Indian Institute of Technology Madras

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National Programme on Technology Enhanced Learning

CHEMICAL ENGINEERING THERMODYNAMICS
by
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Lecture 13

Models for the Excess Gibbs free energy

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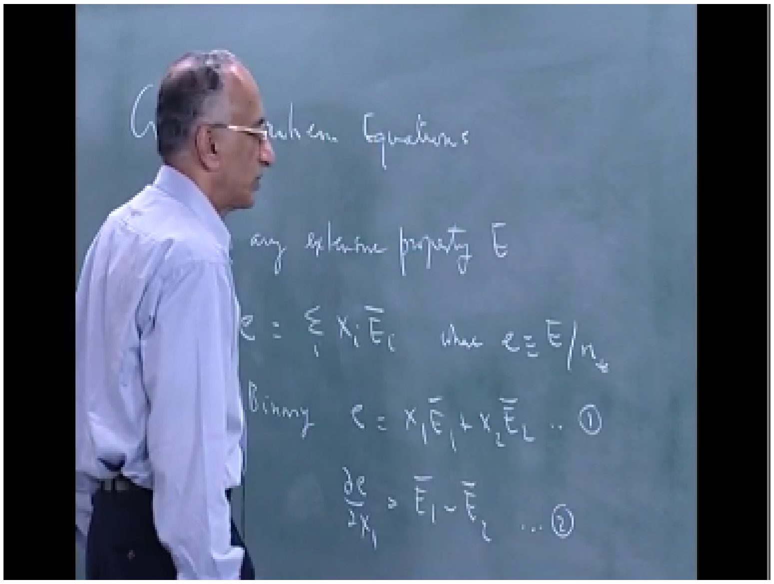

Primarily about day Gibbs Duhem equation this is actually applicable for any extensive property what we have seen is for any extensive property I will write everything in terms of specific properties where e is identically E/n by the total numbers of moles this is one equation the other equation says and say example binary we will discuss binary mixtures and then I will extend it to multi component mixtures e=x1 then we shown this is one and this is two.
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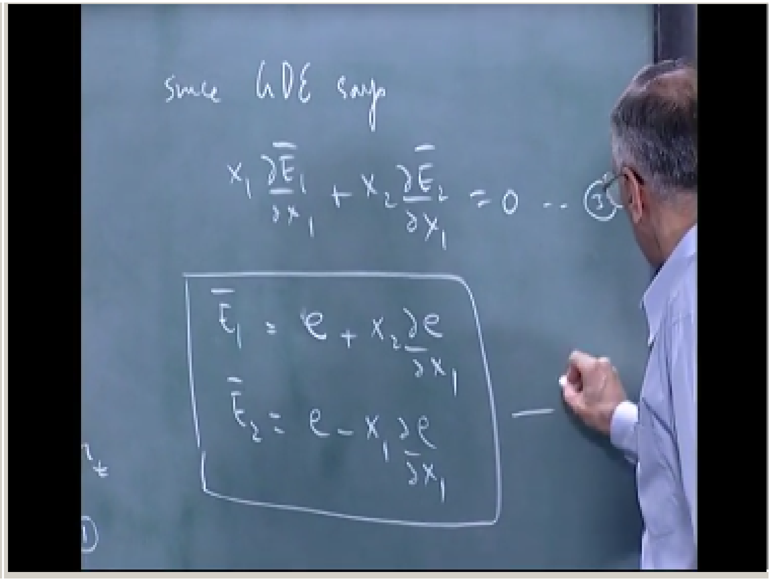

Since GDE says

$$x_1 \frac{\partial \bar{E}_1}{\partial x_1} + x_2 \frac{\partial \bar{E}_2}{\partial x_1} = 0 \quad \ldots \text{③}$$

$$\boxed{\begin{aligned} \bar{E}_1 &= e + x_2 \frac{\partial e}{\partial x_1} \\ \bar{E}_2 &= e - x_1 \frac{\partial e}{\partial x_1} \end{aligned}}$$

Since, Gibbs equation says two follows from three from differentiating one and using equation three so we have this simple result that I can solve equations one and two simultaneously for E1 and d2 so I have E1 =e+x2 ∂e/∂x1 then E2=e-x1∂e/∂x1 just switch one and two but differentiation with respect to two is same as differentiation with respect to 1e-1 so this is the set of this is the simplest way of solving for e1.e2 it has the advantage that because, this is one degree of freedom this as the advantage that this equation are symmetric you can simply module E and you do not have to module any one of the components so if you have a module for E then you automatically have these are general results these are very important.

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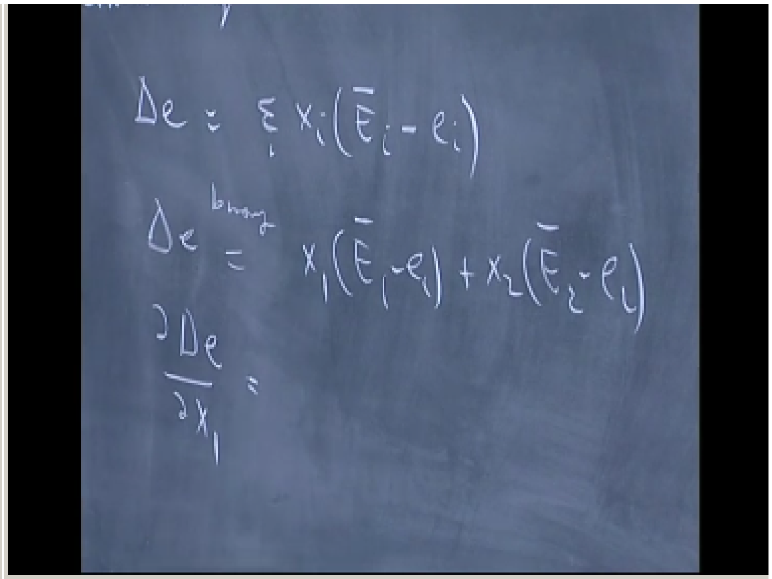

And in particular the most important affect the three quantities that are important I will e=g which is the most important thing g, h and v these two are measurable and this is important from a theoretical point of view you know that g with respect g/t with respect to t will give you-h/t^2 g with respect to p will give you v so the pressure depends in the temperature dependences are covered through measurements of h and v because enthalpy and volume are also extensive properties these conditions are satisfied so if I can measure enthalpy change for example actually.

I should have written this I wrote I think everything as we will make a small change here I should actually have written everything in terms of Δe this is what I did last time right I will just repeat it here I will say more conveniently because what I have written there is correct we write the same equations we write equations like this Δe=∑xi(Ei-ei) and you will get partial of ∂Δe/∂x1 I have to write it specifically for binary just I am repeating the whole thing for I do not know what to do about this chicken kunai I want to some cases in camps because, he is health officers.

And he said he watched doing it okay I will double check it otherwise why did not you tell the ward in charge also tell the wardens make sure some this thing is not fatal but apparently it causes near unbearable pain in the points for about 3,4 days okay we will come back to this I am rewriting all these equations so these are not new equations but these are equations written this will be 1` in terms of mixture properties so this is e1-e1-e2-e2 okay.

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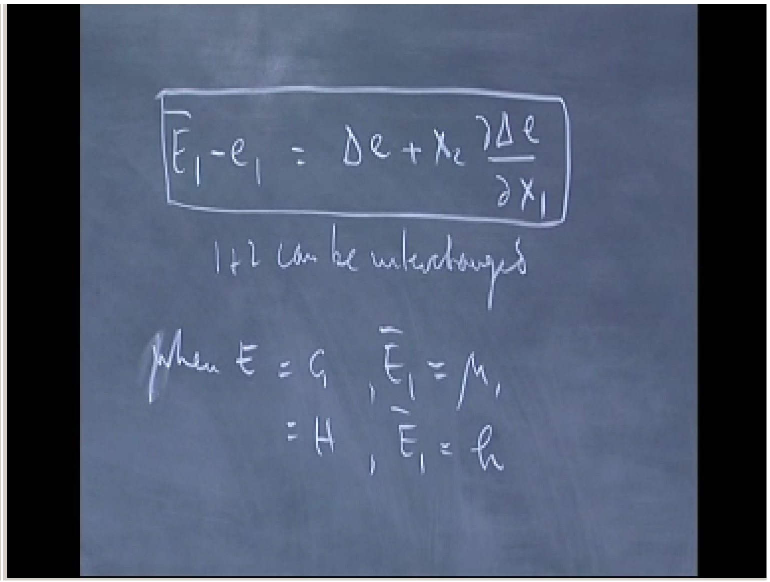

$$\boxed{\bar{E}_1 - e_1 = \Delta e + x_2 \frac{\partial \Delta e}{\partial x_1}}$$

1+2 can be interchanged

when $E = G$, $\bar{E}_1 = \mu_1$

$= H$, $\bar{E}_1 = h$

Then we have $E1-e1=\Delta e+x2\partial\Delta e/\partial x1$ and so on then 1+2 can be integers what you are looking for is this property here e1 because if you are doing phase equilibrium you have already shown in particular remember that g1 is same as $\mu 1$ so we have shown in phase equilibrium that $\mu 1\alpha=\mu 1\beta$, $\mu 2\alpha=\mu 2\beta$, phase equilibrium so if I know the chemical potential as a function of composition then I can do the phase equilibrium calculations so the purpose of this entire exercise is to get the composition depended of the chemical potential since it is more general then that the theory actually applies to all partial properties.

I am deriving it in general for obituary partial mall property I said three are of importance Δg because that will give you the chemical potential as a functional composition Δh, Δv because the governs temperature and the pressure dependents of the chemical properties and those are the measurable quantities these are not actually what is measurable is the change in- the volume off course specifically measurable so we have these equations so what we have when $E=g$ $E1=\mu 1$ and $E=h$ $E1=h1$ for others we do not have the name this is g1 which is identical with $\mu 1$ yeah because E after mixing is XiEi we integrate it the basic equations show that you remember otherwise I recall it for you here through this here.

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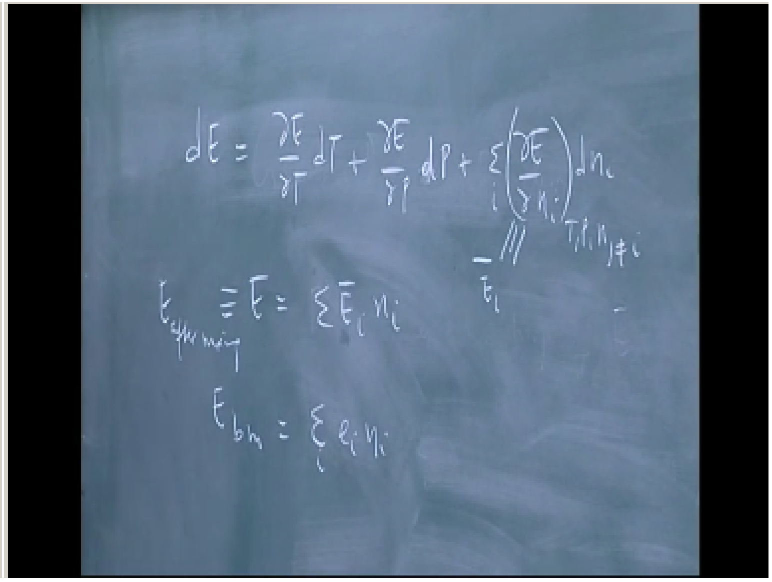

We did it for g the basic equation simply tell you this quantity holding TP in j_0=I is called DI it is the definition of partial molecule we integrated this at constant T and P but at obituary T and P the initial state was characterized by TP and some composition when we took this start experiment in which we expanded this system by a factor of k to calculated differences from that we got $E=\sum$ Ei ni for a property of a mixture it is not sufficient for you to know the specific property of pure I you have to know its value the per mole value in the mixture this is the function of composition.

This is also equal to E after mixing if I am considering a process this is identical with the E before mixing in some over ei ni this Ei is pure I I take n1 moles of 1 its value of E is e1 so I just add it all up so this is before mixing after mixing in the mixture the property changes from Ei so I want to understand the mixing process I have to know how to calculate Di that's the central thing in mixture theory because it was not done this way actual science progress by iteration by various things since this is 100, 75 years in solids this was done effect model.

In 1947 when people started doing this process and when it gives introduce passion properties as well so it is been refined over a period of time now we see it on perspective the way we look at it is simply to look at the process of mixing in which you can make measurements you can mix two components at constant T and P quantities you can measure are actually Δh and Δv you cannot measure Δg but so happens the Δg is the most important quantity because it governs facial liberal chemical equilibrium we have through equality of chemical potentials in energy so I have to look at Δg although it is not measurable Δh and Δv are measurable.

So I am looking at E before mixing and after mixing if I take the differences between these two you get Ni.Ei-e if I take per more mixture I get this equation I take x1 moles of 1 and x2 moles 2 and form one mole of the mixture so per mole of the mixture they change in the it is simply given by xi I am doing binary because primarily we will be dealing in this course with binaries and I will show you that the extension to multi compound system it is only algebraic complexity in practice though if you went to a refinery they will tell you, you guys are being theoretical the actual refinery as 21 components but all your is to do is extend this.

And hit the radian box in the head in computer you just have to hit it on the head it will give you spread of all the answers just simultaneously equations instead of solving two equations you will solve a n equations in an component system they are all absolutely trivial in principles this is all the rest but what we found from thermo dynamics also is that the equation for the chemical potential or E1 for that matter for any Ei you have n variables and only n-1 equations so there is one decrease of freedom thermodynamics cannot give you the decrease of freedom there is uncertain that comes from experiments only way to do it is try.

And measure do something experiment or emphasis you guess a model either modeling or experimentation for Δh, Δv you can get it from experiment if you can get it from experiment you do not do modeling when you are uncertain you do modeling you start telling about way mixtures occur classical thermodynamics does not provide you with any method for calculating this directly molecular thermodynamics gives you mechanism because there are molecules you can say this molecules is replaced by this molecules.

For example if I want to talk about mixing I will imagine a box full of molecules of type 1and I will bring a molecule far away from infinity molecule 2 to the middle of this mixture then I ask what is the configuration around this molecules what was the configuration before what is the difference in entropy I can do this calculations in a molecular theory as far as classical thermodynamics is consent and I am sampling guessing what Δe in the case of g in the case of H and V.

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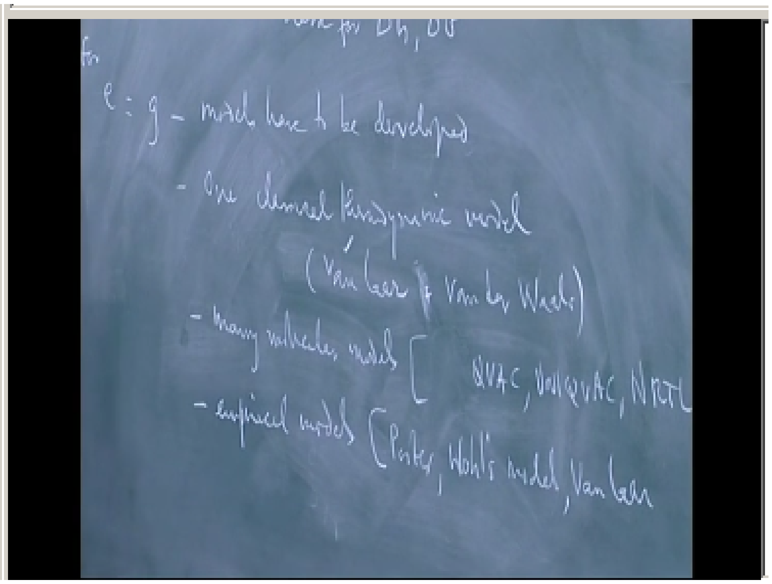

So I will say for E=h or v use experimental data for Δh, Δv for E=g modules here to be developed we have exactly one model one model in variations of that this was done in 1898 as I told you by van law read V as f the Germans do that much here I have heard only one law here and in the US so I have to check with some Dutchman and I will sing operatically vanderwalls and then any number of molecular models then empirical models you will have to know the wander model one thing it works very well and it is also beautifully derived I will derive it there you do not need any extraordinary concepts with the anguished concepts it is a really clever one I mean after it is derived you can say what is the big deal if you go back 1898 at look at the state of thermodynamic.

And ask for you could have guessed it and you said yes in a better we noble price if you are honest mostly probably you will say no would not practical molecular models there are many of them once you have to know in this course are all of these are actually a walk first like then unique quack then the model is called NRTL I should have mentioned Wilson these are the only once we put have no but these are the tested once the empirical models starts from what is called forties model is the whole series of models I will add one land again van law is actually derived of very good model it had only one parameter in it then people did not later people who came along used this equations without realizing.

There is only one parameter there were two parameters they are related to one method they did not realize it so they made it into two parameter model in the two parameter model is so successful that is fully established so we will use the empirical model of van law which is the same model as we derived here the people forgot how it was derived this kind of things happened all the time then finally there is a model by Dolts it should come under theoretical models I will law here van law one classical model suppose I should say also say this comes under slightly different it comes under what is called chemical theory of solutions all of these come under.

So called physical theories that means these theories for mixtures are derived without assuming any chemical reactions those are like said all mixtures are ideal except you are looking at the wrong species so therefore it is chemical theory it assumes it partial chemical reactions that actually occur in mixtures as a result of which if you mix A and B you do not get a mixture of A and B but, you get an ideal mixture of A to B and AB3 if you like some combinations it postulates there are reactions that takes place in solutions in the final mixture if you looked at the right component it is imply ideal.

But all others are physical theories there are some evidence for chemical theory, chemical theory is now used in all cases where there is clear associations salvation we have mixtures where the components in solution form diverse or for example HF in mixture always seems to exist effect 6F6 if you take that in account and does form ideal mixtures rather substances similarly you have salvation where solution molecule is surrounded by the solvent molecules because of high interaction so if you take that complex as one entity then you have an ideal so these are very special cases other than that these are the models I will just say a few words about these acronyms this is actually called quasi chemical theory is called quasi chemical theory.

Because the form of the final result looks like the result you would have got have you assumed chemicals reaction it is sort of recalls theory but, there is no chemical reactions postulated yet reaction postulated is of this form I mean postulated in the sense the final result ;looks like it in the sense that what is done by Google this is the big name here there is a serious of goodie name lectures goofier name this thing in Europe students, students all combined to form these lectures in the very prestigious anyway Google name suggested that if you take a flatus model for the you do not have to go to the molecular thermodynamics for this you simply imagine that 1 and 1 are neighbors.

And he says if you have a 1 and 1 then 2,2 in the mixture you are replacing this 1,1 burns by 1,2 and 2,1 bonds the 2,2 and the 1,1 are breaking up and you are forming 1 2 simply did a counting on that and assumed that 11+22=2(12) if you imagine the reaction of this kind where you go from a 1,1 pair and a 2,2 pair and 2, 1 pair then you try to chemically equilibrium equation which tells you the number of 12 pairs by the number of 1,1 pairs times 2,2 pairs is equal to constant that is the equation that comes out on the theory and therefore the theory is called quasi chemical theory this is called the universal quasi chemical theory this was derived by sprouts nets.

So I will write the names down it is probably 75 and he is weekly even now NRTL is again due to nets but the name associated with okay I will tell you for unit quake the name associated with Abrahams for NRTL it is sprouts net and renown Wilson is due to Wilson so he generalized this theory again made a mistake ended with two independent parameter that co-related data so well, that you cannot argue again against unique mean if you say should not be whose people laugh at then further correction are been made in fact we are ourselves are made the correction unlike there was a mistake but what is called the it is not yet widely used there is no point teaching at under graduate course is called it is essentially a self consistent theory NRTL is actually again I do not want to get you guys to get very skeptical NRTL is derived by a mistake by the resulting equation correlate data.

So well that people have accepted it again it is called non random to liquid theory there is a corresponding theory actually you must have mentioned that here apart from these there is a another whole list of theories that go by the name of corresponding states I will discuss that separately to this corresponding states theory due to and what from that theory this NRTL theory was derived I mean that is the bases I am going to discuss all these in the greater detail just gibing you general stories between but any way this is the this theory is a very successful theory for liquid mixtures.

So we will use it Wilson is a guy who started the whole concept of liquid mixtures theory of liquid mixtures actually it is very small paper in 1962 think it is in if I remember correctly in general of ACP and it is very small one page paper Wilson simply said may be I am jumping the done but let me say this a bit suppose you have 1,1 here you introduce a molecule of 2 here what is judged was for example this could be suppose you looked at a liquid mixture closely and locally you could take a look at let us say this is late us configuration I have one four neighbors arranged like this around centered molecule actual later configuration set different.

I am only insulating a point if I have cells like this inside the liquid then I have 50, 50 mixture of 1 and 2 all around all it see is neighbors are 1 and here it is 2 and I will show you the following physical result we have already seen this result you have seen that the work done in a process in a isothermal process at a constant temperature and pressure the work done is equal to –Δg we saw that for a open systems correspondingly this number the work done in bringing a molecule to 1 mole of 2 into for one molecule of 2 into a mixture of four molecules of 1.

And so on it is determined completely by the chemical potential μ2 I will show you that μ2 is change in the μ2 from the pure state gives you the work done in bringing this molecules 2 from ∞ to here that is the physical interpretation so this the work done in this mixture 50, 50 mixture is actually not dependent of the global composition but on the local composition so what Wilson said was you should not be talking of x2 but you should be talking of x21 that means the mole fraction of 2 in the neighborhood of 1 and that is what determines the work done and that is what determines Δg that is standard of whole space of theories called local composition.

And all these come under local composition tools this does not quite come under local composters derived before Wilsons theory but the unequaled and NRTL come under local configures all these so these three are called local composition theories I think that is all as far as these what I will do now I will derive the theory of van law, basically said I am interested in model for Δg I want the composition dependents of a free energy of mixing.

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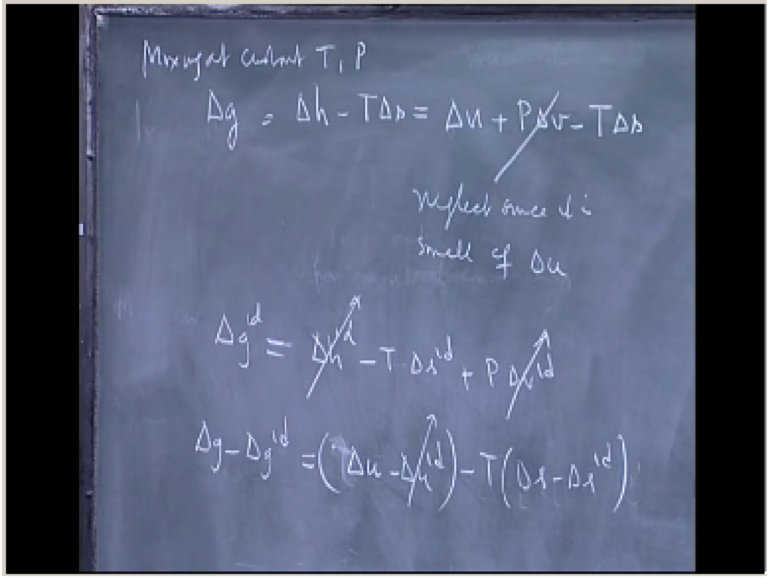

Mixing at constant T, P

$$\Delta g = \Delta h - T\Delta s = \Delta u + \cancel{P\Delta v} - T\Delta s$$

neglect since it is small cf Δu

$$\Delta g^{id} = \cancel{\Delta h^{id}} - T\Delta s^{id} + \cancel{P\Delta v^{id}}$$

$$\Delta g - \Delta g^{id} = (\Delta u - \cancel{\Delta h^{id}}) - T(\Delta s - \Delta s^{id})$$

This is clearly equal to $\Delta h\text{-}t\Delta$ we are doing mixing at constant TNP this is the process of interest and looking at $\Delta g = \Delta h\text{-}t\Delta s = \Delta e\text{-}p\Delta\text{-}t\Delta s$ constant T and P so Δt and Δp will not come in no change in temperature and pressure of these this is the argument you can make the change but this is the valid argument for a large number of mixture the change in Δv is so small that $p\Delta v$ is compared to Δe so I am going to neglect this because this is small this is reasonable assumption very rarely is Δv large enough for you to worry about so in assumption it is made very often then I said I am going to have an ideal mixture I already understand a ideal mixture I showed you that one solution to equation is logx but let us say I assume Δg ideal$=\Delta h\text{-}t\Delta d+p\Delta vd$.

But in the ideal mixture there is no change in volume there is no change in enthalpy I do not have to worry about those in ideal mixture you have the molecules that do not whose interactions are not different from in the mixture from the pure state so there is no change in enthalpy there is no change so this difference $\Delta g\text{-}\Delta g=\Delta u$ I will write $-\Delta u$ ideal but this is actually zero this is written identically as g excess similarly this will be written as u excess this is written as x excess super script p is for excess it means over and above the ideal case all theories the molecular theory or the classical theory.

So far we have a problem with finding both they either assume uxx is 0 or x access is 0 I must say one more modeled here in the molecular models there is one more model which is due to against model it is polemical solutions where he said the big difference is not in energy but it is arrangements so if you putting one polymer molecule here the polymer molecule is so large that has about 10,000 neighbors so your actual polymer concentration will be in parts per million but it will have a tremendous influence in property.

So it is of the dissipative so if you take the weight fraction the polymer will be very high but if you take mole fractions the polymer will be very low because the polymer molecular weight will be 100, 1000 the other molecular weight will be 10 so the factor of thousand or 10,000 so he was looking at special case of polymer solution and he derived the theory that is beautiful theory but it is one of the earliest as far as so Flory is another it is called Flory against theorem.

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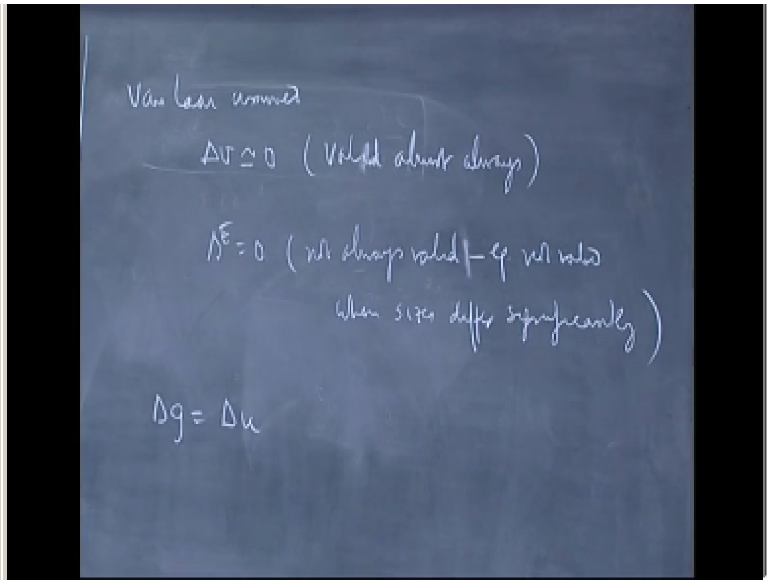

Van Laar assumed

$\Delta v \simeq 0$ (valid almost always)

$s^E = 0$ (not always valid – eg not valid
when sizes differ significantly)

$\Delta g = \Delta u$

But anyway coming back here all theories Flory for example said is effectively zero it is negotiable it is the entreaty change that is most important and in many other theory as shown that sx is 0 it means the mixing is ideal but the energy are important so van law for example said van laws assumption are the following assumed first Δv is approximately zero it is the very valid assumption I will say valid almost always then he assumed sx=0 this is not always valid certainly not valid for solutions of mixtures of substances that are very different in size but this is not dilute valid I will say for example not valid when size is differ significantly so he finally said therefore Δg=Δu you can relax among those assumptions not trivial but you can but now you are going back in 1898.

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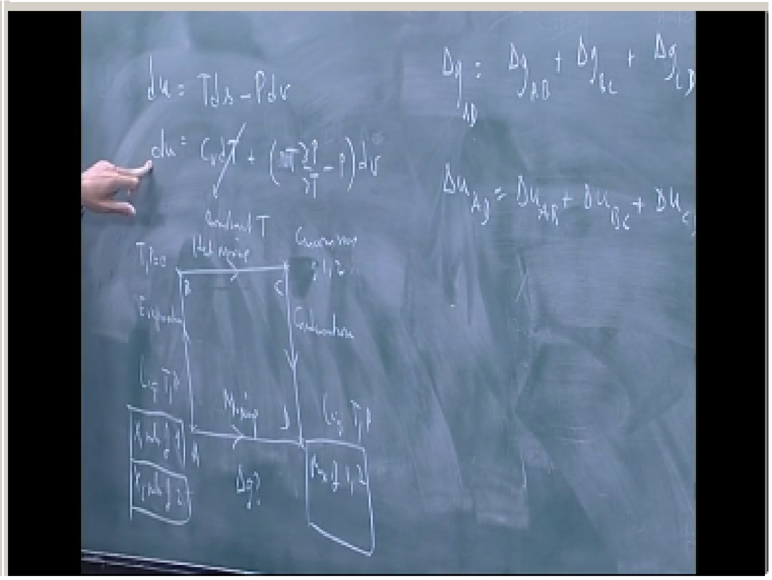

He went back to this equation, he did not do it with exactly like this also equal to CV it starts with this equation du talking of constant temperature process so this is zero so the real interest was in mixing of liquids that is of interest even now in thermodynamics in mixing of gases not much happens gases behave reasonably well less very high pressure so what van law did a very clever thing he said he wants to mix 1 and 2 let me say x1 moles of pure 1 and x2 moles of 2 separately in 2 boxes from here you have to go to mixture of composition x1 this is liquid this is also liquid and you want to know what is Δg? The progress we made is Δg is same as Δu but I do not know Δu here.

So I have not made much progress what he said was at this is at pressure Pv is also at same temperature and pressure I said we will go here t,p=0 this is the thought experiment so you just imagine that you evaporate completely 1 and 2 go to p=0 you have to be below the critical temperature actually for this you do not have I am sorry so you just go to p=0 then you mix the 2 this is so you produce a gaseous mixture of 1 and 2 then you can dense it so this is evaporation this is condensation so you are replacing mixing this is ideal mixing this is mixing so the process of mixing you replace by evaporation ideal mixing and condensation.

And you looking at the step by step if you look at this you want only Δu for each of them Δg for this is same as Δu, Δg for these three steps because G is function of state Δg does not matter if I calculate Δg from here to here or from here to here then I add this so this as BCD so first is Δg A to D $\Delta G=\Delta G_{AB}+\Delta G_{BC}+\Delta G_{CD}$ now you said you can replace this by $\Delta u_{AD=}\ \Delta U_{AB}+\Delta U_{BC}+\Delta U_{CD}$ actually he did not say this sorry this is Δu-Δs please correct this and we said because Δs for the real process he said was the same as the Δs for the ideal process the ideal process entropy is still have to take into account I think I am going to stop here.

And repeat what is said as I said a lot I will continue in the next class actually the calculation steps are fairly straight forward imagine first of all the quantity of interest is the chemical potential for all basic calculations for reaction equilibrium calculations because on the one hand for reaction equilibrium I am going to use the fact that g should be a minimum and g again I given by niμi so if I know μi as the function of composition and I can p-lay games of this so I want g to be a minimum I used the usual callus but I have to use it in terms of measurable quantity so I have to express g=niμi in terms of composition variable so I need chemical potential as a function of composition.

Now thermodynamics will give you the temperature dependency of the chemical potential through the enthalpy measurements it will give you the pressure dependences of the chemical potential through volume changes measurements but it cannot give you the composition depends except through equations as I told you constituent n-1 equations for n variables there is one degrees of freedom the way to deal with decrease of freedom is look at the mixing process and derive all the results in terms of change in G during mixing so that is all I have done instead of change in G I have looked in any extensive property.

Because in particular I am not only interested in changing n G I am also interested in change in enthalpy and volumes the change in G is given by as we derived those expressions and you know how to get that e1,e2 once I know the change in g I have to know change in G as a function of composition so that is all I am looking at what van law said was we do not understand liquid mixing it is too complex but we understand the ideal gas mixing so he will go from here evaporate this in order to evaporate this all he as to do is integrate this from p=0 if you integrate this you just write this ∂v/∂p dp and integrate it and if I have an equation of I can calculate all these parts and it is not ideal after that it is going on increasing the pressure it is going to be non ideal so you put in the van law equation.

And state for p do this differentiations and get this differences in particular you will get A/b^2 van law equation into v-b is constant sop when you do p with respect to t you will essentially end up here $a./v^2$ so if you integrate that you get directly a nice expression in terms of ways you will get Δu so to change in internal energy here is measured by the constant a11 for pure 1 in a22 it got two subscripts because in a mixture a changes then you do the ideal mixing there is only entropy change when you ideal mixing and calculate the entropy change separately.

So Δs ideal is known Δu =0 then I have to do this calculation for concentration again vanderwas equation had to be used is the mixture A and B are functions of composition and what function of composition you have to use I know how mixture of mixing occurs for example the size of the mixture here is treated as if it was one molecule or one su8bstance with certain parameters certain size and certain so here again already had mixing rules we will use those mixing rules and calculate the convection it will also come out in terms of way mix so the whole process this will give you this expression once I have Δg I can get $\mu 1 \mu 2$ by differentiation you have already written those equations.

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