Indian Institute of Technology Madras

NPTEL

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Thermodynamics and
the Chemical Industry

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Lecture 11

Refrigeration/ Thermodynamics
Of mixtures

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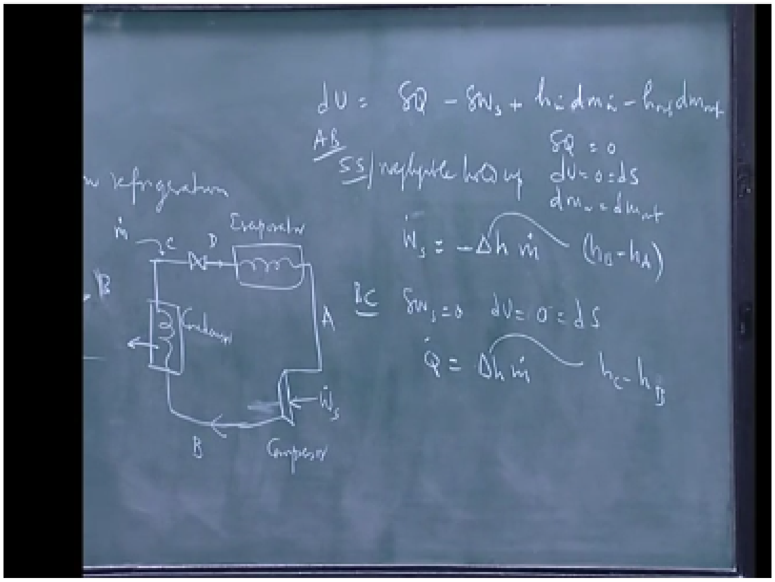

I have discussed let me finish this vapor compression refrigeration, and the PH diagram that is have already, basically the basic refrigeration system looks like this, there is a thoroughly one and this is an evaporator after the cooling occurs, you get vapor which is compressed, the compressed vapor again condensed there is fluid flowing at some rate m. looking at a steady state operation, the throughtling operate starts at C.

So this is CD and DA is the evaporation AB is the compression and BC is the condensation, you can hardly see the refrigerator at the back now days because everything is close these days but this let take this operation of compression, the compressor you can all see, at the back usually at the bottom. This compressor usually it is treated as an adiabatic compressor because there is no time for heat exchanger.

BC is the set of coils now days your refrigerator gets hot on the side and the back because you got all these coils it exchange the heat with the surroundings at the room temperature, Q condenser, it exchanges the heat till the material completely condenses the classical refrigerator a expansion, each of these are very easily analyzed. The basic equation all of these are treated as it is just a flow system and it is steady state you have du I will write the open system equations.

For each of these this is an open system du = Tds I am considering reversible operation right now – δ Ws + hn dmn, so if you looking at the evaporator either steady state if you are looking at steady state let us look at we will start with AB, it is either steady state or negligible. My system is the compressor the hold up in the system is negligible compared to the mass flowing through system.

Which means du and ds can be neglected, because u refers total internal energy of the open system, in the open system consist of mass inside the compressor. So this part, this become 0 and you have the compressor work δ Ws and for the negligible hold up first of all du is 0 ds is 0 dm in = dm out. And divide through by dt you get Ws. = h out – h in, so – δ m. δ h is of course B – A. This is hb – ha, then you can do the analysis for the condenser here.

Here no shaft work is done again you are looking at the steady state or you looking at the negligible hold up, so you are really looking at du and Ws. I think I should write this in term, Tds is not 0 I will write done the 1st part itself it is much easier, and it show you exactly where the 2nd law kicks in right now. In terms of the 1st law I have this is adiabatic operation now I have to add q = 0.

This part δ Ws is 0 AB and then BC δ Ws = 0, and again du = ds = 0, du = 0 and ds = 0. So you get δ h x m. is simply Q, Q. = δ h x m. and the δ h in this case is C – T, it si not C- T, it is C – D. hc – hb is negative so Q is actually, process CD I have δ Ws is 0, so is δ Q again you are looking at negligible holder, so dm in = dm out, the same thing.

So you have h in = h out or I will write in terms of hc = hd and the last step DA the evaporator is exactly like the condenser so you get Q. this is δ h it is – hd, this enthalpy is > this using simply evaporating the whole thing, it is completely vapor and then you are compressing the vapor. Let me write this here, if the operation is actually adiabatic notice this work done = δ h x m. is always valid.

Say the 1st law, if the process is isotropic you go along the line, if the process is not isotropic, the actual work done more than, this is work done on the system you have to do more work. So you will end up at some point B` and I do not know the path. You just draw the line you do not actually the reversible parts are always variable by depending upon the efficiency because work is the function of the path and I do not know the path beforehand depending on the condition of your compressor.

You will do more work and this actual work done will be always δ h this value here is δ h at constant entropy. So this is reversible work is this is the actual work, so the thermo dynamics status in this system will be different that is all, instead of B it will go to B` it will get, it will go to higher temperature therefore the higher enthalpy. The condenser and the evaporator effectively operated at the constant pressure thermo dynamically.

But if you are doing the design for an industry you will worry about pressure drop here, so basically what you have to do is design this condenser first for the heat that you expect and then the rest of it will design itself because you know the total heat load here / δ h will give you m. that determmi8nes free on refrigerator should circling inside, that is the seal system and normally this is operated just to little above atmospheric pressure.

Because you do not want air to leak in you will rather the fuel to leak out but this pressure is determined to really close to atmospheric pressure it may just below. This pressure is anything convenient for safety in. in case if it blows up, you make sure nobody gets injured to badly, so these two pressures then you look at the thermo dynamic charts to see which fluid would work between these two pressures and which as see this is the cooling you get.

That means pictorially you looked at the graph and tell which is the widest on the same scale, the one that has the widest liquid vapor envelope will be one which as the largest enthalpy change, this / this will give you the efficiency or the co efficient of the performance, the maximum cooling you get for the work done okay this is about the vapor compression refrigeration.

Another thing that I have to mention in the work cycles is the rank, have you done the rank and the other course, similar you must have done the TS diagram but you can trace the same thing on PH diagram, so I will skip rank cycle stuff.

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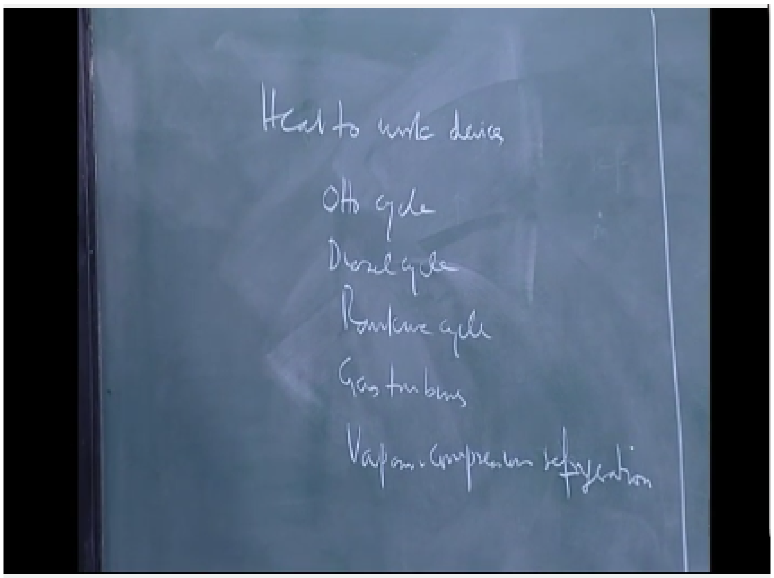

Heat to work devices

Otto cycle

Diesel cycle

Rankine cycle

Gas turbines

Vapor compression refrigeration

I will just summarize for heat to work devices, what do you need to know is that the ortho cycle the diesel cycle, then the rank hand cycle and the gas turbines. And then I expect you to, then the vapor compression refrigeration, I think going beyond that I have to go to mixture thermo dynamics because chemical engineering thermo dynamics really about multi component system.

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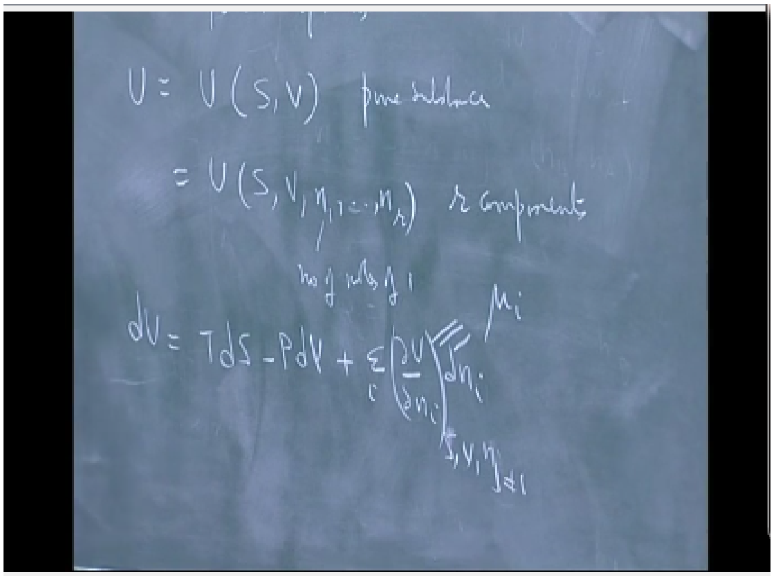

$U = U(S, V)$ pure substance

$= U(S, V, n_1, \ldots, n_r)$ r components

no of moles of 1

$$dU = TdS - PdV + \sum_i \underbrace{\left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_{j \neq i}}}_{} dn_i \quad \mu_i$$

So let me start discussing multi component systems, I write internal energy I know it is the property of state, so it has to be property it has to function of measurable variable. For example it U functional S V for pure substances, I told you the number of variables is determined experimentally you will come up face tool but there is empirical input applying the phase rule also = SV let say it is R component system.

R components n1 is the number of mole so 1 and so on, since it is property of state I can use calculus partial of u is with respect S holding V n1, n2 etc constant. Since all the moles are held constant and the volume it is an same partial of an pure substances, so you will get Tvs, partial of u with respect s is T. and the partial of u with respective V is – P + some over right. Holding S nj i.

It means all mole numbers other than ni, the reason I can use calculus is because I have asserted from two last U is the function state and the S is the function of state. This incidentally what I defined Mi, I have 4 equation of this kind because I have simply introduced, I will write them all down.

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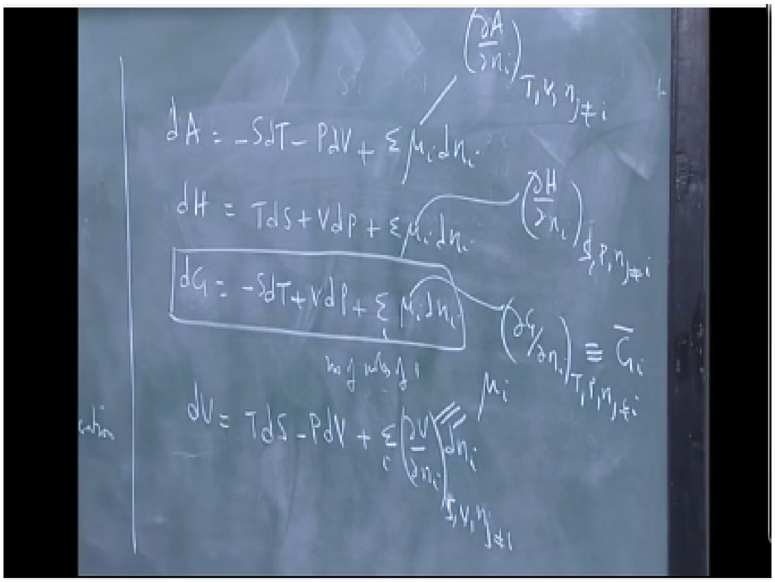

$$dA = -SdT - PdV + \sum \mu_i dn_i \qquad \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}}$$

$$dH = TdS + VdP + \sum \mu_i dn_i \qquad \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j\neq i}}$$

$$\boxed{dG = -SdT + VdP + \sum \mu_i dn_i} \qquad \left(\partial G/\partial n_i\right)_{T,P,n_{j\neq i}} \equiv \bar{G}_i$$

no of moles of i

$$dU = TdS - PdV + \sum_i \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} dn_i \qquad \mu_i$$

DA A is still U – TS, so we will get – Sdt, - Pdv μi partial of A with respect to ni, so only difference is the variables that are held constant and T, V, n are not equal. If you differentiate holding S, V and ≠ i, if you differentiate u you get the chemical potential, you get the same chemical potential, because A is still U – TS, so d H u + Pv , so this is Tds + Vdp + μi dni. This is h with respect to ni again, S T ≠ i, this last partial g with respect to any extent variable with the respect to the number of moles.

Holding T and P and other mole numbers constant keeps coming again and again it is called a partial mole property. Turns out to be very important because ideally what would like, you will have a mixture property what you would like to is simply x i/ property and add you should get the answer. It happens exactly that way provided partial properties and not other property. So for example from this, I am going to integrate this equation for convince exactly as I did in the pure state.

If I integrate this I will show you G is simply μi, some over mi that means if I know the chemical potential in the mixture of component i, I can simply add it up and get the answer, but μi in the mixture is not evenly pure. In the pure state chemical potential is different from the chemical potential in the mixture because the environment is different you are talking about molecules, energy and entropic properties.

If you have a mixture I have more rearrangement possibilities for the entropy is higher the energy is different because the inter molecular force is set different between like and unlike molecules. So I am going to this integration, what we will show is.

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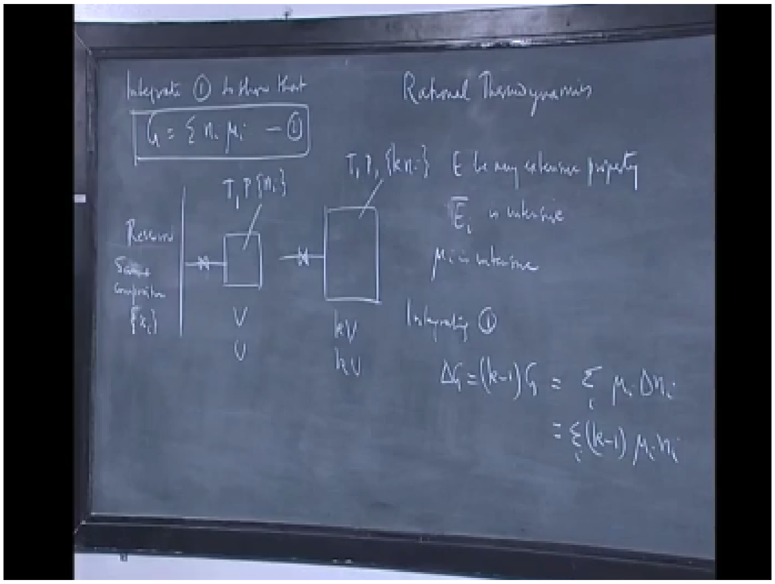

Integrate ① to show that

$$\boxed{G = \sum n_i \mu_i \quad - ①}$$

Rational Thermodynamics

E be any extensive property

$\bar{E}_i$ is intensive

μ_i is intensive

Integrating ①

$$\Delta G = (k-1)G = \sum_i \mu_i \Delta n_i$$

$$= \sum_i (k-1)\mu_i n_i$$

Show that V = I forgot this so integrate I will call this equation 1 the results can be derive from any one of these but g is the most convenient for chemical so I will use this, the arguments are identical. Integrate 1 we will show g is ni μi show that trivial thing but it is conceptually very important then of course like the almost fundamental thing done by Gibbs. During his 10 years of meditation apparently nobody ever met him he did not bother he just walked in did thermodynamics went back.

And then wrote a 150 page book he wrote 3 such books and all of which are absolute classics, is not a single conception error of any of the books, this is a after 100 years little over 100 years. What you have is a system with the number of moles ni and I put a bracket. I have the system in the final state k times larger, I have a reserve wire that is connected to, properties here do not change at all it has 10^{6ni} or whatever it is.

Same composition that means I have xi the mole fraction, this is automatically 1 – r the last one is determined, same composition but infinite amount of fluid P = 0, this is in state T this is also state T, P K times larger all extensive properties for k times larger here. so if I have the volume

Sv the volume will be k times v, any property if you take internal k times it is just the larger system is one.

Now I make an assertion that g with respect to ni, doing two extensive variables and I make the assumption that g is the number of moles so partial of g with respect to ni is an intensive variable, it is actually an assertion in thermodynamics, you do not need a separate law if you this is whole theory of homogeneous functions which this can be shown as correct result.

This is done I do not know whether you have seen this book, there is a book called rational thermo dynamic, it is typical of the author truce dell passed away recently, cllifer truce dell was a great thermo dynamics. He said thermo dynamics is guys are loose and the normal lecture they have to do things correctly. So he uses fairly regress mathematical language to describe thermo dynamics.

He called this thermo dynamics a rational implying everybody as well as rational and in rational thermo dynamics he will show what happens if it is not a homogeneous function like when g is not a homogeneous so on. So fundamentally Δ g / Δ ni because this is property per mole, this is assumed to be a intensive variable, it does not depend on the extent of the system. So the assert here all the incentive properties let say let E be any extensive property increases it size.

Then E I bar is intensive, E I bar is E per mole, specific properties are also intensive if I if small e because it is per morn, but E I bar is thing in question, so G I bar or μi is intensive, if it is intensive then for this process you can take this equation apply for the open system, the change in the number of moles, so I want to integrate it at constant T and P. so this is 0, μi is constant because it is composition remains constant. If μi constant what you have to do is integrate this g = μi = ni.

Actually you will get integrating 1 you get Δ G = K – 1 G because this system is simply k times larger than that, this is = on the right hand side and I get some more I, μi times Δ ni which is = k -1 times μi ni. Since k is not identically 1 you can cancel it off, you will get this result. It crucially depends on the fact on the μi is an intensive variable. That one other thing about this nano technology that they are taking about no big deal.

It is just suddenly the nano has become very fashionable molecular scale measured in Armstrong and I do not know whether you know it started with fin men lecture, typically plenty with the bottom. What he meant was lot of space and you can rearrange the molecules and so on but it is quiet an interesting lecture you should read that independently but nano has become a buzz word but the fact is in small systems if you are talking systems, nano systems kind of dimension.

You are not talking about system with very large number of molecules then you are talking about a very small number of molecules all of these must remember classical thermodynamics does not depend on molecule structure but it assumes that the average property vary continuously. That means very large number of molecules so that if you have density variation so you are actually adding or subtracting molecules in change in the density.

But the number of molecules added or subtracted you can treat the whole thing in calculus if you 10 and take away 1 then the change is too much you cannot use calculus. So in nano system the total number molecules is property fluctuations are larger than the property itself, and in such system for example the chemical potential need to be an intensive variable at all it will depend on the number of the molecules in the system.
In that sense it is not an intensive variable but for our purpose we will resolve this thing will never treat less than 10^{-13} so you do not have to worry, it is very hard for you to deal with less. Now if you take a drop and you are already talking of 10, so k will cancel you write G = ni μi. You might say I did the integration for 1 process but notice the final result as only the variables that belong to the initial state and initial state is entirely arbitrary.

The process is described in parameter k I have chosen a particular process but the result is independent as a process, once k is cancelled out the result is independent to the process, result is applicable to initial state which could be arbitrary. I am full of bugging arguments of this kind, so you will get a result and then you will use it everywhere then you will get all your answer, if you have nagging doubt did I do that right.

This is what Gibbs is book of full single experiment he did everything sitting at his table, so this result is very important it is central to mixture thermo dynamics and typically having done that. I have integrated now I would like differentiated you think a kid playing.

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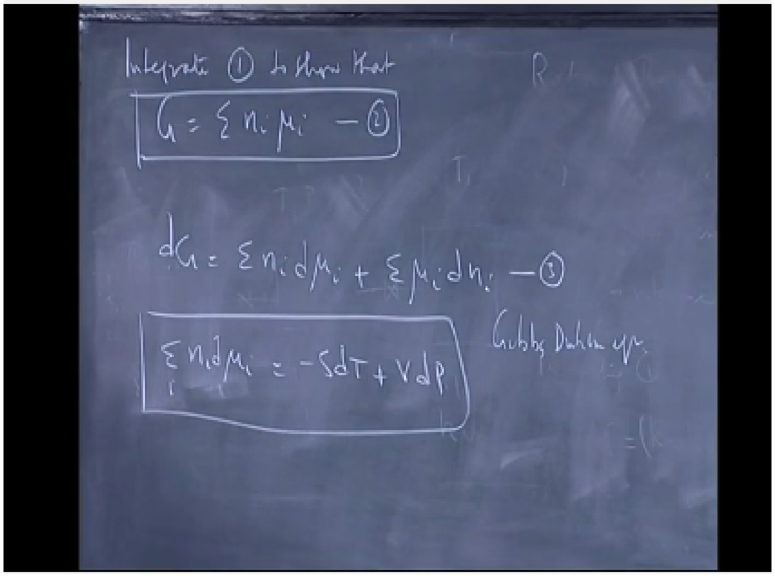

Integrate ① to show that

$$\boxed{G = \sum n_i \mu_i \quad - ②}$$

$$dG = \sum n_i d\mu_i + \sum \mu_i dn_i \quad - ③$$

$$\boxed{\sum_i n_i d\mu_i = -SdT + Vdp}$$

Gibbs Duhem eqn

Differentiate this you get dg = μi right. Then I insist if I differentiate I should get this same answer as before, so I have to compare 3 with 1 and declare the 2 and the 1 are same. If I declare both 1 and same I get ni dμi – St + Vdp, this is the other central equation in thermodynamics, it is called Gibbs equation, I will stop here, this is again very central to mixture thermo dynamics I will put it another form that we actually use. When I did the integration I used a physical input that μi intensive variable, therefore I was able to write this form. Now I do calculation and come up with this you might say where did this come from?

It comes from the fact the μ1 variable should be described by the temperature pressure and R – 1 intensive variables right, if I use composition I would used pressure x1, x2 Xr – 1. So mole fraction satisfy the condition that sum over dxi = 0, looks a little more ugly but it is the same thing. Some over ni, = something. It is entirely dxi =0, so any set of intensive used to describe the system independent variables will be only R – 1.

The R intensive describes composition it is differential will always be determine by others that is Gibbs equation. So we will continue from there I have to do some work on this to produce the final form that we actually use.

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