# Chemical Engineering Thermodynamics
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## Lecture – 13
## Virial Equation of State

Hello and welcome back. So, in the previous lecture we were trying to calculate various thermodynamic properties using G over RT as the generating function. And once we have an expression for G over R T the Gibbs free energy in terms of the compressibility factor Z and measurable quantities such as P V and T; we have derived relations as to how G over RT is related to these.

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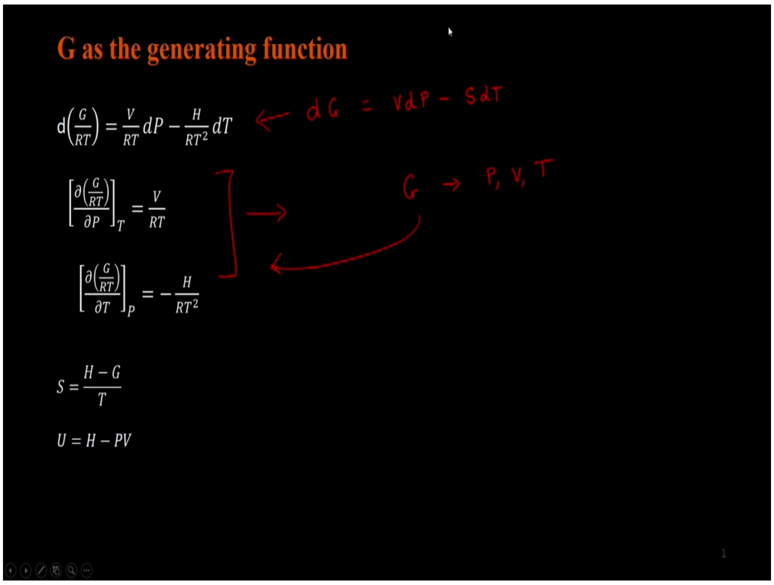

G as the generating function

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

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

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

$$G \rightarrow P, V, T$$

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

$$U = H - PV$$

And then for the other thermodynamic properties you can use the expressions given here to relate them to the measurable quantities. For example, since d G is V d P minus S d T; remember we said we like this expression because the Gibbs free energy change is expressed as a function of temperature and pressure or changes in temperature and pressure which are readily measurable in a laboratory. So, d G is a convenient function to work with in that sense.

And once we have an expression for T G over RT we can rewrite it eliminate S and rewrite it in terms of V and H. And the partial derivatives of G over RT with respect to P and T are given over here. And if I have a relation for G in terms of P V and T then I can use these equations here to calculate all the thermodynamic quantities I am interested in.

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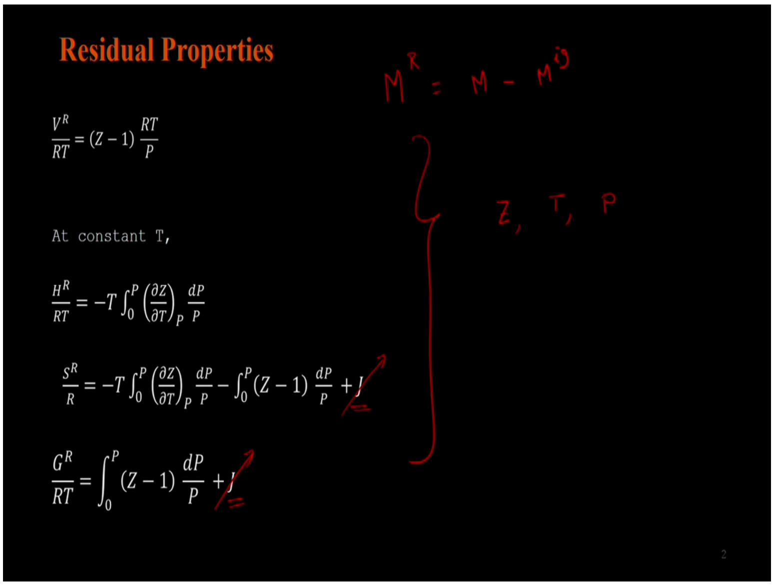

## Residual Properties

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

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

At constant T,

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

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

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

$Z,\ T,\ P$

Then we have defined what are known as residual properties we defined the residual property any residual property M R as M minus M i g everything taken at the same temperature and pressure conditions. So, i g stands for the ideal gas condition R for the residual property and M is the total property.

So, once we have that relation we can express various residual properties V R, H R S R and G R in terms of the compressibility factor Z T and P essentially. And in expressions for the entropy and the Gibbs free energy there appears a constant J and we have shown yesterday that this constant J is independent of temperature and in most cases I am interested in delta of these quantities. So, it does not matter what that value of J is going to be I can arbitrarily set it to 0. So, we are going to ignore that J from now on. So, we had expressions for H R S R and G R and once I have that I can calculate total property or add this to the ideal gas value to get the total property.

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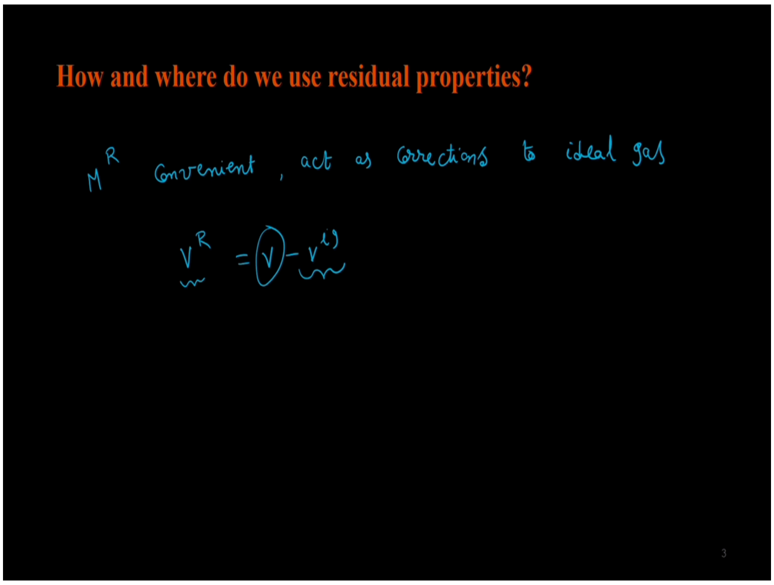

## How and where do we use residual properties?

$M^R$ Convenient , act as corrections to ideal gas

$$\underset{\sim}{V^R} = \boxed{V} - \underset{\sim}{V^{ig}}$$

It turns out that the residual properties are convenient right; it is convenient and they act as corrections to the calculations based on ideal gas properties right. So, for example, if I have a residual volume it is a correction over the ideal gas volume; if I know the ideal gas volume I can add the residual volume to get the total volume. So, this is sort of a correction and for gases it works out because most of these corrections are usually small major contribution comes from the ideal gas, value. And then you have a small collection on top of that to get to the total property and this whole for all the other properties as well H as etcetera right.

On the other hand for liquids these corrections become pretty large because there is vaporization enthalpy of vaporization is pretty large. So, it might not be as convenient, but definitely for non ideal gases; if they do not obey ideal gas law then I can always use the residual property and use it as a correction over the ideal gas value. And again these residual properties are going to be related to the P V T or the compressibility factors as we have derived the equations previously. What we are going to do next is look at some of the more common approaches for obtaining the compressibility factor or the P V T relationships.

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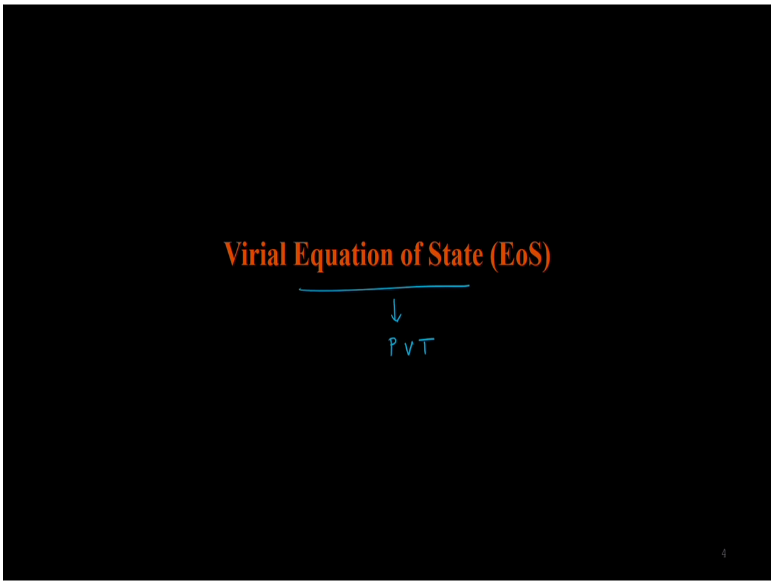

Virial Equation of State (EoS)

$\downarrow$

P V T

One of the easiest one and to relate the P V T quantities in a gas is through what is known as virial equation of state. So, equation of state usually is a term we use in thermodynamics for P V T relationship; how one of them is related to the other 2 values now. When we talked about the ideal gas early on in this course we looked at a virial question of state and we said that it is sort of a power series expression for P V relationship.

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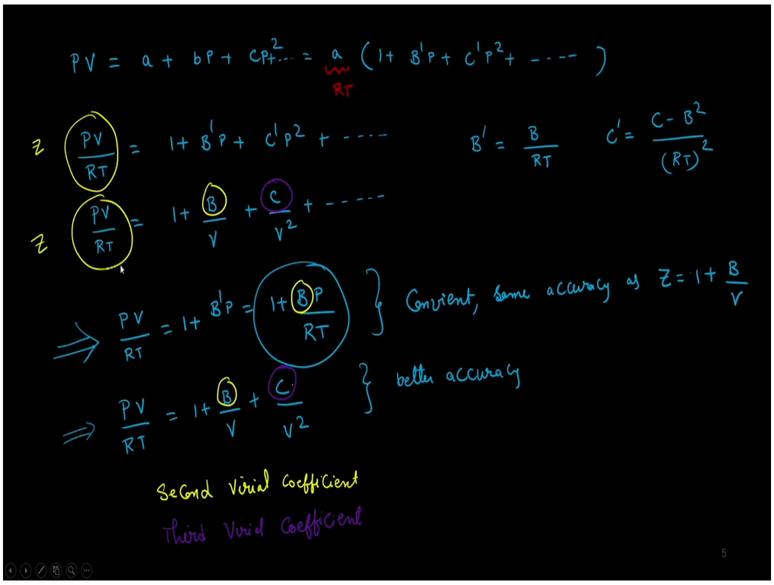

$$PV = a + bP + cP^2 + \dots = \underbrace{a}_{RT}\left(1 + B'P + C'P^2 + \dots\right)$$

$$Z \quad \frac{PV}{RT} = 1 + B'P + C'P^2 + \dots \qquad B' = \frac{B}{RT} \qquad C' = \frac{C - B^2}{(RT)^2}$$

$$Z \quad \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots$$

$$\Rightarrow \frac{PV}{RT} = 1 + B'P = 1 + \frac{BP}{RT} \quad \Big\}$$ Convient, Same accuracy as $Z = 1 + \frac{B}{V}$

$$\Rightarrow \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} \quad \Big\}$$ better accuracy

Second Virial Coefficient

Third Virial Coefficient

So, for example, what we said is the product P V can be expressed as a plus b P plus c P squared etcetera right. And if I factor out a it would be 1 plus B prime P plus C prime P square plus so on. This is an infinite power series in terms of P for an ideal gas only the first term is sufficient and we have already seen that this value of a is going to be equal to RT. All these subsequent terms drop out for an ideal gas, but if the gas is not ideal; then we are going in a use as many terms as they are necessary to express this product P V alright.

So, the other way of writing this is P V over I will bring that a to the other side RT to the other side so that this will be 1 plus B prime P plus C prime P squared plus so on right. And these quantities here are known as the virial coefficients right; this is power series in P an equivalent expression can be written for power series in terms of V. So, the coefficient is going change will replace B prime with B and C prime with C over V squared plus so on. And in fact, these quantities are related B prime is going to be equal to B over RT C prime is going to be equal to C minus B squared over RT whole squared and so on; those equations can be derived.

But the main idea of this is that I am expressing this P V term as a power series in P or in other words I am expressing this quantity P V over RT as 1 plus B prime P plus C prime P squared etcetera. And recall that P V over RT is what we called as the compressibility factor for an ideal gas; it will simply be 1, if the gas is non-ideal then we will have the additional terms in these power series.

Now, which one of these two forms; is better it turns out that if there is only one term we are going to use in addition to the ideal gas. So, for example, if I am going to use only P then P V over RT is 1 plus B prime P or in terms of B, it is 1 plus B P over RT. This equation is convenient and same accuracy it has the same accuracy as that of Z is 1 plus B by V.

On the other hand if I need more than one term in P then it turns out the second form which is this is a better it has better accuracy. Now, let us give some names here we call this B as the second virial coefficient this is a virial equation of state. So, B is the second virial coefficient and this C here is what we call as the third virial coefficient.

Depending on the requirement we will use either one or two terms higher order terms are rarely used they have it is very difficult to obtain B; even C it is very difficult to obtain, so any term higher than c cannot be obtained experimentally. So, it does not make sense to be using higher order terms at most for practical applications we are going to use the second virial coefficient or maybe the third virial coefficient depending on the acquirement if the pleasures are a little higher at moderate pressures second virial coefficient usually works.

And again like I said the form of the equation for really expression we will use; we will depend on how many terms I am using. If I am going to use only the second virial coefficient then this equation here is enough; if I am going to use both the second and the third virial coefficients then we will use this equation the essential difference is; if you see on the right hand side in the first case in this case here, there is only P and T; in the second case there is volume. So, one of them is explicit in terms of pressure, the other one is explicit in terms of volume.

So, if I do not know volume I will have to solve the cubic equation in the second case, but in the first case it is a straightforward calculation. Well if it is a power series expansion how do these curves look like. So, let us look take an example.

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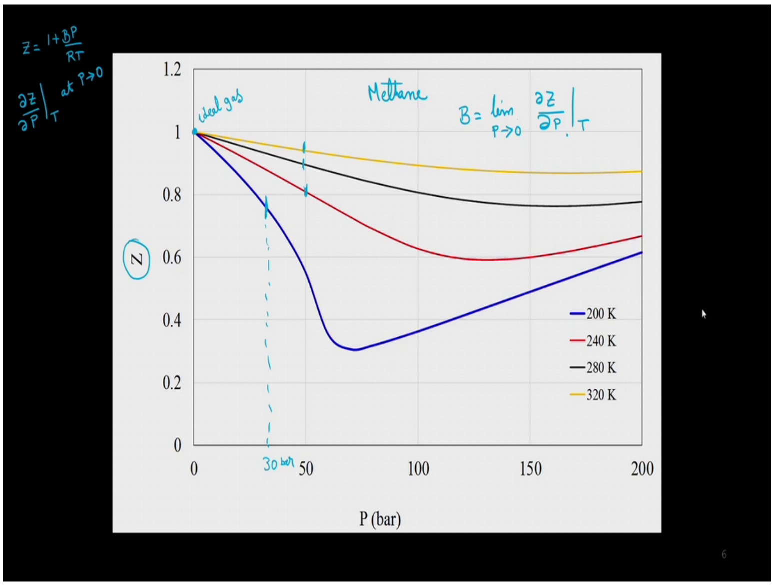

This is methane at 4 different temperatures and what we are plotting on y axis is the compressibility factor for methane at 4 different temperatures from 200 to 300 Kelvin and going from pressure of 0 to 200 bar. The curve that is at the bottom well first this point here is essentially the compressibility factor at the 0 pressure limit, all gases have to reach the ideal gas limit. So, the compressibility factor value will be 1; so all of them start right there.

At the highest temperature the compressibility factors are closer to 1; as you see with this yellow curve here whereas, the globe as the temperature decreases; the compressibility factor value is going to move farther away from 1 indicating more and more non ideality remember Z equal to 1 is the ideal gas limit. So, as I move away from this value of 1; it means the gas is more and more norm ideal right; so, the as the temperature increases the gas non ideality increases as well.

Then there are other things we can notice from this curve for example, we said we can express the compressibility factor Z as 1 plus B P over RT if I am going to use only the second virial coefficient. So, if you plot this curve or this expression 1 plus B P over RT; if B is not a function of temperature I am sorry not a function of pressure then this should be a straight line and this is obeyed only until moderate pressures.

And as you can see fairly until this limit for these gases and maybe until that point for this gas; the part of that curve until those pressures is fairly linear. So, the second virial coefficient is going to be sufficient to define or to fit the behavior of the gases until the pressures indicated of course, it changes with temperature right. So, for example, at 200 Kelvin; I would use only the second term if I have to predict the behavior until about maybe 30 bar right. But at a higher temperature of course, I can push that pressure a little bit more maybe until 50 bar and I could still use only the second virial coefficient and get away with it.

So, if this is the experimental data and one wants to estimate the second virial coefficient; how do I get that? All we need to do is simply take the derivative of this curve dou Z over dou P at constant temperature. And take the derivative not at any condition, but as you approach at the lower pressure limit.

So, at the low pressure limit or limit as P goes to 0; if you take this derivative then that will give you the value of the second virial coefficient. So, another way of defining second virial coefficient is; it is the derivative of compressibility factor with respect to pressure right at constant temperature of course, and then let us rewrite that it is the derivative at the 0 pressure limit for Z over P as at constant temperature that is the second virial coefficient right. Now, let us use these ideas and see if we can solve one quick problem.

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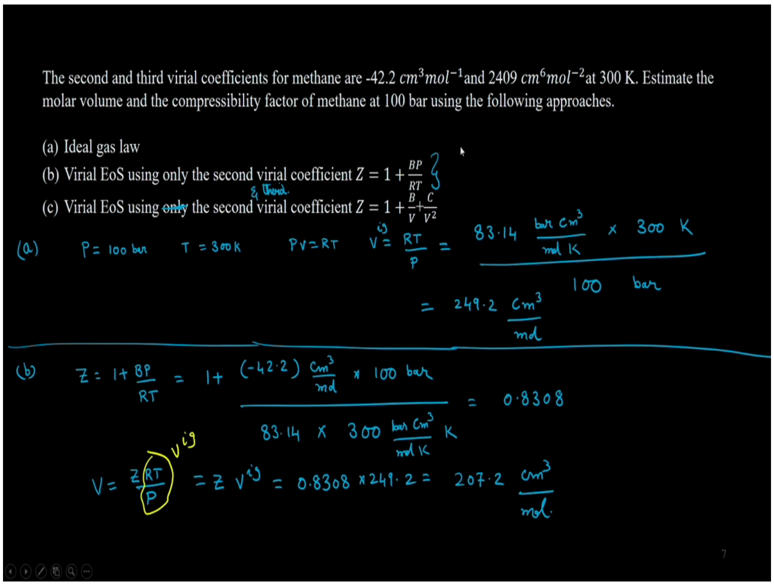

The second and third virial coefficients for methane are -42.2 $cm^3 mol^{-1}$ and 2409 $cm^6 mol^{-2}$ at 300 K. Estimate the molar volume and the compressibility factor of methane at 100 bar using the following approaches.

(a) Ideal gas law

(b) Virial EoS using only the second virial coefficient $Z = 1 + \frac{BP}{RT}$

(c) Virial EoS using ~~only~~ the second & third virial coefficient $Z = 1 + \frac{B}{V} + \frac{C}{V^2}$

(a) $P = 100 \text{ bar}$ $\quad T = 300 K$ $\quad PV = RT$ $\quad V^{ig} = \frac{RT}{P} = \frac{83.14 \frac{\text{bar cm}^3}{\text{mol K}} \times 300 \text{ K}}{100 \text{ bar}}$

$= 249.2 \frac{cm^3}{mol}$

(b) $Z = 1 + \frac{BP}{RT} = 1 + \frac{(-42.2) \frac{cm^3}{mol} \times 100 \text{ bar}}{83.14 \times 300 \frac{\text{bar cm}^3}{\text{mol K}} K} = 0.8308$

$V = Z \underbrace{\frac{RT}{P}}_{V^{ig}} = Z V^{ig} = 0.8308 \times 249.2 = 207.2 \frac{cm^3}{mol}$

What we are given is the second and third virial coefficients for methane at 300 Kelvin and we going to estimate the molar volume and the compressibility factor for methane at 100 bar using the following approaches. First is an ideal gas law then we want to use only the second virial coefficient and then we want to use both the second and third virial coefficient. So, let us see if I can estimate the molar volumes and compressibility factors for methane in this scenario. I am given the pressure it is 100 bar and the temperature is 300 Kelvin.

If it is an ideal gas then P V is RT or the molar volume V is going to be equal to RT over P and recall that R is 83.14 bar centimeter cube per mole Kelvin times 300 Kelvin over the pressure is the 100 bar. So, if we simplify this number then let us call this as ideal gas volume. So, V I G if I simplify that what I get is 249.2 centimeter cube per mol this is case a.

Now, for case b I want to use the second virial coefficient alone Z is 1 plus BP over R T. So, we will first estimate the compressibility factor using the second virial coefficient alone. So, it is going to be 1 plus the value for B is negative 42.2 centimeter cube per mol times a 100 bar over RT 83.14 bar c c per mol per Kelvin times 300 Kelvin right.

And then if you simplify these numbers bar centimeter cube over mol Kelvin times 300 Kelvin. And if you simplify these numbers it turns out that the value of Z is going to be 0.8308. So, remember Z for an ideal gas is 1, but at these conditions if I use the second virial coefficient I end up with a compressibility factor of 0.83 right which means it is 17 percent lower.

And the actual volume then using this value of compressibility factor is going to be Z RT over P. Remember RT over P is anyway V i i g; so this is also going to be equal to Z times V ig. So, that will be 83 percent of what we have calculated as the ideal gas volume and that number turns out to be 207.02 centimeter cube per mol. So, our molar volume actually is lower by using the non ideal equation of state; in this case we have used a varial equation of state with the second virial coefficient.

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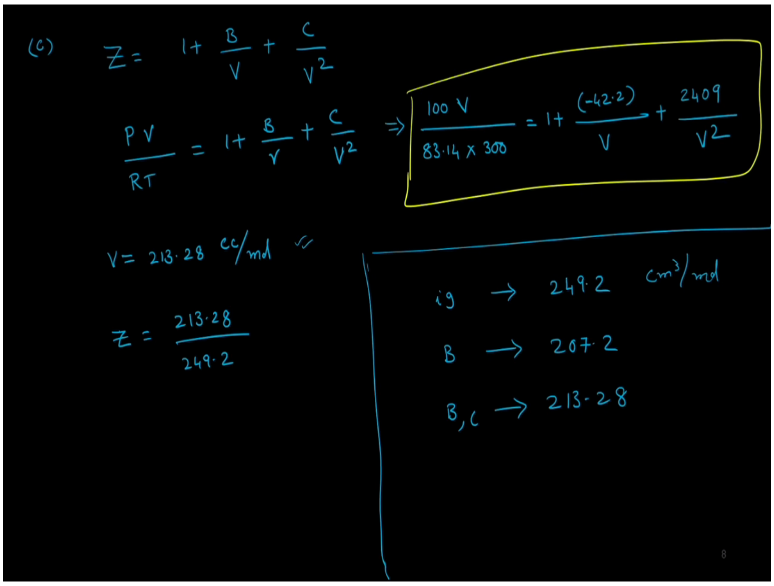

(c) $Z = 1 + \frac{B}{V} + \frac{C}{V^2}$

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} \Rightarrow \boxed{\frac{100\,V}{83.14 \times 300} = 1 + \frac{(-42.2)}{V} + \frac{2409}{V^2}}$$

$V = 213.28$ cc/mol ✓✓

$$Z = \frac{213.28}{249.2}$$

ig → 249.2 $cm^3/mol$

B → 207.2

B, C → 213.28

And the third one we want to use both the second and the third virial coefficients; so, the form of the equation we should be using is this Z is 1 plus B over V plus C over V squared the values are given to us, but I have to solve this for volume. So, what we will do is rewrite the compressibility factor as P V over RT is 1 plus B over V plus C over V square and if you look at this equation now you will realize that everything in this equation is known except the volume.

This is a 100 bar times the volume or 83.14 times 300 just make sure that we are we are using the correct consistent set of units negative 42.2 centimeter cube per mol over V plus the value for C was 24; 2409; so, 2409 over V squared.

So, now I have to solve this equation this would be a cubic in V everything except V is known. I could use any suitable software excel maybe and then get what the value of V is going to be. And in this case that V turns out to be 213.28 centimeter cube per mol. If I want to calculate Z it is going to be 213.28 over the ideal gas value which is 249.2 at this condition.

But the value of V now as you see is different from what we have calculated then let us list that ideal gas value just the B or B and C; ideal gas was 249.2 just using the second virial coefficient was 207.2 using both B and C that is 213.28; all of them in centimeter cube per mol. As you can see each one will give us different results depending on our experience and what we know about the gas and its behavior; we should be choosing the correct form of the expression we have to use for the particular condition.

This is our will use the virial equation of state to calculate the molar volume. What we are going to do next is try to derive some expressions some expressions for the residual properties and then enhance the total property changes and how we can use this information to calculate the total property changes from virial equation of state.

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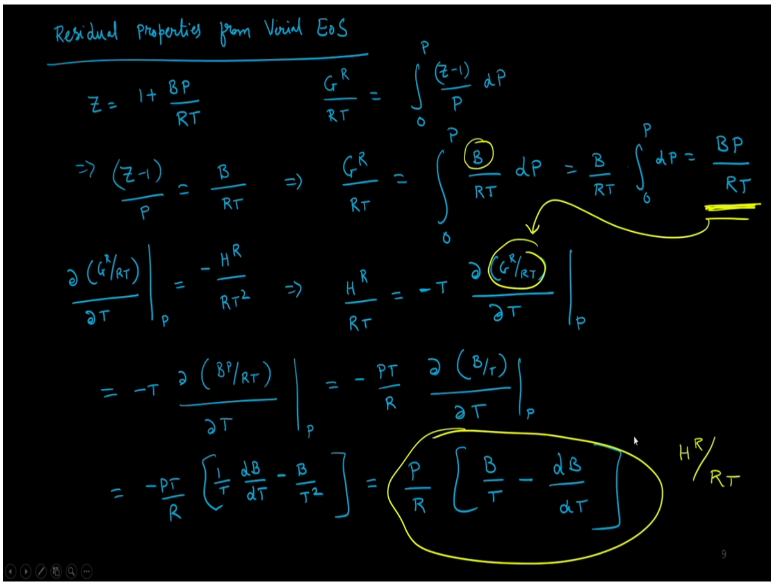

Residual properties from Virial EoS

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

$$\Rightarrow \frac{(Z-1)}{P} = \frac{B}{RT} \Rightarrow \frac{G^R}{RT} = \int_0^P \frac{\boxed{B}}{RT}\,dP = \frac{B}{RT}\int_0^P dP = \underline{\underline{\frac{BP}{RT}}}$$

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

$$= -T\left.\frac{\partial (BP/RT)}{\partial T}\right|_P = -\frac{PT}{R}\left.\frac{\partial (B/T)}{\partial T}\right|_P$$

$$= -\frac{PT}{R}\left[\frac{1}{T}\frac{dB}{dT} - \frac{B}{T^2}\right] = \boxed{\frac{P}{R}\left[\frac{B}{T} - \frac{dB}{dT}\right]} \quad H^R/RT$$

So, first let us see or derive some expressions for residual properties using virial equation of state we will restrict our discussion only to the second virial coefficient. So, the form of the equation we will use is the compressibility factor is 1 plus B P over RT. Remember the equation we derived yesterday that the Gibbs free energy G R over RT that residual Gibbs free energy is integral 0 to P Z minus 1 by P d P. And now I know that the compressibility factor from from virial equation of state is given by this expression.

So, I can write Z minus 1 over P to be B over RT which implies G R over RT is going to be integral of 0 to P B over RT d P. The second virial coefficient we can show this rigorously from statistical thermodynamics; it depends only on temperature it is independent of pressure. So, I can bring everything within the integral sign out of that. So, it will be B over RT integral 0 to P d P or B P over RT this is the expression for G R over R T.

Now, for H R over RT we will use G R over RT as generating function; recall that the derivative of this guy G R over RT with respect to temperature at constant pressure is negative H R over RT squared. Then H R over RT is negative T right times the derivative of G R over RT with respect to temperature at constant pressure; now the pressure is constant.

So, let us use this expression for G R over RT right here and put it here and try to take the derivative. What happens is negative T; the derivative of B P over RT with respect to T at constant pressure. So, I can bring because P is constant I can bring P and R out of that derivative. So, it will be P T over R and the derivative of B over T with respect to T pressure is constant that is obvious right. And this value right here P T over R derivative of B over T is going to be 1 over T derivative of B with respect to T right minus B over T squared; that will be the derivative right.

Notice that I got rid of the partial derivative because B is only a function of temperature; so, I can write just d B over d T. And then if I simplify this it will be P over R times B by T minus d B by d T; this is the expression for H R by RT. So, this is the expression for H R by RT.

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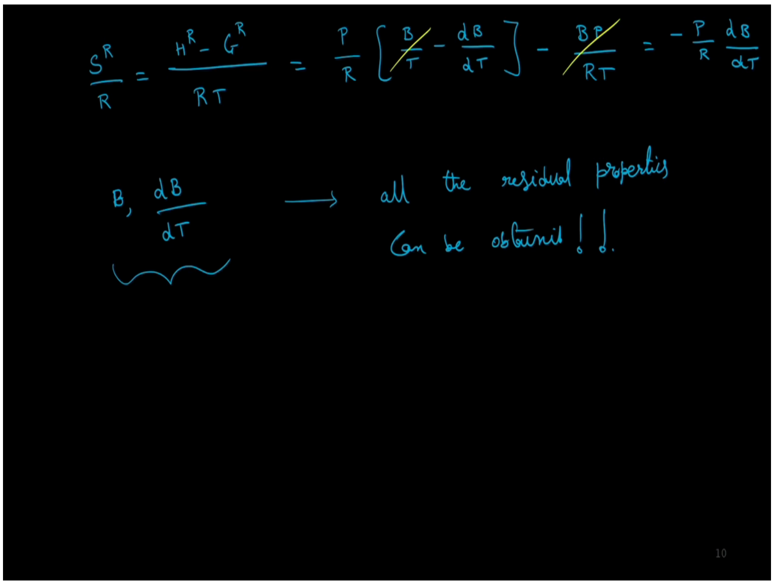

$$\frac{S^R}{R} = \frac{H^R - G^R}{RT} = \frac{P}{R}\left[\cancel{\frac{B}{T}} - \frac{dB}{dT}\right] - \cancel{\frac{BP}{RT}} = -\frac{P}{R}\frac{dB}{dT}$$

$$\underbrace{B, \frac{dB}{dT}} \longrightarrow$$ all the residual properties can be obtained!!

Now, once I have H R by RT and G R by RT; S R is pretty easy to calculate it turns out that S R over R is H R minus G R by RT. I have both H R and G R from the previous slide one of them is P by R; B by T d B by d T P by R B by T minus d B by d T that is H R by RT minus B P by RT that is G R by R T.

So, it turns out that the 2 terms cancel and all I have left is minus P over R d B d T all right. So, that is the expression for S R over R; then it turns out I can derive similar expressions for u R and a R then boils down to is I can express all the thermodynamic quantities only as if I know what the second virial coefficient B is and how it varies with temperature what is d B over d T.

If I have these 2 pieces of information I can get all the residual properties can be obtained. And once I have the residual properties and I have the ideal gas specific heat, then I can calculate all the property changes that are of interest. So, then the next thing to ask is how the second virial coefficient changes with temperature.

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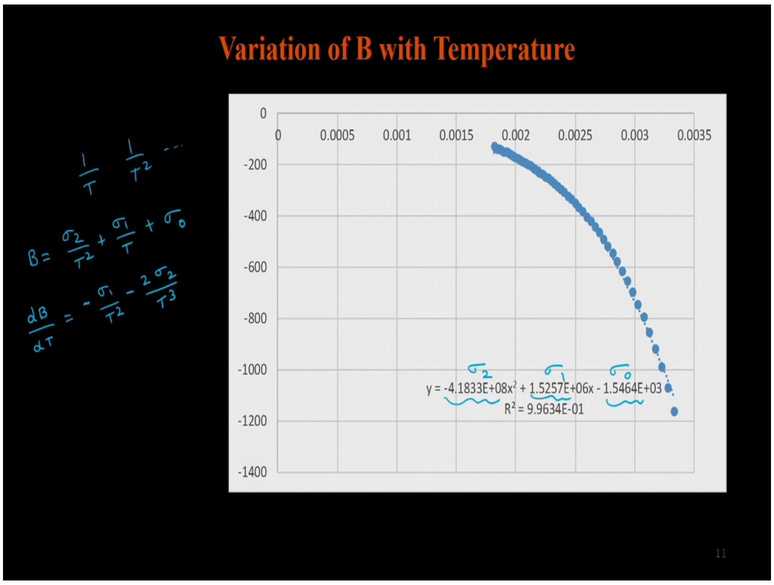

Variation of B with Temperature

$$\frac{1}{T} \quad \frac{1}{T^2} \quad \cdots$$

$$B = \frac{\sigma_2}{T^2} + \frac{\sigma_1}{T} + \sigma_0$$

$$\frac{dB}{dT} = -\frac{\sigma_1}{T^2} - \frac{2\sigma_2}{T^3}$$

$$y = \underbrace{-4.1833E+08}_{\sigma_2}x^2 + \underbrace{1.5257E+06}_{\sigma_1}x - \underbrace{1.5464E+03}_{\sigma_0}$$

$R^2 = 9.9634E-01$

This is second virial coefficient for water and as you can see usually it does vary with temperature in some sort of a power series; depending on the compound we have. There are several expressions that we can use the most convenient one is a polynomial either in T or 1 over T; more often the case 1 over T; 1 over T squared etcetera.

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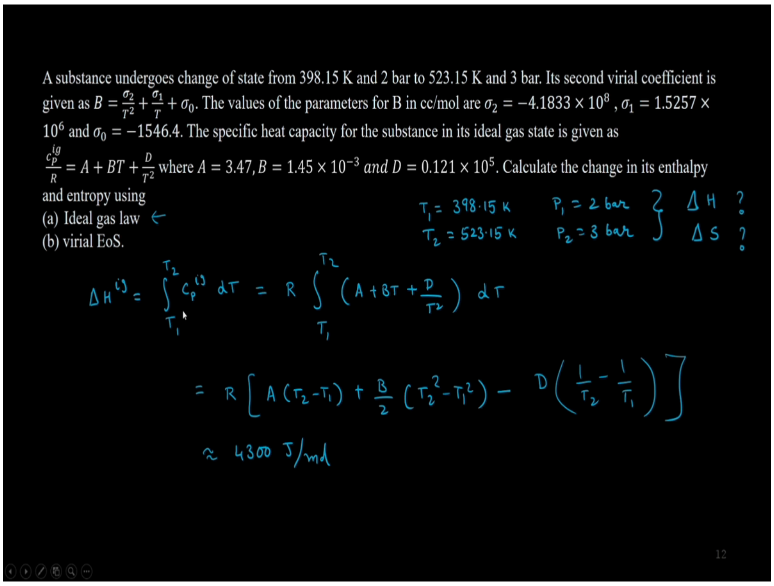

A substance undergoes change of state from 398.15 K and 2 bar to 523.15 K and 3 bar. Its second virial coefficient is given as $B = \frac{\sigma_2}{T^2} + \frac{\sigma_1}{T} + \sigma_0$. The values of the parameters for B in cc/mol are $\sigma_2 = -4.1833 \times 10^8$, $\sigma_1 = 1.5257 \times 10^6$ and $\sigma_0 = -1546.4$. The specific heat capacity for the substance in its ideal gas state is given as $\frac{c_P^{ig}}{R} = A + BT + \frac{D}{T^2}$ where $A = 3.47, B = 1.45 \times 10^{-3}$ *and* $D = 0.121 \times 10^5$. Calculate the change in its enthalpy and entropy using

(a) Ideal gas law ←

(b) virial EoS.

$$\left.\begin{matrix} T_1 = 398.15\text{ K} & P_1 = 2\text{ bar} \\ T_2 = 523.15\text{ K} & P_2 = 3\text{ bar} \end{matrix}\right\} \quad \begin{matrix} \Delta H \ ? \\ \Delta S \ ? \end{matrix}$$

$$\Delta H^{ig} = \int_{T_1}^{T_2} C_p^{ig}\, dT = R \int_{T_1}^{T_2} \left(A + BT + \frac{D}{T^2}\right) dT$$

$$= R\left[A(T_2 - T_1) + \frac{B}{2}(T_2^2 - T_1^2) - D\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

$$\approx 4300 \text{ J/mol}$$

And as you see here B is written as this; sigma over T square plus sigma 1 over T plus sigma naught right sigma 2 over T squared plus sigma 1 over T plus sigma naught and the values of sigma are given here.

Those are the values of sigma 2 sigma 1 and sigma naught and once I have this I can readily differentiate this equation d B over d T right; I can readily differentiate this equation to get d B over d T right. So, it will be negative sigma 1 over T squared minus 2; sigma 2 over T cube that would be d B over d T. So, if I know an expression for being with temperature then I can do a differentiation get d B by d T and all the other information I need.

So, let us use this idea and try to solve a problem a substance undergoes a change of state from an initial condition; a temperature of 398.15 Kelvin to a final and a pressure of course, at 2 bar to a final condition T 2 is 523.15 Kelvin and P 2 is 3 bar. This is a change of state the specific heat capacity for the substance in its ideal gas state is given c p i g over R is given as A plus B T plus D over T square values of A B and D are given to us.

And its second virial coefficient is given what we want to calculate is delta H and delta S. First thing we want to do is use an ideal gas law to calculate these changes. So, I am interested in delta H i g as you recall delta H i g for an ideal gas delta A or H is only a function of temperature. So, in this case delta H i g is simply going to be c p i g d T integral of that quantity from T 1 to T 2.

And that value will be is easy to obtain c p i g over R is given to us. So, it is going to be R times integral T 1 to T 2 A plus B T plus D over T squared d T. And this value right here is R A T 2 minus T 1 plus B over 2 T 2 squared minus T 1 squared minus D; 1 by T 2 minus 1 by T 1. Now, if I can simplify this equation I can get what the value of delta H i g is going to be what I get is about 4300 joules per mol. So ideal gas value is fairly easy to calculate if I know the ideal gas specific heat capacity because enthalpy depends only on c p i g or temperature in this case.

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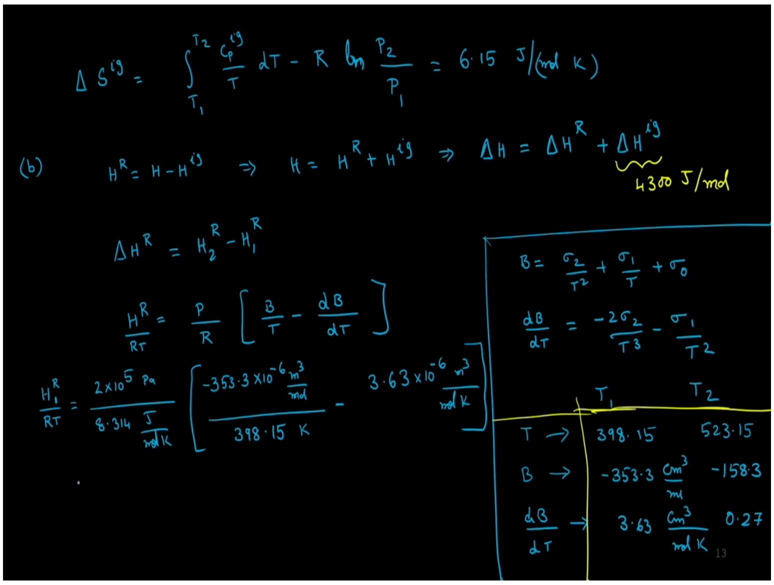

$$\Delta S^{ig} = \int_{T_1}^{T_2} \frac{C_p^{ig}}{T} dT - R \ln \frac{P_2}{P_1} = 6.15 \ J/(mol\ K)$$

(b) $$H^R = H - H^{ig} \Rightarrow H = H^R + H^{ig} \Rightarrow \Delta H = \Delta H^R + \underbrace{\Delta H^{ig}}_{4300\ J/mol}$$

$$\Delta H^R = H_2^R - H_1^R$$

$$\frac{H^R}{RT} = \frac{P}{R}\left[\frac{B}{T} - \frac{dB}{dT}\right]$$

$$\frac{H_1^R}{RT} = \frac{2\times10^5\ Pa}{8.314\ \frac{J}{mol\,K}}\left[\frac{-353.3\times10^{-6}\ \frac{m^3}{mol}}{398.15\ K} - 3.63\times10^{-6}\ \frac{m^3}{mol\,K}\right]$$

$$B = \frac{\sigma_2}{T^2} + \frac{\sigma_1}{T} + \sigma_0$$

$$\frac{dB}{dT} = -\frac{2\sigma_2}{T^3} - \frac{\sigma_1}{T^2}$$

|  | $T_1$ | $T_2$ |
|---|---|---|
| $T \rightarrow$ | 398.15 | 523.15 |
| $B \rightarrow$ | $-353.3\ \frac{cm^3}{mol}$ | $-158.3$ |
| $\frac{dB}{dT} \rightarrow$ | $3.63\ \frac{cm^3}{mol\,K}$ | 0.27 |

If I am interested in calculating the entropy change for an ideal gas recall the expression it is going to be integral T 1 to T 2 c p i g by T d T minus R l n P 2 over P 1; this was the expression for change in entropy of an ideal gas; we can run through the calculation similar to the integral we have done earlier for enthalpy. And in this case we can get the value to be about 6.15 joule per mol Kelvin right.

So, those two are pretty straightforward to calculate. Now if I am interested in using a virial equation of state as the next part of the problem asks right; use a we virial equation of state to calculate the changes in enthalpy and entropy. How are you going to do that? Remember by definition H R is H minus H i g which means H is going to be H R plus H i g or delta H; the change in entropy or enthalpy is going to be the change in the residual values of enthalpy plus change in the enthalpy under ideal gas conditions.

We have already calculated the change in enthalpy under ideal gas conditions it was 4300 joules per mol. So, if I got to calculate the total enthalpy change then all I need is to calculate the difference in the residuals between the initial and the final states or delta H R. So, delta H R is what I am looking for right now which is H 2 R minus H 1 R difference between the final and the initial states. And I am going to use virial equation of state to calculate these residual quantities to calculate these residual quantities. And remember from a virial equation of state H R was P over R or H R over RT rather was P over R B by T minus d B by d T; B by T minus d B by d T; I need to calculate B and d B by d T at initially in the final conditions.

Then I can plug those numbers here to get H R over RT or H R. What I will do is calculate B and d B by d T at the initial and final conditions. Let me do that here B is given to me it is sigma 2 over T squared plus sigma 1 over T plus sigma naught values of sigmas are given in the problem statement right.

If this is this then d B by d T like I said earlier is 2 sigma 2 over T cube minus sigma 1 over T squared. Once I have these two expressions and I have the values of sigmas given to me; sigma 2 sigma 1 and sigma naught; I can use these 3 values of sigmas here and calculate at the initial and the final conditions; I can calculate all the 3 all the both the quantities I require and the initial and the final conditions.

The initial temperature is through 398.15 Kelvin; the final temperature is 523.15 15 Kelvin. The B this is T the B is at this temperature the value of B; we calculate is negative 353.3 centimeter cube per mol. At the second temperature at the higher temperature it is slightly lower its negative 158.3.

And d B over d T at the first temperature it is 3.63 centimeter cube per mol Kelvin and at the second temperature it is 0.27 right. So, I can use the given values of sigma and based on the expressions for virial equation of state; I can calculate what the values of B and d B over d T R. Once I have B and d B over d T all that is left is to come back and calculate H R at the first and the second conditions.

This is going to be let us write expression out for the first condition at least; H R at the first pressure or the first condition the pressure is given to us; it is 2 bar and the final pressure is 3 bar. So, this is 2 bar. So, 2 into 10 power 5 Pascal's over 8.314 joule per mol Kelvin is the value of R. Remember now I am converting everything into psi units to be consistent. So, I have to convert B into meter cube per mol

So, it is going to be negative 353.3 into 10 power negative 6 meter cube per mole; the 10 power negative 6 is to convert c c per mol to meter cube per mol over the temperature in the first at the first condition. So, I am going to write it this is the first condition is 398.15 Kelvin minus d B over d T is 3.63 over that is 3.63.

And again it is centimeter cube per mol Kelvin. So, it is going to be 10 power minus 6 centimeter cube per mol Kelvin; since we have put in 10 power minus 6, it is going to be meter cube per mol Kelvin. So, this is meter cube per mol this is Kelvin this is meter cube per mol Kelvin and then everything else balances out here I can calculate H R over R T.

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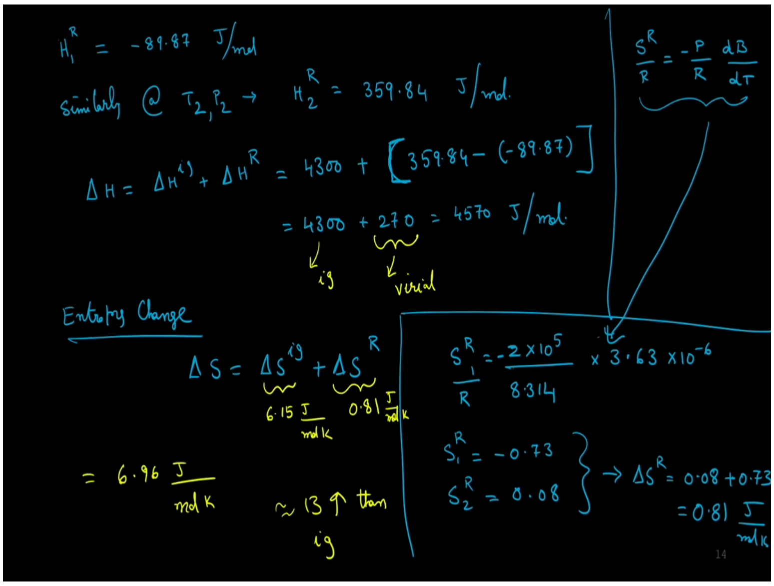

$H_1^R = -89.87 \ J/mol$

similarly @ $T_2, P_2 \rightarrow \ H_2^R = 359.84 \ J/mol.$

$\Delta H = \Delta H^{ig} + \Delta H^R = 4300 + [359.84 - (-89.87)]$

$= \underset{\swarrow \atop ig}{4300} + \underbrace{270}_{\swarrow \ virial} = 4570 \ J/mol.$

$\frac{S^R}{R} = -\frac{P}{R} \underbrace{\frac{dB}{dT}}$

Entropy Change

$\Delta S = \underbrace{\Delta S^{ig}}_{6.15 \frac{J}{mol K}} + \underbrace{\Delta S^R}_{0.81 \frac{J}{mol K}}$

$= 6.96 \frac{J}{mol K}$

$\approx 13 \uparrow$ than ig

$\frac{S_1^R}{R} = \frac{-2 \times 10^5}{8.314} \times 3.63 \times 10^{-6}$

$\left.\begin{array}{l} S_1^R = -0.73 \\ S_2^R = 0.08 \end{array}\right\} \rightarrow \Delta S^R = 0.08 + 0.73$

$= 0.81 \frac{J}{mol K}$

So, notice that if I do not involve the corrections using the virial equation of state then I would have calculated only the ideal gas value which is the negative 4300 joules per mol. And if I use the correction then I added another 2 seventy to that which is about what 6 percent higher.

So, the estimate for enthalpy change is about 6 percent higher in this case and for a process that is a lot if it is energy requirement for the process; then it is essentially 6 percent more. So, these corrections are necessary for process calculations depending on how far away I am from no ideality. And we can accomplish this by using the residual properties and then appropriate equation of state in this example we have used ideal gas equation of state.

I can run through a similar calculation for the entropy change right and in fact, all the other thermodynamic quantities delta S is going to be delta S for the ideal gas plus delta S in the residual property. And remember we have calculated delta S for the ideal gas already earlier and we said that value is 6.15 joule per mol Kelvin.

What I have left is to calculate delta S R right and delta S R will calculate it by calculating the residual properties at the first and the second conditions right. And remember we said S R over R is negative P by R d B by d T.

So, I can use this calculate S R at condition 1 is negative the pressure initial pressure I have is 2 bar. So, 2 into 10 power 5 Pascal over 8.314 joule per mol per Kelvin negative of that multiplied with d B over d T is 3.63 into 10 power minus 6 to correct centimeter cube to metre cube.

This is S 1 over R and this value turns out to be negative 0.73. In these examples we looked at today what we have done is use the idea of the residual properties and employed virial equation of state to calculate property changes in the process. When we come back to tomorrow we are going to look at other types of equation of state I can use to achieve the same objective.

Thank you.