

Thermodynamics And Kinetics Of Materials

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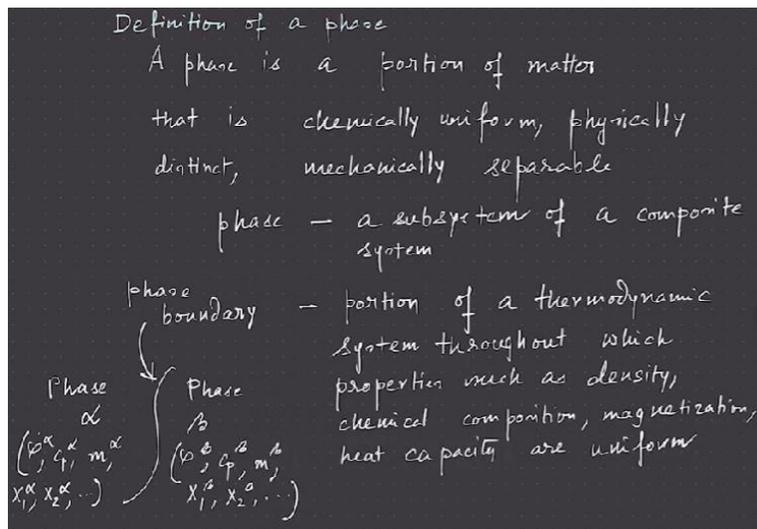
**Dept of Materials Science and Metallurgical Engineering,
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Lecture 17

Phase equilibria and phase transition in unary systems 1

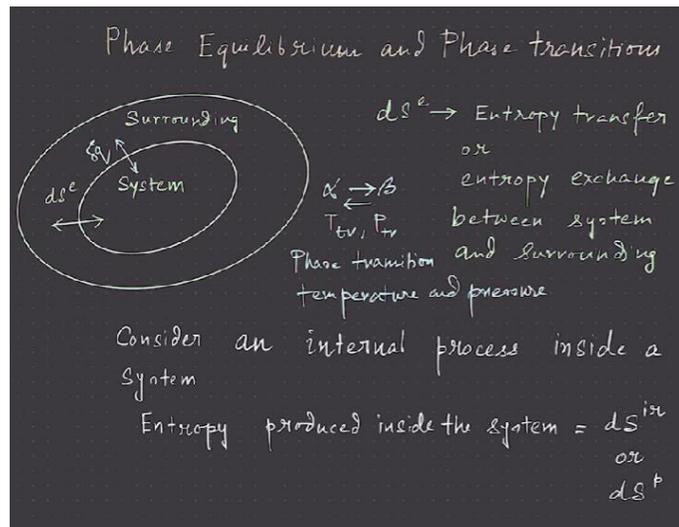
I will start with the definition of phase and as you know and this is well known if you have studied physical metallurgy and you have looked at phase diagrams then I will define phase diagram and what are the principles behind phase diagram these will be described in this course but you might have seen some phase diagrams whether it is a unary system or a binary system you might have seen some phase diagrams but what is a phase? These also we know it is a portion of matter that is chemically uniform, physically distinct and mechanically separable right this is something a textbook definition right it is given that it is chemically uniform, physically distinct and mechanically separable right and but I can also define the phase as a subsystem of a composite system if you remember when you define a composite system a composite system contains subsystems but overall the composite system is isolated it is isolated from the surroundings and but it has several subsystems and the subsystems are separated by walls and each subsystem is characterized by its own internal energy, volume and mole number of species right so basically you can think of phase as a subsystem no so again if I think of phase the way another definition of phase it is portion of a thermodynamic system right instead of telling portion of matter I am telling that it is a portion of a thermodynamic system throughout which properties such as density, chemical composition, magnetization, heat capacity these type of properties are uniform so it is a portion of a thermodynamic system instead of telling it is a portion of matter I am talking of it as a portion of a thermodynamic system so as a result what happens is with these ideas see phase is a subsystem of a composite system or portion of a thermodynamic system you can immediately identify the previous idea the concepts that we have been given that for a thermodynamic equilibrium that has been given in terms of subsystems of a composite system so it's a portion of a thermodynamic system means it's a subsystem throughout which properties such as density, chemical composition, magnetization, heat capacity, electric polarization or susceptibility these are uniform so these should have physically distinct physically and chemically distinct properties right so a phase has its own composition for example right so that is exactly what I am talking about and if there are two phases say in a microstructure in a material you often see these internal structures under a microscope in this internal structures you different you see

different types of contrast now and these contrasts are often identified as phase now if you see when you see the contrast the main thing that distinguishes these two phases is the phase boundary or the interphase between the phases right now if you think of a phase boundary the phase boundary is drawn here it's like a hypothetical phase boundary or you can think of it as a physical phase boundary so right so basically if you look under a microscope in a system say in a eutectic system you will see that there is these two different phases like cementite and ferrite and there is a distinct phase boundary that you can identify that separates these two phases right so this is one phase boundary I have shown schematically



and if you look at that you have on one side alpha phase another side beta phase how is alpha phase characterized it will have alpha which is uniform throughout it will have a heat capacity okay which is again uniform throughout then it will have some magnetization say for example it will have also mole fractions of different components that make up this phase like x_1^α x_2^α and so on right it will also have its own energy its own molar volume etc etc similarly our lattice parameter again phase beta like it has its own density we can think of and it has its own molar volume so therefore it has its own unique lattice parameter and then you have phase beta say again phase beta has a unique density ρ^β it has a unique heat capacity CP^β then unique magnetization say for example iron-chromium system the iron rich phase is magnetic while the chromium rich phase is not so as a result you have now again so the band so the chromium rich phase when we identify a chromium rich phase one of the characteristics that we see is that it has no magnetization right but if I look at the iron rich phase on the other hand I look at that I see that it is ferromagnetic and it has a spontaneous magnetization associated with it again chromium rich phase has more chromium and the iron rich phase has more iron and throughout the phase the composition of iron will more or less become uniform again throughout the phase for beta phase x_1^β x_2^β x_1^β x_2^β this will be uniform right so basically it will be chemically and physically uniform in terms of chemical and physical properties right and

it is mechanically separable now when we talk about phase transition we when we talk about phase transition one of the common phase transitions that come into means that immediately come to our mind is like water evaporating right water boiling and it got a done into water vapor or water freezing and becoming ice or ice melting and becoming water and so on right so basically this is the exactly the or some phase alpha transforming so basically the idea is some phase alpha is transforming to beta and then when you look at phase transition we also characterize something called a phase transition temperature phase transition temperature and pressure when talk about phase transition temperature and pressure what we are telling is that there is a given pressure and given transition temperature at which alpha can transform to beta or vice versa beta can transform to alpha in one case say for example for alpha to beta conversion alpha may require heat from outside while for beta to alpha conversion heat can be released to the surroundings from the system right so this is a so as you can see there is this arrow that is moving from alpha to beta there is another arrow which is from beta to alpha and as you can see at the phase transition temperature and pressure this alpha beta conversion can go either way so that means it is reversible right so there is a phase transition temperature and pressure now I told that whenever there is heat transfer or heat exchange between the system and the surroundings if there is a heat exchange between the system and the surroundings say some δQ is added to the system or δQ is removed from the system you will always have a corresponding entropy exchange right there will be an entropy exchange right so this is called entropy transfer or entropy exchange between system and surroundings right now think of an internal process like this phase transition internal process



such as a phase transition inside a system now if this internal process is spontaneous if this internal process is spontaneous or natural or irreversible then there will be also a nonzero entropy produce so there is entropy exchange between the system and surroundings due to heat transfer but there is also entropy produced inside the system and there can be also entropy produced inside the surrounding if there is some process

happening in the surrounding but the entropy produced so if I considering only an internal process which is happening only inside the system an entropy produced is called DSIR or DSP that means this P means entropy is produced right entropy production or entropy that is happening due to this irreversibility again irreversibility is associated with any natural or spontaneous process so any natural or spontaneous process will produce some entropy so there will be some entropy that is coming from the exchange between system and surroundings it is like an exchange of thermal matter if you remember it is like an exchange of thermal matter and that exchange of thermal matter is due to heat transfer and if there is this exchange of thermal matter where when there is a temperature gradient for example that part that that part is you will see that that part can always happen if there is a heat transfer whether it is a reversible process or irreversible process that is immaterial however when the process is irreversible then there will be also a nonzero entropy produced this is the most important part so basically if I go further so if I if I describe further so this DSIR will be equal to 0 when the process is reversible right when the process is reversible now first law when we talk about if I think of these quantities like DV right there is a DV or DN as exchange quantities like exchange between the system and surroundings for example DVE is the change in volume of the system or volume exchange between the system and the surroundings again DNE is basically nothing but change in amount of component inside the system or matter exchange between system and surroundings this can happen when the system is open in the DVE it can happen when even when the system is closed right

$$dS^{irr} = 0 \quad \text{When the process is reversible}$$

First law

$$dV^e = dV = \text{change in volume of the system}$$

or, volume exchange between system and surroundings

$$dN^e = dN = \text{change in amount of a component inside the system}$$

or, matter exchange between system and surrounding

you can have mechanical energy transfer or energy transfer when the system is closed but DNE or matter transfer between the system and the surrounding can only happen when the system is open or we are considering a subsystem which is separated by a permeable membrane which is permeable to the exchange of matter or exchange of species right so now if I look at this internal process that is happening inside system and I am look and I derive the thermodynamic the first law it is the combined first law second law then what I

will write I will write T DSE minus PDVE plus mu DNE which is nothing but for a reversal process this is same as TDS that is change in entropy minus PDV that is change in volume and there is multiplied by pressure and as you remember that U as a function of S VN you have expanded and you have written this coefficient so D equal to TDS minus PDV plus mu DN right

$$dU = TdS^e - pdV^e + \mu dN^e$$

$$= TdS - pdV + \mu dN \quad \text{--- reversible process}$$

Irreversible or natural or spontaneous process
 Creates entropy dS^{ir}

$$\therefore dS^e = dS - dS^{ir}$$

$$dS_{system}^{ir} > 0$$

$$dS_{sur} = dS$$

$$= dS^e + dS^{ir}$$

$$dU = TdS - pdV + \mu dN - TdS^{ir}$$

Hillert - Phase Diagrams and Phase Transformations - Their Thermodynamic Basis
 L. Q. Chen - Thermodynamic Equilibrium and Stability of Materials

so this is signifying a reversible process however and for reversible process you have only exchange terms but for an irreversible or a natural or spontaneous process we have told that there is a DSIR which is greater than 0 right so it is like a DSIR in this case if it is an irreversible process is happening inside the system then DSIR system has to be greater than 0 right if it is happening the surrounding then DSIR surrounding also has to be greater than 0 right wherever there is an irreversible or spontaneous or natural process natural or spontaneous process or an irreversible process they are all same right if there is a natural process the natural process there is a natural reaction to the process and or there is a and the process will happen spontaneously or irreversibly right so DSIR system in that case will be greater than 0 now if you see if I now rewrite the first law taking into account this irreversibility component then DS exchange that is the amount of entropy exchange between the system and the surrounding is nothing but DS of the system in entropy of the system overall DS sys means this is like a DS system so basically what I am trying to say here is DS system which is equal to DS is nothing but DS exchange plus DSIR right so if that is so so DS exchange is nothing but DS DS minus DSIR right DS minus DSIR right so that's what I am writing DS but change now becomes equal to DS minus DSIR now if that is so if that is so then we can write DU in the case of an irreversible process happening inside the system equal to TDS minus PDP plus mu DM and DS exchange is DS exchange term is what DS total change in entropy minus the irreversible part right so DS minus TDSIR right so that is the idea and this is something that has been used this DSIR has been used in by Hiller right in his phase diagram phase transmission book recently by Long King Chen in his book on thermal stability of materials it is to basically understand and

also understand and also quantitatively explain the contribute or quantitatively calculate the contribution of the entropy that is produced in the system when there is an irreversible process right so you have this equation now whether process is reversible or irreversible does not matter this equation tells you the change in technology of the system equals to TDS that is the change in entropy times the temperature by the way temperature and entropy and conjugate variables then minus P DV this is the mechanical work done the reversible mechanical done and then is mu dn by the way there is this TDS IR now this entropy produced can be because of exchange irreversible exchange of mole number can be because of some irreversible exchange of pressure it can happen for various reasons right so but there is this T minus TDS IR and that is because of the entropy that is produced in the system if the process is irreversible now this TDS IR we often write as TDS IR can also be written as as shown in Hiller's book or Long King Chen's book that it can also be written as d d zeta where d where d is the amount of dissipation of internal energy right or this is basically driving force means this amount of dissipation again as I told you previously entropy basically measures the dissipation of the internal energy right so basically the amount of dissipation of internal energy or you can think of this as a driving force for a spontaneous or a natural or an irreversible process right for example heat flow from hot body to a cold body is a spontaneous or natural or irreversible process right it has to be a natural process because it does not require any engine right it does not require an external what to be done or stuff so you have a hot body or a cold body you put them together heat will flow spontaneously from a hot body to a cold body unless there is equilibrium established right so now zeta what is this zeta so instead of TDS IR I am representing by d d zeta in those books in the books they use xi but I am using zeta here so zeta is the extent of the process the extent of the process means it is zeta is some sort of an internal process variable or an order parameter you can think of it as an order parameter or an internal process variable

$$dU = Tds - pdv + \mu dn - Tds^{ir} \quad Tds^{ir} = Dd\xi$$

$D \rightarrow$ amount of dissipation of internal energy (driving force for the spontaneous process)

ξ (zeta) \rightarrow Extent of the process (internal process variable or an order parameter)

$\xi = 0$ or ξ_i at the start of process
 $\xi = 1$ or ξ_f at the end of process

this basically tells the say basically if I tell it's the extent or progress of the process I am tracking the progress of process so at the start of process zeta is equal to 0 at the start of process zeta equal to 0 now as I go to the end my zeta increases and as it and at the end of

the process once the process is completed then zeta goes to becomes 1 right so that is how we can define zeta which is an order parameter on which quantifies the extent the process or it is an internal process variable which tracks the progress of a spontaneous process now remember the driving force is equal to 0 for a reversal process there is no driving force alpha can transform to beta beta can transform to alpha when it is a reversible process right in if it's a reversible phase transition alpha can transform to beta beta can transform to alpha for example at 1 bar pressure and 0 degree Celsius like 273 Kelvin ice to water transformation is a reversible process because ice can transform to water water can transform to ice it's a reversible process however d becomes greater than 0 for an irreversible or spontaneous process and as I told you TDSIR is written as d d zeta and d is given as now this d variable there is a driving force or that extent of dissipation is given by or amount of dissipation of internal energy basically which produces this irreversibility is given by minus Δu Δ zeta and at constant entropy volume and more right it's called minus Δu Δ zeta so as I was telling you this is zeta is like an order parameter in a phase transition process now zeta equal to 0 in the so basically if I tell zeta equal to 0 that is the parent phase now if 0 and if zeta lies between 0 and 1 it's a mixture of parent phase and product phase for example there is some some phase transition that is happening from a cubic phase to a trigonal phase then when I am talking about cubic phase cubic phase is the parent phase where zeta equal to 0 now there is a value of zeta between 0 and 1 which basically quantify or which basically signifies a mixture of the parent phase and product phase and zeta equal to 1 is basically the product phase zeta equal to 1 is the product phase right

$D = 0$ for a reversible process
 > 0 for an irreversible or spontaneous process
 $Tds^{in} = D d\zeta$
 $D = -\left(\frac{\partial U}{\partial \zeta}\right)_{S, V, N}$
 ζ - order parameter in a phase transition process
 $\zeta = 0$ is the parent phase
 $0 < \zeta < 1$ is a mixture of parent + product phases
 $\zeta = 1$ is the product phase

so now if we have that if we know this $dSIR$ and minus $dSIR$ now $dSIR$ is nothing but d by t d zeta right according to this definition $dSIR$ is nothing but d by t d zeta now d by t d zeta right so according to this definition it follows that $dSIR$ equals d by t d zeta and now if I integrate from the initial state to a final state remember this is another very important point that I want to tell you if I have two points see the advantage of using state functions is that

we are only interested in the two states what is the path followed whether the path is reversible or irreversible it does not really matter right as long as I know the two states I know the properties of these two states in terms of entropy change or internal change I can quantify the amount of entropy produced or amount of some quantity consumed and stuff right we require for state functions we only require the final and initial states we don't require to know how this initial to final state transition has happened whether through a reversible path or through an irreversible path right so we don't require to know now if you see when I am integrating this is like $\int_{initial}^{final} d\zeta$ means I instead of writing initial to final $\int_{initial}^{final} dS$ I can also do $\int_{initial}^{final} d\zeta$ that $d\zeta$ signifies the extent or the progress of process of ζ is an internal process variable or it's like an order parameter when there is when cubic and the tetragonal phases are coexisting then the order parameter is between 0 and 1 when it completely becomes the product phase that is the tetragonal phase then ζ becomes equal to 1 otherwise ζ equal to 0 right so that's how you can define a cubic to tetragonal phase transition means a lattice a solid lattice a solid is transferred from cubic phase cubic phase means it has a cubic crystal structure then at a certain critical temperature for example it changes from cubic crystal structure to a tetragonal crystal structure it can be because of certain temperature it can be also because of some type like application of something strange that you get such a transition again you can think of liquid to solid transition the same way or when it is an irreversible process for example if I take up some ice in water and then I take it to room temperature from 0 degree Celsius from 0 degree Celsius I take it to room temperature then that ice that is there or the ice cubes that we have put inside water these ice cubes will start melting right so they will start melting and they will melt irreversibly and they will produce water so I am at room temperature say 25 degree Celsius and I have a bucket full of ice and this ice bucket ultimately once we see we will see that the ice bucket has converted to water completely all the ice in the bucket have converted to water right it has melted to water so that's an irreversible process now how much is the amount of irreversibility this type of definition will help us quantify right so again if so now think of an isolated system if I have an isolated system isolated system means no way there is any exchange of energy means it does not allow exchange of energy it does not allow exchange of volume it does not allow exchange of exchange of matter right isolated system does not allow any exchange whatsoever now in such cases D can be written as $T dS - d\zeta$ right it can anyway be written as $T dS - d\zeta$

Amount of entropy produced or energy dissipated

$$\Delta S^{in} = \int_{\text{initial}}^{\text{final}} dS^{in} = \int_{f_i}^{f_f} \frac{D}{T} df$$

$$dS^{in} = \frac{D df}{T} = dS \text{ for an irreversible process in an isolated system}$$

Isolated system

$$D = T \left(\frac{\partial S}{\partial f} \right)_{U, V, N} = T \left(\frac{\partial S^{in}}{\partial f} \right)_{U, V, N}$$

$D = 0$ for an initially equilibrium state
 $D > 0$ for an initial nonequilibrium state

now if you see here so for such a process for an isolated system D can be 0 if the initial state inside the isolated system is at equilibrium if the initial state is at equilibrium then D is equal to 0 that means there is no driving force or thus for any spontaneous process because you are already in the equilibrium state however if you are away from the equilibrium state that means you have an initial non equilibrium state then D has to be redutive right so for a closed system that is system that is in contact with say a thermal and mechanical reservoir for example now if it is thermal and mechanical reservoir

Closed system (constant temperature + pressure)

- System in contact with thermal and mechanical reservoir

$$U(S, V, N) \rightarrow G(T, P, N)$$

$$dS^{in} = dS - dS^e \quad dU = \delta Q_P - p dV$$

$$= dS - \frac{\delta Q_P}{T} \quad \text{or, } \delta Q_P = dU + p dV$$

$$= dS - \frac{dH}{T} \quad = dH \quad (\because dp = 0)$$

$$= \frac{T dS - dH}{T} \quad G = H - TS$$

$$dG = dH - T dS - S dT$$

$$dT = 0$$

$$\therefore dG = dH - T dS$$

we know from the Legendre transform that instead of using this potential U instead of using U SVN we will try to use G or Gibbs free energy as a function of temperature, pressure and mole number so S and T are conjugate so S will be replaced by T S is replaced by T and V is replaced by P and N remains N so this is now so we use G T now if you see what is d S IR d S IR is d S minus d S exchange right now d S exchange is nothing but del Q P by T again a mechanical reservoir so del Q P by T and d U and del Q P is nothing but

$dU + PdV$ which is nothing but so the heat transfer at constant pressure is nothing but change in enthalpy so you can configure it as change in enthalpy since $dP = 0$ right now so this can be written as $dS - \frac{dH}{T}$ or $dS - \frac{dH}{T}$ and this is which is nothing but if I take this if I simplify this further I can write P comes here so $TdS - dH$ but if you see G is nothing but $H - TS$ so dG equals to $dH - dS - TdS$ but this is in contact with the thermal reservoir so this is a fixed temperature so $dT = 0$ so dG equals to $dH - TdS$ if you see $TdS - dH$ is nothing but $-dG$ so dS_{int} is nothing but $-\frac{dG}{T}$ which is equal to $-\frac{dG}{T}$ right so ζ is again the internal so driving force is negative derivative of partial derivative of the Gibbs free energy with respect to the internal process variable at fixed temperature pressure and right so and the ΔG that is the free energy that the change in free energy for this entire process for this entire spontaneous process is nothing but a negative of the T into ΔS_{int} right so $-\Delta G = T\Delta S_{int}$ right so $-\Delta G$ is nothing but that is the amount of extent of dissipation right extension of dissipation of internal energy is nothing but that right $-\Delta G = T\Delta S_{int}$ in this equation

$$\begin{aligned}
 dS^{int} &= \frac{TdS - dH}{T} = -\frac{dG}{T} = \frac{Dd\xi}{T} \\
 D &= -\left(\frac{\partial G}{\partial \xi}\right)_{T, P, N} \\
 &= T\left(\frac{\partial S^{int}}{\partial \xi}\right)_{T, P, N} \\
 \Delta G &= -T\Delta S^{int}
 \end{aligned}$$

in the equation that I showed here so if you see this entire term is nothing but in this case in the closed system which is in contact with the mechanical and thermal reservoir it is nothing but that this much engine that is free energy right now we take an example a quick example in fact I have given this as one of the assignments and I have also explained there I think that most of you have done it correctly so if you see you have means a part of the problem has been given as an assignment right now I just discussed this problem in the light of this new new stuff that you learned that ΔH_{fusion} because to and as you know ΔH_{fusion} and $\Delta H_{melting}$ are synonymous right and then an opposite of $\Delta H_{crystallization}$ or this die solidification right so $\Delta H_{solidification}$ so the enthalpy change due to solidification is minus of the enthalpy change due to fusion or melting right melting or fusion of the same process right so so these that so if you think of the definition of ΔH

fusion or ΔH melting that is the amount of heat absorbed right a solid has to absorb this amount of heat right and one mole of solid absorbs this amount of heat that is ΔH fusion that is nothing but the latent heat so latent heat and it converts to to convert to one mole of liquid at one bar pressure so ΔH fusion is given again at the transition temperature remember when I am talking about when I am signifying when I am telling that ΔH fusion or ΔH melting that is the latent of melting or latent of fusion and that is always specified at the given temperature that given temperature is in general the transition temperature and one bar pressure right and as I told you ΔH crystallization this basically when liquid is transferred to solid now when the liquid transfers to solid it releases it to the surrounding right it releases it to the surrounding so it is the amount of heat released from the system to the surrounding when one mole of liquid solidifies or crystallizes to form one mole of so one mole of liquid solidifies to form one mole of solid at one bar pressure let us call it one bar pressure sometimes we do use one atmosphere pressure but let's call it one bar pressure right so in this case I am thinking of ice to water conversion now ice to water conversion the transition temperature or the temperature of the reversible process is zero degrees Celsius and one bar pressure right one bar pressure means 10^5 Pascal pressure and this is an ice so at this temperature and pressure ice to water transformation or transition is reversible right ice can go to water water can means it can at zero degrees Celsius and one bar pressure water can exist in the solid state as well as in the liquid state right both are in equilibrium right ice and water are in equilibrium right and this when ice and water that means they're free energies are equal right ice and water free energies are equal now in such a case ice can transform to water or water can transform to ice there is no no no no no spontaneity means there is no spontaneous transformation from ice to water or water to ice however if I raise the temperature above zero degree ice will melt to water spontaneously if I lower the temperature below zero degree water will transform to ice irreversible right so that is the problem so how much is that is what we will quantify right so in this small example so as you know again this is the combined first second law when we are talking about some process which can be a natural process or a reversible process taking place in the system and again we know all this math and it quickly quote through this and what I am trying to say that at constant pressure dP equal to zero and then dH is dU plus PdV which we know so we can write dH equals to TdS right from here dH equals to TdS plus μdN minus TdS plus μdN because dU plus PdV is dH right dH equals to TdS plus μdN what I have done is I have taken this here so this becomes dU plus PdV and that is equal to dV right so once we have done that

$$\begin{aligned}
 dU &= Tds - PdV + \mu dN - Tds^{ir} \\
 H &= U + PV \\
 dH &= dU + PdV + VdP \\
 \text{At constant pressure} \\
 dP &= 0 \\
 dH &= dU + PdV \\
 dH &= Tds + \mu dN - Tds^{ir}
 \end{aligned}$$

now we are telling that and the melting point right or melting point or freezing point is zero degrees Celsius right that is the critical temperature right that the phase transition temperature so this is the phase transition so zero degrees Celsius is the phase transition temperature from solid to liquid or liquid to solid associated with so phase is zero degrees Celsius at one bar pressure remember at zero degrees Celsius and one bar pressure ice to water conversion or water to ice conversion is are both possible because ice and water are in equilibrium and the process is a reversible Now we also define the molar volume of ice which is 19.66 centimeter cube per mole it is per mole and of water is 18.02 centimeter cube per mole. Note that the molar volume of water is smaller than that of ice what does that mean what is the molecular weight of water molecular weight is 18.02 grams per mole so if that is so then rho is equals to 18.02 grams per mole by now if I think of rho water if I think of rho water it is 18.02 centimeter cube which is equals to one gram per cubic centimeter right so density of water is one gram per cubic centimeter so rho water so basically rho is equals to m by for any material right now for ice what it will be ice and water they have the same composition right chemical composition is water H2O right which has a molecular weight of 18.02 grams per molecule right so if you have that then rho ice equals to this is here it will be Vm is 19.66 right and here it will be 18.02 so this comes out to be I think approximately 0.916 say this is gram per c c or cubic centimeter so gram per centimeter

$\rho = \frac{M}{V_m}$
 $M = 18.02 \text{ gm/mol}$
 $\rho = \frac{18.02 \text{ gm/mol}}{18.02 \text{ cm}^3/\text{mol}} = 1 \text{ gm/cc}$

$T^m = 0^\circ\text{C} = 273 \text{ K}$ (Phase transition temperature)
 $1 \text{ bar} = 1.01325 \text{ atm}$

$V_m^{\text{ice}}(273\text{K}, 1 \text{ bar}) = 19.66 \text{ cm}^3/\text{mol}$
 $V_m^{\text{water}}(273\text{K}, 1 \text{ bar}) = 18.02 \text{ cm}^3/\text{mol}$

Amount of heat released per mole of water solidified
 $Q_{\text{ice}} = \frac{18.02}{19.66} \cdot Q_m = \Delta H^{\text{crystallization}} = -\Delta H^{\text{fusion}} = -6006 \text{ J}$
 $= 0.916$

$\Delta H = \Delta U + P\Delta V$
 $= Q_p = T\Delta S$

$\Delta H^{\text{fusion}} = \Delta H^{\text{melting}}$ $1 \text{ atm} = 1.01325 \text{ bar}$
 is the amount of heat absorbed during the melting of 1 mole of solid to 1 mole of liquid at 1 bar pressure.

$\Delta H^{\text{crystallization}} = -\Delta H^{\text{fusion}}$
 is the amount of heat released when 1 mole of liquid solidifies or crystallizes to form 1 mole of solid at 1 atm. pressure

0°C $1 \text{ bar} = 10^5 \text{ Pa}$
 $\text{ice} \rightleftharpoons \text{water}$
 1 bar

as you can see ice at this so at 273 K and one bar that 273 K means 0 degree Celsius is nothing but 273 K and at this temperature and at this pressure the ice is lighter than water right now amount of heat released per mole of water per mole so amount of heat is when water solidifies to ice per mole is given by delta H crystallization which is negative of delta H fusion which is given as say negative of delta H fusion and delta H fusion is 6006 say let us assume

delta H fusion because 6006 joules per mole so delta H crystallization is nothing but minus 6006 joules per mole now delta H is delta U plus Pd now delta U plus P delta V is nothing but QP and QP is the heat transfer at constant pressure right heat input the system at constant pressure which is nothing but equal to T delta H right now the entropy released now if you think of entropy release because see water transfer to ice means heat is released to surrounding so there is an entropy released to the surrounding and that amount of entropy released will be minus 6006 by 273 so first of all the heat released is minus 6006 joules per Kelvin right it is minus 6006 joules per Kelvin and the entropy release is basically coming from this equation QP plus minus T and delta Hc right which is basically given by minus 22 joules per Kelvin now if that is so if there is an entropy released right so basically there is an entropy exchange so inside the system entropy gets reduced right entropy gets reduced when water converts to ice right there is this delta Hc is minus 22 right delta Hc is minus 22 that means in the surrounding because it is released there is a negative of delta Hc that is basically so because the delta Hc system plus delta Hc surrounding should go to 0 right delta Hc system plus delta Hc surrounding should go to 0 so delta Hc surrounding is nothing but minus delta Hc which is 22 joules per Kelvin it is also understandable because there is heat released to the surrounding and as a result the entropy the entropy of the exchange the amount of entropy that will go up in the surrounding will be like it will be the same as the entropy that is transferred to that is the entropy that is changed in a system right this is due to heat transfer right or 6006 joules per joules and that's minus 6006 joules is the amount of heat that is released by one mole of water when it converts to ice right now 6006 by 273 is that delta Hc but it is negative right is minus Tm delta Hc because an entropy is released from the system so to the surrounding so the entropy of the surrounding will go up and that will go up exactly by

the same amount so it is 22 so that delta Hc surrounding and delta Hc system they add up to see so delta S is delta S system which is nothing but delta Hc which is minus 22 joules per Kelvin and this plus 22 joules per Kelvin again remember this is all calculated per mole right we have taken one mole of ice and I'm looking at one mole of ice converted to water or one mole of water converted to ice here we are looking at one mole of water converted to ice now if you see you have delta Hc which is minus 22 you have delta SiR which is delta S minus delta Hc which has to be C so for a reversible process the irreversible component of entropy of the entropy produced has to be C right and so you have now this delta S total which is delta S system plus delta S surrounding which is basically 22 at plus 22 in inside the surrounding right inside surrounding it is plus 22 so I should have written this way minus 22 plus 22 which is equal to 0 so delta S total that is the total entropy change is 0 see for a reversible process entropy is conserved right the process is reversible right there is no change in total entropy right

entropy released from system to surrounding

$$Q_p = -T_m \Delta S^e = -6006 \text{ J/K}$$

$$\Delta S^e = \frac{-6006}{273} \text{ J/K}$$

$$= -22 \text{ J/K}$$

$$\Delta S^{\text{surrounding}} = -\Delta S^e = 22 \text{ J/K}$$

$$\Delta S = \Delta S^{\text{system}} = \Delta S^e = -22 \text{ J/K}$$

$$\Delta S^{\text{univ}} = \Delta S - \Delta S^e = 0$$

if a process is irreversible there will be a positive change in entropy but if the process is reversible then delta S total that is the system surroundings or that is or this is also called delta S universe universe includes system and surrounding which is equal to C right now I have means we have been asked to calculate the change in enthalpy or the difference in enthalpy between water and ice at 273 K and 1 bar pressure so water to ice is basically nothing but see delta H so when I write delta H water to ice water transform to ice what I mean is it is H ice minus H water again this H means I can use small small H or even if I tell one mole then small H or capital H doesn't matter so this is it is basically the enthalpy per mole so is H ice minus H water right so basically delta H fusion will be H water minus H ice so delta H water minus delta H ice sorry H water minus H ice that is basically is nothing but delta H fusion ice to water right so ice has to absorb it so it is minus of the delta H oscillation so which is delta H fusion which is nothing but 6006

$$\begin{aligned}
\Delta S^{\text{universe}} = \Delta S^{\text{tot}} &= \Delta S^{\text{system}} + \Delta S^{\text{surrounding}} \\
&= -22 + 22 \\
&= 0
\end{aligned}$$

Process is reversible

$$\begin{aligned}
\Delta h_{\text{water} \rightarrow \text{ice}}^{\text{cryo}} &= h_{\text{ice}} - h_{\text{water}} \\
h_{\text{water}} - h_{\text{ice}} &\left(273 \text{ K}, 1 \text{ bar} \right) \Delta h_{\text{ice} \rightarrow \text{water}}^{\text{fusion}} \\
&= -\Delta H_{\text{water} \rightarrow \text{ice}}^{\text{crystallization}} \\
&= \Delta H_{\text{ice} \rightarrow \text{water}}^{\text{fusion}} = 6006 \text{ J}
\end{aligned}$$

joules now if you look at the molar volume then you can also estimate U_{water} minus U_{ice} because H_{water} minus H_{ice} is nothing but U_{water} plus PV_{water} minus U_{ice} plus PV_{ice} which is equal to 6006 joules now we can calculate $P(V_{\text{water}} - V_{\text{ice}})$ P is basically one bar which is like but one it can be 10^5 Pascal or 101325 Pascal and then you have this difference 19.66 is equal to 8.02 and this is centimeter cube per mole so you can convert into meter cube so you have to multiply by 10^{-6} so you have to multiply by 10^{-6} so what you get the contribution that you get if you see this is these are both condensed phases see there is no gaseous phase so the PV work is really really small compared to the the enthalpy of fusion see the enthalpy of fusion or heat of fusion is 6006 whereas this PV work the difference in the PV in water and ice or this pressure one bar pressure is only 0.166 so 6006 plus 0.166 is basically this is a like like the numbers in thousands and this like numbers in tens and so 6006 plus 0.166 is actually 6006.166 but the 0.166 is negligible compared to this number right

$$\begin{aligned}
u_{\text{water}} - u_{\text{ice}} &= ? \\
h_{\text{water}} - h_{\text{ice}} &= \left(u_{\text{water}} + pV_m^{\text{water}} \right) - \left(u_{\text{ice}} + pV_m^{\text{ice}} \right) \\
&= 6006 \text{ J} \\
u_{\text{water}} - u_{\text{ice}} &= 6006 \text{ J} + p \left(V_m^{\text{ice}} - V_m^{\text{water}} \right) \\
&= 6006 + 1 \text{ bar} \times 101325 \text{ Pa} \\
&\quad \times (19.66 - 18.02) \times 10^{-6} \text{ m}^3 \\
&= 6006 + 0.166 \\
&\approx 6006 \text{ J}
\end{aligned}$$

so you can take same that means we work I can neglect right now if that is so another thing that we are talking about is water minus is ice so is water minus is ice is basically ΔS so it is basically $\Delta S_{\text{ice to water}}$ obviously again common sense tells us that ice which is solid will have lower entropy than that of water right water which is liquid which will have more right which will have more mobile atoms and which has slight plus one another we can slight means be slightly more disorder than solid in solid it is very closely packed compared to water then you can immediately see that is water minus is ice is nothing but the amount of entropy that was produced in this that that that that was changed the system during this reversal process we should not use the word produced that the amount of entropy that was required for this this transformation to take place was 22 joules per Kelvin right 22 joules per Kelvin was was was the amount of entropy that happens to exchange and that is going to plus 22 happens surrounding and plus the minus 22 happens in the system but in this case this is ice to water right so basically ice to water means ice will require heat so heat is coming inside the system if it is coming inside the system there is a change there is also thermal metal thermal matter coming inside the system that means the entropy is increasing right although there is no irreversibility but the entropy is increasing and the entropy difference is nothing but plus 22 right this plus one joules per kelvin inside the system now think of one interesting case now see this is basically I am looking at so if you look at I am actually developing thermodynamics for a unary system unary means one component system water is a single component right we are not talking about hydrogen and oxygen because we are not caring about that reaction of hydrogen and oxygen coming into form water we are just looking at phase transitions in water and water is a single component as a result a single component system we are looking at phase equilibrium in a single component system and the equilibrium that we are specifically looking at is the equilibrium solid liquid equilibrium that is coexistence of ice and water at 273 Kelvin and one bar now let us consider irreversibility that means we will consider the temperature at which the process of converting to water from water to ice or ice to water becomes irreversible now if that is so if we consider 298 Kelvin and one bar one mole of ice in this case is irreversibly melting to one mole of water right one mole of ice is irreversibly melting to one mole of water

$$S^{\text{Water}} - S^{\text{Ice}} = 22 \text{ J/K} \quad \Delta S_{\text{ice} \rightarrow \text{water}}$$

Consider 298 K (25°C) and 1 bar

1 mole of ice irreversibly (spontaneously) melts to 1 mole of water

Assume enthalpy difference and entropy differences between water and ice same as that at 273 K, 1 bar

$$\Delta S^{\text{melting}}(298 \text{ K}, 1 \text{ bar}) = \Delta S^{\text{melting}}(273 \text{ K}, 1 \text{ bar}) = 22 \text{ J/K} = \Delta S^{\text{water}}$$

now think of enthalpy difference and entropy difference that is $H^{\text{water}} - H^{\text{ice}}$ or $S^{\text{water}} - S^{\text{ice}}$ basically to be the same as that of 273 Kelvin right that is that that is the same as that of so at 298 Kelvin we are telling that the change is it is very insensitive that $H^{\text{water}} - H^{\text{ice}}$ or $S^{\text{water}} - S^{\text{ice}}$ the change in that with respect to temperature is very very small right that the basically the CP contribution is small is what we are talking about right so the enthalpy difference and entropy difference do not change they are same as that at 273 Kelvin and one bar pressure at 298 Kelvin and one bar pressure it is the $\Delta S^{\text{melting}}$ right per mole and $\Delta S^{\text{melting}}$ per mole at 273 Kelvin and one bar pressure are the same and that is equal to 22 joules per Kelvin right you require the system requires 22 joules per Kelvin for this conversion or this transition to take place however note this that at 25 degree Celsius this is an irreversible transformation now when ice melts heat is absorbed by the system from the surroundings now so in the surrounding the the the there is from the surroundings so if there is a negative heat input to the surrounding right heat is getting absorbed right so it is coming from the surrounding so which is basically now surrounding as is at what temperature 298 Kelvin how much of it is required that is enthalpy is required it is 6006 right so it when ice melts it requires 6006 joules right per mole so in one mole requires 6006 joules now minus 6006 by 298, 298 is the temperature of the surrounding right it is because 298 is the temperature of the system so it is the temperature of the surrounding also right so 290 because system and surrounding should have the same temperature thermal equilibrium so then $\Delta S^{\text{surrounding}}$ is minus 20.15 in this case because it is transferred from the surrounding to the system right so that entropy or thermometer of the surrounding goes down right but it goes down by minus 20.15 but the amount of it that entropy exchange that is required for ice melting to water is basically plus 20.

15 joules per Kelvin right so the entropy exchange during ice melting to water right ice

melting to water so basically you are producing entropy and the amount of entropy that is not producing you are you there is a change in entropy but the change in entropy is positive again don't call it entropy so this is something that I am sorry for means I have told entropy produced we should not call entropy produced it is the entropy that is exchange or the entropy that is basically exchange or transferred between the system surrounding so this is ΔS_e or you can call it $\Delta S_{transfer}$ means the amount of entropy that is we transfer to the system for this ice melting to water at 298 Kelvin and one bar pressure is 20.15 joules per Kelvin now ΔS_{total} is basically ΔS_{system} but ΔS_{system} remember has something called ΔS_e that is the amount of entropy that has is to be transferred for ice melting to water and that amount of entropy that is exchanged between the system the surrounding because $\Delta S_{surrounding}$ is nothing but $\Delta S_{surrounding}$ and ΔS_e inside the system right basically they have to add up to 0 right so if it is minus 20.15 then there will be plus 20.15 right this is plus 20.15 but you see ΔS_{system} is slightly more than ΔS_e because ΔS_{system} is given as 22 right it is 22 joules per Kelvin right it was given as the enthalpy difference between water and ice is at 298 Kelvin is 22 joules per Kelvin so 22 joules per Kelvin is ΔS_{system} but the entropy that is exchanged is only plus 20.

15 as you can see here this is minus 20.15 so the exact amount with opposite sign will be transferred to the system which is minus 20.15 the minus of minus 20.15 is plus 20.15 that will be transferred to the system but there is a entropy difference which is 22 so if you see there is the ΔS_{system} is 22 which includes this part plus the irreversible part and for the surrounding there is no irreversible part right the process is happening inside the system the irreversible process is happening inside the system so this is negative 20.

When ice melts, heat is absorbed by system from surrounding

$$\Delta S_{surrounding} = -\frac{Q}{T} = \frac{-6006}{298}$$

$$\approx -20.15 \text{ J/K}$$

Entropy exchange during ice melting to water at 298 K, 1 bar

$$\Delta S_e = +20.15 \text{ J/K}$$

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}$$

$$= 22.0 - 20.15 = 1.85 \text{ J/K}$$

15 this is plus 20.0 so you get a plus 1.85 joules per Kelvin as you can see it is indeed a

spontaneous process because the delta S total or delta S universe is positive right it is indeed a spontaneous process and the delta S irreversible right the delta S irreversible that is the amount of entropy produced inside the system is 1.85 joules per Kelvin right so basically as I told you that delta S system is nothing but it is 22 which is 20.15 plus delta S IR and delta S IR is 1.85 and if you add them basically you get 22 right so basically 22 is 20.15 plus 1.85 and 1.85 that means is the amount of entropy that is produced in the system during this continuous transformation from I to 1 right now if you think of delta G as I told you this is nothing but the minus T delta S IR which is basically minus 551.3 joules right this is the chemical energy which is changed this is the amount of chemical energy or the display energy change or this minus 551.3 right

$$\Delta S^{\text{system}} = \Delta S = \Delta S^e + \Delta S^{\text{irr}}$$

$$22 = 20.15 + \Delta S^{\text{irr}}$$

$$\therefore \Delta S^{\text{irr}} = 1.85 \text{ J/K}$$

$$\Delta G_{\text{1 bar}}(298 \text{ K}) = -T \Delta S^{\text{irr}}$$

$$= -298 \times 1.85 \text{ J}$$

$$= -551.3 \text{ J}$$

This is the chemical energy changed to thermal energy

2 into T minus 2.8 into 1.85 is nothing but delta G and this is the chemical energy that is changed to thermal energy right that is converted to thermal energy right so we will discuss further in the next lecture we will discuss further about the unary system the equilibrium in unary system and we will discuss how to represent this using a phase diagram and the phase boundary and we will also discuss the concept of there is something called a phase rule to quantify these transformations so we will discuss all of these in the next lecture.

Unary system

$$\mu = \left(\frac{\partial G}{\partial N_i} \right)_{T, P, N_{j \neq i}} = \left(\frac{\partial U}{\partial N_i} \right)_{S, V, N_{j \neq i}}$$

N moles of component 1

$$\therefore \frac{G}{N} = G_m \text{ or } \bar{G} = \frac{\Delta G}{\Delta N} = \left(\frac{\partial G}{\partial N} \right)_{T, P} = \mu$$