Indian Institute of Technology Madras

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National Programme on Technology Enhanced Learning

Chemical Engineering Thermodynamics
by

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Lecture 33

Summary of
Classical Thermodynamics

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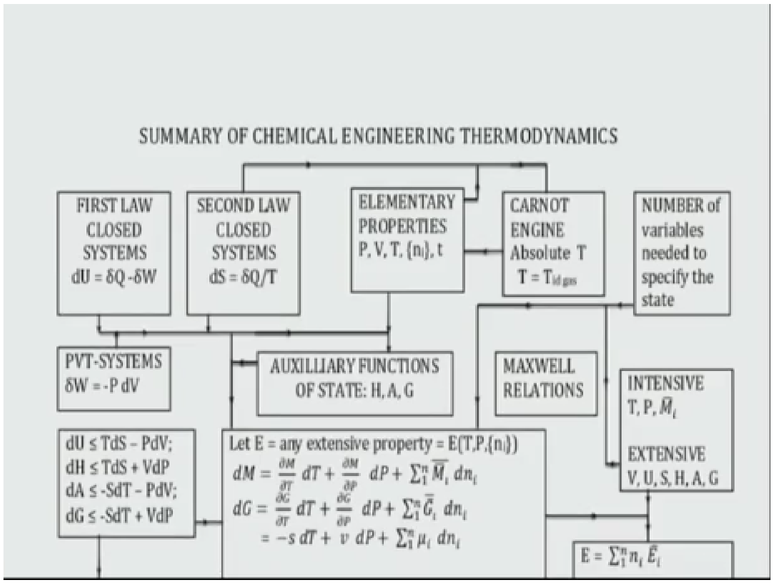

SUMMARY OF CHEMICAL ENGINEERING THERMODYNAMICS

FIRST LAW CLOSED SYSTEMS $dU = \delta Q - \delta W$

SECOND LAW CLOSED SYSTEMS $dS = \delta Q/T$

ELEMENTARY PROPERTIES P, V, T, $\{n_i\}$, t

CARNOT ENGINE Absolute T $T = T_{id\ gas}$

NUMBER of variables needed to specify the state

PVT-SYSTEMS $\delta W = -P\,dV$

AUXILLIARY FUNCTIONS OF STATE: H, A, G

MAXWELL RELATIONS

INTENSIVE T, P, $\bar{M}_i$

EXTENSIVE V, U, S, H, A, G

$dU \le TdS - PdV$;
$dH \le TdS + VdP$
$dA \le -SdT - PdV$;
$dG \le -SdT + VdP$

Let E = any extensive property = E(T,P,$\{n_i\}$)

$$dM = \frac{\partial M}{\partial T}\, dT + \frac{\partial M}{\partial P}\, dP + \sum_1^n \bar{M}_i\, dn_i$$

$$dG = \frac{\partial G}{\partial T}\, dT + \frac{\partial G}{\partial P}\, dP + \sum_1^n \bar{G}_i\, dn_i$$

$$= -s\, dT + v\, dP + \sum_1^n \mu_i\, dn_i$$

$E = \sum_1^n n_i \bar{E}_i$

You rate the first law for closed systems there is an assumption that you have elementary concepts of Q and W straightened out but you are always in conflict about them there is an assumption of continuum that it is not made up of molecules it is actually made up of molecules but you do not recognize that simply say that anytime you are dealing with the system you are leaving with such a large number of molecules that any change in density can be treated as continuous.

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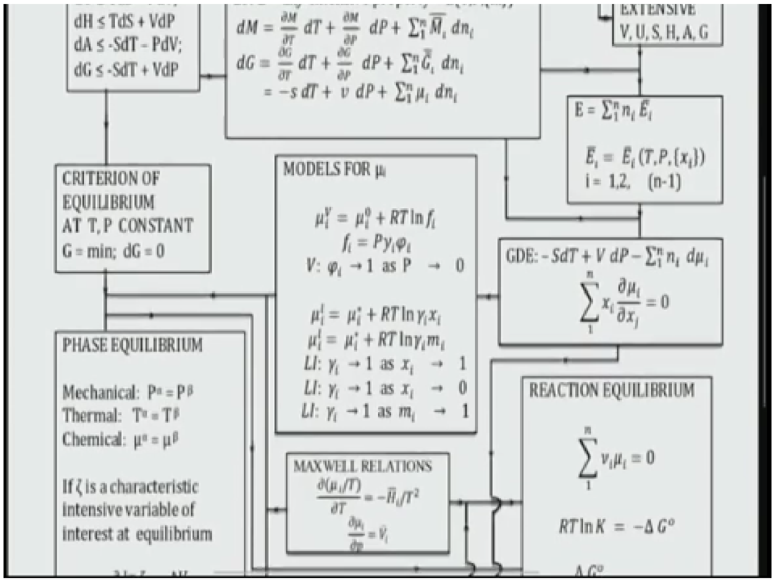

$dH \le TdS + VdP$
$dA \le -SdT - PdV;$
$dG \le -SdT + VdP$

$dM = \frac{\partial M}{\partial T} dT + \frac{\partial M}{\partial P} dP + \sum_1^n \bar{M}_i \, dn_i$
$dG = \frac{\partial G}{\partial T} dT + \frac{\partial G}{\partial P} dP + \sum_1^n \bar{G}_i \, dn_i$
$= -s \, dT + v \, dP + \sum_1^n \mu_i \, dn_i$

EXTENSIVE
V, U, S, H, A, G

$E = \sum_1^n n_i \bar{E}_i$
$\bar{E}_i = \bar{E}_i (T, P, \{x_i\})$
$i = 1, 2, \ (n-1)$

CRITERION OF
EQUILIBRIUM
AT T, P CONSTANT
G = min; dG = 0

MODELS FOR μ_i
$\mu_i^V = \mu_i^0 + RT \ln f_i$
$f_i = P y_i \varphi_i$
$V: \varphi_i \to 1 \text{ as } P \to 0$
$\mu_i^l = \mu_i^* + RT \ln \gamma_i x_i$
$\mu_i^l = \mu_i^* + RT \ln \gamma_i m_i$
$LI: \gamma_i \to 1 \text{ as } x_i \to 1$
$LI: \gamma_i \to 1 \text{ as } x_i \to 0$
$LI: \gamma_i \to 1 \text{ as } m_i \to 1$

GDE: $-SdT + V \, dP - \sum_1^n n_i \, d\mu_i$
$$\sum_1^n x_i \frac{\partial \mu_i}{\partial x_j} = 0$$

PHASE EQUILIBRIUM
Mechanical: $P^\alpha = P^\beta$
Thermal: $T^\alpha = T^\beta$
Chemical: $\mu^\alpha = \mu^\beta$
If ζ is a characteristic intensive variable of interest at equilibrium

MAXWELL RELATIONS
$$\frac{\partial(\mu_i/T)}{\partial T} = -\bar{H}_i/T^2$$
$$\frac{\partial \mu_i}{\partial p} = \bar{V}_i$$

REACTION EQUILIBRIUM
$$\sum_1^n v_i \mu_i = 0$$
$$RT \ln K = -\Delta G^o$$

Actually the molecules are either that many a + 1or - 1 you cannot change it continuously but the change of + 1 or- 1 in 10^{23} molecules is so small that you can treat it as differential so you make that assumption and treat as far as thermal classical thermodynamics is concerned treat smatter as if it was continuous all the variables are continuous you assume that there are measurable quantities like PVT and you have the empirical evidence that reproduce the state of a system you need to measure in a pure substance only two of the three quantities if you measure P and T.

All these are not written down here all these are implicit in your entire treatment so then you can say given all that in addition to all that I discovered that there is a quantity u such that dU is a perfect differential although it is the difference of two quantities which are not perfect differentials that is an achievement to say that took nearly two thousand years because people it is sort of vaguely groped and said various things then Joule came along with his calorimeter.

And asserted that that was true so it became a hypothesis and so far it is not been contradicted at all the second law was even more subtle to discover it took but after the discuss although the second law came before the first law entire discovery of the concept of entropy energy although it was not well-defined it was understood reasonably well people are using energy as if it was a state variable.

They did not define it in calculus but they understood it quite well and tribute much more difficult concept it is really amazing that somebody should after lot of work accumulation of knowledge discovered that there is a differential quantity called dS which can be produced by dividing δQ by absolute temperature so the whole idea of introducing an absolute temperature and proving that it is the only factor that will produce a perfect differential out of a non perfect differential δQ.

That is sort of a symmetric there is nothing common about it know if not it is δQ then cannot you do the same thing with δ W you cannot nobody has done it so if you discover another property where you take a path dependent quantity if I divide it by an absolute quantity and produce a perfect differential you can apply for a Nobel price right away so far nobody else has done it the whole history of mankind that is the only case where you found a perfect differential therefore you found another property S with which you can do exactly as you *δ* with PVT etc…

Then there are elementary properties like PVT T ideal gas that came from Gay - Lussac's measurements you know you take the volume and you produce an absolute temperature and that absolute temperature for an ideal gas at which the volume is 0 is - 273^0 C so that is an empirical information number of moles again you think you can identify the species you can measure them you can do it reproducibly.

So those are elementary properties I must also say Q and W are taken as elementary concepts I should have drawn a box there the first one you can add a box elementary concepts like Q and W the difficult thing there again in the development was that Q and W are equivalent according to Joule but are different and there are exactly 2 ways in which energy can be exchanged with the surroundings.

No more than two ways otherwise you could have written down this law if there was a third way you have to produce another symbol and add to it and again you are ready for a noble price if you find it then you have you applied it to Carlos ideal engine you the concept of entropy you came up with reversible engines in the maximum possible efficiency and then it turns out that P was equal to T ideal gas that had already been done of course the whole of thermodynamics will go through if P was equal to α times the ideal gas our α is any constant.

It is just luck that α was chosen to be 1 then work done in PV systems is always defined by PDV it is a concept of mechanical work and we put that concept in and then derive various properties we also introduce auxiliary properties we have U and S + P V P etcetera by combining those in various forms you produce other properties these are not independent properties they are combinations of existing properties.

Now these properties you use you write for closed systems therefore you are able to write differential equations first order differential equations describing the change in internal energy the change in enthalpy change in Helmholtz free energy and so on and by putting down the in equality sign which is what the second law told you the second law is basically an inequality you were able to come up with fundamental equations for closed systems having done that in order to extend it to open systems you allowed change in the number of moles.

So you simply wrote BG is equal to for example- SDT + VDP + μi dNi right simultaneously you went back to calculus and wrote the other equation for any extensive property that is DMS partial of M with respect to T DT + partial of M with respect to PDP + Mi bar DNA one example of that is this now you have a criterion of equilibrium you ask under P and P when is the system at equilibrium and you showed that for example if TP are constant G should be minimum or DG 0 incidentally in all of this there is another thing that you have taken on faith which is the law of conservation of mass.

Which again has not been contradicted so far so you have to put that in order to put the criterion of equilibrium and derive expressions for phase equilibrium simply put two phase together and ask that the combined two phase be at equilibrium similarly you asked about chemical equilibrium the formulation is always ν i μ i is = 0 or if you have multiple equations ν_{ij} μi = 0 and you found RTLnK = - δg0 δg0 contained everything that you do not know but you isolated quantities that are functions only of temperature on the right hand side.

So essentially what you said was k at one temperature is a constant regardless of the pressure and that is a very useful concept to have then you have this B of δg0 / T = δH0 and then similarly D of δ 0 / dT is δCP so you have to measure Δcp CP0 is the ideal gas specificity of no it is a function of temperature you have to know δ 0 at 1 temperature CP0 you have to know at one temperature for all.

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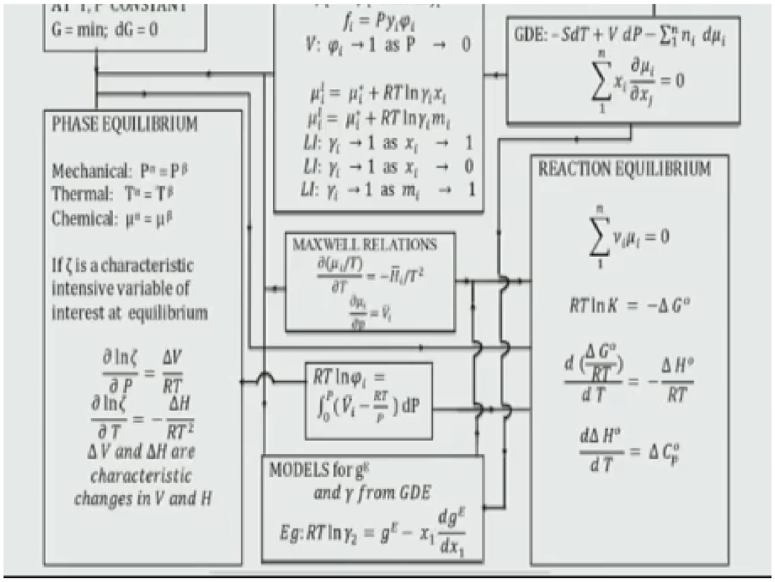

As a function of temperature you have to integrate that to get δH CP0 you have to know as a function of temperature at all temperatures as far as phase equilibrium is concerned you got rid of U0 and therefore you had all measurable quantities you simply play games with these equations because the equations I have written down here are for solvent- solvent systems for solvents – solute systems you have to give different models in do the equation.

Now on the right hand side again the number of properties required to specify the state of a system is a completely empirical quantity told you there is a Gibbs phase rule but the phase rule assumes that you know the number of components in the number of phases and you may not be able to in macroscopic thermodynamics you may not be always able to detect the number of phases.

For example in solid as long as it is distinct phase solid liquid vapor you very clever just look at it and say there are 3 phases but if there are three solid phases you are in trouble you do not know simply the structure may be different only if you look at it in a microscope you will know so the number of properties required to specify the state of a system is always an empirical quantity we have known from experience at a pure component single phase system there are two variables that required to specify the state of this.

Similarly in each case you know the number you can use the Gibbs phase rule if provided you know the number of components in the number of phases then of course the Gibbs phase rule is a very rigorous rule then you then again big make the post elation that some quantities are intensive some quantities are extensive intensive variables do not vary with the size of the system T and P are alright in Mi bar the partial molar property is also an intensive variable that is an assertion.

In fact in nano systems where the number of molecules is very small this is no longer true in the whole of classical thermodynamics we will break down in the way in which you use it if you go to systems with small number of molecules because then the changes are not continuous you no longer have the applicability of the continuum but and it does not mean you have to throw away all the concepts you have tore work it and a lot of it with hold but with some reservations for example the fact that mi bar the partial molar property is independent of the size of the system will no longer be true.

So you cannot do the simple integration that you already did so you have to divide properties intensive and extensive and what you do is then you are able to integrate the fundamental equation we wrote the fundamental equation DG is equal to for example - STDT +VTDP + μ IDNI you integrate this equation and produce the Gibbs duhem equation I have got the next step is you have you prove that M is equal to Ni Mi bar for all macroscopic systems and then we have asserted for in particular Mi bar for m equal to g is the chemical potential.

It is so important that we give it a name it comes again and again we have to we have already asserted that Ni bar is a function only of TP X 1 to XR- 1 only are the mole fractions not of small numbers given that you can derive a Gibbs duhem equation which is the equivalent of composition variables of the equation that gives you four compression wave but sum over XI =1 instead of that you get a more complicated equation for chemical potentials but remember well the Gibbs duhem equation says I have written then down are actually R – 1 equations because for every J you will get one equation.

The solution to it lies there is only one independent function there so if I know gXS I can calculate all the others so the nature of the equation because they first-order ordinary differential equations they lead to a single solution provided you know one function as a function of a composition which is δ which is G Xs or G so if you know one mixture property as a function of composition then you can calculate all the others using the gives you equation there for mixing becomes very important it is central in thermodynamics.

So you ask what are the models for mixing I have that here in the bottom row you have models for GXS so that essentially has to do with mixing this is for the condensed phase for the gas phase you avoid the whole thing because solving the Gibbs duhem equation for the chemical potential is equivalent to solving the Gibbs Duhem equations for the partial molar volume in the partial volume molar volume is measurable.

So you do not bother to solve the Gibbs duhem equation for the gas phase the partial molar volume can be solved for either from empirical data you can measure it or from equations of state you can go to Van Der Waals equation of state there dlich-kwong equation of state and derive expressions for Vi bar and from Vi bar you can calculate Vi so you got the chemical potential model which satisfies the Gibbs duhem equation.

So for vapor you write μi = μ 0 + RT ln ϕ is simply Pyi times V_I and RTln ϕi is integral V_i bar -RT by PDP so if you know V_i bar you know ϕ I bar you know ϕi and therefore you know μi for liquids you write μ I * + RTln X 1 I am going to do the next one from the next class shall discuss this case of electrolytes or solutes where it is more convenient to use morality as a measure unit of measurement rather than the mole fraction but in all these cases you have liquid 1 γ I = to 1 when X I goes to 1 that is the solvent components.

The solute components γ I goes to 1when XI goes to 0 and finally the third type of solid components and molality XI goes to 0 it means very dilute solutions if molarity of 1 is a very dilute solution you are talking one mole of solute per thousand grams of solvent therefore you have the molarity units and in a very dilute solution you are saying am I goes to on so use that and then all the time you can do manipulations because you have introduced a redundancy in thermodynamics by introducing three additional functions H A and G.

Originally you had only U and S along with PVT you introduced a change in g so; instead of two variables you introduced three others so there is a ϕ C to do redundancy in thermodynamics.

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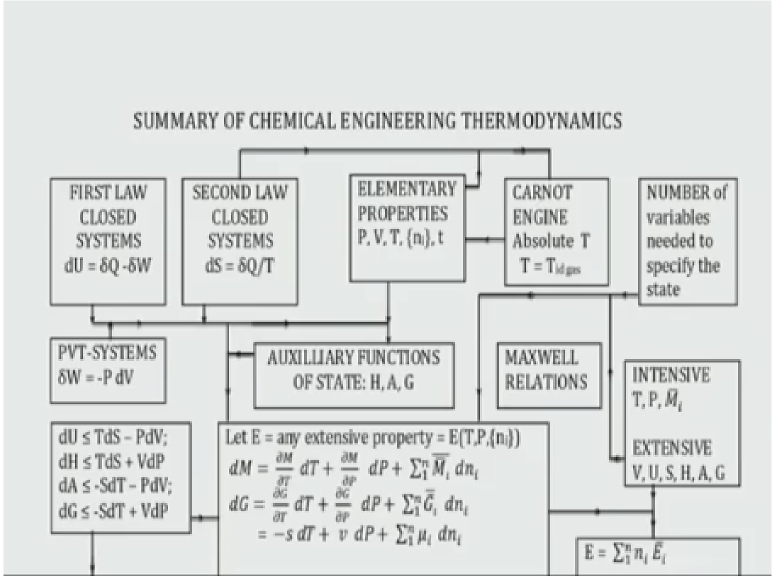

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$E = \sum_1^n n_i \bar{E}_i$

HAG are additionally introduced their only combinations of US and other properties, so to that extent every equation in thermodynamics has ɸ C 2 equivalent in fact if you allow permutations that is if you put 1 in the denominator doing asking for G with respect to P you can ask P with respect to G so if you allow permutations you are talking of ɸ C ɸ P 3 which is even larger number.

So that is the number you have in terms of combinations and permutations actually in principle what you do is take PVT HAG U and S means 8 out of 8 any three variables are the independent variables so there are HC 3 ways of writing every equation in thermodynamic sin principle that is why when people list Maxwell's relations it is meaningless it is absurd to go on listing them you simply recognize that if you take any three variables as the base variables and write the differential equations you can produce Maxwell relations of any you want.

So Maxwell relations you produce whenever you need them write down what the independent variables are entering and the purpose of all this manipulation is first thing is to understand the overall picture as I told you thermodynamics is so general that even though all the models in if you ever go to astrophysics you will discover that their model for the universe is that of an ideal gas and therefore when they calculate your background radiation they do it from PV^{γ} is equal to constant because the planets are very small compared to the intervening space.

So you can treat them like point particles it is all a matter of scale and in that scale you have a large number of non interacting point particles practically ideal gas.

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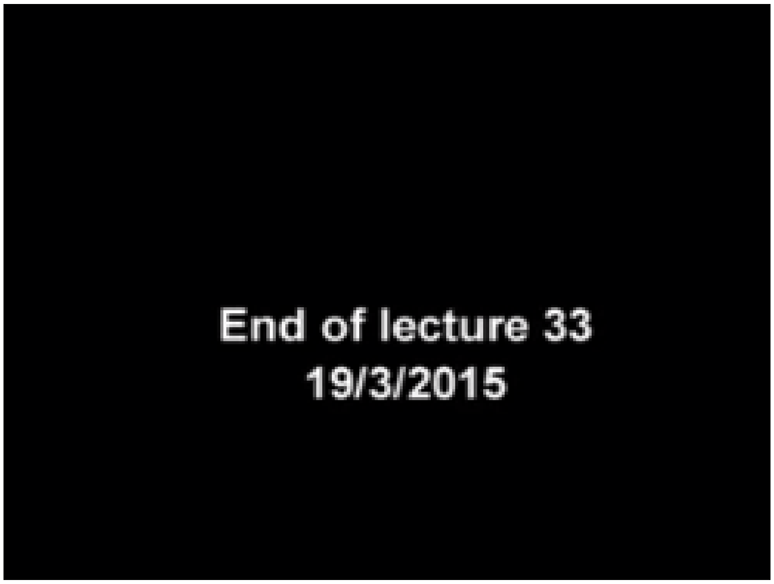

End of lecture 33
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That you can describe systems the way they are in fact I do not know if I mentioned it.

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