Chemical Engineering Thermodynamics
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Lecture – 18
Generalized Correlations for Liquids

Hello and welcome back, today we are going to look at Generalized Correlations for Liquids.

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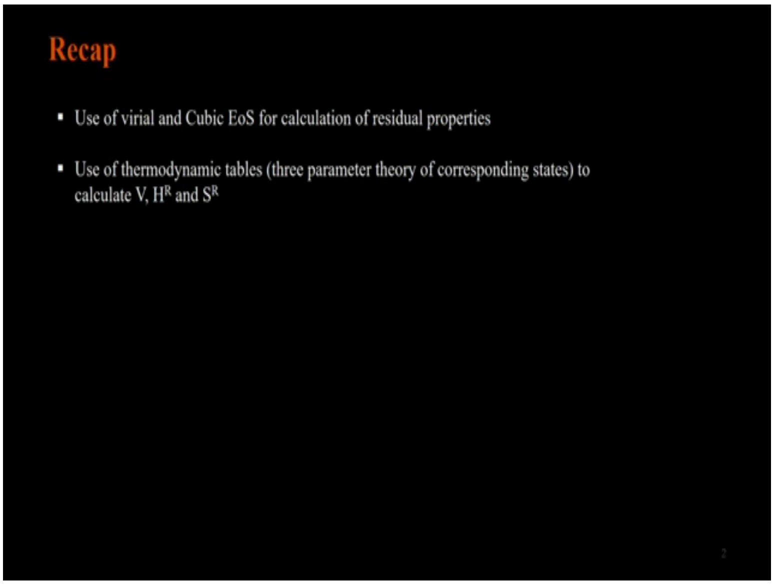

Recap

- Use of virial and Cubic EoS for calculation of residual properties
- Use of thermodynamic tables (three parameter theory of corresponding states) to calculate V, H^R and S^R

Just a quick recap; so far we looked at using virial equation of state and cubic equations of state for calculation of the residual properties. We have also looked at use of thermodynamic tables to calculate the; molar volume, residual enthalpy, and residual entropy. Most of our focus so far has been on the vapor phase.

Although we talked about vapor liquid region beneath the dome in case of cubic equations of state but most of our focus has been on the vapor phase. What we will do today is try to look at some of the correlations that are available for calculation of the liquid molar volume and enthalpy changes due to vaporization.

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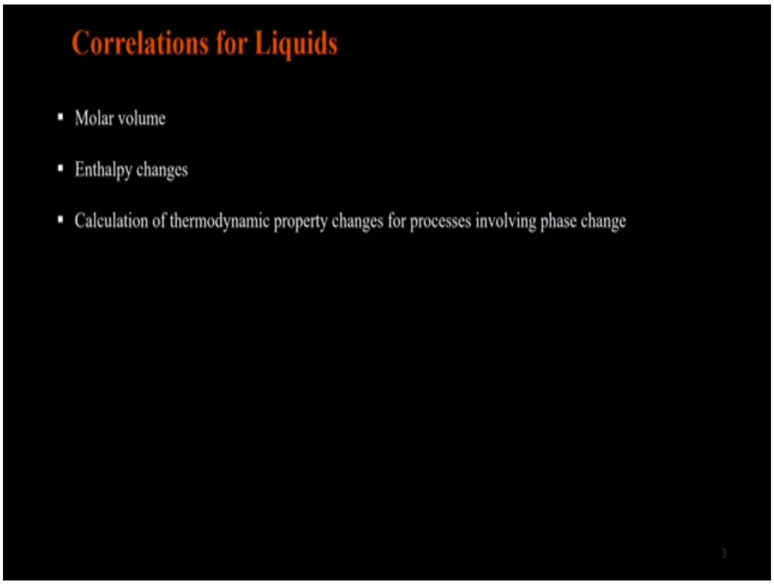

Correlations for Liquids

- Molar volume
- Enthalpy changes
- Calculation of thermodynamic property changes for processes involving phase change

So, let us start our discussion with some of the correlations for liquid molar volumes.

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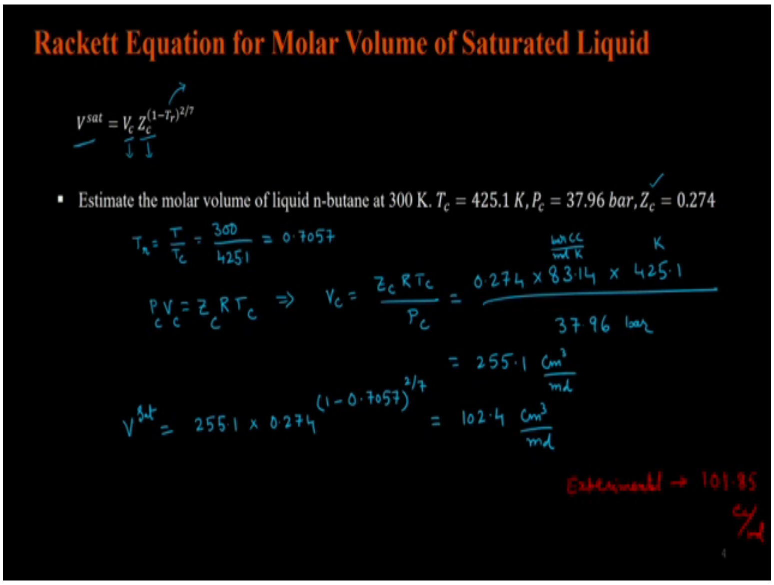

Rackett Equation for Molar Volume of Saturated Liquid

$$V^{sat} = V_c Z_c^{(1-T_r)^{2/7}}$$

- Estimate the molar volume of liquid n-butane at 300 K. $T_c = 425.1\ K, P_c = 37.96\ bar, Z_c = 0.274$

$$T_r = \frac{T}{T_c} = \frac{300}{425.1} = 0.7057$$

$$P_c V_c = Z_c R T_c \Rightarrow V_c = \frac{Z_c R T_c}{P_c} = \frac{0.274 \times \overset{\frac{bar\,cc}{mol\,K}}{83.14} \times \overset{K}{425.1}}{37.96\ bar}$$

$$= 255.1\ \frac{cm^3}{mol}$$

$$V^{sat} = 255.1 \times 0.274^{(1-0.7057)^{2/7}} = 102.4\ \frac{cm^3}{mol}$$

Experimental → 101.85 cc/mol

The Rackett equation is one of the more popular equations to estimate the molar volume of a saturated liquid. As you can see in this expression, we can calculate the molar volume of the saturated liquid V sat. If we know the molar volume at the critical point the compressibility factor at the critical point and then the reduced temperature at whatever temperature we are interested in calculating the saturated liquid molar volume.

So, let us quickly run through an example for this calculation. We would like to estimate the molar volume of liquid n-butane at 300 Kelvin. The critical temperature, critical pressure, and the compressibility factor at the critical point are given to us. To be able to do this calculation as you can see we have Z C the compressibility factor at the critical point which is given to us.

And because I know the temperature and T C I can calculate T r or the reduced temperature at these conditions which is essentially T over T C. So, that would be 300 over 425.1 which will give me a T r of 0.7057. So, two of the variables on the right hand side I have now; Z c, the reduced the compressibility factor at the critical point and the reduced temperature T r.

What I do not have is V c. Some of the tables list this volume at the critical point some tables do not. If they do not as in this case we can actually calculate it using the compressibility factor right. we know that PV is Z RT this is true even at critical point. So, it will be P C V C will be Z C RT C or if I am interested in V C it is essentially Z RT over P at the critical point.

I have a value for Z 83.14 this is in bar C c per mole Kelvin and temperature is 425.1 Kelvin over P c is the critical pressure 37.96 bar. So, if I do this calculation I end up with a value for P c. in this case this value of P c turns out to be 255.1 centimeter cube per mole. What I am interested in is then V sat or the saturated liquid volume at 300 Kelvin whatever pressure that saturation occurs at right.

And if I want that then all I need to do is plug in the numbers I just have readily available to me now. Times 0.274 to the power 1 minus 0.7057 to the power 2 over 7 and if I simplify this the number I will get is 102.4 centimeter cube per mole. Turns out this is a fairly good estimate the actual experimental value at this conditions is or the measured experimental value at these conditions is a 101.85 C c per mole.

So, that is a decent calculation remember we have no experimental data we have just estimated this value so that is a pretty good estimate. Rackett equation works in some scenarios it does not for example, in case of water I think it is off by about 30 percent or so at it is boiling point etcetera. So, it depends in certain cases it works well in certain cases it may not work well, but it gives us a ballpark figure without any prior experimental data.

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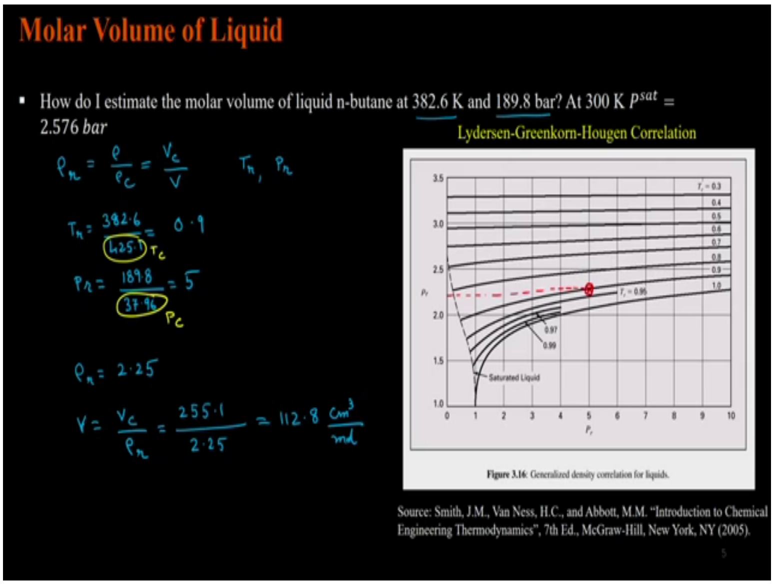

Molar Volume of Liquid

- How do I estimate the molar volume of liquid n-butane at 382.6 K and 189.8 bar? At 300 K $P^{sat} =$ 2.576 *bar*

$\rho_r = \frac{\rho}{\rho_c} = \frac{V_c}{V}$ T_r, P_r

$T_r = \frac{382.6}{425.1} = 0.9$ T_c

$P_r = \frac{189.8}{37.96} = 5$ P_c

$\rho_r = 2.25$

$V = \frac{V_c}{\rho_r} = \frac{255.1}{2.25} = 112.8\ \frac{cm^3}{mol}$

Lydersen-Greenkorn-Hougen Correlation

Figure 3.16: Generalized density correlation for liquids.

Source: Smith, J.M., Van Ness, H.C., and Abbott, M.M. "Introduction to Chemical Engineering Thermodynamics", 7th Ed., McGraw-Hill, New York, NY (2005).

What we have looked at in case of Rackett equation is estimation of the molar volume at saturated conditions. Now let us say I want to estimate the molar volume for n-butane again but not at saturated condition, but in a sub cooled state. In this case as you can see I want to estimate it is molar volume at 382.6 Kelvin and 189.8 bar very sub cooled liquid.

And what I have as additional information is at 300 Kelvin the vapor pressure is 2.567 bar right. So, in cases like this what we do is use what is known as; Lyderson Greenkorn Hougen equation or Hougen correlation. In this case in this scenario we are given a correlation for the reduced density which is essentially density over the critical density or in terms of volume it is V c over V.

This is given as a function of T r and P r. So, if we think about it is a two parameters theorem of corresponding states right. We have two parameters T r and P r which determine what the reduced density is. So, we can use this equation straight away right. For example, if in this scenario what I can do is, I can actually calculate what T r and P r will be in this case; T r would be 382.6 over 425.1 which would be 0.9 and P r will be 189.8 over P c.

Again P c in this case was 37.96. So, it will be 5 remember these values of T C and P c are same as in the previous problem. So, these are the values of T r and P r what I will do; is take these values of T r and P r and locate the corresponding point on the correlation chart; this is 5 and this is 0.9.

So, I am there on the chart and I can go back and see at this point what the value for reduced density is it is about halfway in between 2 and 2.5. So, let us say it is 2.25. So, the reduced density I have obtained at these conditions is 2.25.

So, if I am interested in calculating the molar volume then V is going to be P c over the reduced density look at this equation here right it is rho over rho C or P c over V. So, the molar volume itself will be P c over rho r. And remember we calculated P c for n-butane in the previous problem given Z C. So, it was 255.1 over 2.25 and that number there turns out to be a 112.18 centimeter cube per mole.

So, not just at saturation condition there are correlations that are available to estimate the molar volume of the liquid even in a sub cooled state we one of the correlation as we have just used is an example. Now these two correlations are widely used for estimating the molar volume of the liquid in saturated state and in the sub cooled state.

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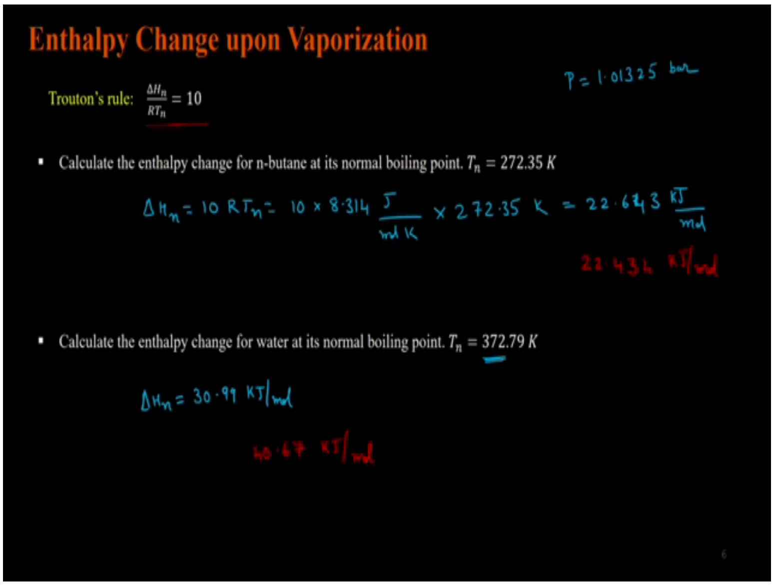

Enthalpy Change upon Vaporization

$P = 1.01325$ bar

Trouton's rule: $\frac{\Delta H_n}{RT_n} = 10$

- Calculate the enthalpy change for n-butane at its normal boiling point. $T_n = 272.35\ K$

$$\Delta H_n = 10\, RT_n = 10 \times 8.314\ \frac{J}{mol\ K} \times 272.35\ K = 22.643\ \frac{kJ}{mol}$$

22.434 kJ/mol

- Calculate the enthalpy change for water at its normal boiling point. $T_n = 372.79\ K$

$\Delta H_n = 30.99$ kJ/mol

40.67 kJ/mol

The other thing we are interested in is calculation of enthalpy change upon vaporization right. If there is a phase change from liquid to vapor or vice versa what would be the enthalpy change. One of the easy estimate of enthalpy change upon vaporization is obtained using what is known as troutons rule. It says that the enthalpy change for vaporization at it is normal boiling point is given by this expression right here for most liquids.

So, if I were to calculate the enthalpy change for n-butane and I know that it is normal boiling point is 273.35 Kelvin. Normal boiling point being the boiling point at atmospheric pressure so P is 1.01325 bars right at this pressure if the boiling point is 272.35 Kelvin I am interested in calculating it is enthalpy change. All I need to do is simply use troutons rule 10 times RT n.

So, 10 times R is 8.314 joule per mole Kelvin times, T n is 272.35 Kelvin which is 22.643 joules per a mole I am sorry kilojoules per mole notice that I have converted joules to kilojoules which turns out to be actually a fairly good estimate turns out the experimental value for n-butane is about 22.434 kilojoules per mole so fairly good estimate in this scenario. However, if you take another example as in this case for water what we get using troutons rule is delta H n of 30.99 kilojoules per mole for water the normal boiling point is this.

We do a similar exercise as earlier and we end up with a value of 30.99 kilojoules per mole whereas, the actual experimental value is 40.67 kilojoules per per mole. So, in this case troutons rule does not perform as well as in the earlier case it is about 300 percent off. But then gives a ballpark figure it is a quick estimate of enthalpy of vaporization.

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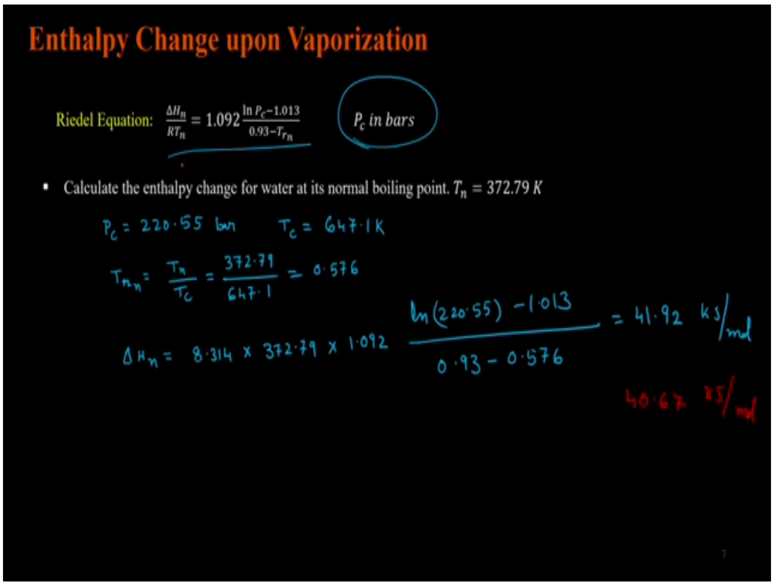

Enthalpy Change upon Vaporization

Riedel Equation: $\frac{\Delta H_n}{RT_n} = 1.092\frac{\ln P_c - 1.013}{0.93 - T_{r_n}}$

P_c in bars

- Calculate the enthalpy change for water at its normal boiling point. $T_n = 372.79\ K$

$P_c = 220.55$ bar $T_c = 647.1$ K

$T_{r_n} = \frac{T_n}{T_c} = \frac{372.79}{647.1} = 0.576$

$\Delta H_n = 8.314 \times 372.79 \times 1.092 \frac{\ln(220.55) - 1.013}{0.93 - 0.576} = 41.92$ kJ/mol

40.67 kJ/mol

We can improve the accuracy by using other correlations one of the more popular correlations used for estimating enthalpy of vaporization at normal boiling point is what is known as Riedel equation right. which is given by this expression here the only thing I want to stress is that in this case the critical pressure P c needs to be in bars for this equation written as such to be applicable.

Now let us quickly run through this calculation for estimating enthalpy change for water at it is normal boiling point right. In this case we will try to use it for water again if I were to use this equation the first thing I would need is P c. And the critical pressure for water is 220.55 bar. And because I have to calculate T r at the normal boiling point I would also need T C and for water the critical temperature is 647.1 Kelvin.

So, T r n is going to be T n over T C the reduced or 372.79 over 647.1 which turns out to be 0.576. Once I have T r n I can actually plug it every of everything else in that Riedel equation to get delta H n. It is going to be R T n R is 8.314 times T n is 372.79 times 1.092 logarithm of P c. P c needs to be in bar we have it in bar it is 220.55 bar minus 1.013 over 0.93 minus T R n which is 0.576.

If I run through the calculation I would end up with a value of again I am converting joules into kilojoules it would be 41.92 kilojoules per mole. Now this turns out to be a better rep estimate for water the experimental value again is 40.67 kilojoules per mole much closer to the experimental value. Remember this is completely predictive in nature there is no experimental data that goes into this calculation so that is a decent estimate.

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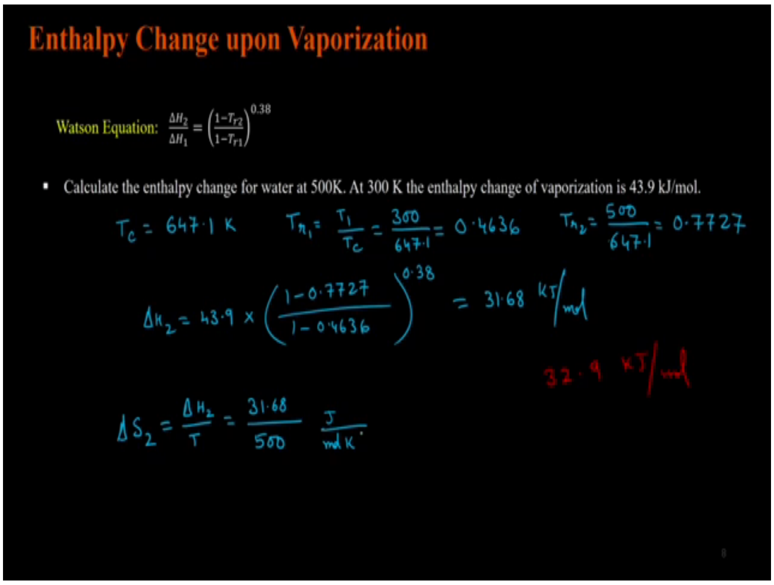

Enthalpy Change upon Vaporization

Watson Equation: $\frac{\Delta H_2}{\Delta H_1} = \left(\frac{1-T_{r2}}{1-T_{r1}}\right)^{0.38}$

- Calculate the enthalpy change for water at 500K. At 300 K the enthalpy change of vaporization is 43.9 kJ/mol.

$T_c = 647.1 \text{ K} \qquad T_{r_1} = \frac{T_1}{T_c} = \frac{300}{647.1} = 0.4636 \qquad T_{r_2} = \frac{500}{647.1} = 0.7727$

$\Delta H_2 = 43.9 \times \left(\frac{1-0.7727}{1-0.4636}\right)^{0.38} = 31.68 \text{ KJ/mol}$

32.9 KJ/mol

$\Delta S_2 = \frac{\Delta H_2}{T} = \frac{31.68}{500} \frac{\text{J}}{\text{mol K}}$

In the previous calculation was for enthalpy change upon vaporization at it is normal boiling point either using troutons rule or using Riedel equation. Now let us look at calculating enthalpy change upon vaporization at different conditions not at it is normal boiling point, but at other temperatures. So, let us take this example and to be able to do that of course, we are going to use the equation I have shown here which is known as Watsons equation it relates the enthalpy of vaporizations at two different temperatures to the reduced reduce conditions.

So, to be able to do this calculation we need enthalpy change of vaporization at one temperature then we can calculate it at the other temperature. So, let us take this example we are interested in calculating the enthalpy change of vaporization for water at 500 Kelvin at 300 Kelvin the value is known it is 43.9 kilojoules per mole. So, to be able to do this again what we need to calculate is the reduced temperature at the two conditions.

So, I need the critical temperature which is 647.1 Kelvin for water. And the T r 1 turns out to be T 1 over T c. So, that is 300 over 647.1 which turns out to be 0.4636. Similarly T r 2 is going to be 500 over 647.1 which turns out to be 0.7727. So, once I have T r 1 and T r 2 I can actually calculate delta H 2 directly. It will be delta H 1 which is 43.9 kilojoules per mole times one minus T r 2 which is 0.7727 over 1 minus T r 1 which is 0.4636 to the power 0.38.

According to the Watsons rule and this value here turns out to be 31.68 kilojoules per mole and again this is a good estimate the experimental value turns out to be 32.9 kilojoules per mole. So, then let us summarize what we have done. So, far in today's lecture we looked at calculation of the liquid molar volume at saturated condition and at other conditions using the correlations.

We also looked at enthalpy change due to vaporization at it is normal boiling point as well as enthalpy change due to vaporization at other temperatures other than the normal boiling point right. So, why are we interested in this it turns out if we have a process where there is a phase change from liquid to vapor or vice versa. These type of calculations come in handy to be able to do enthalpy change enthalpy calculations for enthalpy change upon vaporization or entropy change upon vaporization etcetera.

Before we do that let me quickly talk about entropy change upon vaporization. If we take this example here delta H 2 is 31.68 kilojoules per mole. And if I ask you what would be the entropy change upon vaporization at 500 Kelvin delta S 2 turns out vaporization occurs at a constant temperature. So, delta S 2 has to be equal to delta H 2 over T. We will come back to this calculation later when we talk about phase equilibrium.

But for now let us just say that delta S 2 is delta H 2 over T. And because I already have delta H 2 for phase change. I can simply divide it with the temperature at which this change occurs. So, it would be 31.68 over 500 this would be in joules per mole Kelvin. So, not just enthalpy change I can also calculate the entropy change upon vaporization.

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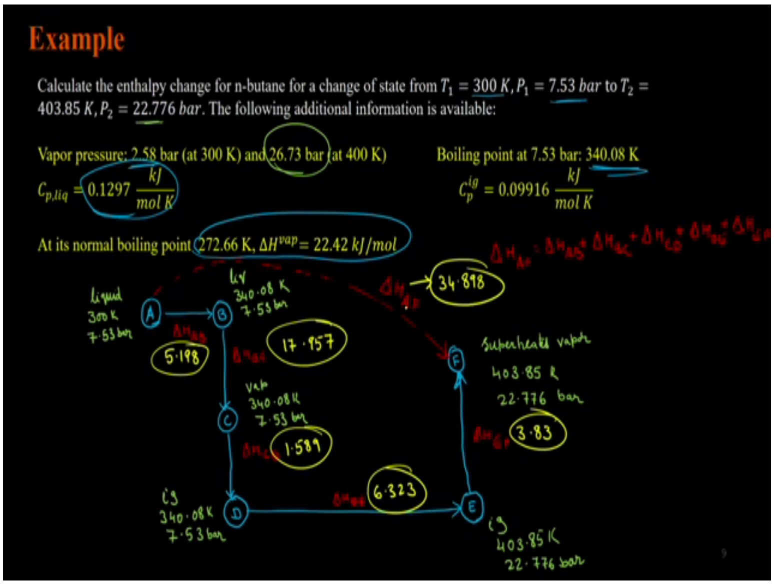

Example

Calculate the enthalpy change for n-butane for a change of state from $T_1 = 300\ K, P_1 = 7.53\ bar$ to $T_2 = 403.85\ K, P_2 = 22.776\ bar$. The following additional information is available:

Vapor pressure: 2.58 bar (at 300 K) and 26.73 bar (at 400 K)

Boiling point at 7.53 bar: 340.08 K

$C_{p,liq} = 0.1297\ \frac{kJ}{mol\ K}$

$C_p^{ig} = 0.09916\ \frac{kJ}{mol\ K}$

At its normal boiling point 272.66 K, $\Delta H^{vap} = 22.42\ kJ/mol$

Let us run through a problem and see how we can put all of this together whatever we have talked about so far together. We are interested in calculating enthalpy change for n-butane at 300 Kelvin and 7.53 bar, if it changes to a final state of 403.85 Kelvin and 22.776 bar. Bunch of other information is given to us to be able to help us in the calculations. So, let us see what it means.

So, I have A right and I have a final state let us call this as F; that is the final state this is my initial state. At the initial state what is the condition of my species. The temperature is 300 Kelvin and the pressure is 7.53 bar, but I am given the vapor pressure at 300 Kelvin vapor pressure is 2.58 bar. So, the pressure is more than the vapor pressure which means the system is going to be in a sub cooled liquid state.

So, this would be a liquid let us use a different color for this is a liquid right. And this liquid is at 300 Kelvin and 7.53 bar. Similarly at it is final state F right let us look at what the final state F is. It is at 403.85 Kelvin and at 400 Kelvin already the vapor pressure is 26.73 bar at 403 Kelvin it is going to be more than 26.73 bar that is going to be slightly higher right.

But definitely more than 22.776 bar. So, the final condition I have not even reached the vapor pressure which means it is going to be in a superheated state. So, lower the total pressure of the system is lower than the vapor pressure. So, I am in a superheated vapor phase the temperature is 403.85 Kelvin and the pressure is 22.776 bar that is where I am.

So, I am going from a sub cooled liquid state to a superheated vapor state. And I am interested in calculating the enthalpy change for this process we can follow a similar logic if one is asked to calculate an entropy change. But let us look at it look at enthalpy change for this particular problem. What we will do is in because enthalpy is a state property instead of directly going from state A to state F we are going to go through a series of steps such that I will choose these steps such that I can readily calculate the enthalpy change for each step very easily.

If I were to go from A to F directly it is going to be very difficult for me to calculate the enthalpy change. So, what I would do is break this process down into a series of steps I would choose the step such that at each step I can easily calculate the enthalpy change for that particular step right. So, here is a way to do it one of the ways to do it I should say.

I will transform or I would change the state of this liquid at 300 Kelvin and 7.53 bar to it is boiling temperature remember the boiling temperature is given to us it is 340.08 Kelvin. So, what I will do is, I will make it into a liquid alright. But the temperature is going to be 340.08 Kelvin and I will keep the pressure as it is 7.53 bar. So, this is liquid to liquid temperature has changed the pressure did not change ok.

Then I will take this B and vaporize it and make it into a vapor at the same conditions. Vapor at 340.08 Kelvin and 7.53 bar; let us call this as state C. From state C this is vapor this is a real vapor or a non ideal vapor, but it is not going to behave as an ideal gas. So, what I will do is, I will take this vapor and move it to it is ideal gas state.

So, let us call that state as D and I am going to give it ideal gas state at 340.08 Kelvin and 7.53 bar the same conditions, but now in an ideal gas state. Once I am in an ideal gas state I am going change the temperature and take it to it is final temperature still in the ideal gas state but the temperature is it is final temperature.

Ideal gas 403.85 Kelvin and 22.776 bar I have actually taken to the final temperature as well as the final pressure and finally, from this case I will take it to a real gas state or superheated vapor for that particular species F. So, these are the series of steps I will use to go from state A to state F.

Let us draw that actual process is going to be along this red dotted line. And I am interested in delta H let us call that as A F for that particular process I cannot calculate it directly. So, what I will do is calculate delta H AB delta H BC delta H CD delta H DE and finally, delta H EF. So, delta H AF is going to be right sum of these delta H AF is delta H A to B plus B to C plus C to D plus D to E plus E to F alright.

So, this is what we are going to do. Now let us see how we can find delta H for each of these steps we have just decided to use delta H A to B. Now, if you look at the process delta H A to B is at the same pressure we are only changing the temperature and this is for a liquid. I have C p for the liquid given to me write C p for the liquid is given 0.1297 kilojoules per mole.

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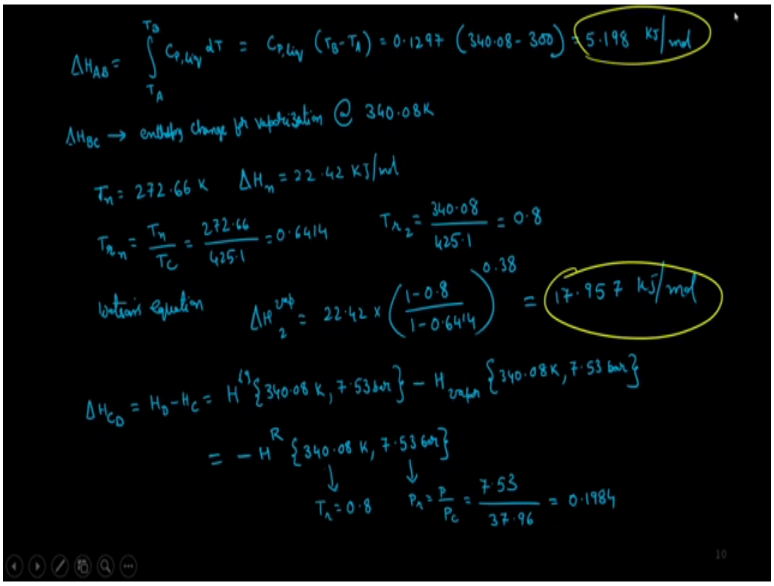

$$\Delta H_{AB} = \int_{T_A}^{T_B} C_{P,liq}\, dT = C_{P,liq}(T_B - T_A) = 0.1297\,(340.08 - 300) = \boxed{5.198\ \text{kJ/mol}}$$

$\Delta H_{BC} \rightarrow$ enthalpy change for vaporization @ 340.08K

$T_n = 272.66\ \text{K} \quad \Delta H_n = 22.42\ \text{kJ/mol}$

$$T_{r_n} = \frac{T_n}{T_c} = \frac{272.66}{425.1} = 0.6414 \qquad T_{r_2} = \frac{340.08}{425.1} = 0.8$$

Watson's equation

$$\Delta H_2^{vap} = 22.42 \times \left(\frac{1-0.8}{1-0.6414}\right)^{0.38} = \boxed{17.957\ \text{kJ/mol}}$$

$$\Delta H_{CD} = H_D - H_C = H^{ig}\{340.08\ \text{K}, 7.53\ \text{bar}\} - H_{vapor}\{340.08\ \text{K}, 7.53\ \text{bar}\}$$

$$= -H^R\{340.08\ \text{K}, 7.53\ \text{bar}\}$$

$$\downarrow \qquad \downarrow$$

$$T_r = 0.8 \qquad P_r = \frac{P}{P_c} = \frac{7.53}{37.96} = 0.1984$$

So, if I were to calculate delta H A B it is simply T A to T B C p liquid D t in this case C p liquid is constant it is not a function of temperature. So, I can take it out of the integral this will turn out to be T B minus T A. So, that is 0.1297 times 340.08 minus 300 which is 5.198 kilojoules per mole that is delta H A B.

If C p liquid is not independent of temperature I can still do the same integration it is going to be a little bit more elaborate expression. And then I will end up with the numerical result anyway for delta H B C right. Let us see what it means; this is the enthalpy change due to vaporization at 340 Kelvin all right going from liquid to vapor this is not at the normal boiling point.

The normal boiling point will be; obviously, much lower because the boiling point at 7.53 bar is 340 at 1 bar is going to be much lower. So, we are not at normal boiling point. But we are at a different condition right. So, we are interested in estimating the delta H vaporization at this condition. And we are of course, given the normal boiling point itself which is 272.6 Kelvin and delta H vaporization at this condition is 22.42 kilojoules per mole.

So, what we will do is then use the Watson equation we looked at earlier. Use condition one as the normal boiling point and calculate it for condition 2 which is the condition of our interest right let us do that. So, delta H BC let us write that down delta H BC is the enthalpy change for vaporization at 340.08 Kelvin. What we know is that the normal boiling point is 272.66 Kelvin. And delta H at the normal boiling point is given to us.

It is 22.42 kilojoules per mole right. So, what we will do is we will use Watsons rule to calculate. And for using Watsons rule we need T r 2 and T r 2, T r n is T n which is 272.66 over T C which is 425.1 Kelvin. Let us write that down T n over T C so that is 272.66 over 425.1. So, that is 0.6414 and T r 2 is going to be 340.08 over 425.1 which turns out to be 0.8 so this is T r 2.

So, we can use Watsons equation or Watsons correlation to calculate delta H 2 it is going to be delta H n which is 22.42 times 1 minus 0.81 minus T r 2 by 1 minus T r 1 0.6414 to the power 0.38. And this value right here turns out to be 17.957 kilojoules per mole. So, let us keep that in mind this is the first value that is the second value right this is delta H P c.

So, enthalpy of vaporization we have calculated using the Watsons rule. Then the third one going from vapor at 340.08 Kelvin right and 7.53 bar to an ideal gas state at the same condition what would that be what would that difference be delta H CD. If you think about it right if you think about it delta H CD is H vapor at 340.08 or rather it is actually H for the ideal gas right H D minus H C.

So, that is H for the ideal gas at 340.08 Kelvin and 7.53 bar minus H for the vapor at the same conditions that is H C 340.08 Kelvin and 7.53 bar. Should take the difference if you remember the way we have defined the residual properties it is the value for the gas minus the ideal gas value. This is opposite of that ideal gas minus that of the enthalpy for the gas.

So, this is going to be negative of the residual value H R negative of the residual enthalpy at the conditions we are looking at in this case 340.08 Kelvin and 7.53 bar. How do we calculate the residual enthalpy? One of the ways to do it is use Lee Kessler tables let us say right. We could use Lee Kessler tables and calculate the residual enthalpy at these conditions right.

So, let me quickly run through what T r and P r values are going to be. At this condition 340.08 T r remember what we said is 0.8 P R is going to be P over P C. So, that is going to be 7.53 over P c our P c is 37.96 bar for n-butane which turns out to be 0.1984.

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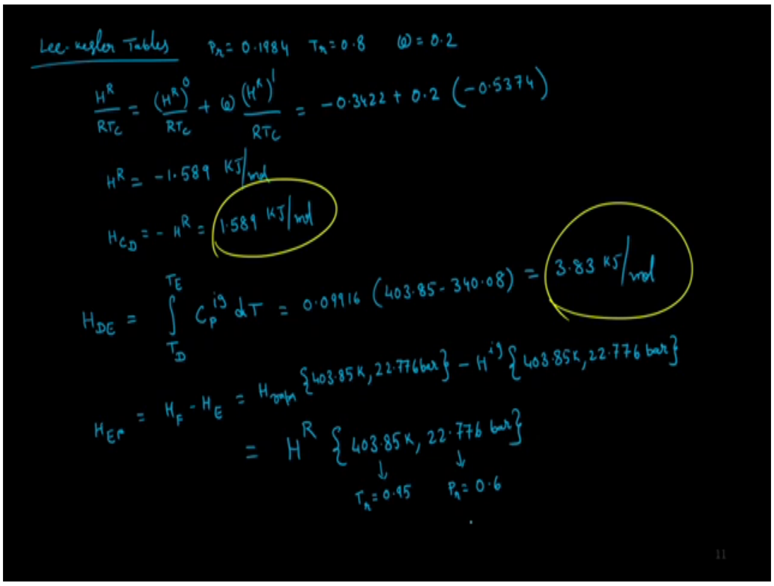

Lee-kessler Tables $P_r = 0.1984$ $T_r = 0.8$ $\omega = 0.2$

$$\frac{H^R}{RT_c} = \frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c} = -0.3422 + 0.2\,(-0.5374)$$

$$H^R = -1.589\ \text{KJ/mol}$$

$$H_{CD} = -H^R = \boxed{1.589\ \text{KJ/mol}}$$

$$H_{DE} = \int_{T_D}^{T_E} C_p^{ig}\, dT = 0.09916\,(403.85 - 340.08) = \boxed{3.83\ \text{KJ/mol}}$$

$$H_{EF} = H_F - H_E = H_{vap}\{403.85\text{K}, 22.776\text{bar}\} - H^{ig}\{403.85\text{K}, 22.776\text{ bar}\}$$

$$= H^R\{\underset{\substack{\downarrow \\ T_r = 0.95}}{403.85\text{K}},\ \underset{\substack{\downarrow \\ P_r = 0.6}}{22.776\text{ bar}}\}$$

So, what I am after then using Lee Kessler tables is or you can use any suitable correlations for calculating this residual enthalpy. But what I am interested in is residual enthalpy for n-butane at P r of point 0.1984 T r of 0.8. And for n-butane it turns out the eccentric factor is 0.2. I am using Lee Kesler tables from Lee Kesler tables what I get is H R by RT C is H R naught by RT C right plus omega times H R 1 by RT C.

At the given T r and P r I am going to look at the tables and find the values of H R naught and H R 1. If need be I can interpolate and get these numbers the final value I have from the tables after interpolation is negative 0.3422 for H R naught by RT C plus omega times H R 1 by RT C is negative 0.5374 at the given T r and P r I can simplify this and calculate H R right. And the value I have for H R is 1.589 kilo joules per mole.

So, I go back H C to D H C to D is negative of H R right. So, it is going to be negative of H R or this will be 1.589 kilo joules per mole. That is H C to D this is the residual enthalpy or negative of residual enthalpy at the desired conditions. I have H C to D then I need to calculate H D to E. And if you look at it H D to E is essentially the change in an ideal gas state the pressure is changing as well as the temperature is changing. But if you recall for an ideal gas the enthalpy change is independent of pressure it depends only on temperature.

So, I can write this equation fairly easily the enthalpy change for H D to E is going to be a function of temperature alone T D to T E C P i g d T. Remember this is an ideal gas state so even if the pressure changes it will not affect enthalpy the temperature change will affect and it will be integral of C P i g d T and what we are given is the value of C P i g for n-butane. Usually it is a function of temperature in this case we are given that it is a constant independent of temperature.

So, the calculation will be a little easier right; 0.00 0.09916 times 403.85 minus 340.08. And this value here turns out to be 3.83 kilojoules per mole. So, I have also calculated H D to E it is an integral of C P i g d T and the final thing I am interested in is H E to F. Let us look at what this number is; H E to F again the temperature and pressure are not changing what is changing is the state of the substance it goes from an ideal gas state to a superheated vapor right.

So, this is exactly the residual property at this condition. If you recall the definition for residual property H E to F is H F minus H E. So, this is H for the vapor at 403.85 Kelvin and 22.776 bar minus H for the ideal gas at exactly the same condition. This difference we call it as residual property as you know by now. So, this is H R the residual property at 403.85 Kelvin and 22.776 bar. So, so this is exactly the residual property at these conditions 403.85 Kelvin and 22.776 bar.

We are going to use Lee Kesler tables as we did earlier to calculate this residual property. To be able to do that we are interested in calculating the reduced temperature in this case it turns out to be 0.95 and the reduced pressure this case turns out to be 0.6. So, this reduced temperature and reduce pressure of 0.95 and 0.6 respectively we are going to go back to the Lee Kesler tables and look at the values for H R naught by RT C and H R 1 by RT C.

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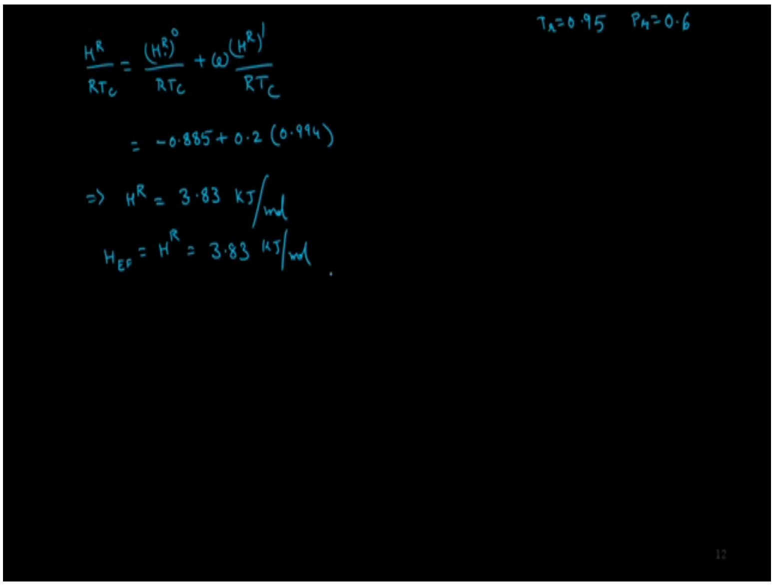

$T_r = 0.95 \quad P_r = 0.6$

$$\frac{H^R}{RT_c} = \frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c}$$

$$= -0.885 + 0.2\,(0.994)$$

$$\Rightarrow H^R = 3.83 \text{ KJ/mol}$$

$$H_{EF} = H^R = 3.83 \text{ KJ/mol}$$

So, I did just that and it turns out that H R by RT C. Then will be H R naught by RT C plus omega times H R 1 by RT C. Remember T r is 0.95 P r is 0.6, I go to Lee Kesler tables and look for these residual values of enthalpy at these temperature reduced temperature and reduced pressure. And what I have is negative 0.885 for H R naught omega if you remember is 0.2 for n-butane and H R 1 is 0.994 right.

And what this gives me is a value of H R if I multiply it with RT C and that value turns out to be 3.83 kilojoules per mole. So, I have a value of H R and we said H EF is exactly same as H R at these conditions. So, it is going to be 3.83 kilojoules per mole. So, we have calculated everything we need in this particular case.

So, let us write some numbers here delta H AB we calculated it to be 5.198 all these numbers are in kilojoules per mole. Delta H B to C is 17.957, delta H C to D is 1.589, D to E is 6.323, E to F is 3.83. Now if you look at these numbers let me circle them as you can see and the total we said delta H is 34.898. Out of this 34.898 more than half of it is coming from delta H B to C which is essentially the enthalpy change due to vaporization that is the major contributor.

The residual properties both of them put together add to about you know 5, 5.3 which is less than 10 to 15 percent. The other big contribution comes from the change in temperature of the gas even in the ideal gas stage it is about 6.3 kilojoules per mole. So, this sort of gives a summary of the percentage contributions of each of these steps to the total change in the entropy like I said again majority of it of course, comes from more than 15 percent of it of course, comes from the enthalpy change due to vaporization.

So, this is how we can combine everything we learned today on generalized correlations for liquids. We can use it for calculating enthalpy changes due to vaporization or calculating the enthalpy changes for processes; that involve phase change as in going from a liquid at one condition a sub cooled liquid to a superheated vapor as we demonstrated in this particular example.

And like I said earlier once we calculate enthalpy change it should be fairly straightforward calculation even for entropy change. We follow a similar path for each of these small steps we can calculate the entropy change and for the step that involves the phase change from liquid to vapor like I said earlier. We just divide delta H by T that will give us delta S for the vaporization part. And we add all of them up we can come up with an entropy change for the total process. So, with that we end today’s lecture.

What we have done so far then in the lecture is try to use various methods to calculate changes in thermodynamic properties. Such as enthalpy, entropy, Gibbs free energy, etcetera. And in the process we have used a cubic equation of state we have used virial equation of state we have used generalized correlations for liquids etcetera to achieve this particular objective. When we come back in the next lecture we will start looking at more closely at two phase systems which are actually of interest for a lot of chemical engineering separation processes.

Thank you.