

Thermodynamics And Kinetics of Materials

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Lecture 8

First and Second Laws Combined

Now, we have defined first law, second law and third law. So, having defined all of these laws I will just recap the statement of third law. So, what was the statement of third law? That at absolute 0 Kelvin that is the, so third law defines the absolute scale of temperature. Now, at the absolute 0 temperature all perfect crystalline substances have the same entropy, and the value of the entropy is 0 right. So, all perfectly crystalline substances will have 0 entropy at absolute 0 temperature right, S at 0 k is equal to 0 for all substances in perfectly crystalline form. So, this is what we know. Now, as I ah so as you can see here now you have first law which is the conservation ah law and then you have second law it defines entropy, convectionality or inversibility of a process. Now, you have third law which tells about the absolute 0 temperature and also gives you a way to define absolute entropy. See in general what we basically measure is the change in entropy, change in energy. So, we are basically interested in the change not the absolute value. However, like delta S. So, if I want to know delta S or delta U for a process right. Now, when I am talking about delta S from 0 to T if you look at if you remember the integration because again del Q it will be again it is a reversible $T dS$ and if you do it at constant pressure this is equals to dH which is $C_p dT$ and C_p itself can be a function of temperature. So, dS equals to $C_p dT$ by T and C_p itself can be a function of temperature, but when I integrate from initial state to final state or T_i to T_f I require to know what is the value at T_f right.

Statement of third law

At absolute zero ($T=0$ K) all perfect crystalline substances have the same entropy, and it is zero.

$S(0\text{K}) = 0$ for all substances in perfectly crystalline form

Third law lets us calculate absolute entropies.

$$\Delta S_{0 \rightarrow T} = \int_0^T \frac{C_p(T)}{T} dT$$

$\delta q_{rev} = T dS = dH$
 $dS = \int_{T_i}^{T_f} \frac{C_p}{T} dT$

$S(0) = 0 \rightarrow S^\phi(T)$ or $S^\circ(T)$
Standard entropy at temperature T

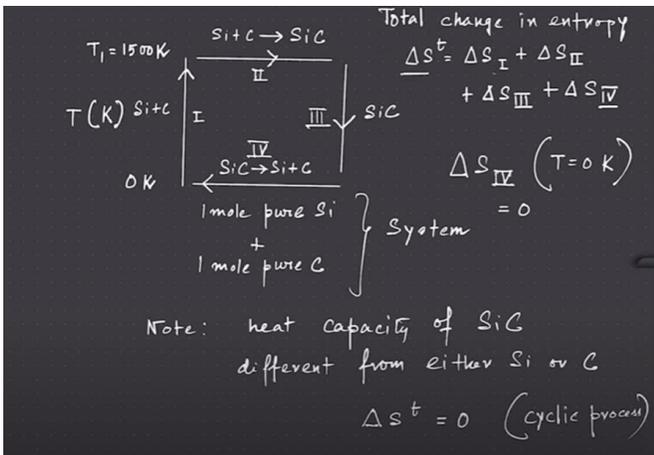
S_m^ϕ (J/mol·K)

Graphite, C(s)	5.7
Diamond, C(s)	2.4
Water, $H_2O(l)$	69.9
Hydrogen, $H_2(g)$	130.7

So, I require to find out the value of T_f , but I require to know also the value at T_i right. So, the point is when I have this dS . So, it is basically S . So, if you look at the left hand side it is S of final state

minus S of initial state. Now, so the value at S_i . So, for example, the previous problems you have seen you have some like S_0 right. So, that is the or S_{m0} right. So, molar entropy at 0 kelvin. So, here once you have third law. So, you can basically calculate the or estimate the absolute entropies how because you will do the same integral ΔS from 0 to T , but now it is at 0 and it is at T and as you know S_0 equal to 0. Now, S_0 equal to 0 basically gives you a way to define standard entropy at some temperature which is defined as $S_{\phi T}$ or $S_0 T$ right. You often define it as $S_{\phi T}$ or $S_0 T$ which is the standard entropy at temperature T and this is basically called third law entropy and this $S_0 T$ we generally for example, it is often reported for different substances we report $S_0 298$, 298 is your room temperature right 25 degree Celsius. So, S say for example, this is the standard entropy at room temperature for different substances that is listed here. So, if you see these are the different substances listed here and for these different substances when I want to define the standard entropy at 290 kelvin I am basically using the fact of S_0 equal to 0 right and then for graphite say for example, I will. So, graphite solid which is solid form of carbon one of the electrodes of carbon which is I think which you will later see is the most stable of carbon is having entropy standard entropy of 5.7 joules per mole kelvin defined at 298 kelvin and then diamond has 2.4 water in the liquid state has 69.9 and hydrogen has 130.7 right this is the and as you can see here that the trends look fine because in solids the entropy the standard entropy is also less in liquid this is higher and in gas it is much, much larger. So, now if you have that now think of a process now think of a process and one of the very well-known processes that is often cited in the literature or in the text books is the formation of silicon carbide and what is there we have pure silicon and you have pure carbon and you form silicon carbide at a given temperature. However, you are thinking of a process like this you have if you think of the process now from 0 kelvin I am at 0 kelvin I have silicon and carbon is a pure form now I take it to a temperature of 1500 kelvin from 0 kelvin and that is my first that is my stage 1 of the process and at 1500 kelvin silicon and carbon combine to form silicon carbide that is the stage 2 of the process. So, at 1500 kelvin this is the stage 2 of the process where silicon and carbon combine to form silicon carbide. Now I take this silicon carbide at T_1 equal to 1500 kelvin. So, this is hypothetical experiment because I cannot really go to 0 kelvin. So, but you go to. So, now you take this silicon carbide and take it to 0 kelvin say from 1500 to 0. Now at 0 kelvin silicon carbide can say decompose into silicon and carbon because silicon carbide silicon and carbon all have remember here in the perfectly crystalline form silicon carbide silicon and carbon all will have the same entropy and the value of entropy at 0 kelvin is 0. So, this is the fact that we will want to use. Now if you look at this entire cycle if you look at this entire cycle which contains 1, 2 and this is what is number stage number stage 3 of the process and this is the final stage 4. So, you have 1, 2, 3 and 4. So, basically the total change in entropy ΔS_T is the total change in entropy during this entire process right. What is the process? Silicon and carbon you take from 0 kelvin to 1500 kelvin at 1500 kelvin silicon carbon combined from silicon carbide. Now stage 3 silicon carbide is taken from 1500 kelvin to 0 kelvin where silicon carbide can turn back to silicon and carbon right can compose into silicon and carbon. And we start with 1 mole of pure silicon and 1 mole of pure carbon that is your system and the total change in entropy is equal to change in entropy in stage 1 of the process stage 2 of the process stage 3 of the process and stage 4 of the process right there are 4 stages of the process. Now remember heat capacity of silicon carbide is different from that of silicon or carbon. Silicon has a different heat capacity silicon

carbide has a different heat capacity carbon has a different heat capacity again carbon in different form. So, what is the form? Let us assume that we have taken carbon in the form of graphite right. So, silicon and carbon in 1 mole you have taken and carbon is in the form of graphite, but all of these silicon carbide silicon and carbon this is the most important point will have different heat capacities right will have different heat capacities. Now see at delta S 4 right there is a thing delta S 4 the stage 4 of this entire cyclic process is taking place at T equal to 0 kelvin at T equal to 0 kelvin silicon carbide individually has an entropy of 0 right and silicon also has an entropy of 0 and carbon has an entropy of 0 right. So, the change in entropy in the stage 4 of the process is basically going to be same right. So, that is what I have written here delta S 4 equal to 0 because the entropy of pure silicon carbide is the same as the entropy of silicon and carbon at T equal to 0 kelvin SSI C is the entropy of silicon carbide at 0 kelvin. So, in brackets are put 0 equal to SSI at 0 kelvin at S C at 0 kelvin this is the entropy of carbon and these are all equal to 0 therefore delta S 4 is same.



$$\Delta S_{IV} = 0$$

∴ the entropy of pure SiC is the same as entropy of Si and C at T = 0 K ($S_{SiC}(0) = S_{Si}(0) = S_C(0) = 0$)

$$\Delta S_{III} = S_{SiC}(0) - S_{SiC}(T_1) = -S_{SiC}(T_1)$$

$$\Delta S_I = S_{Si}(T_1) + S_C(T_1) - S_{Si}(0) - S_C(0) = S_{Si}(T_1) + S_C(T_1)$$

$$\Delta S_{III} = S_{SiC}(0) - S_{SiC}(T_1)$$

$$\Delta S_I + \Delta S_{II} + \Delta S_{III} = 0 \quad \text{--- (A)}$$

From (A)

$$\Delta S_{II} = -\Delta S_I - \Delta S_{III}$$

$$\Delta S_{II}^{reached} = \frac{S_{SiC}(T_1) - S_{Si}(T_1) - S_C(T_1)}{Si + C \xrightarrow{1500} SiC}$$

So, now you have delta S T which is delta S is a cyclic process right it is a cyclic process. So, now, it is initial state and final state right. So, ultimately delta S T should be equal to 0 now delta S T for a cyclic process that is the delta S total is also 0 right it is a cyclic process my initial state and the final state of the same and entropy is a state function right. So, the delta S T is 0 delta S 4 is also 0. So, delta S 1 plus delta S 2 plus delta S 3 is equal to 0. Now think of delta S 1 right think of delta S 1 what you have is silicon delta S 1 is silicon and what is the process you are going from 0 to T 1 right. So, the change in entropy is S of silicon pure silicon at T 1 plus S of your carbon at T 1 right S of your silicon at T 1 S of your carbon at T 1 minus S of silicon at 0 kelvin and S of carbon at 0 kelvin these are 0 right this is equal to 0 this is equal to 0. So, basically delta S 1 is nothing but S S i plus S S c at temperatures T 1 right. Now delta S 2 if you see this equation you can write delta S 2 equals to minus delta S 1 minus delta S 3. Now let us look at delta S 3 delta S 3 if I look at delta S 3 you have formed already silicon carbide right in stage 2. Now in delta S 3 you have basically taken silicon carbide that is formed and taken from 1500 kelvin. So, 1500 kelvin is your initial temperature here and 0 kelvin is your final temperature. So, S S i c at 0 minus S S entropy of silicon carbide at T 1 right that is your initial. So, that is going to be equal to again S S i c at 0 is 0 so it is minus S S right. So, delta S 3 minus S S S. Now if you see now delta S 2 from this equation from this equation that you have here let us call it A from A

what can we write ΔS_2 equals to minus ΔS_1 minus ΔS_3 and this ΔS_2 is the entropy of the reaction what is the reaction silicon plus carbon at stage 2 at 1500 kelvin on silicon carbide right that is the. So, this is basically the entropy of reaction. Now the entropy of reaction is nothing but minus ΔS_1 minus ΔS_1 ΔS_1 is minus S_{Si} minus sorry plus S_{Si} plus S_C . So, minus ΔS_1 will basically minus S_{Si} and minus S_C at T equal to T_1 and minus ΔS and it is minus ΔS_3 ΔS_3 is minus S_{SiC} . So, there is a minus sign here there is a minus sign here it becomes plus. So, it becomes S_{SiC} T_1 minus S_{Si} T_1 and S_C as an S_{carbon} T . So, as you can see here the ΔS reaction basically exactly tells you the same thing right it is product entropy of the product minus entropy of the reactants at T equal to T_{naught} at kelvin entropy of product what is the product silicon carbide minus the entropy of the reactants at temperatures at temperature T_1 right. And as you can see we are using this process of this understanding that of third law that at in stage 4 where you have silicon carbon and silicon carbide all of them have 0 entropy in the perfectly crystalline form right. So, in fact this is the way we can basically relate ΔS_2 to ΔS_1 and ΔS_3 . So, this is the idea and this is how third law basically gives you a way to define the absolute entropy or define the standard entropy right. So, this is something that you can understand even in this the reaction that we consider of silicon and carbon forming silicon carbide right how we are making use of third law right. Now, we are always considering say some equilibrium right we in thermodynamics equilibrium thermodynamics we have to consider equilibrium. Now, what does that entail that means that we are thinking of say for a simple system in a simple system we are considering say chemical work mechanical work and thermal work right. So, heat input is also considered. So, when we are talking about a system which is in thermal equilibrium with the surroundings, we know that the temperature has to be the same right temperature of the system has to be same as the surroundings as long as the wall between the surroundings allow heat transfer. Now, if there is heat transfer allowed the system and the surroundings will finally arrive at the same temperature T at thermal equilibrium. Now, as you know in Clausius inequality what we have learnt P_s is greater than equal to ΔQ by T right. Now, think of heating at constant volume I will heating a system at constant volume.

System in thermal equilibrium with the surroundings at temperature T

Clausius Inequality

$$dS \geq \frac{\delta q}{T}$$

Heating at constant volume

$$\delta q_v = dU \quad (\text{no non-expansion work})$$

$$dS \geq \frac{dU}{T} \quad (\text{constant } V)$$

$$T dS \geq dU$$

Constant internal energy ($dU=0$)

$$dS_{U,V} \geq 0$$

Constant entropy

$$dU_{S,V} \leq 0$$

$$dV=0$$

$$dS=0$$

$$\Rightarrow dU_{S,V} \leq 0$$

$$dS \geq \frac{\delta q}{T}$$

$$\geq \frac{\delta q_v}{T}$$

$$\geq \frac{dU}{T}$$

Now, ΔQ_V ok. So, there is no non expansion work ok no non expansion work and we are telling that heating at a constant at constant volume right. So, now you have no non expansion work means

there is no chemical work and stuff and also an expansion work also is like change in volume right, but we are doing heating at constant volume. So, ΔQ_V is going to be just $T \Delta S$ right change in the let us now as you can see here in Clausius inequality what we are telling is now dS is greater than equal to $\Delta Q_V / T$. Now, it is at constant volume. So, we are telling it is greater than equal to $\Delta Q_V / T$ which basically means that this is greater than equal to $T \Delta S$ and that is exactly what we have written right at constant volume it is dS is greater than equal to $T \Delta S$. So, I will just write this down. So, as you know you are you can get confused as you can see here at constant volume dS is greater than equal to $T \Delta S$ by T or $T dS$ is greater than equal to this is all coming from Clausius inequality right $T dS$ is greater than equal to ΔQ_V . Now, think of this if we assume the internal energy to be constant if we assume the internal energy to be constant that means du is equal to 0 then $T dS$ is greater than equal to 0 or dS is greater than equal to 0 right. If you if you consider T greater than 0 then $T dS$ greater than equal to 0 means dS is greater than equal to 0, but dS is greater than equal to 0 with what are the constraints volume is fixed and volume does not change internal energy does not change. So, if volume does not change and internal energy does not change now we get a very interesting corollary of the Clausius statement right we get a Clausius inequality that the entropy either dS can be equal to 0 or it is greater than 0 at if the system is at constant energy and constant volume right. Now, you can also think the other way say for example I fix dS means at constant entropy then what happens the dS equal to 0 so du is less than equal to 0 this implies, but what is what are the constraints dS equal to 0 and dv equal to 0 that means du is less than equal to 0. Now, you see in one case you are telling that if you take a constant internal energy that the internal energy of the system is constant then du is less than equal to 0. See we are focusing on the system here right and another is constant entropy problem is constant entropy means whether entropy does not change entropy is kept fixed volume is kept fixed then du has to be either equal to 0 or less than 0 right. These basically give me two extremum conditions right it gives me that at equilibrium the dS at for a given internal energy and volume the dS has to be either equal to 0 or greater than 0 right at a constant entropy du has to be less than 0 or equal to 0 right. So, now think of heat transfer that is actually taking the heat transfer that is happening at constant pressure. Now, when you take constant pressure we have already discussed this ΔQ_P so ΔQ_V when we write ΔQ_V equal to $T \Delta S$ similar ΔQ_P equal to $T \Delta S$. Now, $T dS$ has to be again cautious inequality comes in so $T dS$ greater than equal to ΔQ_P . Now, if you think of constant enthalpy that means dh equal to 0 then dS right change in entropy at constant enthalpy and pressure should be equal to greater than equal to 0 right. Now, again if we go to constant entropy that means dS equal to 0 and you have this constant pressure so dh is less than equal to 0 right. Again you get two different conditions right from cautious inequality now it is in terms of changing enthalpy and changing entropy. Now, if you see $T dS$ greater than equal to du gives you another consequence one very interesting consequence which is $du - T dS$ is less than equal to 0 because $T dS$ is greater than equal to du since $T dS$ greater than equal to du therefore $du - T dS$ is less than equal to 0. Now, see I define a new thermodynamic function or thermodynamic variable called f which is Helmholtz free energy I will so show that how all of these potentials connected all of these different thermodynamic functions are connected but you see with this definition of $du - T dS$ less than equal to 0 I can define something called f which is basically called Helmholtz free energy which is $u - T s$ right f equals to $u - T s$. Now, this is called

Helmholtz free energy so this is another type of energy so we have now encountered there is u then we have h and then we have s and with using u and s we can define f which is the Helmholtz free energy and then with h and s so as we have done already so $dh - T ds$ is greater than equal to $dh - T ds$ is greater than equal to dh so since $T ds$ is greater than equal to dh right so $dh - T ds$ has to be less than equal to 0 so g we define another type of energy is called Gibbs free energy which is g which is equal to $h - Ts$. We will show the equivalence of that and we will show the equivalence of these different statements of entropy maximization and energy minimization or Gibbs free energy minimization or Helmholtz free energy minimization but what you can see here is that by using simple Gaussian inequality and focusing on the system and thinking of different constraints like adding different constraints like constant volume lifting or constant pressure heat transfer we can basically define different forms of the Gaussian inequality and we can also define different functions like different new thermodynamic functions or new thermodynamic energies which are like Helmholtz free energy or Gibbs free energy right. Now we can tell since $du - T ds$ is to be less than equal to 0 so we can tell and here what we have talked about when we talked about $du - T ds$ so we told that the volume has to be fixed right and temperature has to be fixed right if you see that volume and temperature so basically instead of volume and entropy we are now telling volume and temperature and if I do that F is basically equal to minus Ts so dF if I look at dF dF is $du - T ds - S dT$. Now when I am defining Tf we are telling there is a heat transfer at constant volume right so heating at constant volume is involved now if I tell constant temperature then dT is also equal to 0 dT equal to 0 that means constant T so now $du - T ds$ less than equal to 0 means dF at constant temperature and volume less than equal to 0 right so this is another way of writing the same Gaussian inequality right this is again indicating thermodynamics the same thermodynamics equilibrium.

Heat transfer at constant pressure

$$\delta q_p = dH \quad \delta q_v = dU$$

$$T ds \gg dH$$

Constant enthalpy $dH = 0$

$$dS_{H,p} \gg 0$$

Constant entropy $dS = 0$

$$dH_{S,p} \leq 0$$

U
H
S
F

$$dU - T ds \leq 0 \quad ; T ds \gg dU$$

$$F = U - TS \quad \text{Helmholtz Free Energy}$$

$$dF = dU - T ds - S dT$$

$dT = 0$ (constant T)

$$dH - T ds \leq 0 \quad ; T ds \gg dH$$

$$G = H - TS \quad \text{Gibbs Free Energy}$$

$$dU - T ds \leq 0$$

$$\Rightarrow dF_{T,v} \leq 0$$

Now if you think of this here what we have used is constant temperature and volume but previously we used constant entropy right when we talked about du less than equal to 0 we told constant entropy and constant volume here we have replaced it by constant temperature and constant volume. Similarly when I took at Th say G let us look at G so G is $H - Ts$ so dG equal to Th minus $T ds$ minus $S dT$. Now dH is du plus dv plus pdv minus ds . Now think of constant pressure so here if P equal to 0 and constant temperature that is T equal to 0 so then what you basically get is $dH - T ds$ less than

equal to 0 implies that it is constant pressure and at constant temperature now if you tell also constant temperature so what does it mean it means dG_P right P is constant P is constant is less than equal to 0 right so we get another form where we now so in dF when we looked at Helmholtz free energy what we tell that the change in Helmholtz free energy should be less than equal to 0 at constant temperature and volume right $dF_{T,V}$ right so we told dF this basically tells you $dF_{T,V}$ is less than equal to 0 now if you fix temperature and pressure then the convenient way is to express $dG_{T,P}$ is less than equal to 0. So this leads to a very interesting and nice approach and this is an approach that was initially established by Callum in and in his classic text it is described in detail thermodynamics and introduction of thermostatics and recently again using this approach of different potentials there is this book by Long King Chen thermodynamic equilibrium and stability of materials in Springer very decent book all of these both these books basically this is the classic text where Callum introduces this postulatory approach where basically or axiomatic approach so where there are some axioms that are given and we assume if we tell that these are true then all the laws first law second law third law in accordance with those laws these axioms follow these laws and we can show that we can use these axioms to understand these different types of thermodynamic equilibrium right so that is the end. Now before we go to complex systems complex systems is where you have like magnetic work electrical work and all the surface contribution from surface etc we will start with very simple system right we are always in all these cases we have been considering simple systems simple systems means we consider there is a thermal contribution to energy there is a mechanical contribution to energy total energy thermal contribution mechanical contribution and chemical contribution right so now if you think of that then if you look at these books you can understand here we I basically following this axiomatic approach that is given by Callum and what we can define here is entropy or given by Longing Chen recently so basically what is thermal matter? Thermal matter is basically given by entropy and mechanical matter is given by volume or change in volume right if there is a mechanical work there is a change in volume if there is a change in if there is heat transfer involved then there is a change in entropy right so entropy the total entropy of the system is the measure of thermal matter volume is the measure of mechanical matter and mole number of species say species i th species so it can be a multi component system we can have species 1 2 3 1 2 3 or a b c and each of these can have some mole numbers right mole numbers is number of moles or amount of species and that number of moles of certain species i is basically measure of chemical matter contributed by species i right so the mole number is the measure of chemical a mole number of species volume is the measure of mechanical matter and entropy is the measure of thermal matter right now if we define that and what we told that we will define some now what we can think of is that we define something like potential right there are different so we look at like thermal potential what does thermal potential mean we will come to that if you look at the very standard law of electrical matter electrical energy then it becomes very easy to understand say for example electrical energy is Uq energy due to charge right Uq and electrical matter is charge q now electric potential ϕ is Uq by q or dUq/dq right so this is something that we are very familiar right electric potential which is basically change in electric energy change in electric matter or change in charge right so that is basically going to be the electric potential similarly we can define thermal potential how you have thermal energy which is say in T right that is the thermal contribution to

the total energy ok total energy is U and since we are considering simple system so we can think of U is basically decomposing to U_p plus U_m that is the mechanical contribution and then U_c U_c is the chemical contribution now if you have thermal energy which is U_p right then you have thermal matter which is S the thermal potential is $\partial U / \partial S$ which is basically T we have shown that right dU equals to dS minus T dP when you get the combined first and second law and when you looked at the exact differential and compare the positions $\partial U / \partial S$ indeed is T right for a given $\partial U / \partial S$ for a given V and for a given M is indeed T so thermal potential is ∂U by dS ok so similarly we can write say mechanical potential now if you see what is mechanical energy is U_m which is basically PV work right you can think of PV work or force times displacement right so that is the mechanical energy and you have mechanical matter which is equal to V and you have mechanical potential which is P which is U_m by V or more accurately it is change in mechanical by ∂U right so and there is a so this is minus P in general so minus P is equal to $\partial U / \partial P$ right as pressure increases volume decreases so if you think that way so there is a minus sign right so minus P equals to $\partial U / \partial P$ similarly we can think of chemical energy ok this is basically because of chemical interactions and because the species that come in right they form bonds and stuff so that gives rise to chemical energy and chemical energy let us call it U_c ok and chemical matter is so if you think of single component system you can think of the mole number of single pet component to be N then chemical potential you can find that chemical potential is U_c by N or more accurately it is ∂U_c so in this case we are taking basically S and so thermal matter is kept constant here and N is kept constant here and this is basically ∂U by ∂N and what are kept constant S and U right so this is how we can define these potentials and then once we have defined these potentials then we can basically think of stating the thermodynamic problem what is the thermodynamic problem?

$$dF_{T,V} \leq 0$$

At constant T and V

$$dF = dU - TdS \leq 0 \Rightarrow dF_{T,V} \leq 0$$

$$dG_{T,P} \leq 0$$

At constant T and P

$$dG = dH - TdS \leq 0$$

$$dH - TdS \leq 0$$

$$dG_{T,P} \leq 0$$

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$= dU + VdP + PdV - TdS - SdT$$

$$dP = 0$$

$$dT = 0$$

Postulatory approach

- Classic text
Thermodynamics and Introduction to Thermostatistics (2nd edition) — Herbert B Callen
- Defining potentials
- Recent text
Thermodynamic Equilibrium And Stability of Materials — Long-Qing Chen
Springer 2022

The thermodynamic problem is in general this so you have different say think of this you have different phases and these phases share some phase boundaries and you want to find out the equilibrium between the phases now instead of thinking of phases we will come to the exact definition of phase but what I am thinking is phase as subsystem so you already know about an isolated system open system closed system now let us think of a isolated composite system so something like I will just change color of ink so if you see I am thinking of an isolated system right in that isolated system I am thinking of two

subsystems okay like subsystem alpha and subsystem beta and I am also telling that this isolated system it is completely isolated completely isolated base there is no heat and mass transfer that is happening between the system and surroundings but this is a composite system right it has two subsystems this is alpha subsystem and there is beta subsystem and then there is this wall right this is the wall now this wall are constrained what can this be? This wall can be flexible or rigid this wall can be permeable to transfer of matter or impermeable so wall basically gives you constraints right it gives you constraints of rigidity and if you remove the constraints it is flexible right it is flexible means it is adaptable to volume change right it adjust right if there is a difference in volume and if there is some work done then basically it is flexible so it will adjust the volume by moving the flexible wall however it is rigid the rigid wall cannot move right so rigidity is a constraint flexibility basically removing the constraint right wall can be flexible wall can be rigid wall can be permeable permeable means it allows the matter to flow through the wall right matter flow through the wall between two subsystems alpha and beta between the subsystems that we have constrained right now it is flexible it is permeable then there is another thing which is basically allows heat transfer between alpha and beta and that is basically diathermal and if I now use a constraint then that is basically adaptable now this is a simple system right we are considering only the what are the constraints what are the contribution we are considering one is thermal another is mechanical and another is species right the mole number of species right so for example so if you think of this so if I am just thinking of the same two subsystems so here we call the subsystem 1 and this is subsystem 2 or you can call them alpha and beta whatever be the naming convention or you can call it like roman 1 roman 2 it does not really matter so whatever naming convention in purpose now you see in subsystem 1 you have internal energy you have volume and you have mole number of different species right you have species 1 species 2 species 3 you can think of like different species like 1 2 3 or a b c or whatever you think of and now you have please note that these are all extensive variables right these are all variables that depend on the extent of the system that is why I wrote them so you should understand that we are describing with three extensive variables one is u means b that is n and n for different species so it can be a multi component system so you have n_1 which is the mole number of species 1 in subsystem 1 and then you have n_1 in subsystem 2 that is the mole number of species 1 in subsystem 2 right which are different which can be different right and then you have say another species called n_2 which is in 1 some the mole number is n_{21} and here it will be n_2 in sub system similarly you can have n_i in sub system 1 and you can have n_i so you have like many components n_i in subsystem right and then this entire system is isolated however this is a composite system right this is an isolated composite system now we want to see so we can initially make the wall completely constrained like it is rigid it is impermeable to matter right matter flow it is impermeable to the flow of species between the subsystems it is rigid it cannot move and it is also adiabatic that means it does not allow heat transfer in the subsystems now I remove all these constraints and after I remove all these constraints what will be the final state of this different sub systems in these two sub systems right which are in contact right when we remove all the constraints that gives me the equilibrium states right the equilibrium states of the subsystems right and that is the goal of that is the major goal in thermodynamics right if you look at phase equilibrium that is the problem so think of the subsystems as phases again we can think of this as phases and we I do not give the concept of reservoir right now but I

am thinking of like you have one phase alpha and then we have another phase beta right now if I want to define alpha and beta so if I define a phase what is phase? A phase by itself is the portion of matter that is chemically homogeneous chemically as well as structurally homogeneous and right chemically as well as structurally homogeneous and it has its physically distinct physically distinct means distinct physical characteristics so for example density refracting index heat capacity and all these things are distinct right for alpha and beta now physically distinct chemically homogeneous and then mechanically separated now we have for example we have separated with them and we can separate them right by doing some mechanical work or some such process I will come to this mechanically separable in some later also so when we discuss phase equilibrium when we discuss phase equilibrium multi component multi phase systems but here we are also considering exactly there is a problem

$$\begin{aligned}
 \text{Electrical matter} &= q \\
 \text{Electrical energy} &= U_q \\
 \text{Electric potential } \phi &= \frac{U_q}{q} = \frac{dU_q}{dq} \\
 U &\rightarrow U_T + U_M + U_C \\
 \text{Thermal energy} &= U_T \\
 \text{Thermal matter} &= S \\
 \text{Thermal potential} &= \frac{dU_T}{dS} = T
 \end{aligned}$$

$$\begin{aligned}
 \text{Mechanical potential} \\
 \text{Mechanical Energy} &= U_M \\
 \text{Mechanical Matter} &= V \\
 \text{Mechanical potential } - p &= \frac{U_M}{V} \\
 &= \left(\frac{\partial U_M}{\partial V} \right)_{S, N} \\
 \text{Chemical energy} &= U_C \\
 \text{Chemical matter} &= N \\
 \text{Chemical potential} &= \frac{U_C}{N} = \left(\frac{\partial U}{\partial N} \right)_{S, V}
 \end{aligned}$$

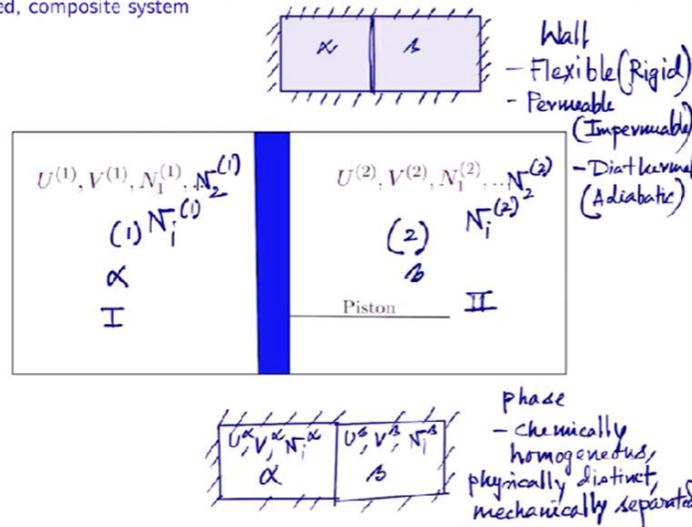
So this alpha phase is like a subsystem which has its own internal energy say U_α and it has V_α alpha is a volume and it has also this different species U_α V_α and so here it is like U_β V_β and N_β and this is the alpha system and this is the beta subsystem and we are trying to find out and now overall I have put some I have made it isolated however I have put a wall or boundary or phase boundary between this alpha and beta and this phase boundary can be such that it has all these constraints like rigid and impermeable and everything but I am removing all these constraints and then I am trying to find out what will be at what will be the equilibrium state what will be the final state of the when we remove all these constraints and that final state is going to be the equilibrium state and the equilibrium state of alpha phase in equilibrium with beta phase right so alpha phase by itself is homogeneous beta phase by itself is homogeneous both of them come together now they have although they are chemically homogeneous they are physically distinct you initially have some alpha and beta and now you want to put them together once you put them together and you remove any all the internal constants that means allow the phase boundary to be flexible that means the phase boundary can move you allow it to be permeable that is the species can there is exchange of species through the wall right it allows species of lower species through the wall and also diathermal that is it allows heat transfer to the wall then you want to understand the equilibrium conditions of alpha and beta and that is exactly the problem of phase equilibrium right that is exactly the problem of phase equilibrium now to solve it you have this different postulates and these in this axioms and one of these axioms is that you have an

entropy function S which is defined for all equilibrium states right all equilibrium states which is a function of these extensive variables u, v, n extensive means they basically so S itself is an extensive variable and it is a function of other extensive variables u, v, n so this is so it is a so defined for all equilibrium states and this is the values are assumed with extensive parameters of internal constant are those right the extensive parameters u, v, n are those the values that are those that the values will be such that it maximizes the entropy over the manifold of constrained equilibrium states so that is the most important point that the entropy basically the subsystems will assume values of $u, v,$ and n such that the total entropy of the entire composite system is maximized ok over the manifold of all these different constant equilibrium states so basically in absence of an internal constant remember this point that you have to you have the wall wall can give you constraints now if you remove this constraints then basically the values assumed by $u, v,$ and n values assumed by $u, v,$ and n will be such that the entropy of the total system is maximized right or change in so the total system entropy is maximized again it has come from the same thing that ds u, v so this is basically in one sense we are telling that there is a function s in such that this $ds, u, v,$ and n has to be greater than right it is maximized now by the way if I look at this function so basically if I look at entropy as a function and if I look at any function which is to be maximized how we find maximum minima we first find out ds equal to 0 that is the extremum condition once we know the extremum condition then we want to find out where whether the second derivative is going to be negative if it is negative then obviously entropy is maximized right so again we will go into this definitions more minutely so for example s is an extensive property that means it is additive that we have already proved right from second law so this is something that we are telling it is a slightly different approach where we are telling that s is a function and this is a function of $u, v,$ and n which are also extensive parameters right of the system like u is the energy is extensive parameter volume extensive parameter right this is not molar volume this is not molar internal energy this is total internal energy total volume and the mole number right these are all additive and therefore s is also additive and total s of a composite system is sum of entropies of constituent subsystems so if you have subsystems α and β it is nothing but s is nothing but s_α plus s_β right so that is what I have done summation over α for all the constituent subsystems and entropy of each subsystem is a function of the extensive parameters of that subsystem right if s_α if I consider f_α s_α is a function of $u_\alpha, v_\alpha, n_1, \dots, n_r$ that is multi components say up to n_1 to n_r so you have species 1, 2, 3, 4, r so basically if you think of 1, 2, 3, 4, r you will tell what is 1, 2, 3, 4, r these are nothing but say for example copper, aluminium, niobium so you can think of like see some elements or you can think of some compounds which are the which form the components of the system right chemical components these are different chemical components so you can have one component system like you have like a unary system or you can have a multi component system here you have multiple components like and each component has its own mole number right in each subsystem or in each phase right another very important thing that we will come to the so I will come I will describe all of this in detail in the next class onwards so I have talked about the what is the problem thermodynamic problem is finding the phase equilibrium right where you are finding the equilibrium states of this composite isolated composite system okay in which you want to and the equilibrium states are such that the entropy of the total entropy of the whole composite system is maximized right after removing the in the absence of the

un internal constraint right so that is the thing so and the entropy is continuous and differentiable so this is also a very important part of the statement of the axiom that the entropy is continuous and differentiable function and is monotonically increasing function of energy, energy means internal energy right so we will continue in the next class about this so in the next lecture I will continue about this and we will talk about the other two postulates or other two axioms right this is the axiomatic approach so we have these postulates and we will see that these postulates finally are in such a way that the no thermodynamic law is violated and you get back the equilibrium state of this multi-phase multi-component system or this isolated composite system containing many many subsets right.

Thermodynamic problem

Determination of equilibrium states which results after the removal of internal constraints in an isolated, composite system



Entropy function $S = S(U, V, N)$ defined for all equilibrium states: values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states.

$$dS = 0 \text{ Extremum condition}$$

S is an extensive property - additive. Total S of a composite system: sum of entropies of constituent subsystems:

$$S = \sum_{\alpha} S^{(\alpha)} \quad S = S^{\alpha} + S^{\beta}$$

Entropy of each subsystem: function of the extensive parameters of that subsystem

$$S^{(\alpha)} = S^{(\alpha)}(U^{(\alpha)}, V^{(\alpha)}, N_1^{(\alpha)}, \dots, N_r^{(\alpha)})$$

The entropy is continuous and differentiable and is a monotonically increasing function of energy