, let us say P 1 V 1 to some final volume let us say P 2 and V 2. Now the question is, how would I do this transformation? So, this is an expansion as we have drawn it.

So, this is an example of an expansion and in this case, I am showing the work done in an P V diagram, because the dimension of pressure times, volume is the dimension of energy or work. Now if we can do it in many different ways, we can do it in a single step. Then we can actually set the opposing pressure equal to P 2, and this system basically expands and then the work done will be nothing, but the area under this curve. We have already done it, because of the expression for work done or we can write it as a differential expression for work done, is nothing but the negative of external pressure times the change in volume and for any finite spray. I mean a finite value of the work done. It will be nothing, but integration of that P external into d V, where actually the volume chains in a finite limit.

So, now the question is, this work done which we are describing here if I set the external pressure to be equal to P 2, then the volume change is nothing, but V 2 minus V 1, and the work done will be just area under this curve. However, if I go to an intermediate pressure first, which is say P prime, which is somewhere say here and which corresponds to volume which is say V prime here, then the work done in our first step will be something like the area under this curve; the red shaded zone and then in the second step it will be the area under this curve.

So, you see that the work done is very different. So, work done is a path function and that is why the differential. We are not actually mathematically exact differential, so it is an in exact differential and that is why we use a cross sign similarly for heat withdrawn or heat supplied to the surrounding, that also we write it as d cross Q.

Now, we already discussed in the earlier course or it is also explained in the textbook why? Actually we use a negative sign here. Usually we the convention will follow here is, the work done on the system is a positive and work done by the system is negative. Now you can think that or classic example for work done thus or the system is actually a gas which is confined in a cylinder and one side we have a movable piston which is frictionless and massless, so that it does not, the movement of the piston does not actually cause any dissipation of energy.

Now the question is, if the gas expands then actually the system is working, but always the weight of the piston or the opposing pressure acts in the downward, because if we think that we are, we have put piston or we have put the cylinder vertically then the force acting on the opposite pressure acting on the gas is actually always downward, but the gas is doing work in the other direction, because its expanding.

So, from that point of view we took the work done to, with the expression, in the expression. For the work done we usually take a negative sign to make things consistent. Similarly heat flown into the system from the surrounding is a positive quantity, but if it is released from the system and goes into the sounding that is a negative quantity.

So, any energy input either in form of work or heat if it is formed into the system, it is a positive and if it is flown out of the system into the surrounding that we take as a negative, take to be negative. Now then we say that we basically write the statement of the first law of thermodynamics and we say that for any cyclic process the work done will be equivalent to the heat withdrawn.

Now, what is a cyclic process? Now cyclic process is that you basically change, you start from a state of the system. Suppose this is a system, is just an gas constant in a cylinder and then it is its macroscopic properties at the state of the system is completely defined by three parameters; pressure, volume and temperature. And of course, the pressure volume and temperature actually has a relation meaning, they are not linearly independent.

So, you can choose any two parameters as like variables. Like suppose I have one particular pressure and volume that defines the system. So, automatically the temperature will be defined and that will be followed from a by an equal. I mean usually the gases will follow an equation of state which you approximate. We can approximate with a ideal gas equation of state which is not a very good approximation, which is valid only for dilute gases as well as that, like at a very low pressure limit analyzer, a high temperature limit also. And then we can actually model it slightly better way using Van der Waals gas equation.

But whatever it is, it is a model and there is a equation of state corresponding to that model and the gas more or less may obey that a real gas more or less may obey that equation of state under for certain region of pressure and volume, and then the pressure and volume. If I change and go to a new pressure and volume then I do as change in the state of the system, and if we do a change in the state of the system in such a way that after the transformation the system actually comes back to the original change, original pressure following original state. So, then it is known as the cyclic process.

But after the cyclic process the surroundings may not come back to the initial step and we discussed it. Suppose if I expand that gas in one step and then again compress it again by one step and to make sure that we have to send my final pressure, is actually equal to the initial pressure, then we will see that there will be some imbalance of the work done and that we discussed that those who are eternally equivalent to the lifting of masses; in the altitude, the lifting of masses in the altitude, the lifting of masses in the at different altitudes in the surrounding.

Now, so it means that the heat withdrawn is basically equivalent to the work done by the system and again both work and heat are, as I said that these are called path functions, so the these the differential work done or differential heat withdrawn are basically in exact differential. So, we have to actually use a cross sign here and we know that for any cyclic process the system will always come back to the initial state. If the surrounding also comes back to the initial sate, which means there was no work or heat exchange involved. So, both side will be 0, but it may be nonzero also, and that nonzero thing is basically the system, actually was used during the transformation. Although it came back to the original state it is kind of like surrounding used the system to convert some amount of work into heat, something like that or a heat into work.

Now, the question is, that conversion work into heat and heat into work in a cyclic process due to conservation of energy, we can write it, but since it is a basically we are saying the work done by the system will be equivalent to the heat withdrawn from the surrounding. Now heat withdrawn from the surrounding is a positive quantity work done by the system is a negative quantity, so to keep consistency we are we are using a negative sign here.

So, in other words if I just arranged this equation, we will get d cross Q plus d cross W is equal to 0, now if we write this d cross Q and d cross W, which is addition of two differential as a d U and we see that the cyclic integral of d U is 0. Now cyclic integral means actually you started from a particular state of the system and you are actually coming back from the same state; like in the P V diagram, we can actually show; what is a cyclic integral. Suppose this was my original state P 1 and V 1, and then I am doing, I am just traversing some path and finally, I see that I come back in the same original state.

And what we are finding that the, although d cross Q and d cross W their differential or their cyclic integral, which basically tells that when you come back to the original state, are actually nonzero or they are the differentials are actually in exact differential. Their addition if I take, a cyclic integral of that is 0, which means actually that quantity is independent of path.

So, whichever path we take, the cyclic integral will always be 0. So; that means, actually this quantity; that is why I am writing it as d U, not d cross U, because it is an exact differential now. And that we defined as the internal energy or the energy of the system and then you wrote the first law of thermodynamics as d U is d cross Q plus d cross W.

Now, using this value of d cross w which we already used like minus P external into d V, the first law can be rewritten as d U is d cross W minus P external or P opposing. Some textbook write it as a P opposing into d V, so this is basically the expression for the first law. Now the only thing which we did not discuss here is that we assume that the work done here is a kind of pressure following work. We only considered the P V type of work. We can also consider the non P V type of work which are important, particularly in a subsequent sections like, when you talk about electrochemistry and other things, but it can readily be introduced in the same way like. So, this expression is exact d U is equal to d cross W plus d cross Q and for d cross W we are actually replacing it by minus P external into d V.

Assuming that on the external work is, all the work is basically mechanical work, pressure volume work. Otherwise we have to use the original equation and just write it as in terms of pressure volume work and non pressure volume here, and sometimes we write it as d cross Q plus we write it as minus P external into d V; that is the pressure volume work plus d cross W, which is the non P V work.

So, that will also we can, we could have written the first law, and then from the first law what we further study, is that we want to further first study this state function which we got from the right away from the statement of the first law, that I have an a state function which is U, which is known as internal energy and we explained why it is called internal energy and that we can actually write in terms of volume and temperature. And then we can just expand a differential, it is just chain rule of, I mean partial differentiation, and then what you discover is that this d U the total differential of the internal energy can be written as the partial differential.

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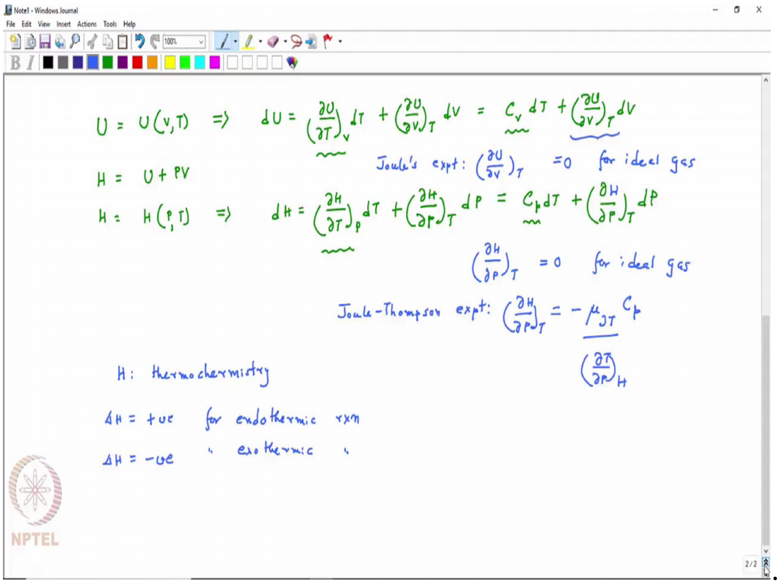

$$U = U(V,T) \Rightarrow dU = \underset{\sim}{\left(\frac{\partial U}{\partial T}\right)_V} dT + \left(\frac{\partial U}{\partial V}\right)_T dV = \underset{\sim}{C_V}\, dT + \underbrace{\left(\frac{\partial U}{\partial V}\right)_T} dV$$

Joule's expt: $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for ideal gas

$$H = U + PV$$

$$H = H(P,T) \Rightarrow dH = \underset{\sim}{\left(\frac{\partial H}{\partial T}\right)_P} dT + \left(\frac{\partial H}{\partial P}\right)_T dP = \underset{\sim}{C_P}\, dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$\left(\frac{\partial H}{\partial P}\right)_T = 0$ for ideal gas

Joule-Thompson expt: $\left(\frac{\partial H}{\partial P}\right)_T = -\underset{\left(\frac{\partial T}{\partial P}\right)_H}{\underline{\mu_{JT}}}\, C_P$

H: thermochermistry

$\Delta H = +ve$ for endothermic rxn

$\Delta H = -ve$ " exothermic "

So, this is just straightforward if we just do it and plus del U del V e d V and which we can further write it, this should be d T and then we can further write it as C v d T plus del U del V T d V. Now the C v is nothing, but the heat capacity at constant volume. Similarly we can also define another thermodynamic quantity which we said, named as enthalpy and which was defined as nothing, but U plus P V. And similarly we can write the H as a function of pressure and temperature and then we actually wrote the equation for d H and that was a del H del T P d T plus del h del P T d P. And again just like we showed that the C v is basically change in internal energy at a constant with respect to temperature at constant volume.

Now, C p is nothing, but the heat capacity at constant pressure and d H is nothing, but the heat withdrawn at constant pressure. So, by definition C p is nothing, but del H del T P and using that notion, we got similar equation. Now then we talked about the second term, which is this term; del U del T V, how do you calculate that and then we talked about an experiment which was known as Joule's experiment, where we talked about some adiabatic expansion and how Joule actually tried to measure this term, and he found that del U del V T d V is actually 0 and, but it is actually will be nonzero for a real gas.

So, we write it that for ideal gas it is 0. Similarly about the same token, this should be H. Similarly by the same token we can also say that for ideal gas del H del P T, that term is 0 for ideal gas, but for other gas there was an fantastic experiment which we discussed and that is known as Joule Thompson experiment, and Joule Thompson did this experiment to figure out what is the value of del H del P T for any gas. And if you remember final expression for the Joule Thompson coefficient was something like mu J T into Cp, where Cp is the heat capacity at constant pressure and mu J T was known as Joule Thomson coefficient which was identical to the temperature drop per unit pressure at constant enthalpy.

So, that basically gave us, and an equation to measure the quantity which is del H del P T. And next we, we actually then usually discuss about the properties of H or the enthalpy and then we talked about thermo chemistry, where we talk about the Hess Law of thermo chemistry. And we talked about how the heat change is associated with various reaction and we can, how we can actually talk about the enthalpy change. Basically enthalpy change will be nothing but the heat change at constant pressure.

So, most of the chemical reactions are also happen at constant pressure, so that is why enthalpy is a natural quantity to discuss about. And then we talked about the endothermic and exothermic reaction, where an endothermic reaction is defined as when heat is flown into the system. So, by definition for endothermic reaction delta H is positive for endothermic reaction.

And similarly if it is produced in the in the reaction and that we call as exothermic reaction, and if it is flown into the surrounding the, by convention we take the delta H to be negative. And then usually we switch to the second law of thermodynamics, and the connection for the first law and the second law when we discuss this thing, we again.

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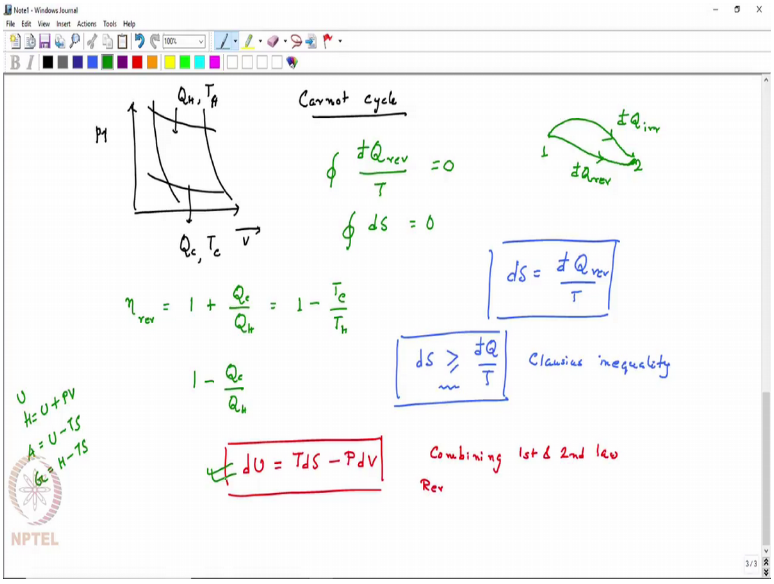

Carnot cycle

$$\oint \frac{đQ_{rev}}{T} = 0$$

$$\oint dS = 0$$

$$\boxed{dS = \frac{đQ_{rev}}{T}}$$

$$\eta_{rev} = 1 + \frac{Q_c}{Q_H} = 1 - \frac{T_c}{T_H}$$

$$1 - \frac{Q_c}{Q_H}$$

$$\boxed{dS \geq \frac{đQ}{T}}$$

Clausius inequality

U

$H = U + PV$

$A = U - TS$

$G = H - TS$

$$\boxed{dU = TdS - PdV}$$

Combining 1st & 2nd law

Rev

Usually all the textbook actually start with some conceptual cycle which was developed for a cyclic process, which was developed to understand the efficiencies of engines and that is known as Carnot cycle, which is developed by the or which is basically put forward by the French engineer Sadi Carnot, and he basically said if we have basically two isotherms which are connected by two Adiabats and if we consider a process like a cyclic process, wherein the when the isothermal change is happening, some amount of heat is withdrawn which is Q h at some temperature T h from a hot reservoir.

And then when I am having the isothermal compression, some amount of heat we see is released at temperature T c that Carnot ask this question what is the efficiency of this engine, and which is basically withdrawing some heat from a hot reservoir, releasing some less amount of heat to the cold reservoir, and basically converting the rest of the heat to the into work. And then there are many again this is a pressure volume diagram and, so this whole, these are basically two isotherms and two Adiabats all of you know this thing. And then when in order to understand the work done, which is produced in inter cyclic process.

We figured out that not only just like we did for the first law of thermodynamics that we figured out that the cyclic integral of this quantity that d cross Q plus d cross W is equal to 0. From the second law from the Carnot cycle we figured out that the cyclic integral of this quantity d cross Q reversible by T is 0 and that quantity we named as d S, where S is nothing, but entropy of the system which was defined as the reversible heat change at the constant temperature.

Now, this reversibility is very important. If I have some change of state from suppose the system is undergoing a change in state from state 1 to state 2 along some path. So, if the path does not follow a reversible path, then that heat change divided by temperature is not actually d S, but rather we have to always consider our reversible path, an equivalent reversible path and that heat change which is associated with the reversible path as opposed to the irreversible path, that heat change divided by temperature, will be the entropy, identical to the entropy of the system. So, that is just a definitional thing.

And then we talked about the efficiencies of the Carnot engine and for a reversible Carnot engine, because all these paths which I have drawn in the Carnot diagram, is basically our, each of them are reversible paths and we told that it is a nothing, but 1 plus Q c by Q h. Now when I write Q c it means that when I write, when I say suppose thirty calorie of heat is released into the surrounding, then automatically Qc will be negative, and so that is why some textbook actually write this expression as 1 minus Qc by Q h.

But the Qc inherently does not have any sign, it is just a magnitude and which is also in terms of the temperature, we could write it as 1 minus T c by T h. And since T c is always less than T h the efficiency of the Carnot engine will always be less than 1 or you can think that if I have the hot temperature, hot reservoir temperature to by in finite, I will be approaching to close, I mean approaching very close to the unit efficiency of the engine or the cold reservoir temperature is close to absolute 0 temperature that way also I can reach to the unit efficiency.

But in reality of course, the efficiencies are much lower, this is all for reversible engine. We usually talk about are the Carnot Theorem also which says that between two temperature limits. All reversible engines are equally efficient and the reversible engine actually is more efficient than an irreversible engine. So, these are the two theorems which are known as a Carnot theorem, and then we ask this question fine. So, d S are the change in entropy is basically defined as d cross Q reversible by T, but what is the relationship of d cross Q by T, if it is not an irreversible process or any general process, and then we talked about a very interesting thing which is known as Clausius inequality and which basically says that d S will be greater than or equal to d cross Q by T, it will be equal to d cross Q by T.

If the d cross Q is d cross Q reversible of the processes reversible, but if it is not, if it is an irreversible process then d S will be greater than d cross Q by T. We already derived the Clausius inequality in that course and then using that. Now we can actually using this fundamental relation which is again known as Clausius inequality, there as you can see that there is an inequality involved here.

So, using these Clausius inequality we can actually combine the first law and the second law and that basically, if you remember first law was d U is d cross Q plus d cross W and here we are writing d U is instead of d cross Q I can write T d S, if it is equal, if it is a reversible process. So, I can write it as d U is equal to T d S, and for any reversible process the external pressure. By reversible process again you mean that, we make the changes in such a way that the change in pressure always follows the state of the system itself.

So, P external is always P itself, the pressure of the system. So, we write it as d U is T d S minus P d V. So, that is one of the most fundamental equation in thermodynamics which is, which you get by combining the two laws, combining first and second law of thermodynamics, but this is again true for reversible process, not for irreversible process. And for an irreversible process all you will always get the heat change will be greater, the heat change by temperature, the d S will be greater than the heat change by temperature.

Now, from this relation which is only for the reversible process, then we can actually get many other processes, and there we apart from the enthalpy which was defined as U plus P V. We can also define many other state functions; for example, the Hell mouths free energy which was u minus T S and also the Gibbs free energy which is H minus T S. And then for and already we have the expression for internal energy, which is already for the first law. And then starting from this fundamental equation which is a d U is T d S minus P d V, we can actually derive many other interesting relation.

And all these relations actually lead to some interesting relationship between the differentials of the thermodynamic properties. For example, if I take this d U and first take the derivative with respect to say entropy, so keeping the volume constant.

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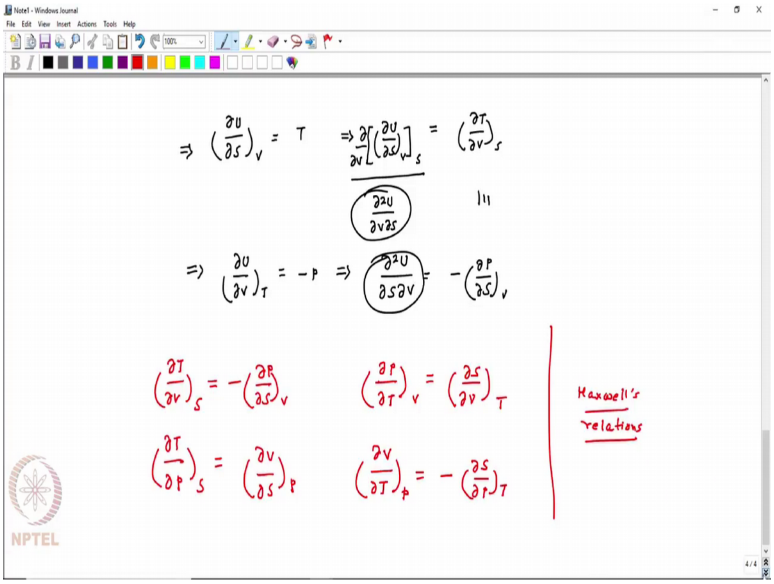

$$\Rightarrow \left(\frac{\partial U}{\partial S}\right)_V = T \quad \Rightarrow \underline{\frac{\partial}{\partial V}\left[\left(\frac{\partial U}{\partial S}\right)_V\right]_S} = \left(\frac{\partial T}{\partial V}\right)_S$$

$$\boxed{\frac{\partial^2 U}{\partial V \partial S}} \qquad \parallel$$

$$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = -P \quad \Rightarrow \boxed{\frac{\partial^2 U}{\partial S \partial V}} = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

Maxwell's relations

So, what I will have is, nothing but del U del S V that will be T and minus 0, because d V is 0, I am considering at constant volume process. And then in the second step we can do, we can take a derivative with respect to volume and then what I will have is del S del V, is nothing, but del T del V at constant entropy. And similarly, so in this case it is we can actually write it more explicitly what is del 2 del S del V. So, we first took the derivative with respect to S keeping V constant and then in the second step, we took the derivative of this quantity with respect to volume, keeping S constant and that is nothing, but del 2 U del V del S.

Similarly we could also, I mean use the starting from this fundamental equation, we could also first take temper the volume derivative, keeping the temperature constant and that if I do that that will give you minus P and then if I now again to the second derivative, but this time I am taking the entropy derivative as, in the later part and then what I will get is minus del P del S V.

Now, these two quantities are basically identical, because U is a state function and by the chain rule of differentiation, it does not depend on the order of differentiation for the state function. So, basically these two quantities are identical. So, what we establish, what we can establish very quickly, is basically the differential relationship between very nice relationship, let we just write it at the bottom.

So, we can actually get very interesting relationship; something like del T del V S is minus del P del S V, and this is one of the Maxwell’s equation which we got from this particular fundamental equation. Similarly just like we wrote d U is T d S minus P d V, we could also get another equation for d H, because we know that H is U plus PV.

So, I can write d H is d U plus P d V plus V d P, but d U is already T d S minus P d V and I have plus P d V plus V d P, so this P d V cancels. So, I will get it is basically T d S plus V d P and again from this equation which is d H is T d S plus V d P, which is another important equation. We can actually get another relation something like del T, it will be T and P as you can see del T del P, and in the first case I have to take S, this S to be constant and then it will be nothing, but del V and del S and P constant.

So, similarly for the other two like for using (Refer Time: 34:38) free energy and Gibbs free energy will also get similar equation, so it will be minus S d T plus V d P and all these things which you already studied, and I am only writing the differential forms which the four equations which you get, it will be del P del T V is nothing, but del S del V and it will be T or P V S T, and then we have del V del T P for the equation of our Gibbs free energy.

So, we will get minus del S del P T. So, all these four equations are known as Maxwell’s relations, and these are extremely important thermodynamic relations which we often use to derive many interesting thermodynamic properties. Now one thing we always want to keep in mind is that, these equations were developed for any general system. Now, moment you have, but you, in order to actually apply this equation, you sometimes need that equation of state you start from something and then you first focus on the process; like is it an irreversible process or it is an irreversible process. If it is a reversible process say for example, am I doing it in isothermal way or I am doing it in adiabatic oil.

So, all these things first come into picture and then we use the equation of state, how the transformations are happening and are we a can approximate if it is a gaseous system can approximate it as a ideal gas or you have to actually consider that deviations or the departures from ideal behavior, or can we actually use the van der Waals equation of state for our model system.

So, those things we will be important; that is number 1. Secondly, the conditions has to be applied in the sense that under what condition as I said is it adiabatic or is it isothermal all these things. Those things has to be first checked then, then we apply to the specific cases and then we basically try to solve the problems. And then also two more quantities that we particularly often use are defined as the coefficient of thermal expansion and compressibility that we usually write these two equations, these two expressions or these two physical quantities as alpha and beta. So, alpha is defined as the coefficient of thermal expansion.

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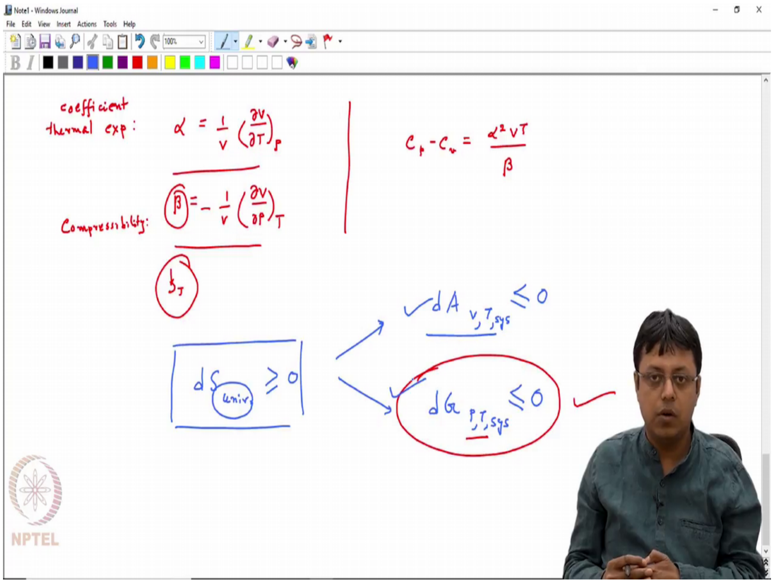

coefficient thermal exp: $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

Compressibility: $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

β_T

$C_P - C_V = \frac{\alpha^2 V T}{\beta}$

$dS_{univ} \geq 0$

$dA_{V,T,sys} \leq 0$

$dG_{P,T,sys} \leq 0$

Now, thermal expansion means as I increase the temperature how the volume is changing. So, it will be del V del T at constant pressure and it is per unit volume, because otherwise alpha will depend on volume, so that is the definition of alpha. Similarly beta is written as, I mean defined as the compressibility and. Compressibility means how much volume will change, if I apply the pressure. So, del V at a constant temperature and then per unit volume change, but del V del P is a negative quantity, because if I apply pressure any physical any matter will actually string, and that is why to keep the alpha beta a positive number we actually use a negative value in the a minus sign in the definition.

And then we from these actually you can calculate what is the difference between the heat capacity Cp minus Cv, which you can get for other, there are also other generalized expression. And from that you will get that it will be nothing, but alpha square V T by beta which also we kind of like formulated or we kind of derived its, its a very easy derivation.

So, you just have to find out first general relationship between Cp minus Cv and how do you get it. You already know that the Cp is coming from here and then the C v is coming from here. So, you can now, basically Cv is related to del U del T V d T, and Cp is related to del H del T P d T and there is a relation between U and H, because we know that h is U plus PV that you write and then you calculate what is the Cp minus Cv for those using that relation. And then you basically use these expressions or the definitions of coefficient of thermal expansion ah

So, this is thermal expansion or better to call it as a coefficient of thermal expansion, coefficient for thermal expansion, and then this one we call it as a compressibility. Some textbook actually write it or denote it as kappa T instead of beta, so the suffix T is basically constant temperature, but we will be using the beta notation here on them.

Now, the next thing what we study is, basically what are the directionality for a spontaneous process which is actually irreversible process, and then we say that all we can say from using the Clausius inequality is that the entropy of the system plus surrounding together which is the entropy of the universe, will be always greater than 0 for a spontaneous process and will be equal to 0 for a reversible process.

A reversible processes are mostly, not mostly they are indeed idealized process, all natural processes are spontaneous in nature and they are actually irreversible, and then we say that this is not an useful relationship. The reason being this equation is for the entropic change for the universe, but what you want is basically entropy change of the system, because we want to actually do some measurement on the system and see the effects on the surrounding.

So, you want some quantity which will be positive or negative and that quantity that positive or negative will give me the directionality of a spontaneous or non spontaneous process. So, then we say that, let us actually find some other quantities which, on which we can actually say that, not for the universe, but for the system, if we can actually trace this fundamental requirement that this universe must be greater than or equal to 0 for a spontaneous or reversible process.

Then can you actually get a useful relationship, which actually is a property of the system itself. And we figured out that yes there are two quantities; and one is the hemisphere energy, if we look at the hemisphere energy at constant volume and temperature, if that is less than or equal to 0. The less than 0 means it is a spontaneous process and equal to 0 means it is a reversible process and similarly if the changes are happening at constant pressure and temperature, then we can say the Gibbs free energy change is the correct quantity to look at and for chemist actually most of the chemical reactions happen at constant pressure and temperature and that is why this, we always talk about the changes in the Gibbs free energy.

And we have I mean transformations are mostly at the constant pressure and temperature, and then we look at the differential Isolus finite changes is the Gibbs free energy. And then we want to see whether how much Gibbs free energy is changing, and then we formulate many other I mean requirements or the conditions from this fundamental equation.

So, just keep in mind that sometime we say that the d g should be negative. Its not a correct statement, it is actually the dg for the system. So, it should write actually this is dg pt for the system that is negative, and not only that its not only the dg of the system, its taken at constant pressure and temperature.

If the process or the change happens at constant volume and temperature, then the Hellmouth free energy is the right thing to look at. So, from quantity which actually is the entropy change, but which has to be applied for the universe, you cannot talk about only the change in entropy of the system or the change in entropy of the surrounding. You have to think about the system and surrounding together and which is not an useful thing, because then you cannot observe, because you are also part of the universe, you only want to make changes in the system and see the effects in the surrounding. So, better useful quantities are basically hemisphere energy and Gibbs free energy and considering the chemical processes are happening mostly at under constant pressure and temperature, the Gibbs free energy is the automatic choice to look at.

Now we will in a next lecture we will see how we can actually focus on the changes in the Gibbs free energy, and then we can talk about many interesting properties or changes in the system, particularly how we can actually formulate the equilibrium constant and how can I catch; actually we can talk about the phase transitions.

So, those already we covered in the earlier lecture, earlier course on basic thermodynamics. So, you can always again go back to and watch the YouTube video lectures or you can actually refer to the textbooks which have been referred to you.

Thank you.