Introduction to Chemical Thermodynamics and Kinetics
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Lecture – 13
Spontaneity and equilibrium - part 1

So, in the last lecture, we discussed about entropy and we defined what is entropy, and we also showed how entropy changes happen for different processes. And we showed that in general for any the irreversible process the entropy change of the system must be greater than 0 and entropy change for the system and surrounding together or the entropy change of the universe also must be greater than 0. Now natural processes are irreversible process for example, let us just take the example of say growth of any animal or tree. So, we get born and then we get old and then we die. So, that is an irreversible process there is an arrow of time associated with it a old man never gets younger with time. So, there is a concept of directionality or time arrow of time of any irreversible process.

Now, we are going to consider this directionality and for any reversible process the system can actually go back to it is original state. So, we are going to consider first, what are the conditions for spontaneity of a process and what are the conditions for the processes at equilibrium, by processes at equilibrium we mean that; it is a reversible process because at equilibrium we know that reversibility has to be maintained that is the meaning of equilibrium and by spontaneity of the process. We mean that the process has to be irreversible there is a directionality that it goes from say in a particular direction.

For example, we know that water flows from high altitude to low altitude because of gravity or heat flows from a hot body to cold body because of differences in temperature those are called spontaneous processes. And if for a equilibrium system we are also going to discuss what are the conditions. So, the first thing first we can argue from our previous discussion is that we can relate everything to the changes in entropy of the system.

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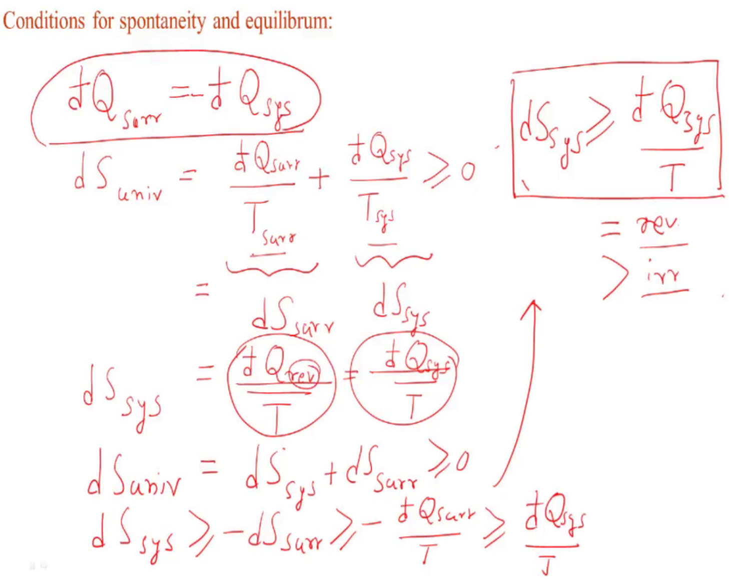

Conditions for spontaneity and equilibrum:

$$\text{đ}Q_{surr} = -\text{đ}Q_{sys}$$

$$dS_{univ} = \underbrace{\frac{\text{đ}Q_{surr}}{T_{surr}}}_{dS_{surr}} + \underbrace{\frac{\text{đ}Q_{sys}}{T_{sys}}}_{dS_{sys}} \geq 0 \qquad \boxed{dS_{sys} \geq \frac{\text{đ}Q_{sys}}{T}} \quad \begin{matrix} = rev \\ > irr \end{matrix}$$

$$dS_{sys} = \frac{\text{đ}Q_{rev}}{T} = \frac{\text{đ}Q_{sys}}{T}$$

$$dS_{univ} = dS_{sys} + dS_{surr} \geq 0$$

$$dS_{sys} \geq -dS_{surr} \geq -\frac{\text{đ}Q_{surr}}{T} \geq \frac{\text{đ}Q_{sys}}{T}$$

Which means that we already discussed that the heat change for any reversible process, associated with the surrounding will be heat change associated with the system.

So, the dS universe which is the d cross Q surrounding divided by temperature of the surrounding plus d cross Q system divided by the temperature of the system, which has to be greater than equal to 0. If it is 0 we know that it is a reversible process and it will be 0 only when you can see here that if I make it 0 the condition is T surrounding must be equal to T system; which means it is also isothermal. Now for any irreversible process which we naturally adiabate. So, we have a condition that dS universe is greater than 0, and we can easily argue that this dS universe is nothing but this part is coming from dS of surrounding and this part is coming from the dS of the system, but for any process the dS of the system then if this condition has to be valid. DS of the system can be equal to d cross Q reversible it is defined as d cross Q reversible by t, but which can be equivalent to the d cross Q system of divided by T if the processes because this is the definition remember; however, it is not always true that these only for reversible changes the heat changes are equal, but for irreversible change we know that the dS of the system must be greater than equal to the dS of the surrounding. This follows let us just use this equation first we can easily then understand how we arrive at the condition for spontaneity.

So, we just discussed that dS universe which is nothing but dS system plus dS surrounding is greater than equal to 0. Which follows that dS system must be greater than equal to minus dS surrounding, but we know that dS surrounding is nothing but d cross Q surrounding by t. Which is minus d cross Q surrounding by t. And then we also know that there should be a negative sign here because the heat withdrawn from the surrounding is heat gained in the surrounding. So, which is greater than equal to d cross Q system divided by t. So, from here we can just rewrite the condition for spontaneity is that we have or we can write it just like we discussed dS of the system is greater than equal to d cross Q system divided by t.

Now, this holds for any reversible as well as irreversible process this is not only the reversible process this heat change because that by from first law we know that the heat changes must be equal. So, we get a very interesting relationship. So, the equality if it is equal it is a greater than equal to you can see it is will be a reversible process. If it is greater than it will be an irreversible process. So, these 2 are the conditions for spontaneity and equilibrium. So, what we just showed is that the entropy of the system which is defined as the reversible heat change at constant temperature, which again is can be equated to the heat change associated with the process, but that heat change may be identical to the reversible heat change if the path is reversible; which means the process is I n reversible process; however, if it the path is irreversible then the associated heat change will always be greater or less than the reversible heat change and then you can show that the dS system will always be greater than or equal to d cross Q system by d.

Now, we will use this condition to understand what are the conditions for spontaneity, and what are the conditions for equilibrium. Now we can right away use the first law of thermodynamics to get relation between these condition of spontaneity and equilibrium and the internal energy.

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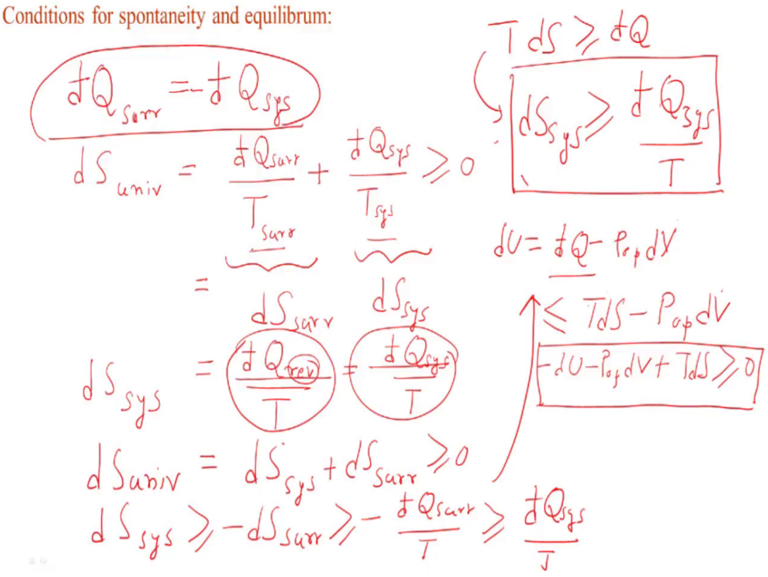

Conditions for spontaneity and equilibrum:

$$\boxed{\text{đ}Q_{surr} = -\text{đ}Q_{sys}}$$

$$dS_{univ} = \underbrace{\frac{\text{đ}Q_{surr}}{T_{surr}}}_{dS_{surr}} + \underbrace{\frac{\text{đ}Q_{sys}}{T_{sys}}}_{dS_{sys}} \geq 0$$

$$dS_{sys} = \frac{\text{đ}Q_{rev}}{T} \neq \frac{\text{đ}Q_{sys}}{T}$$

$$dS_{univ} = dS_{sys} + dS_{surr} \geq 0$$

$$dS_{sys} \geq -dS_{surr} \geq -\frac{\text{đ}Q_{surr}}{T} \geq \frac{\text{đ}Q_{sys}}{T}$$

$$TdS \geq \text{đ}Q$$

$$\boxed{dS_{sys} \geq \frac{\text{đ}Q_{sys}}{T}}$$

$$dU = \text{đ}Q - P_{op}dV$$

$$\leq TdS - P_{op}dV$$

$$\boxed{-dU - P_{op}dV + TdS \geq 0}$$

Now, for that we just write dU from the first law is nothing but d cross Q minus P opposing into dV now all we have to do is to get the equation for the entropy or you can see that since dQ is nothing but if the process is reversible instead of dQ we can write as TdS or where actually TdS is nothing but the entropy of the so, the this is we can we could have written it as TdS is greater than equal to P cross Q and we are dropping the notation sys or system because it is obvious that we are only dealing with the systems notation. So, we could write that since TdS is greater than equal to dQ. So, this dQ. So, this dU will be less than equal to TdS minus P opposing into dp or we could write that if we just rearrange this term that minus dU minus P opposing into dV plus TdS that is greater than equal to 0.

So, this is the condition for spontaneity and equilibrium together if it is 0 it is spontaneous if it is greater than 0 it is sorry if it is 0 it is at equilibrium and if it is greater than 0 it is a spontaneous process. Now the question is of course, we got a relationship for the spontaneity and equilibrium now we will move on and discuss the conditions for equilibrium we just said that

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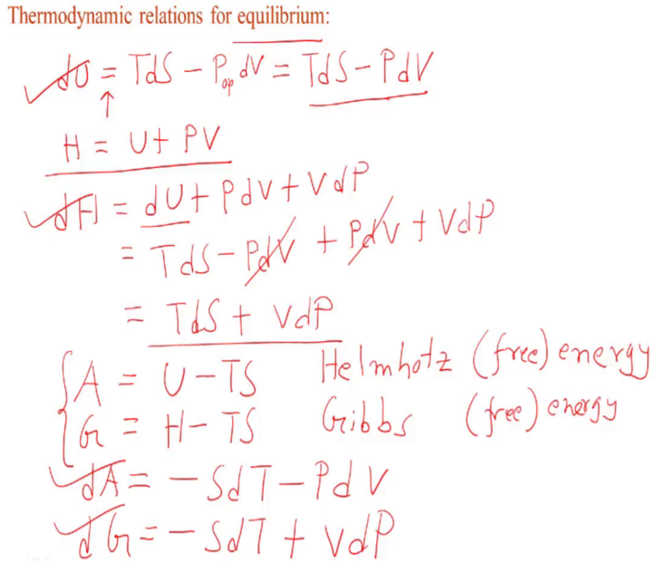

Thermodynamic relations for equilibrium:

$$dU \underset{\uparrow}{=} TdS - P_{op}dV = TdS - PdV$$

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

$$= TdS - \cancel{PdV} + \cancel{PdV} + VdP$$

$$= TdS + VdP$$

$$A = U - TS$$ Helmholtz (free) energy

$$G = H - TS$$ Gibbs (free) energy

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

we can write the first law, instead of writing as dU is d cross Q. We write it as TdS and this equality sign holds only for equilibrium remember minus P opposing into dV.

So, this is and if it is an equilibrium also remember that the opposing pressure will be nothing but equal to the pressure of the system because equilibrium means reversibility is maintained. So, dU is TdS minus PdV and that will be our first equation to start with now we will use the other definitions of say for example, enthalpy and will also define some new energy terms today and then we will see how the differential relations look like. So, we know that H is U plus PV. So, you can write dH is equal to dU plus we are just following the chain rule PdV plus plus pdp and then for dU we can write TdS minus PdV this is the value of dU plus PdV plus VdP and then this PdV cancels then we get dH is nothing but TdS plus PdV.

So, similarly we can define 2 new quantities we call it as A which is U minus TS just like we defined H as U plus PV and this a is called Helmholtz energy or sometimes called Helmholtz free energy. And similarly, another quantity which we will call as G which is nothing but H minus TS and is known as Gibbs free energy. So, this if we use these 2 relations and just try to understand what is the differential for da it is again will be a change rule chain rule for example, dA will be dU minus TdS minus SdT and we can easily show that it is nothing but minus SdT minus PdV and similarly dG is nothing but minus SdT plus VdP.

Now, we have 4 equations one is for dU which is TdS minus PdV. One is for dH which is TdS plus pdp, one is for dA which is SdT minus PdV, and the 4th one is for dG which is minus

SdT plus VdP now we will move on and see how one can use these relations very cleverly to build many differential relationships between different thermodynamic quantities. Now what we mean by that is suppose we have some function Z which

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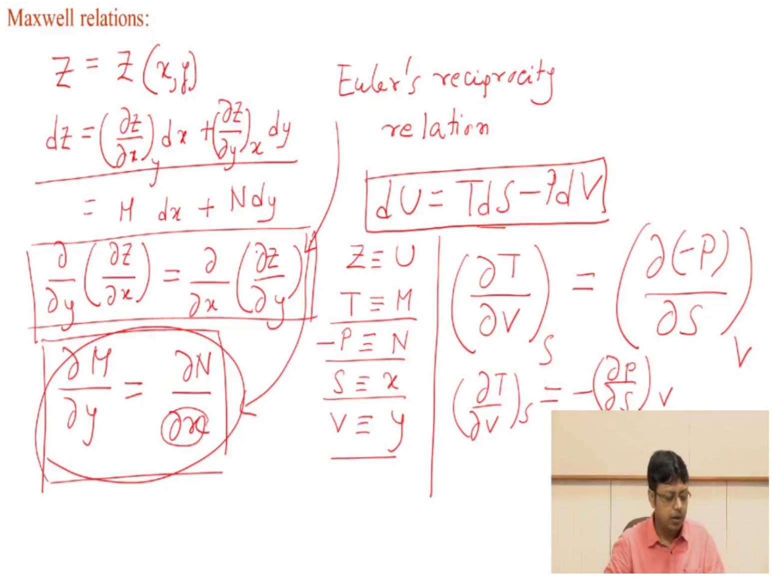

Maxwell relations:

Suppose we can write it as a function of x and y. So, the total derivative we discussed is earlier can be written as a partial derivative with respect to x keeping the y constant plus partial derivative with respect to y, keeping x constant and we can write it suppose as Mydx plus or we just write it as M we drop the notation y plus Ndy.

So, m is nothing but the partial derivative with respect to Z and n is nothing but the partial derivative to x and n is nothing but the partial derivative with respect to y. Then if we further take the differential of Z we know that due to the reciprocity relation we can write that the order of the differentiation does not matter this is known as the Euler's reciprocity relation, and due to this reciprocity relation, we can write that del M because del Z del x was nothing but M del M del y is nothing but del N del x

So, let us now use this or use this Euler's reciprocity relation to this is actually known as Euler reciprocity relation and which comes from the notion that the order of differentiation does not matter. So, we can now use the relation say for dU which was TdS minus PdV, now we can actually make a connection that here U is here our Z is nothing but u and T is just follow this equation, T is nothing but m and P is nothing but N. So, it is associated with dS you can see mdx. So, x is nothing but x and V is nothing but y, I was using small x and small y. So, I will just use that same notation.

So, we can now use this reciprocity relation which is del N del y will be del n del x and that right away tells us that del S you can just follow from here, we have del M delta y M is T. So, it is del M which is del T and del y y is V del T del V will be equal to and when we did this differentiation we kept x constant. So, it is at constant entropy which is equal to N. N is nothing but P here, but in this case it is not P it this it should be minus P because there is a minus sign it will be del of minus P with respect to x x is nothing but S, when we get the V constant or we can just rearrange a little bit which is del T del V S is nothing but minus del P del S.

So, this kind of relations are basically writing helps us to write a formulate a differential relation between various thermodynamic quantities and these differential relations are known as Maxwell relations, now we have just used only one equation which is dU equal to TdS minus PdV, we could use or we could apply the same general process for other differentiation to get other Maxwell relations let us just calculate one more we already discussed that

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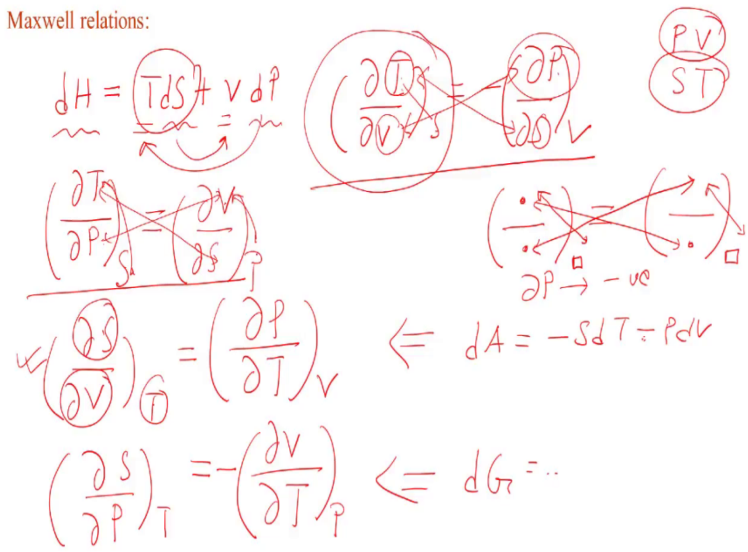

The equation for dh will be nothing but dh was TdS plus VdP.

So, in this case a easy way to remember is that we will take the partial derivative again with respect to P and with respect to x. So, if we take the percent derivative with respect to say S because the differentials are here dS and dP. So, what we will get is del T and then del P. We are taking this quantities partial derivative with respect to this differential. Del P keeping S constant will be equal to del V, now this quantity taking the partial derivative with respect to S del S keeping P constant. Similarly, will have del S del VT which will be which we can use for the third relation which was basically dA is minus SdT minus PdV that will give us a relation for this we are coming back how to get the relation and from the equation of dG. We can equivalently dG was minus SdT plus VdP we can equivalently get a relation for del S del PT.

Now, from the first relation which was dU equal to TdS minus PdV. We already showed that del T del VS is nothing but minus del P del S V. Now how do you judGe that what are the relations how do you remember it now look at it that I am asking suppose what is del V del T del V S or partial derivative of temperature keeping the entropy constant, now what are our energy terms? We know that PV is an energy term because it is a pressure volume work is equivalent to energy.

Similarly, ST is also an energy term, because if you remember we wrote that de is TdS or dH is TdS. So, st must have an dimension of energy and you already know that S is the dimension of heat divided by temperature multiplied by temperature will be dimension of heat which is a form of energy. So, just keep that in mind how the energy terms are coming. So, here look at here like I have ST here and then on the right-hand side I will just use to memorize it I will just use this mnemonic to keep that in mind that I have del T here I have del S here. So, these are STR energy term.

So, if I have P here I should have P here. That is one thing and then I am keeping S T. So, that is the energy term. So, I have to keep the V here as constant let us take the second example here I have T and S which are energy terms and here I should then have a V here P and V and then T S. So, then P P only thing you have to keep in mind wherever I have a del P either in the numerator or denominator I will have a negative sign. So, the way to remember is something like this I have relation like this, and then if it is S here it will be T here or if it is P it will be V here something like that.

Similarly, I will just look for the energy terms and also this constant term here will have a relation with this term keeping in mind that I will have only PV term, PV like term or ST like term and the second thing is that anything if del P is there should be negative. Now let us using this rule or using this this strict try to get what we will should get for the del S del VT now since it is del S. So, it should be del T here since it is del V it should be del P here and since it is T, where S T is the energy term I should have V here. Similarly, here it is del S. So, I will have del T here it is del P I will del V here and then it is st I will have P here PV, but since it is a derivative with respect to pressure I will have a negative sign.

So, this is easy way to memorize all these relations which are in general known as Maxwell's relation. So, we have 4 Maxwell's solution one is the first one del T del V S is del P del S V then the second one del T del P S is del V del S P and so on. So, we have basically 4 Maxwell's relation now we are going to use this Maxwell's relation to figure out how we can write some other relations from this very interesting relations which are known as Maxwell's relations.

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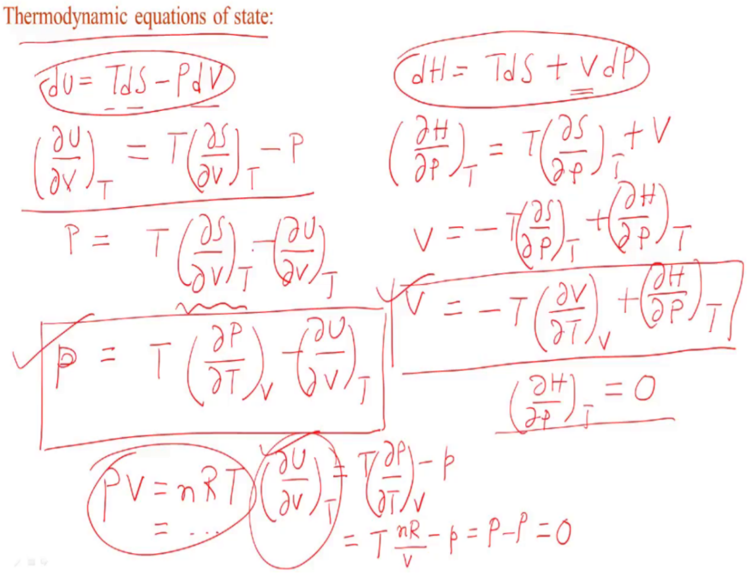

Thermodynamic equations of state:

$$dU = TdS - PdV$$

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

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

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

$$PV = nRT$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T\frac{nR}{V} - P = P - P = 0$$

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

$$V = -T\left(\frac{\partial S}{\partial P}\right)_T + \left(\frac{\partial H}{\partial P}\right)_T$$

$$V = -T\left(\frac{\partial V}{\partial T}\right)_V + \left(\frac{\partial H}{\partial P}\right)_T$$

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

Now, let us first write the first equation which is dU is TdS minus PdV. Again, remember that we are using the equal sign keeping in mind that equality means the system is at equilibrium.

If it is spontaneous we have to write it that fundamental condition that minus dU minus PdV plus TdS must be greater than 0. We are only considering systems at equilibrium not for any spontaneous process. So, that is why you are using the equality sign. Now we already said let us just take a derivative with respect to volume if we do that we can get a equation for pressure. So, which means if we take the derivative with respect to volume keeping the temperature constant we have to keep the temperature constant, because on unless we keep the temperature constant if we take the volume derivative the line have 2 terms here, one are the derivative with respect to volume and then again derivative with respect to temperature that is what we are not doing. So, we will have the temperature constant and del S del V T remember it is a differential with respect to volume and then I have minus P.

So, we get a very interesting relation which basically tells us how the pressure can be expressed. So, it is nothing but T del S del V T minus del U del V T. Now we can now use Maxwell relation to instead of writing it in terms of entropy we can write it the other way it is del S remember. So, I will have a del T here and it is del V here in the numerator. So, alpha del P here and since it was TST combination. So, I will have PV combination minus del U del VT. So, that is a new expression for pressure and these equations are such equations are known as thermodynamic equations of state.

So, we are actually not writing this PV equal to nRT at the ideal gas equation or something like a Van der waals gas equation which we discussed, but this is a independent of the system and we wrote the pressure, as in terms of partial derivatives of pressure temperature volume internal energy and some other quantities which we can measure. So, this is a new way of writing the equation of state for any arbitrary system. We can actually apply it to ideal gas we can also apply it for real gases. Now let us see if we had proceeded with the other equation for dH which is TdS plus VdP.

So, as before if we take a derivative with respect to pressure I may get I will get a expression from following. So, let us calculate it del H del P keeping the temperature constant. So, I will have T del S del P T plus V. So, volume is nothing but what we get here is minus T del S del P T plus del H del V T now again we can use Maxwell's solution minus T into del s. So, we will have del T here because it is a Sd term and we had dP in del P in the denominator. So, you should have del V here and in since it has st it will pv combination plus I have del H del P T.

So, this is another thermodynamic equation of state that we just discussed. Now we know that del u del V T for ideal gas should be equal to 0. We can actually quickly check we can use the pv equal to nrt relation here. So, if we use it what we get is del u del V T. So, this quantity we are measuring is nothing but T into basically we are using this equation or the second equation T into del P del T P minus P, now what is T into del P del T V? So, we have to write pressure in terms of temperature which will be nrt divided by V. So, if I take the derivative of energy divided by V keeping the following constant it will be nothing but NR divided by V minus V. So, that is nothing but P minus P which is 0. So, which we already know that del U del V T is 0 for any ideal gas.

So, this equation or this equation is a general equation, similarly you can also test for ideal gas you will find that del H del PT is 0 and remember these 2 are some interesting quantities which we discussed that del U del VT was 0 for ideal gas and it was measured by joule in joules experiment although later on people found that actually it is non 0, because if you are doing an experiment of course, you are working with real gases for ideal gas it is 0, but it for real gas it will be nonzero and if you do a enough refined experiment where the sensitivity of the experiment is good enough that you can detect the change then you will find that del U del V T will be nonzero.

Similarly, the del H del PT remember was measured in joule Thomson effect and joule Thomson experiment and where they found that del H del PT can be connected to the drop-in temperature with respect to pressure and that they termed as joule Thomson coefficient and from that you can calculate the del H del PT. Now we will proceed on this discussion and where on based on the discussion where we will be using this relationship of pressure and volume on the thermodynamic relations, and then we will use it to calculate other thermodynamic quantities something like say Cp minus Cv now Cp minus Cv we have already discussed for ideal gas, but what happens for say exam for example, if you ask this question what is Cp minus Cv for a solid. Then we cannot use an ideal gas equation to begin with and then we have to use a general equation for that we will use similar relationships because all these fundamental relations like dU equal to TdS minus PdV or dH equal to TdS plus VdP.

These are just fundamental equations we do not make any approximation or any assumption here, always said that these are fundamental relations coming from the concept of entropy and the concept of spontaneity and equilibrium we are only considering the equilibrium process because it is a equation of state, and equation of state means it will only describe the properties of the state this equations will describe the properties of the state which means the system must be in equilibrium. Thermal equilibrium as well as material equilibrium and then the equality signs holds, otherwise there will be an greater than or less than sign which we can always derive from the fundamental condition which we just discussed that d U minus d U minus PdV plus TdS will be greater than equal to 0.

Now, suppose we are dealing with a piece of metal which is a solid and for that solid or gas we can actually define some other quantities say for which we can measure experimentally. So, one of these quantities is known as coefficient of thermal expansion.

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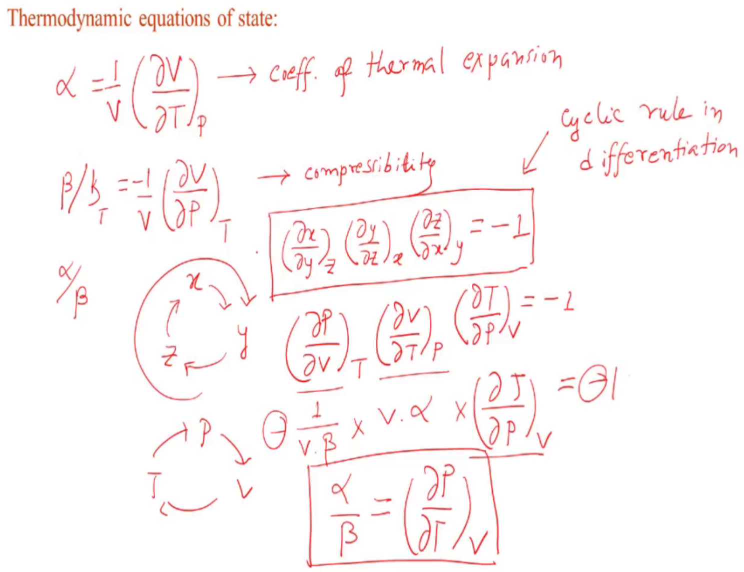

Thermodynamic equations of state:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \rightarrow \text{coeff. of thermal expansion}$$

$$\beta / \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \rightarrow \text{compressibility}$$

cyclic rule in differentiation

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1}$$

$$\alpha / \beta$$

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$$

$$-\frac{1}{V.\beta} \times V.\alpha \times \left(\frac{\partial T}{\partial P}\right)_V = -1$$

$$\boxed{\frac{\alpha}{\beta} = \left(\frac{\partial P}{\partial T}\right)_V}$$

Which usually is denoted as alpha. So, alpha is defined as coefficient of thermal expansion. Remember what is thermal expansion as the name suggests. So, it is if I increase the temperature how the material expands. So, keeping the pressure constant I will measure the change in volume with respect to temperature.

So, this is nothing but coefficient of thermal expansion. And similarly, the other quantity which sometimes people write as beta or sometimes people write is kappa or sometimes they also write it as kappa suffix T which is known as compressibility. Now as the name suggest that compressibility. So, it is basically tells how much you can get a compression for say a piece of metal or a gas. So, compression means you have to apply pressure and see that change in volume. So, it is nothing but derivative of volume with respect to pressure, but you have to define it per unit volume otherwise you have a problem.

So, we always define it as 1 over V keeping the temperature constant now if you increase the pressure you know that the volume will also decrease. So, in order to make the parameter constant we use a negative sign in the definition. So, that the beta or the kappa becomes positive. Now let us see what is the value of say for example, alpha by beta because that will be useful for our subsequent purpose. Now in order to do that you see that we have used all these parameters pressure volume and temperature and we can use the cyclic rule for differentiation if we have say 3 parameters,

Well let me write it as the xyzy, x, y and z. Where x can be written as a function of y and z, similarly y can be written as a function of and x, and similarly for z which is the case here because I can write the pressure in terms of volume temperature of volume in terms of pressure and temperature and so on. So, then if I follow a chain of differentiation in a cyclic order by cyclic order I mean; I have to maintain a order like if I take the derivative of x with respect to y keeping z fixed. So, it is xyz the next one will be y z, keeping x fixed and the third one is z x and keeping y fix. So, we have to always maintain this order xyz or yzc or zxy we cannot write xzy. So, that this is a reversal of order. So, then it will be minus 1. So, this is known as the cyclic rule in differentiation.

So, using this cyclic rule if we take the instead of xyz as pressure volume temperature we can easily get a very nice relation. So, I have del P del V, say I am writing say pressure to volume to temperature this cycle I am maintaining. So, then the next term will be volume then temperature keeping pressure constant the third differential will be temperature pressure and volume that should be equal to minus 1.

Now, we have to connect it to alpha and beta now remember what is alpha? In the definition of alpha there will be also one of our volume because the volume you will have to define it per unit volume, otherwise if it will be dependent on the volume of the gas or the substance itself. So, we are dividing it per unit volume in in that to maintain that per unit volume we are dividing it by volume. So, alpha is del V del T P. So, this quantity is nothing but V into alpha. Similarly, beta is del V del P T now this is nothing but 1 over we can write it as 1 over del P del V T.

So, this is nothing over nothing but 1 over there is a V missing similarly. So, we will write it as V into beta, with a negative sign and times this del T del P V that is equal to minus 1. So, what we get this volume actually gets cancelled this minus 1 here will gets cancelled here. So, all we get is alpha by beta is nothing but if I take this on the other side it will be nothing but del P del T V. So, you got a very nice relation between alpha and beta where alpha is the coefficient of thermal expansion and beta is the compressibility which are measurable quantities and we can measure the thermal expansion and compressibility for even solids also not only for gas, but of course, for solids the value will be very less the compressibility value, but still we can get some value.

Now, we will be using this relation to get the relationship between Cp minus Cv now before that if you remember.

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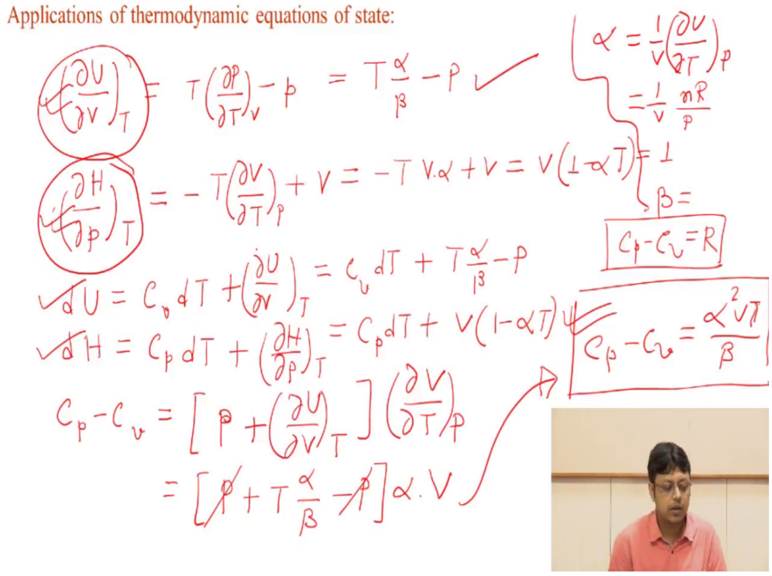

Applications of thermodynamic equations of state:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T\frac{\alpha}{\beta} - P \quad ✓$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V = -TV.\alpha + V = V(1-\alpha T) = 1$$

$$✓\, dU = C_v\, dT + \left(\frac{\partial U}{\partial V}\right)_T = C_v\, dT + T\frac{\alpha}{\beta} - P$$

$$✓\, dH = C_p\, dT + \left(\frac{\partial H}{\partial P}\right)_T = C_p\, dT + V(1-\alpha T)$$

$$C_p - C_v = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$= \left[\cancel{P} + T\frac{\alpha}{\beta} - \cancel{P}\right]\alpha.V$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\frac{nR}{P}$$

$$\beta =$$

$$\boxed{C_p - C_v = R}$$

$$\boxed{C_p - C_v = \frac{\alpha^2 VT}{\beta}}$$

So, when we are discussing the Cp minus Cv relation or usually for any many other problems also we always calculate these 2 quantities which we discussed many times one is del U del V T now already we saw that del U del V T is nothing but P if we take the del U del V T it will be minus P. So, we can use the original notation which we have been using. So, it is T into del P del T V minus P and similarly we will also notice that del H del P T is nothing but we had minus T into del V del T P and there will be a plus volume and there is a minus sign yes.

So, if you just go back we just defined the compressibility alpha divided by beta as del P delta V. So, this del P delta V is nothing but alpha by beta minus P, similarly for del H del PT we have I will have here a volume term and then there is a minus T. Now del V del T P by definition is V times alpha because alpha is the coefficient of thermal expansion this is also thermal expansion you can see, but alpha had it is fine as per unit volume. So, there was a divided by volume and plus V so we can just organize it a little bit. So, we can take the V common and it will be 1 minus alpha T.

So, thus we see that we get a very beautiful relation for delta alpha T and del H del PT which are 0 for ideal gas, but nonzero for any other system in a real system it will have a volume, but when you are writing the value in terms of alpha and beta which are measurable quantities. Now the next thing let us try to do is we can actually write dU from the first law as CpdT plus del U del VT because I am just exploring right now where we can utilize these 2 relation.

So, d U can be now written as very nicely that instead of del U del V T we could use the relation right away which is T into alpha by beta minus P, similarly for the relation for enthalpy th we could write sorry for dU it will be Cv it is Cv is associated to will dU and dH is always associated with Cp and then the next term is del H del PT which was discussed many times, and then we can use the second equation for del H del PT. So, it will be CpdT plus P into 1 minus alpha T. So, we basically got 2 new expression for dU and dH.

Now, what about Cp minus Cv now Cp minus Cv we discussed earlier when we discuss that joule terms on effect and there we got a relation like it will be P plus del U del VT times it was del V del T P. Now what is del U del V T we just discovered it is this equation it is T into alpha by beta minus P and what is del V del T P? Del V del T P is nothing but related to thermal expansion. So, it will be alpha times V we can just simplify this. So, the P is get cancelled. So, I will have one alpha and there is one alpha. So, it will be alpha square V times T minus beta. So, what we get is Cp minus Cv is alpha square V T divided by beta.

So, this is a general relation now you can always go back and check with your ideal gas equation you have to get a value of alpha from ideal gas equation for example, alpha is nothing but one of our V is a coefficient of expansion. So, it is del V del T P. Now can if I use the ideal gas equation pv equal to nRT. So, P will be nothing but nrt divided by P. So, the derivative will be nR divided by V. So, we can write it down here 1 over. So, it is n R nRT by V nrt by P sorry and then I will have P here. So, then what I get is PV and numerator is nR. So, that is 1.

Similarly, beta will you can easily discover will also be 1. So, alpha and beta will be actually equal to 1 excuse me and since it is actually alpha square you can see here that we will have one extra V term that will also cancel and let us try to try at home this is you can try at home that just get the alpha value first and get the beta value, and then explore what is the Cp minus Cv value and for ideal gas you should get the Cp minus Cv equal to R, but the point here is that this equation is a very, very general equation and you can use it for any other system as well.

Now, let us summarize what we discussed so far. We discussed the condition for spontaneity and equilibrium and remember that we had the everything is coming from the second law of thermodynamics, where we discussed that dS of the universe must be greater than equal to 0 if it is an reversible process the system is at equilibrium it is equal to 0 if it is greater than 0 then it is a spontaneous process and then we ultimately ask this question, how the entropy of the system changes for a reverse as on a spontaneous process or a reversible process spontaneous processes are by definition irreversible process.

Then we got our relationship writing the dS as equal to dQ by T if it is reversible, but it will be always greater than dQ by T if it is irreversible if the dq is irreversible. Then we can actually plug in into the first law and then get equation for dU which we wrote at TdS plus PdV and then we also TdS minus PdV and then we also used the same relation to build up other relations for example, that what will be the differential d H and we also defined 2 new thermodynamic quantities a which is the Helmholtz energy defined as U minus TS and G which is the Gibbs free energy which is the G minus H minus ts and we got a relation for dA and dG also.

Then we just use the method of differentiation partial derivatives and to get some differential notation or relations between several thermodynamic quantities. Which is pressure temperature volume entropy etcetera and all these relations are known as Maxwell's relations and we discussed a trick how to remember these Maxwell relations and we use those Maxwell's relation to get a new expression for pressure and volume in terms of thermodynamic quantities. Which we called as thermodynamic equation of state, which is a independent of the system you can plug in your ideal gas equation you can use your real gas equation and check what are the values.

And then we moved on and we discussed what are the fellows of del U del V T, which we often discuss and what is the value of del H del PT for any thermodynamic system in terms of the coefficient of thermal expansion and compressibility, and then we build up then we got very nice interesting relations and then we got a new expression for Cp minus Cv which is alpha squared VT by beta and we will use these relations in future to solve problems. Now as a homework problem what you can try instead of using the ideal gas equation you use the real gas equation you take the Van der waals equation of state. You plug in and you see how these fellows look like del u del V T del H del PT because everything is provided here. So, all you have to do is to plug in the federals equation and check how the Cp minus Cv is what expression you get for Cp minus Cv for an van der waals equation.

Now, in the in the next lecture we will discuss we will start from this and we will build on the discussion based on the free energies mostly, because we will see that what are the so far we are only discussing the conditions first continuity conditions for equilibrium where the system is under equilibrium now we will see what are the conditions for the spontaneity, how we can connect it to the differentials like dU or dH or dG or dA and which one will be most useful. We will see the change in Gibbs free energy which is a dG will be most useful because of some reasons we will see that this condition of equilibrium or spontaneity imposes that the pressure and temperature must be constant during the change. If we make a change in the Gibbs free energy and usually in for any chemical reaction chemist also keep the pressure and temperature constant during the change of transformation. So, the natural choice is to choose Grips free energy we will discuss it in the next class.

Thank you.