# Course on Phase Equilibrium Thermodynamics
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## Lecture 17
## Tutorial

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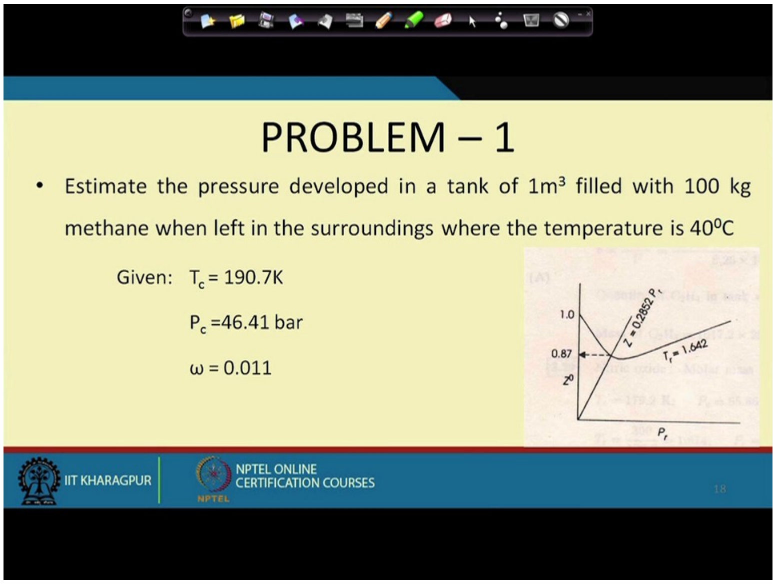

## PROBLEM – 1

- Estimate the pressure developed in a tank of 1m$^3$ filled with 100 kg methane when left in the surroundings where the temperature is 40$^0$C

Given: $T_c = 190.7K$

$P_c = 46.41$ bar

$\omega = 0.011$

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Well, let us see the first problem. The first problem is written here we need to estimate the pressure in a tank of 1 meter cube filled with100 KG methane when left in the surroundings temperature is 40 degree centigrade, what are the data which are given to you? The data of TC PC and omega are given to you. What is the gas? It is methane; you know the molar mass of methane, what is the molar mass of methane?

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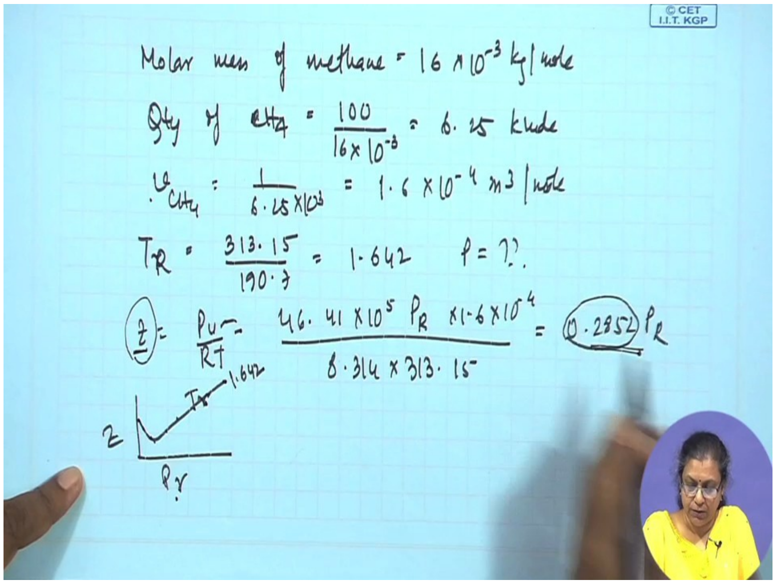

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Molar mass of methane = $16 \times 10^{-3}$ kg/mole

Qty of $CH_4$ = $\frac{100}{16 \times 10^{-3}}$ = 6.25 kmole

$v_{CH_4} = \frac{1}{6.25 \times 10^{3}} = 1.6 \times 10^{-4}$ m3/mole

$T_R = \frac{313.15}{190.7} = 1.642$ $P = ??$

$\boxed{z} = \frac{Pv}{RT} = \frac{46.41 \times 10^{5} P_R \times 1.6 \times 10^{-4}}{8.314 \times 313.15} = \boxed{0.2852} P_R$

It is very, you can always find it out this is equals to 16 into 10 to the power minus 3 KG per mole, right? TC PC and VC are given, so quantity of methane in the gas CH4 this is equal to 100 by 16 into 10 to the power minus 3 which is 6.25 kilo moles you know it, fine. What is the molar volume of methane? VCH4 this will be equal to 1 by 6.25 into 10 to the power 3, fine. This is nothing but equal to 1.6 into 10 to the power of minus 4 meter cube per mole.

What is TR in this particular case? The temperature is given as 313.15 Kelvin by 190.7 Kelvin which is 1.642. So therefore you know TR and what is z equals to that is equals to Pv by RT your P is given, v you have already found out this is the V the P is already given it is P is not given sorry, R is given P is given at 40 degree centigrade. So if you substitute all these terms what do you get? You get 46.41 into 10 to the power of 5 PR into 1.6 into 10 to power minus 4 divided by 8.314 into 313.15 you get z as 0.2852 PR, right?

See one thing what are the data you have at hand? With the data you have at hand you are supposed to find out pressure, agreed? You know TR you can find out z as a function of PR, agreed? But and you also have a compressibility factor chart which gives you z as a function of PR for particular Tr, so in this particular case if you have a Tr, Tr of 1.642, so in your particular condition will lie at any particular point on this particular isotherm, agreed?

But where it is going to lie you do not know. You just know it is going to lie on this particular isotherm you need a trial and error method to find out exactly where it lies? It is a very difficult thing to do without anything you cannot do a trial and error method but at the same time you know something else, you know that z has a linear relationship with Pr as well with the slope of 0.2852, so what do you do?

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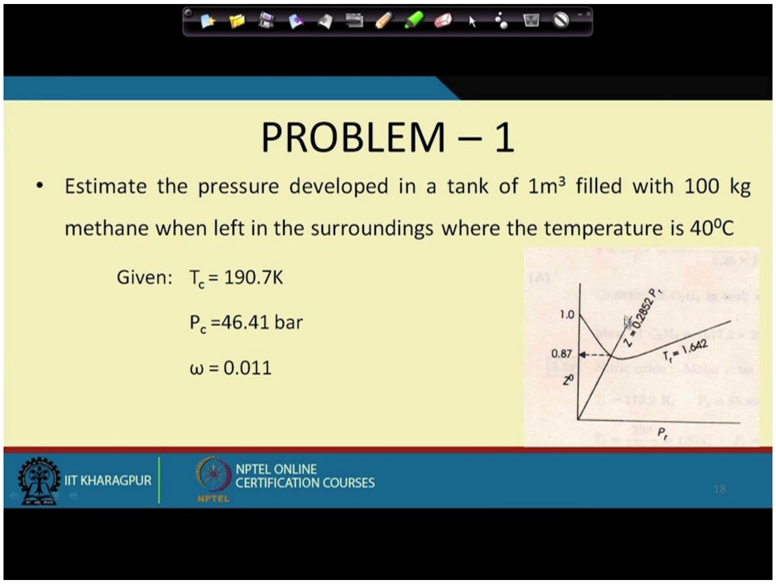

## PROBLEM – 1

- Estimate the pressure developed in a tank of 1m$^3$ filled with 100 kg methane when left in the surroundings where the temperature is 40$^0$C

Given: $T_c$ = 190.7K

$P_c$ =46.41 bar

ω = 0.011

The best way is to do is you draw a straight line from the origin with z equals to 2.582 Pr and you see where it intersects with the isotherm at Tr equals to 1.642. So naturally this is going to be the point in question and for that particular point in question you know what is z0? You find that the z0 is nothing but 0.87.

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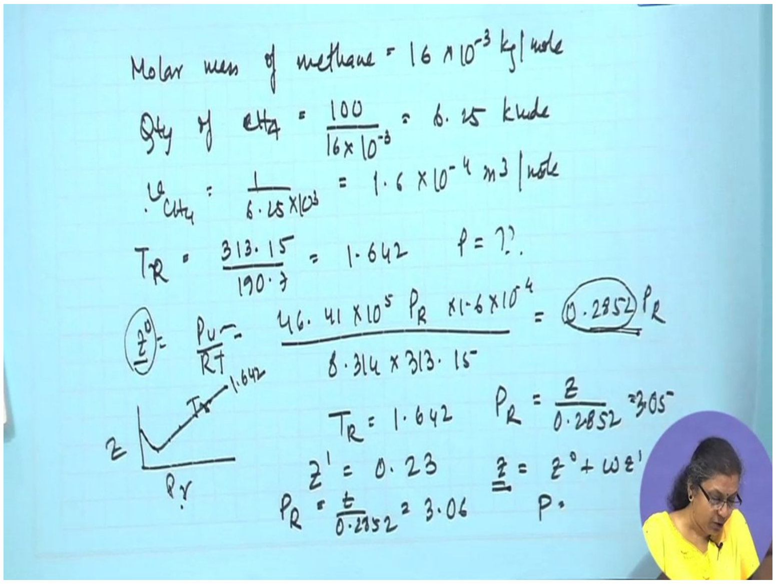

Molar mass of methane = $16 \times 10^{-3}$ kg/mole

Qty of $CH_4$ = $\frac{100}{16 \times 10^{-3}}$ = 6.25 kmole

$\therefore v_{CH_4} = \frac{1}{6.25 \times 10^{3}} = 1.6 \times 10^{-4}$ m3/mole

$T_R = \frac{313.15}{190.7} = 1.642$   $P = ??$

$\boxed{z^0} = \frac{Pv}{RT} = \frac{46.41 \times 10^{5} P_R \times 1.6 \times 10^{-4}}{8.314 \times 313.15} = \boxed{0.2852} P_R$

$T_R = 1.642$   $P_R = \frac{z}{0.2852} = 3.05$

$z^1 = 0.23$   $\underline{\underline{z}} = z^0 + \omega z^1$

$P_R = \frac{z}{0.2852} = 3.06$   P.

So naturally you from here you know that at TR equals to 1.642, what is your PR going to be? Your PR is going to be z by 0.2852. So you know the PR is going to be 3.05, right? So you know PR you know TR and for better accuracy you would like to refer to the z1 versus Pr Tr chart. From the z1 versus PRTR chart if you since you know PR and TR you can find out z1, the z1 you will be finding out just check it up, this is data I am giving you this is nothing but equals to 0.23.

Once you know z1 you know z then what is the next thing? This is basically z0; you can find z as z0 plus omega z1, omega is already given. So from there you can find out the final z using this final particular z you can find out PR as z by 0.2852 you get PR as equal to 3.06 and from there you can find out P and this particular iteration possibly it has to be done a number of times. So from here you get a particular z again you start from this particular with z0 equals to 0.86 z1 equals to 0.23 PR equals to 3.06, TR equals to 1.602. You get a PR as 3.024, right? With this particular PR as 0.324 there are several iterations may be which you have to do.

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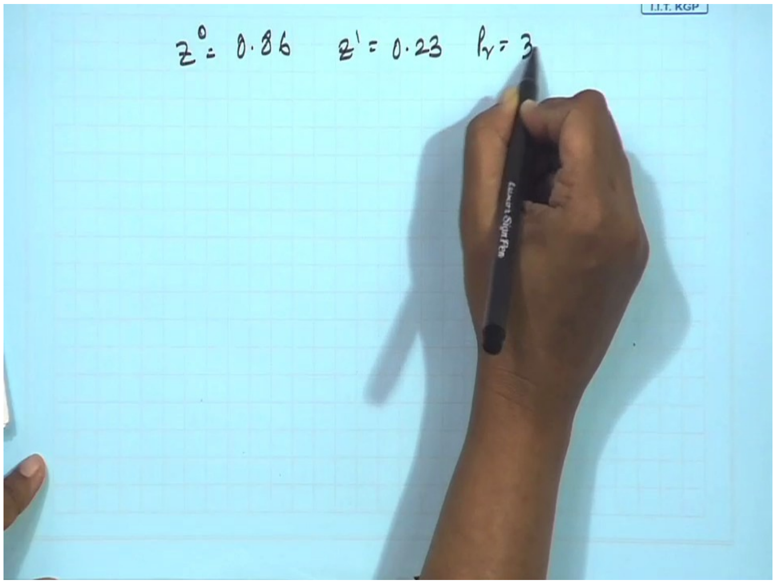

Finally you get your z as your z0 as 0.86, z1 equals to 0.23 Pr at Pr equals to 3.204, TR equals to1.642, from where you get your final PR as 3.024 when the calculations converge from where you get your P as 140.34 bar. So this was the first problem.

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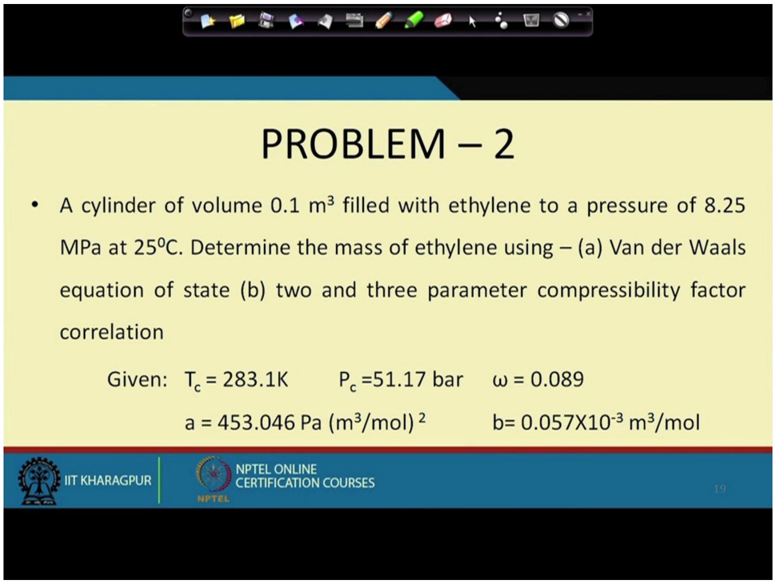

## PROBLEM – 2

- A cylinder of volume 0.1 $m^3$ filled with ethylene to a pressure of 8.25 MPa at 25$^0$C. Determine the mass of ethylene using – (a) Van der Waals equation of state (b) two and three parameter compressibility factor correlation

Given: $T_c = 283.1K$ $P_c = 51.17$ bar $\omega = 0.089$

$a = 453.046$ Pa $(m^3/mol)^2$ $b = 0.057X10^{-3}$ $m^3/mol$

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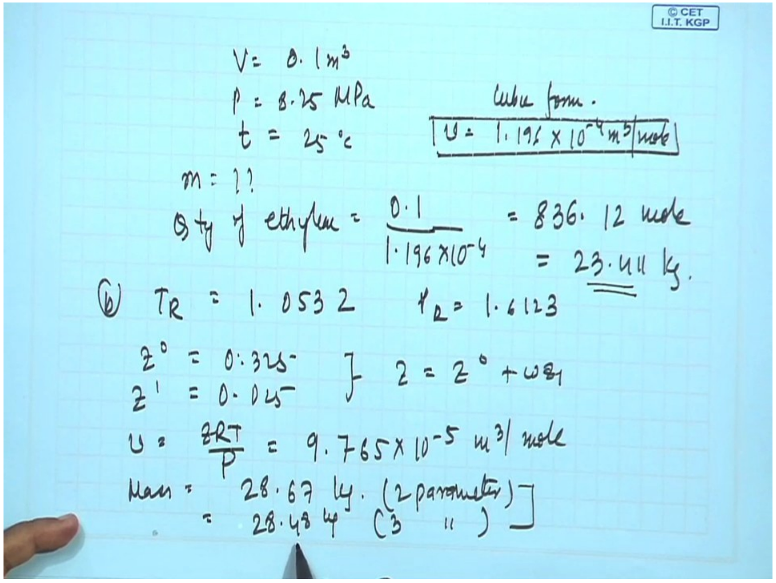

$V = 0.1 m^3$

$P = 8.25$ MPa

$t = 25$ °c

$m = ??$

Cubic form.

$\boxed{v = 1.196 \times 10^{-4} m^3/mole}$

Qty of ethylene $= \dfrac{0.1}{1.196 \times 10^{-4}} = 836.12$ mole

$= \underline{\underline{23.41 \text{ kg}}}$.

ⓑ $T_R = 1.0532$ $P_R = 1.6123$

$\left.\begin{array}{l} Z^0 = 0.325 \\ Z^1 = 0.045 \end{array}\right\} Z = Z^0 + \omega Z_1$

$v = \dfrac{ZRT}{P} = 9.765 \times 10^{-5} m^3/mole$

$\left.\begin{array}{l} \text{Mass} = 28.67 \text{ kg. (2 parameter)} \\ \quad\;\; = 28.48 \text{ kg} \;\; (3 \;\; \text{"} \;\; ) \end{array}\right]$

Let us go to the second problem it is a pretty straightforward problem you have a cylinder of 0.1 meter cube, so your volume is 0.1 meter cube, the pressure is also given 8.25 mega-Pascal, temperature is given as 25 degrees centigrade you are required to find out the mass of ethylene and you are supposed to do it by the Van der waals equation of state 2 and 3 parameter compressibility factor chart, right?

So for the Van der waals equation a is given b is given but it has to be a trial and error technique you need to find out, see you know the total volume if you can find out the molar volume then you can find out the mass of ethylene inside this. In order to find out the molar volume you need to write down the Van der waals equation in the cubic form, once you write it down in the cubic form you need to solve it iteratively.

Now remember one thing when you have to do iterative calculation, first guess which you should be using is the value of v obtained from the ideal gas state, right? So therefore that will be your first guess value for solving this particular cubic form of equation. So therefore from the initial guess value you get v equals to 1.196 into 10 to the power minus 4 meter cube per mole this initial value, the initial value has been obtained from the ideal gas equation.

Once you know the molar volume so then from that you can find out the quantity of ethylene as the total volume divided by the molar volume this has been obtained by solving the cubic equation of state the first guess value for the cubic equation of state was from the ideal gas value. So therefore from here you get that the total moles of ethylene in the cylinder was this and the total mass of ethylene was 23.411 kg provided ethylene obeys the Van der waals equation of state.

As far as finding it out from the 2 and 3 parameter compressibility correlations what you need to do? You need to find out TR, find out TR it will be equal to this, find out PR this is going to be 1.6123, since you know TR PR in this case there is no need of any particular trial and error you can very well find out z0 from the graphs which I have given.

You can also find out z1 the graph is also provided here, once you know these 2 you can find out z omega is also given I believe, so you can find z as z0 plus omega z1, substitute these 2 and omega is 0.089 from there you get z. Once you get z you can find out V from this particular equation. The V from the 2 parameter law it comes out as this is the molar volume 9.765 into 10 to the power of minus 5 meter cube per mole, from where you get the mass of ethylene it is obtained as 28.67 kgs and from this is from the 2 parameter laws.

Similarly if you proceed with the 3 parameter law you get the mass to be 28.48 kgs, it is worth noting that there is slight quite amount of difference between the Van der waals prediction and the 2 and 3 parameter law of corresponding states, naturally this particular deviation it occurs due considering the approximate nature of the Van der waals equation as well as the inaccuracies inherent in the 2 and 3 parameter law of corresponding states. It is also important to know that the predictions from 2 and 3 parameter models they do not vary much which automatically implies that we can safely use the 2 parameter law of corresponding states provided we are not very near the critical conditions and not very near the saturation curves.

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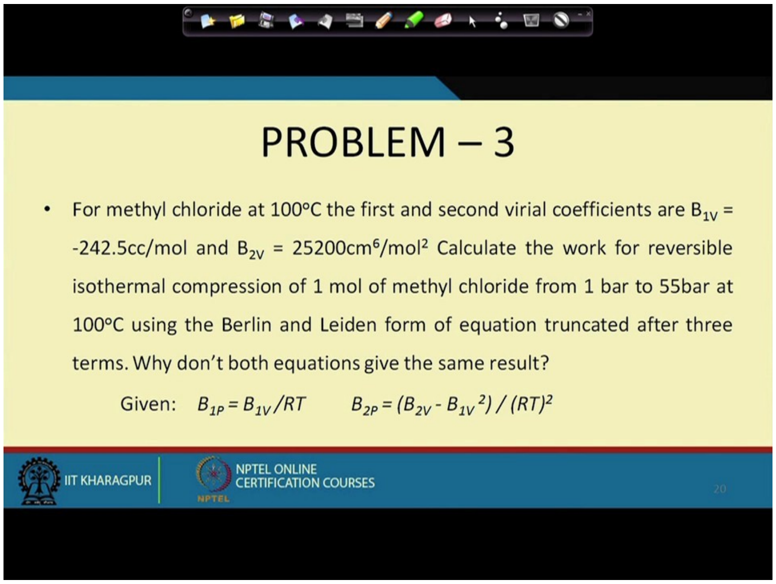

## PROBLEM – 3

- For methyl chloride at 100°C the first and second virial coefficients are $B_{1V}$ = -242.5cc/mol and $B_{2V}$ = 25200cm$^6$/mol$^2$ Calculate the work for reversible isothermal compression of 1 mol of methyl chloride from 1 bar to 55bar at 100°C using the Berlin and Leiden form of equation truncated after three terms. Why don't both equations give the same result?

Given: $B_{1P} = B_{1V}/RT \qquad B_{2P} = (B_{2V} - B_{1V}^2)/(RT)^2$

Now let us go to the third problem, a slightly different problem. What do we have here? This is a problem on the virial equation, what do we have here? We have methyl chloride at 100 degrees centigrade the first 2 coefficients are provided and we would like to find out the work required for reversible isothermal compression of one mole of this Methyl chloride from say one bar to 55 bar at 100 degree centigrade and you are required to work it out both in terms of the Berlin form of equation and the Leiden form of equation or in other words from the volume explicit form and as well as the pressure explicit form.

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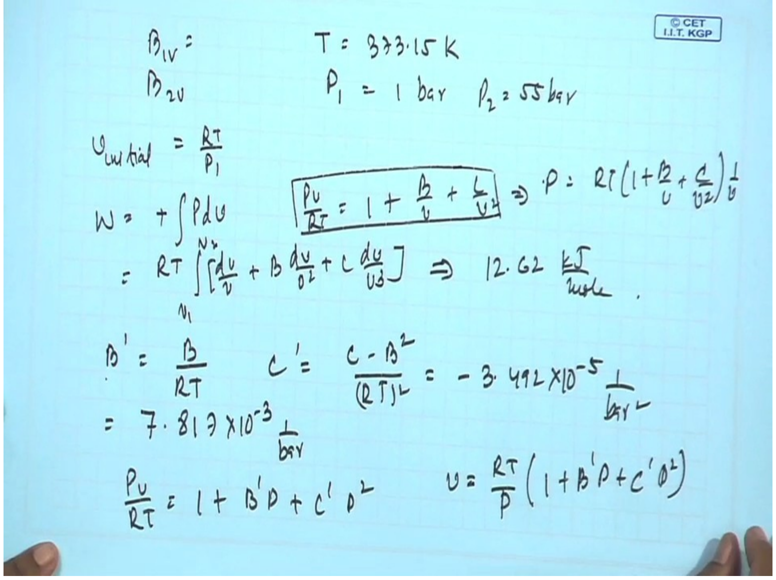

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$B_{1v} =$ $\quad T = 373.15\ K$

$B_{2v}$ $\quad P_1 = 1\ bar \quad P_2 = 55\ bar$

$v_{initial} = \frac{RT}{P_1}$

$W = +\int P\,dv \quad \boxed{\frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2}} \Rightarrow P = RT\left(1 + \frac{B}{v} + \frac{C}{v^2}\right)\frac{1}{v}$

$= RT\int_{v_1}^{v_2}\left[\frac{dv}{v} + B\frac{dv}{v^2} + C\frac{dv}{v^3}\right] \Rightarrow 12.62\ \frac{kJ}{mole}$

$B' = \frac{B}{RT} \quad C' = \frac{C - B^2}{(RT)^2} = -3.492\times10^{-5}\ \frac{1}{bar^2}$

$= 7.817\times10^{-3}\ \frac{1}{bar}$

$\frac{Pv}{RT} = 1 + B'P + C'P^2 \quad v = \frac{RT}{P}\left(1 + B'P + C'P^2\right)$

This is a pretty simple problem you have got B1v you have got B2v you have got T you have got P1 you have got P2, right? From here again you start with a v initial value remember one thing v initial value will be nothing but RT by P1, from there you are required to find out V final, what is W equals to? Minus of integral Pdv, you know Pv by RT is nothing but 1 plus B by v plus c by v square, agreed? So we can easily substitute this in terms of P, in terms of P this equation becomes RT into 1 plus B by v plus c by v square into 1 by v, right?

So therefore we are going to substitute it here, we are going to get this as RT integral v1 to v2 dv by v plus B dv by v square plus C dv by v cube into this equation from where we get the work done as 12.62 kilo joules per mole, right when we are using this particular equation, fine. Now suppose we use the other equation then in that case we need to find out B prime and we need to find out C Prime, we know the equations it is B by RT in this particular case also we know the equation it is C minus B square by RT whole square.

We can find these 2 values, this value is going to be minus 7.817 into 10 to the power minus 3,1 by bar this is going to be minus 3.492 into 10 to the power minus 5, 1 by bar square, once this B prime and C prime are found the rest is pretty simple we know Pv by RT equals to 1 plus B prime P plus C prime P square, we know what is v equals to, again we can substitute it in terms of RT by P one plus B prime P plus C prime P square, fine.

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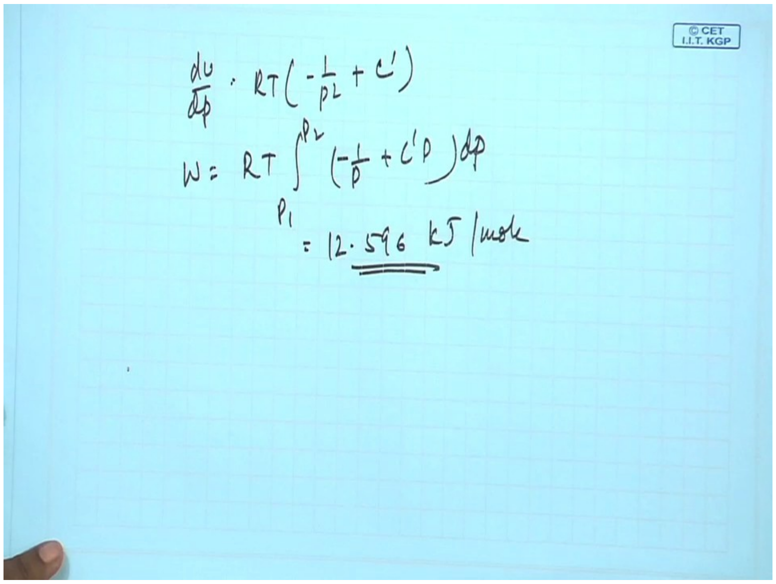

$$\frac{dv}{dp} = RT\left(-\frac{1}{P^2} + C'\right)$$

$$W = RT\int_{P_1}^{P_2}\left(-\frac{1}{P} + C'P\right)dP$$

$$= \underline{12.596}\ \text{kJ/mole}$$

Or else we can write we can just expand and write it down, so therefore from this particular equation we know what is dv dp equals to? It is equals to RT into 1 by P square plus C prime, fine. And we know what is W? This is equals to RT integral P1 to P2 minus 1 by P plus C prime P into dP which gives you the value of 12.596 kilo joules per mole. So therefore this is one particular way that we can do it there is just one thing which I would like to point out.

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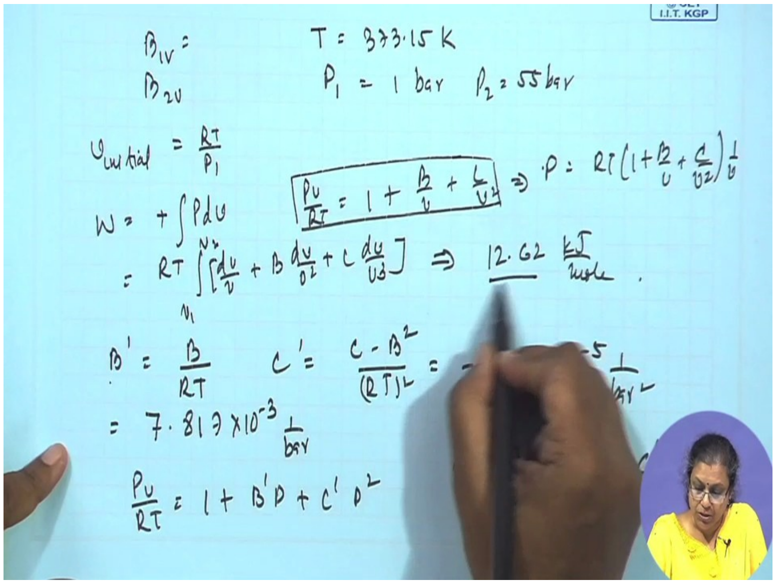

$B_{1V} =$

$B_{2V}$

$T = 373.15\ K$

$P_1 = 1\ bar \quad P_2 = 55\ bar$

$v_{initial} = \frac{RT}{P_1}$

$$\boxed{\frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2}} \Rightarrow P = RT\left(1 + \frac{B}{v} + \frac{C}{v^2}\right)\frac{1}{v}$$

$$W = +\int P\,dv$$

$$= RT\int_{v_1}^{v_2}\left[\frac{dv}{v} + B\frac{dv}{v^2} + C\frac{dv}{v^3}\right] \Rightarrow \underline{12.62}\ \frac{kJ}{mole}.$$

$$B' = \frac{B}{RT} \qquad C' = \frac{C - B^2}{(RT)^2} = \ldots{}^{-5}\ \frac{1}{bar^2}$$

$$= 7.817\times10^{-3}\ \frac{1}{bar}$$

$$\frac{Pv}{RT} = 1 + B'P + C'P^2$$

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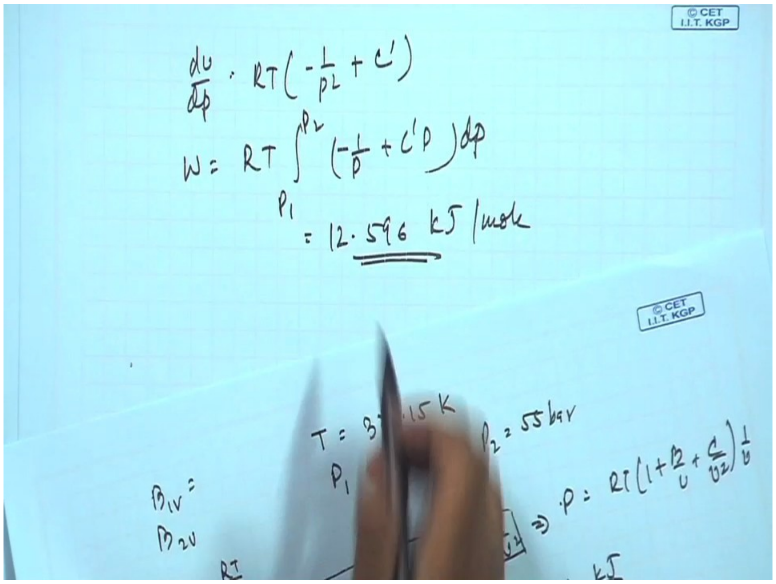

$$\frac{dv}{dp} = RT\left(-\frac{1}{p^2} + C'\right)$$

$$W = RT\int_{P_1}^{P_2}\left(-\frac{1}{p} + C'p\right)dp$$

$$= 12.\underline{596}\ kJ/mole$$

$T = 3\ \ .15\ K \quad P_2 = 55\ bar$

$P_1$

$B_{1V} =$

$B_{2V}$

$\Rightarrow P = RT\left(1 + \frac{B}{v} + \frac{C}{v^2}\right)\frac{1}{v}$

If you if you observe the work done which you have obtained by using the same equation in 2 particular forms in one case you get the result as 12.62 in the other case you get the result as 12.596 they are not completely identical this suggests or this happened, why? Just because we had taken the virial equation truncated after the third term, this shows that if you would have taken additional terms the predictions would have been better in this particular case, right?

So in this particular way you can try several other equations for several other problems there are a lot of problems which are available in a large number of textbooks you can try this out you can try problems involving cubic equations of state, virial equations of states and we will also be providing assignments to you for the same.

Now before I end there is one more problem also which I would like to do, it is not exactly on the PvT Behavior of the gases but on phase equilibrium that you have already covered, what is the problem?

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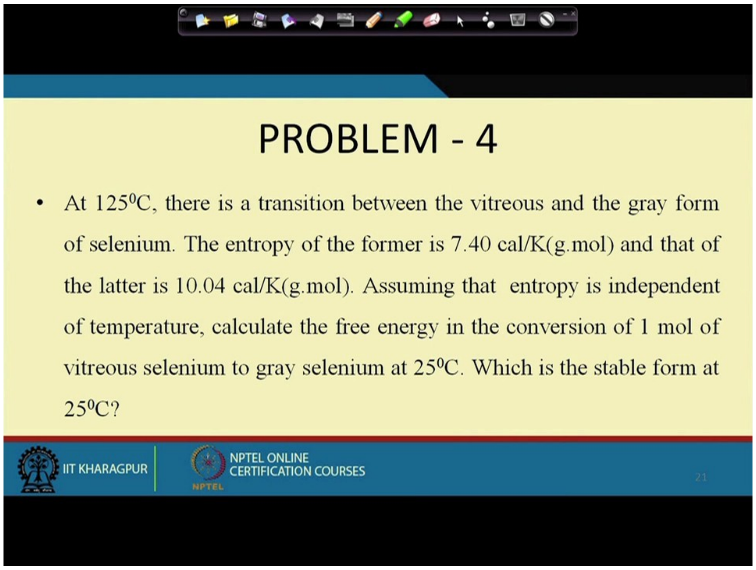

## PROBLEM - 4

- At $125^0$C, there is a transition between the vitreous and the gray form of selenium. The entropy of the former is 7.40 cal/K(g.mol) and that of the latter is 10.04 cal/K(g.mol). Assuming that entropy is independent of temperature, calculate the free energy in the conversion of 1 mol of vitreous selenium to gray selenium at $25^0$C. Which is the stable form at $25^0$C?

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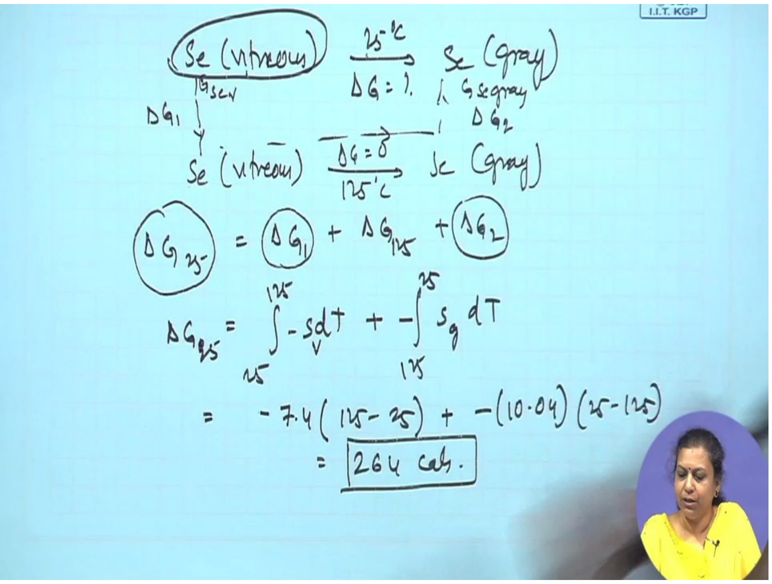

$$\begin{tikzcd}
\text{Se (vitreous)} \arrow[r, "25^\circ C", "\Delta G = ?"'] \arrow[d, "G_{Sev}", "\Delta G_1"'] & \text{Se (gray)} \\
\text{Se (vitreous)} \arrow[r, "\Delta G = 0", "125^\circ C"'] & \text{Se (gray)} \arrow[u, "G_{Se\,gray}"', "\Delta G_2"]
\end{tikzcd}$$

$$\Delta G_{25} = \Delta G_1 + \Delta G_{125} + \Delta G_2$$

$$\Delta G_{25} = \int_{25}^{125} -S_v\, dT + -\int_{125}^{25} S_g\, dT$$

$$= -7.4(125-25) + -(10.04)(25-125)$$

$$= \boxed{264 \text{ cals.}}$$

A very interesting problem it tells you about the transition from the vitreous to the gray form of selenium, right? What does it tell you? It tells you that suppose we have selenium in the vitreous state we would like to convert it to selenium in the grey state. It is given that you are supposed to find out Delta G for this at 25 degrees centigrade, fine. And what is the data given to you for finding this out? The data given to you is that at 125 degrees centigrade they are at equilibrium, what does it mean? It means that at 125 degrees centigrade Delta G equals to 0, fine. Using this data you are supposed to find out this. How to do this? You want to go from this state to this state.

Remember here it has say some particular value say some say Gse here it has got something say Gse grey and here it has Gse v suppose, right? From here to here we wish to go we can devise any path for it. So what do I do? Instead of this path I devise a path this, then this, then this. In this path what are things that I know? Here the change is Delta G,1 here the changes Delta G2 and here in this case the changes Delta G equals to 0. So therefore can I write Delta G at 25 it is equal to Delta G1 plus Delta G at 125 plus Delta G2?

Delta G1 is the Gibbs free energy change of selenium vitreous when it goes from 25 to 125 degree centigrade and Delta G2 is the change in the Gibbs free energy when the grey selenium goes from 125 to 25 degrees centigrade, right? Now if I can find out Delta G1 I can find out

Delta G2 I can find out the Delta G transition at 25 degrees centigrade. What are the data I have for finding these 2 out? The data which I have is the entropy of transitions data, right?

So from the entropy of transition data what do I know? I know Delta G1, this is equals to minus SdT from 25 to125 this is for the vitreous case and since it occurs under a constant pressure so therefore this just entropy change which happens and this is this Delta G is going to Delta G 25 this is 125 to 25 again minus S the grey variety dT.

You know the changes in dT, you know Sv, Sg which is independent of temperature. So from here if you substitute the values what do you get? You get this is nothing but minus 7.4, 125 minus just I am substituting the values minus 10.04, 25 minus 125 which gives you the value as 264 calories. Transition for this transition Delta G is positive which automatically states that this transition from vitreous selenium to grey variety of selenium it cannot be a spontaneous process but the reverse case has to be spontaneous process.

So therefore it is obvious that at 25 degrees centigrade the vitreous form is going to be much more stable and the reverse reaction is going to be the spontaneous reaction and at 125 degree centigrade either of the states can be stable and if we know the condition at 1 particular state we can find out the condition at the other state.

So this completes or rather I have tried to do a few tutorials on PvT behavior to give you a better feel and since I had some time I thought I would just show you the importance of phase equilibrium conditions to find out any particular transition or any particular state from some known particular state at some other conditions we will be continuing our discussions regarding the estimation of properties and then we will be going for mixtures from the next class onwards, have a good day.