Engineering Thermodynamics

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Lecture – 29

Properties of a Pure Substance: Gibbs energy. Helmholtz function. Property relations

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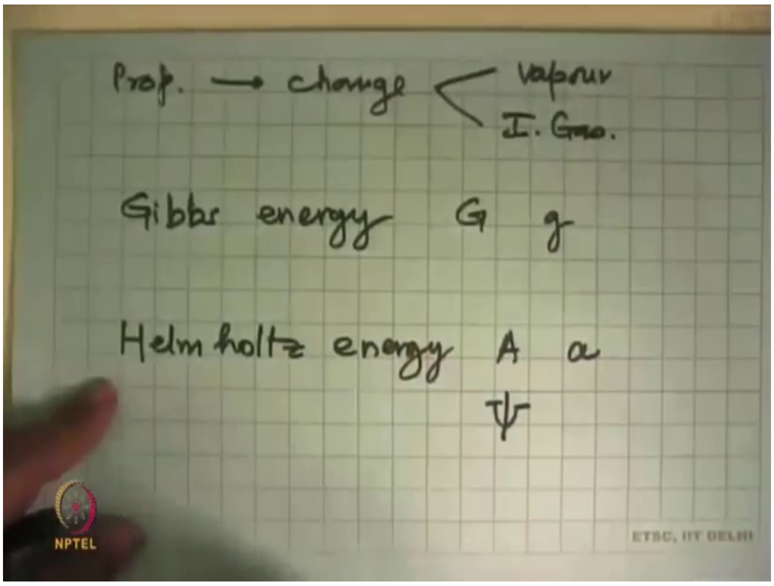

Prop. → change < vapour / I. Gas.

Gibbs energy G g

Helmholtz energy A a ψ

So, we have come to the conclusion of what we had been looking at that we remember that all the properties and the change in the properties. So, we have defined many properties, and we got change in properties for both vapour like behaviour and ideal gas that is what we were looking for. So, what we can do now is use this data to go back to those equation that we wrote in this second module after that analysis of the laws. And now we are at the position to put numbers in there and start getting the answers.

So, this last part as you see in the total problem solving process really one small little thing, the initial part when we formulated the problem, get the approximations, and what the equation that you have to solve. If you made a mistake at that point anywhere, the next point where we put numbers into the equation turn really help us. So, we have to be very clear on that part, after we are done with that whichever ok.

Now, let me put numbers wherever they comes from, and this to this way, but I will do to complete the discussion on properties is to introduce two new properties. You might have come across these in physics or chemistry courses, one is called the Gibbs energy, and the other is the Helmholtz energy. Sometime this is referred to as Gibbs free energy; sometimes this is referred to as some as Helmholtz free energy. And some text, you will find this refer to as Helmholtz functions. Gibbs energy is denoted by G, specific Gibbs energy is small g. Helmholtz is to use symbols A, but in some books you will find the symbols psi as also be used. (Refer Time: 02:22) capital A for total Helmholtz energy, small a for specific Helmholtz energy.

And this definitions complete the set of properties that we would like to have for a pure substance. The Helmholtz energy actually is much more attractive, because it is from here that we develop that equations for a P V T curve, and then by using properties differentials we calculate all the other properties of the pure substance. We do not need to go very deep in to this, but one should be aware that this is the totality of properties that we are working with. So, for completing the discussion sake I am showing you.

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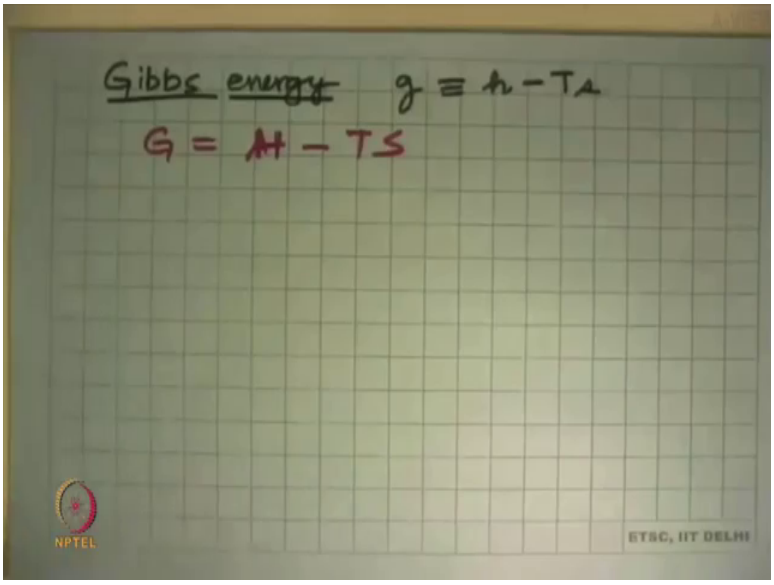

Gibbs energy $g = h - Ts$

$G = H - TS$

So, Gibbs energy is defined as H minus TS or g is equal to small h minus Ts. And Helmholtz energy is A is equal to U minus T S or small a is specific internal energy minus T s.

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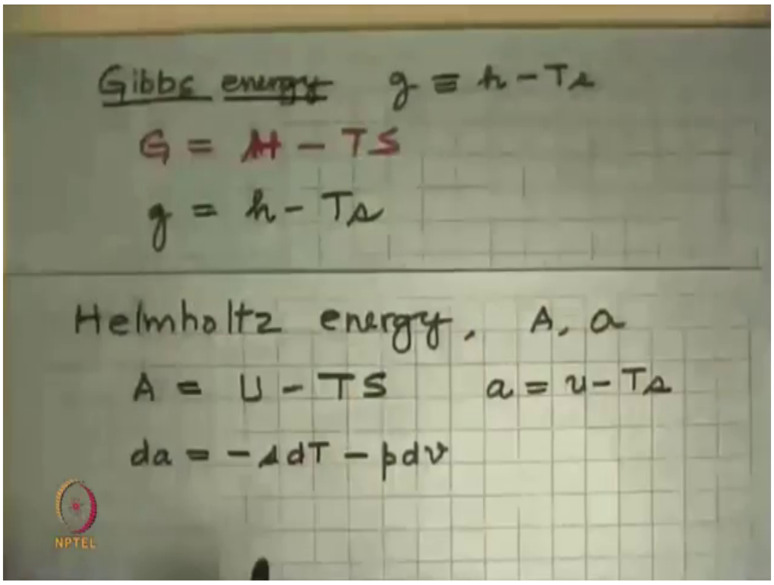

Gibbs energy $g \equiv h - Ts$

$G = H - TS$

$g = h - Ts$

Helmholtz energy, A, a

$A = U - TS \qquad a = u - Ts$

$da = -s\,dT - p\,dv$

So, what we have done something within both cases, we have somehow got something less than Ts. And this becomes important, when we look at what is call the work potential of a reaction or work potential of a change changes taken in. And this tells us, what is the maximum possible work that you can get. And the case like a fuel cell or a battery that is why this property comes in. This property also comes very important in looking at reactions, where we ask if I burn the fuel in air, what is the species that I will get, what is the temperatures I will get.

And then the Gibbs energy will tell you what is in the final composition of that. This is also good for mixtures and say look at I mix, so much water with. So, much air what is the pressure and temperature that I get with the Gibbs energy that helps us to get the laws. So, these are the two functions two energy functions that are there.

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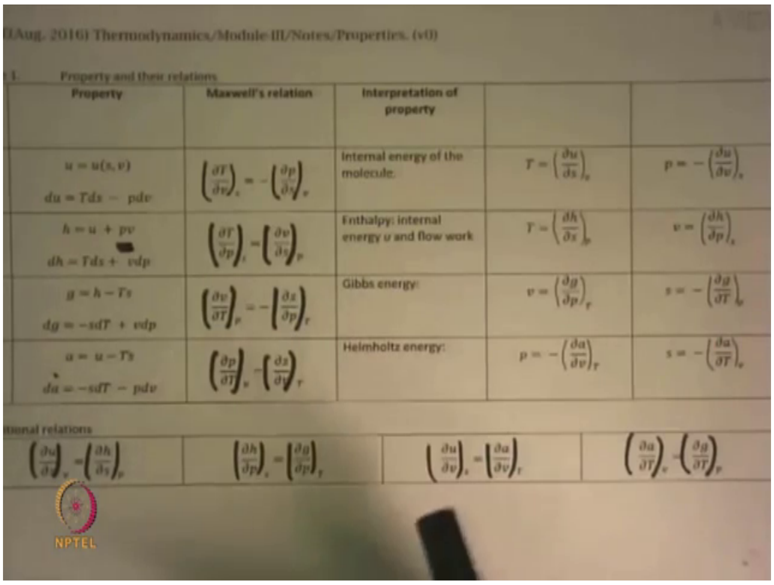

Aug. 2016) Thermodynamics/Module III/Notes/Properties. (v0)

1. Property and their relations

Property	Maxwell's relation	Interpretation of property		
$u = u(s, v)$ $du = Tds - pdv$	$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v$	Internal energy of the molecule.	$T = \left(\frac{\partial u}{\partial s}\right)_v$	$p = -\left(\frac{\partial u}{\partial v}\right)_s$
$h = u + pv$ $dh = Tds + vdp$	$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p$	Enthalpy: internal energy u and flow work	$T = \left(\frac{\partial h}{\partial s}\right)_p$	$v = \left(\frac{\partial h}{\partial p}\right)_s$
$g = h - Ts$ $dg = -sdT + vdp$	$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T$	Gibbs energy:	$v = \left(\frac{\partial g}{\partial p}\right)_T$	$s = -\left(\frac{\partial g}{\partial T}\right)_p$
$a = u - Ts$ $da = -sdT - pdv$	$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$	Helmholtz energy:	$p = -\left(\frac{\partial a}{\partial v}\right)_T$	$s = -\left(\frac{\partial a}{\partial T}\right)_v$

tional relations

$\left(\frac{\partial u}{\partial s}\right)_v = \left(\frac{\partial h}{\partial s}\right)_p$	$\left(\frac{\partial h}{\partial p}\right)_s = \left(\frac{\partial g}{\partial p}\right)_T$	$\left(\frac{\partial u}{\partial v}\right)_s = \left(\frac{\partial a}{\partial v}\right)_T$	$\left(\frac{\partial a}{\partial T}\right)_v = \left(\frac{\partial g}{\partial T}\right)_p$

And now I plotted a graph of chart, which summarises all this properties that we have looked at. This is there in your notes, we do not need to really memorize or go deep into this, but it is put to know that all these things are there, and they have an importance in thermodynamics. So, yes in the table we have property, here Maxwell's relations, interpretation of that property, and what functions came out of this property.

From this side we start with u, u is said the function of entropy and into the d u is T d s minus p d v, which means that u the function of s and v that is u is equal to u s, v. And by doing little bit of small differentials, which I have given in the notes than put it up very soon in that dT dv, and there a bracket missing here is equal to minus dp ds at constant volume.

And you also get from here that temperature is du ds at constant volume and pressure is minus du dv at constant entropy, so that is why we begin to see that how all these properties are related to each other a very nice mathematical functions. So, if only we have a PVT diagram is satisfies only these thinks, just differentiation is coding of to get all the analysis ok. So, this tells you that this is the internal energy of the molecule that includes its vibrational energy, translational energy, rotational energy, electrical energy, and any other types of internal energy that a molecular may have that is all there inside this.

To that we had a pv, which we called as the flow work, h equal to u plus p v. And we got this equations d h is equal to T d s plus v d p, and that gave us the expression that dT dp s is equals to dv ds p or temperature is dh ds at p and v is dh dp at constant entropy. And I looking at Gibbs energy is a maximum work that is possible from a process g going to h minus Ts, dg equal to minus ds dT plus v dp. And again we get these two differential equations or specific volume is dg by dp and T, and s is minus dg dT.

And the last one is of the Helmholtz energy a equal to u minus Ts, da is minus ds dT minus p dv. And you get these two differential equations. And pressure is minus da dv at constant temperature, s is minus da dT here constant specific volume. I have listed here four more equations, which are useful. And these are the equation that we start using to get some PVT diagram or the other properties that we are looking for.

And the nice thing about during such a formulation, if that if we have the right formulation just a few set of differentials, and we get all the answers. There is no approximation involved, and this process is superior to saying that I take data, and it do a polynomial research. Polynomials are very badly in behaved between data points, and differentiating them gives serious mistakes. So, we be very very careful that here working with polynomials, whether it is of properties or any other case differentiation is very very dense best to avoid that.

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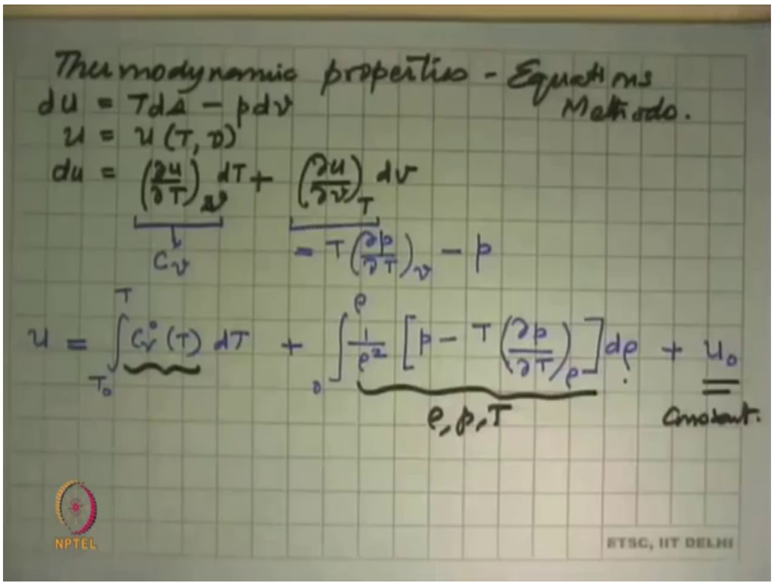

Thermodynamic properties - Equations Methods.

$$du = T\,ds - p\,dv$$

$$u = u(T, v)$$

$$du = \underbrace{\left(\frac{\partial u}{\partial T}\right)_v}_{C_v} dT + \underbrace{\left(\frac{\partial u}{\partial v}\right)_T}_{= T\left(\frac{\partial p}{\partial T}\right)_v - p} dv$$

$$u = \int_{T_0}^{T} \underbrace{C_v^{\circ}(T)}\, dT + \underbrace{\int_0^{\rho} \frac{1}{\rho^2}\left[p - T\left(\frac{\partial p}{\partial T}\right)_\rho\right]}_{\rho,\,p,\,T} d\rho + \underbrace{u_0}_{\text{Constant.}}$$

So, how we got those equations, these are one little thing u is T ds minus p dv. u is a function of s and v. And we get which are differentiated to get this part, and then we can put various other substitutions, and you get this big equations do not worry what is there inside this, but you just see what it means that if I want to vibrate you, I need C v 0 as the function of T.

And I can integrated with temperature, I have this big expression which is what rho p, and T rho p and T. So, if I have an equation for the PVT relationship, I can put that and integrate with respect rho. And this is some constant which is some what arbitrary, you can pick what you want, so that is how we do all these operations and we get u.

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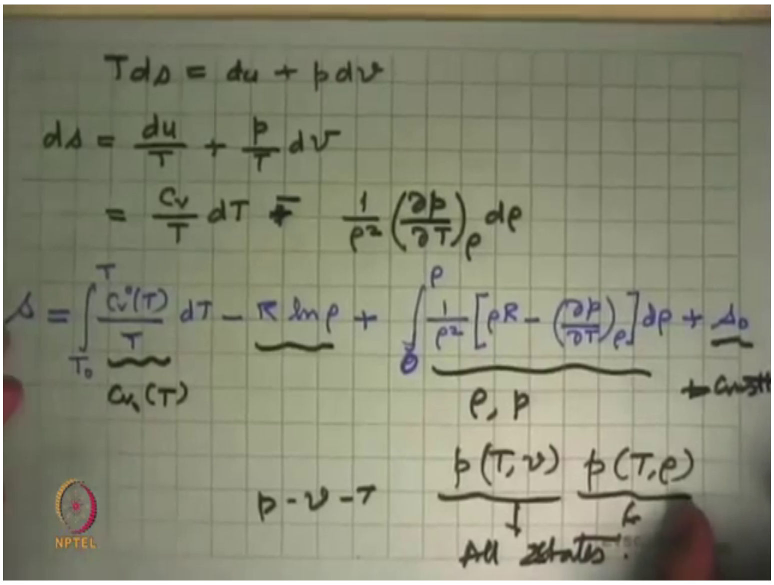

$$T\,ds = du + p\,dv$$

$$ds = \frac{du}{T} + \frac{p}{T}\,dv$$

$$= \frac{C_v}{T}\,dT \mp \frac{1}{\rho^2}\left(\frac{\partial p}{\partial T}\right)_\rho d\rho$$

$$s = \underbrace{\int_{T_0}^{T} \frac{C_v^\circ(T)}{T}\,dT}_{C_v(T)} - \underbrace{R \ln \rho} + \underbrace{\int_0^{\rho} \frac{1}{\rho^2}\left[\rho R - \left(\frac{\partial p}{\partial T}\right)_\rho\right] d\rho}_{\rho,\, p} + \underbrace{s_0}_{\text{constt}}$$

$$p - v - T \qquad \underbrace{p(T, v)}_{\downarrow} \quad \underbrace{p(T, \rho)}_{}$$

All states

And similarly, there is a second function, how we get S from PVT data just to know that second method is there. S can be written from T ds is equal to du plus p dv is substituted that here we substitute some more substitutions, and this we get that s is the function of C v 0 at the function of T that is what you need here. This is R ln rho, rho is the density you need density there. And this whole thing is an integration of density, then here rho and dp, dT coming in there. And then this one the constant depending on there the reference take here.

So, what these two equations showed us that if you have a functional relationship between p, and T, and rho, so p as a function of T and v or p as a function of T, rho. Then we can differentiated, put it in this equation, and where the entropy change. And this is vary for every state there is no approximation here, because we are looking at a P V T relationship or this relationship that we have which is good for all states. So, we do not have depend on somebody giving us the charge, and the properties and the number. We have a little bit of entrepreneurship, we can make this charge ourselves, because so that is two of the properties.

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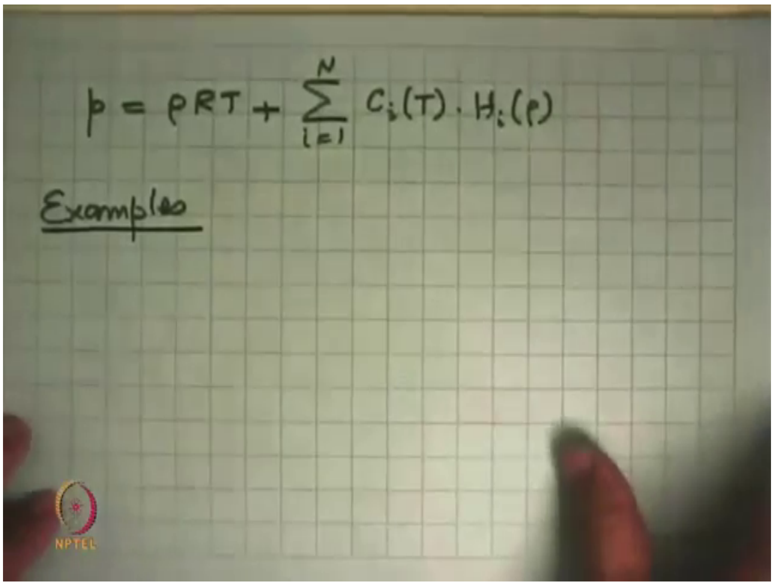

$$p = \rho R T + \sum_{i=1}^{N} C_i(T) \cdot H_i(\rho)$$

Examples

And now I will just give some examples of how we get this p rho R T type of a thing. And what we have done is p equal to rho R T, which is the ideal gas equation of state, and added to this big term here. And then which is C i which is some sort of constants as the function of temperature, and another function which is the of density. So, (Refer Time: 10:56) separation of the variables or source, and this is where if you look of mathematics. You would have come across the Helmholtz partition function, then it what we have done here. And then we do curve fitting and get values of C i and H i we should in many many constants. So, I just show you a few of these formulations ok.

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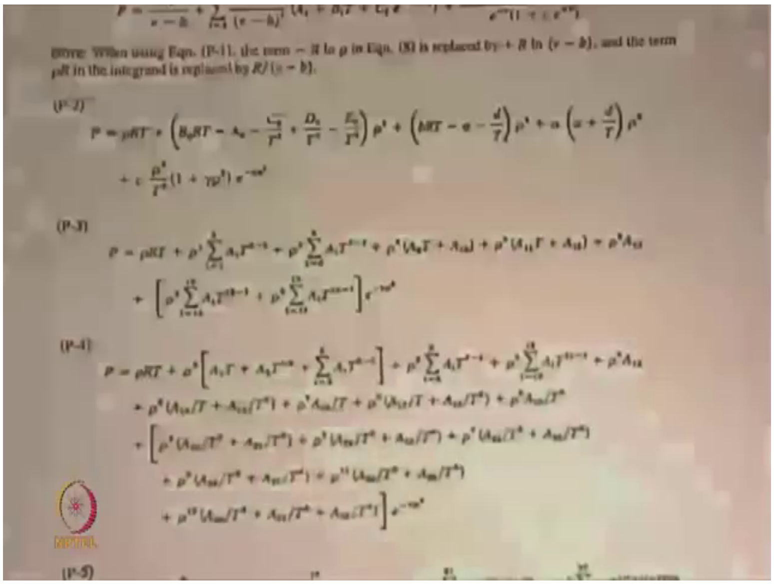

Note: When using Eqn. (P-1), the term − R ln ρ in Eqn. (X) is replaced by + R ln (v − b), and the term ρR in the integrand is replaced by R/(v − b).

(P-2)

(P-3)

(P-4)

(P-5)

Here is a equation of state which fix all the data, it will not that based on the one equation, which we can use for fitting all these data. We have see here this is a first equation p is RT upon b, and then whole bunch of things put in there which are only functions of temperature and density explicitly.

And to this formulation p equal to rho R T plus whole bunch of other things sort of a various unconscious coming there. Then p equal to rho R T plus some other form of these abbreviations. On that formulation is got whole bunch of other things 28, 32 constants coming in over there, so that is ok. And the reason we put these is that some some materials some equation fits best or some other materials some other equations fits best.

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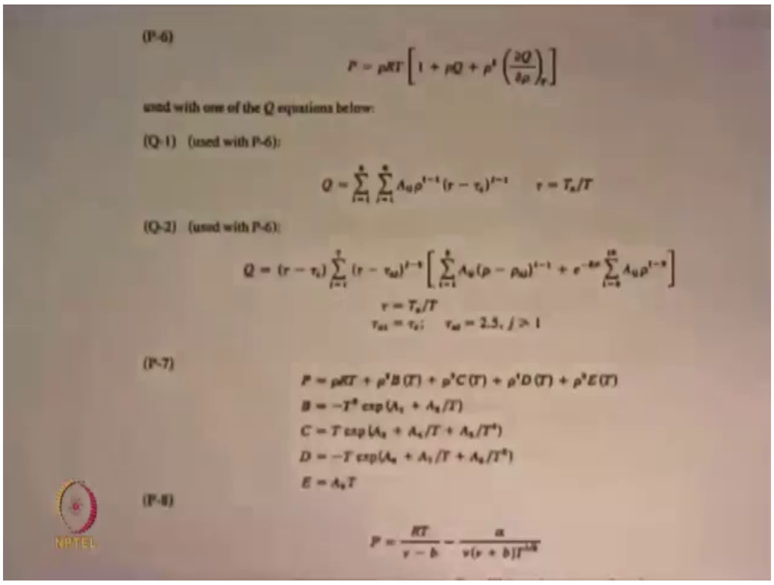

(P-6)

$$P = \rho RT\left[1 + \rho Q + \rho^2\left(\frac{\partial Q}{\partial \rho}\right)_\tau\right]$$

used with one of the Q equations below:

(Q-1) (used with P-6):

$$Q = \sum_{i=1}^{9}\sum_{j=1}^{6} A_{ij}\rho^{i-1}(\tau - \tau_c)^{j-1} \qquad \tau = T_c/T$$

(Q-2) (used with P-6):

$$Q = (\tau - \tau_c)\sum_{j=1}^{7}(\tau - \tau_{aj})^{j-2}\left[\sum_{i=1}^{8} A_{ij}(\rho - \rho_{aj})^{i-1} + e^{-E\rho}\sum_{i=9}^{10} A_{ij}\rho^{i-9}\right]$$

$$\tau = T_c/T$$

$$\tau_{a1} = \tau_c; \quad \tau_{aj} = 2.5,\ j > 1$$

(P-7)

$$P = \rho RT + \rho^2 B(T) + \rho^3 C(T) + \rho^4 D(T) + \rho^5 E(T)$$

$$B = -T^{8}\exp(A_1 + A_2/T)$$

$$C = T\exp(A_3 + A_4/T + A_5/T^2)$$

$$D = -T\exp(A_6 + A_7/T + A_8/T^2)$$

$$E = A_9 T$$

(P-8)

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b)T^{1/2}}$$

So, like this we have many other equations coming in here, and that is equation that is of use to us for water is this equation p equal to rho RT multiplied by this thing. Q is a partition function, which is given by this which is got so many constants in it or by this this is the one is for water. So, you get this long equation which what lots of constants, which are given separately, and from there we can then use put it into this equation differentiated as much as we want, and can compute any properties that you have.

So, we can make our own program, and say that look I can do this. But, the trouble is the two independent variables in all these formulations are pressure and density or specific volume. So, if we are know if we know state, then pressure and enthalpy are known, then direct use of this equation is not possible. We have to develop some other techniques of interpolation, and some approximation to get to the correct answer. Most of the web based programs or other that you see may not have that flexibility that if I specify specific enthalpy, and specific entropy what is the pressure, and temperature that question most of these programs will not be able to answer ok.

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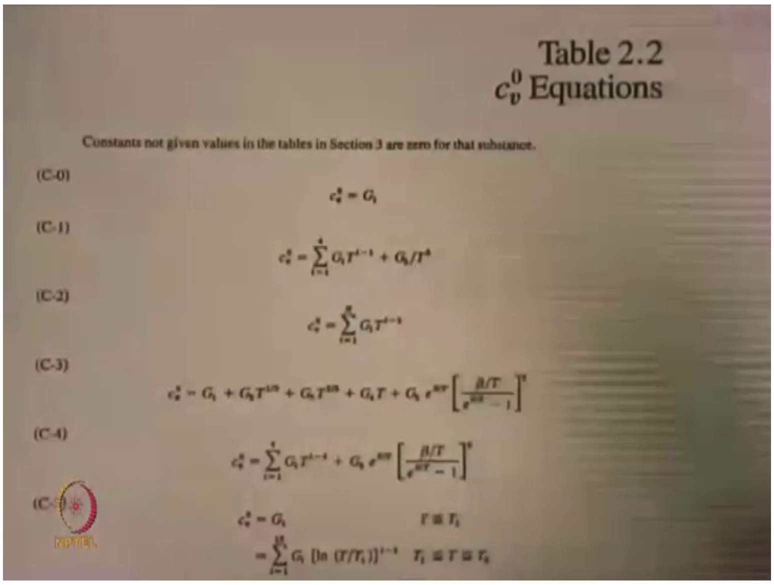

Table 2.2
c_v^0 Equations

Constants not given values in the tables in Section 3 are zero for that substance.

So, these are type of equations we have, these are equations for C v 0 constant volume specific v technique. We talking of depending on the material, we have various type of things which are vary (Refer Time: 13:31) depends on temperature that is all there is constants and temperature to various probabilities T square, T cube, T to the power 4 like that.

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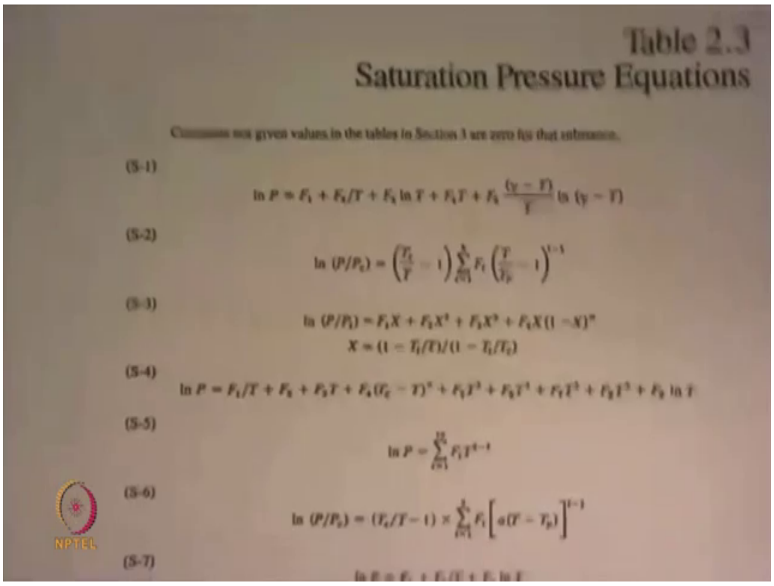

Table 2.3
Saturation Pressure Equations

Constants not given values in the tables in Section 3 are zero for that substance.

The saturation pressure curves that we do, yesterday they can be expressed by any of these type of equation ln P is equal to some function plus function 1 by T ln T and things like that or P by P c is a function of temperature. And so this of 1 by 1 minus to an equation, you specify the temperature you know the saturation pressure that, so that many all the co-ordination that are possible. Again some are good for some substances some are not good for.

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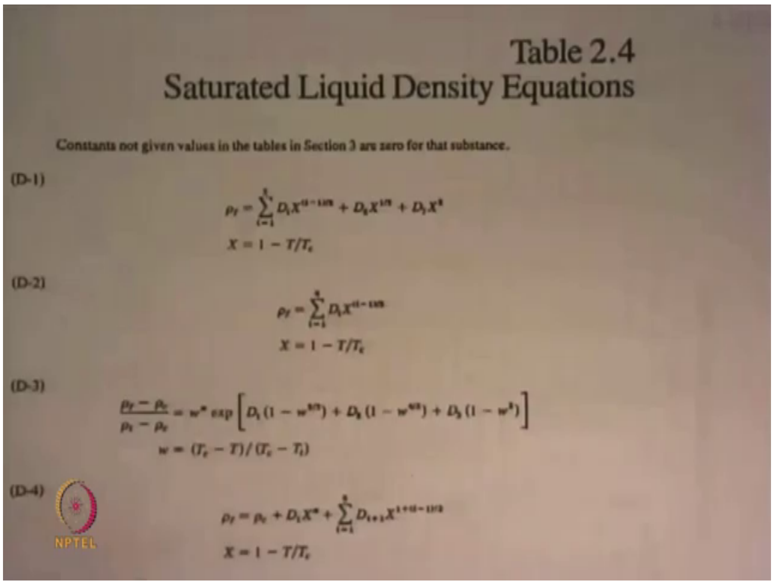

Table 2.4

Saturated Liquid Density Equations

Constants not given values in the tables in Section 3 are zero for that substance.

(D-1)

$$\rho_f = \sum_{i=1}^{5} D_i X^{(i-1)/3} + D_6 X^{1/2} + D_7 X^2$$

$$X = 1 - T/T_c$$

(D-2)

$$\rho_f = \sum_{i=1}^{6} D_i X^{(i-1)/3}$$

$$X = 1 - T/T_c$$

(D-3)

$$\frac{\rho_f - \rho_c}{\rho_t - \rho_c} = w^{\alpha} \exp\left[D_1(1 - w^{2/3}) + D_2(1 - w^{4/3}) + D_3(1 - w^2)\right]$$

$$w = (T_c - T)/(T_c - T_t)$$

(D-4)

$$\rho_f = \rho_c + D_1 X^{\alpha} + \sum_{i=1}^{5} D_{i+1} X^{1+(i-1)/3}$$

$$X = 1 - T/T_c$$

This is a formulation of saturated liquid density; the density of the saturated liquid state rho f or specific volume p f. This is given as the function of this, we can only have the function of temperature. So, we know the temperature, we know the rho f explicitly function; we can make similar things for rho g value.

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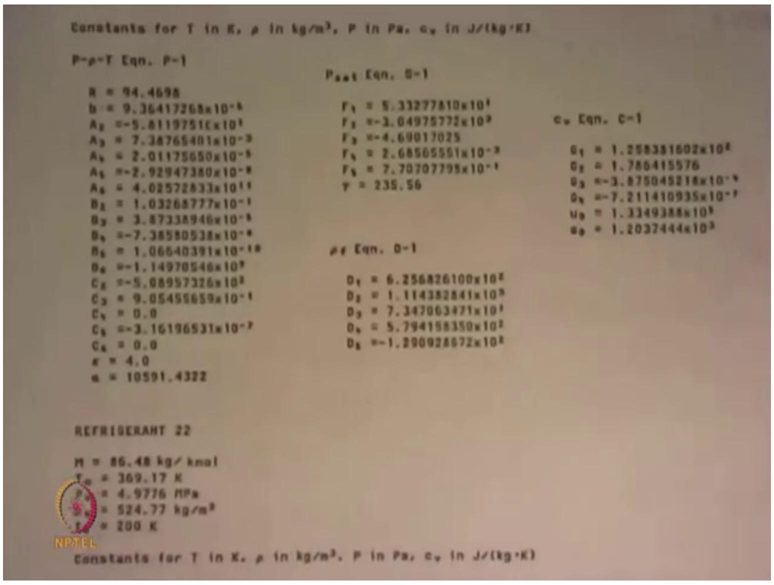

Constants for T in K, ρ in kg/m³, P in Pa, c_v in J/(kg·K)

P-ρ-T Eqn. P-1

$R = 94.4698$
$b = 9.36417268 \times 10^{-4}$
$A_2 = -5.81197510 \times 10^{1}$
$A_3 = 7.38765401 \times 10^{-3}$
$A_4 = 2.01175650 \times 10^{-5}$
$A_5 = -2.92947380 \times 10^{-8}$
$A_6 = 4.02572833 \times 10^{11}$
$B_2 = 1.03268777 \times 10^{-1}$
$B_3 = 3.87338946 \times 10^{-5}$
$B_4 = -7.38580538 \times 10^{-8}$
$B_5 = 1.06640391 \times 10^{-10}$
$B_6 = -1.14970546 \times 10^{9}$
$C_2 = -5.08957326 \times 10^{3}$
$C_3 = 9.05455659 \times 10^{-1}$
$C_4 = 0.0$
$C_5 = -3.16196531 \times 10^{-7}$
$C_6 = 0.0$
$\kappa = 4.0$
$\alpha = 10591.4322$

P_{sat} Eqn. S-1

$F_1 = 5.33277810 \times 10^{1}$
$F_2 = -3.04975772 \times 10^{3}$
$F_3 = -4.69017025$
$F_4 = 2.68565551 \times 10^{-2}$
$F_5 = 7.70707795 \times 10^{-1}$
$\gamma = 235.56$

ρ_f Eqn. D-1

$D_1 = 6.256826100 \times 10^{2}$
$D_2 = 1.114382841 \times 10^{3}$
$D_3 = 7.347063471 \times 10^{1}$
$D_4 = 5.794158350 \times 10^{2}$
$D_5 = -1.290028672 \times 10^{2}$

c_v Eqn. C-1

$G_1 = 1.258381602 \times 10^{2}$
$G_2 = 1.786415576$
$G_3 = -3.875045218 \times 10^{-4}$
$G_4 = -7.211410935 \times 10^{-7}$
$u_0 = 1.3349388 \times 10^{5}$
$s_0 = 1.2037444 \times 10^{3}$

REFRIGERANT 22

$M = 86.48$ kg/ kmol
$T_c = 369.17$ K
$P_c = 4.9776$ MPa
$\rho_c = 524.77$ kg/m³
$T_0 = 200$ K

Constants for T in K, ρ in kg/m³, P in Pa, c_v in J/(kg·K)

And for every material say represent 14, I am showing this the example the critical constants are known T c pc rho c the reference temperature is given T 0 as 125 Kelvin, molecular weight 88.01. And the constant that I used in the equation, it tells you, which is the equation that we use from those. And what is the constants to be use for that what for saturation pressure, what are the which is the equation, and what are the constant. And like that we can put all these together, and to all those property tables and charts that will we have to use.

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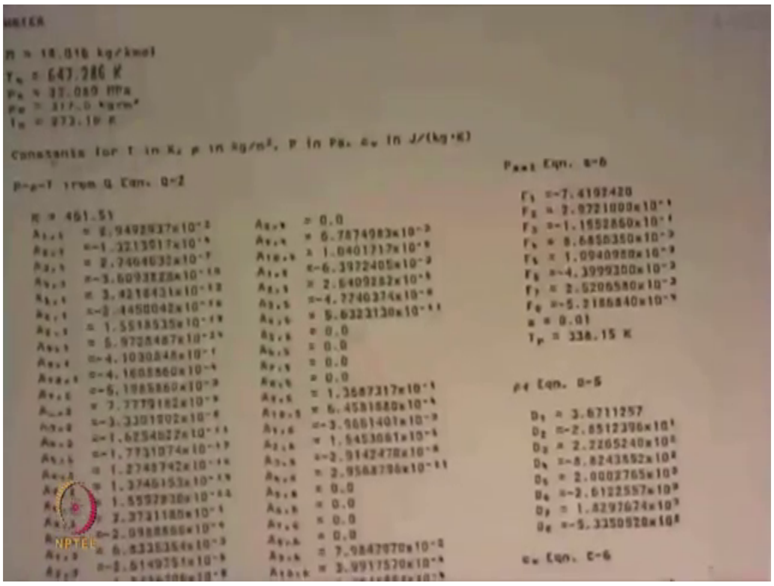

WATER

$M = 18.016$ kg/kmol
$T_c = 647.286$ K
$P_c = 22.089$ MPa
$\rho_c = 317.0$ kg/m³
$T_0 = 273.16$ K

Constants for T in K, ρ in kg/m³, P in Pa, c_v in J/(kg·K)

P-ρ-T from Q Eqn. Q-2

$R = 461.51$

P_{sat} Eqn. S-6

$F_1 = -7.4192420$
$F_2 = 2.9721000 \times 10^{-1}$
$F_3 = -1.1552860 \times 10^{-1}$
$F_4 = 8.6856350 \times 10^{-3}$
$F_5 = 1.0940980 \times 10^{-3}$
$F_6 = -4.3999300 \times 10^{-3}$
$F_7 = 2.5206580 \times 10^{-3}$
$F_8 = -5.2186840 \times 10^{-4}$
$a = 0.01$
$T_p = 338.15$ K

ρ_f Eqn. D-5

$D_1 = 3.6711257$
$D_2 = -2.8512396 \times 10^{1}$
$D_3 = 2.2265240 \times 10^{2}$
$D_4 = -8.8243852 \times 10^{2}$
$D_5 = 2.0002765 \times 10^{3}$
$D_6 = -2.6122557 \times 10^{3}$
$D_7 = 1.8297674 \times 10^{3}$
$D_8 = -5.3350520 \times 10^{2}$

c_v Eqn. C-6

For water that the type of formulations you see, the same equation I showed that the so many constants that we need even for the P-rho-T equation, which is q and p 6. Saturation equation as about 10 constants rho f has 8 C v has about 7 constants there. So, there is a general way in which people have developed all those properties and we have the made effect of using all of that in the problems that we have been solving.

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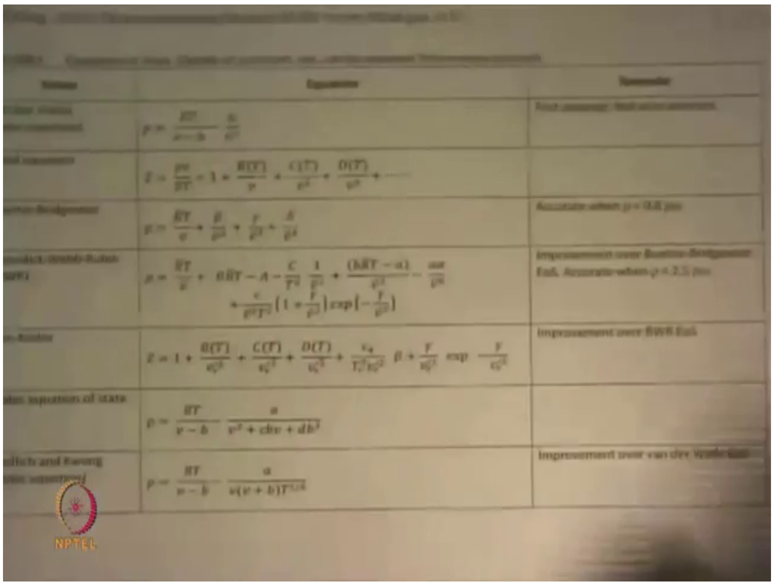

The last thing is how we get the compressibility for ideal gases. P v equal to R T got modified. And you are come across some these in your other courses, there was different types of equations of state. Starting here in the top left, first one is that involves equation of state, you might be familiar with that. And this is p equal RT or v minus b minus a over b square. In the form that it took was that under some conditions, then martial is denser, some cases it is less dense depending on the pressure and temperature.

So, these two terms take care of those physical phenomena of gravitational attraction and with a repulsion between them, does not fit very well your first equation. Then came that Williams equations, where z equal to p v equal to RT was defined as the function of v temperature, and specific volume specific volume spare specific volume, it works a little better and give you the value of z.

In the Beattie Bridgeman equation of state RT upon v bar plus various constants with b bar v square, v cube, v 4, this is specific volume. Then the Benedict Webb Rubin equation, it will get little more complicated, but same thing that RT upon v plus some constant into RT plus whole bunch of constants and combinations of temperature and specific volume that is the common feature in all these.

Lee-Kesler, little more simpler 1 plus BT upon the specific volume square, cube, 5th power, square power with T cube, and like that. The cubic equation of state Redlich Kwong equation of state. And so for depending on what one is interested in and say that only interested in looking at the vapour phase of a refrigerant in a compressor or in air conditioning system, then we can say the this equation is good in forming. I am not too worried about what is the equation of state the liquid thing.

From there I will get some simple state, and from there I will pick up all my equation. And the liquid state, I will just say h is going to C p dt and get my data from there. So, one can do a mix and match of some properties from here, some properties from there, and solve the problem. Now, you can see we would not go into those details, please just take either in the ideal gas solution or we look at the property tables and calculate (Refer Time: 18:02).