Indian Institute of Technology Madras

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National Programme on Technology Enhanced Learning

Chemical Engineering Thermodynamics

by

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Lecture 16

Separation work / Equation of state

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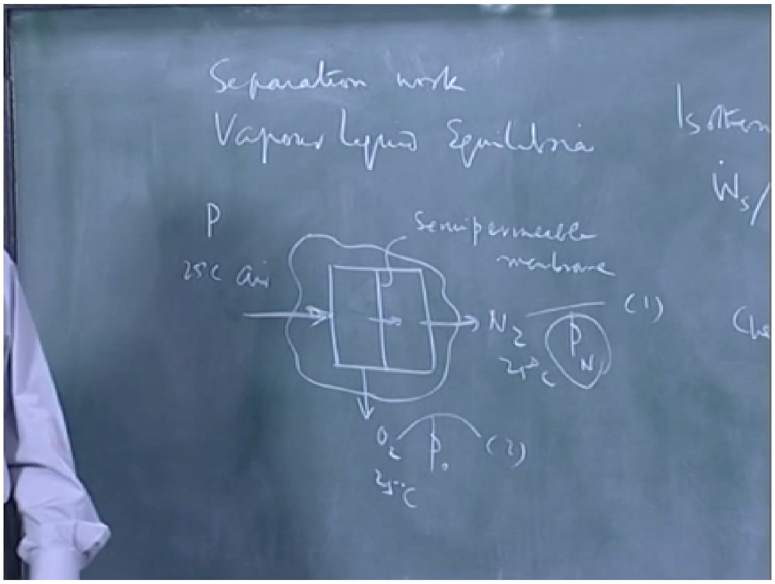

Separation work is very simple the simplest case would be air where I put the air here and relates assume here consist only in nitrogen and oxygen for the case of for the sake of simplicity what I really have is a membrane as I said all these are thought experiments let us assume I have a semi permeable membrane that can be distinguish between the size of oxygen in size of nitrogen would go write through you can pull out nitrogen here oxygen will come out here, air is at some pressure P and one nitrogen at pressure P and this at pressure Po.

As well as thermodynamics is concerned even this sketch is very complicated and drawn envelope like this all I have is air going in an oxygen nitrogen coming out, so if I take one mole of air let us assume 79% is nitrogen 21% is oxygen all I am saying is I have a mass balance I have Δg.

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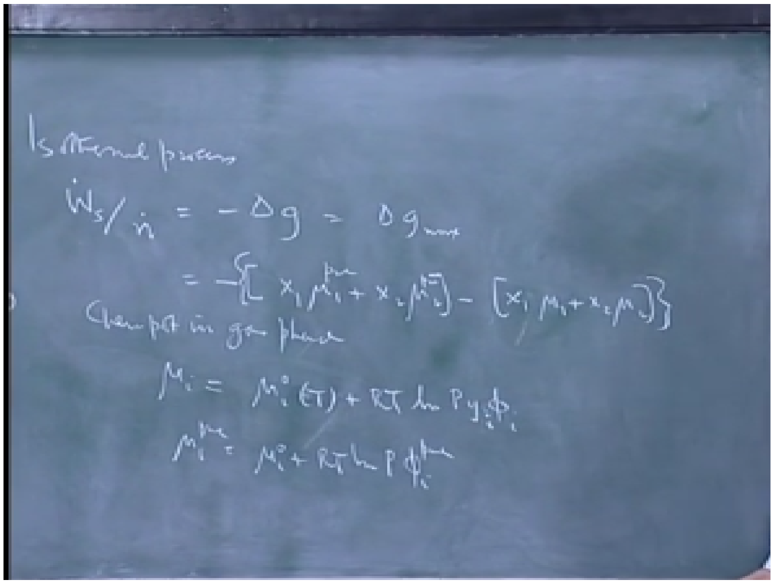

Isothermal process

$$\dot{W}_s/\dot{n} = -\Delta g = \Delta g_{mix}$$

$$= -\{[x_1\mu_1^{pure} + x_2\mu_2^{pure}] - [x_1\mu_1 + x_2\mu_2]\}$$

Chem pot in gas phase

$$\mu_i = \mu_i^0(T) + RT\ln P y_i \phi_i$$

$$\mu_i^{pure} = \mu_i^0 + RT\ln P \phi_i^{pure}$$

You know the W_S. / m. – Δg isothermal the what happens inside is immaterial this is a 250^0 this is a 250^0 all I want to do is to calculate how much work I have to do to separate air into oxygen and nitrogen in then gaseous mixtures, so all I have to do is to calculate according to thermodynamics – Δg you can make this if you like n. usually m is used mass make this m dot /m for 1m /hour /s flowing through I want to calculate the rated which work has to be because this is very simple so Δg is simply g.

Of nitrogen or μ nitrogen sorry we will nitrogen as a component this will be component 2 so it is – of x_1 μ_1 + x_2 μ_2 – μ air sorry this is x1 μ1 pure these are the products this is pure – x_1 μ_1 + x_2 μ_2 this is g before in this case it is – Δg this is not Δg of mixing this Δg for the process so this is equal to if you like Δg mixing beaks this is Δg separation which is – of Δg mixing this according to the equations the models we have this is gas phase so let me write gas phase models only one model for the gas phase.

Or μi saturation at temperature T okay I wrote it as not saturation I do not need μi0 sorry μi0 of T + RT ln Py_1 times Ø1 or yi and μi pure again μi0 + R_T ln P into Ø pure μ0 is the chemical potential of pure I at the temperature of the mixture to find the atmosphere pressure so normally this is written at one atmosphere and therefore P has to be an atmospheric units otherwise you will get the numbers wrong because you taking log P this is actually Log P / 1 which corresponds to 1 atmosphere pressure.

At which μ0 is recant so if we use millimeters here you will be off by a large number we have to be careful, so this difference therefore Δg mix or W_S./m.

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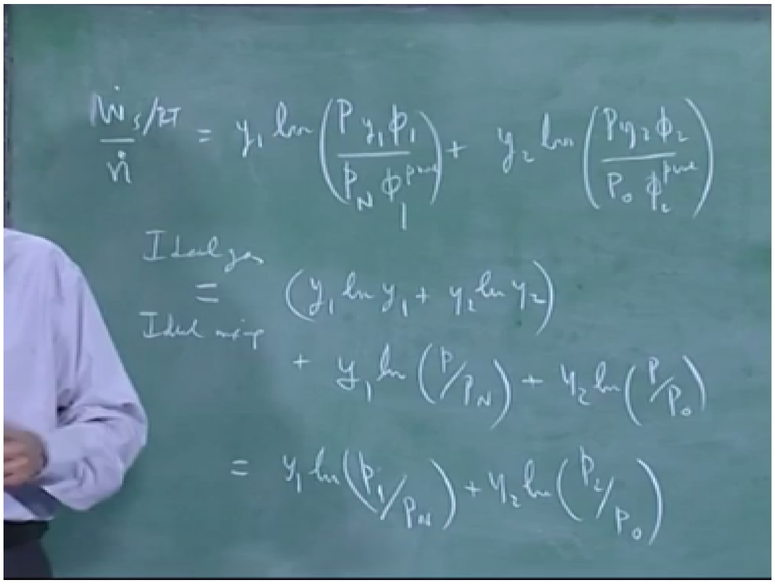

$$\frac{\dot{W}_s/RT}{\dot{n}} = y_1 \ln\left(\frac{P y_1 \phi_1}{P_N \phi_1^{pure}}\right) + y_2 \ln\left(\frac{P y_2 \phi_2}{P_o \phi_2^{pure}}\right)$$

Ideal gas = Ideal mix

$$= (y_1 \ln y_1 + y_2 \ln y_2) + y_1 \ln(P/P_N) + y_2 \ln(P/P_o)$$

$$= y_1 \ln(P_1/P_N) + y_2 \ln(P_2/P_o)$$

/ m. = R_T into difference between these two log in the mixture it is pressure P in the mixture composition is y_1 P_1 / pressure if you complete talking component 1 component 1 is at pressure P_1 into $ϕ_1$ pure and mixed have another x_1 in front sorry we will divide WS./R_T we will take R_T to the side this is x_1 as this is y_1 now sorry + y_2 log Py_2 $ϕ_2$ / ϕ oxygen $ϕ_2$ here the simplest case is S if you assume ideal gas and ideal mixing if you assume ideal gas ϕ1 pure and $ϕ_2$ pure are 1 and ideal mixing means ϕ1 = ϕ pure that is all so equal to.

So the ϕ will cancel and you have y_1 log y_1 + y_2 log y_2 + also written slightly differently than this as p1 p into y1 in this the partial pressure of 1 in the mixture p_2 is partial pressure of 2 in the mixture notice that work is exactly 0 if p1 – pn and P_2 = Po that means if this is at the partial pressure that nitrogen exacts here, and this is at the partial pressure that oxygen exacts here you do not need any work of separation all you need to do is to find this magic membrane through which, you get oxygen on one side and this is what you do in.

Regular reverse or masses where you separate solute in the solvent but in this case right now I will discuss that case in a minute, you have now work done at all but you actually want this usually at P, so normally you get everything at one atmosphere for at the same pressure and normally Pn = Po = P in which case your work done.

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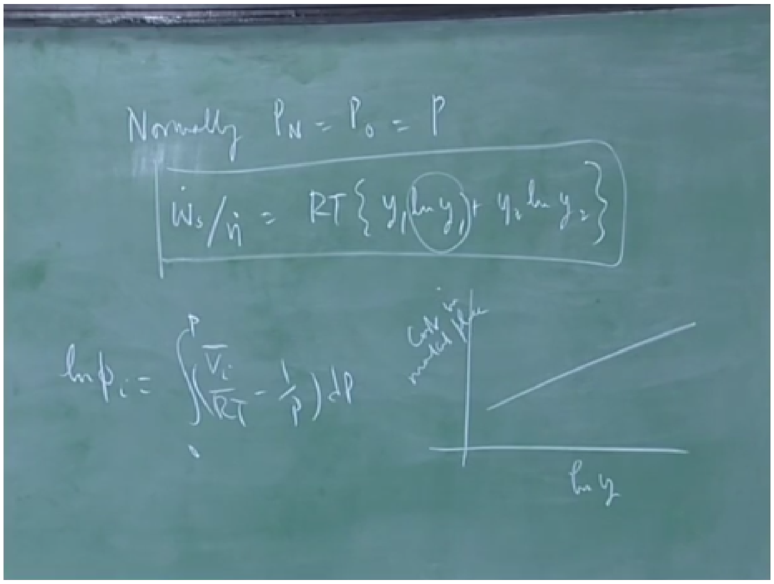

Normally $P_N = P_0 = P$

$$\boxed{\dot{W}_s/\dot{n} = RT\{y_1 \ln y_1 + y_2 \ln y_2\}}$$

$$\ln \phi_i = \int_0^P \left(\frac{\bar{V}_i}{RT} - \frac{1}{P}\right) dP$$

W_S./ m. is simply R_T times y_1 log y_1 + y_2 log y_2 because of pressures if there is non- ideality you have to make these corrections but you can calculate them quite easily you know if you want to calculate non-ideal corrections you know log ϕi is simply in ∫ Vi bar / RT – 1 /P BP from 0 to P you have to take experimental data on V_1 bar Vi bar I ∫ only you get ϕi, so you can through in the ϕi and the ϕi pure for ϕ pure is simply put Vi bar = specific volume of I so we need a fare amount of experimental data.

But these are available for gases not a problem very often in spite of non-ideality ϕ1 and ϕ pure are the same because your Vi bar and Vi specific volume Vi pure are really the same in gaseous systems, so the non=ideality here usually cancels out so this is a pretty good estimate of the work quite so that in al, gaseous substances if you plot log y1 against the cost in the market place across this is the amount of work I put it so if you plot the actual cost which is the plot that I indicated to you.

If you put mark cost in mark place I think I showed you a slide in the very first lecture cost in market place places log y1 log y which is log of the mole fraction as it occurs in nature usually get a straight line for various substances, we will get an exact straight line in the case of gases even the case of liquids it is proportional to this, so you can take this data from chemical age of India I do not know if you look at trade journals so worth you are while looking at you will give you some idea.

Next to where the emphasis in the chemical enwinding market place so this take this cost in the market place plot the gains that mole fraction which this substance occurs natural you get a straight line track that US market you get a perfect straight line in the Indian market you would have few aberrations, petrol for example is much higher than it will be here because that is because it is a additional taxation of the government uria in order to place the farmer they give it to him very cheap.

So uria will be somewhere here sugar will be somewhere here so the cost except for those irrational things where there is market intervention by the government presumably I think they were all introduced with good reasons, but now they are going one by one because of that you have a artificial price difference but otherwise 90% other things it will be perfectly in the international market Europe was it is much more even more rational even here in India also the changes are only in about 34 substances.

Where the exercise duty is in other things are artificially either increased or substitutes and nice plot is given in jet something, so first point about separation work is this is the cost get to give some idea you can look at numbers notice that WS./m. will come out to be negative which means the work is done on the system our convention is work done by the system is positive, so you have to do work that separate air into oxygen nitrogen okay let me discuss the non-ideality part of it.

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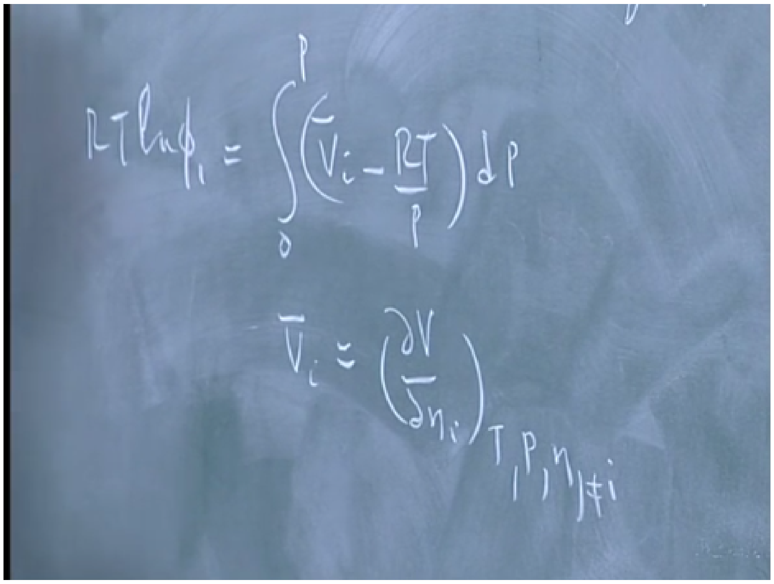

$$RT\ln\phi_i = \int_0^P \left(\bar{V}_i - \frac{RT}{P}\right) dP$$

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

In gas base basically all known ideality corrections have to do with calculating this integral Vi bar – RT /P dP okay this is RT ln ϕi so all you need is Vi bar if you look at Vi bar by definition partial of V with respect ni holding TP all other mole numbers constant, so all you need in the expression for V and you do the differentiation, so what I need is equations or state.

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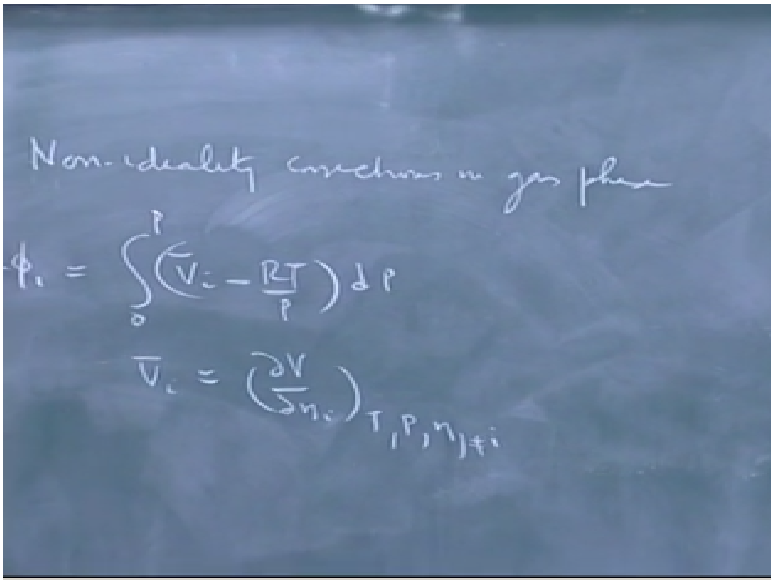

Non-ideality corrections in gas phase

$$\phi_i = \int_0^P \left(\bar{V}_i - \frac{RT}{P}\right) dP$$

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

I will tell you the equation of state that I expect you to know one of the problems with equations or state is that we are all usually implicit in the volume that means you will get multiple roots we have to find the correct root and then do this differentiate so normally you do it numerically.

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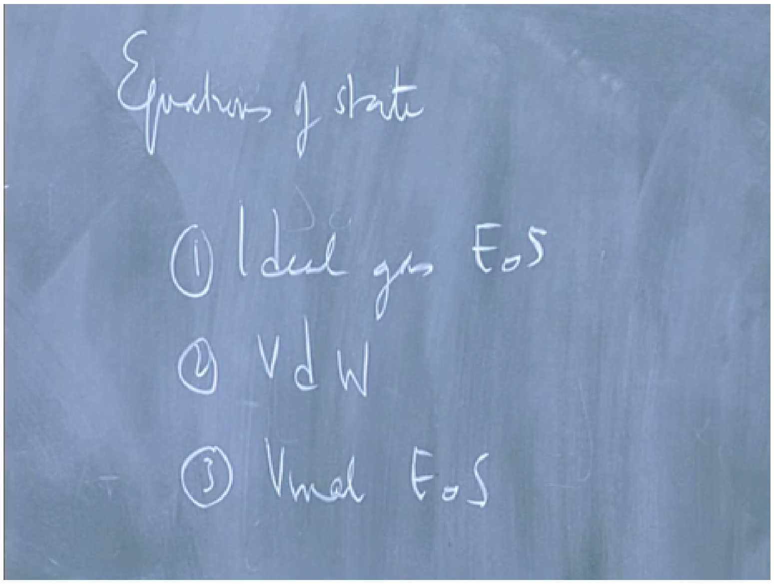

Equations of state

① Ideal gas EoS
② VdW
③ Virial EoS

But let me explain the equation state that you should in of course ideal gas law ideal gas equation state second for simply the historical record you have to know the Van der waals equational state third you have to know virial equation state I will discuss this little more this is the only equation of state that can be derived regress from theory if you are looking at molecules you are looking at inter molecular potentials and depending on different intermolecular potentials so you will get different equations of state.

So in principles there is one intermolecular potential that will give you each equation of state ideal gas comes from $\phi = 0$ the intermolecular potential being 0 it is not clear what the Van der waals comes from there is no simple you can get Van der waals like expressions from many potentials but the exact form of the Van der waals equation does not come out from theory virial equation of state comes out very nicely because this is a really a density expansion and this was originally due to a person called Kammerling owners I think I told you about kammerling owners then theory.

It is due to mayor and mayor this is the husband and wife team oh derived this actually it was derived even before but mayor and mayor give exact expressions in from statistical mechanics for the virial coefficients this is very important equation purely from a theoretical point of view when I say Van der waals here you must add here RK RK this is K for kwang I think this is for kister equation of state and then the other sets and you have to know this multi parametric equations of state.

Thing we use the BT equation in adsorption isotherms and I put down one uses have to know at least one so I will choose 1 wall as all these things and wall as this integration also we will give expression for ϕ for each equation of state all this has been done then you will have a set of equation substrate which are really interpolative based on we have to introduce in other word it is acentric factor what you do is you ask what is the cause of non ideality in the Cos of non-ideality in the molecular terms.

And this is not necessarily this pictures this thing was derived and classical thermodynamics but it basically has to do with the concept that the center of force and the center of mass do not coincide if I have two molecules at interact I can take the line joining the centers of mass but there is also a line of force if I take even a simply molecule like carbon dioxide I have carbon and oxygen in the bigger than carbon so I am trying it little bigger O and O now if I have two carbon dioxide.

Molecules the total interaction between two molecules is between the carbon oxygen and so on and oxygen you take a average of all these and find out how the interaction occurs the center of mass may be write in the middle here, but the center of force need not be located there because the force between oxygen and oxygen may be much larger than the force between carbon and oxygen so on, so that can be at distortion so the question is in fact it is better for me take carbon monoxide.

Because carbon dioxide is quite symmetric if I take carbon monoxide then you can see that the center of mass will be shifted towards oxygen but the carbon, carbon interaction may be stronger than the oxygen and interaction in which cases center of force we will shifted towards the carbon atom there will be a separation between these two when there is a separation you get eccentricity non centric forces if you get a eccentricity it leads in the non ideal behavior so which are defined in a centric factor he actually defined in classical thermodynamics I will tell you how it is defined and what he said was eccentricity factors typically vary from 0 to 0.5 so he said find of fluid for which it is 0.5 find a fluid for which it is 0 and then do an interpolative calculation for all other fluids that is what we will do.

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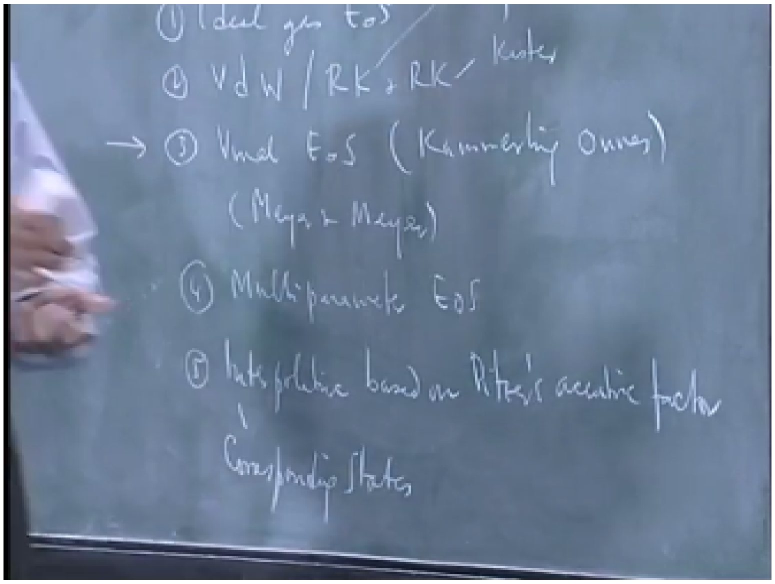

These all derived interpolative once are derived from the principle of corresponding states, so I will do is discuss equations state a little more today and I will start with the discussion of corresponding states so very appealing idea you, I think you already know about the simple principle of corresponding states it was again in the first idea was due to van der waals, let us start with the.

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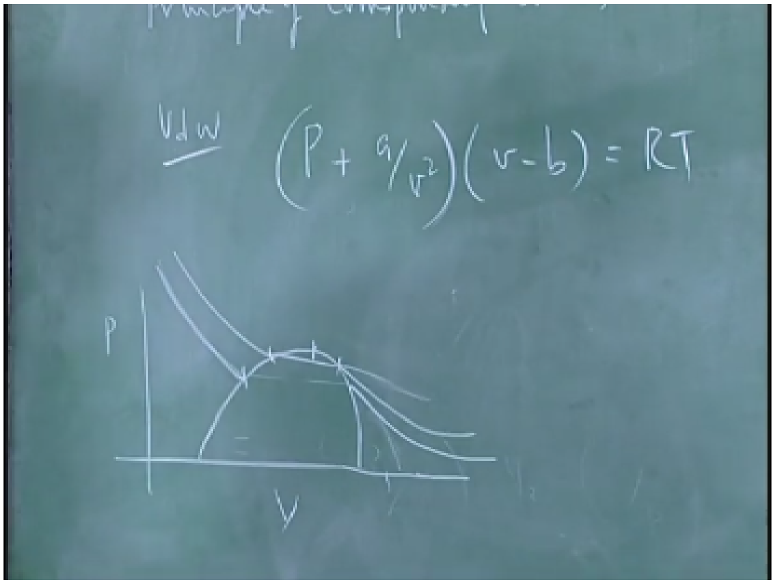

So I will talk about the principle of corresponding states, it is much more general than let us start with Van Der Waals you look at $(P+a/v^2)$ if you look at these plots I can do it on the PV diagram if you like I am distracting the scale is the isothermal towards this end will go like finally at very low pressure PV=constant so the isothermal will go like a rectangular hyperbola. So this part is a rectangular hyperbola and this can be steep is actually steep because liquids are incompressible.

But the point as there if you go up towards a critical point these roots come closer and closer till they finally go inside here, this equation is cubic if I rearrange this equation.

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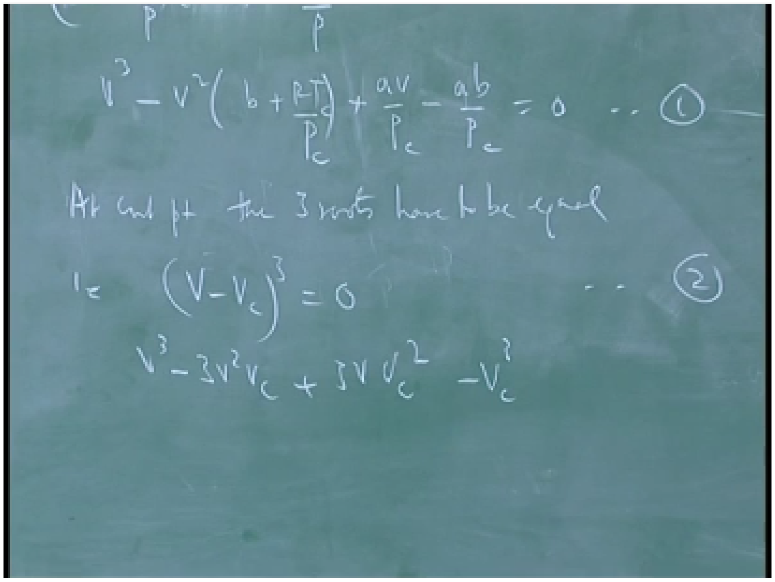

$$V^3 - V^2\left(b + \frac{RT_c}{P_c}\right) + \frac{aV}{P_c} - \frac{ab}{P_c} = 0 \quad .. ①$$

At crit pt the 3 roots have to be equal

$$\text{ie} \quad (V-V_c)^3 = 0 \quad .. ②$$

$$V^3 - 3V^2V_c + 3VV_c^2 - V_c^3$$

I get $(Pv^2+a)(v-b)=RTxv^2$ if you multiply this out let me divide through by P I am looking at the polynomial expression for you get v^3+v^2 into there is a $-b$ here, that is so I can write this as $-b+RT/P$, $-av/P=0$ so I have got v^3 ab/P sorry, there is a constant term, $-ab/P=0$ this is $+ab/P$ this is a cubic equation this three roots what the experimental diagram tells you is two roots are real below the critical point at the critical point all the roots go inside so you will get if two roots are real and a cubic the third root is also real but it is unphysical it is not realizable in the lab.

So you get three roots at critical point actually let me say this yeah at critical point the three roots are equal that means at critical point I can write this as Tc Pc=0 because the roots are equal this equation should also be, you should be able to write it as $(v-v_c)^3=0$. So this is 1 if you like and this is 2, and these two represents the same polynomial you should be able to equate the coefficients so I get $v^3-v_c^3-3vv_c$ x $v-v_c$ and – or + I think this is correct, this is correct.

So therefore if you have two parameters Van Der Waals argued that you should be able to find the parameters by making a comparison between these equations, so if you look at the comparison you get three v_c is $b+RT_c$.

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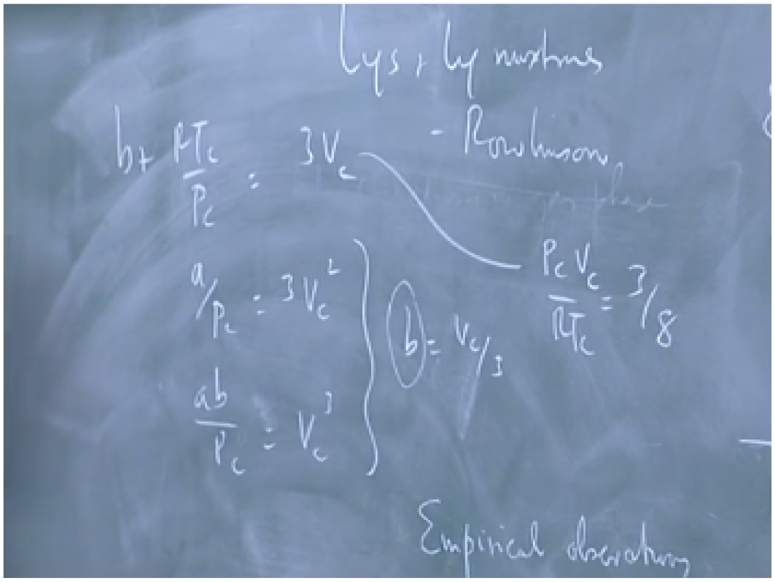

$b+RT_c/P_c=3vc$ it is one equation, another equation is $a/P_c=3v_c^2$ in the last one is $ab/P_c=v_c^3$ so these two implies that b=vc/3. If you look at experimental data on liquid there is a nice book that you should look at suchly a graduate level book it is called liquid zinc liquid mixtures this is the Rowlinson. I think now it is Rowlinson and somebody the original version we have several editions, the first edition was by Rowlinson and he wrote it, he was in imperial college that book has stable of data for several substances if you look at the critical that and look at the volume specific volume at the triple point it is almost always 1/3th the wall critical volume.

They give you both they will give the critical volume, they will give you the volume of the specific volume of the liquid at the triple point, the exception is oxygen unfortunately it one of the first ones it come, because of para magnetism oxygen alone has a very wide range of liquid behavior so you will find otherwise you will find and almost all other cases this is true. The other empirical observations are like this about generalization I mean there will be exceptions, but if you want to generalize something empirical observations v liquid is approximately constant so we will v triple point I will say vt is a specific volume at the triple point of the liquid is approximately vc/3.

Then the absolute temperature at the boiling point is approximately 0.7 times Tc which is why a large amount of data see the boiling point normal boiling point this is normal boiling point, normal means at a total pressure 1 bar how an atmosphere the data is at one atmosphere. So very large amount of data this is the easiest to measure Tb is the easiest measure extensively available

Tc is somewhat difficult to measure because actually critical point measurements are done by looking at what is called critical opalescence.

You know the interface disappears and it is very difficult to experimentally observe and detected at exactly I mean to within 0.1 or point even 05° it is easy but to get exactly the critical point is very difficult. But this is a good thumb rule you can use Tb/0.7 and estimate critical temperature for engineering purposes in correlations we will need the critical temperature it is convenient to use that estimate if you do not have data.

Having said this so this was a b you remember Van Der Waals argued b was actually the volume occupied by molecules and liquid phase because he said in the liquid phase essentially you compress the molecules as much as can, so he said the free space available is v-b, so this estimate of b is a I mean this interpretation of b came in very handy Van Der Waals taught the head, heard a good equation state with him because a is simply $3P_cv_c^2$.

And then if you combine these here if it Pc vc/RTc=3/8 this is well known, this is vc/3 so Pcvc/ if we divide this by RTc/3 is equal to now +1 and I will work out it is 3/8, so any two parametric equation or state that is if you have a cubic equation state and many equation state are cubic and if you have only two parameters in it, it will give you both the parameters and terms of Pv vc and Tc.

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