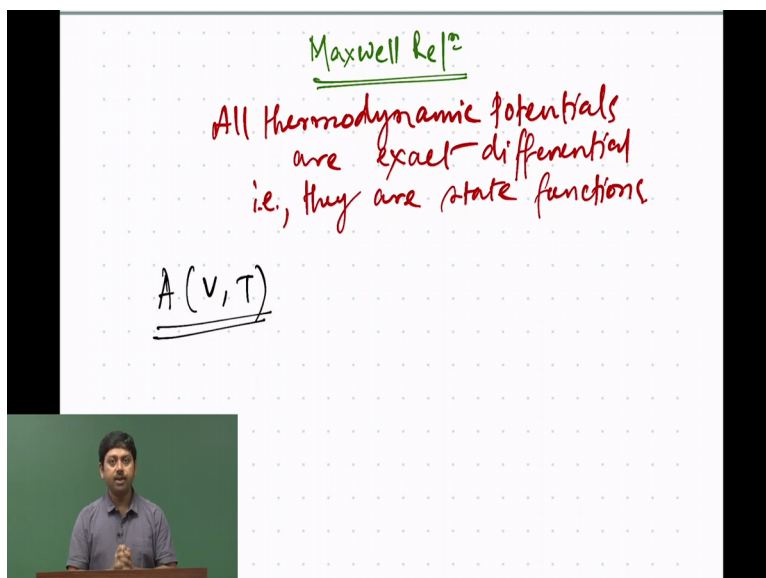


Chemical Principles II
Professor Dr Arnab Mukherjee
Department of Chemistry
Indian Institute of Science Education and Research, Pune
Maxwell Relationships and Applications

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So, to help us understand the thermodynamic relation, there is something called Maxwell relationship which is very famous in thermodynamics. And typically people try to remember it. But I will show you a way that you do not have to remember at all. You have to just number-one thing, that all thermodynamic potentials, all thermodynamic potentials are exact differential and i.e. they are state functions. Just let U , U is a state function, A is a state function, G is a state function, H is a state function. So, they all state functions and therefore they are all exact differential.

What it means is that, either told you that exact differential for example I give you that definition of exact or example of exact differential as height of the ground. So whether you go along X and then along Y or go along Y and then along X , Height does not matter. Height of a particular point is just the characteristic of that point itself, it does not matter how you go to that particular point. You can make 5 rounds and then go to the point, still the height will be the same. So, height is you can say is an exact differential when we talk about the ground.

Similarly A which depends on N V T or I will just write V T because, we are not talking about N here. We are talking about 1 component system, so I will just say that A is a function of V and T . Now, this is a function of multidimensional variables and A is known to be or it is at

least, it is an exact differential. So, since it is an exact differential, it does not matter whether we change the V and then change T or change the T and then change the V, the value will remain the same. And that can be exploited in order to obtain different Maxwell relations.

So I will show you how. So, for example if I do $dA = dU - Tds - SdT$, which means that I am talking about, or let us say, let us make it a little bit more simpler. So, let us say I take a derivative of A 1st at a constant T and then this quantity I take the derivative of that again with respect to T at a constant V, it is the same as if I take the derivative with respect to T 1st at a constant V and then this quantity I take the derivative with respect to V at a constant T. So, they are the same. And they are the same because it is an exact differential. So, you see that by exploiting the properties of exact differentials, we can get now many more relations. For example, we know that dA by dV at a constant T is what? So, we have discussed that here.

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$$\begin{aligned}
 A(T, V, N) &\rightarrow dA = \left(\frac{\partial A}{\partial T}\right)_{V, N} dT + \left(\frac{\partial A}{\partial V}\right)_{T, N} dV \\
 A &= U - TS \\
 dA &= dU - Tds - SdT \\
 &= -pdv - SdT \rightarrow \left(\frac{\partial A}{\partial T}\right)_{V, N} = -S \quad \left. \begin{array}{l} \text{of} \\ \text{state} \end{array} \right\} \\
 &\qquad \qquad \qquad \left(\frac{\partial A}{\partial V}\right)_{T, N} = -P \\
 dU &= Tds - pdv \\
 G(T, P, N) &\rightarrow dG = \left(\frac{\partial G}{\partial T}\right)_{P, N} dT + \left(\frac{\partial G}{\partial P}\right)_{T, N} dP \\
 G &= H - TS \\
 dG &= dH - Tds - SdT \qquad \qquad \qquad = -SdT + vdp
 \end{aligned}$$

Exact-differentiation.

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

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

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

dA by dV at a constant T is nothing but $-P$. So, this is nothing but $-P$. So, we write $\partial \partial T$ of $-P$ at a constant V is $\partial \partial V$ of, what is dA by dT at a constant V , dA by dT at a constant V , I will show you is $-S$, $-S$ at a constant T . So, $-\partial P$ by ∂T is $-$ at a constant V is $-\partial S$ ∂V at a constant T and minus minus cancels, so we get ∂P ∂V at a constant V is ∂S ∂V at a constant T . And that is so much more helpful.

We can easily design an experiment where the volume is fixed. We change the temperature and measure the pressure. And that is somehow, if we did an isothermal experiment where we change the volume and measure the entropy. 1st of all measuring the entropy is very difficult and, but we are getting the same information that if we let say for example, if I talk about an isothermal expansion. So, we know that an isothermal expansion entropy increases, right.

So, we do not isothermal expansion and you cannot tell me the entropy, right but the entropy change that will happen in that isothermal expansion is same as if we did the same experiment by fixing the volume and change the temperature and calculate the pressure. So, that means we fix the volume, increase the temperature, pressure is going to change and that is somehow reflective of the change in entropy with expansion. Without doing this derivation it is impossible to even physically expansion why that will be the case. So, this is one of the Maxwell relation that you will get. So, this is one Maxwell relation.

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$$G \equiv G(P, T)$$

$$\left[\frac{\partial}{\partial P} \left\{ \left(\frac{\partial G}{\partial T} \right)_P \right\} \right]_T = \left[\frac{\partial}{\partial T} \left\{ \left(\frac{\partial G}{\partial P} \right)_T \right\} \right]_P$$

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

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

Similarly, we can exploit free energy, Gibbs free energy in order to do that and we know that Gibbs free energy, G depends on 2 quantities, so and G depends on P and T , right. So, G is a function of P and T , so we can write $\text{del } G$ by $\text{del } T$ at a constant P and the same thing we not take a derivative with respect to T at a constant, no, okay, P at a constant T . So, this will be the same as if I take the derivative with respect to P 1st at a constant T and then take the derivative with respect to T at a constant P . Now we have to just put the values of what is $\text{del } P$ by $\text{del } T$ at a constant P .

So, for that I will just tell you, remind you that dG is $V dP - S dT$. I will just check once. Yes, here it is. Again, you do not have to remember, you can derive again from, you know, directly from U and then do the Legendre's formation of both the variables, make it PT , you get $H - TS$, take the derivative, dG equal to $dH - dS - H dT$ and you will arrive at this. It will take time but you do not need to memorise it, you can actually derive it.

Now, you know that $\text{del } G$ by $\text{del } T$ at a constant P , so when you say constant P your this quantity goes to 0, $\text{del } G$ by $\text{del } T$ will give you $-S$. So, $\text{del } P$ by $\text{del } T$ of $-S$ at a constant T is nothing but and what is dG by dP at a constant T that is nothing but V . So, $\text{del } P$ by $\text{del } T$ of V at a constant P . So, what do we get now, $-\text{del } S$ by $\text{del } P$ at a constant T is nothing but $\text{del } V$ $\text{del } T$ at a constant P . And, how remarkable is that? We can maintain the pressure, positive pressure, change the temperature and calculate the volume, that is somehow calculating the change in entropy by changing the pressure.

So, Maxwell relations make us, make it possible to obtain these kind of relations. So, as you can see we have got 2 relations with 2 thermodynamic potentials, A and G. Similarly we can use H and U to get 2 more thermodynamic relations and there are 4 such thermodynamic relations, but without calculating that we can introduce a mnemonic and help you remember this particular thing.

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$$\frac{\partial^2 H}{\partial S \partial P} = \frac{\partial^2 H}{\partial P \partial S}$$

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

So, the mnemonic that is typically used and why we are using mnemonic, not to memorise but to just you know they can derive everything again, we can use U as, let us say U, we know that U is a function of S and V. So, our formula for U will be $\partial^2 U$ as a function of $\partial S \partial V$, so we are writing in a short notation, that 1st we take the derivative with respect to V at a constant S and then with respect to S at a constant V is same as $\partial^2 U$ by $\partial V \partial S$.

If we use this relation, we will get another Maxwell relation and for H is a function of P and S , so this will give you another Maxwell relation. But, instead of remembering that, instead of deriving that, we can also remember it, there is a pretty easy way to remember it, that is called mnemonic. And in that mnemonic you have to remember this thing, you can, say this, I do not know any, in the want of any better mnemonic I can write this, Sun, please turn violet. Okay, you can find some mnemonic for SPTV. So, what I wanted to mean is that S, P, T, V , that you have to put it in this order. Or you can write another mnemonic as some people are truly, what is with V ? veautiful.

Anyway, so you can decide. The point is that you have to remember S, P, T, V . Okay, so you have, so basically you to write S, P, T and V in this order and then you can do derivative like this. If you do that $\left(\frac{\partial P}{\partial S}\right)_V$ at a constant V , it, the arrow comes just like this and that will correspond to $\left(\frac{\partial T}{\partial V}\right)_S$ at a constant S , okay, so we write in that, right that here. $\left(\frac{\partial P}{\partial S}\right)_V$ is $\left(\frac{\partial T}{\partial V}\right)_S$. However as you can see one arrow is going down and another arrow is going up. So, therefore there is a negative sign.

We can put the negative sign for either of them but for going down you can suit the negative and for going up you can put a positive one. So, you get one Maxwell relation like this. The reason that you have to write S, P, T, V is because your, if you write SPTV, your internal energy depends on S and V , your enthalpy depends on S and P , your Gibbs free energy depends on P and T and your Helmholtz free energy depends on A, T . So, that is the reason you need to write this S, P, T, V because these are the thermodynamic potentials that are governing these 4.

So that is the reason S, P, T, V are required and that is the reason you are getting this So. Whenever you are getting a relationship between this S and V , so that is coming from U . I showed you the relation between for A and G , right. So let us do that. So, for that we need V and T . So, in order to do that again, we can write S, P, T, V and we want to do V and T . So, if we want to do, with respect to V and T , so we can go this way, $\left(\frac{\partial P}{\partial T}\right)_V$ will be same as $\left(\frac{\partial S}{\partial V}\right)_T$.

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And in the, in both cases are coming down so, both are negative. So how do I write that? I write $\partial P / \partial T$ at a constant V coming down means negative let us say, is same as $\partial S / \partial V$ at a constant T , that is also negative, negative negative cancel each other, so we get $\partial P / \partial T$ at a constant V is equal to $\partial S / \partial V$ at a constant T . So, you see how I got that, from this particular arrow I got that. So, ∂P , I took $\partial P / \partial T$ at a constant V , so the arrow goes this way.

Now I have to do the parallel arrow. So, $\partial P / \partial S$, so $\partial S / \partial V$ going this way and both are going downwards, so therefore the arrows R downwards and both are negative, so I will put the negative sign and this is obtained, exactly obtained above as you can see when we derived the Maxwell relations from letter a. You see this is the relation we got, $\partial P / \partial T$ at a constant V is $\partial S / \partial V$ at a constant T . So, this is from A, similarly from G you can get that and from H also you can get that, so we will get all of them.

So let us do another one. So, for another one we want to do with respect to, you know H depends on S and P , right. So, we want to do on S and P , so we can do $\partial T / \partial P$ at a constant S which in that case the arrow goes this way, so therefore the alternate arrow will go this way, so that will be equal to $\partial V / \partial S$ at a constant P . And now both the arrows are going above, so both are positive.

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$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \left[\text{from } H \right]$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \left[\text{from } G \right]$$

Compressibility factor \Rightarrow second derivative of fundamental eq

Compressibility factor \Rightarrow second derivative of fundamental eq:
 Coeff. of thermal expansion, $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$
 Isothermal Compressibility, $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$
 Heat capacity, $C_p = T \left(\frac{\partial S}{\partial T}\right)_P$
 $C_v = T \left(\frac{\partial S}{\partial T}\right)_V$

Now one more is remaining, so this is from H and one more remaining is P and T. We want P and T, so tell S by del P at a constant T we want to do that. So, del H by del P at a constant T is equal to then use a different colour, del P by del T at a constant P. Now, you can see that one is coming down, another is coming up, so del S by del P at a constant T will be the -1. So, this is again obtained from G. So, these are the 4 Maxwell these are the 4 Maxwell relations that you got. And they are all obtained because of the fact that how many potentials are exact differentials.

And we just used their intrinsic variables to obtain these particular quantity. Remember the most important thing is that they are used to make our life simpler, so that experiments can be done on something which is measurable and simple and then can be related to something

which cannot be measurable or very difficult to measure. So, there are some experimentally measurable quantities, they are like, easily experimentally measurable quantities, such as you know ΔV by ΔT at a constant P .


So as I said like earlier also, for example this is difficult to measure but let us say this is easy to measure. So, the thing is that there are some quantities which are, you know easy to measure and they are in general called compressibility factors. And they are 2nd derivative of fundamental equations. For example, these are the 3 quantities, one is coefficient of thermal expansion, known as α which is defined to be $1/V \Delta V$ by ΔT at a constant P . 2nd one is isothermal compressibility, which is called κ_T , which is $-1/V \Delta V$ by ΔP at a constant T .

You see, isothermal compressibility means temperature has to be fixed. Compressibility means what? Volume decreases, and therefore there is a - sign is there because when you increase the pressure, when P is positive, V will be negative and by putting a negative term we get the positive value of compressibility. And one by V is just to normalise it. Similarly coefficient of thermal expansion says that if you put the temperature, then the volume will expand, $1/V$ is again to normalise it.

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Heat capacity, $C_p = T \left(\frac{\partial S}{\partial T} \right)_P$
 $C_v = T \left(\frac{\partial S}{\partial T} \right)_V$

Any thermodynamic derivatives can be expressed in terms of the above heat capacities.



And the, in that case the pressure is kept constant. And heat capacity, heat capacity we know as C_p as $T \Delta S$ by ΔT P for C_v as $T \Delta H$ by ΔT V . Now, any thermodynamic quantity, that is you know, very important quantity, that any thermodynamic quantity, any thermodynamic derivatives or changes can be expressed in terms of the above heat capacity.

They are called in general all heat capacities. Because we can do that, we can express anything in terms of this thing. Since these are measurable, therefore any other thermodynamic derivatives are measurable.

So, although it might look very intimidating that we are you know told us to convert one to another but believe me that is the easiest part, the difficult part is actually to measure them, quantify them, those are more difficult things. A simple change of one derivative to another derivative is not such a difficult thing, once you understand that how to do that. So, therefore this is a great advantage that any of the thermodynamics variables can be written in terms of these heat capacities that are mentioned above.

Okay, so why these compressibility factors are 2nd derivative? Because as you can see that κ is obtained from derivative, taking derivative of V with respect to P . Now V itself is obtained from taking the derivative of the fundamental equations like mentioned above that if you can go above, you will see this V is, this V is obtained as $\left(\frac{\partial G}{\partial P}\right)_T$. So, V itself is 1st derivative of therefore when you take the derivative of V , then it becomes a 2nd derivative. So, now we are going to show you the usefulness of this Maxwell relations.

Remember, in, during the calculations of Joules coefficients, we encountered a term called $\left(\frac{\partial U}{\partial V}\right)_T$ and at a constant T and we did not have any expression of U from the equation of state and therefore we could not calculate that. But, now since we have, now since we know that how to get the equivalent derivatives from Maxwell relations, we can use that in order to calculate the quantity.

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Handwritten derivation on a grid background:

$$dU = Tds - pdv$$

divide both sides by dv

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

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

Diagram illustrating the Maxwell relation used in the derivation:

s	p
v	T

A square with a clockwise arrow around it, indicating the cyclic relationship between the variables s, p, v, T .

For example I will show you, so we know that dU is $T dS - P dV$, that we already know, I am just writing it here. And then we are going to take the derivative, okay, now we are going to take the derivative with respect to V . So, here is a very important point, I used to be myself, get lot of confused, used to get confused a lot earlier when I was learning myself that how do I take the derivative of this particular thing. So, when I have written already the U in a differential form, taking derivative is nothing but dividing by another differential form.

So, let us say I want to take a derivative with respect to V , so what simply I am going to do is that divide both sides by dV . Now that gives us dU by dV and I want to do that at a constant temperature. So, now $T dS$ by dV at a constant temperature - $P dV$ by dV at a constant temperature. Now, that simply I am writing as $\frac{dU}{dV}$ at T and since T is just a constant will come out $\frac{dS}{dV}$ at a constant T - dV dV will cancel and I am going to get P . So, that is how you have to take derivative of this, in this differential.

Now we wanted to calculate this particular quantity dU by dV in the Joules expansion case. Now how do I get that? Because we encountered this particular quantity $\frac{dS}{dV}$ at a constant T and that is difficult to measure, we do not do how to do that. So you remember that $\frac{dU}{dV}$ at a constant T is equal to $-C_V \alpha_J$, where α_J is the Joules coefficient and isothermal version of the Joules coefficient is $\frac{dU}{dV}$ at T . And we said that for ideal gas it would be 0 and for a nonideal gas like Van der Waal gas or the real gas, it will be nonzero.

So what it means is that when you expand the volume at a constant internal energy U and then temperature is not going to change for an ideal gas, whether it will decrease for a real gas or for one was. So, basically, basically this is the coefficient that one has to calculate. So, but in order to calculate $\frac{dU}{dV}$ at a constant T , I have to get this particular quantity $\frac{dS}{dV}$ at a constant T and that is, that is I do not know how to calculate that unless I talk about the Maxwell situation.

And what is that Maxwell's relation, we will do that again, we will not remember, we will just do SPTV and we know that $\frac{dS}{dV}$ at a constant T is nothing but $\frac{dP}{dT}$ at a constant V and both are going down, so both are positive. So, I can write that as $\frac{dP}{dT}$ at constant V - P . Now that is very easy for us to calculate.

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

Ideal gas, $PV = nRT$
 $P = \frac{nRT}{V}$
$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{nR}{V} \left(\frac{\partial T}{\partial T} \right) = \frac{nR}{V}$$


①
$$\left(\frac{\partial U}{\partial V} \right)_T = T \times \frac{nR}{V} - P$$

$$= P - P$$

$$= 0$$



$P\bar{v} = RT$ $\bar{v} = \frac{V}{n}$
 $P(\bar{v}-b) = RT$
 $P = \frac{RT}{\bar{v}-b}$
 $P = \frac{RT}{\bar{v}-b} - \frac{a}{\bar{v}^2} \rightarrow$ Van der Waal gas eqn of state.



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

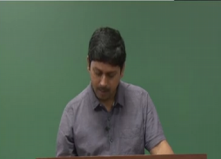
$$= \frac{TR}{\bar{v}-b} - P$$

$$= \frac{RT}{\bar{v}-b} - \frac{RT}{\bar{v}-b} + \frac{a}{\bar{v}^2}$$

$$= \frac{a}{\bar{v}^2} > 0$$

$$= -C_V \eta_J$$


$$\eta_J = -\frac{1}{C_V} \frac{a}{\bar{v}^2}$$



$$\eta_J = -\frac{1}{C_V} \frac{a}{V^2} < 0$$

-9-

Joule's coeff is -ve



So, for ideal gas you know that PV equal to nRT , so P equal to nRT by V so, let us take the derivative with respect to temperature at a constant volume. So, $\frac{\partial V}{\partial T}$ at a constant V is wala with constant, nR is constant, so nR by V $\frac{\partial P}{\partial T}$, which means nothing but nR by V . Now, I put that are above in that particular equation 1. $\frac{\partial U}{\partial V}$ at a constant T is now T into nR by $V - P$. And you know nR by V is nothing but P , so $P - P$ is equal to 0, so you can see that $\frac{\partial U}{\partial V}$ at a constant T is 0.

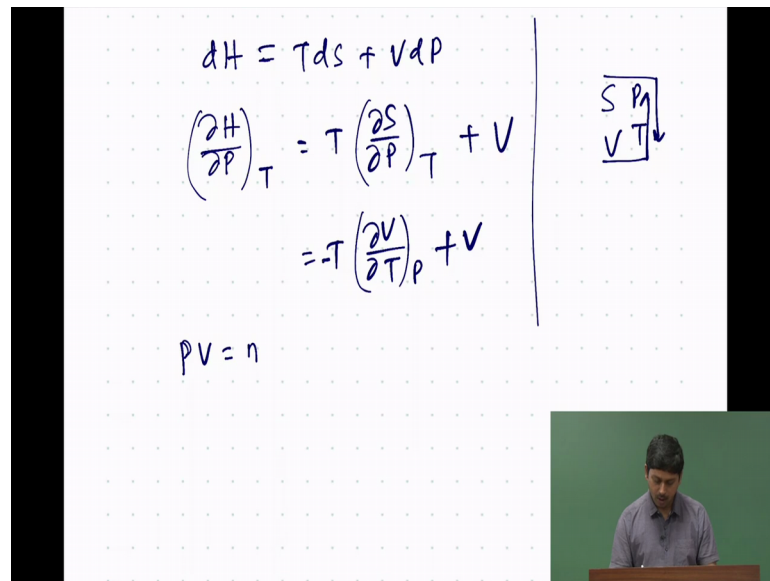
Since that is 0 and C_V is nonzero η_J must be 0. So, Joules coefficient is 0 for an ideal gas. However that is not true for a real gas. And that we are going to show you. So, real gas is very difficult to do anyway, so Van der Wal gas is something that is intermediate between real gas and ideal gas because Van der Wal has that small volume V . So you know that for ideal gas PV equal to RT , PV bar, bar means V by n , so for a real gas we use some b factor for the size. And we write as this, however in order to have attraction between the particles, we put another term as a by V square.

So that is our Van der Wal's gas equation of state. Now, if we want to calculate for this quantity $\frac{\partial P}{\partial T}$ at a constant V , what do we get? We get R by $V - b$, that said, we get R by $V - b$. So, $\frac{\partial U}{\partial V}$ at a constant T is, I just want to see a T $\frac{\partial P}{\partial T}$ V , T $\frac{\partial P}{\partial T}$ $V - P$. Now TR by $V - b - P$. And we know what P is, right, P is this quantity. So, RT by $V - b - RT$ by $V - b + a$ by V square. Now, this term cancels, giving me a by V square.

So, as you can see that this V square of course is a positive quantity and a is also a positive quantity, so therefore this is greater than 0. Since this is greater than 0, you know that this is equal to $-C_V \eta_J$. So, therefore η_J is -1 by $C_V a$ by V square. And C_V is positive quantity, V

square is positive quantity, therefore nJ is less than 0. Therefore the Joules coefficient is negative, indicating that for a free expansion, the temperature of the system will decrease if there is an attraction between the particles. And that is indicated by a , if a would be 0, that means there is not reason between the particles, every of the particles have some size, the tools coefficient will not be affected because a is nonzero, because a is a positive quantity, because there is an attraction between the particles, when there is expansion, particles have overcome that attraction.

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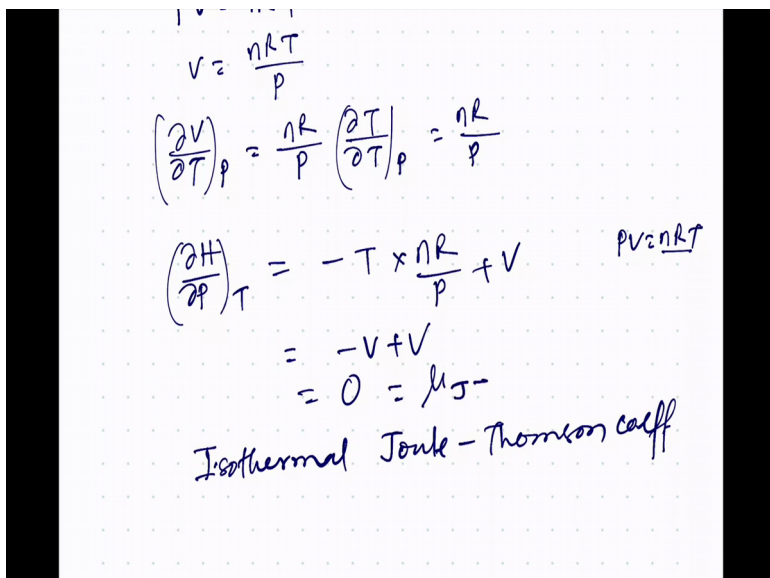
Handwritten derivation on a grid background:

$$dH = T ds + V dP$$

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

$$= -T \left(\frac{\partial V}{\partial T}\right)_P + V$$

Below the equations, it says $PV = n$. To the right, there is a small diagram with a box containing S and P on the top axis and V and T on the bottom axis, with a downward arrow next to it.



Handwritten derivation on a grid background:

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

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

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

$$= -V + V$$

$$= 0 = \mu_{JT}$$

Below the equations, it says "Isothermal Joule-Thomson coeff" and "PV = nRT".

And that will reduce the temperature of the system and that we can see from, after we make this Maxwell's relation, it was possible for us to calculate that. So, we can do the similar things with enthalpy. So, we know that dH is $T ds + V dP$, so I take derivative with respect to

P on both sides, so at a constant temperature, so we get ΔS by ΔP at a constant temperature + V. So, now I again use Maxwell's relation, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$, so ΔS by ΔV at a constant T is nothing but ΔP by ΔT at a constant P + V.

So, that is my ΔH by ΔV at a constant T. Now we know that PV equal to, oh yeah, because now you see that the errors are going up and down, so one will be -, so ΔS by ΔV at a constant T is - ΔV by ΔP at a constant P. Now, PV equal to nRT for an ideal gas, so we need to calculate V, so V is nRT by P, so if I take a derivative with respect to T at a constant pressure, then it is nR by P, that is it, ΔT by ΔT at a constant pressure, which is nothing but nR by P.

So, which means ΔH by ΔP at a constant T is equal to - T into nR by P + V. So, as you know that PV equal to nRT, right, so PV equal to nRT, so therefore nR by P is nothing but V, so - B + PV equal to 0. So, ΔH by ΔT at a constant T is 0 for an ideal gas, and if you remember that is nothing but the isothermal Joules Thomson coefficient. Recalled that is μ_{JT} . So, that means in isothermal condition if you change the pressure, then enthalpy is not going to change and therefore the temperature is also not going to change because there is a (0)(31:00) temperature.

(Refer Slide Time: 31:07)

The slide features a white background with a light gray dot grid. At the top, the text "Special Role of $G(T,P)$ " is written in green and underlined. Below this, two equations are written in black: $S = -\left(\frac{\partial G}{\partial T}\right)_P$ and $V = \left(\frac{\partial G}{\partial P}\right)_T$. Underneath these, the equation $H = G + TS$ is written, followed by $= G$ on the next line. In the bottom right corner, there is a small video inset showing a man in a blue shirt sitting at a podium against a green background.

$$\begin{aligned}
 U &= H - PV \\
 &= G - T \left(\frac{\partial G}{\partial T} \right)_P - P \left(\frac{\partial G}{\partial P} \right)_T \\
 \\
 A &= U - TS \\
 &= G - T \left(\frac{\partial G}{\partial T} \right)_P - P \left(\frac{\partial G}{\partial P} \right)_T + T \left(\frac{\partial G}{\partial T} \right)_P \\
 \\
 \boxed{C_p} &= T \left(\frac{\partial S}{\partial T} \right)_P = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_P
 \end{aligned}$$

So, now I am going to show you some special role, okay, so before I do that, you can do the same thing for Van der Waal gas as well, that I am not doing. So, special role of GTP. So, GTP is very special in the case that we can get everything from GTP, I am going to write down some of that here. If you have GTP, that means you have free energy at constant temperature and pressure, that means you get basically many many quantities. For example, as you know S already, it is ΔG by ΔT at a constant P. Which means if you want to get your S, you vary temperature and calculate, at every temperature calculate the G, get the slope and do the experiment in constant pressure, get the slope and you will get the value of entropy.

That is one of the way to get the entropy. In a lot of examples, for example when we talk about solvation entropy, that means protein or bio molecule is in water, sugar and that, whether that changes the entropy or not or iron, when you put sodium chloride in water, you know what happens is that sodium and chloride, they attracted to each other. Which means that they would like to be close together. But what happens is that when you put water, they get separated because each of them get solvated by water.

So, 1st minima that was there, that is an energetic minima because that was solvated, that was together by Coulombic attraction. But the later one, when the water molecules actually come and solvates both of them, that is called an entropic minima because that is solvent mediated minima that comes by, after you put the water to solvate them. So, the thing is that we want to calculate that. What you have to calculate is you have to vary the temperature and get the free energy of the process. Free energy calculation is easy because it typically can be associated as you can see later, for when you talk about equilibria binding constant and all, you will see that ΔG is related to something like an equilibrium constant.

So, once you know the equilibrium constant, then, so once you know the number of unbound and bound species, so number of or mole of reactant and product, you get an equilibrium constant. Once you have an equilibrium constant you get free energy, once you are free energy, as you can see, then actually you can get to entropy by varying the temperature. So, that is what is very important, people often forget how to get that but this thermodynamic relations can tell you that already.

How do you get V then? So, you can get V by $\frac{\partial V}{\partial P}$ at a constant T . You can get H as, you know $H - TS$ is G , so H is $G + TS$. G you already know, so only thing you need to know is S . So, it is $G - T$ into $\frac{\partial G}{\partial T}$. And then you want to get let us say U , U is $H - PV$, U is $H - PV$ because H is $U + PV$. So, how do you get H then? So you get H as, okay, again H you already have from here, so you can write $G - T$ $\frac{\partial G}{\partial T}$, you want P and V , so you have V here, T , okay, so that also you got. And then you want to get A , A is $U - TS$, U already got from above, S already got from above, you can get that.

And you can show that it can be written as $G - T$ $\frac{\partial G}{\partial T}$ - P $\frac{\partial T}{\partial P}$, so this is $U - TS$. And SS is already given above, you, so it will be $+ T$ $\frac{\partial G}{\partial T}$ at a constant P . So, we can see that, we can get pretty much everything from G . C_P , C_P as you know as T $\frac{\partial S}{\partial T}$ at a constant pressure, which again is $- T$ and S is again the derivative with respect to energy, right. So, it is $- T$ $\frac{\partial^2 G}{\partial T^2}$ P . Now, you see why heat capacity is 2nd derivative of the thermodynamic potential. And that can be shown for every other quantity as well.