Chemical Principles II
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Thermodynamics Free Energy

Okay, so we have finished till now a first law of thermodynamics, second law of thermodynamics both from classical and statistical approaches and we have seen that for spontaneous process for an isolated system entropy always increases, so which means that either we consider something like an universe, beyond which nothing is there and energy is conserved within that and all processes within that universe will be spontaneous because and entropy will increase or we consider whatever the system, it is for example a glass of water in a bottle of water we take into account of the surrounding as well and then together the entropy of the system and surrounding has to increase for spontaneous process.

Now let say if you did not want to look into the surrounding at all, let say we want to only look into the system and try to identify the process will be spontaneous or not, in that case we rely only on the entropy of the system because we are see many times, especially for let say transfer of heat from you know one part to another part that entropy decreases for subsystem and then entropy of the other subsystem increases and together the entropy increases.

So therefore if you look into only the system then entropy is not the criteria to talk about spontaneous processes, so there are new things called free energies which you may be already familiar with are introduce in order to see whether the process is spontaneous or not, and we will get into that today, so today we are going to look into ways of only looking into the system and then find out whether the process is spontaneous or not, so for that will introduce something called fundamental equation of thermodynamics and also we combine the first law and second law and introduce new properties, new calculation, new properties, new thermodynamic potentials.

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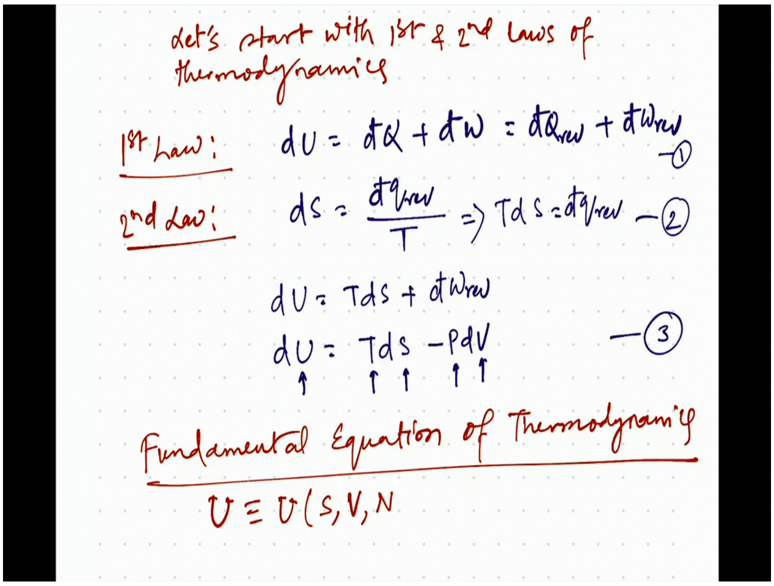

Let's start with 1st & 2nd Laws of thermodynamics

1st Law: $dU = đQ + đW = đQ_{rev} + đW_{rev}$ — ①

2nd Law: $dS = \frac{đq_{rev}}{T} \Rightarrow TdS = đq_{rev}$ — ②

$$dU = TdS + đW_{rev}$$

$$\underset{\uparrow}{dU} = \underset{\uparrow}{T}\underset{\uparrow}{dS} - \underset{\uparrow}{P}\underset{\uparrow}{dV} \quad — ③$$

Fundamental Equation of Thermodynamics

$U \equiv U(S, V, N$

So let us start with what you already know, so let start with first and second law of thermodynamics, so what is the first law? So first law says that DU is equal to DQ plus DW, so you know that this cut here denotes the process is part depend, whereas DU is straight depend property and you also know that the process can be reversible, irreversible does not matter D will remain the same, so we can write for a reversible process as DQ reversible and DW reversible.

What the second law says? Second law says that DS is DQ reversible by T, T is the temperature of the system and DQ reversible, is the reversible change in the heat, remember that often we have found out that DQ is 0 but DQ reversible is not 0 for some systems in isolated case, for example, we talked about the free expansion inside an isolated system and what we saw there is that since the system was kind of isolated, no our system was isolated, there was no change in the heat.

So DQ was 0, yet we found the entropy was increasing because DQ reversible was not 0 and that DQ reversible essentially means that if you take the process in a reversible manner then it will be not be 0 or you can think of in a different way that although the DQ was 0 but the surrounding entropy was not 0, so, but since we are talking about an isolated system, we are not talking about a surrounding entropy that time because there was no heat released to the environment, so therefore we always have to construct an equivalent description, equivalent path going from part of the system to the full part or the system for the free expansion and there found that for a reversible process that DQ will not be 0.

So entropy, whenever you want to calculate we have to always calculate with DQ reversible and not with DQ, so that is an important point, now combining these two above equations, equation 1 and equation 2 what we get is that DU or okay, from here we can get TDS is equal to reversible, so now combining the 2 equations we get DU equal to TDS plus DW reversible and we know that TDS is nothing but PDV, so DU equal to TDS minus PDV.

So here you see that UTSPV are all state dependent property, so given any kind you will be able to calculate this properties, it does not depend how we have arrived at that particular state, for example whatever state, it is, you know internal energy of the system because in depends only on the conflagration of the system and then similarly temperature, entropy all are state dependent quantity, so this equation is valid for any process is reversible or irreversible, it does not matter is, so now will introduce a fundamental equation of thermodynamics, fundamental equation of thermodynamics says that U which is an internal energy is a function of S entropy, V volume and N.

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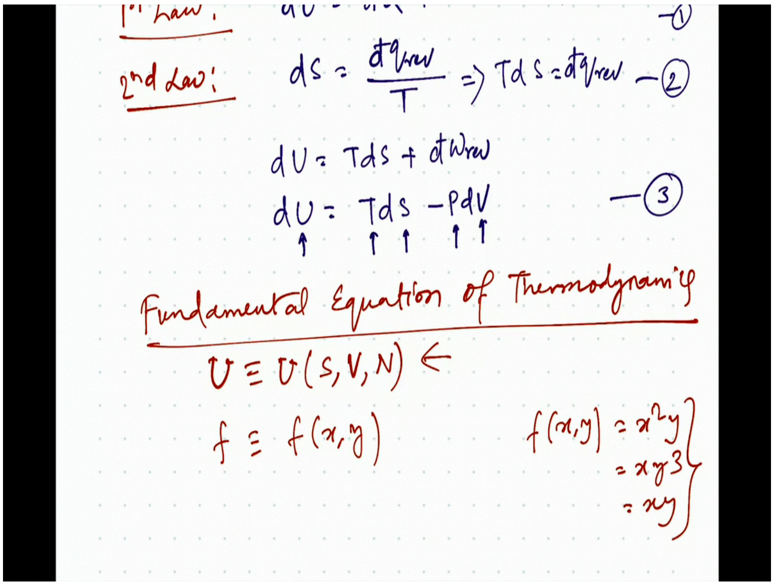


1st Law: $dU = dq$ — ①

2nd Law: $dS = \frac{dq_{rev}}{T} \Rightarrow TdS = dq_{rev}$ — ②

$dU = TdS + dW_{rev}$

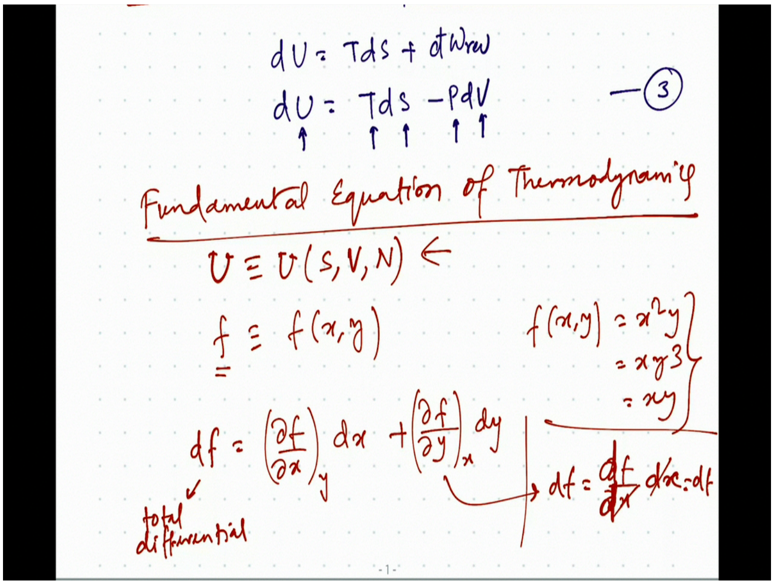
$\underset{\uparrow}{dU} = \underset{\uparrow}{T}\underset{\uparrow}{dS} - \underset{\uparrow}{P}\underset{\uparrow}{dV}$ — ③

Fundamental Equation of Thermodynamics

$U \equiv U(S, V, N) \leftarrow$

$f \equiv f(x, y)$

$$f(x,y) = x^2 y \\ = xy^3 \\ = xy$$



$$dU = TdS + đW_{rev}$$

$$dU = TdS - PdV \quad — ③$$

Fundamental Equation of Thermodynamics

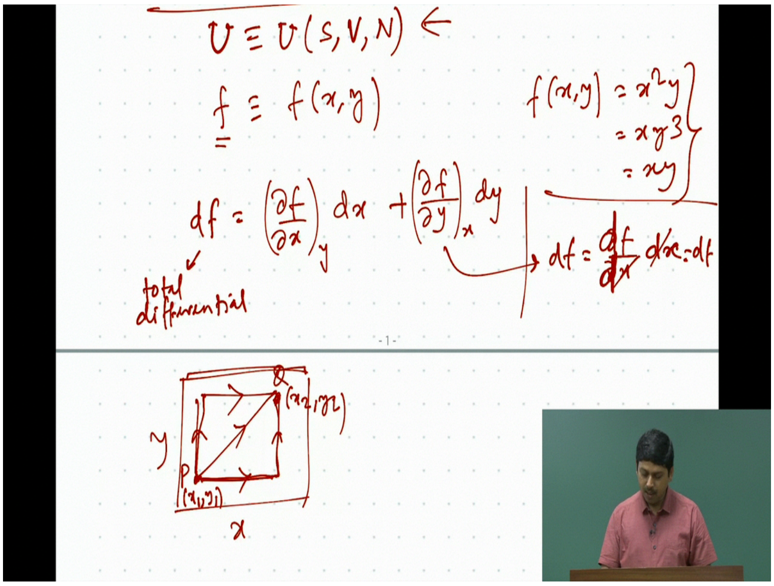
$$U \equiv U(S,V,N) \leftarrow$$

$$f \equiv f(x,y)$$

$$f(x,y) = x^2y$$
$$= xy^3$$
$$= xy$$

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \rightarrow df = \frac{df}{dx}dx = df$$

total differential



$$U \equiv U(S,V,N) \leftarrow$$

$$f \equiv f(x,y)$$

$$f(x,y) = x^2y$$
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total differential

So know that here, it only says that it is dependent on this quantity, it does not give you the type of functions, it only says that it depends on it, for example if I say that I have a function F that depends on X and Y, I do not specify what is nature of dependence, if X, Y could be X square into Y or it could be X, Y cube or simple X, Y, it can be any of this forms, so therefore I do not specify the exact functional form of U with respect to S, V, N, it only specifies that it depends on these 3 quantities which also means that given these 3 variables S, V and N, one can uniquely identify the value of U.

So that is all meant by this particular quantity U, this particular fundamental equation of thermodynamics, now you know that for any multi variable quantity, so whenever there is a change in that variable, then it depends on the changes of the individual quantity, for example if I want to talk about the changes in F, which is called total differential, do not be alarmed by the name, differential is change of in the small amount and total differential means that, that whatever is change in that particular amount F, which is DF but that change can happen either by changing the X or by changing the Y or by changing the both and that can be written as the partial changes.

For example change in F with respect to X, when the Y is constant multiplied by DX or it could be change in Y, changing F with respect to change in Y at a constant X multiplied by Y, so you can notice that here F is a two-dimensional variable, for example if I talk about F as a height of a mountainous area, then you to specify both X and Y in order to talk about the height, imagine in a Google map and if you, you know, you put it in the height information there, we will see that you know, in the map which has both X and Y, you will see certain regions, the height will be higher or certain regions height will be lower.

So there depending on X and Y, you can always get that height, it does not matter how you go to that particular point, either you can go along X and then along Y you can go along Y first and then along X or you can go both by changing X and Y, ultimately if you reach that particular value of X and Y, you will get the same value of height in the map and that is what is meant by exact differential, will come to that later on but it only says that.

Let say few talk about only one variable, so in case of one variable what happens is that, let say our F would be just function of X, then this quantity you become DF equal to dell F by dell X because there is only one variable to DX and see DX, DX will cancel giving DF or dell F will not be there because it is not a partial derivative, so it will just simple DF by DX into DX giving me DF.

So if it is just function of one variable then what we say is that the changing the value of the function is the slope multiplied by the change in the variable, so slope is DF by DX multiplied by the variable will give you the value just like that happens for a single one-dimensional case, however, if you have two-dimensional system, where you have specified X and Y and if you want to go from here, so you can go either this way and then this way or you can go and then this way, so let say this point X1, Y1 and this point is X2, Y2.

So if you can change X1 to X2 keeping, Y1 fixed and then Y1 to Y2 keeping X2 fix or you can go this way and that way, this way and that way you can go this way, there is what I was mentioning earlier, imagine this is just a map and you talking about height of the points, let say P and Q,

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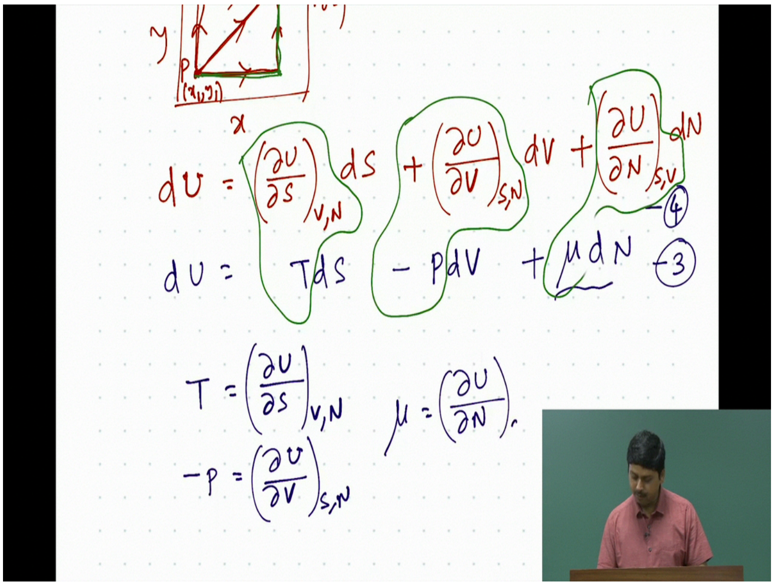
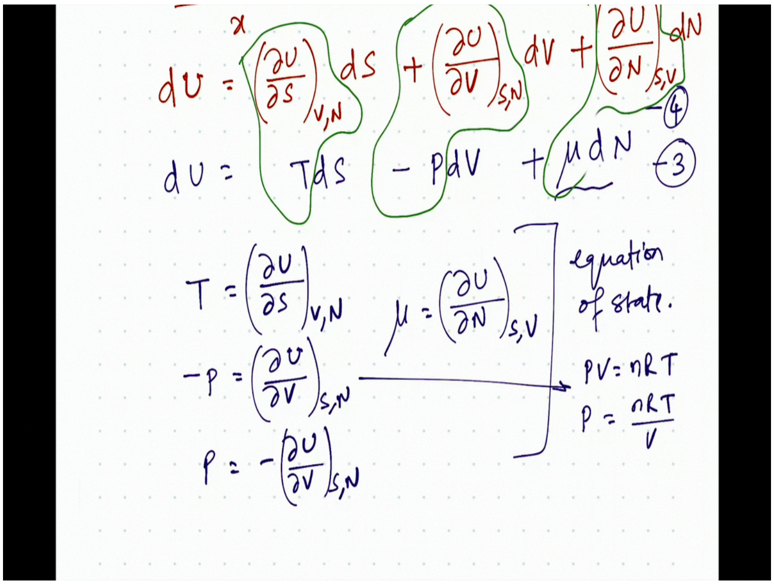


$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN \quad -\textcircled{4}$$

$$dU = T\,dS - P\,dV + \mu\,dN \quad -\textcircled{3}$$

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \qquad \mu = \left(\frac{\partial U}{\partial N}\right)$$

$$-P = \left(\frac{\partial U}{\partial V}\right)_{S,N}$$



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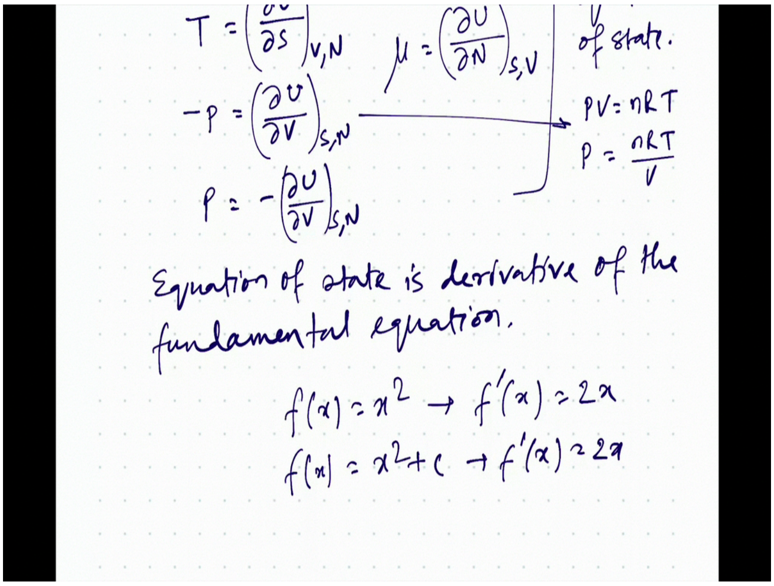
$$dU = T\,dS - P\,dV + \mu\,dN \quad -\textcircled{3}$$

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \qquad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

$$-P = \left(\frac{\partial U}{\partial V}\right)_{S,N} \longrightarrow PV = nRT$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} \qquad P = \frac{nRT}{V}$$

equation of state.



$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \qquad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

of state.

$$-P = \left(\frac{\partial U}{\partial V}\right)_{S,N} \longrightarrow PV = nRT$$

$$P = \frac{nRT}{V}$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$$

Equation of state is derivative of the fundamental equation.

$$f(x) = x^2 \rightarrow f'(x) = 2x$$

$$f(x) = x^2 + c \rightarrow f'(x) = 2x$$

Similarly here we are talking about U which is a function of three variables S, V and N, so therefore the change in U a total differential U can be written as their partial derivatives with respect to all those 3 quantities, so I can write dell E by dell X for a fixed V and N, into DS, DS is change to this plus dell U by dell V at a constant S and N DV plus dell U by dell N at constant S and V DN, this constants are absolutely important because unless we put them constant we are not going to do anything.

So remember what we are doing here that essentially we are not taking this particular path, we are taking this path and then this path, so we are keeping one variable fixed and going in one direction and then we are keeping the other variable fixed and going in that direction in order to make a change in the U or make a change in that particular function, so here also be doing the same thing, so now you see if I now compare this particular equations, let us call that question number 4 and let us right down again question number 3, which was DU equal to TDS minus PDV and 3rd part was not there because we are talking about only two variables but I can tell you for now that the 3rd one if you wrote then it would be plus mew N.

So this one I did not mention before because we are only talking about 1 components system, it will only appear for multi-components system that means when there are more than one type of components is present, let say will talk about mixture of A and B, then it will be, if there is a mixture of more than 2 components, let us say 3 or 4, then also it will be there, so in those situations it will be there.

Now let us compare the question number 3 and 4 and what we also, we see that this one is similar because if I just take the DS out then we get to see this one, similarly we see that this is same and this is same we see that right, so then began right that T is nothing but DU by DS at a function V and N and minus P is DU by DV at a function S and N and mew is DU by DN at a function S and V, so you see that we can 3 different quantities and all are, this all this things are called equation of state.

So you can see equation of state, remember our PV equal to NRT for idea gas equation of state, I could have written as NRT by V and this P equal to NRT by V resembles the this particular equation P equal to minus DU by DV at a constant S and N, so basically we are talking about the same thing minus DU by DV is nothing but NRT by V for idea gas, so you see interestingly here, first of all we get that by taking the derivative of U, so that means the equation of state is derivative of the fundamental equation.

So equation of state is derivative of the fundamental equation, fundamental question has all information about the system, however, when you take a derivative we lose information, for example if I give you a function F equal to X square, now if you take a derivative, you get derivative of F will be 2X, so let say right, if you are FX equal to X square, the derivative of X you get as 2X, if I give you a FX equal to X square plus C then also you will get FX as 2X, so she can be any different values.

So therefore for multiple different values your derivatives can give you the same value, derivative loses information, derivatives is something like projection on that particular variable, for example when you go from three-dimension to two-dimension, so for any difference heights you get the same line on the floor when you project on that, so this is called projection this is like a shadow that comes, so when you project on this you get the same value irrespective of the height on this particular pen, so you lose information.

Similarly the question of state is not have all information because it loses information, whenever you take a derivative the fundamental equation, but fundamental question has all the information, however we do not know the function of form of it, so therefore the do not know the functional form will change from one system to the another system, so therefore the will not know unless but we know how the vary with respect to the variable.

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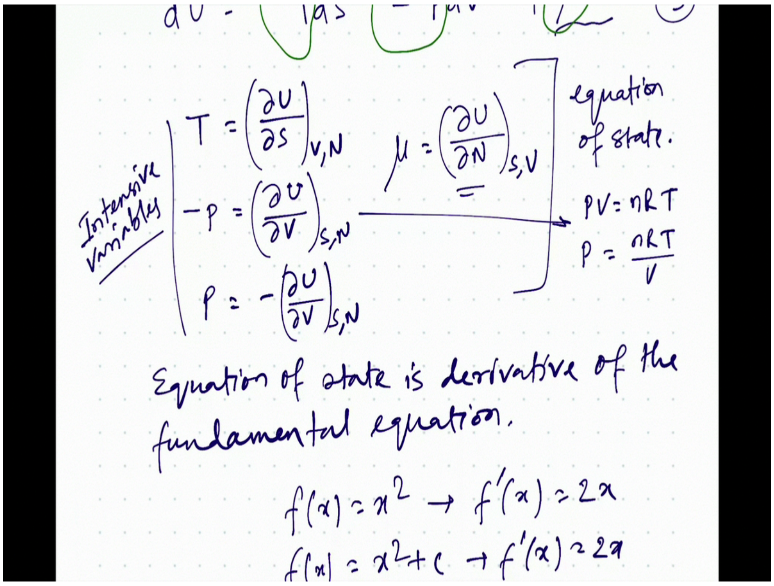

Intensive variables

$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$ $\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$

equation of state.

$-P = \left(\frac{\partial U}{\partial V}\right)_{S,N} \rightarrow PV = nRT$

$P = \frac{nRT}{V}$

$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$

Equation of state is derivative of the fundamental equation.

$f(x) = x^2 \rightarrow f'(x) = 2x$

$f(x) = x^2 + C \rightarrow f'(x) = 2x$

Another important point of the equation of state is that, there are all intensive variables, I have discussed about intensive and extensive variables long back, if you remember that intensity variables are variables that do not change with the size of the system, since we are taking in the derivative and if you notice that in this derivative, we are taking derivatives of two extensive variables, for example if you look at U and S they are both extensive variables.

So when two extensive variables are divided, then essentially it give rise to an intensive variable, similarly look at P there also it is, you know ratios of 2 extensive variables E and V and you when you talk about mew that also ratios of 2 extensive variables U and N, so therefore mew T and P all are intensive variables and they do not change with the size of the system.

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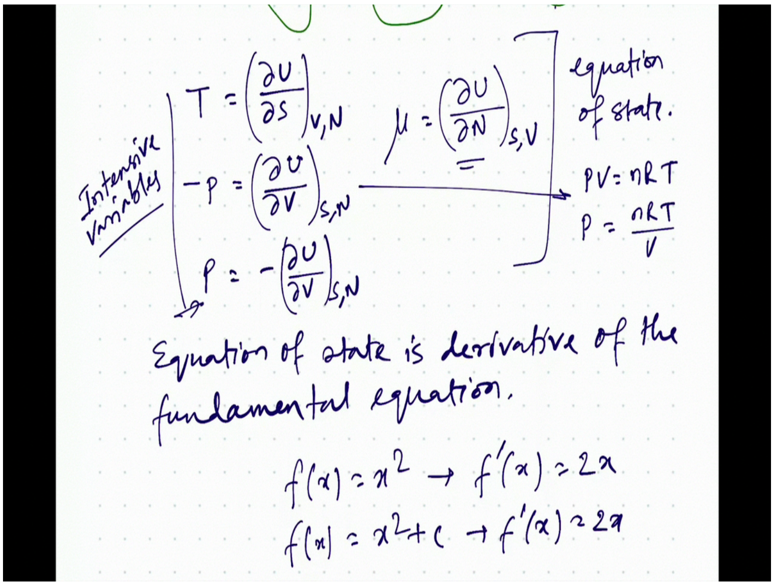

Intensive variables

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \qquad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

$$-P = \left(\frac{\partial U}{\partial V}\right)_{S,N} \longrightarrow PV = nRT$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} \qquad P = \frac{nRT}{V}$$

equation of state.

Equation of state is derivative of the fundamental equation.

$$f(x) = x^2 \rightarrow f'(x) = 2x$$

$$f(x) = x^2 + c \rightarrow f'(x) = 2x$$

Okay, so now we got the 3 quantities, another interesting thing you notice which we talked about briefly while talking about statistical thermodynamics, that the temperature is nothing but changing U with respect to change in S, so it means that whenever there is for a fixed volume, of course and the number of particles wherever there is a change in entropy, there will be changing energy, so it is a monotonically increasing function of, entropy is a monotonically increasing function of energy because I can write 1 by DS dell S by dell U.

So if U changes, S changes and we saw that in case of let say of particle in a box system, wherever the energy is increasing that the number of particle in 3-D box, number of possibilities are number of degenerative of micro-states were increasing, so that is very simplest example of showing you that, if energy increases that the number of possibilities increases and that was another reason that we talked about when heat flows into the system and there we saw that wherever there U was increasing then the number of possibilities were also increasing.

So and because what happens is that whenever increase the energy than the particles can have multiple states accessible to it and therefore there are number of ways of doing it and S increases, so and that essentially is temperature, you know that the temperature cannot become 0 or negative, so therefore it will be always monotonically increasing function, similarly when you talk about U and V, we know that whenever V increases, U will decrease because and then only you will get a positive pressure on the system, so whenever you have increase the V that the particles we separate from each other and the internal energy will decrease and that will give rise to a positive pressure on the system.

So that makes sense and chemical potentially is again by changing the number of particles, one can change the energy of the system, so for example we talked about a salt solution and then depending on the water and the salt particle your this thing will change, the energy of the system will change, so thus we see that how this internal energy is related to this 3 different variables on which they depend on.

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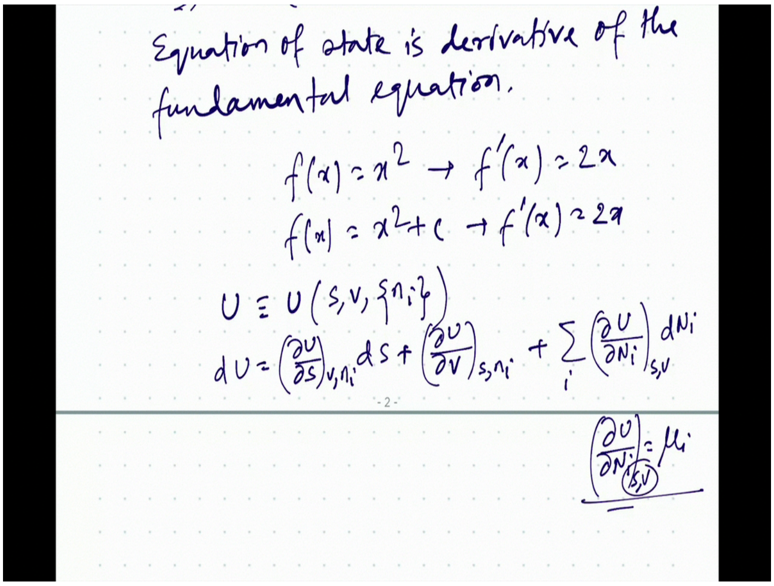

Equation of state is derivative of the fundamental equation.

$$f(x) = x^2 \rightarrow f'(x) = 2x$$

$$f(x) = x^2 + c \rightarrow f'(x) = 2x$$

$$U \equiv U(S, V, \{n_i\})$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_i} + \sum_i \left(\frac{\partial U}{\partial N_i}\right)_{S,V} dN_i$$

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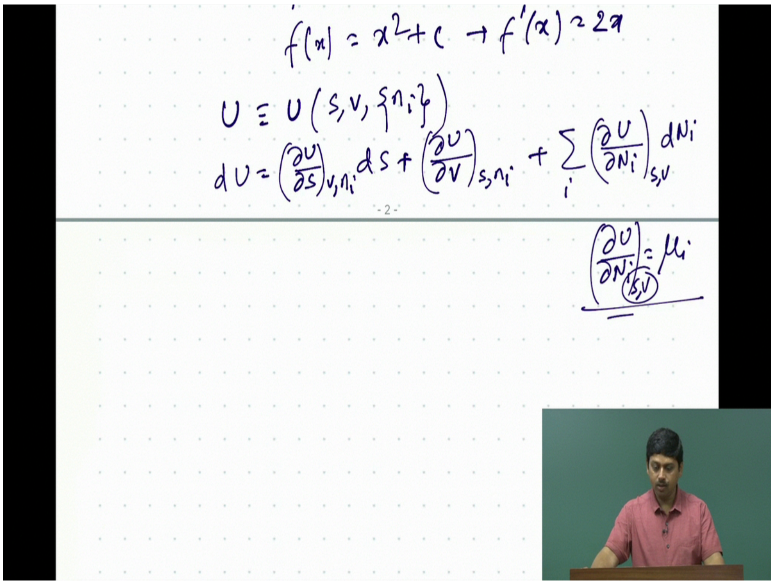
$$\left(\frac{\partial U}{\partial N_i}\right)_{S,V} = \mu_i$$



$$f(x) = x^2 + c \rightarrow f'(x) = 2x$$

$$U \equiv U(S, V, \{n_i\})$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S, n_i} + \sum_i \left(\frac{\partial U}{\partial N_i}\right)_{S,V} dN_i$$

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$$\underline{\left(\frac{\partial U}{\partial N_i}\right)_{\boxed{S,V}} = \mu_i}$$

Now that we talked about that, we can say that, we can actually extended this particular one more than one components, more than 2 components system and multicomponent system and in that case, generally we can write U a function of S, V and NI where I can go from one to the number of components and in that case we can simply see that, we can write the DU dell U by dell S at a function V and all NIs DS dell U by dell V at a function of S and all Nis plus sum over I dell U by dell NI at a function of S and V DNI.

Where, which means that dell U by dell NI for a multicomponent system at a function of S and V is nothing but mew I, never forget this subscripts, because without that it will be not meaningful and mew I are just, for a multi-components system, for a mixture of 3 or more components each of them, we have their own chemical potentials and chemical potentials you will know in the late of course, will not discussing in this course, something like pressure, like for example pressure try to equalises and change the volume, similarly chemical potentials drive the change in the number of particles of different components and make the chemical potential equal between two components and that is what we see in osmotic, you know whenever there is permeable membrane there is a change in the number and the chemical potential actually play a role to change that across a membrane.

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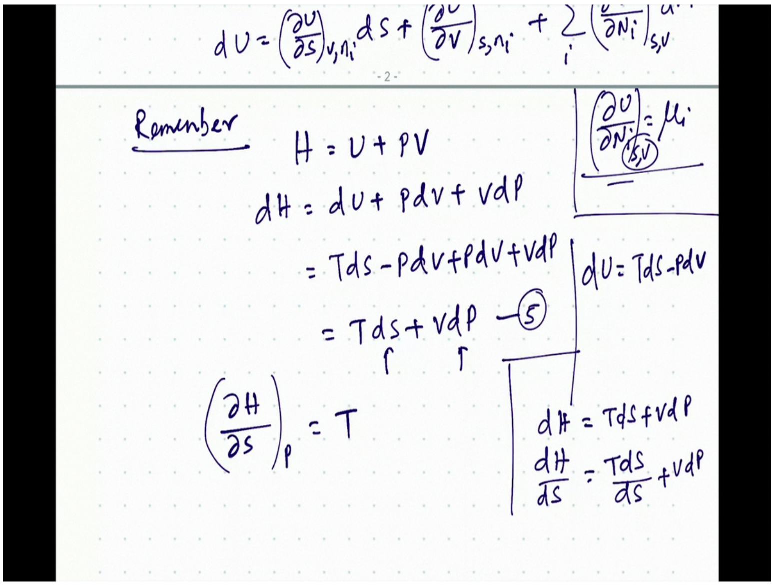


$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_i} + \sum_i \left(\frac{\partial U}{\partial N_i}\right)_{S,V}$

-2-

Remember

$H = U + PV$

$dH = dU + PdV + VdP$

$= TdS - PdV + PdV + VdP$

$= TdS + VdP$ ⑤

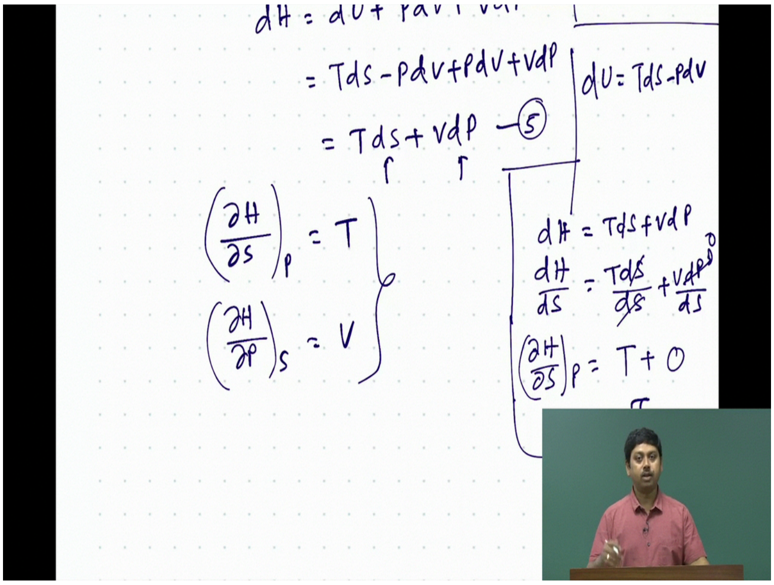
$\left(\frac{\partial H}{\partial S}\right)_P = T$

$\left(\frac{\partial U}{\partial N_i}\right)_{S,V} = \mu_i$

$dU = TdS - PdV$

$dH = TdS + VdP$

$\frac{dH}{dS} = \frac{TdS}{dS} + VdP$



$dH = dU + PdV + VdP$

$= TdS - PdV + PdV + VdP$

$= TdS + VdP$ ⑤

$dU = TdS - PdV$

$\left.\begin{aligned}\left(\frac{\partial H}{\partial S}\right)_P &= T \\ \left(\frac{\partial H}{\partial P}\right)_S &= V\end{aligned}\right\}$

$dH = TdS + VdP$

$\frac{dH}{dS} = \frac{T\cancel{dS}}{\cancel{dS}} + \frac{VdP^{0}}{dS}$

$\left(\frac{\partial H}{\partial S}\right)_P = T + 0$

Okay, so now we remember, now we are going to discuss a new thermodynamics variable, so remember that we define H as U plus PV, so therefore taking the differential in both sides it will be DU plus PDV plus VDP but we know that DU from our earlier, for example is TDS minus PDV from our equation 3, so we can write that TDS minus PDV plus PDV plus VDP and we get TDS plus VDP, so you see natural variables of each are S and P, so from here itself, we can write that okay, we are omitting the changes in number of particles from now onwards.

So we can write as dell H by dell S at a constant P is T, so how did I do that, so what I did here, I just write it here, so from this equation which is let say question number, we have gone up to 4, we can call it 5, so the way we did is that we had DH is equal to TDS plus VDP, we divided both sides by DS and we took the pressure constant, so DS, DS will cancel and pressure constant will become 0, so that is what we get as T, so that is what we precisely we did that, we need not really differentiate because already H differential amount.

Similarly when we do that with respect to P and take S constant, we get dell H by dell P at a constant S is V, so you see that you are getting completely different, you know different, different current thermodynamic potentials using different expressions, so for example here we find that if we change the pressure and we see a change in enthalpy, when the process is done at the abiotic condition and reversible at the abiotic condition are called iso-entropy condition than that is nothing but the volume.

Similarly we see that if you change the entropy of the system and measuring enthalpy and a constant pressure, we get nothing but temperature, so some of the things we not seem very physical right now, however you will see that some of the unphysical quantities can be mapped into something which is physical and measurable and therefore we need to know all this thermodynamic relations in order to understand that how to calculate each and every quantities possible.

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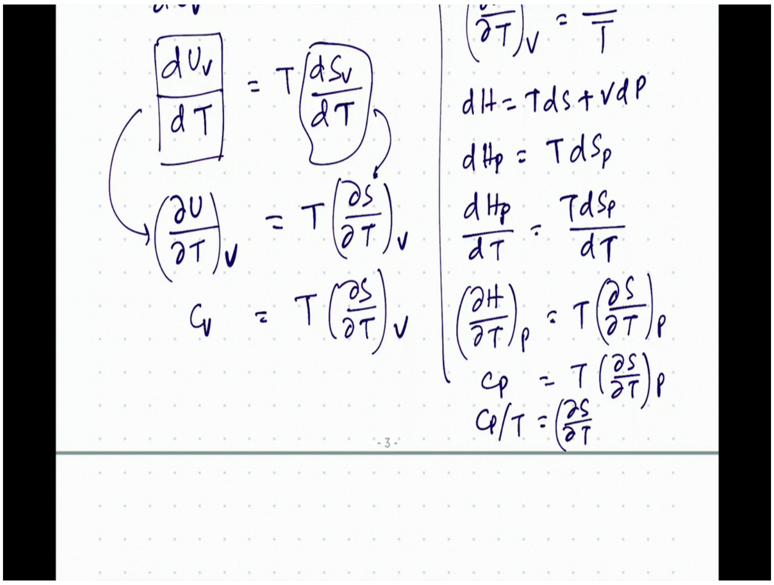


$$\boxed{\frac{dU_V}{dT}} = T\frac{dS_V}{dT}$$

$$\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$dH = TdS + VdP$$

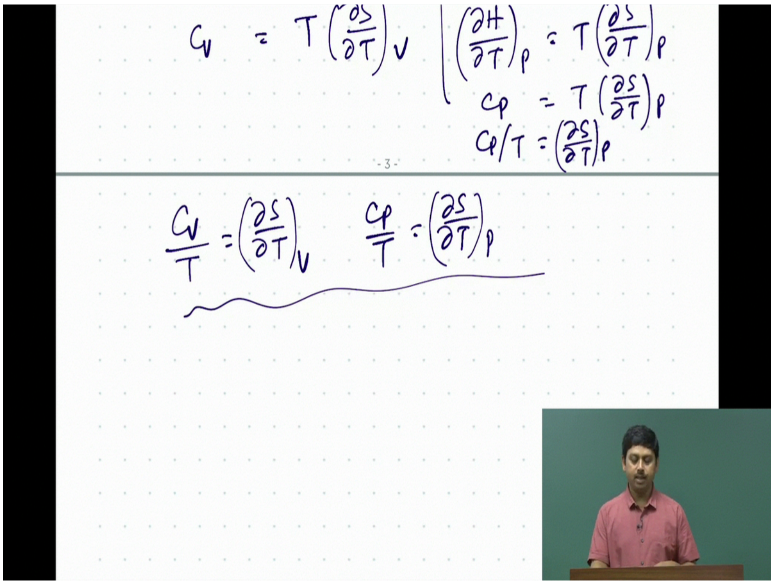
$$dH_P = TdS_P$$

$$\frac{dH_P}{dT} = \frac{TdS_P}{dT}$$

$$\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$C_P/T = \Big(\frac{\partial S}{\partial T}$$



$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \qquad \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$C_P/T = \left(\frac{\partial S}{\partial T}\right)_P$$

-3-

$$\frac{C_V}{T} = \left(\frac{\partial S}{\partial T}\right)_V \qquad \frac{C_P}{T} = \left(\frac{\partial S}{\partial T}\right)_P$$

So now that I got that, we can also write that in terms of something measurable quantities and we can see that how this entropy depends on specific heat something like that, we can write it as again we are using the question number 3 as DU equal to TDS minus PDV and now we can take V fixed and that we can denote by a subscribe V, so TDS V and DU become 0 because we are using that, so now at this stage we are going to take derivative respect to T, both sides, so we will just do one more step, will not jump here, we are divided by T here, what we get? We get this kind of the expression.

We are dividing just by dell T on both sides and taking dell T limit to be 0, so then this quantity that wrote here, this particular quantity what it is saying is? That there is a differential amount of changing U at a constant V for a change in T, so that is precisely nothing but dell U by dell T at a constantly V, that is what is meant, so this writings are equivalent and right-hand side what we should write then T, I have T only and that this quantity, this particular quantity can be written as dell S by dell T at a constant V, now dell V by dell T at a constant V you know that CV, that is call CV right, specific heat at a constant volume that is nothing but this quantity.

So therefore we can write here that dell S by dell T at a constant V is nothing but CV by T, similarly we can use that expression of H also, we know that DH is TDS plus VDP, again we take pressure as constant, so we can write as TDSP divide by temperature on both sides, we get TDSP by DT and then we are writing in a dell form, giving us this one, and by definition it is CP, so therefore CP by T is dell S by dell T, so we got that CV by T is dell S by dell T at a constant V, whereas CP by T as dell S by dell T at a constant P, so here seen that how the changes in entropy with temperature at a constant volume on pressure is gives rise to the specific heat divided by temperature.