# Chemical Engineering Thermodynamics
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## Lecture – 12
## Thermodynamic Tables

Hello and welcome back. The previous lectures we looked at using ideal gas equation of state for calculating various changes in properties across a process, then we have used thermodynamic diagrams to be able to calculate these changes. In today's lecture we are going to look at what are known as Thermodynamic Tables and following it up we will talk about using a cubic equation of state or other equations of state, for non ideal gases and how we can use these approaches to calculate the property changes. To begin with let us quickly summarize what we have done so far.

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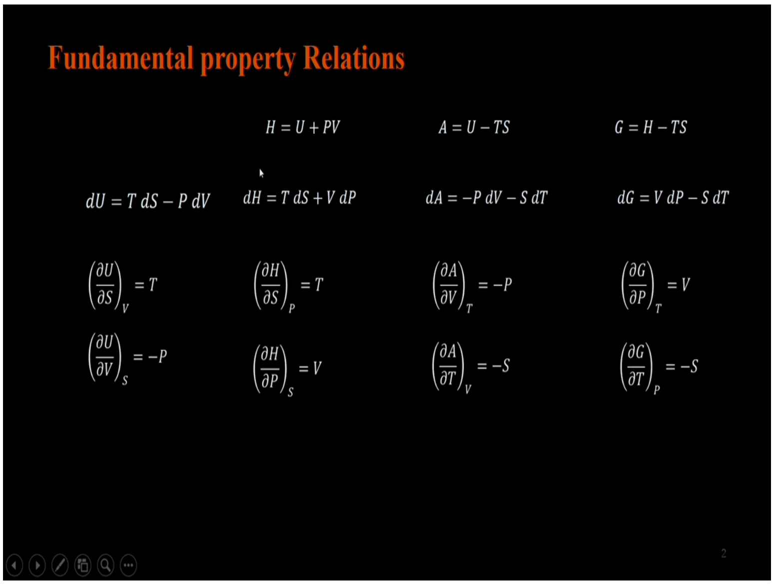

Fundamental property Relations

$H = U + PV$ $\quad A = U - TS$ $\quad G = H - TS$

$dU = T\,dS - P\,dV$ $\quad dH = T\,dS + V\,dP$ $\quad dA = -P\,dV - S\,dT$ $\quad dG = V\,dP - S\,dT$

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \left(\frac{\partial H}{\partial S}\right)_P = T \quad \left(\frac{\partial A}{\partial V}\right)_T = -P \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \quad \left(\frac{\partial H}{\partial P}\right)_S = V \quad \left(\frac{\partial A}{\partial T}\right)_V = -S \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

We define a variety of thermodynamic properties enthalpy, Helmholtz free energy, Gibbs free energy. How these changes are dependent on one another and the derivatives or partial derivatives for these variables in terms of other thermodynamic quantities and then we derive some very important relations known as Maxwell's relations that relate things that we can measure to things that we cannot directly measure laboratory setting.

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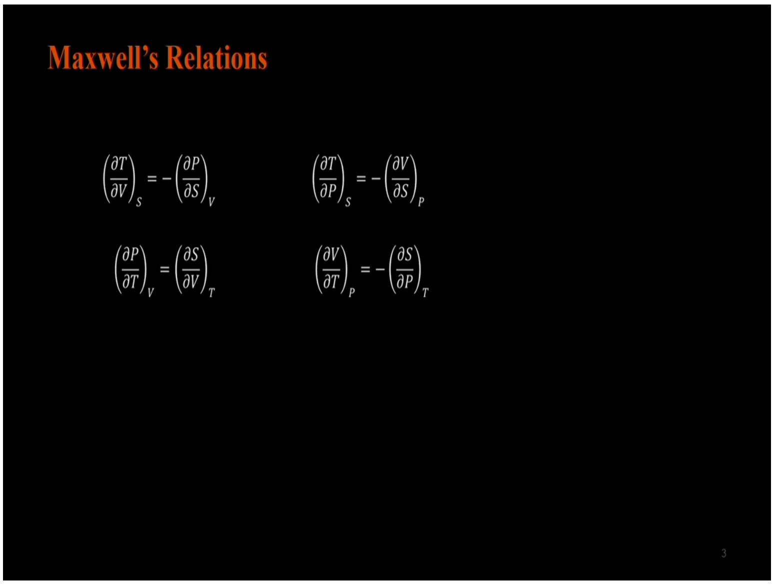

## Maxwell's Relations

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

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

These type of equations will help us extract information we need from the information we can measure in the lab.

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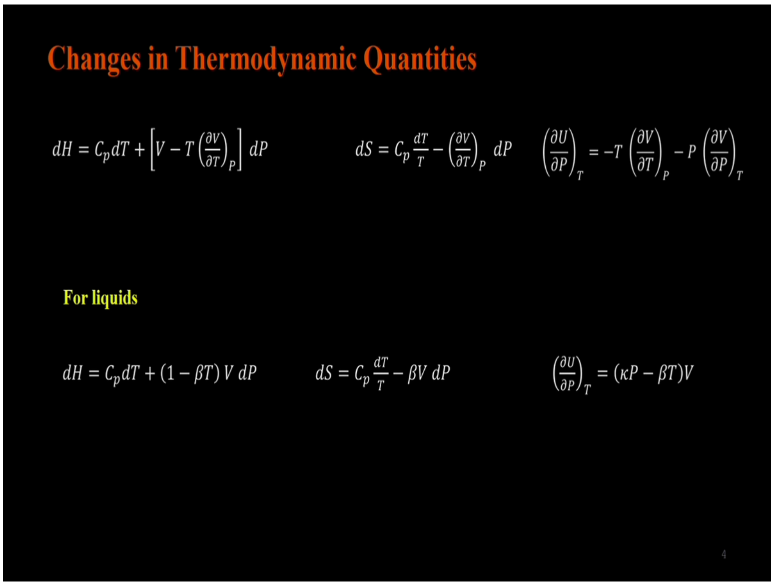

## Changes in Thermodynamic Quantities

$$dH = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP \qquad dS = C_p \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP \qquad \left(\frac{\partial U}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T$$

For liquids

$$dH = C_p dT + (1 - \beta T)\, V\, dP \qquad dS = C_p \frac{dT}{T} - \beta V\, dP \qquad \left(\frac{\partial U}{\partial P}\right)_T = (\kappa P - \beta T)V$$

Then we looked at how we can use these equations for recruits in terms of the isothermal compressibility and volume expensivity beta and kappa.

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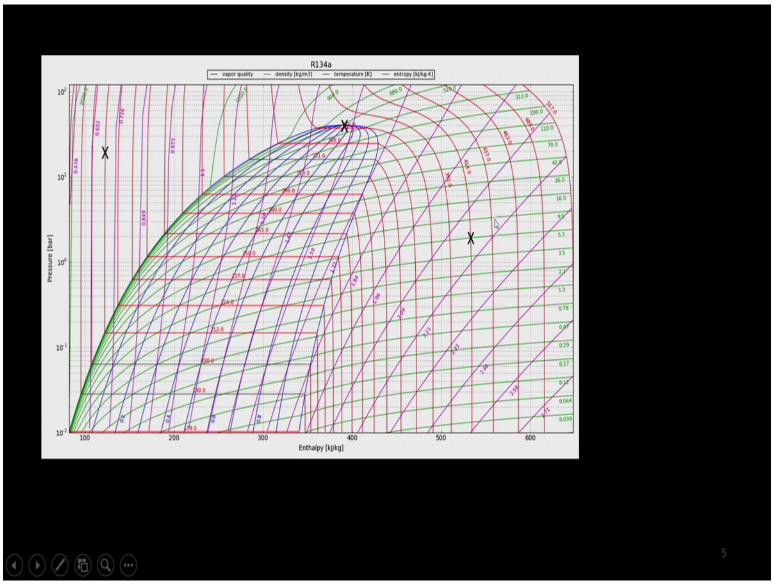

And finally, we looked at thermodynamic diagrams and how these diagrams have a wealth of information in them including entropy, molar volume or specific volume density the 2 phase region below the dome represented in this region etcetera.

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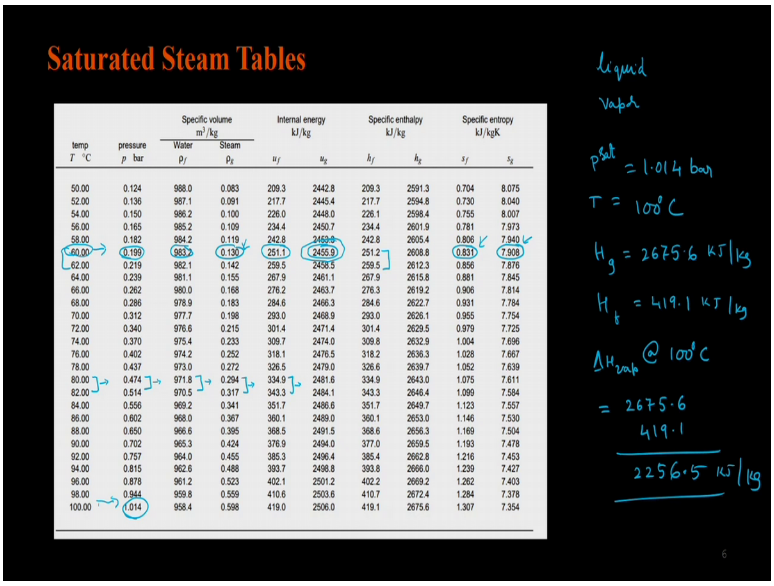

## Saturated Steam Tables

| temp | pressure | Specific volume $m^3/kg$ | | Internal energy kJ/kg | | Specific enthalpy kJ/kg | | Specific entropy kJ/kgK | |
|---|---|---|---|---|---|---|---|---|---|
| | | Water | Steam | | | | | | |
| $T$ °C | $p$ bar | $\rho_f$ | $\rho_g$ | $u_f$ | $u_g$ | $h_f$ | $h_g$ | $s_f$ | $s_g$ |
| 50.00 | 0.124 | 988.0 | 0.083 | 209.3 | 2442.8 | 209.3 | 2591.3 | 0.704 | 8.075 |
| 52.00 | 0.136 | 987.1 | 0.091 | 217.7 | 2445.4 | 217.7 | 2594.8 | 0.730 | 8.040 |
| 54.00 | 0.150 | 986.2 | 0.100 | 226.0 | 2448.0 | 226.1 | 2598.4 | 0.755 | 8.007 |
| 56.00 | 0.165 | 985.2 | 0.109 | 234.4 | 2450.7 | 234.4 | 2601.9 | 0.781 | 7.973 |
| 58.00 | 0.182 | 984.2 | 0.119 | 242.8 | 2453.3 | 242.8 | 2605.4 | 0.806 | 7.940 |
| 60.00 | 0.199 | 983.2 | 0.130 | 251.1 | 2455.9 | 251.2 | 2608.8 | 0.831 | 7.908 |
| 62.00 | 0.219 | 982.1 | 0.142 | 259.5 | 2458.5 | 259.5 | 2612.3 | 0.856 | 7.876 |
| 64.00 | 0.239 | 981.1 | 0.155 | 267.9 | 2461.1 | 267.9 | 2615.8 | 0.881 | 7.845 |
| 66.00 | 0.262 | 980.0 | 0.168 | 276.2 | 2463.7 | 276.3 | 2619.2 | 0.906 | 7.814 |
| 68.00 | 0.286 | 978.9 | 0.183 | 284.6 | 2466.3 | 284.6 | 2622.7 | 0.931 | 7.784 |
| 70.00 | 0.312 | 977.7 | 0.198 | 293.0 | 2468.9 | 293.0 | 2626.1 | 0.955 | 7.754 |
| 72.00 | 0.340 | 976.6 | 0.215 | 301.4 | 2471.4 | 301.4 | 2629.5 | 0.979 | 7.725 |
| 74.00 | 0.370 | 975.4 | 0.233 | 309.7 | 2474.0 | 309.8 | 2632.9 | 1.004 | 7.696 |
| 76.00 | 0.402 | 974.2 | 0.252 | 318.1 | 2476.5 | 318.2 | 2636.3 | 1.028 | 7.667 |
| 78.00 | 0.437 | 973.0 | 0.272 | 326.5 | 2479.0 | 326.6 | 2639.7 | 1.052 | 7.639 |
| 80.00 | 0.474 | 971.8 | 0.294 | 334.9 | 2481.6 | 334.9 | 2643.0 | 1.075 | 7.611 |
| 82.00 | 0.514 | 970.5 | 0.317 | 343.3 | 2484.1 | 343.3 | 2646.4 | 1.099 | 7.584 |
| 84.00 | 0.556 | 969.2 | 0.341 | 351.7 | 2486.6 | 351.7 | 2649.7 | 1.123 | 7.557 |
| 86.00 | 0.602 | 968.0 | 0.367 | 360.1 | 2489.0 | 360.1 | 2653.0 | 1.146 | 7.530 |
| 88.00 | 0.650 | 966.6 | 0.395 | 368.5 | 2491.5 | 368.6 | 2656.3 | 1.169 | 7.504 |
| 90.00 | 0.702 | 965.3 | 0.424 | 376.9 | 2494.0 | 377.0 | 2659.5 | 1.193 | 7.478 |
| 92.00 | 0.757 | 964.0 | 0.455 | 385.3 | 2496.4 | 385.4 | 2662.8 | 1.216 | 7.453 |
| 94.00 | 0.815 | 962.6 | 0.488 | 393.7 | 2498.8 | 393.8 | 2666.0 | 1.239 | 7.427 |
| 96.00 | 0.878 | 961.2 | 0.523 | 402.1 | 2501.2 | 402.2 | 2669.2 | 1.262 | 7.403 |
| 98.00 | 0.944 | 959.8 | 0.559 | 410.6 | 2503.6 | 410.7 | 2672.4 | 1.284 | 7.378 |
| 100.00 | 1.014 | 958.4 | 0.598 | 419.0 | 2506.0 | 419.1 | 2675.6 | 1.307 | 7.354 |

liquid

vapor

$P^{sat} = 1.014$ bar

$T = 100^{\circ}C$

$H_g = 2675.6$ KJ/kg

$H_f = 419.1$ KJ/kg

$\Delta H_{vap}$ @ $100^{\circ}C$

$$= \begin{array}{r} 2675.6 \\ 419.1 \\ \hline 2256.5 \text{ KJ/kg} \\ \hline \end{array}$$

What we will do today is look at what are known as thermodynamic tables first. The information that is stored in thermodynamic tables is similar to what is given in form of thermodynamic diagrams. One of the more popular thermodynamic tables is what are known as a steam tables are. This is of course for water, right there are 2 types of steam tables 1 corresponding to what is known as the saturated steam indicating that, we have both liquid and vapor phases coexisting with 1 another at equilibrium. And then thermodynamic properties such as internal energy, enthalpy, entropy density or volume etcetera are listed for saturated steam. Because it is saturated there are 2 phases 1 component. So, there is only 1 degree of freedom which indicates I just need to pick 1 property be it enthalpy, be it entropy or pressure or temperature whatever it is I pick 1 property and the state of the system is going to be fixed.

So, for example, if I say that I have saturated steam with an internal energy of the vapor phase being 2455.9 which corresponds to this quantity here 2455.9 then there is only 1 condition at which that happens, the corresponding temperature is going to be 60 degree centigrade, the pressure at this condition is going to be 0.199 bar which also means that the vapor pressure at 60 is 0.199 bar. The densities of the liquid and vapor phases are given for the liquid phase it is 983.2 meter cube per kg, for the vapor phase it is 0.13 meter cube per kg, the entropy of the liquid and vapor are given etcetera.

So, because this is saturated steam table, at each condition we are going to have there are 2 phases which means all thermodynamic properties in these 2 or most of the thermodynamic properties will come back to that later, most of the thermodynamic properties in these 2 phases are different. It has different internal energy, it has different enthalpy, it has different entropy etcetera.

If there happens to be a condition which falls in between the 2 values listed in this table for example, if I need something at 81 degree centigrade that falls between 80 and 82, we can simply interpolate suitably between the 2 conditions do an interpolation and then get the quantities we need. So, these tables in that sense usually are closely spaced, and if there is a requirement for information in between the 2 data points in this table, we can always interpolate and get what we need.

So, again saturated steam table there is one for the liquid phase; one property listed for the liquid phase and one property listed for the vapor of the gaseous phase. So, internal energy there is liquid internal energy and vapor internal energy liquid enthalpy and vapor enthalpy and incidentally, this difference between the liquid and vapor enthalpy is corresponds to the heat of vaporization at that condition. So, for example, at 70 degree or let us 100 degree centigrade that is more popular one, at 100 degree centigrade right the pressure is 1.014 bar.

So, the vapor pressure at 100 degree centigrade is 1.014 bar, the temperature of course, was 100 degree centigrade. The enthalpy of the vapor is 2675.6 the units are kilo joule per kg and the enthalpy of the liquid or the enthalpy of the vapor we are using a subscript g for a gaseous state and for the fluid we are using l in this table so let us stick with that. These are the specific values and the enthalpy of the liquid is 419.1 kilo joule per kg. The difference between these quantities is going to be the enthalpy of vaporization at 100 degree centigrade or 1.014 bar whatever it is you want to express it as there is going to be 2615.7 minus 419.1 which is 52 and 2, 2256.5 kilo joule per kg.

So, 2256.5 kilo joule per kg is the enthalpy of vaporization and this condition, similarly I can calculate the internal energy of vaporization or entropy change due to a vaporization etcetera at the same condition. So, this is how we can use the saturated steam table similar to the thermodynamic diagram, I do not have to read it off the plot, I can use the table directly and get the values I want right.

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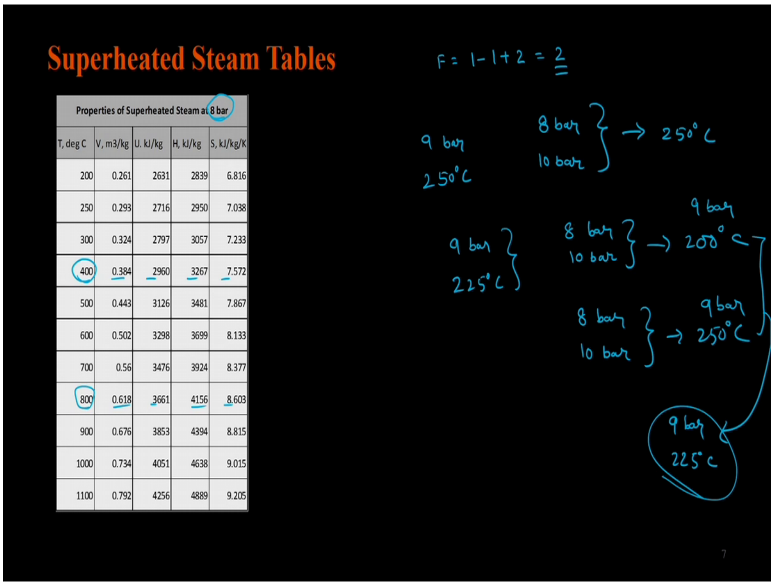

## Superheated Steam Tables

| Properties of Superheated Steam at 8 bar | | | | |
|---|---|---|---|---|
| T, deg C | V, m3/kg | U. kJ/kg | H, kJ/kg | S, kJ/kg/K |
| 200 | 0.261 | 2631 | 2839 | 6.816 |
| 250 | 0.293 | 2716 | 2950 | 7.038 |
| 300 | 0.324 | 2797 | 3057 | 7.233 |
| 400 | 0.384 | 2960 | 3267 | 7.572 |
| 500 | 0.443 | 3126 | 3481 | 7.867 |
| 600 | 0.502 | 3298 | 3699 | 8.133 |
| 700 | 0.56 | 3476 | 3924 | 8.377 |
| 800 | 0.618 | 3661 | 4156 | 8.603 |
| 900 | 0.676 | 3853 | 4394 | 8.815 |
| 1000 | 0.734 | 4051 | 4638 | 9.015 |
| 1100 | 0.792 | 4256 | 4889 | 9.205 |

$F = 1 - 1 + 2 = \underline{\underline{2}}$

9 bar
250°C

$\left.\begin{matrix}\text{8 bar}\\ \text{10 bar}\end{matrix}\right\} \rightarrow 250°C$

$\left.\begin{matrix}\text{9 bar}\\ 225°C\end{matrix}\right\}$

9 bar

$\left.\begin{matrix}\text{8 bar}\\ \text{10 bar}\end{matrix}\right\} \rightarrow 200°C$

$\left.\begin{matrix}\text{8 bar}\\ \text{10 bar}\end{matrix}\right\} \rightarrow \begin{matrix}\text{9 bar}\\ 250°C\end{matrix}$

9 bar
225°C

And then we have what are known as superheated steam tables, this corresponds to the superheated condition right.

So, there is only 1 phase. So, the degrees of freedom is 1 component 1 phase plus 2. So, that is going to be 2 degrees of freedom. So, I need to fix 2 variables, let us say at 8 bar and I fix the temperature to be 400 degree centigrade, then other values are given to me V U H and S and similarly at 8 bar and 800 degree centigrade the values are given to me etcetera right. As the temperature increases of course, the entropy is going to increase, the enthalpy is increases the pressure is same, but the temperature goes from 400 to 800 U H S etcetera increase right.

So, I need now 2 variables to fix the state of the system unlike in the saturated case where I just needed 1 variable. Once these 2 variables are fixed I can read other quantities off the table and we usually have a long list or a lengthy table a different closely spaced pressure say at 8 bar, then at 10 bar then a 12 bar etcetera and then the temperatures being 200 250 300 400 etcetera.

And again as in the previous class if I need something in between, I need to do an interpolation. If I need it at 9 bar, then I take the table at 8 bar and I take the table at 10 bar and then if I need it at 9 bar and 250 degree centigrade I take these 2 tables and then interpolate between these 2 pressures at 250 and I am home free. Otherwise if I need it at 9 bar and say 225 degree centigrade, then I first need to do an interpolation for 9 bar and 200 degree centigrade and then I do an interpolation between the tables at 8 bar and 10 bar, again for 9 bar at 250 degree centigrade right.

So, first I do this for 9 bar 200 then I do this for 9 bar 250 and then I take these 2 quantities and interpolate again for 9 bar and 225 degree centigrade. We call this as double interpolation, the first time for 200 the second time for 250 and then we interpolate again for 225 degree centigrade that is how we get the value at 225.

So, we can suitably use these tables interpolate and get to the point we want depending on how closely these values are spaced, the accuracy is going to increase of course.

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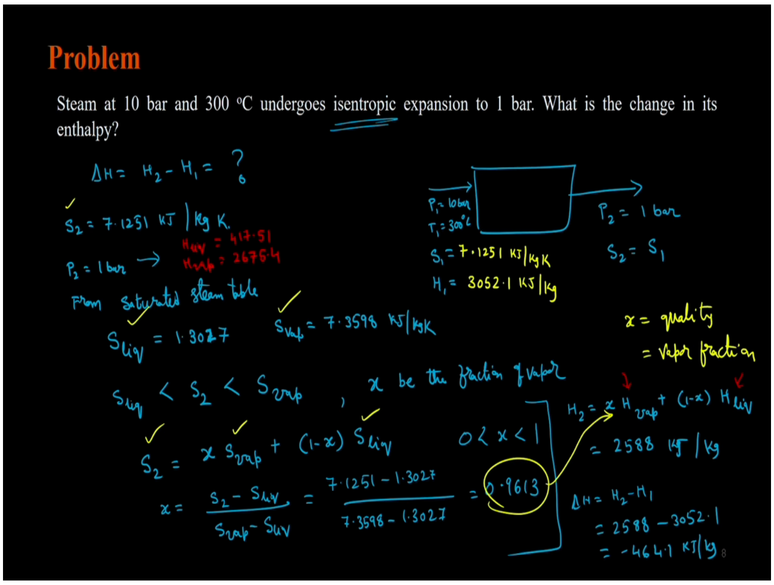

## Problem

Steam at 10 bar and 300 °C undergoes isentropic expansion to 1 bar. What is the change in its enthalpy?

$\Delta H = H_2 - H_1 = ?$

$S_2 = 7.1251$ KJ/Kg K.

$P_2 = 1$ bar $\rightarrow$ $H_{liq} = 417.51$, $H_{vap} = 2675.4$

From saturated steam table

$S_{liq} = 1.3027$ $S_{vap} = 7.3598$ KJ/KgK

$S_{liq} < S_2 < S_{vap}$, $x$ be the fraction of vapor

$S_2 = x S_{vap} + (1-x) S_{liq}$ $0 < x < 1$

$x = \frac{S_2 - S_{liq}}{S_{vap} - S_{liq}} = \frac{7.1251 - 1.3027}{7.3598 - 1.3027} = 0.9613$

$P_1 = 10$ bar, $T_1 = 300$ °C $\rightarrow$ $P_2 = 1$ bar

$S_1 = 7.1251$ KJ/KgK $S_2 = S_1$

$H_1 = 3052.1$ KJ/Kg

$x =$ quality $=$ vapor fraction

$H_2 = x H_{vap} + (1-x) H_{liq}$

$= 2588$ KJ/Kg

$\Delta H = H_2 - H_1$

$= 2588 - 3052.1$

$= -464.1$ KJ/Kg

So, that is how we are going to use these tables what we will do next is quickly solve 1 problem based on these tables. I have steam at 10 bar and 300 degree centigrade it undergoes isentropic expansion to 1 bar. The question is what is the change in its enthalpy during this process right. So, we have steam that 100 was an expansion, the expansion is said to be isentropic and we want to know the change in enthalpy right.

So, what I have is a process right steam is entering at 10 bar and the temperature is 300 degree centigrade and it comes out, I do not know at what condition or at what temperature what I do not know is it comes out at 1 bar and what I again know is that the entropy is same as 2 is S 1 because the process is isentropic. Similar to isobaric process where the pressure is same, isentropic process indicates the entropy is same and if that be the case then S 2 is going to be equal to S 1 I know P 1 and T 1 I know P 2.

Now, we want to find out what the change in enthalpy is or delta H for this process which is H 2 minus H 1 is we want to find this quantity, let us see how we can do it using the steam tables this is steam right. So, because I know 2 conditions P 1 and T 1 I can go back to the steam table and look at the values for entropy and enthalpy at these conditions. So, I am going to read these 2 numbers off the table directly and it turns out that at 10 bar and 300 degree centigrade the entropy is 7.1251 kilo joule per kg Kelvin and H 1 is 3052.1 kilo joule per kg.

So, we are going to read it off superheated steam table as we have done earlier right coming out. So, I know what it is at the initial condition. Now the process is isentropic right, which means S 2 is going to be equal to S 1 or S 2 is 7.1251 kilo joule per kg Kelvin. We are coming out at 1 bar so, the first question to ask is am I going to be near 2 phase region or am I going to be in a single phase region at 1 bar because I do not know the temperature, I cannot answer the question right away, but if I look at the entropy maybe I can.

So, what I will do is, I will take 1 bar right and go to a saturated steam table. P 2 is 1 bar from the saturated steam table, let me look at the entropy values for the liquid it is 1.3027; obviously, this value S 2 is much higher than that of the liquid. So, it cannot be only liquid and for the vapor it is 7.3598 kilo joule per kg Kelvin. So, from the saturated steam table when I look at the entropy at 1 bar it turns out that the liquid entropy is lower than S 2, the final total entropy of whatever is coming out which in itself is lower than the vapor entropy. What this tells me is that whatever is coming out cannot be liquid, cannot be vapor the only way this can happen is if it is in between or if it is a mixture of both liquid and vapor right.

So, whatever comes out is going to be a mixture of both liquid and vapor, let x be the fraction of vapor. Then S 2 is going to be the fraction of vapor multiplied the multiplied with the vapor entropy plus the fraction of liquid which is 1 minus x multiplied with the liquid entropy. So, then depending on the value of x which is; obviously, going to be between 0 and 1 we can always end up with the value of S 2, that is in between these 2 numbers which is as liquid and as vapor which is what we have S 2 is 7.1251 which is in between s liquid which is 1.3027 and S vapor which is 7.3598.

So, my situation is I am going to have a 2 phase mixture coming out and the fraction of the vapor in this 2 phase mixture is going to be x and we usually call this x as the quality of the steam, it is the vapor fraction in the steam. So, now, since I know S 2 I know s vapor I know S liquid S 2 is right here S liquid is here S vapor is here. So, once I know these 3 quantities I can always go back and calculate x right. So, let me see x is going to be S 2 minus S liquid over S vapor minus S liquid.

So, that is going to be 7.1251 minus 1.3027 over S vapor is going to be 7.3598 minus S liquid is 1.3027. And if I solve for this number it turns out to be 0.9613. So, the fraction of vapor at the outlet is 0.9613. Once I have this number I can always go back and calculate the entropy it sorry in this case enthalpy at the outlet which is x times H for the liquid no or sorry because I have excess the vapor fraction it is x times H for the vapor plus 1 minus x times H for the liquid.

At 1 bar I am going to go back to saturated steam write down the values of H for liquid and H for vapor, the numbers I have are 417.51 and 2675.4. Once I put these 2 numbers back in here for calculating H 2 what I get is 2588 kilojoules per kg. I already know x all right, I already know x from here I am going to put that value here and then the 2 values of H liquid and H vapor from the saturated steam tables here. Once I do that I can calculate H 2 to be 2588 kilo joules per kg.

And finally, delta H is going to be H 2 minus H 1, I already know H 1 2588 minus 3052.1 that will be delta H which is going to be minus 464.1 kilo joule per kg. So, the value for change in enthalpy is negative 464 kilo joule per kg. So, to solve this problem all we have done is simply use the steam table and the condition that the entropy change for the process is 0, its an isentropic process. The moment we have the steam tables it is pretty straightforward to solve this particular problem.

Now, so far what we have looked at is using thermodynamic tables and thermodynamic diagrams or the ideal gas scenarios for calculating the property changes in a process. But then in a chemical process industry we have millions of compounds, it is not possible to tabulate the properties for all these compounds or you know draw diagrams for properties of all these compounds. In addition we are going to make several more millions of mixtures when we combine these chemical species which is what it is in a chemical process industry most of them occur as mixtures.

So, its going to be challenging to be able to use these diagrams or tables in most cases. For special cases like water or refrigerant which where we looked at the diagram r 134 m its fine, but in a chemical process industry its not going to be very easy to use such diagrams or tables right away. So, we need to come up with a way where we can handle chemical species or millions of chemical species and their mixtures. We have looked at how to do that if it is an ideal gas like scenario, but for other cases we still have to find a way to do it. So, the way we handle these property changes in case of non ideal gases is, introducing what are known as residual properties, in some books you may see the usage of the word departure functions.

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## Residual Properties

Departure Functions

So, either one essentially means, the difference between what it is in a non ideal scenario to what it is in an ideal scenario at the same temperature and pressure conditions. We will come back to that in a minute, but before we go there let us quickly introduce an idea.

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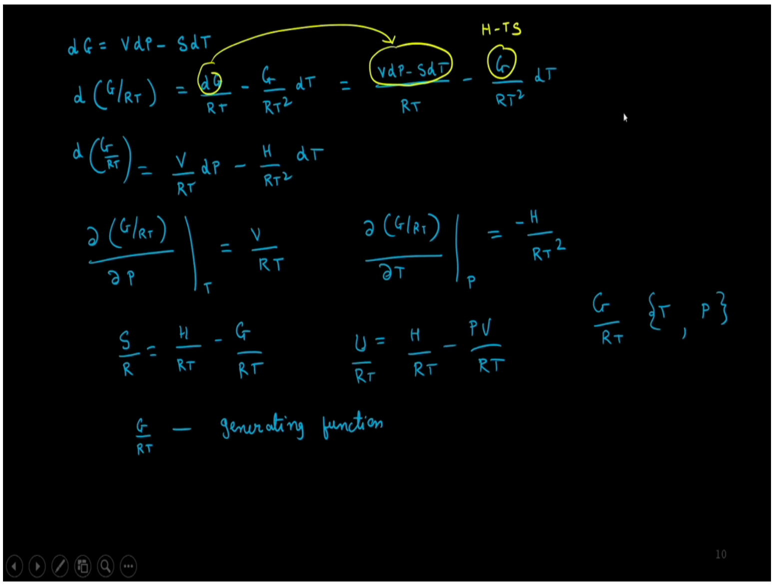

$$dG = VdP - SdT$$

$$d\left(G/RT\right) = \frac{\boxed{dG}}{RT} - \frac{G}{RT^2}dT = \frac{\boxed{VdP - SdT}}{RT} - \frac{\overset{H-TS}{\boxed{G}}}{RT^2}dT$$

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT}dP - \frac{H}{RT^2}dT$$

$$\left.\frac{\partial\left(G/RT\right)}{\partial P}\right|_T = \frac{V}{RT} \qquad \left.\frac{\partial\left(G/RT\right)}{\partial T}\right|_P = \frac{-H}{RT^2}$$

$$\frac{G}{RT}\ \{T, P\}$$

$$\frac{S}{R} = \frac{H}{RT} - \frac{G}{RT} \qquad \frac{U}{RT} = \frac{H}{RT} - \frac{PV}{RT}$$

$\frac{G}{RT}$ — generating function

Now, if we have a homogeneous fluid of constant composition, then we have written several relations for thermodynamic properties. One of the more important ones for a chemical process industry as, I have talked about earlier is d G is V d P minus S d T. This is important because the change in Gibbs free energy is related to the changes in temperature and pressure on the right hand side which can be directly measured.

So, this in that sense is a special case which we like for our calculations. Now I am going to take this and try to rewrite it a little bit let us see if I write d of G over R T, then it is going to be d G by RT minus G by RT square d T. I am just opening these parentheses and writing it as d G and dT right. Now d G itself is V d P minus S d T. So, it is going to be V d P minus S dT over RT minus G by RT square dT right. And again I am going to replace that G with H minus TS here I have replaced d G with V d P minus S dT and then do a little bit of simplification. So, that in the end what I end up with is going to be V by RT d P minus H by RT square dT this is going to be d of G by RT.

So, d of G by RT is going to be V by RT d P minus H by RT square dT right. And remember how we have taken the partial derivatives, if I say what would be the partial derivative of G over RT with respect to P at constant temperature its going to be straightforward, its going to be simply V over RT and similarly the partial derivative of G over RT with respect to the temperature at constant pressure is going to be its constant pressure. So, the first term drops out and we are taking the derivative of this and from the second term that derivative is going to be negative H over RT square right.

So, if I have g over RT as a function of temperature and pressure, then I can take the derivative with respect to pressure at constant temperature I can get V, I can take its derivative with respect to temperature at constant pressure I can get negative H and then once I have V and H I can calculate S because S is simply H minus G by T. So, it is going to be H by RT minus G by RT this is going to be S over R and U because I know H I can calculate U, U or RT is going to be H over RT minus P V over RT and so on. So, once I know g over RT as a function of temperature and pressure then I can calculate all the thermodynamic properties. In fact, you can derive a relation for the Helmholtz free energy also I can calculate V H S U everything.

So, in that sense we are using G as a generating function for all the thermodynamic properties, we generate or calculate all the thermodynamic properties using G. So, it is called as the generating function.

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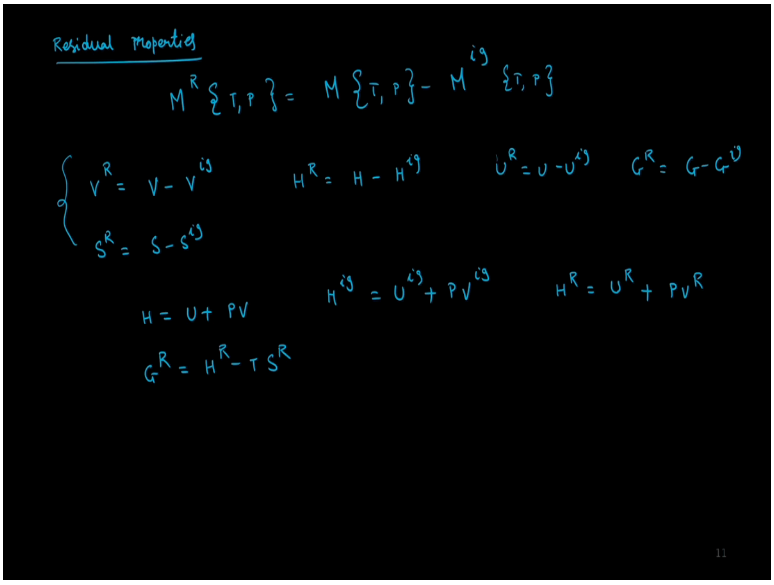

Residual Properties

$$M^R\{T,P\} = M\{T,P\} - M^{ig}\{T,P\}$$

$$V^R = V - V^{ig} \qquad H^R = H - H^{ig} \qquad U^R = U - U^{ig} \qquad G^R = G - G^{ig}$$

$$S^R = S - S^{ig}$$

$$H = U + PV \qquad H^{ig} = U^{ig} + PV^{ig} \qquad H^R = U^R + PV^R$$

$$G^R = H^R - TS^R$$

Now, let us introduce the concept of residual properties keeping this in mind; residual properties and like I said at the beginning of this section, by residual property all we mean is the difference between the property and that in its ideal gas state at the same temperature and pressure right. Some properties such as enthalpy might not be dependent on pressure, some like volume will be dependent on pressure for an ideal gas, but we want to take and calculate them at the same temperatures and pressures to calculate the residual property.

So, we are going to use the superscript r to denote the residual property, it can be for any thermodynamic property M, M R is going to be M minus M i g where i g stands for the ideal gas condition. So, for example, the volume or the residual volume V R is going to be V the actual volume minus the ideal gas volume. So, the gas itself is behaves as an ideal gas then; obviously, V also will be i g and V R or the residual volume will be 0 if it is a non-ideal gas or a real gas then of course, there will be a non-zero value for the residual volume similarly enthalpy H R is going to be H minus H i g. And dropping the condition that all of them they have all of them have to be at the same temperature and pressure, it is implied in that equation when I write H R is H minus H i g etcetera U R is going to be U minus U i g G R or the residual Gibbs free energy is going to be G minus G i G S R is going to be S minus S i g and so on right.

Now, are these residual properties related to one another is H R related to U R for example, let us see H I know is definitely U plus P V and if I write it for an ideal gas H i g is going to be U i g plus PV i g where V i g is a volume of the ideal of gas enthalpy and internal energy are also for the ideal gases. So, that equation also holds and if I subtract 1 from the other H minus H i g will be H R on the right hand side it will be U minus U i g which is; obviously, U R plus PV R the original equation was H as U plus PV for the total property, for the residual property H R will be U R plus PV R exact similar equation I am replacing everything with residual properties and similarly other equations follow for example, G R G is H minus T S. So, G R is going to be H R minus T S R and so on right.

So, this is the definition of residual property and how residual properties are related to the other thermodynamic properties. Now there is a very important idea which we are going to introduce here about the residual properties, what would be various thermodynamic residual properties at the limit of 0 pressure. Limit of 0 pressure is an important limit because as we know most gases tend to become ideal gases as we approach the 0 pressure limit.

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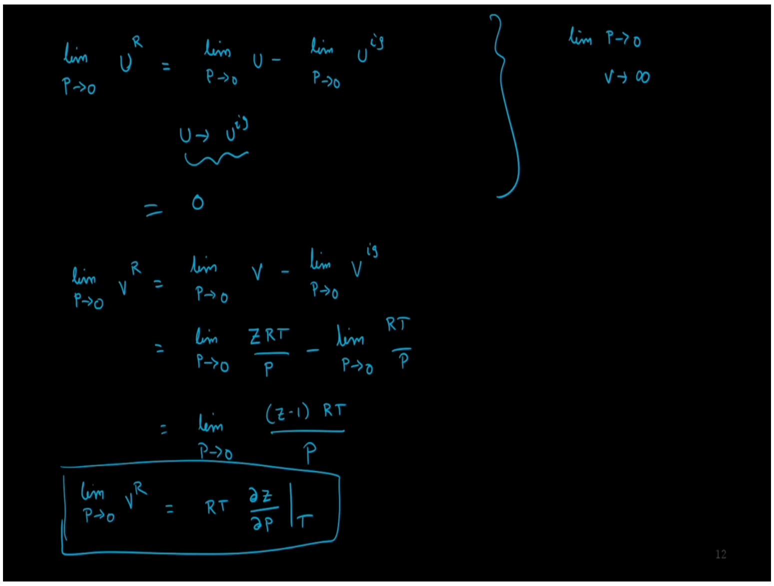

$$\lim_{P\to 0} U^R = \lim_{P\to 0} U - \lim_{P\to 0} U^{ig}$$

$$\underbrace{U \to U^{ig}}$$

$$= 0$$

$$\lim P\to 0$$

$$V \to \infty$$

$$\lim_{P\to 0} V^R = \lim_{P\to 0} V - \lim_{P\to 0} V^{ig}$$

$$= \lim_{P\to 0} \frac{ZRT}{P} - \lim_{P\to 0} \frac{RT}{P}$$

$$= \lim_{P\to 0} \frac{(Z-1)\,RT}{P}$$

$$\boxed{\lim_{P\to 0} V^R = RT \left.\frac{\partial Z}{\partial P}\right|_T}$$

So, let us see what happens for each of the thermodynamic properties at this limit of P going to 0 U R residual internal energy, what would be this value by definition U R is U minus U i g.

So, its going to be P going to 0 U minus limit of P going to 0 U i g. As we approach the 0 pressure limit the volume goes to infinity and as the volume goes to infinity the molecules are pulled apart. So, far apart that there is a decrease in their intermolecular forces when they are pulled apart and eventually there are no intermolecular forces at very very large molar volumes or as V goes to infinity. And when that happens, the internal energy which is a result of the molecular level kinetic potential and other forms of energies because the intermolecular forces go to 0 they exactly behave as if they are an ideal gas and U will tend to go to U i g at this limit and so, this U R is going to go to 0 right the temperature is same.

So, other types of intra molecular level energies are going to be same for ideal gas as well as for a real gas only thing as you approach the 0 pressure limit, the real gas in the real gas the intermolecular forces go to 0 and then the total internal energy will be same as that of an ideal gas and so, the residual internal energy is going to go to 0 as we approach the 0 pressure limit. Now on the other hand let us see what happens to molar volume, limit of P going to 0, what is the value of the residual volume V R. This will be limit of P going to 0, V minus limit P going to 0 V i g right V minus V i g.

So, this is limit of P going to 0, V in terms of compressibility factor is z RT over P z is the compressibility factor the ideal gas compressibility factor is 1. So, it is simply RT by P or this will be limit of P going to 0, z minus 1 RT by P. Now if you observe as P goes to 0 the gases behave as an ideal gas. So, z will go to 1. So, you have a numerator which is 0 and a denominator which is 0, z minus 1 goes to 0, P goes to 0.

So, both the numerator and the denominator go to 0. So, that limit is indeterminate and the only way we can determine at its going to be taking a derivative by the LHopital’s rule which will give us derivative of z with respect to P at constant temperature. So, this limit as P goes to 0 for residual volume is going to be determined by the slope of z versus P curve at constant temperature as we approach the 0 pressure. So, it is finite, but then it does not have to be 0.

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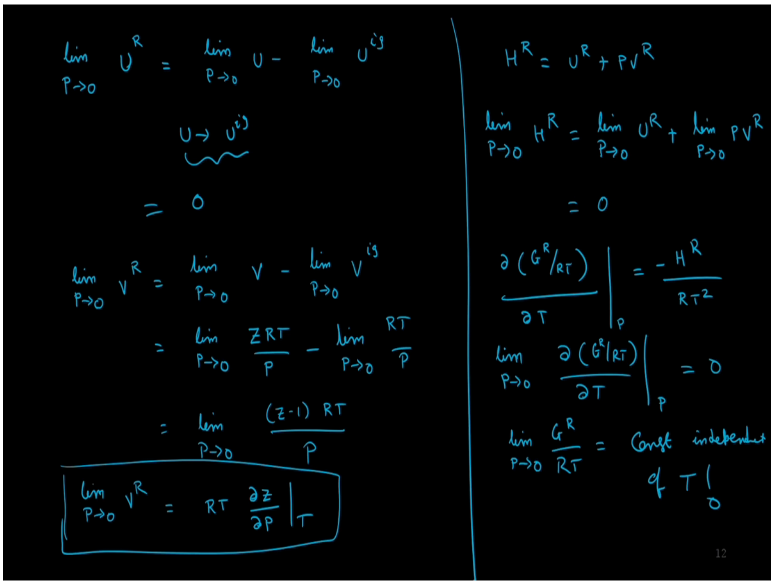

$$\lim_{P\to 0} U^R = \lim_{P\to 0} U - \lim_{P\to 0} U^{ig}$$

$$\underbrace{U \to U^{ig}}$$

$$= 0$$

$$\lim_{P\to 0} V^R = \lim_{P\to 0} V - \lim_{P\to 0} V^{ig}$$

$$= \lim_{P\to 0} \frac{ZRT}{P} - \lim_{P\to 0} \frac{RT}{P}$$

$$= \lim_{P\to 0} \frac{(Z-1)\,RT}{P}$$

$$\boxed{\lim_{P\to 0} V^R = RT \left.\frac{\partial Z}{\partial P}\right|_T}$$

$$H^R = U^R + PV^R$$

$$\lim_{P\to 0} H^R = \lim_{P\to 0} U^R + \lim_{P\to 0} PV^R$$

$$= 0$$

$$\left.\frac{\partial (G^R/RT)}{\partial T}\right|_P = -\frac{H^R}{RT^2}$$

$$\lim_{P\to 0} \left.\frac{\partial (G^R/RT)}{\partial T}\right|_P = 0$$

$$\lim_{P\to 0} \frac{G^R}{RT} = \text{Const independent of } T\,!$$

Now, what happens for H R? H R is; obviously, U R plus PV R ok. So, what happens to the residual enthalpy H R as we go to 0 pressure limit? Then it P going to 0 H R is going to be limit P going to 0 U R plus limit P going to 0 PV R V R is finite. So, PV R also will go to 0. So, H R in that sense will go to 0 what happens to G R? Derivative of G R over RT with respect to T at constant pressure we said is minus H R by RT square.

So and H R is 0 so, this derivative is 0 at the limit of 0 pressure limit P going to 0 derivative of G R over RT with respect to temperature at constant pressure is 0, which implies G R over RT is a constant independent of temperature right. At the limit of 0 pressure G R over RT is a constant independent of temperature, because the derivative with respect to t goes to 0 and so on.

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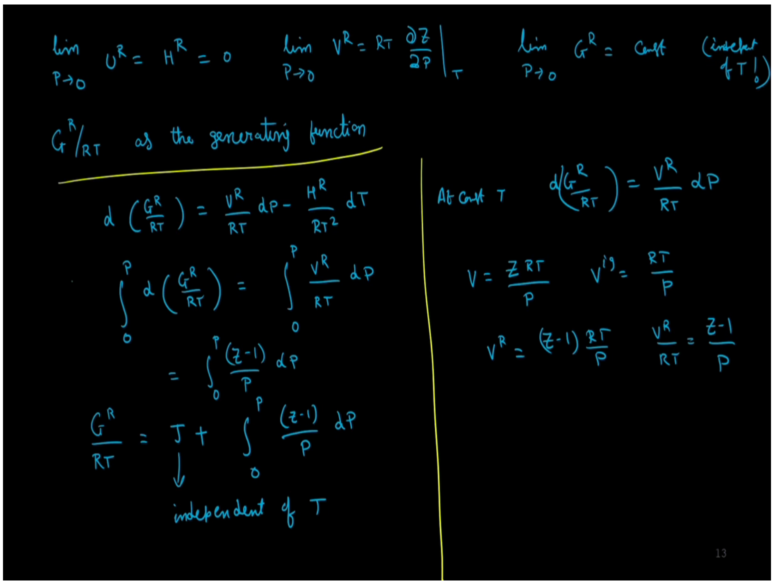

$$\lim_{P\to 0} U^R = H^R = 0 \qquad \lim_{P\to 0} V^R = RT \left.\frac{\partial Z}{\partial P}\right|_T \qquad \lim_{P\to 0} G^R = \text{Const} \quad (\text{indep of } T!)$$

$G^R/RT$ as the generating function

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}\,dP - \frac{H^R}{RT^2}\,dT$$

$$\int_0^P d\left(\frac{G^R}{RT}\right) = \int_0^P \frac{V^R}{RT}\,dP$$

$$= \int_0^P \frac{(Z-1)}{P}\,dP$$

$$\frac{G^R}{RT} = \underset{\substack{\downarrow \\ \text{independent of } T}}{J} + \int_0^P \frac{(Z-1)}{P}\,dP$$

At Const $T$ $\quad d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}\,dP$

$$V = \frac{ZRT}{P} \qquad V^{ig} = \frac{RT}{P}$$

$$V^R = (Z-1)\frac{RT}{P} \qquad \frac{V^R}{RT} = \frac{Z-1}{P}$$

So, what we have done is looked at the limits at the 0 pressure, limit P going to 0 U R the residual internal energy and the residual enthalpies are 0 limit of P going to 0 the residual volume is derivative or rather it is RT dou z over dou P at constant temperature and limit of P going to 0, G R is some constant independent of temperature.

Now, how does this information help me? So, for example, we want to calculate the residual enthalpy at some condition, how do I do this using this information? So, now, I have some idea about what happens to various residual properties at the 0 pressure limit let us see how I can use this information and calculate residual properties at other conditions. We start with G R over RT as the generating function, remember we have used generating function idea earlier.

So, we are going to use G R over RT as the generating function and try to derive all the thermodynamic properties based on this idea. So, first let me write what d G R by RT is. It is V R by RT d P minus H R by RT square dT right, at constant temperature this equation simply reduces to d G R over RT V R by RT d p. So, let me take the equation at constant temperature and let us see what happens if I integrate this equation integral going from 0 pressure to pressure P, d of G R over RT is going to be equal to integral going from 0 to P V R by RT d P right.

Now, I am going to make a few notes on the other side, V is in terms of compressibility factor it is z RT over P, V i g is RT over p. So, V R is z minus 1 RT over P or V R over

RT is z minus 1 by P right. So, then this equation becomes integral 0 to P, z minus 1 by P d P or in other words G R by RT at any given temperature and pressure at a temperature T and pressure P is going to be some constant J plus integral 0 to P z minus 1 by P d P noting that this constant J needs to be independent of temperature, that is what we said at the 0 pressure limit it is independent of temperature.

So, J this constant J is independent of temperature and G R by RT is J plus integral 0 to P z minus 1 by P d P. So, I have how G R by RT changes with both temperature and pressure. So, I can take this information, take the derivative with respect to temperature get enthalpy etcetera because I am going to use it as the generating function.

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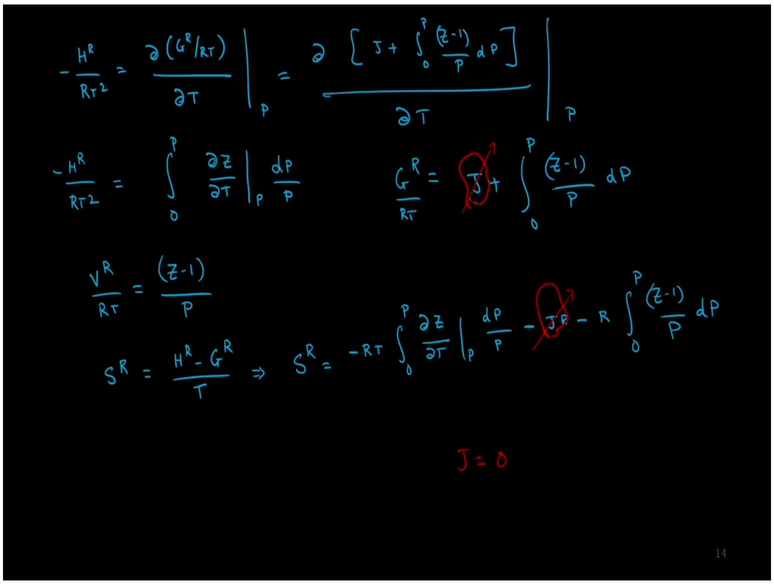

$$-\frac{H^R}{RT^2} = \left.\frac{\partial (G^R/RT)}{\partial T}\right|_P = \left.\frac{\partial \left[ J + \int_0^P \frac{(z-1)}{P} dP \right]}{\partial T}\right|_P$$

$$-\frac{H^R}{RT^2} = \int_0^P \left.\frac{\partial z}{\partial T}\right|_P \frac{dP}{P} \qquad \frac{G^R}{RT} = \cancel{J} + \int_0^P \frac{(z-1)}{P} dP$$

$$\frac{V^R}{RT} = \frac{(z-1)}{P}$$

$$S^R = \frac{H^R - G^R}{T} \Rightarrow S^R = -RT \int_0^P \left.\frac{\partial z}{\partial T}\right|_P \frac{dP}{P} - \cancel{JR} - R \int_0^P \frac{(z-1)}{P} dP$$

$$J = 0$$

So, for example, H R by RT square is the derivative of G R by RT with respect to temperature at constant pressure. So, it will be derivative of J plus integral 0 to P z minus 1 by P d P with respect to temperature at constant pressure, remember J is a constant independent of temperature so, that first derivative will go to 0 so, that this becomes integral 0 to P dou z over dou T at constant P d P over P that will be negative H R by RT square right.

Remember earlier I have G R by RT or some constant J plus integral 0 to P z minus 1 by P d P, I have H R V R by RT is anyway simply z minus 1 by P we are away RT is simply z minus 1 by p. So, it has this quantity right here, if I divide everything with RT S R over RT is going to be H R let us not do that, let us just write them as they are then S R is going to be negative RT integral 0 to P derivative of z with respect to t P d P by P minus J R minus R times integral 0 to P z minus 1 by P d P.

So, I can write S R also in terms of the compressibility factor and finally, in most cases what I am interested in is not the absolute value, it is the change in the thermodynamic properties delta H delta G delta V delta S etcetera and in such cases specially for delta G and delta S and for such cases it is really material what this value of J is going to be irrespective of what of what value I take, it is going to get cancelled when I take the difference because it is independent of temperature and because of that reason it is convenient to choose J to be 0 and completely drop this term because it does not appear in the differences.

And that being the case we are completely off that constant and all the thermodynamic quantities can be expressed only in terms or the residual properties of thermodynamic quantities can be expressed only in terms of the compressibility factors and how they change with temperature and pressure their integrals derivatives etcetera.

We know how to calculate the residual property, but for process calculations the total property we are interested in how do we transfer this information of residual property into the total property, well that is pretty straightforward.

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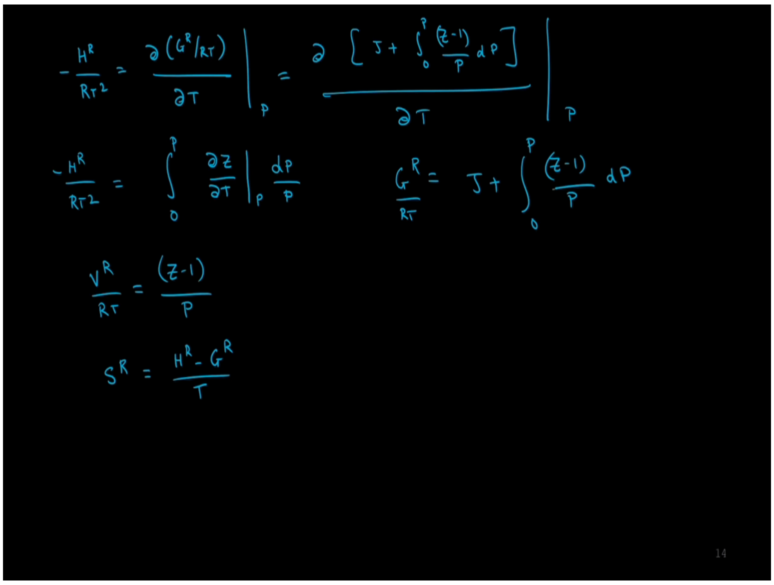

$$-\frac{H^R}{RT^2} = \left.\frac{\partial (G^R/RT)}{\partial T}\right|_P = \left.\frac{\partial \left[J + \int_0^P \frac{(z-1)}{P} dP\right]}{\partial T}\right|_P$$

$$-\frac{H^R}{RT^2} = \int_0^P \left.\frac{\partial z}{\partial T}\right|_P \frac{dP}{P}$$

$$\frac{G^R}{RT} = J + \int_0^P \frac{(z-1)}{P} dP$$

$$\frac{V^R}{RT} = \frac{(z-1)}{P}$$

$$S^R = \frac{H^R - G^R}{T}$$

Since we know H is H i g plus H R, the change in property delta H is going to be delta H i g plus delta H R. So, delta H i g is very simple its it simply is integral C p i g dT, I can express it as an integral of the specific heat capacity or with respect to temperature plus delta H R; and H R is something which we have written earlier, it is minus RT square integral 0 to P dou z by dou T at constant P d P.

So, I can calculate use this equation calculate H R at condition 1, calculate H R at condition 2 take the difference that will give me delta H R and then I can calculate the total delta H. So, to be able to do this calculation then all I need is the specific heat capacity in an ideal gas like k C p i g and how the compressibility factor which can be calculated from P V T relationship changes with respect to temperature or the derivative of that, once I have these 2 pieces of information I can calculate H straightaway right.

Similarly, if I want to calculate delta S the change in entropy, delta S it is simply delta s for the ideal gas like case plus delta S of the residual properties. So, delta S R is S R at condition 1 or condition 2 minus S R at condition 1 right and we have said that S R we are going to write it as minus T integral 0 to P derivative of z with respect to t d P by P minus integral 0 to P z minus 1 d P by P. We write S R like this and S i g is simply integral T 1 to T 2 C p i g by T dT minus R l n P 2 by P 1.

So, again all I need to calculate delta S is this information for C p i g and how these derivatives change or how z changes as a function of temperature and pressure. Once I have that pieces of information with me I can calculate delta S for any process. Similarly other properties such as delta U and delta G delta a etcetera can also be calculated. So, once I have H R, G R and V R if I want to calculate S R its pretty straightforward S R is going to be H R minus G R over T right since G is H minus T S, S is H minus G by T.