Indian Institute of Technology Kanpur

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Course Title
Engineering Thermodynamics

Lecture – 38

Thermodynamic Property Relations 2

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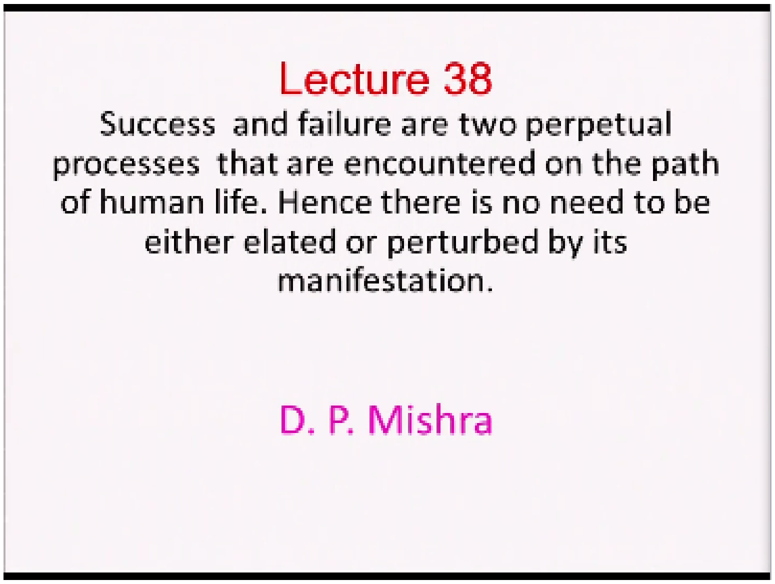

Lecture 38

Success and failure are two perpetual processes that are encountered on the path of human life. Hence there is no need to be either elated or perturbed by its manifestation.

D. P. Mishra

Let us start this lecture with the thought process success and failure are to perpetual processes that are encountered on the path of human life. Hence there is no need to be either elated or perturbed by its manifestation. So if you recall that in the last lecture we discuss about the partial derivative method and Jacobean methods and we have recapitulate the rules which govern this partial derivative method there are basically three rules one is the reciprocal rule, chain rule, and the, what you call cyclic rule.

So these three are to be used and then later on we also find out the relation show to connect these Jacobeans with the deliver partial derivatives, and we have also enumerated the four rules. And later on we looked at the thermodynamic potential we discuss about four potentials basically internal energy, enthalpy, Gibbs function and Elmer’s function or potential whatever you call and we also derived the relationship connecting those change in the potential thermodynamic potential in terms of measurable properties and non valuable property right. And those things we will be now connecting it with the measure and non measurable properties.

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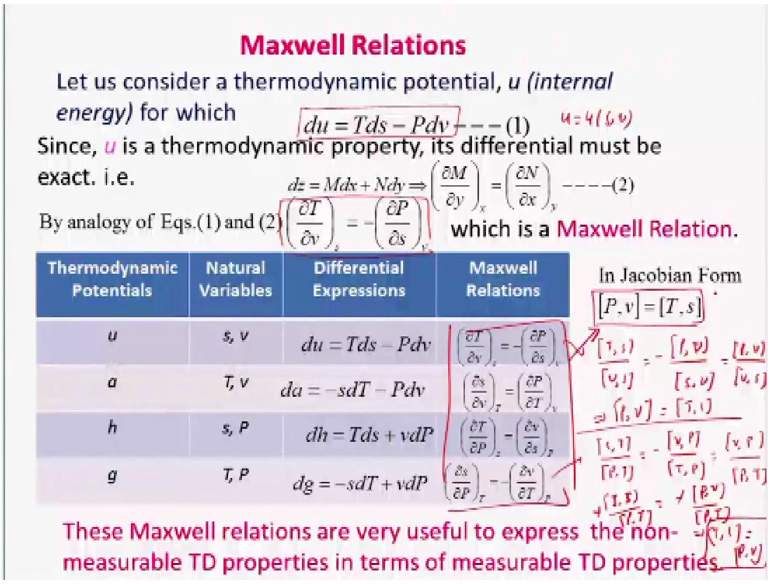

Maxwell Relations

Let us consider a thermodynamic potential, *u (internal energy)* for which $\boxed{du = Tds - Pdv}$ - - - (1) $u = u(s,v)$

Since, u is a thermodynamic property, its differential must be exact. i.e.

$$dz = Mdx + Ndy \Rightarrow \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \text{ - - - - (2)}$$

By analogy of Eqs.(1) and (2) $\boxed{\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v}$ which is a Maxwell Relation.

Thermodynamic Potentials	Natural Variables	Differential Expressions	Maxwell Relations
u	s, v	$du = Tds - Pdv$	$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$
a	T, v	$da = -sdT - Pdv$	$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$
h	s, P	$dh = Tds + vdP$	$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$
g	T, P	$dg = -sdT + vdP$	$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$

In Jacobian Form

$$\boxed{[P,v] = [T,s]}$$

$$\frac{[T,s]}{[v,s]} = -\frac{[P,v]}{[s,v]} = \frac{[P,v]}{[v,s]}$$

$$\Rightarrow [P,v] = [T,s]$$

$$\frac{[s,T]}{[P,T]} = -\frac{[v,P]}{[T,P]} = \frac{[v,P]}{[P,T]}$$

$$\Rightarrow \frac{[T,s]}{[P,T]} = + \frac{[P,v]}{[P,T]}$$

$$\Rightarrow \boxed{[T,s] = [P,v]}$$

These Maxwell relations are very useful to express the non-measurable TD properties in terms of measurable TD properties.

So in today's lecture, so let us consider a thermodynamic potential that is internal energy which is more natural, because it comes from the first law of thermodynamics whereas other properties are derived right. And for which we can write down that is the first Gibbs equation that is du=Tds-Pdv and u as we know is the basically thermodynamic properties and hence its differential must be exact.

And for that what we will do we will use this condition that is ∂M/∂Y when X is equal to constant equal to ∂N/∂X and Y constant if the form is basically you know Z-Mdx+Ndy, there is a lot of similarities between this and also this one right is not it. And if you look at in this case in this equation 1 the M is basically T and in equation 2 you can say N=-P right. So I can write this condition like to a property like internal resistive property as basically ∂T/∂V when S remaining constant is equal to - ∂P/∂S when V is remaining constant.

So if you look at basically this one what it indicates if you look at left hand side that is basically change in the temperature with respect to specific volume whereas the right hand side change in pressure with respect to entropy. As we know that entropy is not a measurable property right whereas temperature, volume, pressure are measurable property that means I can relate the non measurable properties with the measurable properties with this expression right okay.

And this expression is basically known as the maximal relation it is a very important aspect which is being used in thermodynamics particularly for having the thermodynamic relations. The objective of thermodynamic relation is to connect the non measurable properties with the measurable properties. So in the similar manner we will be using others Gibbs equations right there are total four Gibbs equation we have seen or we have derived in the last lecture, so we will be using that.

So let us look at the what are the thermodynamic potential we have discussed till now that is one is internal energy right and which is a function of S and V right is not it if you look at this in from this equation you can write down U is a function of S and V. And by using this U as a property of the system then I can find out these expressions very easily right. And that is the differential and this being derived from the differential relationship what we call Gibbs equation that is equation number one.

So you know we can this is this equation is basically Maxwell equation in similar manner right I can write down that change in the Elmer's function is equal to $– sdT-Pdv$ we have already derived this. And by using the same condition I can get $\partial S/\partial V$ when temperature remaining constant is equal to $\partial P/\partial T$ when volume remaining constant. If you know this expression right differential expression very easily you can get a Maxwell relationship right.

In the similar fashion we can write down that $dh=Tds+vdP$ right and from this expression I can write down $\partial T/\partial P$ when entropy remaining constant is equal to $\partial V/\partial S$ when pressure remaining constant if you look at all are trying to connect entropy with respect to the rest of the, what you call measurable properties like pressure, temperature, you know specific volume.

So in the similar fashion I can get $dg = -sdT + vdp$ and from this I can get that is $\partial s /\partial P$ when temperature remaining constant is equal to minus $\partial V / \partial T$ when pressure remaining constant so these 4 are basically the Maxwell relations right and this is in the differential form but I want to write down in Jacobean form what it would be right it will be very simple one right.

Okay and that is basically Jacobean = Jacobean PS you can say with respect to PR or any other thing right, so is it true right and this is a very important you know expression these Maxwell relations because that you can connect the non measurable property to this measurable properties and coming back to that like this Jacobean form is a very simple and very easy to remember you know like let us consider this one right.

If I consider the first one right here what I can write down I can write down T, s V, s = - P, v - into S, v right, so is equal to can I write down this way that is P,V into V,s can I write down is very easy I am just changing this negative was you know has gone out because I have interchanged these variables here right, so therefore I can write down very easily that is PV Jacobean P, V = Jacobean P, S, yes or no right.

Similarly I can take another one let us say this one I am taking now right I can write down s, T Jacobean P, T = - V, P and T, P similar way I can write down this right this as basically if I write down I can write on V, P right equal to P, T can I have a negative sign has gone right so can I write down this as S, T I can also write down as P, S okay T, S here into P, T - = -P, V into P, T yes or no, so minus, minus will cancel it out so I will get basically P, S = P, V Jacobean.

So the same thing I am getting, so all this thing you can see all for Maxwell relation right all these for maximal relationship can be converted into one equation in case of Jacobean form so that is very easy to remember and handle we will see.
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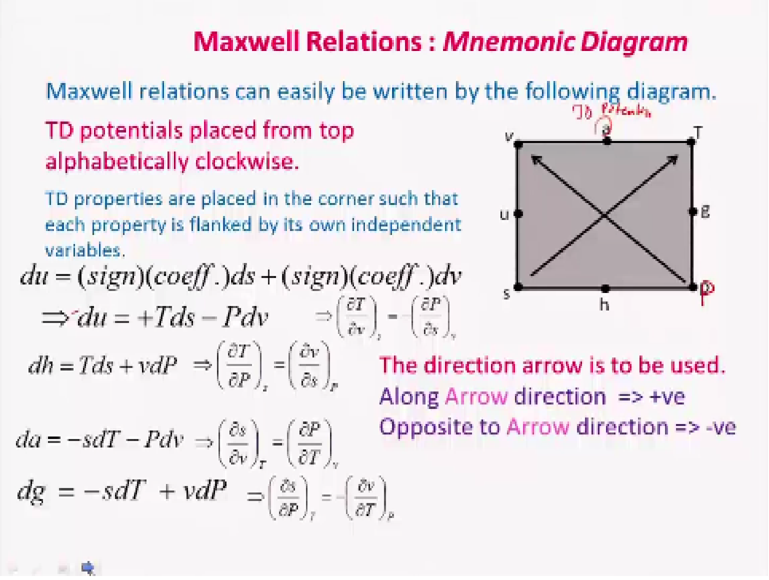

Maxwell Relations : *Mnemonic Diagram*

Maxwell relations can easily be written by the following diagram.

TD potentials placed from top alphabetically clockwise.

TD properties are placed in the corner such that each property is flanked by its own independent variables.

$$du = (sign)(coeff.)ds + (sign)(coeff.)dv$$

$$\Rightarrow du = +Tds - Pdv \quad \Rightarrow \left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$$

$$dh = Tds + vdP \quad \Rightarrow \left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$$

$$da = -sdT - Pdv \quad \Rightarrow \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

$$dg = -sdT + vdP \quad \Rightarrow \left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$$

The direction arrow is to be used.
Along Arrow direction => +ve
Opposite to Arrow direction => -ve

So and also you can think of mnemonic diagrams you know which you definitely might have used you know like in your earlier days to remember certain things you know like Maxwell relation can be easily written in the diagrammatic form like you know I can think of putting this in anti-clockwise if you look at this one here right a, g, h you this is alphabetical order and these are all what you call potentials right and we know that a is basically function of v and d you can write down here similarly g is a function of t and p this is basically capital P okay pressure and h is a function of entropy and P and u is a function of s and v.

And of course you know this is a what you call as I told that this potential a this is potential right this is basically thermodynamic potential right a, g, h is our place you know in anti-clockwise sorry this is in a clockwise facing clockwise direction right because this is the clockwise and it is flanked by the there what you call functions or the independent the variables right and now I can write down the gifts equation you know very easily like vu I am going to take an example is equal to sign into coefficient into ds and also alert we use sign and coefficient v.

So if I take that you know this u if you look at you is basically you know the independent variables s and we so if you look at the sign and the coefficient open for s will be T if it is in this direction you know direction of the arrow then it will be positive sign, so this I can say positive time and what will be coefficient here for du it will be basically T the coefficient is T similarly and sign for this in a way because it is on the opposite direction of the arrow so therefore the it will be negative sign and coefficient will be P.

So if you look at this is ds, dv and is equal to dq so you can write down this basically du is equal to $TdS - PdV$ this is the gives if you can remember it is fine otherwise also this is the helpful this diagram will be helpful to remember you keeping the sign in to in you know in this so similar way I can have you know like, from of course once you know this relationship I can very easily find out Maxwell relation right $\partial T / \partial V = - \partial P / \partial s$ V is remaining constant right.

And we can from this diagram you know we can have a relationship dh is equal to $TDs + VdP$ let me just tell you again how because if look at h, h is having two independent variable one is s and other is P so if you look at that for the s the coefficient will be T right and it will be positive so therefore this Is positive T and in this case for the P the coefficient is V it is also positive.

So therefore it is dh is equal to Tds + VdP right and you can get the maximal relation very easily and similar way you can you know have the Gibbs function and if you look at Gibbs function is basically two independent variable one is P and T if you look at T the sign will be in this case what it will be it will be you know negative and the coefficient will be s so therefore it is a negative yeah right therefore it is a negative sign here and of course for the P that is the way it is in the same direction of the arrow.

So therefore it is positive in similar way we can also look at the Elmer’s function and that is equal to dq is equal to – sdT - PDv and you can get a maximal relationship so if you look at this is the way how you can remember this Maxwell relationship so that you can utilize for solving the problems.

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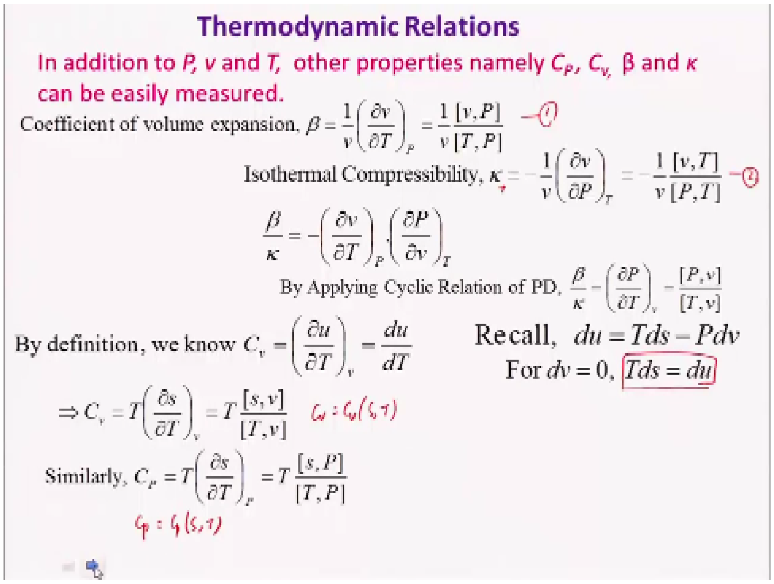

Thermodynamic Relations

In addition to *P*, *v* and *T*, other properties namely C_P, C_v, β and κ can be easily measured.

Coefficient of volume expansion, $\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = \frac{1}{v}\frac{[v,P]}{[T,P]}$ —①

Isothermal Compressibility, $\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = -\frac{1}{v}\frac{[v,T]}{[P,T]}$ —②

$$\frac{\beta}{\kappa} = -\left(\frac{\partial v}{\partial T}\right)_P \cdot \left(\frac{\partial P}{\partial v}\right)_T$$

By Applying Cyclic Relation of PD, $\frac{\beta}{\kappa} = \left(\frac{\partial P}{\partial T}\right)_v = \frac{[P,v]}{[T,v]}$

By definition, we know $C_v = \left(\frac{\partial u}{\partial T}\right)_v = \frac{du}{dT}$

Recall, $du = Tds - Pdv$

For $dv = 0$, $\boxed{Tds = du}$

$$\Rightarrow C_v = T\left(\frac{\partial s}{\partial T}\right)_v = T\frac{[s,v]}{[T,v]}$$ $C_v = C_v(s,T)$

Similarly, $C_P = T\left(\frac{\partial s}{\partial T}\right)_P = T\frac{[s,P]}{[T,P]}$

$C_p = C_p(s,T)$

Very easily and we look at basically thermodynamic relations right and of course for that we need to use some more properties apart from Pv T and those are C_P C_V β, β you know like it is a coefficient of volume expansion K that is the isothermal compressibility and we know that coefficient of volume expansion is β is equal to 1 over V into ∂V by ∂T when pressure remaining constant so I can write down that in the Jacobean form that is one over V is equal to Jacobean VP with respect to TP right just to convert that you know parcel the derivative into the Jacobean form.

In the similar way isothermal compressibility K which is equal to – 1 over V into ∂V by ∂ P when temperature remaining constant and is equal to you know 1 by V into Jacobean VT with respect to PT so if you look at sometimes so you keep in mind I use this isothermal compressibility sometimes I use K_t okay you just check I mean K_t and K are same right that kind of things you can keep in mind so β /K you can think of you know like you can just divide that equation is this if I say this is equation one right.

And equation two you can get β/ K is equal to ∂V / ∂T pressure remaining constant into ∂P by ∂ Vt of course the with a minus sign and you can apply this cycle relationship you know and you can find it out basically that is equal to you can simplify this expression write as ∂P by ∂T into V using the cycle in essence right and by definition we knows CV is equal to u by ∂T when volume remaining constant and that is equal to ∂u by dT and we know that du is equal to TDS - PDV right.

So we can use that and when dv is constant that is nothing but your Tds, Tds is equal to du and I can write down that in place of you know like C_V is equal to ∂s / ∂T when volume car constant is equal to P Jacobean is B with respect to TV right because in place of this row you can utilize this expression right in the similar way we can also express in the C_P in terms of entropy that is C_P is equal to T ∂s by ∂T when pressure remaining constant and right so you can basically can write down C_P is a function of s and T and similarly C_V is a function of what you call s and T.

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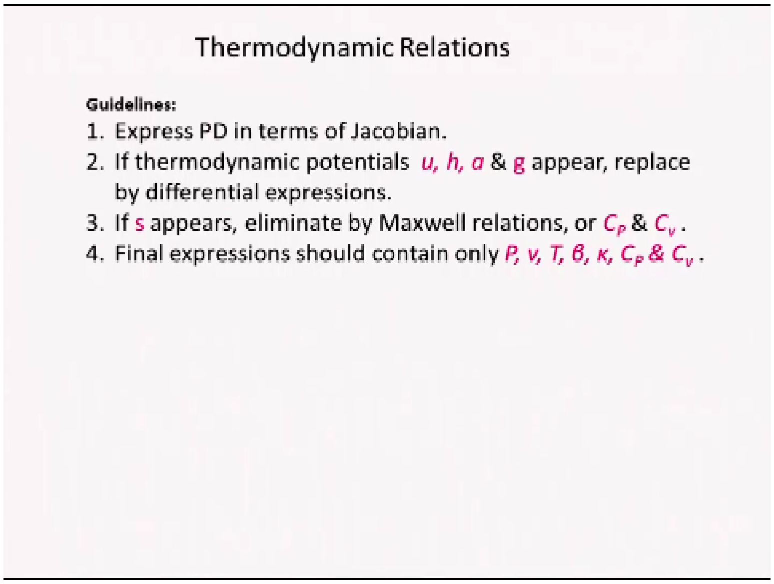

Thermodynamic Relations

Guidelines:

1. Express PD in terms of Jacobian.
2. If thermodynamic potentials u, h, a & g appear, replace by differential expressions.
3. If s appears, eliminate by Maxwell relations, or C_P & C_v .
4. Final expressions should contain only $P, v, T, \beta, \kappa, C_P$ & C_v .

So if you look at like you know these are the guidelines I would like to view how you will you know handle the thermodynamic relations first you express the partial derivative in terms of Jacobean right that is the easier way and if thermodynamic potential u, h, a, g appear in the expression replaced by the differential expression you know like for the oil gives free gives sorry gives equation we have derived four equations and if s appears in the expression you know you eliminate that by using Maxwell relations or CP or CV and final expressions should contain only the measurable properties and those are P, V, T,B and then β K C_P and C_V.

So these are all measurable properties so therefore you should do that and I will tell you like you can use both Jacobean and partial derivatives or you can use the partial derivative itself you know like alone and the equation will be very helpful and it will very faster also in deriving the expressions.

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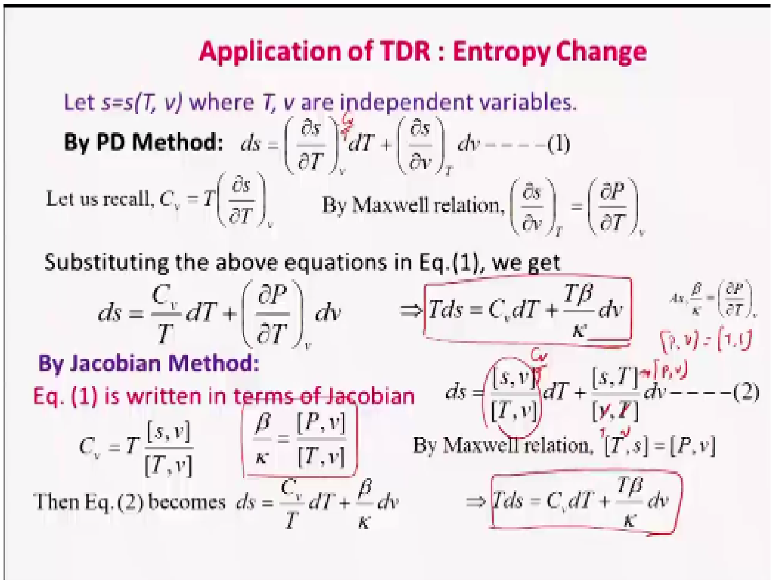

Application of TDR : Entropy Change

Let $s=s(T, v)$ where T, v are independent variables.

By PD Method: $ds = \overset{C_v}{\left(\frac{\partial s}{\partial T}\right)_v} dT + \left(\frac{\partial s}{\partial v}\right)_T dv$ ----(1)

Let us recall, $C_v = T\left(\frac{\partial s}{\partial T}\right)_v$ By Maxwell relation, $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$

Substituting the above equations in Eq.(1), we get

$$ds = \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_v dv \quad \Rightarrow \boxed{Tds = C_v dT + \frac{T\beta}{\kappa} dv}$$

As, $\frac{\beta}{\kappa} = \left(\frac{\partial P}{\partial T}\right)_v$

$[P,v] = [T,s]$

By Jacobian Method:

Eq. (1) is written in terms of Jacobian $ds = \overset{C_v}{\frac{[s,v]}{[T,v]}} dT + \frac{[s,T]}{[v,T]} \xrightarrow{} [P,v]\, dv$ ----(2)

$C_v = T\frac{[s,v]}{[T,v]}$ $\boxed{\frac{\beta}{\kappa} = \frac{[P,v]}{[T,v]}}$ By Maxwell relation, $[T,s] = [P,v]$

Then Eq. (2) becomes $ds = \frac{C_v}{T} dT + \frac{\beta}{\kappa} dv$ $\Rightarrow \boxed{Tds = C_v dT + \frac{T\beta}{\kappa} dv}$

So let us look at some kind of you know how we can derive the relationship we will first consider the entropic change which is you know this thing so we have seen that entropy is a function of T and V where TV are the independent variables right and we will use the partial derivative method that is ds = ∂s/∂T when volume remaining constant into dT + ∂s/∂v temperate for constant temperature into DV right.

And if you look at this is your first term is the M and you can say this is n then you can very easily find out what it would be right so if you look at the recall this one the CV is basically $(\partial s/\partial tT)_v$ right into T, so therefore I can replace this term you know I can replace this term basically by CV/T right very easily and we need to also look at ∂s/∂V when temperature is remaining constant and from maximal relation we know ∂ /∂V T is nothing but your ∂P/∂T for constant volume right.

That we can use here Maxwell relations so if we do use this one I can get that ds = v/T dT + ∂P/∂T when volume remaining constant into dV right that we can we have already replaced this thing so if you look at all these things are basically right hand side you know changing right hand side are what you call measurable properties right and whereas the entropy change can be expressed in terms of measurable properties like C we pressure temperature volume all those things.

So then it will be easier and we can write down Tds = C_vdT + Tß / k dv we have already derived this expression right ß/K is nothing but your dP/dTV in the you know this thing earlier we have done that so therefore this expression is basically now in terms of all measurable properties, okay. So by the Jacobean method we have done the partial derivative means you know without really invoking the Jacobean method you can do that.

But in the partial derivative we'll do it just to illustrate that the equation 1 can be written as the Jacobean S_V with respect to T V X dT plus Jacobean s, T with respect to waiting into DV and we you know this s, V and TV basically CV/T that is we already know CV = P and what you call Jacobean is V with respect to dV, so therefore I can write down here very easily CV/ T and here in this expression if you look at it is basically what you call sT.

We know by the Jacobean that is PV Jacobean is equal to PS right by the Jacobean as from the maximal relationship so I can do that easily right and therefore that became PV and if you look at I can write down here instead of sT I can write on what you call VP and then I will take you know I can in place of these I can write down as basically or to call -PV I can write down -PV here and VT is there.

If I change it this become if I say this is T and this V then will this become minus and minus so it will be plus so that is nothing but your ß/ K right and then I can get the very easily dS = C_V/T dT = ß/K dv bright and we can put that expression you know Tds = C_v dT + T ß/K dv and this is the same expression what we got earlier by the partial derivative methods right so if you look at this is little faster way of doing you need not to remember which relationship we will be using you know which Maxwell in lessons you will be using.

In this case when we do buy the partial derivative I will have to you know look at it and also of course one can say because they entropy the volume a temperature then it has to be convergent to pray expressing pressure and temperature when volume remaining constant but you will have to remember but here it is very easy simpler way of doing the what you call Jacobean method.

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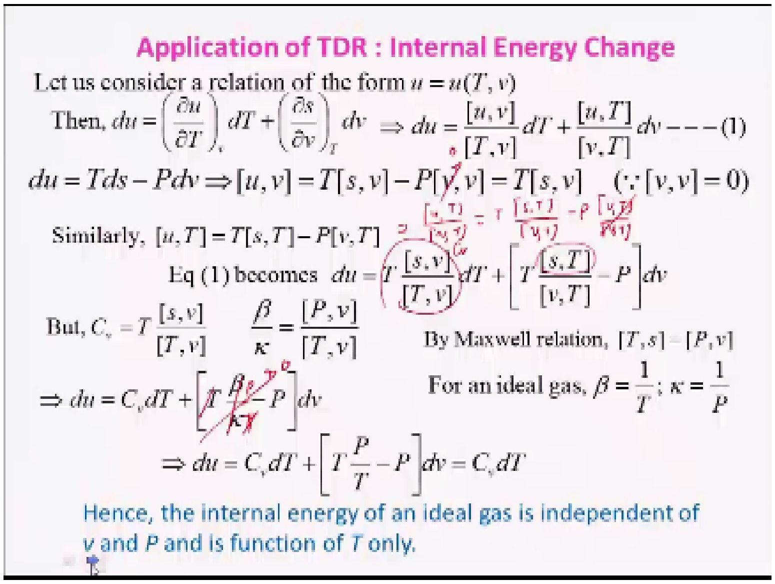

Application of TDR : Internal Energy Change

Let us consider a relation of the form $u = u(T, v)$

Then, $du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv \Rightarrow du = \frac{[u,v]}{[T,v]} dT + \frac{[u,T]}{[v,T]} dv \text{ ---(1)}$

$$du = Tds - Pdv \Rightarrow [u,v] = T[s,v] - P[\cancel{v},v] = T[s,v] \quad (\because [v,v] = 0)$$

$$\frac{[u,T]}{[v,T]} = T\frac{[s,T]}{[v,T]} - P\frac{\cancel{[v,T]}}{\cancel{[v,T]}}$$

Similarly, $[u,T] = T[s,T] - P[v,T]$

Eq (1) becomes $du = T\frac{[s,v]}{[T,v]} dT + \left[T\frac{[s,T]}{[v,T]} - P\right] dv$

But, $C_v = T\frac{[s,v]}{[T,v]}$ $\quad \frac{\beta}{\kappa} = \frac{[P,v]}{[T,v]}$ $\quad$ By Maxwell relation, $[T,s] = [P,v]$

For an ideal gas, $\beta = \frac{1}{T}$; $\kappa = \frac{1}{P}$

$$\Rightarrow du = C_v dT + \left[\cancel{T}\frac{\beta}{\kappa \cancel{T}} - P\right] dv$$

$$\Rightarrow du = C_v dT + \left[T\frac{P}{T} - P\right] dv = C_v dT$$

Hence, the internal energy of an ideal gas is independent of *v* and *P* and is function of *T* only.

Because of fact that the module relation can only one not four as in the case of partial derivative let us consider the relation form u = T, V right and so I can write on D = $(\partial u/ \partial T)_V$ dT and plus $(\partial s/ \partial v)$ when temperature remaining constant into DV and so that we can also express in terms of Jacobean and if you look at this thing we already know from the what you call first gives equation and this expression is nothing.

But you are what you call ∂ u/ ∂ Tv STV and whereas minus P is basically ∂s/ ∂v T you know that one so and of course for this you can find out from this first gives the equation you can express in terms of Jacobean that is Jacobean UV = T[s, v] – P[v, v] and the Jacobean we know it is zero right by the Jacobean rules. So therefore the Jacobean [u,v] is nothing but T[s,v]. Similarly we can write down u with respect to T from this expression that is Jacobean [u,T]=T[s,t]-P[v,T] and then we can write down basically you know equation 1 as du= you know s,v and with respect to [T,v]dT+ in place of what you call [u,T]/[v,T].

I can write down that from this expression I can write down basically as [u,T] Jacobean [v,T]=P[s,T]/[v,T-P[v,T] so this is cancel here so it you get basically [T,s] Jacobean with respect to [[v,T]-P]dv so you can get very easily and this expression is basically you know [s,v] this is nothing but your [s,v] and this we need to look at it and that is nothing but your β/K right, and we can use the Maxwell relations here and then get that one because Maxwell relation is T,s is equal to P,V so therefore we can you know replace this term with the maximal relationship and then after that connect to the β/K.

So therefore we can get du=C_vdT+[Tβ/K-P]dv so this is the expression you know change in internal energy in terms of all what we call measurable properties like C_v temperature coefficient of volume expansion isothermal compressibility and pressure right, and also the specific volume so all these are measurable properties and we can connect you know very easily evaluate the change in internal energy.

And for an ideal gas now we know β=1/T and the K that is isothermal compressibility is equal to 1/P so if I put it here you know β/K become basically P/T instead of this I can write down T so this cancel it out and this term basically will be 0 right, if that is 0 then I can get basically du=C_vdT that means that what you call internal energy for an ideal gas is independent of pressure and volume it is only dependent on the temperature right that we have already seen now we have proved that you know by this expression.

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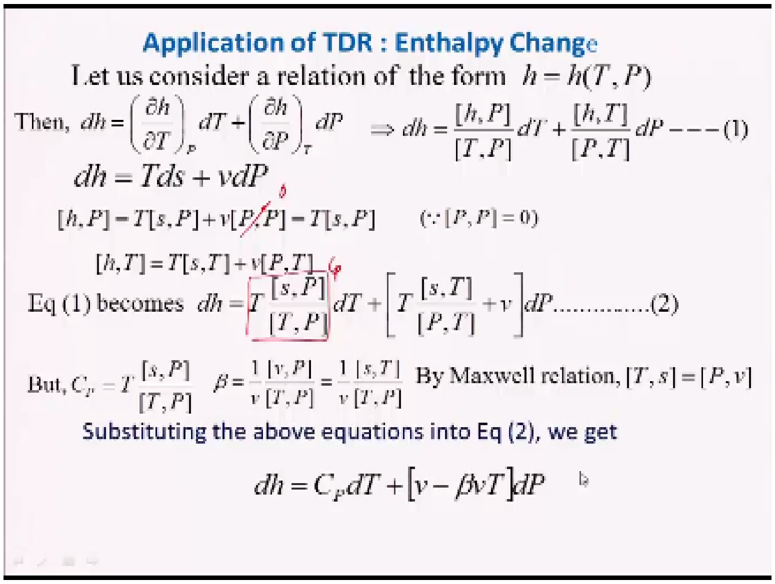

Application of TDR : Enthalpy Change

Let us consider a relation of the form $h = h(T, P)$

Then, $dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP \Rightarrow dh = \frac{[h,P]}{[T,P]}dT + \frac{[h,T]}{[P,T]}dP$ ---(1)

$$dh = Tds + vdP$$

$$[h,P] = T[s,P] + v[\overset{0}{\cancel{P,P}}] = T[s,P] \qquad (\because [P,P] = 0)$$

$$[h,T] = T[s,T] + v[P,T]$$

Eq (1) becomes $dh = \overset{C_p}{\boxed{T\frac{[s,P]}{[T,P]}}}dT + \left[T\frac{[s,T]}{[P,T]} + v\right]dP$..............(2)

But, $C_p = T\frac{[s,P]}{[T,P]}$ $\beta = \frac{1}{v}\frac{[v,P]}{[T,P]} = \frac{1}{v}\frac{[s,T]}{[T,P]}$ By Maxwell relation, $[T,s] = [P,v]$

Substituting the above equations into Eq (2), we get

$$dh = C_p dT + [v - \beta v T]dP$$

So in the similar way we can look at the enthalpy change and will be following the similar procedures right and let us consider a relationship in the form the enthalpy is a function of T and P right, and we can write down dh=∂h/∂T and for a constant pressure into dT ∂h and ∂P for constant temperature into dP and we can write down in the Jacobean forms in the similar manner and $dh=Tds+vdP$ that we know from the second you know expression and we can write down that you know [h,p] that is Jacobean [h,p] keeping the pressure you know like as a variable is equal to T in Jacobean $[s,P]+v[P,P]$ and of course [P,P] is 0.

So therefore you can get this is equal to P[s,P] and we can also write down similar way like of course the T as a variable and Jacobean $[s,T] =T[s,T]+v[P,T]$ and equation 1 you can write down in this similar form like and then we can notice that C_P is basically T[s,P] with respect to [T,P] so therefore this form I can write down as C_P and we can use the vertical maximal relationship for right and we know that maximization $[T,S]=[P,v]$.

And by that we can also find out this β as is equal to 1/v[v,P][T,P] sorry $\beta=1/v$ [v,P] with respect to [T,P] and which is nothing but in 1/v[s,T] with respect to [T,P] right, this we are getting with by using the maximal relationship and substituting these things in expression we can get $dh=C_pdT$ into$[v-\beta vT]dP$ so that with this you know we can get basically the enthalpy change can be expressed in terms of where what you call all measurable properties right.

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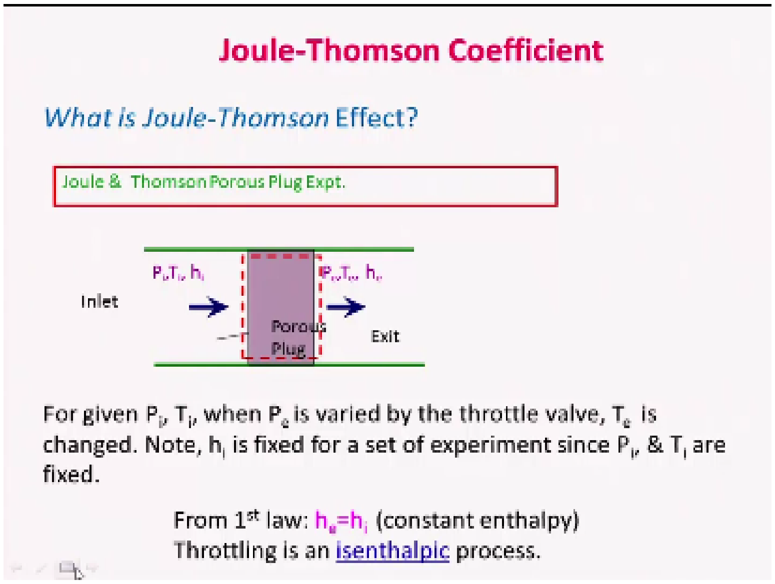

Joule-Thomson Coefficient

What is Joule-Thomson Effect?

Joule & Thomson Porous Plug Expt.

For given P_i, T_i, when P_e is varied by the throttle valve, T_e is changed. Note, h_i is fixed for a set of experiment since P_i, & T_i are fixed.

From 1st law: $h_e=h_i$ (constant enthalpy)
Throttling is an isenthalpic process.

And we also look at another this thing what we have already discussed that is joules thumbs and coefficient right which is a isenthalpic process and which we have seen earlier you know like which you use in your what you call air conditioning systems and capillary tubes and then porous blocks kind of things and we know that if we apply this first law of thermodynamic forces control you know volume systems we will find that enthalpy is remaining constant right and this process is known as isenthalpic process right which we have already derived this thing.

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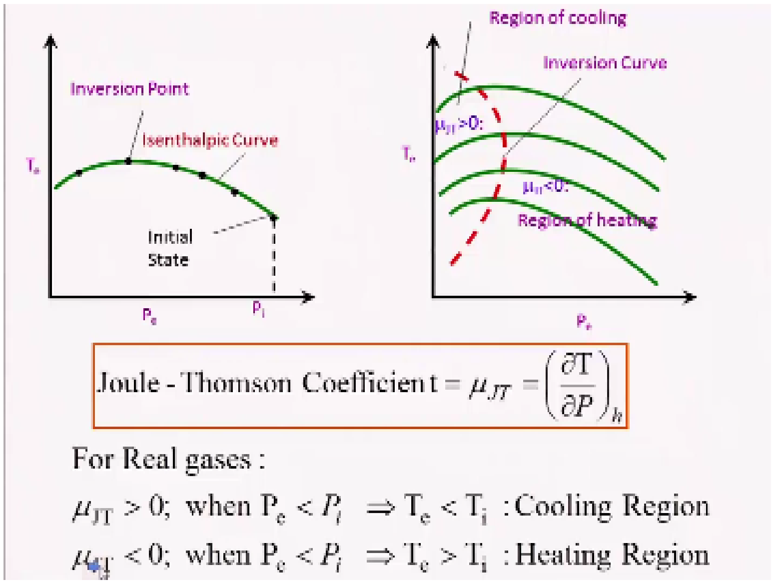

Joule - Thomson Coefficient = $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h$

For Real gases :

$\mu_{JT} > 0;$ when $P_e < P_i \Rightarrow T_e < T_i$: Cooling Region

$\mu_{JT} < 0;$ when $P_e < P_i \Rightarrow T_e > T_i$: Heating Region

And if you look at that this you know like a µ JT what we derived that is the Joule coefficient is nothing but ∂ T / ∂ P when enthalpy is remaining constant right and this reason is basically the µ JT > 0 and that is known as reason appalling because of fact that when P < P I right all the time it will be because the exit pressure will be lower than the inlet pressure otherwise there would not be any flow right then PE will be less than ti because this will be what you call negative in the numerator.

So whereas the TE <T I will be to make it what to call greater than zero so that there will be cooling region and similarly when mu JT is less than zero there will be heating region we have already discussed this thing. Now what we need to do these Joule Thomson coefficient we need to what to Call Express in terms of properties right because it is a very important parameter which is used for design of air can be and the vision system.

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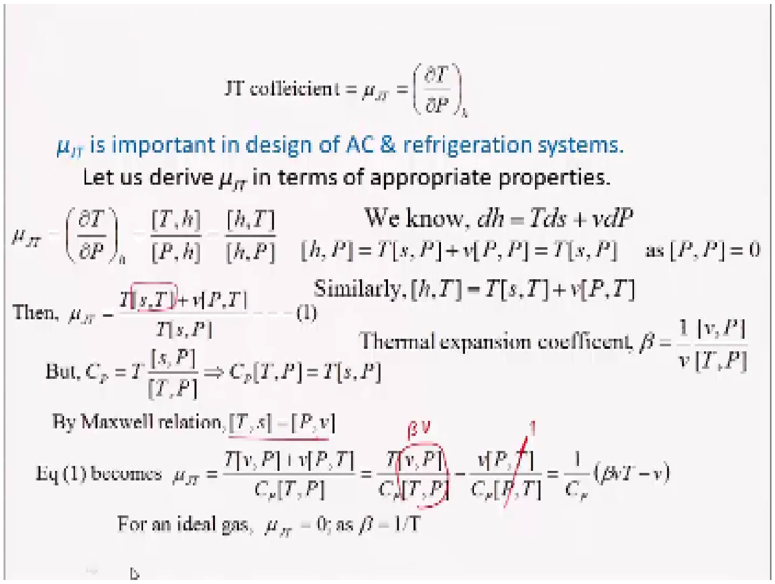

$$\text{JT colleicient} = \mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h$$

μ_{JT} is important in design of AC & refrigeration systems.

Let us derive μ_{JT} in terms of appropriate properties.

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h = \frac{[T,h]}{[P,h]} = \frac{[h,T]}{[h,P]}$$

We know, $dh = Tds + vdP$

$[h,P] = T[s,P] + v[P,P] = T[s,P]$ as $[P,P] = 0$

Similarly, $[h,T] = T[s,T] + v[P,T]$

$$\text{Then, } \mu_{JT} = \frac{T\boxed{[s,T]} + v[P,T]}{T[s,P]} \text{ ---- (1)}$$

Thermal expansion coefficent, $\beta = \dfrac{1}{v}\dfrac{[v,P]}{[T,P]}$

$$\text{But, } C_p = T\frac{[s,P]}{[T,P]} \Rightarrow C_p[T,P] = T[s,P]$$

By Maxwell relation, $\underline{[T,s] = [P,v]}$

$$\text{Eq (1) becomes } \mu_{JT} = \frac{T[v,P] + v[P,T]}{C_p[T,P]} = \overset{\beta v}{\boxed{\frac{T[v,P]}{C_p[T,P]}}} - \frac{v\cancel{[P,T]}^{\,1}}{C_p\cancel{[P,T]}} = \frac{1}{C_p}(\beta vT - v)$$

For an ideal gas, $\mu_{JT} = 0$; as $\beta = 1/T$

So therefore we need to look at it and plate we can express this ∂ T / ∂ P when the enthalpy remaining constant in the Jacobean form that is Jacobean pH with respect to pH right and I can inter change this one and then get this expression right and we know that D H = TDS + VDP that we know very well. So I can write down enthalpy you know with respect to Pin the Jacobean form as shown here and which is equal to basically T into Jacobean SP and similarly we can have Jacobean with respect to temperature you know like as a variable.

So therefore we can express this term as basically you know T into Jacobean s T + V Jacobean PT divided by T Jacobean SP right, so if you look at the earlier is all measurable property whether but now we entropy has entered into pictures which is non-measurable so we need to you know eliminate that so for that we know that thermal expansion coefficient β which is 1/v Jacobean VP with respect to T P and we know also the CP = T Jacobean SP with respect to T P.

So therefore I can write down CP Jacobean TP is equal to Pinto Jacobean SP and with maximal relationship we know that TS is equal to Jacobean TS is equal to Jacobean PV so therefore we can utilize this one right and, so we can write down basically this as the Maxell relationship is T into in place of HP you know I can write down basically VP from the maximal relationship it by using these maximal relationship I can buy do not VP here +V x Jacobean PT / TP.

So if you look at this expression becomes you know like this and then I can look at this VP and TP is nothing but your what you call coefficient of you know thermal expansion coefficient so in place of these I can write down as beta V right and similarly PT by PT so therefore this will be one I can say V P and then joule-Thomson coefficient will be equal to 1 / CP I can take it out then it will be β V T - specific volume right.

So it is a if we look at all our measurable properties and you can get this you know very easily it is not a you know differential whether it is all our measurable properties you can find out joule Thomson coefficient very easily we know that Veda for an ideal gas one over T the joule some concern coefficient will be equal to 0 right.

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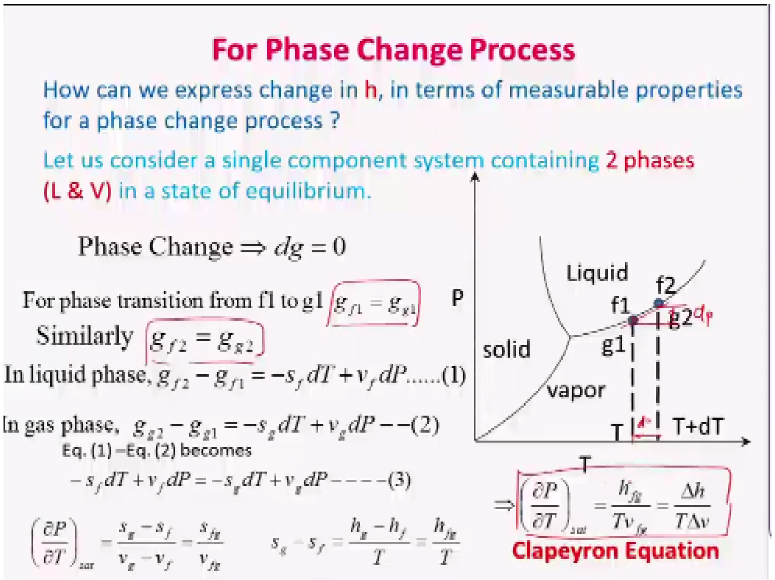

For Phase Change Process

How can we express change in h, in terms of measurable properties for a phase change process ?

Let us consider a single component system containing 2 phases (L & V) in a state of equilibrium.

Phase Change $\Rightarrow dg = 0$

For phase transition from f1 to g1 $\boxed{g_{f1} = g_{g1}}$

Similarly $\boxed{g_{f2} = g_{g2}}$

In liquid phase, $g_{f2} - g_{f1} = -s_f dT + v_f dP$......(1)

In gas phase, $g_{g2} - g_{g1} = -s_g dT + v_g dP$ --(2)

Eq. (1) – Eq. (2) becomes

$-s_f dT + v_f dP = -s_g dT + v_g dP$ ----(3)

$\left(\frac{\partial P}{\partial T}\right)_{sat} = \frac{s_g - s_f}{v_g - v_f} = \frac{s_{fg}}{v_{fg}}$ $\quad s_g - s_f = \frac{h_g - h_f}{T} = \frac{h_{fg}}{T}$

$\Rightarrow \boxed{\left(\frac{\partial P}{\partial T}\right)_{sat} = \frac{h_{fg}}{T v_{fg}} = \frac{\Delta h}{T \Delta v}}$

T

Clapeyron Equation

So if you look at the we have seen the phase change processes you know from the liquid to the gas and liquid to the it is vapor right and also solid to liquid all those things we have seen now and we need to express you know H in terms of measurable properties during a phase change right and for that we will have to look at the phases you know how will express this H in terms of you know measurable properties for example heat of vaporization whenever it is vaporize we need to express in terms of measurable properties.

So let us consider a single component system with two phases liquid and vapor in the state of equilibrium when it is in state of equilibrium you know it will be basically in thermodynamics that means mechanical equilibrium thermal equilibrium they change equilibrium also the chemical equilibrium you know all those things will be valid and what we will do for example we will take this you know phase diagram I am taking because solid vapor and liquid you can describe in a single two dimensional part PT.

So if I consider this is a point here right and what is that this f1 is a state where the properties you know of the liquid and here the properties of the gas and all will be same like at that point and similarly a let us at station 2 like which is another point that also can be same. So you know like that has to be maintained as a result the change phase change right to how we are changing you know the change in the Gibbs free energy will be = 0.

So therefore we can say phase transition from liquid to the gas right will give the condition that gives function you know like at station 1 for the liquid is =gives function for the vapor it is vapor at the station 1. And similar way also we can write down at this you know another point like okay so that is gf 2 = GZ 2.

So we know that for the liquid phase gf 2 - gf 1right = sf dt + $v_f$dp so if you look at there is a some change in the temperature here between these two this is basically dt and if you look at this is nothing but your dp. Right change pressure and if you look at the vapor state right or the gas state right gaseous state that will be g_g2 - g_g1 is =sg dt + vt dp same thing we are writing.

Only thing you know we are putting one is the for the vapor and other is the for the liquid and both the site should be same. So therefore if i - it this equation 1 and 2 you know I will get basically s_fdT + v_fdP =- sddT +vgdp. Right and this is you know we will cancel it out because of this condition.

That this condition you know and these two condition so this will be cancel it out so if you look at if I can separate this you know ∂P all the coefficient for deep in one side and t dT for the other side then I can get the ∂ P /∂T on the saturated concern because it is a saturated condition is =change in entropy that is sD - sF = vZ - v F.

Right you know like what to call that means the slope of this curve right this slope is = change in entropy right we are with the change in the specific volume now we are in trouble in the sense entropy has come into pictures. Right so what we need to do we will have to use you know our definition of the entropy change in entropy is =change in the enthalpy / 2 P.

Right and then I can write down H FG by T so if I put this thing here in this expression I will get ∂ P /∂T is =hfg /tvfg and this equation is basically says you know like the from the slope if I know this law I can evaluate hfg very easily right and are provided I know the change in the specific volume right because I know this pressure and temperature right.

So that I can have conduct experiments and then find out this thing and then we can evaluate H FG and this equation is known as the clapper on equation right this equation is known as the chaperon equation. Which will relate this heat of you know vaporization sublimation x' and others also right into the measurable properties.

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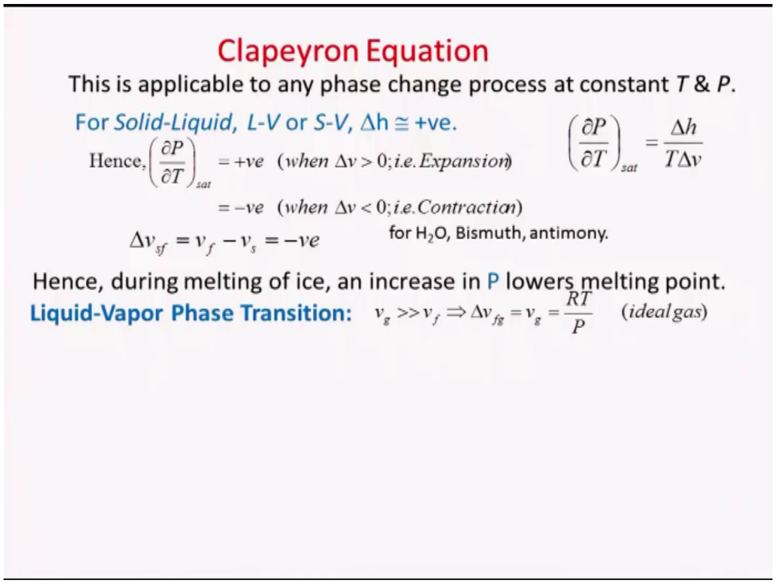

Clapeyron Equation

This is applicable to any phase change process at constant *T* & *P*.

For *Solid-Liquid*, *L-V* or *S-V*, Δh ≅ +ve.

$$\left(\frac{\partial P}{\partial T}\right)_{sat} = \frac{\Delta h}{T\Delta v}$$

$$\text{Hence,} \left(\frac{\partial P}{\partial T}\right)_{sat} = +ve \quad (when\ \Delta v > 0; i.e. Expansion)$$

$$= -ve \quad (when\ \Delta v < 0; i.e. Contraction)$$

$$\Delta v_{sf} = v_f - v_s = -ve$$

for H_2O, Bismuth, antimony.

Hence, during melting of ice, an increase in P lowers melting point.

Liquid-Vapor Phase Transition: $v_g >> v_f \Rightarrow \Delta v_{fg} = v_g = \frac{RT}{P} \quad (ideal\,gas)$

Right so of course as I told this is applicable to any change process at a constant temperature and pressure because you know it is a once pressure is constant temperature is constant that we have seen. But for the solid and liquid you know or the solid is a vapor the change in enthalpy or the vapor vaporization or heat of sublimation. It will always be positive so therefore what you call that if it is $\partial P/\partial T$ is positive.

Right and although we have seen that the change in you know enthalpy will be positive and of course then this term will be positive only if the ΔV will be greater than 0 that is the expansion right if solid is converted into liquid. Let us say okay or it is vapor ray so what will happen that will be what you call expansion.

But there might be some cases where that will be contraction for example like your water bismuth or antimony you know like these are what you call contact right negative. So therefore it will be change in the specific volume will be negative when it is solid is converted into liquid like your eyes being floated. You know like I have been floated in water you know liquid which is a liquid.

So in during melting of ice you know like what he says is a negative so therefore whenever increase in you knows pressure lowers the melting point of that we call this thing that is the reason why you might have seen that you know this ice skaters. Right they press it so that the there will be a melting out and they can move very freely and that process you know the relegation right kind of thing and that is being used for the ice skaters to do that.

So liquid vapor phase transition if you look at late we look at in the solid and liquid right we can think of liquid vapor transition in this case the if you look at specific volume of the vapor is much larger than the specific volume of the liquid is not it. For example like if you look at liquid and steam right if you look at for example if you can look at water and steam like what we you know steam say specific volume is much higher than the liquid specific volume.

So therefore I can write down the change in volume during this liquid vapor phase transition is equal to the VG right and if I assume that ideal gas which need not to but can assume that VG is equal to RT by p. So if I look at then I can express do Pay do T is equal to basically in place of you know what you call this expression in the chaperon equation if I put this in place of what you call Delta V that we can only VG and in place of V Z I will put RT by P then duo P you T is nothing but H FG P by RT square right and if I can separate this thing that is I can write out D In P divided by DT is equal to the g RT square rights.

Then I can integrate this equation and I will get In P is equal to H FG byr1 over T plus constant right and then Ian get this I can plot this In P over 1over C and then I can get the slope is basically this one right and if I plot this thing I can get the slope Ian get the also the intercept and constant and this expression is basically known as the classiest and Clapeyron equation.

Okay so if you look at mean you can use this thing for basically finding out the various temperatures and if you know the heat of vaporization all these things and it is very useful expression relating the what you call heat of vaporization and pressure and temperature kind of things and when you put that thing I can get an expression like this is In P 2 by P 1 is equal to HF G divided by R 1 over t1minus t2 right so I can take an example just to illustrate how you can do that use this expression for finding out you know heat of vaporization and kind of things so let us say that in order to decrease their time right.

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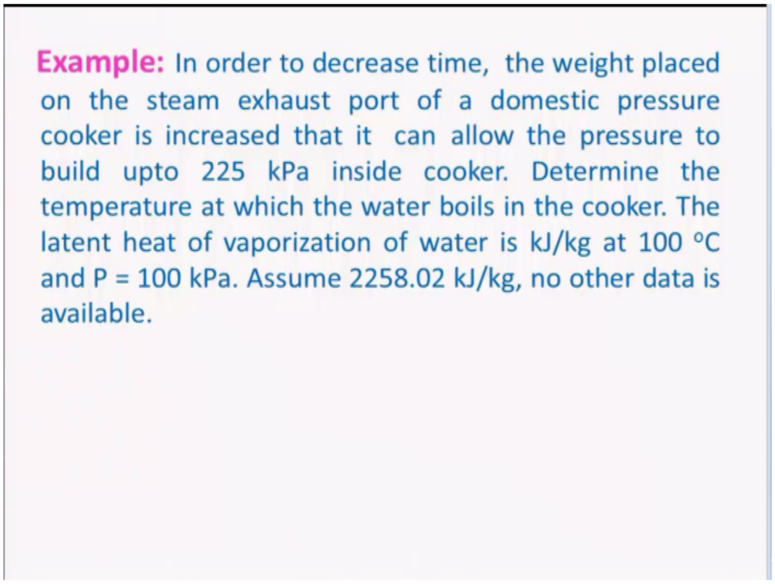

Example: In order to decrease time, the weight placed on the steam exhaust port of a domestic pressure cooker is increased that it can allow the pressure to build upto 225 kPa inside cooker. Determine the temperature at which the water boils in the cooker. The latent heat of vaporization of water is kJ/kg at 100 °C and P = 100 kPa. Assume 2258.02 kJ/kg, no other data is available.

Wait place on the steam exhaust port of a domestic pressure cooker is increased so that it can allow the pressure to build up to the 225 kilo Pascal inside the cooker and we determine the temperature at which theaters boils in the cooker and the latent heat of vaporization of water is 258.02o kilo joule per kg at 1000 C and pressure of undead k we need to calculate this temperature at which the water you know boils kind of things so how to go about it so if you look at what other things are given is that p1 is given.

That is 100kPa right and p2 is also given 225 kPa and t1 is given to seven 373 Kelvin sandhog is given to 2580 2kilo joule per kg right of course that is at 100 degree Celsius and pressure of hundred K P right and we'll have to find t2 so what we candor we can basically apply the Clausius-Clapeyron equation righty using we can get basically In P 2 by P 1 is equal to H FG by ah 1 over T 1 minus 1over T 2 so if you look at in this expression P 2 is given P 1 is given temperature That is 100 is equal to F G is given.

vertical specific gas constant this is 8.314 into molecular weight has to be there that is 418 for water 1 over3 7 3 minus 1 over T 2 so from this toucan get T 2 is equal to 120 4.6 degree Celsius from this you know you can get but if you look at your steam table right you will get at 225 KP a you can get temperature T 2 is equal to 124 big in Celsius which is very close to that right so what I'm saying by this way one can know some properties and other player properties can be found out.

Very easily and we can use this Clapeyron clausius chaperon equation and then Clapeyron equations and for very finding out the properties for during the phase change processes with this I will stopover and we have come to the end of this thermodynamic course and I would like to quote from this.

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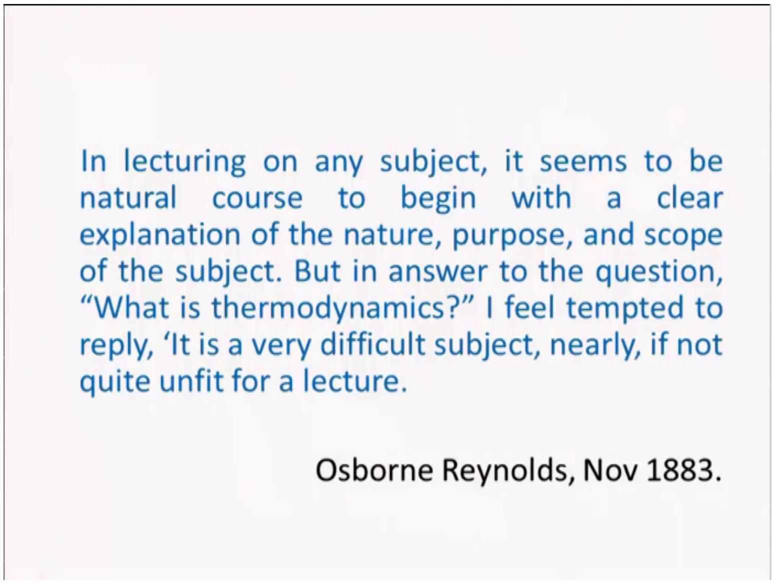

In lecturing on any subject, it seems to be natural course to begin with a clear explanation of the nature, purpose, and scope of the subject. But in answer to the question, “What is thermodynamics?” I feel tempted to reply, ‘It is a very difficult subject, nearly, if not quite unfit for a lecture.

Osborne Reynolds, Nov 1883.

Osborne Reynolds in November 1883 who says in lecturing on any subject it seems to be natural course to begin with a clear explanation of the nature purpose and scope of the subject but in answer to the question what is thermodynamics feel tempted to reply it is very difficult subject nearly if not quite unfit for a lectures with the third process I will stopover here thank you very much.

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