Lecture - 08
Maxwell's Relations - Part I

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So, in the earlier class we had seen about legendary transformations, which was applied to thermodynamic system. So, the idea was that for an isolated system, I usually have for an isolated system, I usually have U as a function of S, V, N and depending on the experimental situation that we have, we can replace the generator extensive coordinates by the corresponding intensive coordinates.

The conjugate the generalized force conjugate generalized force. For example, if I want to replace entropy by temperature because TS T is the conjugate generalized force, then by

construction I define Helmholtz free energy F. which is u minus TS and this F is a function of T, V and N.

And if I want to see how this is a function of T, V and N we do a d F, and which is d u minus T d S minus S d T. Of course, I have the first law which is T d S is d u plus p d V minus mu d N. So, all of this discussion that we are having particularly given this form of the internal energy, where it is a function of V and N implies that we are talking about a hydrostatic system.

So, in principle you can carry out the same argument by writing u as a function of X 1 X 2 X N where your. This is now applicable for any general thermal thermodynamic system you are talking about; this one alternatively can be written down as T d S minus p d V plus mu d N we shall require both of this.

And one can clearly eliminate d u minus T d S from this to write down this as S d T minus p d V minus plus mu d N. Let us just check whether this is correct d u minus T d S is minus p d V plus mu d N right. Now you see here its T, V and N therefore, this quantity is a function of T, V, N.

So, one can do it for the Gibbs free energy also we did that which basically we wrote down u minus T S plus p d P V and for both of this the prescription of getting to the Helmholtz free energy or the Gibbs free energy was to use the legendary transformation which was y minus d y d x times x.

And this is therefore, this is was for a single variable if I want to generalize this, then this would be y minus del y del x i x i. For the enthalpy we used U plus PV, here we replace this is a function of T, P and N; because you have replaced the volume and the entropy and this is a function of S V sorry this has to be H S, V and N.

All of this thermodynamic potentials that we see have their own applications. For example, F is typically conserved, F is conserved if I have for an isothermal process, for an isothermal

process with no mechanical work. Which means d V is 0 d T is 0, d N we take it usually to be 0 because it is a closed system there is no exchange with the particle.

This is typically for an isothermal process. In present in presence of a constant force for example, you are doing the experiment where you have connected the system to a thermostat as well as to a barostat, where the pressure on the system remains constant as well as the temperature remains constant then G is conserved.

So, if you take the system from a to b then the Gibbs free energy is conserved it remains the same and this is typically for an adiabatic process. So, you have replaced V, I am sorry this has to be S, P, N. We have replaced V by the conjugate force which is the pressure adiabatic process in presence of a constant force. So, I hope this clear to you now I mean one can keep on deriving this kind of thermodynamic potentials.

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$$H = U + PV$$

$$U - \circled{S}\frac{\partial S}{\partial U} - \circled{N}\frac{\partial U}{\partial N} = \boxed{U - TS - \mu N} = \Omega(T, V, \mu)$$

$$U = S\left(\frac{\partial U}{\partial S}\right) + V\left(\frac{\partial U}{\partial V}\right) + N\frac{\partial U}{\partial N} \quad \rightarrow \text{ Euler equation : } U \text{ is homogeneous} \atop \text{ of degree 1}$$

$$= TS - PV + \mu N \qquad U - TS - \mu N = -PV$$

$$\Omega(T, V, \mu) = -PV \qquad \Omega/V = \omega(T, \mu)$$

$$\boxed{\omega(T, \mu) = -P} \qquad \qquad \hookrightarrow \text{Density}$$

$$F(T, \lambda V, \lambda N) = \lambda F$$

a Constant force.
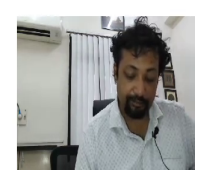
So, one can go further by writing u minus S del S del U minus N del sorry del U del N. And this if I write down this is going to be U minus T S and if you look at the first law which is over here, then you see that del S del N is minus mu.

So, this is going to be plus mu sorry del U del N is plus mu. So, that this is going to be minus mu times N. This is what is called the grand potential omega look at this, here you have started off with U replaced it the entropy by temperature. So, T the volume remains the same and this is a function of mu.

Now, recall what you had done for the, the Euler relation was U is equal to S times del U del S plus V times del U del V plus N times del U del N. So, this is the Euler equation which we had studied because it is a homogeneous because U is homogeneous of degree 1 sorry.

So, therefore, this is T S what is del U del V? If you are confused about del U del V look at the first equation del U del V is minus P. So, this is minus P V plus del U del N is mu N plus mu N. So, look at this structure over here then U minus T S plus sorry minus mu N is minus p V.

So, it follows the omega T V and mu which has the exact structure as this, which you have obtained by eliminating the entropy and the particle number the entropy and the particle number from the functional dependence is minus p times V.

If you define omega by V as small omega which is now a function of T and mu because V has been taken care of then omega T mu is equal to minus p. So, this defines the density and that density must be equal to the negative of the pressure, once again this is a function of T, V, N and the homogeneity would mean this is lambda F.

$$\omega(T, \mu) = -p$$

$$F(T, \lambda V, \lambda N) = \lambda F$$

$$G(T, P, \lambda N) = \lambda G$$

$$H(\lambda S, P, \lambda N) = \lambda H$$

$$\Omega(T, \lambda V, \mu) = \lambda \Omega(T, V, \mu)$$

$$G(\lambda T, \lambda P, N) = G \qquad \text{Density}$$

$$\lambda = \frac{1}{V} \quad \omega(T, \mu) = \frac{\Omega}{V} = -p$$

$$\Omega(T, V, \mu) = V - TS - \mu N$$

G is a function of T P N, so only for the it is homogeneous. So, if you want to write G lambda T lambda P N is just going to be G for the intensive variables if it is a function of an intensive variable, then it is homogeneous with degree of degree 0 with respect to the internal coordinates. We had H which was a function of S, P, and N, S is the extensive quantity this means this is lambda times H it is extensive with respect to only S. Therefore, it is homogeneous of degree 1 with respect to only S.

It is homogeneous of sorry this is lambda with S and N. It is homogeneous of degree 0 with respect to the intensive coordinate which is the pressure P. If you want to look at omega, omega is a function of T V and mu. So, lambda V means lambda omega T V mu right.

So, it is only extensive of with respect to volume which is an it is only homogeneous of degree one with respect to the volume which is expected right. So, this clearly follows from

this if you choose the lambda is equal to 1 by V then this becomes T mu is this becomes omega T mu which is omega over V.

And which we have utilized before and this must be equal to minus of the pressure. So, now, you clearly know for the given the experimental situation I can define the thermodynamic variable which will be relevant. If you look at omega right, what is omega? Omega very quickly let us do this T V mu is U minus T S minus mu N.

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So, let us d omega is d u minus T d S minus S d T minus mu d N minus m d mu. So, I have d u minus T d S minus mu d N minus S d T minus N d mu and d u minus T d S minus mu d N d u minus T d S minus mu d N is minus p d V. So, therefore, this becomes minus p d V minus S d T minus N d mu.

Now, this one has to be careful in defining, you see now no longer I have d N, but d mu this is the potential that you use for an open system. An open system is the one which can exchange particles with the environment. So, you are allowing in the Helmholtz free energy F you are allowing an exchange of temperature energy with respect to the with the bath.

So, that your temperature is kept fixed in the Gibbs free energy you are not only allowing an exchange of energy with the bath, but you are also there is also an exchange of mechanical equilibrium which means the force, the force also has to be same, so that the pressure remains the constant. So, you are allowing for the volume fluctuation.

In this enthalpy, you are allowing for the volume fluctuation, but your container clearly there cannot exchange any energy because it is an adiabatic process or cannot exchange any kind of a heat. In this case omega it is an open system where you are allowed to now not only exchange energy, but you are also allowed to exchange the particle number.

So, in such a system this is the potential that you use is omega and in thermodynamics this is called a grand potential. Isothermal process with no mechanical and chemical work omega remains a constant right. So, this concludes our discussion on thermodynamic potential.

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Now, what we want to do now here is we want to start off with what is called the Maxwell's Relations. And these are set of relations which are extremely useful in thermodynamics and which you can use to manipulate partial derivatives. So, let us start with the first law.

So, d U is T d S minus p d V plus mu d N right. Now I know that this is a state function, if this is a state function this means that d u is and this implies that d u is del U del S d S plus del U del V d V plus del U del N d N.

And therefore, you can immediately identify what are these this corresponds to the temperature, this corresponds to the pressure, this corresponds to the chemical potential is this correct. So, T d S is equal to d U plus p d V minus mu d N and therefore, this is correct.

So, this means that del U del S is equal to T del U del V is minus p and del U del N is mu plus mu right. So, now, you identified this derivatives. Now interestingly since it is a state function therefore, this is an exact differential. Now if it is an exact differential that means, the mixed derivatives would be equal.

So, which means that if I want to take pairwise like this del U del S must be equal to del del S of del U del V. When you had taken del U del V what were the quantities you had to fix S comma N, here you had taken S comma V and here you had taken V comma N right.

When you so this is del U del S V comma N and when you take del l del del V of this this is S constant, this is del U del V S comma N and when you finally, take a derivative with respect to S, what is a held constant? V is held constant, but del U del S is T S V comma N is T. Therefore, this means that del T del V S constant must be del U del V is del P del S volume constant right.

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

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

Maxwell's Relation

$$\boxed{\frac{\partial T}{\partial V}\Big/_{S,N} = -\frac{\partial P}{\partial S}\Big/_{V,N}}$$

$$\boxed{\frac{\partial T}{\partial N}\Big/_{S,V} = \frac{\partial \mu}{\partial S}\Big/_{N,V}}$$

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

$$\boxed{-\frac{\partial P}{\partial N}\Big/_{V,S} = \frac{\partial \mu}{\partial V}\Big/_{N,S}}$$

$U(S,V,N)$
$=$
$F(T,V,N)$
$G(T,P,N)$
$H(S,P,N)$

Let us look at this pair now this and this. If I look at these two pairs then I have del del N of del U del V S comma N, what is held fixed? Volume is held fixed must be equal to del del V of del U del N; S comma V N is held fixed, am I right? Yeah.

But del U del V is minus p. So, this means del P del N volume fixed must be del del V of del mu del del V; N is fixed, correct? And finally, if I want to take this and look at this these two terms. So, that means, what I have I will write down here is del del N of del U del S V comma N and then S is equal to del del S of del U del N S comma V N is being held constant.

But del U del S is, so this means del T del N entropy is equal to del del S of, what is del U del N? Chemical potential mu N held fixed. So, this is the third relation that I get. Now very

quickly, so once I have this please remember that not only here I am holding S as fixed, I have taken a derivative here. So, I am fixing S and N since it is a three variable now.

Here I am fixing V and N. So, this actually has S and V, if I look over here then when I take this derivative I am taking the derivative with respect to, I am holding V and S held fixed and here N and S held fixed. So, V and S, N and S and finally, when I am looking at this derivative I am not only holding I am taking with respect to N and therefore, S and V are held fixed and this is N and V are held fixed.

So, please remember this while you are constructing the these relations. Now these relations are consequence of the fact that your internal energy is an exact differential nothing else purely mathematical origin says that my internal energy is an exact difference. Therefore, it must satisfy the correct criteria that the mixed derivatives must be equal.

These relations are called Maxwell's relations, but you see the problem is that I have derived this relation starting from U, but earlier I just in a little while ago we just derived so many thermodynamic potentials, F of sorry T V and, G of T, P and N omega of sorry first we will write down H of S, P and N.

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Maxwell's Relation

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

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

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

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

$U(S,V,N)$ — 3

Are all $\frac{2}{8}$ these independent?

Maxwell's Relation

- ✓ $F(T,V,N) \times 3$ Thermodynamic potentials
- ✓ $G(T,P,N) \times 3$
- ✓ $H(S,P,N) \times 3$
- ✓ $\Omega(T,V,\mu) \times 3$

And then finally, we had omega what was it function of we eliminated. So, this is T, V and mu. Clearly all of these are thermodynamic potentials and we have only looked at one of them. So, I can derive all such right conditions for each of these potentials nobody can stop me and you are right in doing that also.

So, in principle, you see this one has given you three Maxwell's relation. So, this will give you another 3, this will give you another 3, this will give you another 3, this will give you another 3; 1, 2, 3, 4, 5. So, there are 15 Maxwell's relations, the question is, are all of these independent?

Which means are you finding a repetitive Maxwell's relation when you are looking for F, G, H and omega which you have already obtained. So, that is the question which we want to understand or which we are trying to answer here.

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The straightforward way of doing it is to look at what they are called Jacobians. I am sure you have done Jacobians. Jacobians are very much there when you do coordinate transformation right. When you do coordinate transformations then you the Jacobians are very very useful. So, if you go from x y to u v then you essentially do the Jacobian. The Jacobian is represent written down as this particular way and this determinant of del f del x del f del y del g del x del g del y right.

So, here for example, so, here y is held fixed, here x is held fixed, here y is held fixed, here x is held fixed. And if you want to write down explicitly this is del f del x y constant del g del y

x constant minus del f del y x constant del g del x y constant this is how your Jacobian will look.

Clearly it is a determinant. So, if you exchange the rows and the columns you carry over a minus sign, which means if I want to write down del g del f del x del y then this is going to be del g del x del g del y del f del x del f del y. I do not want to write what is held constant repeatedly you should I know by now know what is and this you see is just done by bringing this over here and this one over here.

And therefore, this is del of f, g by property of determinant is x comma y, del f, g del y del x is again del f del y del f del x del f; sorry del g del y and; terribly sorry for this del g del y del g del x the determinant of this and this is going to be minus del of f, g del of x, y.

Its only for two variables therefore, it is very very easy to understand, but essentially if you have any even permutation of either the numerator or the denominator; then there is no minus sign, but if there is an odd permutation you rearranging the variables there is going to be a minus sign.

$$\frac{\partial(g,f)}{\partial(x,y)} = \begin{vmatrix} \frac{\partial g}{\partial x} & \frac{\partial g}{\partial y} \\ \frac{\partial f}{\partial x} & \frac{\partial f}{\partial y} \end{vmatrix} = -\frac{\partial(f,g)}{\partial(x,y)}$$

$$\frac{\partial(f,g)}{\partial(y,x)} = \begin{vmatrix} \frac{\partial f}{\partial y} & \frac{\partial f}{\partial x} \\ \frac{\partial g}{\partial y} & \frac{\partial g}{\partial x} \end{vmatrix} = -\frac{\partial(f,g)}{\partial(x,y)}$$

$$\frac{\partial(f,g,h)}{\partial(y,y,z)} = -\frac{\partial(g,f,h)}{\partial(x,y,z)} = \frac{\partial(g,h,f)}{\partial(x,y,z)}$$

Even permutation should give you $(+)$

odd permutation $(-)$ ve

So, if you are for example, del f, g, h del of x y z is equal to minus of del g, f, h del of x comma y comma z is equal to del g, h, f.

So, if you once again another take it over here, then this is going to be like this. So, you can clearly understand that you are exchanging the rules twice and therefore, any even permutation should give you a plus sign odd permutation should give you a negative sign.

$$\frac{\partial(f,g)}{\partial(x,y)} = \frac{1}{\frac{\partial(x,y)}{\partial(f,g)}} = \left[\frac{\partial(x,y)}{\partial(f,g)}\right]^{-1}$$

$$\frac{\partial(f,g)}{\partial(x,y)} \frac{\partial(x,y)}{\partial(u,v)} = \begin{vmatrix} \partial_x f & \partial_y f \\ \partial_x g & \partial_y g \end{vmatrix} \begin{vmatrix} \partial_u x & \partial_v x \\ \partial_u y & \partial_v y \end{vmatrix}$$

$$\partial_x f \equiv \frac{\partial f}{\partial x}$$

$$= \partial_x f \, \partial_u y + \partial_y f$$
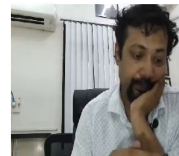
Further del of f, g del of x y is one over del of x y del of f, g. Which I can write down del of x y del of f comma g. If you multiply these two, then you will see that you are going to get 1 the most crucial identity that we want to do del of x comma y u comma v.

Let us write down explicitly what this means del x f, del y f, del x g, del y g. So, my shorthand notation del x f is identical to del f del x y is being held constant. And here of course, I have del x sorry here I have del u x del u y del u stupid error del v x, del u y, del v y, correct?

Let us take just look at the first term the first term is this times this plus this time this. So, del x f, del u y plus del is this correct del y f, I am sorry this into this, what am I doing?

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$$\overline{\left(\frac{\partial(f,g)}{\partial(x,y)} \cdot \frac{\partial(x,y)}{\partial(u,v)}\right)} = \begin{vmatrix} \partial_x f & \partial_y f \\ \partial_x g & \partial_y g \end{vmatrix} \begin{vmatrix} \partial_u x & \partial_v x \\ \partial_u y & \partial_v y \end{vmatrix} = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}$$

$$\partial_x f \equiv \frac{\partial f}{\partial x}$$

$$a_{11} = \partial_x f \, \partial_u x + \partial_y f \, \partial_u y \quad \rightarrow \quad 1^{st} \ term$$

$$= \frac{\partial f}{\partial x}\Big)_y \frac{\partial x}{\partial u}\Big)_v + \frac{\partial f}{\partial y}\Big)_x \frac{\partial y}{\partial u}\Big)_v = \frac{\partial f}{\partial u}\Big)_v$$

$$= \begin{vmatrix} \frac{\partial f}{\partial u}\Big)_v & \frac{\partial f}{\partial v}\Big)_u \\ \frac{\partial g}{\partial u}\Big)_v & \frac{\partial g}{\partial v}\Big)_u \end{vmatrix}$$

So, this multiplies with this so that this is del u x and then I have del y f del u y. So, this is the first term, what do I mean by the first term clearly? This matrix is going to be something like this a 11 a 12 a 21 a 22, what I have written down over here is a 11 you can write down for a 12 and ones the same a 12 and a 21 and a 22, but this is will suffice for us.

This is del f del x y held constant, del x del u v held constant, del f del y x held constant, del y del u v held constant and this is del f del u v held constant. Similarly, if you look at a 22 you are going to get del f. So, this a 11 will be this del f del u v constant, del f del v u constant, del g del u v constant, del g del v u constant. This is going to be the product; this combined thing is going to be equal to this determinant.

$$= \begin{vmatrix} \dfrac{\partial f}{\partial u}\Big)_v & \dfrac{\partial f}{\partial v}\Big)_u \\[1.5em] \dfrac{\partial g}{\partial u}\Big)_v & \dfrac{\partial g}{\partial v}\Big)_u \end{vmatrix} = \dfrac{\partial(f,g)}{\partial(u,v)}$$

$$\dfrac{\partial(f,g)}{\partial(x,y)} \dfrac{\partial(x,y)}{\partial(u,v)} = \dfrac{\partial(f,g)}{\partial(u,v)}$$

$$u=f, \quad v=g \qquad \dfrac{\partial(f,g)}{\partial(x,y)} \dfrac{\partial(x,y)}{\partial(f,g)} = 1$$

$$\dfrac{\partial(f,g)}{\partial(x,y)} = \left[\dfrac{\partial(x,y)}{\partial(f,g)}\right]^{-1}$$

So, but this is nothing, but del of f comma g del of u comma v. So, it follows del f, g del x y is del x y del u, v is equal to del f, g del u, v right. If you choose now u is equal to f v is equal to g then del f, g del x y del x y del f g, I can choose that without any loss of generality because if the right hand side becomes f and del f, g del f, g then this is equal to 1. And therefore, I have del of f, g del of x y is equal to del x y del f, g whole inverse.

So, this is the one that we were trying to show over here, but we have shown it in a different way and we have defined or rather we have derived the more general result which is like this if you are wondering how we came up with this?

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$$\frac{\partial f}{\partial x}\bigg) \frac{\partial x}{\partial u} + \frac{\partial f}{\partial y}\bigg) \frac{\partial y}{}$$

So, if you are wondering, how we came across this? Then we have essentially, we say del f del x del x del u plus del f del y del y. So, if del x just a minute.

So, let us see we want to write see what happens. So, del f del x y constant and then you have del x del u v constant plus you have del f del y x constant and then you have del y del u v constant what we have done was we have written it down as del u del f del u v constant.

If you are wondering how we got this relation the idea is very very simple. So, suppose f is a function of x and y then I know that the differential total differential is del f del x y constant d x plus del f del y x constant d y.

But now I have also told that x is a function of u y is a function of x is a function of u and v, this is stupid. So, I am also told that x is a function of u and v and y is also a function of u and v. That means, d x is del u x d u plus del v x d v and d y is del u y d u plus del v y d v.

Let us substitute this back over here sorry over for d x and this one for d y. If I have that then I am going to write down in a very shorthand notation del x f del u x this multiplies this d u plus del x f del v x d v plus I have del y f del u y d u plus del y f del v y d v.

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If I collect all the terms together then I have del x f del u x plus del y f del u y times d u plus del x f del v x plus del y f del v y times d v, but now if x is a function of u and y and y is a function of u and v, then it follows that f is also a function of u and v therefore, I can also alternatively write down that this as del u f d u plus del v f d v.

And if I compare these two, if I compare these two with this one then it follows that del f del u v constant is del f del x y constant, del x del v v constant plus del f del y x constant del y del

u v constant. So, of course, the second one also follows similarly, and this is the identity that we have used over here to derive this particular relation.