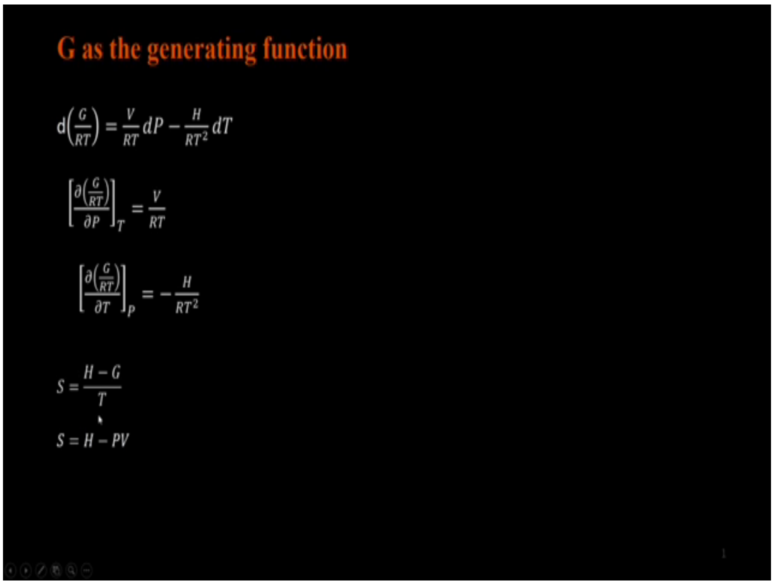
Chemical Engineering Thermodynamics
Sasidhar Gumma
Department of Chemical Engineering
Indian Institute of Technology, Guwahati

Lecture – 14
Residual property relations from EoS

Hello and welcome back. In the previous lecture we were looking at Virial Equation of State.

(Refer Slide Time: 00:42)



G as the generating function

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

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

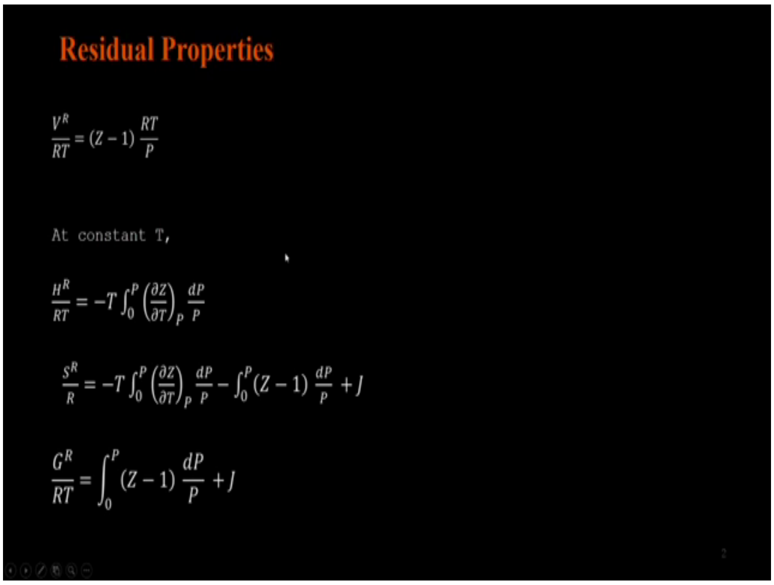
$$\left[\frac{\partial\left(\frac{G}{RT}\right)}{\partial T}\right]_P = -\frac{H}{RT^2}$$

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

$$S = H - PV$$

We started with Gibbs free energy as a generating function to derive all the thermodynamic properties, such as this one where the Gibbs free energy change with respect to temperature is same as the enthalpy or it is related to enthalpy. And once we have enthalpy and Gibbs free energy I can derive entropy, etcetera.

(Refer Slide Time: 00:59)



Residual Properties

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

At constant T,

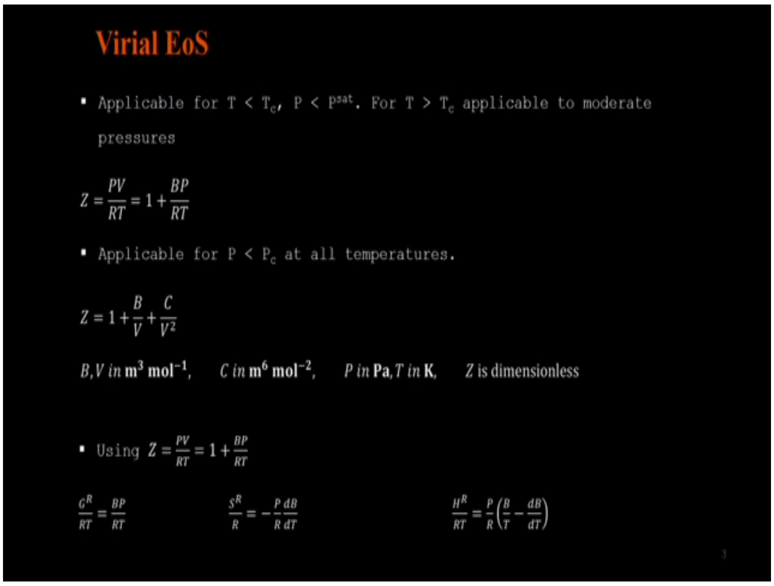
$$\frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}$$

$$\frac{S^R}{R} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1)\frac{dP}{P} + J$$

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

And we have also express the residual properties in terms of the compressibility factor, temperature and pressure. Using Gibbs free energy as the residual as the generating function we can express all the residual properties in terms of these quantities, and once we have done that we have applied to a particular equation of state yesterday we looked at virial equation of state.

(Refer Slide Time: 01:20)



Virial EoS

- Applicable for $T < T_c$, $P < P^{sat}$. For $T > T_c$ applicable to moderate pressures

$$Z = \frac{PV}{RT} = 1 + \frac{BP}{RT}$$

- Applicable for $P < P_c$ at all temperatures.

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2}$$

B, V in $\mathrm{m^3\,mol^{-1}}$, C in $\mathrm{m^6\,mol^{-2}}$, P in Pa, T in K, Z is dimensionless

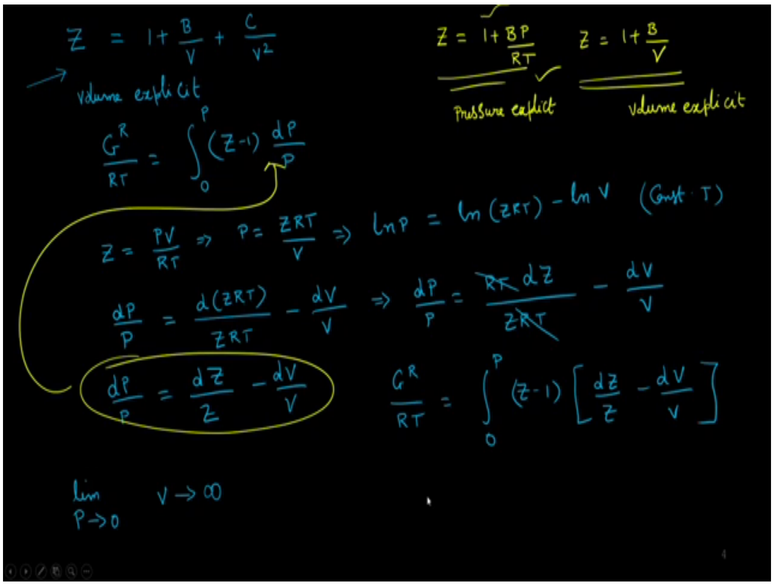
- Using $Z = \frac{PV}{RT} = 1 + \frac{BP}{RT}$

$$\frac{G^R}{RT} = \frac{BP}{RT} \qquad \frac{S^R}{R} = -\frac{P}{R}\frac{dB}{dT} \qquad \frac{H^R}{RT} = \frac{P}{R}\left(\frac{B}{T} - \frac{dB}{dT}\right)$$

So, either using 2 or 3 virial coefficients that is the most number of virial coefficients we generally use in a process industry, we can define the compressibility factor. And we have derived the relation for the residual properties in terms of the second virial coefficient only when there are two terms in the virial equation of state and tried to solve a problem based on that in the last class. Today, what we will do is try to extend this discussion for virial question of state what happens if I have both the second and the third virial coefficient, how do I express these residual properties and then we will move on to other equations of state in particular what are known as cubic equations of state.

So, let us first start our discussion Virial equation of state involving both the second and the third virial coefficients.

(Refer Slide Time: 02:14)



$$Z = 1 + \frac{B}{V} + \frac{C}{V^2}$$

volume explicit

$$Z = 1 + \frac{BP}{RT} \qquad Z = 1 + \frac{B}{V}$$

Pressure explicit   volume explicit

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

$$Z = \frac{PV}{RT} \Rightarrow P = \frac{ZRT}{V} \Rightarrow \ln P = \ln(ZRT) - \ln V \quad (\text{Const. } T)$$

$$\frac{dP}{P} = \frac{d(ZRT)}{ZRT} - \frac{dV}{V} \Rightarrow \frac{dP}{P} = \frac{\cancel{RT}\,dZ}{Z\cancel{RT}} - \frac{dV}{V}$$

$$\boxed{\frac{dP}{P} = \frac{dZ}{Z} - \frac{dV}{V}} \qquad \frac{G^R}{RT} = \int_0^P (Z-1)\left[\frac{dZ}{Z} - \frac{dV}{V}\right]$$

$$\lim_{P \to 0} \quad V \to \infty$$

When we have both the second and third virial coefficients then the compressibility factor Z is as we discussed yesterday, return in terms of 1 plus B over V plus C over V square, right. Now, contrast this with the form we had only when there is two where there is only the second virial coefficient. So, Z is 1 plus BP over RT, I could also write it as Z is 1 plus B over V.

We chose this form because it’s more convenient when I know temperature and pressure, I can calculate the compressibility factor and hence the volume. But the moment we have both the second and third virial coefficients as we discussed yesterday we only tend to use this form of the expression. So, we want to change this integration in terms of volume or density rather than pressure. And let us see how we do that quickly with one example first and then we will just generalize it and try to write the expressions for other thermodynamic properties.

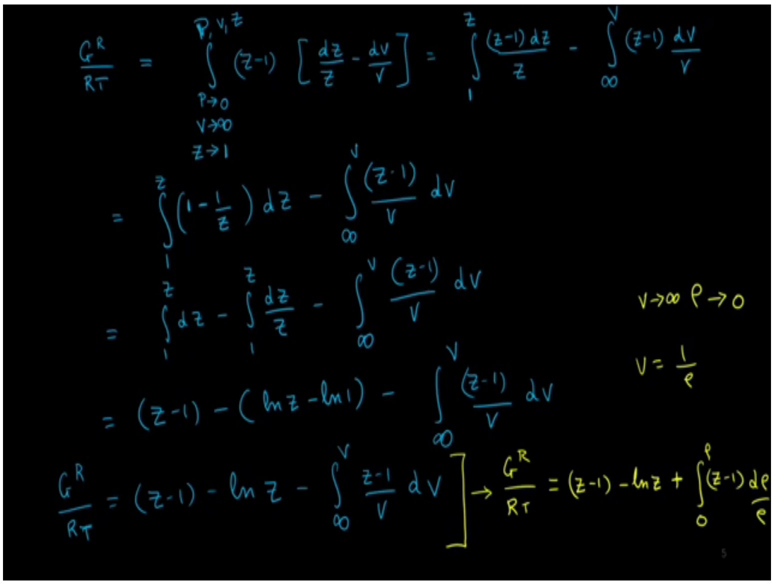
So, my goal then is to take this equation here G R by RT is integral 0 to P Z minus 1 dP over P and somehow convert it in terms of volume. The way we do that is using the definition for compressibility factor. Recall that compressibility factor Z is PV over RT which implies P is Z RT over V. So, if I take a logarithm on both sides log P will be log of Z RT minus log of V.

Now, I am going to take a derivative the left-hand side will be dP over P the right-hand side this is that let us write restrict it to constant temperature, so the temperature is constant. So, RT is constant it can come out, RT. Then all I have left RT d Z or rather let us just write the whole thing out that is easier to write without confusing ourselves its d of Z RT over Z RT minus d of V over V and because temperature is constant RT can come out. So, what I have left then is dP over P is RT d Z over Z RT minus dV over V. So, I can cancel these out T terms. So, dP over P than turns out to be d Z over Z minus dV over V.

So, I can take this expression right here and put it back here in that equation for Z R over RT. Let us see what happens. G R over RT is integral 0 to P Z minus 1 dP over P and I am go a replace that with d Z over Z minus dV over V right, minus dV over V.

Now, limit as P goes to 0 volume will go to infinity as pressure goes to 0 the molar volume goes to infinity, right. So, keeping that in mind let us see what happens to this integral for G R over RT.

(Refer Slide Time: 05:50)



$$\frac{G^R}{RT} = \int_{\substack{P\to 0\\ V\to\infty\\ Z\to 1}}^{P,V,Z} (Z-1)\left[\frac{dZ}{Z} - \frac{dV}{V}\right] = \int_1^Z \frac{(Z-1)\,dZ}{Z} - \int_\infty^V (Z-1)\frac{dV}{V}$$

$$= \int_1^Z \left(1-\frac{1}{Z}\right) dZ - \int_\infty^V \frac{(Z-1)}{V}\,dV$$

$$= \int_1^Z dZ - \int_1^Z \frac{dZ}{Z} - \int_\infty^V \frac{(Z-1)}{V}\,dV$$

$$V\to\infty \quad \rho\to 0$$

$$V = \frac{1}{\rho}$$

$$= (Z-1) - (\ln Z - \ln 1) - \int_\infty^V \frac{(Z-1)}{V}\,dV$$

$$\left.\frac{G^R}{RT} = (Z-1) - \ln Z - \int_\infty^V \frac{Z-1}{V}\,dV\right] \rightarrow \frac{G^R}{RT} = (Z-1) - \ln Z + \int_0^\rho (Z-1)\frac{d\rho}{\rho}$$

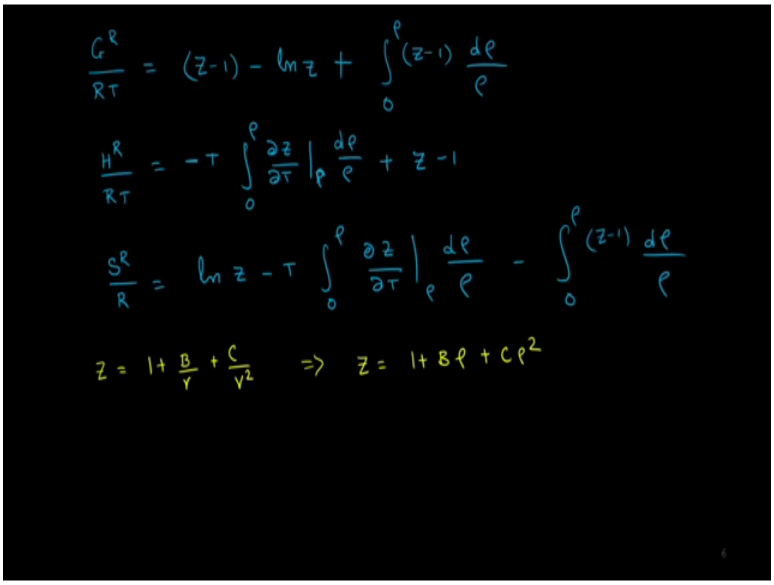
So, what I have is G R over RT right, is integral P going to 0, the volume going to infinity the gas will be an ideal gas. So, it will be compressibility factor goes to 1 right, Z minus 1 d Z over Z minus dV over V. The other end is at a pressure of P the corresponding volume and compressibility factors are simply V and Z whatever those numbers are. But at the lower pressure limit the volume goes to infinity it becomes an ideal gas. So, compressibility factor goes to 1.

Now, I have to do this integration and it turns out that this is a pretty straightforward integration, I can do integral Z going from 1 to Z, Z minus 1 d Z over Z minus integral volume going from infinity to V Z minus 1 dV over V. I have just separated those two parts, and the first one is essentially Z minus 1 minus ln right. So, if you think about it let us write it explicitly maybe that will have it is integral of 1 to Z, Z minus 1 by Z is 1 minus 1 over Z d Z, right, minus integral of infinity to V Z minus 1 over V dV.

Now, if you think about it the first integral it is d Z integral of 1 to Z d Z minus integral of 1 to Z d Z over Z minus integral infinity to V Z minus 1 by V dV. Or the first term is Z minus 1; the second term is ln Z minus ln 1 minus the integral infinity to V right, Z minus 1 by V dV. So, this is Z minus 1 minus ln Z minus integral of infinity to V Z minus 1 by V dV.

So, what we have done in that sense is change the variable that it needs to be integrated we have changed it from P to V. Some textbooks it is the integral is confusing in terms of infinity, if it is for some people then it might help to think of it in terms of density rather than volume. I can write the same equation is Z minus 1 minus ln Z minus or rather plus integral of 0 to rho Z minus 1 d rho over rho. So, this is noting that V is 1 over rho, right. So, we can when the volume goes to infinity then the density goes to 0 and so the limits are from 0 to the density rho Z minus 1 d rho by rho. Either of these two forms whether I write it in volume or density it is a little bit more helpful rather than writing in terms of pressure.

(Refer Slide Time: 09:43)



$$\frac{G^R}{RT} = (Z-1) - \ln Z + \int_0^\rho (Z-1)\frac{d\rho}{\rho}$$

$$\frac{H^R}{RT} = -T\int_0^\rho \left.\frac{\partial Z}{\partial T}\right|_\rho \frac{d\rho}{\rho} + Z - 1$$

$$\frac{S^R}{R} = \ln Z - T\int_0^\rho \left.\frac{\partial Z}{\partial T}\right|_\rho \frac{d\rho}{\rho} - \int_0^\rho (Z-1)\frac{d\rho}{\rho}$$

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} \Rightarrow Z = 1 + B\rho + C\rho^2$$

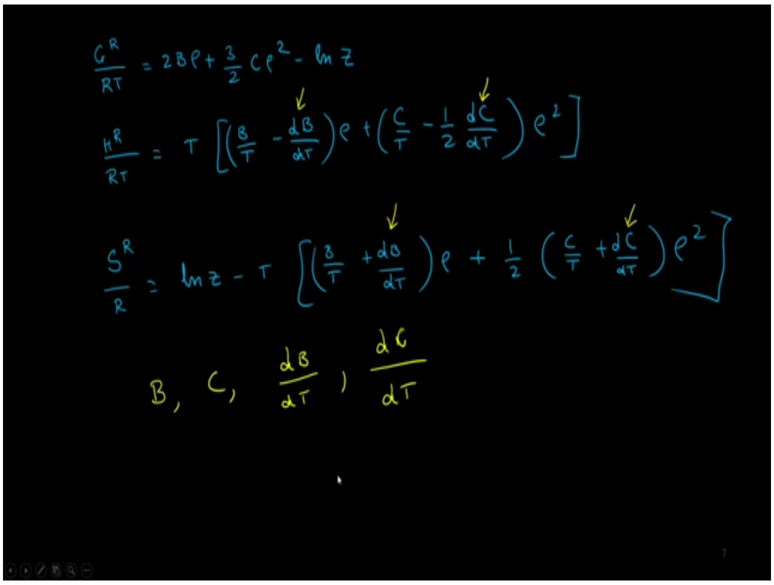
So, we will take this idea forward right, we are going a take this idea forward and write all the three expressions just to summarize the following forms of residual properties are helpful. Z minus 1 ln Z integral 0 to the density Z minus 1 d rho by rho. We have obtained this simply by replacing V is one over rho in the previous expression for G R.

We can take a derivative of this expression with respect to temperature and we are going to end up with an equation for H R by RT turns out to be minus T integral of 0 to density dou Z dou T at constant density d rho over rho plus Z minus 1. And S R over R turns out to be ln Z minus T times integral 0 to rho dou Z over dou T at constant density d rho over rho minus integral 0 to rho Z minus 1 d rho over rho.

So, all the three forms of these equation if you see, all the three equations if you see on the right-hand side it is just the compressibility factor, densities and temperatures derivatives and integrals of these quantities all of which can be measured in the lab and the left-hand side it is the residual property. So, if I have a volume explicit equation of state the right-hand side can be easily obtained and then I can use that form of expression to calculate the residual properties, right.

Now, keeping this in mind if I have now we were talking about, the virial equation of state with both the second and the third virial coefficients this is the form we have. So, the compressibility factor is going to be 1 plus B rho plus C rho squared since we are talking in terms of densities in these expressions, right, and I can take the derivative of this at constant density do derive the expressions for G R by RT etcetera using the above relations and what we will end up with are the following equations.

(Refer Slide Time: 12:04)



$$\frac{G^R}{RT} = 2B\rho + \frac{3}{2}C\rho^2 - \ln Z$$

$$\frac{H^R}{RT} = T\left[\left(\frac{B}{T} - \overset{\swarrow}{\frac{dB}{dT}}\right)\rho + \left(\frac{C}{T} - \frac{1}{2}\overset{\swarrow}{\frac{dC}{dT}}\right)\rho^2\right]$$

$$\frac{S^R}{R} = \ln Z - T\left[\left(\frac{B}{T} + \overset{\swarrow}{\frac{dB}{dT}}\right)\rho + \frac{1}{2}\left(\frac{C}{T} + \overset{\swarrow}{\frac{dC}{dT}}\right)\rho^2\right]$$

$$B,\ C,\ \frac{dB}{dT},\ \frac{dC}{dT}$$

Let us just write them down in a separate slide G R over RT is going to be 2 B times the density plus 3 by 2 C density squared minus ln Z, right. H R over RT is temperature B over T minus dB by dT rho plus C over T minus half d C by dT.

Again, as earlier both the second and third virial coefficients are going to be functions of temperature we need that functionality, so that I can get the derivatives dB over dT as we did yesterday and dC over dT for the third virial coefficient. And once I have both G R and H R is pretty easy to obtain S R over R. It is going to be ln Z minus T times B over T plus dB dT times rho plus half C over T plus d C dT times rho squared.

These are the three equations for G R, H R and S R. Other thermodynamic quantities can be similarly obtained again in both these expressions we have the derivatives with respect to temperature for B and C in addition to B and C itself. So, once I know B C, and their derivatives at various conditions I should be able to calculate the all the residual properties and hence changes for any process when there is three terms in the virial equation of state.

Now, in real life as we have discussed yesterday virial equation of state is applicable only if there are if it is at low to moderate pressures and well below the critical conditions. So, with that we end the discussion for today.

Thank you.