**Chemical Principles 2**
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**First Law of Thermodynamics**

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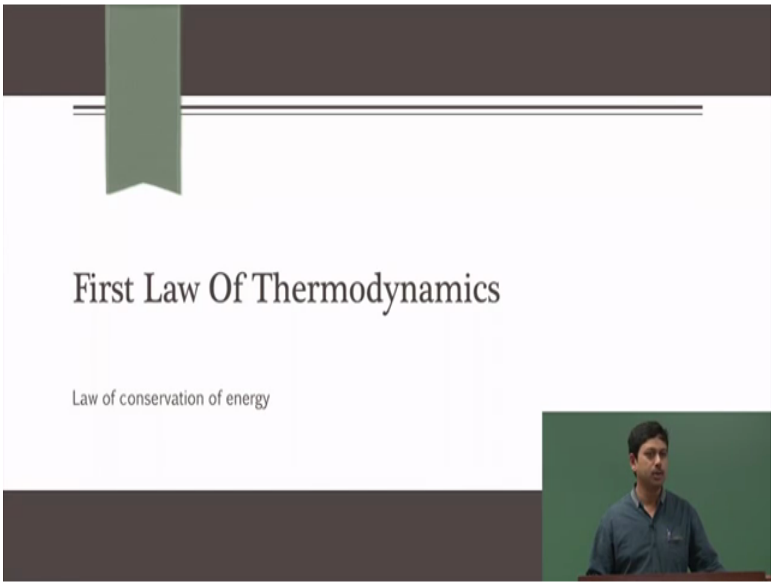


Okay, so welcome to the next lecture so we have introduced the first law of thermodynamics the other day right? So now we are going to move ahead with more formulations of thermodynamics.

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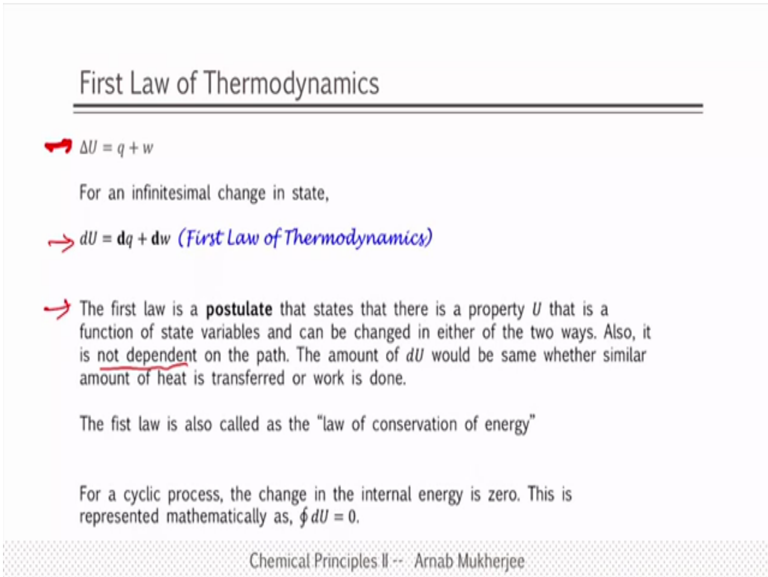


So first law of thermodynamics is a combination of like says that change in the internal energy is a combination of both heat and work and for an infinitesimal change we can write as dU equal to dq plus dw. Now we already mentioned that the first law is a postulate that states that the property U is a function of state variables that can be changed either two ways and also it is independent of path, right it is not dependent on path.

What it means will become clear today, but remember that we are saying that as a postulate taking that to be a state function and also we know that it is law of conservation of energy and because it depends on the state when it comes back whichever path it you know carries on when it comes back to the same point, it will be 0.

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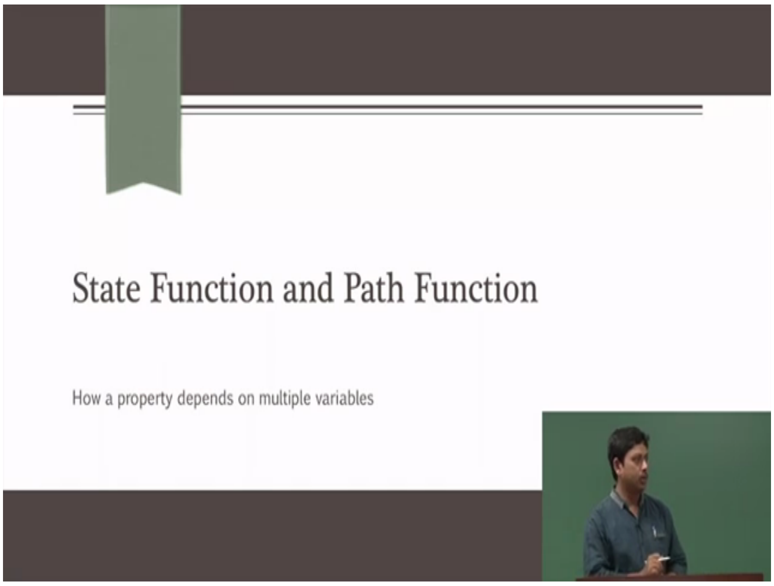


Okay, so now we are going to discuss today about state function and path function, basically what it means is that how a property varies as a function of its own variables that is called state function and path function so it will become more clear today.

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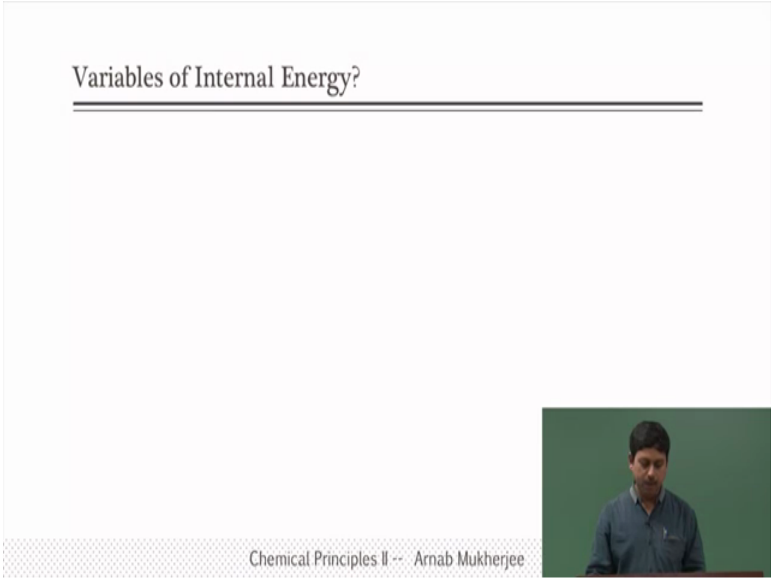


So what are the variables of internal energy?

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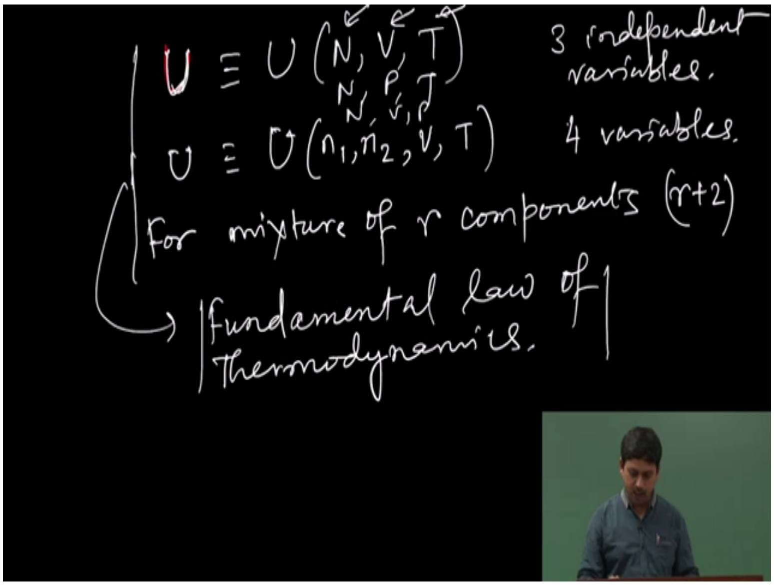


So we say that as a postulate that internal energy U (I will just change that colour) internal energy U is basically a function of N, V and T, 3 variables. So by that what it means is that for one component system it will depend on number of moles, volume and temperature. Therefore, for one component system there are 3 independent variables and when it is a let us say multi component mixture or let us say two component system, then internal energy will depend on chemical composition of the first component, chemical composition of the second component, volume and temperature, so in that case 4 variables.

So in general for a mixture of r variables (how many indepen) r components rather not variables (I will just clarify that) r components how many independent variables will be there? For 1 component 3, so for r component will be r plus 2 independent variables. So the other variables will be dependent on that, okay. So which means that once you specify the number of moles, volume and temperature or let us say number of moles, pressure and temperature or number of moles, volume and pressure U can be determined from that, okay.

And that U will know as fundamental law of thermodynamics, we will come back to that later again after we cover second law and all, we will come back to this fundamental law of thermodynamics later. But right now we will just introduce it, because we now actually so we are mapping the variables like N, P and T into a value of U, it is like a function functional form, only thing that we do not know what is the nature of the function? How nature of the function means how can we can express U in terms of N, V and T that is not known, that will vary from system to system.

However, we can say that for 1 component system these are the variables on which we will depend on and it does not matter how we arrive at that value, it does not matter which path we take from coming from one state to that particular state. So we define the state by N, V and T its independent variables, they define the state just like let us say for example we talk about phase base we define position and momentum and that defines a system, if you define position, movement of all the particles.

Similarly for microscopic variables once we define this independent variables, we define the system all together. Once we know this information we can calculate every property once we have this fundamental law of thermodynamics we can calculate every property from that particular thing, okay. So that is one thing that we wanted to say.

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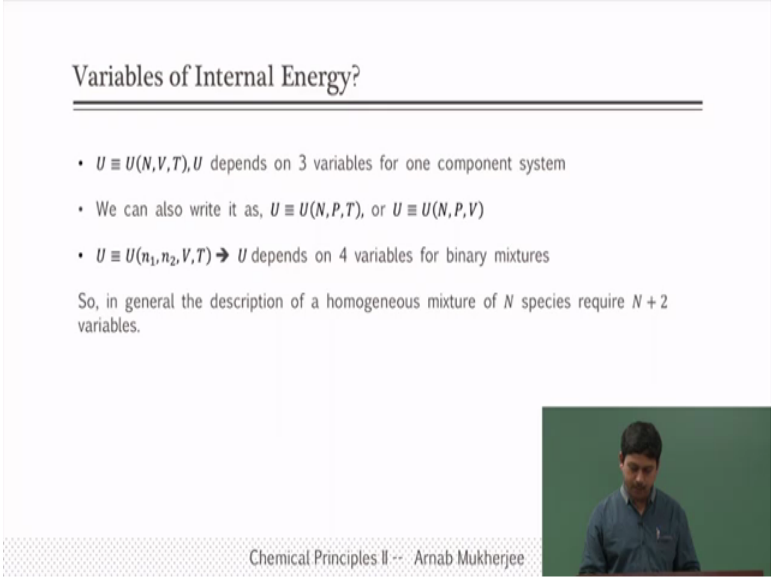


And this we covered that and in yes so that we have covered. So now since it is dependent on multiple variable system, since U depends on multiple variables we can see that when you change those variables the value will change, the property will change. For example when I change number of moles U will change or temperature change then U will change and things like that. So how it changes, depending on change of one variable to another variable can be understood by understanding differentiation.

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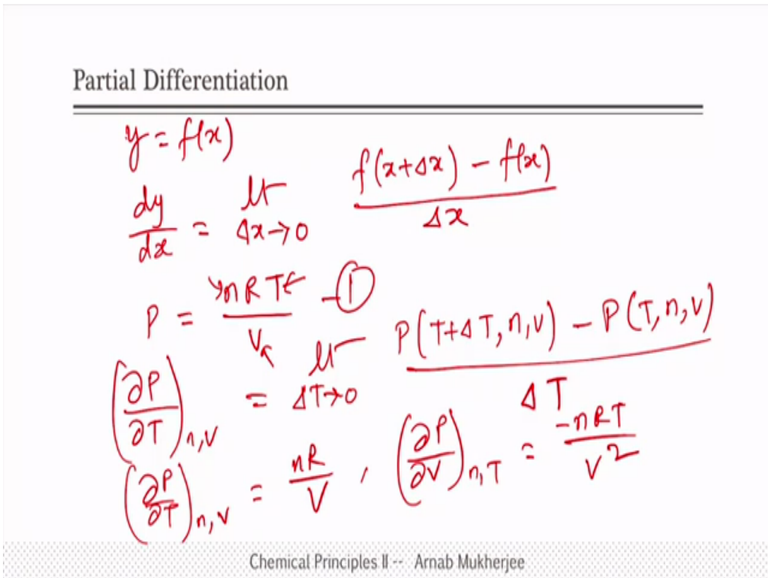


Now if a function depends on only one variable let us say we call it f x as a function let us say y equal to f x is a function and we want to know how this particular function changes with respect to x, then what we say? We do a differentiation dy by dx, so what dy by dx tells us from first principle is that as x tends to 0 how fx changes from fx to f x plus delta x. So this is the definition from first principle that given a function of one variable how one can get the change of that function with small change of the variable by divided by of course the variable difference. So this is from the first principle the definition of a differentiation.

Now let us talk about pressure for part you know ideal gas system, a pressure can be written as n RT by V, right. So here you can see that it depends on (R) it depends on n because R is the constant, T and V three variables, right. So now let us say if I want to calculate for this that how this particular function changes with respect to temperature, but then there are other two variables that on which it depend on, pressure depends on three variables now N, T and V and we wanted to see how it changes with respect to just one variable T and if we do that then we call that as partial differentiation and you see the notation is del instead of d.

So when you write that dP dT we are saying that how P changes with respect to T alone keeping n and v constant. So how we can write from first principle, you can write limit delta temperature tends to 0, pressure as a function of T plus delta T, comma n, v minus P T, n, v by delta T, so this is the definition of partial differentiation, right. So we can give some example, so let us say if I want to calculate del P by del T as a function of n, v for a particle you know from equation 1 let us say then what we are going to get is nR by V.

Similarly we can calculate del P by del V at a constant n and temperature which will give us minus nRT by V square. So I assume that you guys know how to do differentiation from 12th standard and this is so in partial differentiation we just take the other variables as constant, nothing else and that will help us to carry out the changes with respect to one particular variable. Okay, so now we are going to see that if let us say more than one variable change, what will happen?

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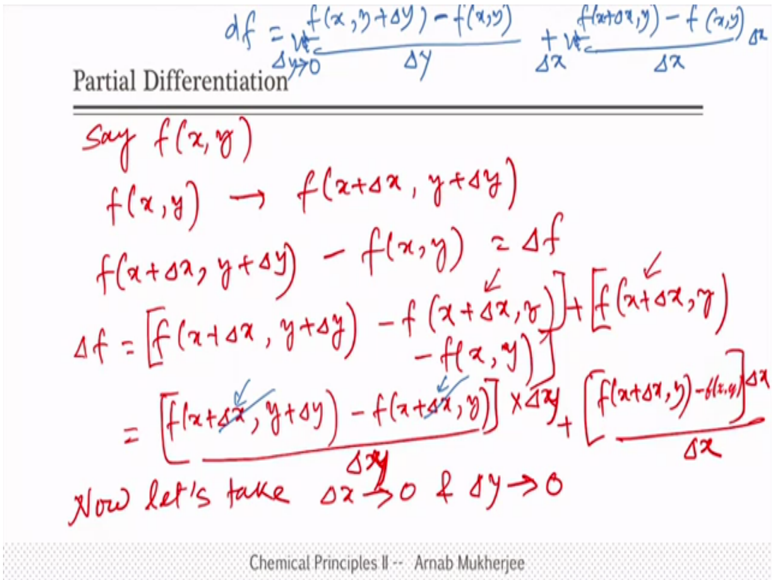


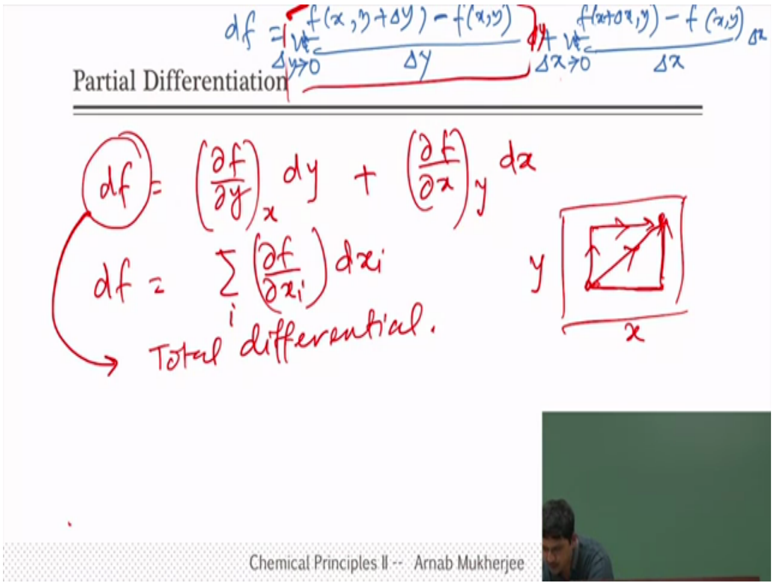


Okay, so now let us say a function f x a function f depends on more than one variable x and y, okay. So in that case I want to see how the function changes with respect to both the variables, how do I look at, how do I understand that? So we want to see that how f x, y goes to f x plus delta x and y plus delta y. So how do I write that? We can say that f x plus delta x, y plus delta y minus f x, y is equal to delta f. So I want to see how the function changes based on the change of both its variables, not just one let us say it depends on only 2, we saw that P depends on 3 variables, but here we are just taking only 2 of the and then see that how it turns out, how we can write that?

So we say that the amount of the amount of changes in f is delta f and that change is happening by change of the variables x and y both. So we can write the difference here like that and then we are going to add and subtract this particular quantity so we write delta f as f x plus delta x, comma y plus delta y and then we are going to add and subtract this quantity x plus delta x, y and add this quantity x plus delta x, y since we are adding and subtracting it does not make any difference it remains the same, correct? Because what we did is that we just added this, subtracted this, added this same quantity two times, delta remains same.

Now we are going to take put them in a bracket, okay. So within the for the first bracket we are going to multiply and divide by delta x. So f x plus delta x, y plus delta y minus f x plus delta x, y this one we are going to multiply by delta x and divide by delta x, I am all going by first principle, okay. Second one no first one we are going to do y, second we are going to do x, f x plus delta x, y minus f x into delta x by delta x so we got two terms.

Okay, so now let us take delta x tends to 0 and delta y tends to 0, what is going to happen? Look at the first term, in the first term if I take the delta x to be 0, then I have delta x in both the cases, okay if I take now I can take the limit right away. So we are taking now limit to delta y and delta x tends to 0 for both of them, okay. So left hand side will become (so actually I do not have space so I should write here then) left hand side will become df is equal to why I am putting df? Because we are taking limit, for them limit delta x tends to 0 and delta y tends to 0.

Now this quantity since we are taking the limit delta x tends to 0, it will be simply 0 and it will also be 0. But here delta y we cannot just take to be 0, because we are dividing by delta y also. So what we are going to have is f x, y plus delta y minus f x, y divided by delta y limit y tends to 0 plus f x plus delta x, y minus f x, y divide by delta x into delta x, now you see what is happening so df becomes now this particular term that we have that particular term is from first principle is nothing but del f by del y at a constant x, right agree? (Oh I forgot to write dy here delta y) and delta y becomes dy because we are taking delta y to be very small and right hand side becomes del f by del x at a constant y because see the y value remains constant dx, is it clear?

So basically what we have done is that we have shown that from first principle if a function depends on multiple variables then the change of function can be associated with the change of either of that variables, if it depends on 3 variables, we have to have 3 such terms we apriory do not know whether y changes or x changes, but we are saying that if y or x change then the overall change in the function will be sum of this partial differentiation with respect to the variable multiplied by the change in variable.

So in principle if quantity depends on many many variables we can write as del f by del x i dx i and i then i can go to 1 to whatever number of variables it has. So this is what called total differential, it is called total differential that that means how much difference is there all together when we change these variables. Now what does it mean basically? It means that let us say I have a 2 dimensional surface and then I want to reach from this point to that point, now I can go along this one and then along this one, so let us say this is my x coordinate and this is my y coordinate.

So I can vary along x and then along y or I can vary along y and then along x or I can have a combination of both, so by changing the amount of x or the amount of y this creates many different paths to reach from one point to another point. If you had only one variable there is only one path to go, but since you have a multiple variables there are multiple paths because all possible combinations x, y will give you a new path, okay.

So that is what that creates this path functions because now this f has the possibility to reach different different paths, okay. So imagine that we are talking about a mountain and then let us say one particular place of a mountain has some height. Now that height is independent of path, so height as a function of x and y coordinates is independent of path because you can reach whichever way to that particular point you will get the same height, okay so that height is we can call at an exact differential, okay.

Whereas, if you get to a property where if you change that then you will get different different values then will be called I exact differential, okay. Now we will see we will see that later on, but before that I just want to show you how this particular differentiation look like.

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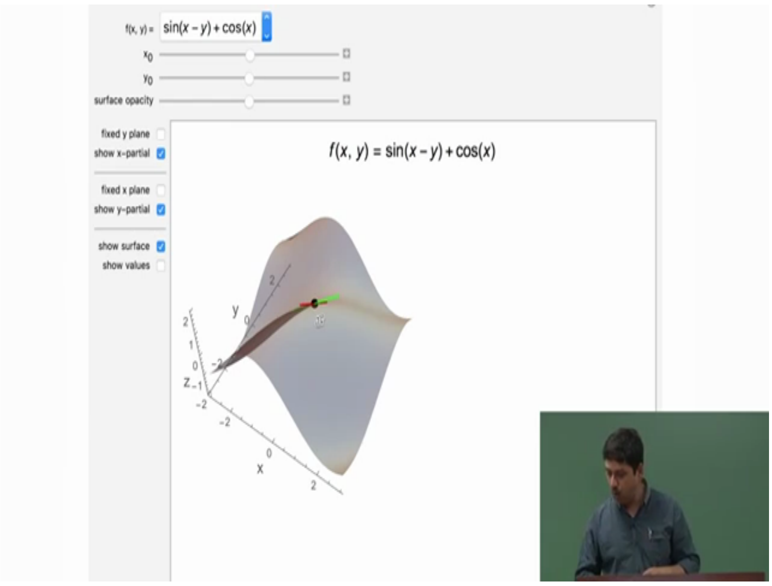


So for example here we are showing a particular function f x, y is Sin x minus y plus Cos x some function is drawn here, okay and this is one particular point here some x 0, y 0 we can we can vary the point also along x 0, see along x 0 it has some minima, along y 0 it has some minima, so let us take that point here and then we can show that how the derivative looks like.

So this is some one plane which is fixed along x, this is a fixed along y plane and now you see that this is partial derivative along y, can you observe that? And I can show you partial derivative along x at that point you see. So at that point for that particular value of y 0 you are looking at how it changes along the x, that slope is going to give you the partial derivative. So ideally these slopes can be different in different directions.

So but however, here the z coordinate do you think will be dependent or independent of paths, the z coordinate will it be dependent on path or independent of path? It will be independent of path, because it is just a function of x and y, just like our U is a function of V and T and n so therefore it is independent of path given a value of V, given a value of T it will give you exact value of U so it is independent of path whenever there is a function of those variables will be independent of path.

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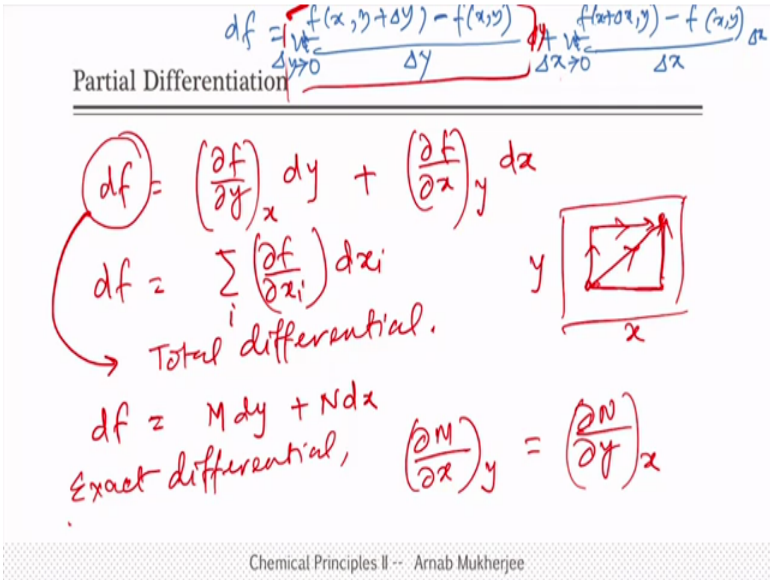


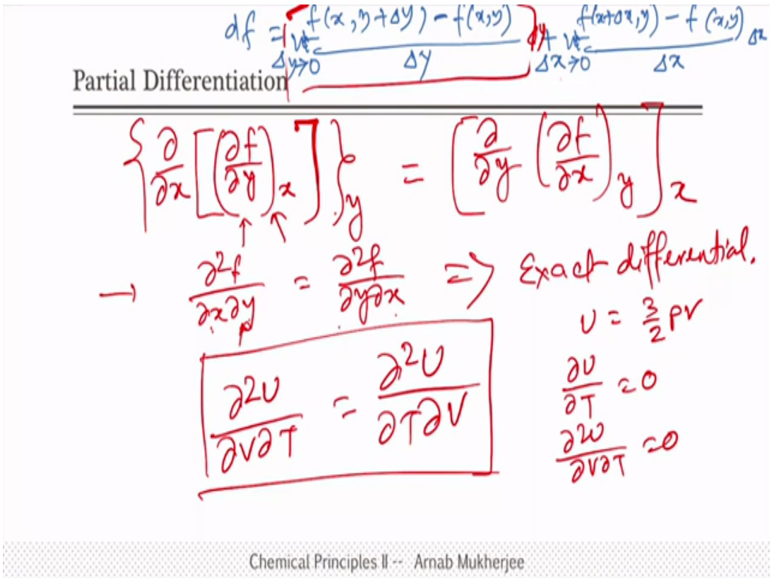


But now how do you actually show that it is independent of path and what is the formula for doing that? So let us say so now we have written total differential in terms of the partial differential, now we simplify a little bit and we say that del f by del y, x is M so we can write M dy plus N dx, okay and for exact differential, the criteria is that del M so M came from differentiation with respect to y, now we have to do with respect to x, del M by del x with respect to y is del N by del y with respect to x. So it is exact differential if it satisfies this criteria otherwise it will be an inexact differential.

So you see why we got that, so now you know that M is already a partial derivative of with respect to y, now if you combine together it essentially means that del f by del y at a constant x is our M, right and that one we are taking a derivative with respect to x at a constant y is equal to the opposite thing. So whenever this condition is satisfied we say that it is a exact differential.

So if you look at physically, instead of mathematically what do you observe? You see that first thing that is changing we can simplify this by the way, we can simplify as d 2 f by dx dy is equal to d 2 f by dy dx. If this is satisfied then it is an exact differential or a state function, what it physically means? It physically means that you go first along y for a fixed value of x here and then you go along x for a fixed value of y, first go along y for a fixed value of x and then you go along x for a fixed value of y on the left hand side.

What the right hand side says? That you go along x for a fixed value of y, then go along y for a fixed value of x. If you look at the derivative dx dy and dy dx they are not same, first we are taking derivative with respect to y then x and here first x and then y. So it only means that if you do one and then the other it does not matter, if there is an exact differential you will reach the same point, otherwise it will be an inexact differential.

Since we know that U to be an exact differential we can for U atleast we can write that del 2U del V del T is equal to del 2U del T del V, okay. U for an ideal gas you know it is 3 by 2 PV, right. So del U by del T is basically going to be 0 and therefore del 2U by del V del T is so it is not that interesting a quantity here, okay. So we are going to show some interesting quantity.

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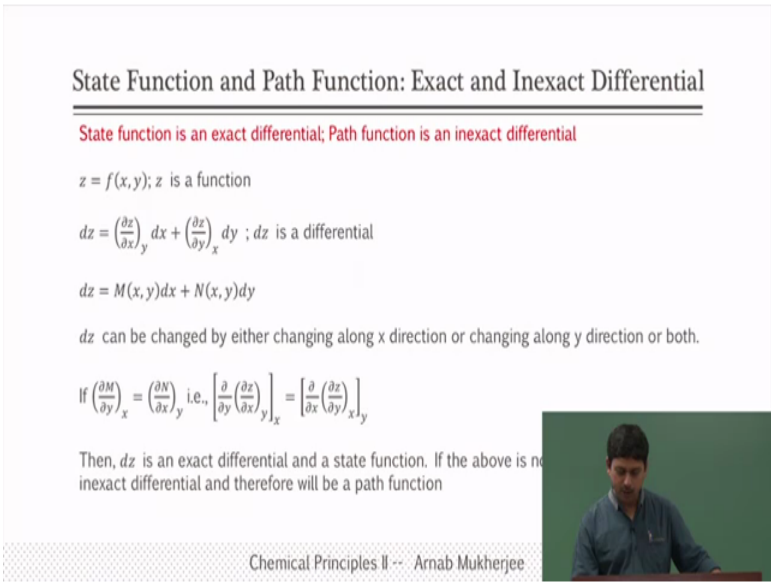


But let me see before that whatever is there. Yes, so this is what we discussed here this is what we discussed.

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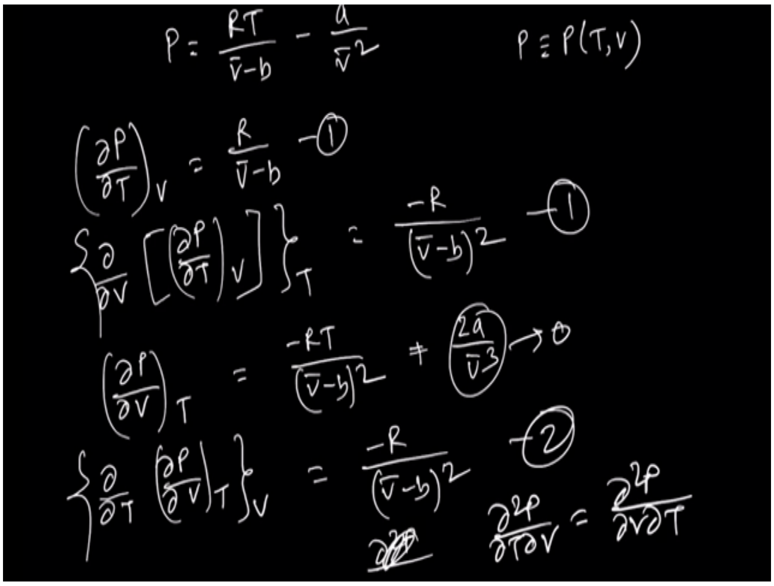


So we are going to just solve for one particular system P equal to RT by V minus b (v bar) minus a by V bar square, right. So here P is a function of T and V, right so we can do first with respect to T at a constant V what we are going to get R by V minus b, right. Now let us say we do we take the derivative of 1 again with respect to V now, now del del V of this quantity del P del T V now this one has to be at a constant T is going to be minus R by V minus b square, right let us call that equation 1.

And (let us do the equation) let us do the other way round, so del P by del V at a constant T is what minus RT by V minus b whole square minus minus minus plus 2a by V cube, correct, is it correct? Now let us do the second one now it is with respect to T and at a constant V so now V will be constant So since with respect to T this quantity goes to 0 and this quantity will give you minus R by V minus b whole square, equation number 2.

Now does it match? 1 and 2 match? Yes, so now we can say that d 2P by dT dV is equal to d 2P by dV dT, which means P is an exact differential for the Van der Waal gas that we have discussed, okay.

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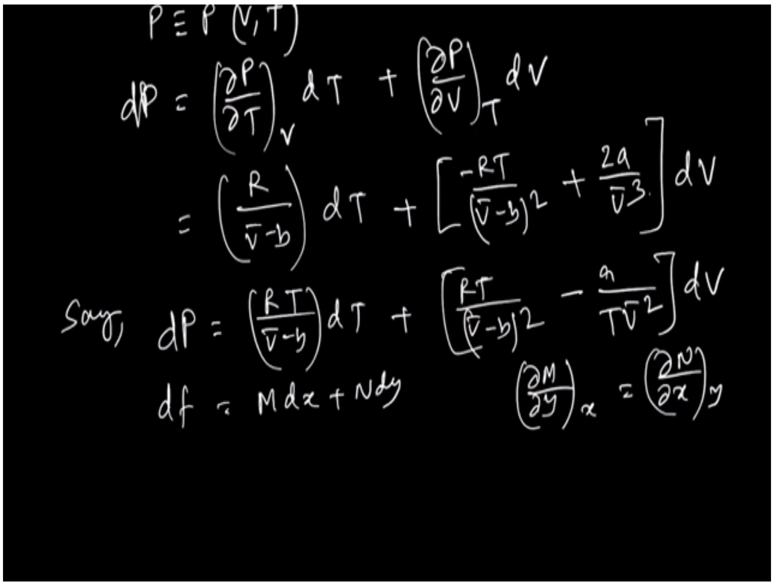

Since P is a function of V and T, we can write dP as del P del T V dT plus del P del V T dV, right we can write that. Now we have already calculated what those quantities are, what was the del P del T at a constant V? It was R by V minus b dT and the second one was minus RT by V minus b square plus 2a by V cube into dV, okay so this was the derivation. Now this gave us perfectly this gave us the exact differential P as an exact differential.

Now let us say we do not want to write that, we want to express dP in this form let us say RT by V minus b dT plus RT by V minus b whole square minus a by TV square dV. Say this is it is lie this. Now can you tell me that P is an exact differential or not? You remember it is a M dx plus N dy formula, remember? So I will remind you df is here M dx plus N dy, in that case what we have to check del M by so M dx means already there was a derivative with respect to x has happened. So with respect to y we have to do at a constant x and we have to check with respect to x at y, are you following?

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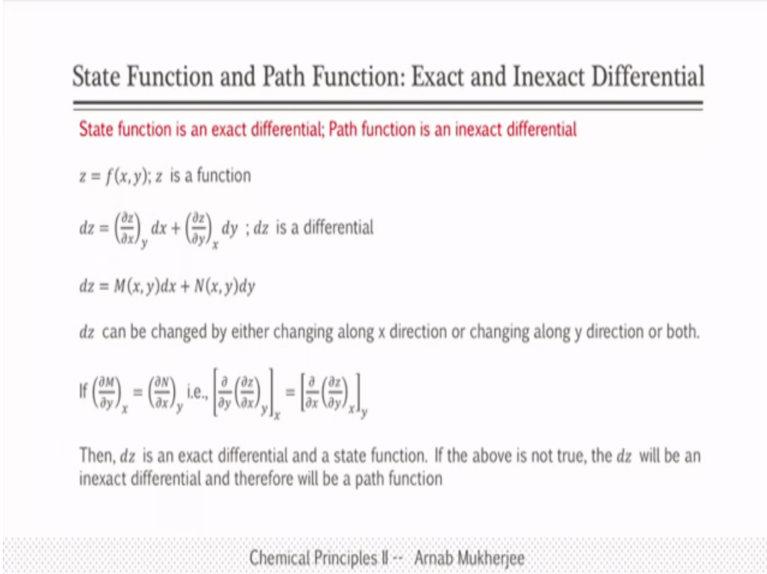


We can go back and check that whether it is a case or not del M by del y see M came because I already derived with respect to x, so the next one would be y, right.

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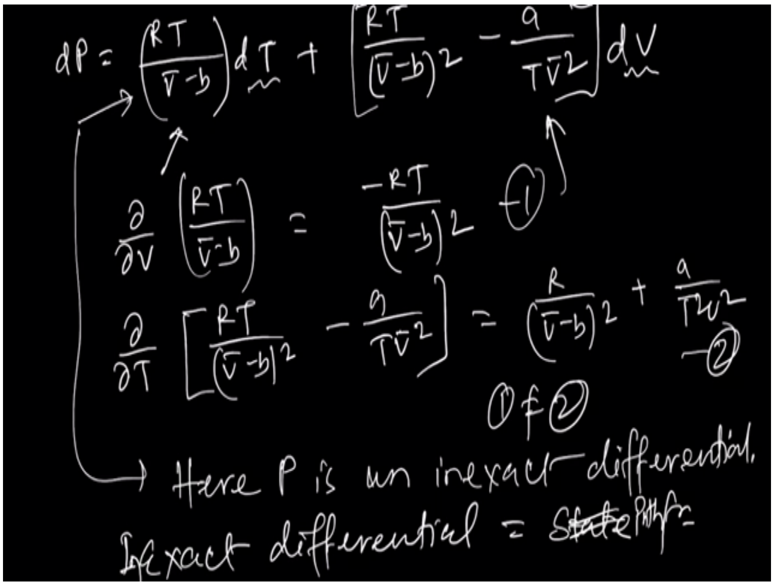


Now if you go back dP is let us say we say that RT by V minus b dT plus RT by V minus b square minus a by TV square, if that is the case that is the case will it be an exact differential? So for that what we have to do is that we have to take this quantity with respect to V del del V of RT by V minus b is going to give us minus RT by V minus b square and this right hand side we have to take with respect to T, you understand why I am doing that right?

Because since I have already V, I know that I have to do with respect to T, since I have T, I know that I have to do with respect to V it is like 2 variable case only, right. So now if I do the right hand side with respect to that RT by V minus b square minus a by TV square what I am going to get? I am going to get R by V minus b square minus plus minus minus plus T square V square, correct.

Now you see this 1 and 2 are not same so therefore this quantity if dP is expressed by this way then here P is an inexact differential, okay. So now I will say I will tell you that exact differentials differential is equal to state function inexact or (I will write here) inexact differential is a path function, okay.

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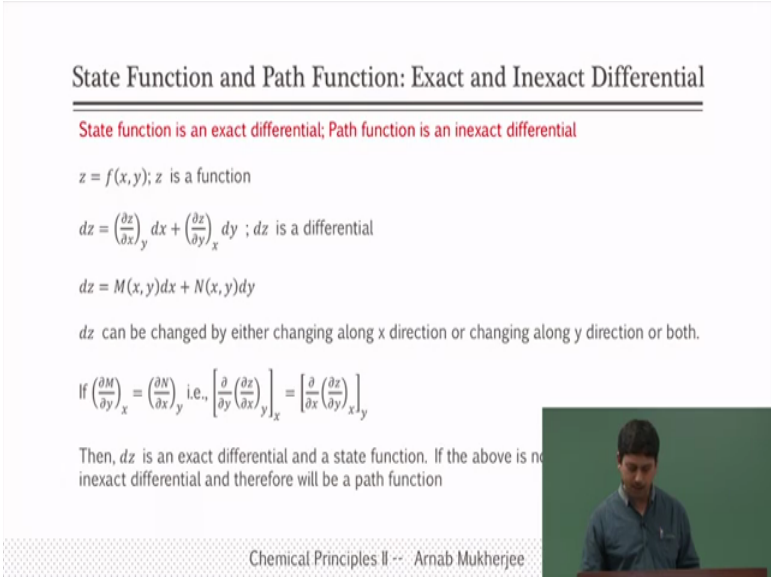


So this is just of the thing, so I will just show you the summary, summary is there in this particular slide, okay.