Chemical Engineering Thermodynamics
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Lecture – 16
Thermodynamic Property Calculations using Cubic EoS

Hello and welcome back. We are going to continue our discussion on Thermodynamic Property Calculations using Cubic Equations of State.

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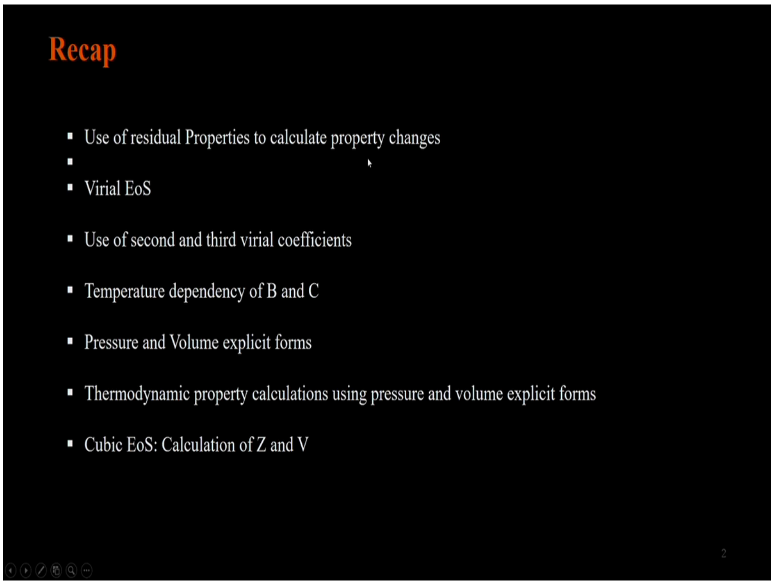

Recap

- Use of residual Properties to calculate property changes
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- Virial EoS
- Use of second and third virial coefficients
- Temperature dependency of B and C
- Pressure and Volume explicit forms
- Thermodynamic property calculations using pressure and volume explicit forms
- Cubic EoS: Calculation of Z and V

So, far our target was to calculate the residual properties and hence the change in the total thermodynamic properties, we have used the virial equation of state, usage of second we have also looked at usage of second and third virial coefficients, we have looked at various forms of generating functions using Gibbs free energy we have generated the residual enthalpy and residual entropy. We have looked at both the pressure and volume explicit forms of these expressions and finally, in the last class we looked at calculation of compressibility factor and the molar volume using a cubic equations of state.

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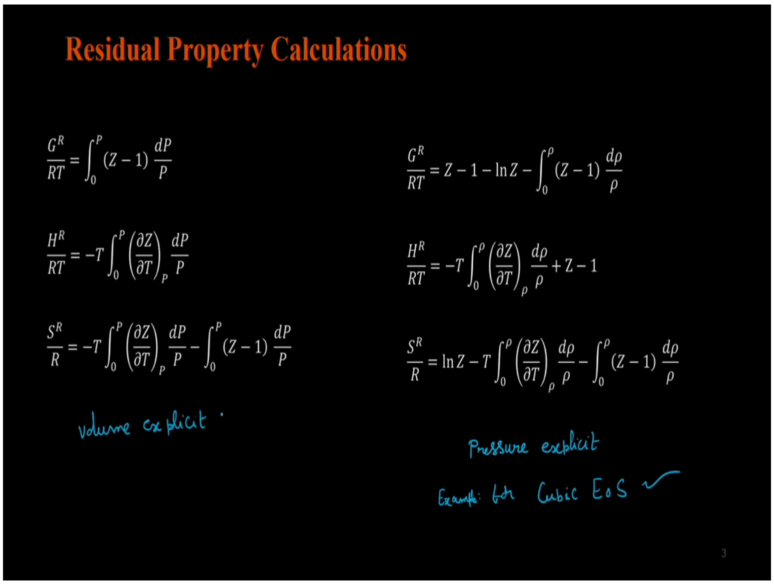

Residual Property Calculations

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

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

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

volume explicit ·

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

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

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

Pressure explicit

Example: for Cubic EoS ✓

Quickly to summarize this discussion; the left hand side in this slide shows the expressions for the residual properties. Then we have a volume explicit equation of state and on the right hand side we have a version which is pressure explicit equation of state more applicable for the cubic equations of state we looked at.

So, this is the pressure explicit form, which is more appropriate for cubic equations of state the virial expression. And on the left hand side I have the volume explicit form of these residual property relations.

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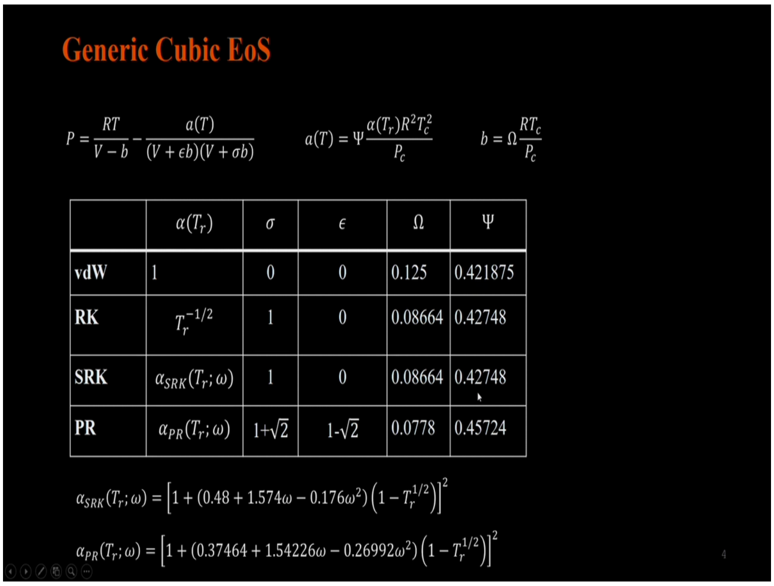

Generic Cubic EoS

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\epsilon b)(V+\sigma b)} \qquad a(T) = \Psi\frac{\alpha(T_r)R^2T_c^2}{P_c} \qquad b = \Omega\frac{RT_c}{P_c}$$

	$\alpha(T_r)$	σ	ϵ	Ω	Ψ
vdW	1	0	0	0.125	0.421875
RK	$T_r^{-1/2}$	1	0	0.08664	0.42748
SRK	$\alpha_{SRK}(T_r;\omega)$	1	0	0.08664	0.42748
PR	$\alpha_{PR}(T_r;\omega)$	$1+\sqrt{2}$	$1-\sqrt{2}$	0.0778	0.45724

$$\alpha_{SRK}(T_r;\omega) = \left[1 + (0.48 + 1.574\omega - 0.176\omega^2)\left(1 - T_r^{1/2}\right)\right]^2$$

$$\alpha_{PR}(T_r;\omega) = \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)\left(1 - T_r^{1/2}\right)\right]^2$$

Now, if we recall our discussion in the last class we looked at a generic equation of state for a variety of cubic equations like Van der waals, Redlich Kwong Soave, Redlich Kwong and Peng Robinson and there were several parameters in these cubic equations of state. The parameter a is a function of temperature or it is not a function of temperature for Van der Waals equation of state.

But for the others it is a function of temperature also for both SRK and Peng Robinson we introduced an additional parameter known as the eccentric factor which is a property of the substance.

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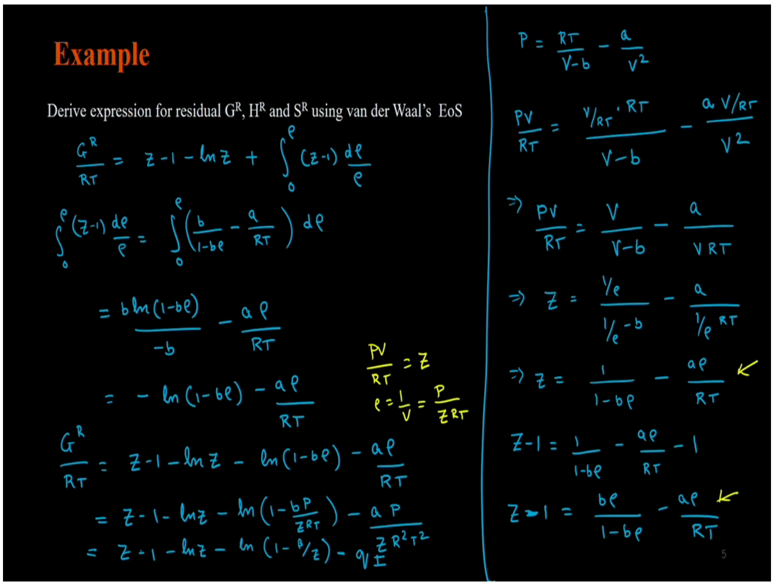

Example

Derive expression for residual G^R, H^R and S^R using van der Waal's EoS

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

$$\int_0^\rho (Z-1)\frac{d\rho}{\rho} = \int_0^\rho \left(\frac{b}{1-b\rho} - \frac{a}{RT}\right) d\rho$$

$$= \frac{b\ln(1-b\rho)}{-b} - \frac{a\rho}{RT}$$

$$= -\ln(1-b\rho) - \frac{a\rho}{RT}$$

$$\frac{PV}{RT} = Z$$

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

$$\frac{G^R}{RT} = Z - 1 - \ln Z - \ln(1-b\rho) - \frac{a\rho}{RT}$$

$$= Z - 1 - \ln Z - \ln\left(1 - \frac{bP}{ZRT}\right) - \frac{aP}{ZR^2T^2}$$

$$= Z - 1 - \ln Z - \ln(1 - B/Z) - q\frac{Z}{I}R^2T^2$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\frac{PV}{RT} = \frac{V/RT \cdot RT}{V-b} - \frac{a\,V/RT}{V^2}$$

$$\Rightarrow \frac{PV}{RT} = \frac{V}{V-b} - \frac{a}{VRT}$$

$$\Rightarrow Z = \frac{1/\rho}{1/\rho - b} - \frac{a}{1/\rho\, RT}$$

$$\Rightarrow Z = \frac{1}{1-b\rho} - \frac{a\rho}{RT} \swarrow$$

$$Z - 1 = \frac{1}{1-b\rho} - \frac{a\rho}{RT} - 1$$

$$Z - 1 = \frac{b\rho}{1-b\rho} - \frac{a\rho}{RT} \swarrow$$

And in the last class we looked at solving these cubic equations of state like I said for compressibility factor and molar volume, what we will do today is look also for both SRK and Peng Robinson we introduced an additional parameter known as the eccentric factor, which is a property of the substance.

And in the last class we looked at solving these cubic equations of state like I said for compressibility factor and molar volume; what we will do today is look at how we can use these cubic equations of state for calculating the residual properties given a condition. Of course, that means, once we calculate the residual and we have the ideal gas value like we have looked at it earlier. We can combine them and then use them for calculating the total property changes.

So, for now we are going to focus on calculation of residual properties using these cubic equations of state. Let us look at one example we will take the simplest 1 the Van der Waals equation of state and we would like to use this equation of state to calculate the expressions for the three residual properties the Gibbs free energy the enthalpy and the entropy. So, let us see how we do that. If you recall our discussion from the earlier lectures, this is a cubic equation of state. So, I want to use the pressure explicit form which is on the right hand side.

So, for example, to be able to calculate the residual Gibbs free energy, I am going to use this expression alright. So, that is what it is then G R let us take that example first. G R over R T is going to be equal to z minus 1 minus logarithm of the compressibility factor plus the integral for density going from 0 to the current state z minus 1 d rho over rho. This is the expression for G R over RT. I would like to use this expression and apply Van der Waals equation of state to calculate G R. Now let me write the Van der Waals equation of state over here, it says P is RT by V minus b minus a over V square right we can use the generic expression, but this is a simpler expression. So, well write straight away use the expression we have.

So, now, if you look at this, I need to convert this equation of state in terms of P into compressibility factor z so, that I can apply it in the expression for G R. So, what I will do is convert it into compressibility factor by multiplying with V over R T. So, that P v over RT is going to be V over RT multiply that with whatever terms we have here v minus b minus a V over RT by V square. So, that would be P v over RT is going to be V by v minus b minus a by V R T right. Now if you look at it on the left hand side is z and the right hand side is in terms of volume and if you look at the expression for G R we are writing it in terms of density.

So, I would like to convert this volume into density terms so, that I can use it readily in that expressions. So, what I will do is replace volume with 1 over the molar density. So, it will be 1 over rho minus 1 over rho minus b minus a by 1 over rho RT now if you simplify this a little further this would be 1 by 1 minus b times rho minus a rho by RT. So, this is z and if you look at the expression for G R again, I have z both z and z minus 1. So, z minus 1 is going to be 1 by 1 minus b rho minus a rho by RT minus 1 I will combine it with this so, that z minus 1 will be b, rho by 1 minus b rho minus a rho over RT.

So, then I am interested in these three two expressions one this and 1 is this these are the two expressions I would be interested in which I can use for calculating GR. So, I will go back to my exercise of calculating GR. So, all that is left then is trying to calculate that integral right of z minus 1 d rho by rho, which would be integral of 0 to rho z minus of 1 d rho, we can simplify that a little further. So, this will be z minus 1 plus a rho by RT minus ln of z minus beta; a rho over RT a by V RT ok. So, now, if I want to integrate this I can do that the first term is going to be logarithm of 1 minus b row over negative b and the second term is going to be a row over RT.

So, that this will be well the first term we have a b there. So, it will be negative ln of 1 minus b rho minus a row over R T. So, then G R over R T is going to be z minus 1 minus ln z minus ln of 1 minus b rho minus a rho over RT right. So, if we want we can convert this row back into the compressibility factors z. So, that this would be z minus 1 minus l and z recall that P v by RT is z. So, rho is going to be 1 over V. So, that will be P by z RT. So, this is rho. So, I can put that back b p by z RT minus ln of 1 minus b P by z RT minus a P by z R 2 T 2 right minus a P by z R 2 T square.

So, that would z minus 1 minus ln z minus b P by RT is beta if you recall. So, this would be ln of 1 minus beta over z minus ap by R 2 T 2 if you recall is q ap by R 2 T 2 is going to be q and I right. So, that would be the expression for G R over R T.

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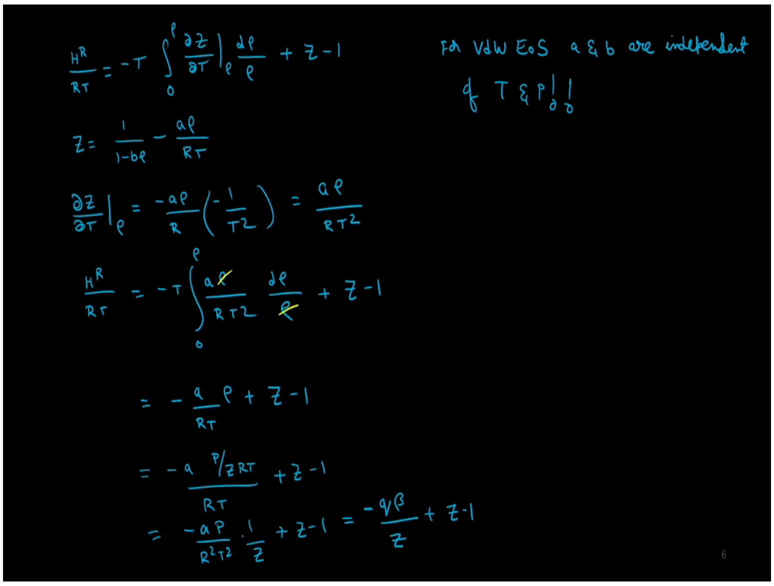

$$\frac{H^R}{RT} = -T\int_0^{\rho} \frac{\partial Z}{\partial T}\Big|_{\rho} \frac{d\rho}{\rho} + Z - 1$$

$$Z = \frac{1}{1-b\rho} - \frac{a\rho}{RT}$$

$$\frac{\partial Z}{\partial T}\Big|_{\rho} = \frac{-a\rho}{R}\left(-\frac{1}{T^2}\right) = \frac{a\rho}{RT^2}$$

$$\frac{H^R}{RT} = -T\int_0^{\rho} \frac{a\cancel{\rho}}{RT^2}\frac{d\rho}{\cancel{\rho}} + Z - 1$$

$$= -\frac{a}{RT}\rho + Z - 1$$

$$= \frac{-a\,{}^{P}/_{ZRT}}{RT} + Z - 1$$

$$= \frac{-aP}{R^2T^2}\cdot\frac{1}{Z} + Z - 1 = \frac{-q\beta}{Z} + Z - 1$$

For VdW EoS a & b are independent of T & P!!

Now, if I want to calculate H R over R T, I will go back to the expression I have for H R over R T. And if you look at our previous slide in terms of the integrals H R over R T is that value right there right. So, we will start from there it is negative T integral 0 to rho dou z over dou T at constant rho d rho over rho plus z minus 1 this is H R over R T right.

So, we will start from here and from our previous slide for Van der Waals equation of state, z we have got it here it is in terms of density, it is 1 by 1 minus b rho minus a row by RT. Now I want to take the derivative of this with respect to temperature at constant density. So, dou z over dou T at constant density is going to be remember b and a for Van der Waals equation of state, they are both independent of both temperature and pressure. So, if I take the derivative with respect to temperature at constant density then the first term is 0, and the second term again is a row by R and the all of them are constants and derivative of 1 over T is negative 1 over T 2.

So, then that would be a rho by RT squared right that is the derivative. So, I can put this derivative back in the expression for H R over RT its going to be minus T right a rho by RT squared integral of that going from 0 to rho d rho over rho plus z minus 1. I can cancel these terms out right and that is integral over density everything else is and I have to integrate it with respect to density. So, it will be simply negative a over RT rho plus z minus 1 negative a over RT plus z minus 1 and again recall that rho is P by z RT. So, we can substitute that. So, this will be negative a P by z RT by RT plus z minus 1.

So, that will be minus a by R 2 T 2 a P by R 2 T 2 times 1 over z plus z minus 1 and we call that a P by R 2 T 2 as q. So, it will be q or rather q times beta. So, this will be q times beta over z plus z minus 1. So, that is our expression for H R over RT. Now finally, we have to calculate S R and that is a straightforward calculation.

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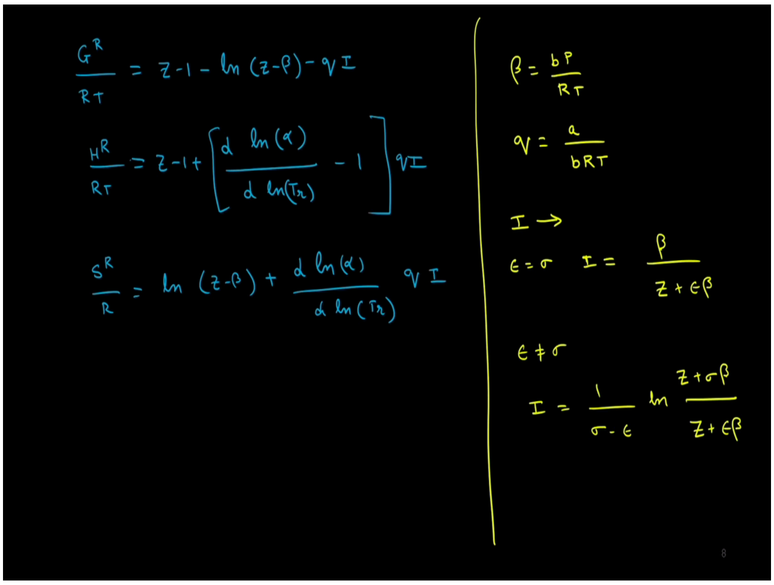

$$\frac{G^R}{RT} = Z - 1 - \ln(Z-\beta) - qI$$

$$\frac{H^R}{RT} = Z - 1 + \left[\frac{d\ \ln(\alpha)}{d\ \ln(T_r)} - 1\right] qI$$

$$\frac{S^R}{R} = \ln(Z-\beta) + \frac{d\ \ln(\alpha)}{d\ \ln(T_r)} qI$$

$$\beta = \frac{bP}{RT}$$

$$q = \frac{a}{bRT}$$

$I \rightarrow$

$\epsilon = \sigma$ $\quad I = \frac{\beta}{Z + \epsilon\beta}$

$\epsilon \neq \sigma$

$$I = \frac{1}{\sigma - \epsilon} \ln \frac{Z + \sigma\beta}{Z + \epsilon\beta}$$

So, I will leave it for you to do it and we simply get S R to be S R over R to be ln of z minus beta. Once we looked at how to calculate the derivatives and integrals for both G R and H R this calculation for S R overall is pretty straightforward. So, essentially then what we try to do is, manipulate the cubic equation of state so, that we can essentially use these expressions on the right hand side to find G R by RT, H R by RT and S R by R.

We have looked at an easy example of Van der Waals equation of state, but then the math is going to be a little bit more elaborate, you should be able to apply it to any cubic equation of state we desire. What we will do next is actually summarize all of these results in a simple form, turns out that I can write the expressions for the three residual properties in a generic fashion like we have done for expressing cubic equations of state themselves. So, ill draw your attention to this slide, where we have summarized for different cubic equations of state depending on the values of sigma epsilon and alpha we get these four forms of the cubic equation of state.

So, we will start here and then we will summarize the three residual properties G R over RT, H R over RT is z minus 1 plus derivative of logarithm of alpha over the derivative of logarithm of T r that is reduced temperature minus 1 times q I. And S R over R is logarithm of z minus beta plus the derivative of logarithm of alpha over the derivative of logarithm of the reduced temperature times q right. These are the three expressions for any cubic equation of state of course, we need to quickly define what we mean by these three terms q right we know a and b. So, let us define the other terms just for sake of completeness beta is b P over RT and q is a by b RT right and we have defined q we have defined beta the last 1 that is left is I. And this I to be able to express it for a general cubic equation of state this is essentially the integral we looked at in the previous example.

So, were going to write this I for two different scenarios if epsilon equal to sigma, then I is beta by z plus epsilon beta, if epsilon is not equal to sigma then this I is 1 by sigma minus epsilon ln of z plus sigma beta by z plus epsilon. So, this is the definition or this is the integral that turns out to be it is the value of the integral that it turns out to be and then once we define I beta in q, you can directly take these expressions and put them here. So, these are the forms of the residual properties we have obtained for a general cubic equation of state, we can do this exercise similar to the way we have handled the Van der Waals equation of state and then get these expressions. So, these expressions are going to be a little bit more friendlier to use rather than going through the complete set of math for each and every cubic equation of state.

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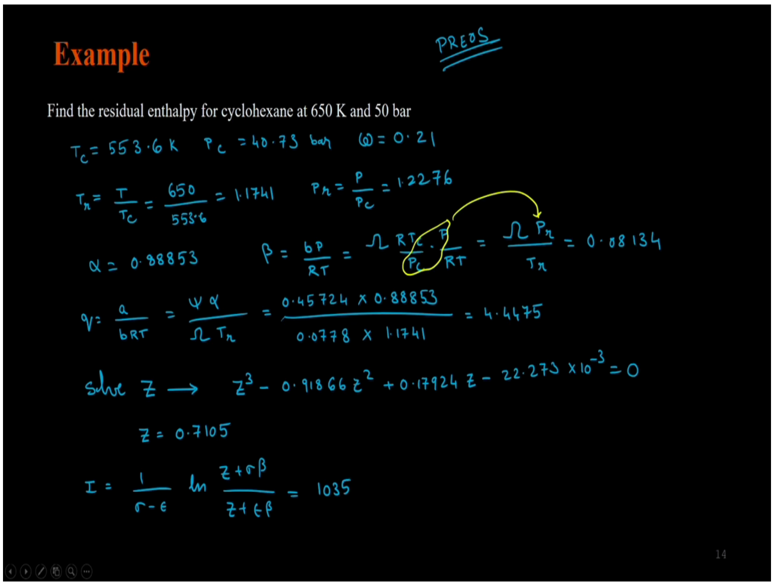

Example

PREOS

Find the residual enthalpy for cyclohexane at 650 K and 50 bar

$T_c = 553.6\ K \quad P_c = 40.73\ bar \quad \omega = 0.21$

$T_r = \frac{T}{T_c} = \frac{650}{553.6} = 1.1741 \qquad P_r = \frac{P}{P_c} = 1.2276$

$\alpha = 0.88853 \qquad \beta = \frac{bP}{RT} = \frac{\Omega RT_c}{P_c} \cdot \frac{P}{RT} = \frac{\Omega P_r}{T_r} = 0.08134$

$q = \frac{a}{bRT} = \frac{\Psi \alpha}{\Omega T_r} = \frac{0.45724 \times 0.88853}{0.0778 \times 1.1741} = 4.4475$

solve $Z \longrightarrow \quad Z^3 - 0.91866 Z^2 + 0.17924 Z - 22.273 \times 10^{-3} = 0$

$Z = 0.7105$

$I = \frac{1}{\sigma - \epsilon} \ln \frac{Z + \sigma\beta}{Z + \epsilon\beta} = 1035$

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So, with that in mind let us solve 1 quick problem. We want to find the residual enthalpy for cyclohexane at a given condition 650 Kelvin and 50 bar. Let us see how we can solve this particular problem. The first thing I want to write then is the critical constants because I want to be able to use the cubic equation of state. So, I am going to go to a handbook and pick these critical constants, I suggest that you do the same. For cyclohexane it turns out that T c is 553.6 Kelvin, P c is 40.73 bar and omega our eccentric factor is 0.21. We are not given a cubic equation of state we should be using here.

So, let us pick 1 I will pick Peng Robinson equation of state. So, I am going to use Peng Robinson equation of state to do this calculation and that is the reason I have picked the omega. Then as you recall the important things we want to calculate straight off are the list reduced conditions, temperature is 650 over 553.6 which is a critical temperature. So, that turns out to be 1.1741 and P r is P over P c which turns out to be 1.2276 for this particular gas. Then what I want to calculate next is alpha no alpha if you recall for Peng Robinson equation of state is given by this expression here. It is a function of omega the eccentric factor and the reduced temperature.

So, we will start with that expression and noting that the reduced temperature is 1.2276 and omega is 0.21, I can calculate alpha for Peng Robinson equation of state and the value I get is 0.88853. Next thing I want to calculate is beta if you recall it as b P over RT right and b is omega RT c by P c P by RT right. So, in terms of this reduced properties beta is going to be omega P r over T r. I have both P r and T r. So, I can straight away calculate beta for this conditions remember that P over P c is P r and similarly T over Tc would be Tr that is how I get this expression for beta.

So, once I have that I do not have to calculate b separately, I am not interested in that if you look at the expressions for G R H R and s are all we have is beta. So, I do not need to worry about b I would rather calculate beta. So, instead of calculating b we calculate beta directly from the reduced properties P r and T r and for this particular scenario it turns out to be 0.08134. Similarly q we said is a by b RT and I can rewrite this in terms of the reduced conditions I will leave it for you to get this expression it will also be equal to psi alpha by omega times the reduced temperature. For Peng Robinson if you look at the table psi is 0.45724 and omega is 0.0778. So, we will take these two values plug them here.

So, it will be 0.45724 times alpha which is we get it as 88853 over omega for Peng Robinson from the table is this times T r which is 1.1741. So, this will be our value for q and the value I get is 4.4475 for q. Once we have this q what I will do is, I will go back and solve like we have done in the previous lecture solve for z from the cubic equation, I get the cubic I have is z cube 0.91866 z square plus 0.17924. At these conditions what I am trying to do is actually calculate the compressibility factor or the molar volume right equal to 0.

So, for that I need to go back and write the cubic expression for Peng Robinson and solve that cubic polynomial or the roots of that cubic polynomial. So, that I can get the three roots and it turns out there will be one real root for this equation and that real root for this equation is at 0.7105 this is the value of z, I will get at this condition. Now once I have z the next thing I need to calculate we need this value of z to calculate G R hrand S R right. So, for a example H R, I need this value of z which is what I just calculated I know alpha well I know alpha, but I do not know this derivative yet, but I do know q I still have to calculate I. For Peng Robinson; obviously, right for Peng Robinson epsilon and sigma are different.

So, because they are different I am going to use this expression here to calculate I right it will be 1 by sigma minus epsilon logarithm of z plus sigma beta z plus epsilon beta and if I solve this what I get is 1035. Next thing that is left for me to calculate the residual enthalpy is I have z I have i I have q, but I do not know this derivative, I still have to calculate this derivative. And to calculate that derivative if you look at the expression for alpha in Peng Robinson equation of state I have it in terms of omega and T r this derivative then is going to be obtained from this expression right here and what I get.

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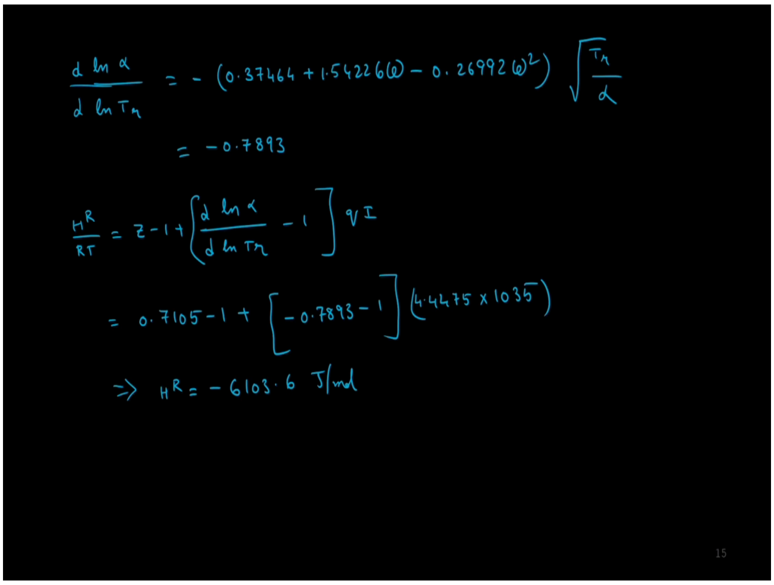

$$\frac{d \ln \alpha}{d \ln T_r} = -\left(0.37464 + 1.54226\omega - 0.26992\omega^2\right)\sqrt{\frac{T_r}{\alpha}}$$

$$= -0.7893$$

$$\frac{H^R}{RT} = Z - 1 + \left\{\frac{d \ln \alpha}{d \ln T_r} - 1\right] qI$$

$$= 0.7105 - 1 + \left[-0.7893 - 1\right]\left(4.4475 \times 1035\right)$$

$$\Rightarrow H^R = -6103.6 \text{ J/mol}$$

If you solve that is d of ln alpha by d of ln T r is negative 0.37464 plus 1.54226 omega minus 0.26992 omega square this is this times square root of T r over alpha. This is the expression you will get if you solve for this derivative I know everything in this expression q i.

So, this will be 0.7105 minus 1 plus negative 0.7893 minus 1 times q times I; q is 4.4475 I is 1035. If I simplify this what I will end up with is a value of H R to be negative 6103.6 Joule per mole. So, essentially it turns out then that we can extend our calculation for compressibility factors with a few additional equations as we have shown here and come up with a value for the residual property. All we need to do is to be able to calculate these terms derivatives and integrals we have shown here.

And once we do that we should be able to calculate the residual properties in a straightforward manner. That well end today’s class, when we come back in the next lecture we are going to look at how we can extend this calculation of residual properties into calculating the thermodynamic property changes using cubic equation of state.

Thank you.